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Advanced Materials Derived from Electronic Waste

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ



O ALLAH, INCREASE US
IN KNOWLEDGE!

To my parents, my wife and my son — for everything...

Abstract (English):

The rapid accumulation of electronic waste (e-waste) and the persistent discharge of dye-contaminated industrial wastewater represent two major environmental challenges facing modern waste management and environmental engineering. This thesis demonstrates that these challenges are interconnected by showing that the non-metallic glass-fibre-reinforced epoxy fraction of waste printed circuit boards (PCBs), commonly disposed of after metal recovery, can be transformed into advanced adsorbent materials for wastewater remediation. Conducted within the framework of the SMaRT-PCBs (Sustainable Materials Recycling Technology for Printed Circuit Boards) project, this research investigated three distinct processing routes: microwave-assisted chemical treatment (MA-CT-PCB), buffered chemical leaching (BL-PCB), and reagent-free mechanical processing (MP-PCB). The resulting non-metallic residues were systematically characterised using X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM–EDS), transmission electron microscopy (TEM), BET nitrogen physisorption, and surface charge analysis. Subsequently, they were tested as adsorbents for water decontamination from organic pollutants. In particular, adsorption tests against methylene blue (MB, 10^{-5} M), selected as molecular probe, were conducted by monitoring the lowering of the concentration of the dye in the liquid phase through UV-visible spectroscopy as a function of the contact time with the adsorbent. Even if MB removal was not always complete, solar-assisted photocatalytic experiments allowed in all the cases complete methylene blue discolouration under simulated solar irradiation following adsorption pre-concentration.

The principal scientific contribution of this thesis is the synthesis of mesoporous silica (MP-PCB-MS, m-SiO₂) from the mechanically processed PCBs, whose adsorption capability was deeply investigated. Compared with the raw PCB precursor, the material demonstrated an approximately two-orders-of-magnitude increase in accessible surface area, resulting in rapid adsorption kinetics. Methylene blue (MB) removal efficiencies of 98–100% at a solute concentration of 1×10^{-5} M were achieved within 1–2 minutes, matching the performance of commercial activated carbon and substantially outperforming natural silica sand. Adsorption behaviour followed the pseudo-second-order kinetic model ($R^2 > 0.99$) and the Langmuir isotherm model, yielding a maximum monolayer adsorption capacity of 76.7 mg g⁻¹. Dye selectivity studies demonstrated strong preferential adsorption of cationic species, while anionic methyl orange (MO) showed minimal adsorption due to electrostatic repulsion. In mixed dye configurations (MB+MO), partial methyl orange co-adsorption occurred through ion-pair-assisted pathways, while MB removal was not reduced.

Regeneration studies using sodium dodecyl sulphate (SDS) suggested excellent cyclic stability of the synthesised $m\text{-SiO}_2$ across at least four adsorption–desorption runs, with only a 0.46% variation in equilibrium adsorption capacity.

In most of the cases, adsorption tests were conducted on a reduced laboratory scale (few mg of adsorbents and few millilitres of contaminated water), but volumetric scale-up experiments were executed at 100 mL and 500 mL configurations using the buffered chemically leached composite (BL-PCB-SU), which was selected since its preparation (performed by Cagliari University) was characterised by a limited environmental impact and could be scaled up. These experiments validated the scalability and thermodynamic invariance also of the adsorption process.

Overall, this thesis demonstrates that non-metallic PCB waste can be transformed into different types of adsorbents for the removal of positively-charged organic pollutants, with excellent performances when converted into mesoporous silica. This work establishes a sustainable pathway for e-waste valorisation while contributing to circular economy approaches for electronic waste management and industrial wastewater remediation.

Abstract (Italian):

Il rapido accumulo di rifiuti elettronici (RAEE) e la contaminazione delle acque reflue industriali da coloranti rappresentano due importanti sfide ambientali per la moderna gestione dei rifiuti e l'ingegneria ambientale. Questa tesi dimostra che tali sfide possono essere interconnesse. In particolare, la tesi dimostra che la frazione non metallica a base di resina epossidica rinforzata con fibra di vetro risultante da schede elettroniche (PCB) di scarto, comunemente smaltita in discarica o incenerita, può essere trasformata in materiali adsorbenti avanzati per la bonifica delle acque reflue. Condotta nell'ambito del progetto SMaRT-PCBs (Sustainable Materials Recycling Technology for Printed Circuit Boards), questa ricerca ha studiato tre distinte frazioni non metalliche derivanti da PCB di scarto, ottenute attuando il recupero delle componenti preziose (svolto dall'Università di Cagliari) attraverso processi differenti: trattamento chimico assistito da microonde (MA-CT-PCB), lisciviazione chimica con soluzioni tampone (BL-PCB) e processo meccanico privo di reagenti chimici (MP-PCB). I residui non metallici risultanti sono stati caratterizzati sistematicamente utilizzando la diffrazione dei raggi X (XRD), la spettroscopia Raman, la microscopia elettronica a scansione con spettroscopia a raggi X a dispersione di energia (SEM-EDS), la microscopia elettronica a trasmissione (TEM), fisisorbimento di azoto e analisi BET, e analisi della carica superficiale. Successivamente, i campioni sono stati testati come adsorbenti per la decontaminazione dell'acqua da inquinanti organici. In particolare, sono stati condotti test di adsorbimento contro il blu di metilene (MB, 10^{-5} M), scelto come sonda molecolare, monitorando la diminuzione della concentrazione del colorante nella fase liquida tramite spettroscopia UV-visibile in funzione del tempo di contatto con l'adsorbente. Sebbene la rimozione del MB non sia risultata sempre completa, gli esperimenti di fotocatalisi assistita da energia solare hanno permesso in tutti i casi la completa decolorazione del blu di metilene sotto irradiazione solare simulata, previa pre-concentrazione del colorante sulla superficie dell'adsorbente.

Il principale contributo scientifico di questa tesi consiste nella sintesi di silice mesoporosa (MP-PCB-MS, m-SiO₂) utilizzando come precursore le schede elettroniche processate meccanicamente, di cui è stato approfonditamente studiato il processo di adsorbimento.

Rispetto al precursore grezzo, il materiale ha dimostrato un aumento di circa due ordini di grandezza dell'area superficiale accessibile, che ha permesso una rapida cinetica di adsorbimento del blu di metilene. Sono state raggiunte efficienze di rimozione del blu di metilene (MB) del 98-100% a una concentrazione di soluto di 1×10^{-5} M entro 1-2 minuti, eguagliando le prestazioni del carbone attivo commerciale e superando sostanzialmente quelle della sabbia silicea naturale. Il comportamento di

adsorbimento ha seguito il modello cinetico pseudo-secondo ordine ($R^2 > 0,99$) e il modello di isoterma di Langmuir, producendo una capacità di adsorbimento monostrato massima di 76,7 mg g⁻¹. Studi sulla selettività del colorante hanno dimostrato un forte adsorbimento preferenziale delle specie cationiche, mentre il colorante anionico metil arancio ha mostrato un adsorbimento minimo a causa della repulsione elettrostatica. In configurazioni di coloranti misti (metilen blue+ metil arancio) si è verificato un parziale co-adsorbimento metil arancio, probabilmente grazie a processi di co-adsorbimento di coppie ioniche, mentre la rimozione del blu di metilene si è mantenuta invariata. Studi di rigenerazione con dodecil solfato di sodio (SDS) hanno confermato l'eccellente stabilità ciclica del m-SiO₂ sintetizzata per almeno quattro cicli di adsorbimento-desorbimento, con una variazione di solo lo 0,46% nella capacità di adsorbimento all'equilibrio.

Nella maggior parte dei casi, i test di adsorbimento sono stati condotti su scala di laboratorio ridotta (pochi mg di adsorbente e pochi millilitri di acqua contaminata), ma esperimenti di scalabilità volumetrica sono stati eseguiti in configurazioni da 100 mL e 500 mL utilizzando la frazione non-metallica attraverso processi di lisciviazione con soluzioni tampone (BL-PCB-SU), selezionata poiché la sua preparazione (eseguita dall'Università di Cagliari) era caratterizzata da un impatto ambientale limitato e poteva essere svolta in grandi quantità. Questi esperimenti hanno ulteriormente convalidato la scalabilità e l'invarianza termodinamica anche del processo di adsorbimento.

Nel complesso, questa tesi dimostra che la frazione non metallica derivanti da schede elettroniche di scarto può essere trasformata in diversi tipi di adsorbenti per la rimozione di inquinanti organici cationici., con performance ottimali quando viene convertita in silice mesoporosa.

Questo lavoro illustra dunque un percorso sostenibile per la valorizzazione dei rifiuti elettronici, contribuendo al contempo agli approcci di economia circolare per la gestione dei rifiuti elettronici e il risanamento delle acque reflue industriali.

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CHAPTER 1: INTRODUCTION

1.1. The Concept of Waste in Modern Society:

Waste, an inherent by-product of human activity, accompanies us from the extraction of raw materials to the final disposal of discarded goods. It represents the tangible remnants of materials whose perceived utility has diminished for both producers and the consumers. This definition belies the complex implications of waste. Industrial expansion, rapid urbanisation, and population growth have greatly accelerated waste generation, turning waste management into a global imperative that demands innovative solutions and international cooperation.

Our ability to create and consume has led to an unprecedented amount of waste, now threatening the very systems that support us. The sheer volume of this waste overwhelms existing infrastructure, leading to overflowing landfills, polluted water, and damaged ecosystems. Such environmental impacts pose serious risks to human health and exacerbate climate change.

Economically, inefficient waste management means loss of valuable resources. The costs of inaction are substantial, including environmental clean-up, public health expenses, and foregone economic opportunities. Socially, waste management also raises equity issues. Communities near disposal sites, often marginalised, face disproportionate hazards. The informal waste sector provides livelihoods for many, but without protections it endangers workers. These inequalities underscore the need for inclusive, equitable waste management strategies

Understanding waste flows from production to disposal, is essential to designing sustainable solutions. This research investigates the interconnected factors driving waste generation and explores innovative approaches to mitigate its environmental and social impacts.

Global municipal solid waste production was estimated to exceed 2.2 billion metric tons in 2022, with projections indicating a 70% increase by 2050 under a business-as-usual scenario (World Bank, 2018). A particularly concerning subset is electronic waste (e-waste), which has been growing at an unprecedented rate. E-waste consists of discarded electrical and electronic devices, including home appliances, laptops, computers and smartphones. In 2021, the world generated an estimated 57.4 million metric tons of e-waste, of which only 17.4% was formally recycled (Baldé et al., 2024). These highlight significant inefficiencies in existing waste management frameworks and the urgent need for innovative solutions.

Although waste is usually viewed as a burden, it embodies recoverable resources (Forti et al., 2020). The circular economy seeks to replace the linear “take-make-dispose” model with reuse and recycling. In the e-waste context, advanced recycling can recover precious metals (gold, palladium, neodymium) vital for electronics (Kumar et al., 2017). Research also explores valorising non-metallic fractions (polymers, ceramics) into new products. Yet recycling e-waste is difficult: the material mix is complex and often contains toxic substances (e.g., brominated flame retardants, mercury, lead) that pose health and environmental risks (Widmer et al., 2005). Moreover, some recycling methods demand substantial energy, raising concerns about overall sustainability.

Waste-based materials for environmental remediation represent a promising avenue for addressing both waste management and environmental pollution. By repurposing discarded materials into functional products, such as adsorbents, catalysts, and membranes, researchers aim to tackle critical issues, including water and air pollution. These materials offer a dual benefit: reducing waste accumulation while addressing environmental contamination, thus aligning with the principles of a circular economy.

This thesis examines current strategies for recycling both metallic and non-metallic e-waste fractions, with an emphasis on the non-metallic components. It evaluates the life-cycle impacts of these processes. The thesis also explores the use of e-waste-derived materials in environmental remediation, especially for water treatment and degradation of organic pollutants.

1.2. E-Waste: Problems and Potentials:

Electronic devices have proliferated rapidly over the past decades. From mobile phones and laptops to electric cars and smart appliances, these technologies are now indispensable. The electronics industry has seen sustained growth ($\approx 3.7\%$ annual increase in systems markets over 30 years). However, widespread use of electronics leads to a corresponding surge in end-of-life waste. This waste, termed electronic waste (e-waste), includes discarded computers, phones, TVs, refrigerators, and similar equipment.

Electronic devices are now integral to communication, manufacturing, healthcare, and daily domestic use, with the electronics industry recording sustained annual growth of approximately 3.7% over the past three decades (Doubrova, 2024). The advent of the transistor in the mid-20th century, followed by the integrated circuit and the microprocessor, laid the foundation for the digital age (Augarten, 1983). From smartphones and laptops to medical devices and industrial machinery, electronic devices permeate nearly every aspect of our existence, driving economic growth, facilitating global connectivity, and enhancing our quality of life.

Figure 1 clearly identifies in terms of revenue and the percentage increase in the electronic systems market over the past 30 years. The total growth has been unprecedented in every industry whether it be automotive, industrial or communication.

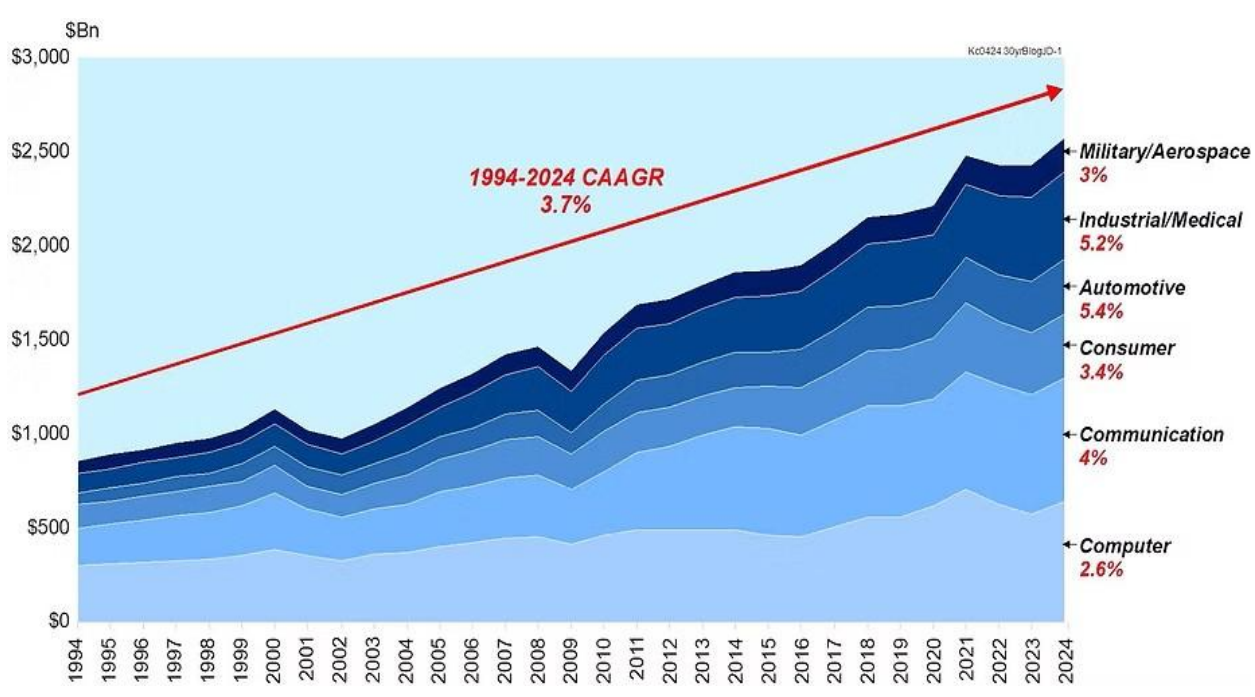


Figure 1: Global electronics market revenue growth over 30 years (Doubrava, 2024)

The chart below shows growth across the electronics value chain over the past thirty years, demonstrating a very strong growth of the components and materials markets, specifically semiconductors, PCBs and PV cells.

As technology has advanced manifold in this century, our society is now deeply reliant on electronic systems and devices. However, this widespread integration also means that, once these products reach the end of their functional life, we are faced with

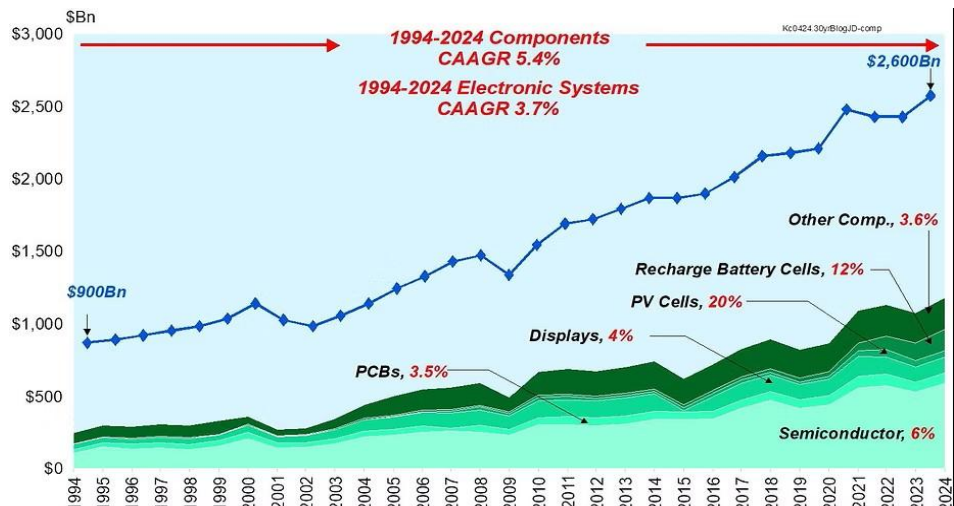


Figure 2: Thirty-year perspective on the production of electronic components and PCBs (adapted from Doubrava, 2024).

the pressing challenge of managing the vast quantities of waste they generate: electronic waste, or e-waste. The vital role electronics play in contemporary society, examines the escalating e-waste crisis,

and analyses its current and future consequences for the environment, human health, and global sustainability (Rigoldi et al., 2019).

The e-waste challenge is already acute and is expected to worsen. Demand for electronics continues to rise, especially in developing countries where growing incomes increase consumption (Baldé et al., 2015). At the same time, rapid technological advancement and the push for new models shorten product lifespans. This planned obsolescence (intentional or perceived) accelerates e-waste generation (Widmer et al., 2005).

Future projections paint a concerning picture. Indeed, the latest Global E-waste Monitor Baldé et al. (2024) reported 62 Mt of e-waste generated in 2022 – an 82% increase since 2010. If current trends continue, e-waste could reach 82 Mt by 2030. Such growth, coupled with low recycling rates, means more toxins (e.g., heavy metals, persistent organics) will be released into soil, water and air, harming ecosystems and human health (Grant et al., 2013). At the same time, unrecycled e-waste wastes valuable materials (gold, rare earths, etc.), depleting finite resources and impeding the circular economy (UNEP, 2013).

Compounding the problem, e-waste has a complex composition. Electronic circuits and casings blend plastics and polymers with numerous metals. Highly conductive metals (Au, Ag, Cu) are deliberately used for wiring and contacts, but hazardous elements (Pb, Hg, Cd) and brominated flame retardants are also present (Widmer et al., 2005). If not properly handled, these toxins can leach into soil, water and air, contaminating ecosystems and endangering wildlife (Robinson, 2009). In short, rapid e-waste growth, limited recycling infrastructure, and the hazardous complexity of the material together underscore the urgent need for sustainable e-waste management.

The combination of increased generation, inadequate infrastructure, complex composition and the resulting environmental and economic consequences underscores the urgent need for effective and sustainable solutions to the global e-waste crisis.

1.3. E-Waste Recycling:

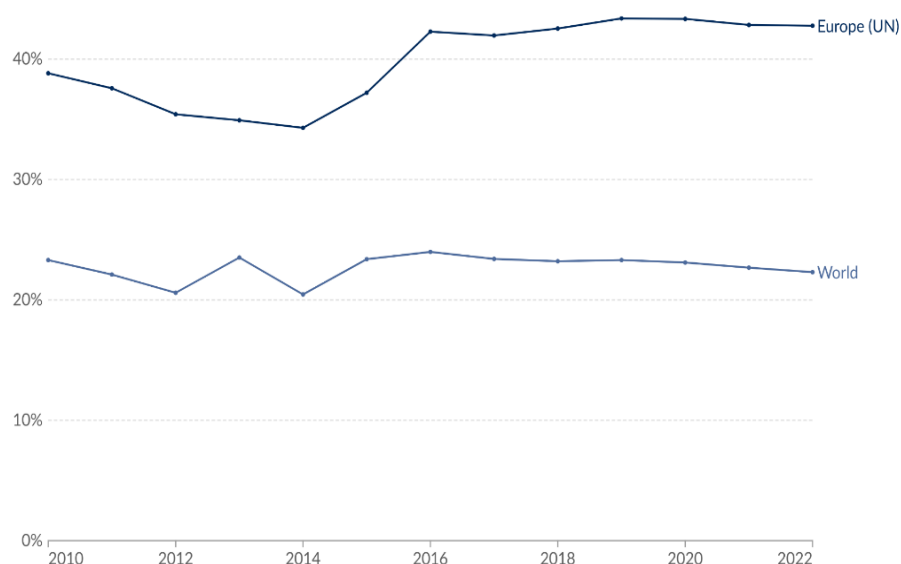
In many regions, especially developing countries, formal e-waste collection and recycling systems are weak or absent. As a result, much e-waste is processed informally under unsafe conditions, releasing toxins (Robinson, 2009). Limited public awareness and weak enforcement further exacerbate these practices (Basel Action Network, 2002). Illegal export of e-waste from developed to developing nations shifts the health and environmental burden to places lacking adequate management capacity.

Recognising these challenges, international and regional policy frameworks have increasingly emphasised recycling, reuse, and resource recovery as the most sustainable pathways for addressing the e-waste crisis. At the global level, the Basel Convention on the Control of Transboundary Movements of *Hazardous Wastes and Their Disposal* (1989), strengthened by its *Ban Amendment* (1995), sought to curb hazardous waste exports, including e-waste, from developed to developing nations. While enforcement remains uneven and loopholes such as mislabelling persist, the Convention has nevertheless created an important foundation for international cooperation (BAN, 2002). At the national level, several countries have introduced Extended Producer Responsibility (EPR) frameworks, requiring manufacturers to take responsibility for collection and end-of-life management of their products. For instance, Japan and South Korea have reported significant success with EPR schemes, mandating the take-back and recycling of discarded electronics (OECD, 2021).

Within the European Union, the *Waste Electrical and Electronic Equipment (WEEE) Directive* (Directive 2012/19/EU) provides one of the most comprehensive legislative frameworks for e-waste management. It identifies e-waste as one of the fastest-growing waste streams and highlights the dual challenge it poses: hazardous substances such as lead, mercury, cadmium, and brominated flame retardants on one side, and critical raw materials such as gold, silver, and rare earth elements on the other. By promoting efficient collection, treatment, and recycling of electrical and electronic equipment, the WEEE Directive aims to improve resource efficiency, minimise environmental and health risks, and advance the EU's transition to a circular economy (European Commission, 2012).

Electronic waste recycling rate, 2010 to 2022

The percentage of total electronic waste that is recycled.



Data source: United Nations Environment Programme, United Nations Statistics Division and the United Nations Institute for Training and Research
OurWorldinData.org/waste-management | CC BY

Figure 3: E-Waste recycling rate 2010 to 2022 (UNEP, 2025).

As anticipated, the ever-increasing volume of discarded electronics has made e-waste recycling a critical solution for addressing environmental, economic, and resource-related challenges. Recycling offers a pathway to

recover valuable materials, mitigate environmental degradation, and preserve finite natural resources. E-waste is composed of a complex mixture of metals, plastics, glass, and other non-metallic components, and effective recycling requires tailored strategies that maximise resource recovery while minimising environmental footprints. Globally, recycling efforts target both the non-metallic and the metallic parts of e-waste, employing physical, chemical, and increasingly biological approaches. These techniques are specifically designed to address the diversity of materials and the varying degrees of recyclability, ensuring efficient and sustainable recovery.

As per the EU WEEE directive the recycling process is commonly organised into five main stages, as represented in the figure. Each stage includes critical sub-stages that together determine the overall effectiveness of recycling and resource recovery.

1. Pre-processing is the essential first stage, this crucial phase significantly influences both the efficiency of resource recovery and the overall environmental impact of the recycling operation. The primary goals of pre-processing are to remove hazardous components, minimise risks to human health and the environment during later stages and to increase material recovery efficiency by separating different material fractions.

The pre-processing stage begins with **collection and logistics**. Efficient collection systems employ various strategies, including municipal collection programs with curb side pickup, designated drop-off centres, and special collection events. Retailer take-back programs, driven by Extended Producer Responsibility (EPR) legislation, where retailers accept old electronics when consumers purchase new ones, also play a significant role. Similarly, manufacturer take-back programs, where producers assume responsibility for the end-of-life management of their products, contribute to organised collection efforts. Efficient logistics, involving the transportation of collected e-waste to processing facilities, are essential to minimise both costs and the environmental impact associated with transportation. (Cucchiella et al., 2015).

Following collection, the e-waste undergoes **sorting and categorisation**. Initially, collected e-waste is often manually sorted based on type, such as large appliances (white goods), small appliances, IT equipment (computers, laptops), and consumer electronics (televisions, mobile phones). This initial sorting streamlines subsequent processing steps by grouping similar materials together. (Hilty et al., 2006).

2. Pre-Treatment: Once WEEE has been collected and transported to authorised facilities, the first technical stage is pre-treatment, which is legally required under the EU WEEE Directive (Directive 2012/19/EU, Article 8 and Annex VII). This crucial step removes hazardous substances that could

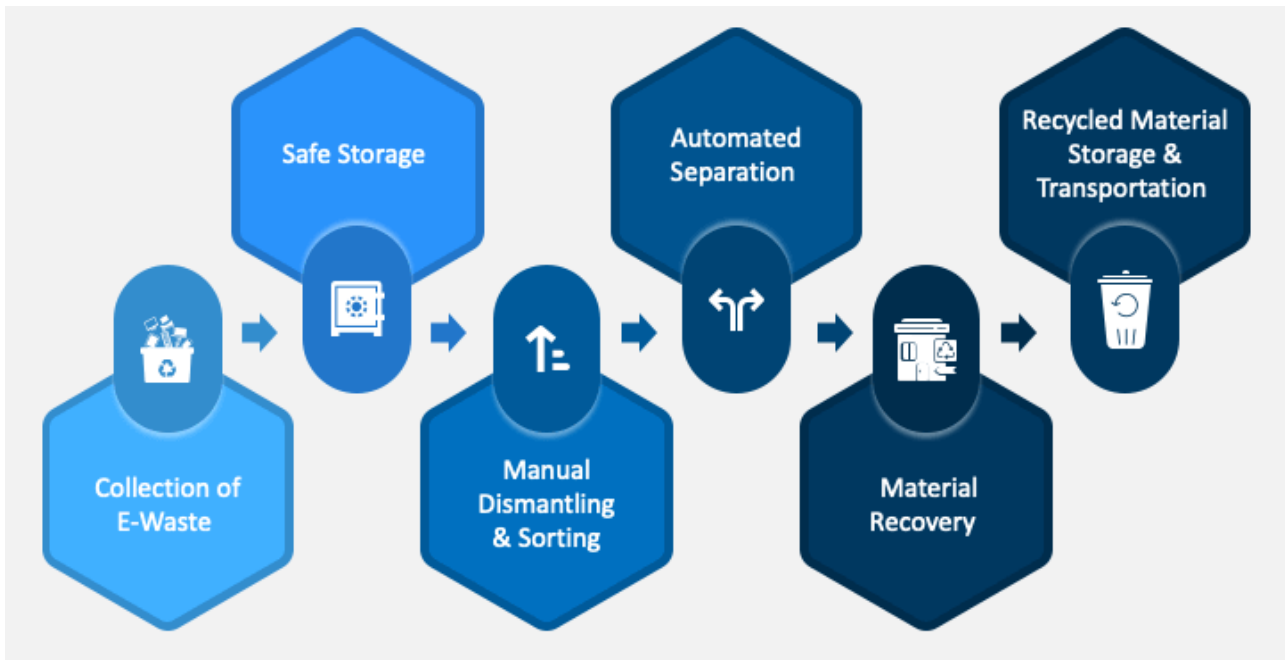


Figure 4: E-Waste recycling flowchart (EU WEEE)

cause environmental contamination and segregates components that can be more efficiently recycled in later stages.

A critical aspect of this stage is **component removal**, which involves manually extracting components that require separate handling due to their hazardous nature or high economic value. This includes various types of batteries, such as lithium-ion (Li-ion), nickel-cadmium (Ni-Cd), and lead-acid batteries, due to their hazardous chemical content (heavy metals and corrosive electrolytes) and the potential for thermal runaway, leading to fires or explosions during processing or storage. Similarly, mercury is also removed from lamps, CFLs and LCD backlights to prevent mercury release during shredding or other processing. (Universal Waste | US EPA, 2024). Additionally, some older capacitors, particularly those used in industrial equipment and older appliances, may contain highly toxic polychlorinated biphenyls, which are persistent organic pollutants (POPs) and require specialised high-temperature incineration or other approved disposal methods. (Breivik et al., 2007).

For devices with data storage capabilities, like computers, laptops, and smartphones, **secure data wiping** is an essential step to protect user privacy (Bovea et al., 2020). This involves using specialised software to completely and irreversibly erase all data from the device's storage media. (Reecollabb, 2024).

A further aspect of pre-treatment is size reduction and initial sorting. Some fractions may be shredded to reduce volume and allow separation of metals and plastics. The efficiency of this stage directly influences both the safety of subsequent processing and the purity of recovered materials (Huisman et al., 2007).

3. Reuse and Refurbishment: The EU WEEE framework prioritises reuse and preparation for reuse over recycling, aligning with the EU Waste Framework Directive (2008/98/EC) and the waste hierarchy. This strategy extends product lifecycles, reducing the demand for virgin resources and minimising environmental impacts. At this stage, collected WEEE is assessed for viability in secondary markets through systematic testing and refurbishment. For instance, computing devices and smartphones undergo functional assessment, secure data sanitization via certified erasure software, and hardware upgrades such as battery or memory replacement. These refurbished devices provide affordable technology access in developing regions while diverting significant e-waste volumes from European disposal streams (Bovea et al., 2020).

While the Directive obliges Member States to establish reuse systems often involving social enterprises, economic barriers persist. The manual labour required for diagnostic testing can occasionally exceed the commodity value of low-end electronics. Nevertheless, reuse yields the highest environmental dividends, as evidenced by life cycle assessment (LCA) studies (Ardente & Mathieux, 2014). Recycling remains the terminal option, pursued only when a device is no longer functionally or economically repairable (Basic Information About Electronics Stewardship | US EPA, 2024).

4. Material Recovery: When refurbishment is unfeasible, WEEE enters the material recovery phase, the technical backbone of electronic recycling. This stage focuses on reclaiming high-value critical raw materials (CRMs), such as gold, silver, and rare earth elements, alongside bulk commodities like steel and polymers. The European Union regards WEEE as a significant “urban mine,” essential for reducing dependency on imported resources and strengthening industrial resilience (European Commission, 2023).

Recovery begins with mechanical treatment, where shredding liberates constituent materials for physical separation. Ferrous metals are reclaimed via magnetic separators, while non-ferrous metals like copper and aluminium are isolated through eddy current separators. Density-based air classification further distinguishes lightweight fractions, such as plastics, from heavier glass and metal particles. Increasingly, facilities employ optical sorting systems to categorise polymers by type, enhancing the purity of recycled plastic streams (CENELEC, 2018). Subsequently, concentrated fractions particularly printed circuit boards (PCBs) are processed via pyrometallurgy, hydrometallurgy, or electrochemical routes. Industrial smelters demonstrate high efficiency in base metal recovery, while hydrometallurgical leaching is preferred for extracting lithium and rare earth elements from complex devices (Tuncuk et al., 2012). Material recovery thus sits at the centre of the EU’s circular economy strategy, balancing environmental protection with resource security.

A comparative environmental impact assessment by Rocchetti et al. (2013), using life cycle analysis applied to a portable prototype hydrometallurgical plant processing WEEE residues from multiple device categories, reported a global warming potential of 25.9 kg CO₂ per kilogram of recovered metal from PCBs a figure that, while lower than primary metal mining for most precious metals, underscores the importance of also valorising the non-metallic residue streams generated downstream of metal recovery rather than consigning them to incineration or landfill.

5. Residual Waste Management and Disposal: Despite advanced recovery processes, certain WEEE fractions remain unrecyclable due to contamination or economic unviability. These include fine sludges, plastics containing brominated flame retardants, and leaded glass from legacy cathode ray tubes (CRTs). These residues require stringent management to mitigate long-term ecological and public health risks (Tsydenova & Bengtsson, 2010).

Disposal involves specialised operations: high-temperature incineration with flue-gas cleaning neutralises toxic organics in contaminated plastics, while heavy-metal-rich wastes may undergo stabilisation or vitrification prior to landfilling. The objective is to ensure only inert materials reach final disposal sites. While improvements in recovery efficiency are reducing residual volumes, the existence of these fractions underscores the need for continued innovation in polymer recycling and the management of legacy hazardous waste streams (Breivik et al., 2007).

Although the proportion of residual waste is gradually decreasing thanks to improvements in recovery efficiency, its proper management remains critical. Operators are required to monitor and report recovery and recycling rates, ensuring that recycling targets are met and that residues are minimised. More importantly, the existence of these fractions underscores the need for ongoing innovation in WEEE processing, particularly in the fields of advanced polymer recycling, safe handling of legacy waste streams, and improved recovery of fine particulate residues.

1.3.1 Conventional Metallic E-Waste Recycling Methods:

E-waste recycling represents a critical industrial response to the escalating environmental, economic, and resource challenges of the digital age. By providing a structured pathway for reclaiming valuable secondary raw materials, recycling facilitates the mitigation of environmental degradation and the preservation of the planet's finite natural reserves. Electronic waste is characterised by its extreme heterogeneity, consisting of a complex blend of precious and base metals, polymers, glass, and specialised ceramics. The effective recovery of these constituents requires highly tailored, multi-stage strategies designed to maximise resource efficiency while minimising the carbon and chemical footprint of the recovery lifecycle itself. Globally, these efforts utilise a synergistic combination of

physical, chemical, and biological methodologies, each engineered to address specific material properties and varying degrees of recyclability to ensure a sustainable circular economy.

1.3.1.1 Physical Separation/Mechanical Separation:

As established by Menad (2016), the initial phase of metallic e-waste recycling is governed by mechanical processing, which serves to liberate and categorise materials before refined metallurgical treatment. **Shredding** constitutes the first and most pivotal operation in this sequence, involving the mechanical comminution of discarded electronics into homogenised fragments. This process is multi-functional: it achieves significant volume reduction, physically detaches disparate components such as resins and copper laminates, and exposes internal elements that would otherwise remain inaccessible within intact housings. Beyond logistical ease, controlled shredding facilitates safer handling by sequestering hazardous components in a regulated environment, thereby minimising the risk of toxic exposure during subsequent processing stages.

Following comminution, the material stream undergoes **magnetic separation** to isolate ferrous components, such as iron and steel. By utilizing high-intensity magnets, these metals are extracted from the bulk mixture, effectively purifying the remaining non-ferrous and non-metallic fractions. This stage is indispensable for preventing cross-contamination in high-temperature metallurgical stages and ensures that ferrous materials are sorted with high precision to meet industrial standards.

The final mechanical stage involves **eddy current separation**, a technique specifically employed to recover non-ferrous conductors such as aluminium and copper. The operational principle of this method relies on the physics of electromagnetic induction, where a rapidly rotating magnetic rotor creates a dynamic magnetic field. As conductive non-ferrous metals pass through this field, they experience a change in magnetic flux, inducing electrical currents or "eddy currents" within the particles. These currents generate their own opposing magnetic fields, resulting in a repulsive force that propels the metals forward into a designated collection area. In contrast, non-conductive materials such as glass and plastics, are unaffected and fall vertically due to gravity. This targeted separation ensures the efficient recovery of valuable metals while reducing the demand for virgin material extraction.

These combined processes of shredding, magnetic separation, and eddy current separation form the backbone of material recovery in e-waste recycling, ensuring the efficient extraction of valuable metals while minimising waste and environmental impact.

1.3.1.2 Metallurgical recovery:

The recovery of refined metals from mechanical concentrates is generally pursued through three distinct technological avenues:

1. Pyrometallurgy
2. Hydrometallurgy
3. Biohydrometallurgy

Pyrometallurgical:

Pyrometallurgical processes, as reviewed by Cui and Zhang (2008), utilise high-temperature thermal treatments to extract valuable metals from complex electronic assemblies. This pathway is particularly effective for the bulk recovery of precious metals like gold and silver, alongside base metals such as copper and lead. While incineration is sometimes utilised to combust organic resins and plastics thereby reducing waste volume, it necessitates stringent emission control systems to prevent the atmospheric release of toxic dioxins, furans, and particulate matter.

The primary pyrometallurgical operation, smelting, involves heating the e-waste in furnaces to temperatures exceeding 1,200°C, causing metals to melt and separate from non-metallic slag.

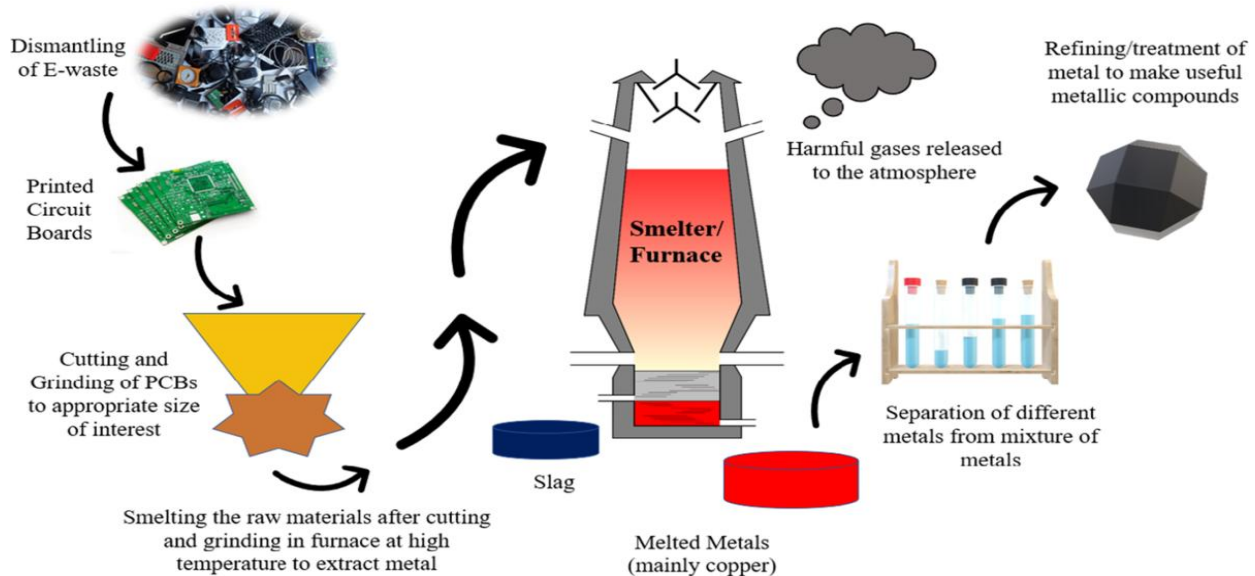


Figure 5: Pyrometallurgical Process (Javed & Singh, 2023)

Although smelting is advantageous for processing vast volumes of heterogeneous waste, it remains energy-intensive and can produce hazardous emissions if not managed with rigorous environmental controls.

Consequently, there is a growing interest in developing more sustainable and less energy-demanding alternatives, such as hydrometallurgical and bio-metallurgical processes, to complement or replace traditional pyrometallurgical techniques.

Hydrometallurgy

The hydrometallurgical process is a chemical-based method widely employed for recovering valuable metals from e-waste. The hydrometallurgical route is a sophisticated chemical-based framework widely recognised for its superior selectivity and significantly lower energy intensity relative to pyrometallurgical smelting. This methodology utilises aqueous chemistry to selectively dissolve metallic components from complex e-waste matrices, such as Printed Circuit Boards (PCBs), facilitating the recovery of high-purity precious metals, including gold, silver, and palladium, alongside base metals like copper, nickel, and cobalt (Cui and Zhang, 2008).

As established by Habashi (2000), the process is fundamentally predicated on the leaching stage, wherein target metals are transitioned into a soluble ionic state within a pregnant leach solution (PLS). The efficiency of this stage is governed by the choice of lixiviant, where acidic leaching utilises high-concentration mineral acids, specifically sulphuric acid, hydrochloric acid, and nitric acid or potent mixtures like *aqua regia* to dissolve base metals and specific

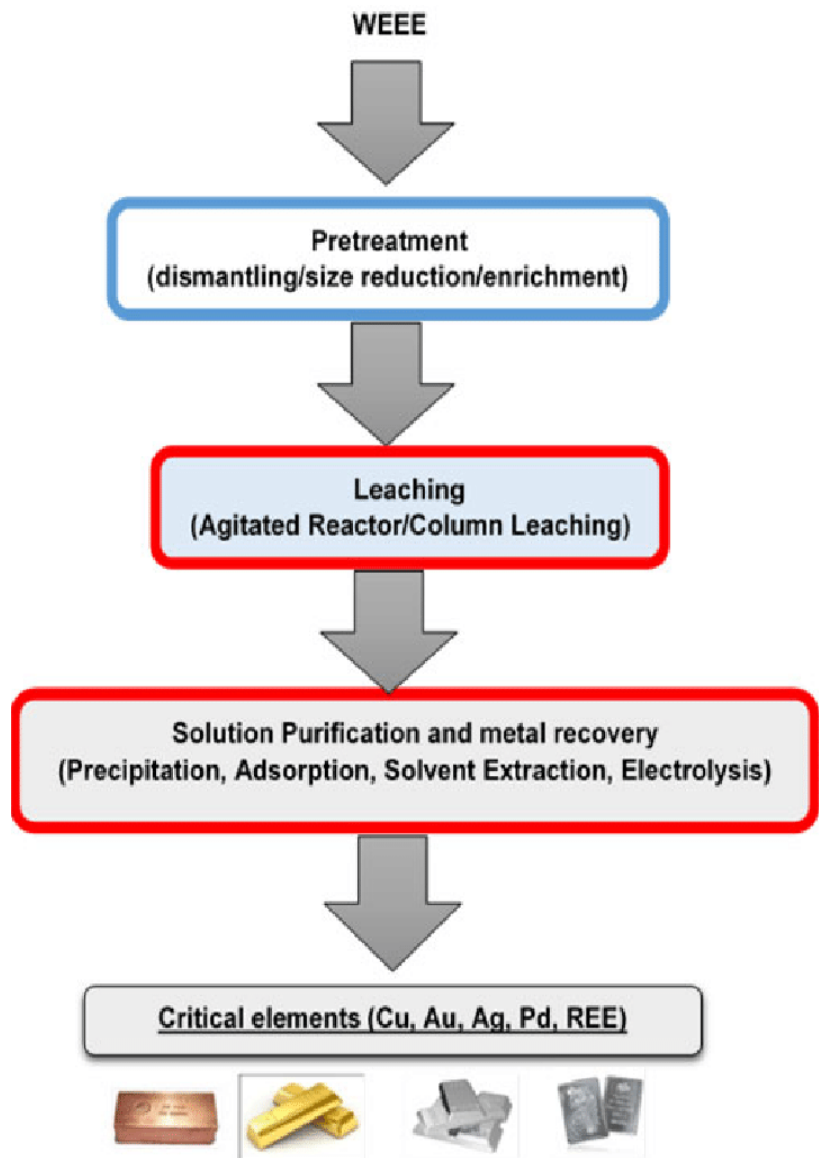


Figure 6: Hydrometallurgical Process (Sethurajan et al., 2019)

noble fractions. Alternatively, alkaline and cyanide leaching are significantly effective for gold and silver extraction, though they necessitate rigorous environmental safeguards due to their high toxicity, leading to increased research into thiosulphate or ammonia-based leaching as more sustainable, less hazardous alternatives.

Following dissolution, the leachate undergoes solution concentration and purification to isolate target metal ions from co-dissolved impurities, which is achieved through solvent extraction, where organic

phases selectively sequester metal ions, or ion exchange, utilizing resins with high molecular affinities for specific elements. The terminal metal recovery phase utilises electrochemical or chemical reduction techniques to revert ions into solid metallic forms. In electrowinning, an electric current is passed through the purified solution to deposit target ions onto a cathode, while cementation involves introducing a more reactive metal to displace and precipitate a less reactive target through a redox reaction. Additionally, controlled thermal or chemical adjustments allow metal salts to be crystallised from the purified solution for industrial reuse. While hydrometallurgy offers precise control and reduced atmospheric emissions, it requires intensive management of chemical reagents and liquid effluents to prevent the contamination of local water systems.

Hydrometallurgy offers several important advantages that make it highly relevant in modern recycling and extractive metallurgy. It is well known for its ability to achieve high recovery rates, particularly when dealing with precious metals and specialty elements that are difficult to extract through other methods. Compared with pyrometallurgy, hydrometallurgical operations generally require lower energy input, which makes them more attractive in terms of energy efficiency and sustainability. Another major strength lies in their selectivity: different metals can be targeted and recovered in a controlled manner, which is especially valuable when treating complex waste streams such as electronic waste. In addition, depending on the reagents and processes employed, hydrometallurgy can generate fewer atmospheric emissions, positioning it as a cleaner alternative in some contexts.

At the same time, the technique presents its own challenges. The reliance on strong acids, bases, or other chemical reagents requires careful handling and strict management of waste streams to avoid occupational and environmental hazards. If effluents are not treated properly, there is a risk of contaminating water sources, which makes environmental monitoring and control essential. The processes themselves are often complex, demanding precise control over parameters such as temperature, pH, and reagent concentration to ensure efficiency and reproducibility. Moreover, the economic cost of chemical reagents and the infrastructure needed for effective waste treatment can be significant, sometimes offsetting the environmental and technical benefits.

Biohydrometallurgy:

Bio-metallurgical processing represents a significant change toward sustainable resource reclamation, utilizing biological agents, primarily specialised microorganisms to facilitate the recovery of valuable metallic fractions from electronic waste. This methodological framework leverages the inherent biochemical capacity of specific microbes to interact with and transform solid-phase metals into soluble forms, positioning it as an ecologically superior alternative to traditional pyrometallurgical

and hydrometallurgical pathways. By significantly reducing reliance on intensive energy inputs and aggressive chemical reagents, bio-metallurgy aligns with circular economy objectives to minimise environmental footprints while potentially enhancing selectivity in the extraction of specific target metals (Brierley & Brierley, 2013).

The fundamental mechanism of this approach is bioleaching, a process that employs acidophilic bacteria, such as *Acidithiobacillus ferrooxidans*, *A. thiooxidans*, and *Leptospirillum ferrooxidans*, alongside fungal strains including *Aspergillus niger* and *Penicillium simplicissimum*. Once cultured and introduced to pre-treated e-waste, these microbes drive metal solubilization through diverse pathways, including the direct oxidation of metal sulphides, indirect oxidation mediated by ferric iron (Fe^{3+}), and acidolysis triggered by the secretion of organic acids. The efficacy of bioleaching is strictly contingent upon the rigorous optimisation of environmental parameters, requiring precise calibration of pH levels, thermal conditions, dissolved oxygen availability, nutrient flux, and pulp density to maintain microbial viability and kinetic efficiency (Pant et al., 2012).

The transition from biological mobilization to final reclamation is managed through integrated Metal Recovery and Residue Management phases. Following the liberation of metals into the aqueous leachate, the solution is partitioned from the solid fraction and processed via conventional hydrometallurgical techniques, specifically solvent extraction, ion exchange, chemical precipitation, or electrowinning to achieve high-purity metal outputs. Concurrently, the residual solid matter necessitates specialised stabilisation and neutralisation to mitigate the risk of secondary environmental contamination, though it may undergo further scrutiny to reclaim trace elements that persist after primary treatment.

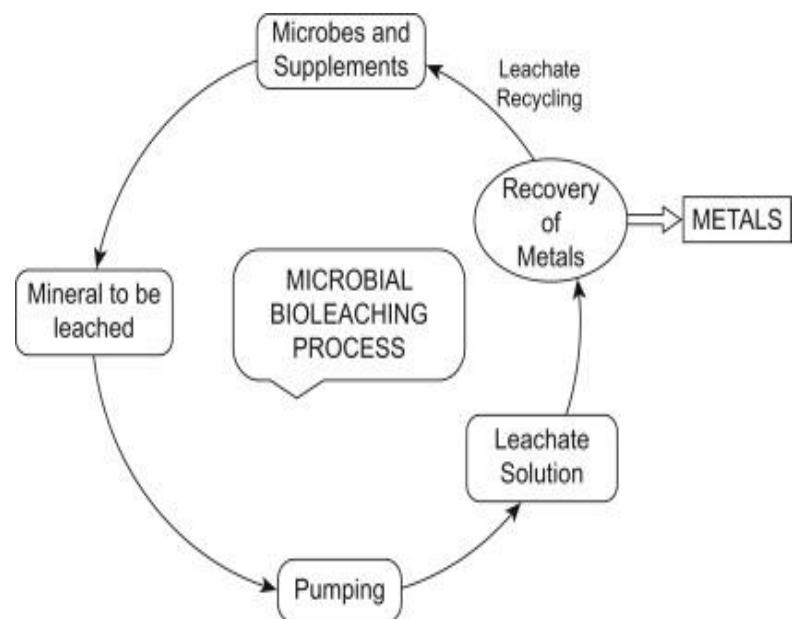


Figure 7: Bio-hydrometallurgical Process Flowchart.
(Kumar & Yaashikaa, 2020)

In the broader context of extractive metallurgy, bio-metallurgy is distinguished by its lower energy intensity and reduced reliance on concentrated chemical reagents. Unlike pyrometallurgy, which is characterised by high-temperature, energy-intensive furnace operations, or hydrometallurgy, which

necessitates the management of concentrated chemical volumes, bio-metallurgical systems operate under ambient pressures and temperatures. This characteristic not only reduces the carbon intensity of the recycling chain but also contributes to potential cost-effectiveness through the use of easily cultured biological consortia that can be tailored for high selectivity in certain systems (Brierley & Brierley, 2013). Consequently, the technology is increasingly viewed as an essential complementary strategy, particularly optimised for low-grade residues or highly complex waste streams where conventional thermodynamic or chemical methods prove inefficient or environmentally prohibitive.

However, the widespread industrial institutionalization of bio-metallurgy is currently constrained by significant technical and kinetic barriers. A primary impediment is the protracted duration of microbial metabolic processes, which necessitates considerably longer residence times than thermal or purely chemical extraction methods. Furthermore, these biological systems exhibit extreme sensitivity to their operating environments; maintaining optimal physiological conditions can be both technically complex and economically demanding at scale. The presence of inhibitory substances within the e-waste stream, including high concentrations of heavy metals or toxic flame retardants, often suppresses microbial activity and reduces overall process yield. These challenges, combined with the complexities of scaling laboratory-proven protocols to industrial volumes, represent the current frontier of bio-metallurgical research (Rawlings & Johnson, 2007). Even though the microbial phase itself is inherently cleaner, the resulting solid residues still demand rigorous end-of-life management to ensure that the promise of a "green" recycling solution does not result in unintended secondary pollution.

While metallic fractions attract the most attention because of their economic value, e-waste also contains a substantial proportion of non-metallic materials, and their recovery is equally essential for achieving a sustainable recycling chain. Metals and non-metals are fundamentally linked in e-waste management: focusing only on metals leaves behind bulky, environmentally harmful fractions, while addressing non-metals closes the loop by reducing landfill dependence and promoting a truly circular economy.

1.3.2 Conventional Non-Metallic E-Waste Recycling Methods:

The recycling of non-metallic fractions from electronic waste represents a major challenge due to the heterogeneous composition of plastics, glass, ceramics, and composite materials present within electronic devices. Unlike metallic components, which often possess high intrinsic economic value, non-metallic materials require more complex separation and recovery strategies to achieve sustainable and economically viable recycling. Nevertheless, effective management of these fractions

is essential for reducing landfill dependency, conserving natural resources, and minimising the environmental impacts associated with e-waste disposal.

Non-metallic materials are commonly separated using differences in physical properties such as density, electrical conductivity, and optical characteristics. **Density**-based separation techniques are widely employed for sorting mixed plastic streams. In these systems, plastics with lower densities float in water-based media, whereas denser materials sink, enabling efficient separation according to material type. Similar principles are applied in air classification systems and hydro-cyclones, where air currents or centrifugal forces facilitate separation based on density differences. Meneses Quelal (2021) emphasised the effectiveness of density-based technologies for the recovery and segregation of mixed plastic fractions generated during e-waste processing.

Electrostatic separation is another important physical recycling method for non-metallic e-waste. Xue et al. (2012) highlighted the application of electrostatic separators for recovering plastics from shredded electronic waste by exploiting the contrasting electrical properties of metals and polymers. Conductive metals respond strongly to electrostatic fields and are deflected accordingly, whereas non-conductive plastic materials remain largely unaffected. This differential behaviour allows efficient separation of plastic fractions from metallic contaminants and improves the purity of recycled materials.

In recent years, **optical sorting** technologies have become increasingly important in advanced plastic recycling systems. Optical sorting utilises light sensors and spectroscopic techniques to identify and separate plastics according to their optical and chemical properties. Hopewell et al. (2009) discussed the importance of near-infrared (NIR) sorting systems in achieving high-quality plastic recycling with reduced contamination levels. NIR spectroscopy identifies plastics based on their specific spectral fingerprints within the near-infrared region, while camera-based systems classify materials according to visual features such as colour, size, and shape. These technologies provide high-speed and high-precision sorting, which is essential for producing recycled plastics suitable for high-value industrial applications.

In addition to physical separation methods, **thermal recycling** approaches are widely employed for managing non-metallic e-waste fractions, particularly plastics that are difficult to recycle mechanically. One of the most significant thermal technologies is pyrolysis, a process involving the thermal decomposition of plastics under oxygen-deficient conditions. During pyrolysis, polymers are converted into valuable products including oil, gas, and char. Fisher (2006) provided a comprehensive

overview of pyrolysis technologies for converting e-waste plastics into secondary fuels and carbon-based materials. The resulting oils may serve as alternative energy sources, while char products can be utilised as industrial carbon fillers. Despite these advantages, pyrolysis processes are often associated with high energy demands and require sophisticated gas treatment systems to control potentially harmful emissions.

Incineration is another thermal management method used for non-recyclable plastic fractions. Through controlled combustion, incineration enables energy recovery in the form of heat and electricity generation. However, Kiddee et al. (2013) emphasised that although incineration offers energy recovery potential, it also poses considerable environmental risks due to the possible release of toxic pollutants such as dioxins and furans. These emissions can have severe environmental and human health consequences if advanced filtration and emission-control technologies are not implemented. Consequently, while thermal methods offer practical solutions for certain waste streams, careful operational control and environmental safeguards remain essential to minimise secondary pollution.

Chemical recycling technologies have also gained increasing attention as sustainable alternatives for recovering high-value materials from plastic waste. These methods involve breaking down polymers into monomers or intermediate compounds that can subsequently be reused in the production of new plastics. Hydrolysis is one of the most extensively studied depolymerization processes, particularly for polyethylene terephthalate (PET). Babaei et al. (2024) described hydrolysis as a key chemical recycling pathway in which water and catalysts are used to decompose PET into its original monomers, including terephthalic acid and ethylene glycol. The recovered monomers can then be repolymerised into high-quality plastics. However, the efficiency of hydrolysis depends strongly on operational parameters such as temperature, pressure, and catalyst selection, and further optimisation is still required for large-scale industrial implementation.

Another important chemical recycling strategy is **solvent dissolution**, in which specific solvents selectively dissolve target polymers while leaving contaminants and unwanted materials behind. Following dissolution, plastics can be recovered through precipitation or re-extraction processes, resulting in highly purified recycled products. Achilias et al. (2007) highlighted solvent-based recycling as an effective approach for processing mixed plastic waste streams and producing recycled polymers suitable for high-value applications.

Glass recovery also constitutes a critical component of non-metallic e-waste recycling. Because glass can be repeatedly recycled without substantial loss of quality, its recovery contributes significantly to resource conservation and waste reduction. Historically, cathode ray tube (CRT) displays represented a major source of recyclable glass in electronic waste. During CRT recycling, panel glass and funnel glass are separated due to differences in composition and contamination levels. Panel glass may be reused in construction materials such as tiles and concrete aggregates, whereas funnel glass, which contains significant amounts of lead, requires specialised treatment for lead recovery or safe reuse in applications such as lead-acid battery production. Jang and Townsend (2003) noted that the decline of CRT technologies has created economic and technical challenges for existing CRT recycling infrastructure.

The transition toward flat-panel and plasma display technologies has introduced new recycling challenges. Wang et al., (2015) discussed recent advancements in recycling technologies specifically designed for modern flat-panel displays. Although these displays contain lower concentrations of hazardous substances such as lead compared to CRT systems, recovering high-purity glass and valuable materials including indium and tin remains technically demanding. Recycling processes typically involve crushing and sorting operations to separate glass from plastics, metals, liquid crystals, and other contaminants before remelting and reuse in new glass products.

Despite advances in recycling technologies, certain non-metallic fractions remain unsuitable for recovery and are ultimately disposed of through landfilling. These residual streams frequently consist of heavily contaminated plastics, mixed composite materials, or hazardous residues that cannot be economically recycled. Modern landfills incorporate engineered systems for leachate collection, groundwater protection, and methane recovery; however, landfilling remains the least desirable waste management option due to its long-term environmental implications and the permanent loss of potentially recoverable resources. Kiddee et al. (2013) identified landfilling as the final management option for non-recyclable fractions generated during e-waste processing.

Overall, the effective recycling and management of non-metallic e-waste fractions are essential for achieving sustainable electronic waste management and advancing circular economy principles. The recovery of plastics and glass reduces pressure on virgin resource extraction while minimising environmental pollution associated with improper disposal. Although significant progress has been achieved through physical, thermal, and chemical recycling technologies, major challenges remain regarding contamination, process efficiency, economic feasibility, and hazardous residue management. Consequently, continued research and technological development are necessary to

improve recovery efficiency, reduce environmental impacts, and support the transition toward more sustainable and resource-efficient e-waste recycling systems.

1.3.3 Circular Economy in E-Waste Management:

The concept of a circular economy (CE) shifts away from the traditional linear “take-make-dispose” pattern to one in which resources are kept in use for as long as possible, the maximum value is extracted from them while in use, then products and materials are recovered and regenerated at end of life. This is achieved through a hierarchy of strategies, often summarised as the **"10 R" principles**: prioritise **refuse, rethink, reduce, reuse, repair, refurbish, remanufacture, repurpose, recycle and recover** with final disposal (incineration/landfill) as the last resort (Potting et al., 2017; Malooly & Daphne, 2023). In the context of e-waste, this means designing systems where metal and non-metal fractions are recovered, reused, remanufactured, or recycled in closed loops, minimising waste and environmental harm.

A central rule is designing for circularity. This means creating electronics that are easier to disassemble and repair, with components that can be readily recovered. The challenges encountered with intricate PCB structures and the complex separation of materials directly highlight why this principle is so vital. When products are designed with their end-of-life in mind, then mechanical and chemical separation methods become far more efficient, allowing for a higher yield of both metallic and non-metallic fractions.

This focus on end-of-life is reinforced by Extended Producer Responsibility (EPR). EPR mechanisms hold manufacturers accountable for their products once they're no longer in use. This isn't just a policy; it's an economic incentive. By shouldering the cost of recycling, companies are encouraged to design products that are cheaper and simpler to process. This directly supports the need for advanced recovery methods, as producers seek out the most cost-effective and efficient ways to handle the e-waste, they are now responsible for. Countries like Switzerland, South Korea and Japan have implemented schemes like EPR, where manufacturers are obligated to finance end-of-life management of their electronic devices. Implementation of this program has demonstrated positive outcomes and increase in recycling rate.

The ultimate goal of these efforts is urban mining. This concept reframes e-waste as a rich, human-made "mine" of valuable materials. Instead of depending on environmentally destructive virgin mining, we can recover critical raw materials (CRMs) like gold, copper, and rare earths from discarded devices. The pyrometallurgical and hydrometallurgical methods previously mentioned for metal recovery are the very tools of this urban mining operation. They allow us to extract these

precious resources from the complex e-waste stream, which is often far more concentrated than natural ore.

The success of a circular economy hinges on closed-loop supply chains. This means that once the metals and non-metals are recovered, they must be fed back into new manufacturing processes. This creates a continuous cycle, minimising the need for new virgin resources and maximizing the value of what have already been produced. The repurposing of non-metallic PCB material for a high-value application like wastewater treatment is a perfect example of closing this loop in a creative and impactful way.

When the principles of a circular economy are effectively implemented in the e-waste management, a vast range of interconnected benefits arise, impacting the economy, the environment, and the society.

A primary benefit is the enhanced resource efficiency. Metals, such as gold, copper, and silver, alongside non-metals like plastics and glass, are recovered and returned to the production cycle. Clarizia (2023) emphasised that urban mining from e-waste provides a sustainable alternative to traditional mining, which is crucial for conserving finite resources. This practice reduces the demand for virgin material extraction, a process that is often energy-intensive and environmentally damaging. The recovery of valuable metals from e-waste substantially contributes to resource conservation.

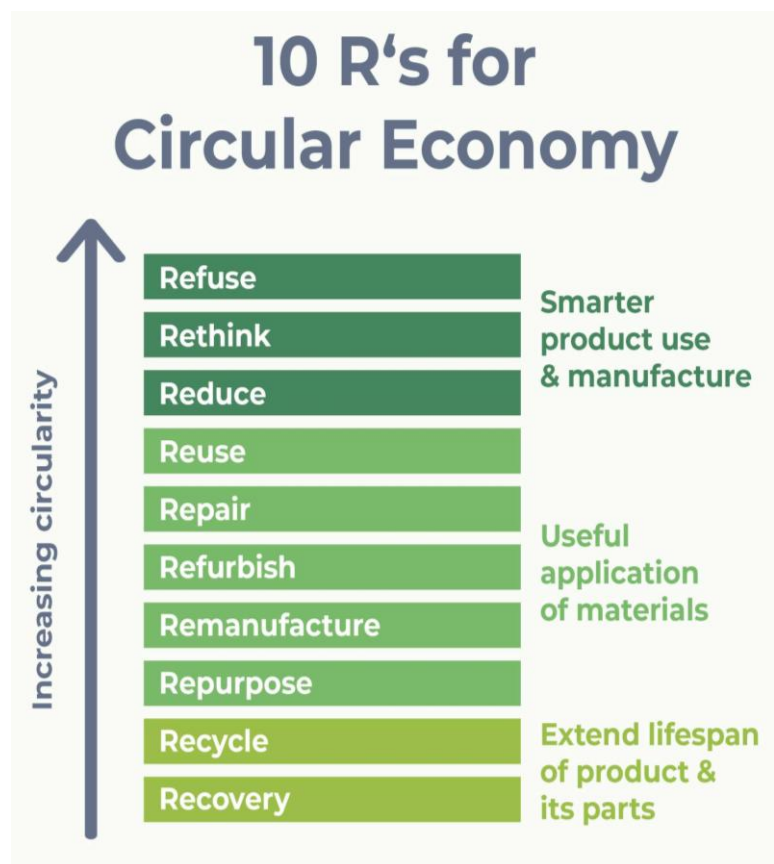


Figure 8: 10R's of Circular Economy

Apart from the resource recovery, the effective implementation of a circular economy in e-waste management provides significant environmental benefits as well. As Murthy and Ramakrishna (2022) note, proper recycling and urban mining techniques are effective in reducing pollution and conserving energy. By reducing the volume of e-waste sent to landfills, the risk of hazardous material leaching

into soil and groundwater is mitigated. This approach also avoids the harmful emissions associated with incineration. The recovery of materials reduces the energy consumption and greenhouse gas emissions linked to mining and processing virgin materials.

From an economic standpoint, circular e-waste management creates substantial economic opportunities. The recovery, reuse, and remanufacturing of electronic components foster new business models and create jobs. Sectors specializing in recycling technology and non-virgin feedstock production gain prominence. The high value of certain metals in printed circuit boards (PCBs) provides a strong financial incentive for investment in efficient recovery methods, driving innovation in the recycling industry.

The transition to a circular e-waste economy is supported by a combination of social and policy drivers. Legislation, such as Extended Producer Responsibility (EPR), holds manufacturers accountable for the end-of-life management of their products. This policy encourages companies to design products that are durable, repairable, and easily recyclable, which aligns with the core principles of a circular economy.

As Murthy and Ramakrishna (2022) mentions that policies like EPR are the right first step, they aren't enough on their own. The reality is that even with regulations in place in two-thirds of the world, a staggering 80% of e-waste still falls through the cracks, often ending up in illegal, harmful processing systems. This glaring gap between policy and practice points to a deeper issue: a lack of global standardization and technological innovation. All e-waste, whether it's generated in Tokyo or Toronto, shares the same mix of valuable resources and dangerous hazards. However, the way it is handled, varies wildly. There's an urgent need for international leaders to come together and establish a shared understanding of what constitutes "best practice" in e-waste processing. By identifying and adopting benchmark technologies for each stage of the cycle, we can create a global standard for effective and safe recycling. This would not only streamline the process but also enhance transparency and curb the illegal, harmful trade of e-waste.

After exploring the core principles and benefits of a circular economy for electronic waste, it's clear that policy and ambition alone aren't enough. By identifying and adopting benchmark technologies for each step of the recycling process, from initial sorting to final material recovery, a global standard could be established. This would not only streamline operations and increase efficiency but also enhance transparency and effectively curb the illegal trade of e-waste. Innovation is the ultimate key to unlocking this potential. By focusing on smart, efficient, and locally adaptable solutions, we can make the circular economy a practical reality for e-waste everywhere. However, the path to a

sustainable future is not just about having the right technology, it's also about its economic feasibility. The development and adoption of these new technologies are directly tied to the financial realities of the industry, as the cost of recycling remains a key factor that either incentivises legal operations or drives the continuation of informal, illicit practices. Cost can be considered as the fundamental barrier to achieving the truly circular system.

1.3.4 E-Waste Recycling Cost and Cost-Benefit Analysis:

E-waste recycling pivots on a careful balance between operational costs and the value recovered from materials. As mentioned before, recycling e-waste have the significant social and environmental benefits, understanding the associated costs is essential for developing sustainable and scalable recycling systems. The recycling costs can be broadly categorised into collection and logistics, pre-processing and treatment, labour, infrastructure, and regulatory compliance and environmental safeguards. Mohamed et al. (2025) identifies collection and transportation as the dominant operational cost driver in regions with sparse infrastructure. Table 1 provides representative indicative cost ranges compiled from established sector studies (GIZ, 2019; Cucchiella et al., 2015; Kang & Schoenung, 2006). These references provide a composite picture of cost structures in the sector, highlighting capital intensity, scale effects, and operational expenditures shaping recycling outcomes.

1.3.4.1 Cost Details:

Table 1: Representative indicative cost ranges for e-waste recycling operations. Sources: GIZ (2019); Cucchiella et al. (2015); Kang and Schoenung (2006). Values are approximate and vary with facility scale, waste composition, and regional conditions.

Category	Description	Estimated range (USD / tonne)
Collection & Logistics	Public awareness, transport, take-back infrastructure, reverse logistics	\$80 – \$150 / t.
Labour	Wages for dismantling, sorting, refurbishment, testing (Skilled + Health and Safety)	\$120 – \$250 / t (Labour typically ~20–35%).
Infrastructure	Facility construction, shredders, sorters, conveyors, utilities, PPE, compliance IT	\$100 – \$200 / t
Material recovery (processing)	Shredding, mechanical separation, chemical/hydrometallurgical/pyrometallurgical steps, refining, emissions control.	\$200 – \$350 / t (Higher for emissions control).
Hazardous waste management	Safe handling/disposal of PCBs, batteries, mercury lamps, CRT glass, sludges	\$50 – \$100 / t (Some hazardous streams e.g., CRT costs more in some cases).

Total Average Cost per Ton of E-Waste Processed: ~\$550–\$1050¹

¹ reflecting formal sector operations in developed economies; informal sector processing costs are substantially lower but omit environmental and health safeguard expenditures.

1.3.4.2 Direct Benefits (Revenue Streams):

On the revenue side, literature estimates return from e-waste recycling in the range of USD 700–1,450 per ton, largely driven by the recovery of precious and base metals, with smaller contributions from plastics, refurbished equipment, and EPR incentives. Metals like gold, in printed circuit boards, can generate up to half of this value, while copper and aluminium form a stable secondary revenue stream (Cucchiella et al., 2015; Chancerel & Rotter, 2009; GIZ, 2019)

Table 2: E-waste revenue streams per tonne of material processed

Revenue Stream	Description	Estimated range (USD / tonne)
Precious metals	Gold, silver, palladium recovered from PCBs, connectors, CPUs	\$400 – \$800 / t (highly sensitive to gold content and global price swings).
Base metals	Copper, aluminium from wiring, frames, motors, heat sinks	\$200 – \$400 / t . Cu alone accounts for 15–25% of revenue potential.
Plastics (if recyclable)	Sorted, flame-retardant-free plastics from housings and casings	\$50 – \$100 / t (limited by contamination and brominated flame retardants).
Refurbished device sales	Sale of tested/refurbished phones, computers, consumer electronics	Highly variable (from negligible to >\$500/t, depending on product mix, testing, demand).
EPR incentives / subsidies	EPR payments, government subsidies, eco-fees	\$50 – \$150 / t depending on the scheme.

Total Average Revenue per Ton: ~\$700–\$1,450.

1.3.4.3 Indirect and Intangible Benefits:

These following benefits are often unpriced in market systems but are critical to sustainable development goals (SDGs).

Table 3: Indirect and intangible benefits of e-waste recycling

Category	Description
Environmental Benefits	Prevents pollution (e.g., mercury, lead, cadmium), reduces landfill volume
Resource Conservation	Saves energy and raw materials (e.g., gold mining, copper extraction)
Climate Impact Reduction	Recycling 1 ton of e-waste saves ~1.44 metric tons of CO ₂ equivalent.
Job Creation	Skilled and unskilled employment in collection, testing, and refurbishment sectors
Digital Access and Equity	Refurbished devices enable affordable access to technology, especially in low-income communities

Reference: US EPA (2024), Global E-waste Monitor (2020), ILO (2019)

1.3.4.4 Net Benefit Evaluation:

Table 4: Net benefit evaluation across recycling efficiency scenarios

Scenario	Cost (USD/ton)	Revenue (USD/ton)	Net Benefit (USD/ton)
Low-efficiency system	\$1,000	\$700	–\$300 (loss)
Mid-efficiency system	\$800	\$1,000	+\$200 (gain)
High-efficiency system	\$600	\$1,300	+\$700 (gain)

These approximate values obtained from various different sources strongly depend on the volume and quantity of the collected material. Along with the market value of the metals and plastics, the efficiency of recovery technologies plays a vital role. The important factor of government support and regulations should also be kept in mind and the Extent of refurbishment and reuse, which can generate high-margin revenue streams.

1.4 Printed Circuit Boards (PCBs): A High-Value but Complex E-Waste

Fraction:

Among the many components present in discarded electronics, Printed Circuit Boards (PCBs) represent one of the most materially valuable and environmentally concerning fractions of e-waste. PCBs form the backbone of virtually all electronic devices, providing the essential infrastructure for interconnecting electronic components. Due to their widespread use in computers, mobile phones, televisions, household appliances, and industrial equipment, PCBs constitute a significant share of e-waste, both in terms of volume and material complexity.

Within this broad category, memory cards such as SD cards, microSD cards, and compact flash cards can be considered a growing sub-group of PCB-based e-waste that has attracted increasing attention in recycling markets. Unfortunately, they typically contain a combination of materials and units, making their recycling very complex and expensive. So, even if recycling e-waste and reusing their components, with a similar purpose to the original one, remain the preferred approaches, the recovery of all the components is often hindered by the intricate nature of electronic devices (Mir & Dhawan, 2021b). Extended activities in research and procedure optimisation have been performed in this sense, leading to the development of specific recycling chains, after the preliminary steps of dismantling, sorting, and the mechanical pre-treatment (such as shredding and crushing) (Niu et al., 2023).

Memory cards have various metal contact pins or connectors made of precious materials like gold or silver, which can be extracted and refined for reuse or resale (Lu & Xu, 2017). Furthermore, memory cards have a small Printed Circuit Board (PCB) responsible for electrical interconnections among different elements. Also, PCBs have an intricate composition: for ~40% weight, they are composed of metals (mainly Cu, Sn, Fe, and Pb, with fractions of Au, Ag, and Pd used as contact materials or

plating layers thanks to their electric conductivity and chemical stability); for ~30% weight, they are composed of polymers; while the remaining ~30% weight is made of ceramic–polymeric materials. For ~23% weight, this last component is made of a glassy plastic support, called fibreglass, composed of glass fibres included in an epoxy resin matrix (Ulman et al., 2018). As anticipated, up to now, the main focus of the recovery processes has been on precious metals that can be extracted from e-waste and recycled (Barragan et al., 2020), but waste PCBs (WPCBs) can be repurposed more extensively as a reservoir of raw materials for diverse applications, following a circular economy approach. Considering that any electric and electronic device contains at least one PCB, and that PCBs represent ~8% of the weight of the electronic device, the high concentration of precious and base metals makes PCBs a potentially lucrative resource for recovery. For instance, the concentration of gold in PCBs is often 40–800 times higher than in naturally occurring ores. They can be considered real “urban mining” sources, enabling the recovery of valuable resources and contributing to sustainability efforts (Hadi et al., 2014).

However, the heterogeneous and multi-layered structure of PCBs also makes them difficult to recycle. The presence of halogenated flame retardants, heavy metals like lead and mercury, and persistent organic pollutants (POPs) such as polychlorinated biphenyls pose serious environmental and health risks if not properly managed (Hagelüken, 2006). During informal or substandard recycling operations; such as open burning or acid leaching, these toxic substances can be released into the environment, contaminating soil, air, and water, and posing direct risks to human health.

Table 5: Typical PCB composition attributed to general materials groups (Blumbergs et al., 2022)

Metals (~40 wt.% in Total)	wt.% of Metals	Ceramics (~30 wt.% in Total)	wt.% of Ceramics	Plastics (~30 wt.% in Total)	wt.% of Plastics
Cu	6–27	SiO_2	15–30	Polyethylene	10–16
Fe	1.2–8	Al_2O_3	6–9.4	Polypropylene	4.8
Al	2–7.2	Alkali-earth oxides	6	Polystyrene	4.8
Sn	1–5.6	Titanates-micas	3	Epoxy resin	4.8
Pb	1–4.2			Polyvinyl chloride	2.4
Ni	0.3–5.4			Polytetrafluoroethylene	2.4
Zn	0.2–2.2			Nylon	0.9
Sb	0.1–0.4				
Au (ppm)	250–2050				
Ag (ppm)	110–4500				
Pd (ppm)	50–4000				
Pt (ppm)	5–30				
Co (ppm)	1–4000				

As a more sustainable and environmentally friendly alternative, recent efforts have explored mechanical and electrochemical processes for PCB recycling. These methods involve size reduction (comminution), followed by magnetic and electrostatic separation to isolate metal-rich fractions from non-metallic substrates such as epoxy and fibreglass. The metal-enriched fraction can then be treated using electrowinning or other electrochemical techniques to recover individual metals with reduced chemical input and lower environmental impact. In one such study, mechanical pre-processing followed by electrochemical recovery demonstrated promising results in efficiently separating and extracting copper and other base metals, without generating significant emissions or effluents. In most of the tests using electrowinning, 98% of copper was obtained. (Veit et al., 2006).

Beyond metal recovery, the non-metallic fraction of PCBs which is often overlooked in traditional recycling, is gaining attention as a functional material for environmental applications. This fraction, primarily composed of glass fibre-reinforced epoxy resin, is thermally stable and non-biodegradable, making it a disposal challenge. However, its high surface area and structural integrity open up possibilities for reuse as an adsorbent material in water treatment systems, especially for the removal of dyes, heavy metals, and other pollutants (Dong et al., 2015). Despite some other studies can be found in the literature regarding the valorisation of the non-metallic component of w-PCBs, they mainly regard its use as fillers for construction materials (phenolic moulding compounds, asphalt, concrete) or composite polymers (mainly, polypropylene and polyester the production of fuels or chemical raw materials or the development of sound-absorbing materials or other advanced materials (Javaid et al., 2024). Transforming this waste fraction into a value-added material not only supports circular economy principles but also reduces the environmental burden of landfill disposal. By utilizing its inherent surface characteristics and structural stability, the study examined its transformation into an adsorbent suitable for water treatment, with particular emphasis on the removal of dyes, heavy metals, and other pollutants. The overarching aim of this PhD thesis is to demonstrate how the conversion of this waste stream into a value-added resource contributes to circular economy principles while simultaneously reducing the environmental burden associated with landfill disposal.

PCBs illustrate the dual nature of e-waste: a rich source of recoverable materials and a complex environmental hazard. Proper recycling and valorisation strategies, particularly those that minimise emissions and maximise the recovery, are essential to harness their economic value while mitigating their ecological footprint. This critical challenge of balancing resource recovery and environmental responsibility forms the core rationale for the **Sustainable Materials Recycling Technology for Printed Circuit Boards** (SMaRT-PCBs) project, and the research herein was performed in its framework.

1.5 The SMaRT-PCB Project:

This PhD work was performed in the framework of The Sustainable Materials Recycling Technology for Printed Circuit Boards (SMaRT-PCBs) project. This is a collaborative initiative aimed at developing and validating an innovative, low-environmental-impact technology for the recovery and valorization of precious metals and plastic-glass components from selected Printed Circuit Boards (PCBs) deriving from computers and mobile phones. To achieve its mission of sustainable e-waste valorisation, the SMaRT-PCBs project is structured around the following four key goals:

1. Development of innovative Metal Recovery Technology: Developing and validating an integrated, environmentally friendly technology for extracting valuable metals such as gold, silver, palladium, and copper from PCBs. This activity is led by University of Cagliari.
2. Production of Market-Ready Recycled Materials: Generating high-quality recycled materials to stimulate market demand for secondary raw materials, thereby promoting the use of recycled content over virgin materials.
3. Minimisation of Process Waste (Zero-Waste): Reducing process residues to a minimum, effectively striving for a zero-waste outcome to limit resource loss and mitigate environmental impacts associated with waste disposal.

4. Assessment of Technical, Economic, and Environmental Sustainability: Evaluating the feasibility of a pilot supply chain dedicated to the innovative and sustainable recovery and valorisation of

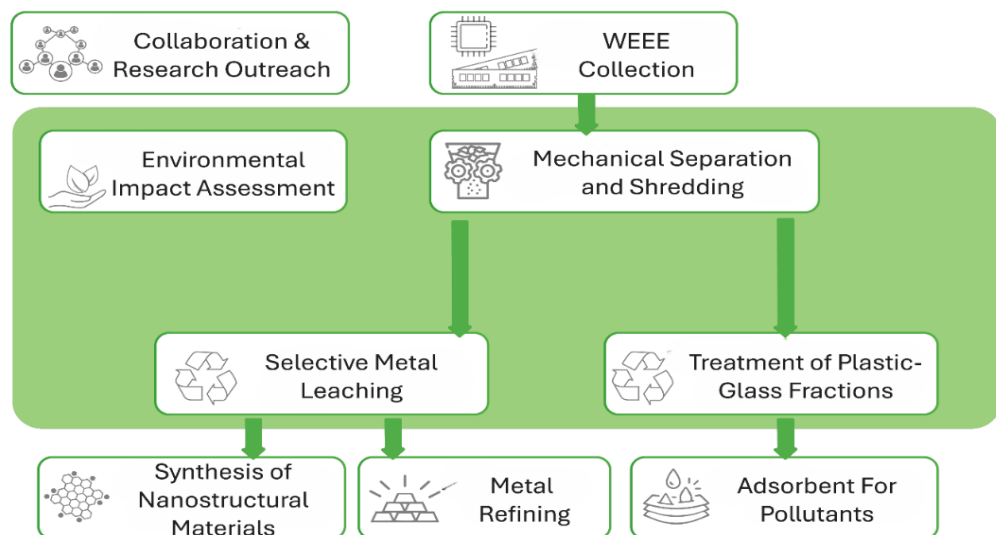


Figure 9: SMaRT-PCB Project Layout

WEEE resources, considering technical performance, economic viability, and environmental impact to ensure a holistic approach to sustainability.

These objectives are pursued thanks to the partnership between the University of Cagliari, University of Brescia and other consortium members, including Gold Fixing S.r.l, Vesti Solidale Soc. Coop., and Lombardy Energy Cleantech Cluster (LE2C). The present work directly addresses the fourth objective and the non-metallic valorisation strand, demonstrating that the residue stream produced downstream of metal recovery can be converted into high-performance water treatment materials, thereby closing the material loop within the project's own process chain.

1.6 Pollutants and Water Pollution:

A pollutant can be a substance or form of energy introduced into the environment that causes adverse effects on living organisms, ecosystems, or natural processes. They can be biological, physical or chemical in nature and they can originate from natural events such as dust storms, wild fires or volcanic eruptions, as well as from human activities including transportation, industrial production, agricultural practices and urbanization. The increasing industrialization and population growth has significantly increased the release of pollutants into the air, water, and soil, unsettling ecological balance and contributing to a range of health and environmental problems.

Pollutants can generally be categorised based on their origin and persistence. Primary pollutants are directly released from identifiable sources, such as carbon monoxide from vehicle exhausts or sulphur dioxide from burning fossil fuels. Whereas, secondary pollutants are formed in the environment through chemical reactions between primary pollutants; ground-level ozone is generated when nitrogen oxides react with volatile organic compounds under sunlight. Another important classification is between biodegradable pollutants, such as domestic sewage, which can be decomposed by natural processes, and non-biodegradable pollutants, including heavy metals, plastics and synthetic chemicals, persist in the environment for long periods and have a tendency to bioaccumulate through food chains.

Environmental contamination presents far-reaching consequences that fundamentally compromise biodiversity, erode ecosystem stability, and endanger public health. The complexity of this challenge is heightened by the tendency of pollutants to act synergistically, compounding their damaging effects and severely complicating efforts toward effective mitigation. Therefore, the successful development of sustainable remediation techniques and robust environmental management policies hinges on a sophisticated grasp of pollutant origins, physicochemical characteristics, and behaviour within natural systems. The repercussions are multifaceted, waterborne contaminants drive public health emergencies; soil contamination diminishes fertility, resulting in reduced crop productivity; and

airborne contaminants are strongly implicated in rising rates of cardiovascular and respiratory illnesses.

Among the environmental compartments affected by contamination, water systems are distinctly vulnerable, serving as the ultimate deposition zones, or final sinks, for numerous pollutants. The input of contaminants, whether from diffuse sources like agricultural runoff and household waste or point sources such as industrial effluents, it leads to their progressive accumulation in rivers, lakes, and oceans. This build-up fundamentally degrades the inherent biological integrity and significantly shifts the chemical equilibrium of these vital water bodies. Addressing this critical environmental issue requires focused research to characterise the specific fate and transport mechanisms of contaminants once they enter the aquatic environment.

1.6.1 Water Pollution:

Water pollution is the contamination of aquatic bodies, such as rivers, lakes, oceans, and groundwater, by harmful substances. As mentioned previously that pollutants can be physical, chemical, or biological, and they have far-reaching consequences for human health, ecosystems, and the environment as a whole. Worldwide different factors and sources are linked to water pollution. This includes Industrial discharge where a of variety of chemicals, heavy metals and toxic waste from industries is directly released into water bodies. In our agricultural sector fertilisers, pesticides, and animal waste from farms can wash into rivers and lakes, causing nutrient pollution and harming the aquatic life. The inadequately treated or sometimes untreated sewage contains pathogens and organic matter that can easily contaminate water sources and spread diseases. Another important and increasing water pollution source is the amount of plastic waste in rivers, seas and oceans. It badly harms the marine life and microplastics can enter the food chain (NRDC, 2024).

1.6.2 Impacts of Water Pollution:

Water pollution has emerged as a critical global challenge. According to the United Nations report (2023), a significant portion of the world's population lacks access to safe and reliable water sources. Specifically, 2.2 billion people lack access to safely managed drinking water, while 785 million individuals lack even basic water services. Furthermore, 3 billion people lack access to water quality monitoring systems, leaving them vulnerable to unknown contamination. The lack of access to safe sanitation exacerbates this issue, with 3.6 billion people lacking access to safely managed sanitation (WHO, 2021). The United Nations (2021) report on water and sanitation for all estimates that contaminated drinking water contributes to 485,000 diarrheal deaths annually.

Chemical contamination of drinking water including by industrial dyes, heavy metals, and persistent organic pollutants poses serious long-term health risks distinct from those associated with microbial contamination. Chronic exposure to synthetic dyes and their metabolites has been linked to carcinogenicity, mutagenicity, endocrine disruption, and dermal and respiratory toxicity (Al-Tohamy et al., 2022).

Beyond human health impacts, water pollution poses significant threats to aquatic ecosystems. Ocean Conservancy (2025) reports that 11 million metric tons of plastic enter the ocean each year, disrupting marine life and food chains. Nutrient pollution can trigger algal blooms, leading to oxygen depletion and the creation of "dead zones" that are detrimental to aquatic life. The economic consequences of water pollution are substantial. It negatively impacts industries such as fishing, tourism, and agriculture, while also increasing the costs of water treatment and healthcare.

Water pollution encompasses various challenges. One major issue is the presence of bacteria and viruses that render water unsafe for consumption. Additionally, chemical pollutants significantly degrade water quality. These pollutants include inorganic molecules such as heavy metals and organic compounds such as microplastics, cosmetics, pesticides, and dyes. At high concentrations, organic dyes can increase oxygen demand, reduce light penetration, and hinder photosynthesis and plant growth. Even at lower concentrations, these dyes may exhibit toxicity, mutagenicity, and carcinogenicity, potentially entering the food chain, causing bioaccumulation and secondary pollution. Exposure to these compounds can lead to skin irritation, allergies, and gastrointestinal or respiratory diseases (Al-Tohamy et al., 2022).

Water pollution is a complex and multifaceted problem that requires urgent action at all levels. By reducing pollution from various sources, improving water treatment and sanitation, and promoting sustainable practices, we can protect our water resources and ensure a healthy environment for present and future generations.

The escalating severity of water pollution underscores the imperative for immediate and comprehensive action. Implementing stringent regulations, enhancing monitoring systems, and investing in sustainable infrastructure are critical steps toward safeguarding public health and preserving environmental integrity.

The extensive impacts of water pollution on human health, ecosystems, and economies highlight the urgency of understanding its underlying sources and mechanisms. Among the various contributors, industrial discharges, particularly from textile and dye-manufacturing sectors represent a major and persistent cause of aquatic contamination. These industries release complex mixtures of chemical

pollutants that not only degrade water quality but also pose long-term ecological and toxicological risks. To better comprehend the scope of this problem, it is essential to examine how specific pollutants, such as synthetic dyes, contribute to the broader issue of water pollution.

The textile and dye-manufacturing industries are among the largest generators of industrial wastewater worldwide. It is estimated that during textile dyeing operations, approximately 10–15% of the applied dyes do not adhere to the fabric fibres and are instead discharged into effluent streams (Yaseen & Scholz, 2019). These effluents often contain not only residual dyes but also a complex mixture of salts, surfactants, heavy metals, and auxiliary chemicals, making the wastewater difficult to treat using conventional methods.

Dyes in wastewater pose several challenges and risks including colour contamination, reduced photosynthesis, non-biodegradation and bioaccumulation. Even at low concentrations of less than 1 mg/L some dyes impart strong colouration. not only aesthetically degrades water bodies but also blocks sunlight penetration, which is essential for aquatic photosynthesis. Reduction in available light decreases the primary productivity by limiting photosynthesis in phytoplankton and submerged aquatic vegetation. This leads to oxygen depletion (hypoxia), which threatens the survival of fish and other aquatic organisms (Verma et al., 2012). Dyes are designed for chemical stability which makes them resistant to biodegradation. Chemically stable Azo dyes account for over 60-70% of global dye use. Non-biodegradability allows them to accumulate in the environment, leading to chronic exposure risks for the aquatic ecosystems (Robinson et al., 2001). Being non-degradable, they can be absorbed by aquatic organisms, potentially entering the food chain and can have hazardous effects to all food chain including humans.

There are many such incidents of dye pollution which are documented and have affected the entire ecosystem. To understand the severity of dye pollution in water systems; one prominent example is of Ganges River in India. The surrounding Kanpur region is home to hundreds of textile mills and tanneries. Effluents from these industries often bypass treatment facilities or receive inadequate treatment. A report by Pollution Assessment: River Ganga published in 2013 (Kamyotra et al., 2013) shows significant dye concentrations along with heavy metals such as lead, arsenic and chromium. The water samples showed high chemical oxygen demand (COD) and low dissolved oxygen which indicates heavy organic and dye pollution. Gastrointestinal issues, skin diseases and respiratory problems have been reported by local communities, linking these problems to the contaminated water.

Another example is Citarum River in Java, Indonesia. It is considered as one of the most polluted rivers in the World. Over 500 textile factories are responsible for the contamination of Citarum river

in Indonesia. Research conducted by Greenpeace International (2013), along with the Indonesian environmental agencies mentioned that frequently untreated dye effluents were released into the river. The water tests found high levels of persistent dyes, lead and mercury. These levels were far beyond the WHO safety limits. Waterborne diseases and aquatic life mortality are common, affecting thousands of residents in the surrounding areas who are dependent on the river for general use and irrigation purposes.

1.6.3 Industrial Dyes: History and Modern Usage:

Industrial dyes can be defined as the ability to add colour to a variety of substrates, including textiles, leather, plastics, paper, cosmetics, pharmaceuticals, and food items. It is a class of synthetic or natural organic compounds. These substances can penetrate and bind with the material to be dyed chemically through covalent or ionic bonding or physically through adsorption because they are usually soluble in the medium in which they are applied (Lellis et al., 2019).

In contrast to pigments, which are insoluble particles suspended in a medium and need a binder to stick to a surface, dyes are soluble and have the ability to interact with substrates at the molecular level. This solubility makes dyes more appropriate for applications requiring consistent and long-lasting colouration by enabling strong fixation and even colour distribution (Gupta & Suhas, 2009).

1.6.3.1 Historical Origins of Dyes:

The history of dyeing is thousands of years old, with the earliest records found in ancient India, China, and Egypt. The initial natural dyes were derived from plants, animals, and minerals. Indigo (derived from *Indigofera tinctoria*) and madder root (the origin of alizarin) were used to a large extent in ancient India and in the Middle East for dyeing material. The renowned Tyrian purple, which was derived from the secretions of the Murex Sea snail, was valuable in ancient Rome and was symbolic of royalty because it was rare and came with an expensive price (Cardon, 2007).

Industrial application of dyes increased significantly with the development of synthetic dyes. The first synthetic dye, mauveine or aniline purple, was synthesised by William Henry Perkin by accident in 1856 while attempting to synthesise an antidote for malaria. This was the beginning of the age of synthetic dyes and transformed textile manufacture by generating reproducible rich colours on a much smaller scale than the application of natural dyes (Travis, 1993).

1.6.3.2 Importance and Modern Usage of Dyes:

Dyes play a vital role in modern industry and daily life, extending far beyond textiles. Their ability to deliver vivid, durable, and diverse colours, along with specific chemical and biological functionalities, has made them essential in sectors such as textiles, plastics, medicine, food, and cosmetics.

The global demand for dyes spans across multiple industrial sectors, each relying on colourants for both functional and aesthetic purposes. Among these, the **textile industry** remains the dominant consumer, accounting for more than 70% of total dye production worldwide (Hunger, 2007). The continuous demand for durable, vibrant, and colourfast fabrics has driven the development of specialised dye classes suited to different fibres. For instance, reactive dyes are widely applied to cotton and other cellulose-based textiles due to their ability to form covalent bonds with hydroxyl groups, resulting in excellent wash-fastness and colour stability. Disperse dyes, on the other hand, are designed for hydrophobic fibres such as polyester, and are applied under high-temperature conditions to ensure proper diffusion into the fabric matrix. Vat dyes are well-known for their superior colourfastness and are employed in the production of denim and workwear through reduction and oxidation processes (Bechtold & Mussak, 2009). As global environmental regulations, such as “REACH” in Europe, have become increasingly stringent, the textile industry has been compelled to innovate towards more eco-friendly and biodegradable dye formulations.

Beyond textiles, dyes play an integral role in the **leather and paper industries**, where they serve both functional and decorative purposes. In leather finishing, aniline dyes are commonly used to enhance the natural grain of the material, producing rich and uniform tones valued in high-end fashion and upholstery. Their deep penetration into the leather matrix ensures long-lasting colour with minimal fading. Similarly, in the paper industry, dyes such as direct and acid dyes are used to impart tint and brightness to products like tissue papers, newsprints, and packaging materials, depending on the desired aesthetic finish (Bechtold & Mussak, 2009).

The **plastics and polymer sector** also relies heavily on colourants to achieve consistency, durability, and visual appeal in synthetic materials. Solvent dyes which are known for their solubility in non-polar media, are extensively used in colouring plastics such as polystyrene, polycarbonate, and acrylics, providing vibrant shades and thermal stability without compromising mechanical properties. In contrast, pigment dyes, which are insoluble but finely dispersed within the polymer matrix, are employed where opacity and UV resistance are required, particularly in large-scale plastic production (Bechtold & Mussak, 2009).

In their work Downham and Collins (2000) mentioned in detail about cosmetics and pharmaceutical industries, food industries and use of dyes in medical and biological sciences. In **cosmetics and pharmaceutical industries** dyes serve critical roles in ensuring product identification, safety, and consumer appeal. Certified cosmetic dyes such as FD&C Red No. 40 and D&C Yellow No. 10 are tightly regulated for purity and toxicological safety by agencies including the FDA (U.S.) and ECHA (Europe). In pharmaceuticals, colourants assist in distinguishing drugs by dosage or purpose and enhance patient compliance by improving product recognition and trust.

The **food industry** represents another major domain where dyes are used to restore or enhance the appearance of processed products. Both natural colorants like curcumin (from turmeric), annatto, and carotenoids and synthetic dyes like tartrazine (E102) are employed to maintain the visual appeal of food items and convey a sense of freshness and quality. However, given rising concerns about the health effects of synthetic additives, regulatory bodies including the FDA, EFSA, and FSSAI have imposed strict safety standards governing their use.

In **medical and biological sciences**, dyes are indispensable for diagnostic, imaging, and analytical applications. Methylene Blue, for example, is employed in sentinel lymph node mapping, as an antimalarial agent, and in the treatment of methemoglobinemia. Similarly, fluorescein is extensively used in ophthalmology for visualizing corneal injuries and assessing retinal blood flow during angiography. In microbiological and histological studies, dyes like crystal violet and safranin play a crucial role in Gram staining, aiding the differentiation of bacterial cell types. These specialised applications demand dyes of significant purity, stability, and biocompatibility to ensure accuracy and patient safety.

All the different types of dyes have significant relevance in various fields and industries. Dyes such as Methylene Blue (MB) and Methyl Orange (MO) have gained particular prominence in environmental and photochemical research. Both dyes are widely used as model organic pollutants due to their well-characterised molecular structures, distinct absorption spectra, and stability under experimental conditions. They have contrasting chemical properties, being MB a cationic thiazine dye and MO an anionic azo dye, and this fact makes them ideal for studying adsorption, photodegradation, and wastewater treatment mechanisms. In this way it is possible to study how they interact with molecules with different characteristics. In this context, MB and MO serve as representative contaminants in numerous laboratory and field-scale studies, forming the basis for understanding dye behaviour, degradation kinetics, and pollutant-removal efficiency in aqueous systems.

Methylene Blue is a heterocyclic aromatic compound belonging to the phenothiazine class of dyes. It has the molecular formula $C_{16}H_{18}ClN_3S$ and a molecular weight of approximately 319.85 g/mol. Structurally, MB consists of a thiazine ring system containing both nitrogen (N) and sulphur (S) heteroatoms

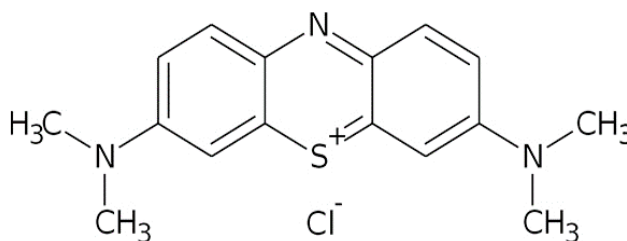


Figure 10: Methylene Blue (MB) Structure

This conjugation enables strong absorption in the visible region, giving MB its characteristic deep blue colour, with a prominent absorption peak near 664 nm in aqueous solution.

MB exists as a cationic dye, with a positively charged central nitrogen atom balanced by a chloride counterion (Cl^-). Its charge and planar molecular structure facilitate strong electrostatic and π - π interactions with negatively charged surfaces such as clay minerals, oxides, or biomaterials. Hydrogen bonding and van der Waals interactions also contribute to its adsorption behaviour. These properties make MB an ideal model compound for studying adsorption, photocatalytic degradation, and redox behaviour in water treatment and environmental remediation processes.

Methyl orange is an azo dye, characterised by the presence of the $-N=N-$ (azo) linkage connecting two aromatic rings. Its molecular formula is $C_{14}H_{14}N_3NaO_3S$, with a molecular weight of about 327.33 g/mol. The molecule contains both sulphonate ($-SO_3^-$) and dimethylamino ($-N(CH_3)_2$) functional groups, which influence its solubility, charge behaviour, and colour. In aqueous medium, MO exists as an anionic dye due to the deprotonated sulphonate group, giving it a strong affinity for positively charged surfaces.

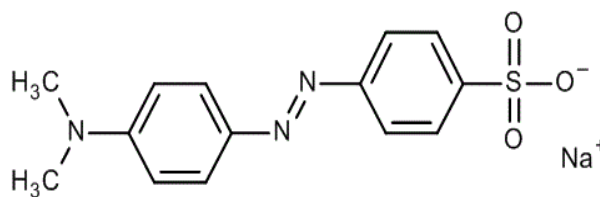


Figure 11: Methyl Orange Structure

The extensive conjugation across its aromatic and azo groups leads to vivid colouration, with an absorption maximum typically around 464 nm in its orange form. The dye also exhibits pH-dependent colour change, where it appears red in acidic medium and orange-yellow in alkaline conditions, making it widely used as a pH indicator. Its chemical stability and well-defined spectral characteristics make MO a valuable model pollutant for examining photocatalytic and adsorption mechanisms, often in comparison with cationic dyes such as MB.

While Methylene Blue (MB) and Methyl Orange (MO) are invaluable in industrial, medical, and research applications, also represent a significant class of organic pollutants when discharged into aquatic environments. Their widespread use in textile dyeing, biological staining, and analytical chemistry means that large quantities of dye-containing wastewater are generated daily. Due to their complex aromatic structures and high chemical stability, these dyes are resistant to natural degradation processes such as photolysis and biodegradation. As a result, even at low concentrations, MB and MO can persist in water bodies for extended periods, leading to long-term environmental and ecological impacts.

The presence of such dyes in aquatic systems not only impairs the aesthetic quality of water but also disrupts photosynthetic activity by reducing light penetration. Furthermore, both MB and MO can exhibit toxic, mutagenic, and carcinogenic effects on aquatic organisms and may enter the food chain through bioaccumulation, posing risks to human health. Their strong colour, stability under varying pH conditions, and solubility in water make them highly detectable markers of chemical contamination, thus serving as model compounds for evaluating water purification and treatment technologies. Consequently, the effective removal or degradation of these dyes from wastewater has become a critical focus in environmental protection and sustainable water management.

Given their persistence and potential toxicity, it is essential to explore efficient strategies for the removal and degradation of MB and MO from contaminated water. Traditional methods for treating dye-laden wastewater can be broadly categorised into biological, chemical, and physical approaches, each with distinct mechanisms and limitations, as summarised in Figure 12. However, the structural complexity and stability of these dyes often render conventional treatments insufficient, prompting the need for advanced and integrated remediation techniques.

The remediation of synthetic dyes from industrial effluents can be executed through distinct primary pathways: biological, chemical, and physical methodologies.

Biological treatment strategies rely on the metabolic activities of microbial consortia, including bacteria, yeasts, and fungi. These processes typically proceed via two main pathways: enzymatic degradation wherein specialised microbial enzymes systematically cleave chromophore structures and assimilate the breakdown products into cellular metabolic pathways or via biosorption, which involves the passive immobilization of dye molecules onto the active functional groups of microbial biomasses.

Alternatively, **chemical treatment methods** leverage targeted chemical transformations initiated by specific reagents or oxidative conditions. Prominent techniques within this category include advanced

oxidation processes (AOPs), ozonation, and heterogeneous photocatalysis, all of which aim to mineralise organic pollutants into benign by-products.

Lastly, **physical methodologies** achieve dye removal through phase separation and mass transfer without altering the chemical structure of the pollutant. These primarily encompass coagulation-flocculation, membrane-based nanofiltration, and chemical precipitation.

Many such traditional methods have been proven ineffective for various organic dyes, specifically biological treatments often lead to limited degradation, while chemical and physical processes often lead to the formation of degradation by-products that can cause secondary pollution, since they are chemical species classified as harmful to the environment. This behaviour is due to the fact that dyes are often characterised by a complex chemical structure, characterised by the presence of particularly stable functional groups, and high molecular weight.

Treatment	Advantages	Disadvantages
Biological methods		
Activated sludge	- Low cost of installation - Low requirement of land area	- Generation of sludge - Rigid process method
Fungal decolorization	- Capable of degrading dyes using enzymes - Flexible method	- Unreliable enzyme production - Lengthy growth phase
Microbial cultures (Mixed bacterial)	- Decolourization occurs in 23-30 hr which is considered fast	- Cationic dyes are not ready for metabolism under aerobic conditions
Adsorption (Microbial biomass)	- Some dyes bind to microbial species with have high affinity	- Effective for a limited type of dyes
Aerobic-anaerobic remediation	- Allow decolorization of azo and water-soluble dyes - No foam formation	- Formation of hydrogen sulfide and methane - Require a large land area - Generation of sludge - Time-consuming
Algae degradation	- Easily assessable - Low operational cost	- Unstable system
Enzyme degradation	- High efficiency - Non-toxic - Reusable	- Unreliable enzyme production
Chemical methods		
Electrokinetic coagulation	- Economically expedient	- High generation of sludge
Electrochemical destruction	- Compounds broken down are non-toxic - No consumption of chemicals - No sludge generation	- High electricity consumption - High flow rates cause a reduction in dye removal
Fenton's oxidation	- Effective decolorization of soluble and insoluble dyes - Removal of all toxins	- Generation of sludge - Narrow working pH range - High cost and risk with handling reagents
Ozonation	- Can be applied in a gaseous state - No increase in sludge and wastewater volume	- Short half-life (20 mins) - Generation of toxic by-products - Unstable system

Figure 12: Advantages and disadvantages of biological, chemical, and physical methods for synthetic dye removal (Kah et al., 2020)

1.7 Adsorption:

The ever-increasing need for clean water is one of the most urgent sustainable development goals, which requires environmentally-friendly strategies for water remediation against different types of pollutants.

The limitations of conventional dye removal methods, such as their potential for incomplete degradation and the generation of harmful by-products, have spurred significant research into alternative approaches.

Adsorption, the process by which molecules or ions accumulate on the surface of a solid material due to intermolecular forces, presents a promising strategy for pollutants removal from water. This technique is particularly attractive due to its simplicity, cost-effectiveness, and environmental friendliness. Unlike many other treatment methods, adsorption generally does not require complex equipment, the addition of harsh chemicals, or does not lead to the generation of harmful by-products.

The efficiency of adsorption processes is governed by the interplay of various intermolecular forces between the adsorbent surface and the adsorbate molecules. These interactions can be broadly categorised into physical and chemical interactions.

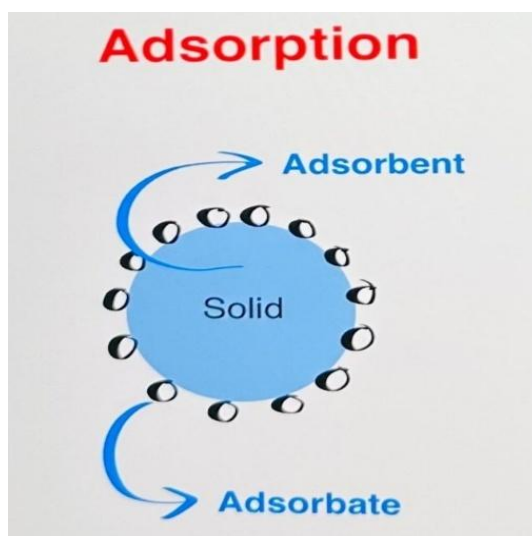


Figure 13: Adsorption

Physical Adsorption:

It could be due to Van der Waals forces which are a weak, non-specific forces, including dipole-dipole interactions and London dispersion forces, which arise from temporary fluctuations in electron distribution. They play a significant role in the adsorption of nonpolar or weakly polar molecules. Additionally, physical Adsorption could be due to hydrogen bonding. This type of interaction involves the formation of a dipole-dipole attraction between a hydrogen atom bonded to a highly electronegative atom (e.g., oxygen, nitrogen) in one molecule and another electronegative atom in the adsorbate. Hydrogen bonding contributes significantly to the adsorption of polar organic molecules.

Chemical Adsorption (Chemisorption):

Chemisorption is fundamentally characterised by the formation of strong, localised chemical bonds, such as covalent, ionic, or coordinate bonds resulting from orbital overlap and electron transfer

between the adsorbate molecules and the active surface sites of the adsorbent. Due to the high specificity of these chemical transformations, chemisorption processes typically exhibit substantially higher adsorption enthalpies ($\Delta H_{ads} > 80 \text{ kJ/mol}$) and greater binding stability compared to physical adsorption.

It is critical to distinguish true chemisorption from high-affinity non-covalent interactions, such as electrostatic attractions and π - π stacking. Electrostatic interactions involve long-range Coulombic forces between oppositely charged species, for instance, the attraction of cationic dye molecules to negatively charged functional groups on an adsorbent surface (e.g., deprotonated silanol groups). Concurrently, π - π interactions drive the interfacial accumulation of aromatic contaminants via the overlapping of localised π -electron clouds with sp^2 -hybridised carbon networks, such as those found in graphene-based materials (Wu et al., 2020). While these driving forces are technically categorised under physical or electrostatic non-covalent regimes due to the absence of formal valence electron sharing, their cumulative binding energy can approach the lower limits of chemisorption regimes, significantly enhancing both adsorption capacity and structural selectivity.

Green Adsorbent Development:

Though the traditional adsorbents such as activated carbon remain highly efficient due to their large surface area and capacity for adsorption, they are encompassed by important drawbacks including costly regeneration, energy-intensive preparation, and potential disposal issues (Kumar et al., 2019). This has motivated the emergence of alternative, sustainable, renewable, and multimodal materials.

In recent years, there has been considerable progress in the concept of designing hybrid bio-based and polymer-functionalised adsorbents. For instance, the use of alginate-derived active mixtures with incorporated oxide macro-beads (TiO_2 , Al_2O_3 , YSZ) by Vassalini et al. (2020) showed enhanced adsorption efficiency for cationic dyes such as methylene blue and crystal violet, and demonstrated photocatalytic activity under weak, visible-light conditions without the assistance of supporting oxidants. Similarly, Da Silva et al. (2021) demonstrated the effectiveness of poly(3,4-ethylenedioxythiophene) (PEDOT) coated on polyvinylidene fluoride (PVDF) mats for methyl orange adsorption with mechanical strength and high dye affinity.

Another study by Vassalini et al., (2024) developed an innovative PEDOT: PSS–chitosan bead system specifically for simultaneous removal of MB and MO from wastewater. The waste shrimp shell-derived biopolymer chitosan possesses intrinsic adsorption sites ($-\text{NH}_2$ and $-\text{OH}$ groups) and biodegradability, while PEDOT: PSS offers electrical conductivity as well as surface charge tunability. Both together constitute a synergistic adsorbent that not only works but is also sustainable

and recyclable in complete harmony with circular-economy principles. These cases demonstrate a clear trend in adsorption research, away from only the efficiency and towards a multi-controller, low-impact products with the ability to be biodegradable, photocatalytic, and easily recovered.

The development of new adsorbents with engineered physicochemical properties is the most crucial in realizing optimal adsorption performance. The ideal adsorbent would possess a set of essential characteristics. With increasing environmental and economic pressures, interest is moving increasingly towards materials of natural, waste, or hybrid origins. This transition has opened the way to a multitude of classes of adsorbents, from bio-chars and zeolites to Metal Organic Frameworks (MOFs) and graphene-based nanomaterials, with specific adsorption mechanisms and sustainability benefits.

1.7.1 Materials for Adsorption:

In the past few decades, the search of sustainable and efficient adsorbent materials has gained momentum considerably. Even though adsorption is conceptually simple, the selection and design of the adsorbent material largely determine the overall effectiveness, cost-efficiency and the environmental impact of the process. The ideal material for adsorption should offer a combination of chemical stability, high surface area, rapid kinetics, re-generatability and a strong affinity for the target molecules. Even after decades of research, there is no single material currently that meets all these criteria. Thus, researchers have explored a wide range of traditional and emerging materials which are often derived either from water sources or from natural resources, to balance the performance with sustainability.

1.7.1.1 Activated Carbon:

For decades, Activated Carbon (AC) has maintained its position as the distinguished adsorbent material. Its superior properties (significantly high surface area, well defined and intricate pores (macro, meso and micro) and its broad-spectrum capacity for effectively sequestering different inorganic and organic pollutants from the wastewater) justified its widespread adoption globally. As mentioned by Kumar et al., (2019) AC has been long regarded as the gold standard among the adsorbents. It remains one of the most used materials for heavy metal and dye removal from the wastewater.

Typically, AC is synthesised through the carbonization of carbon-rich precursors, traditionally fossil-based sources like lignite or coal. This step is then followed by an activation step. Activation may be

physical (e.g., steam, CO₂) or chemical (e.g., KOH, H₃PO₄, ZnCl₂), each precisely designed to optimise pore development and enhance surface reactivity (Ioannidou & Zabaniotou, 2007).

As a result, modern production methods can yield AC with surface areas exceeding 1000 m²/g and a well-balanced pore size distribution, enabling efficient adsorption of pollutants of varying molecular dimensions (Ioannidou & Zabaniotou, 2007). In the case of MB, adsorption proceeds through multiple concurrent mechanisms such as π - π interactions between MB's aromatic rings and the graphitic domains of AC; electrostatic attraction between the cationic dye and negatively charged surface sites (especially under alkaline conditions); hydrogen bonding with oxygen-containing functional groups (e.g., hydroxyl, carboxyl, and carbonyl); and physical pore filling, where capillary condensation dominates in the microporous regions (Tran et al., 2017). These synergistic interactions account for the high dye removal efficiencies consistently reported for AC-based systems.

The significant versatility of AC is its stability across a broad pH and temperature range, its adaptability to both batch and continuous operations, and its availability in multiple commercial forms (powdered, granular, or pelletised), further reinforces its widespread industrial application. In optimised laboratory studies, certain jute fibre based activated carbons have demonstrated methylene blue adsorption capacities exceeding 225.64 mg/g, underscoring their notable affinity and operational efficiency (Senthilkumaar et al., 2005).

However, despite these advantages, several intrinsic challenges have prompted researchers to seek more sustainable alternatives. The production of high-grade AC is energy-intensive, often requiring high-temperature carbonization and activation steps that significantly elevate economic and environmental costs. When derived from non-renewable feedstocks such as coal, these concerns are compounded by a larger carbon footprint and limited long-term sustainability. Even when bio-waste is used as a renewable precursor, achieving consistent pore characteristics and adsorption performance across production batches remains a significant challenge.

Regeneration and reusability are equally critical considerations. Although AC can, in principle, be regenerated through thermal or chemical treatments, these processes often result in partial structural degradation, reduced adsorption capacity, or the generation of secondary waste streams that require additional management. Thermal regeneration, while efficient, can cause pore collapse and carbon burn-off, whereas chemical regeneration, though milder, may introduce secondary contaminants. Moreover, exhausted AC loaded with dyes and heavy metals poses potential risks of desorption or leaching if not properly managed, raising secondary pollution concerns (Tran et al., 2017).

Another key limitation lies in the complexity of real industrial wastewater matrices, which typically contain multiple competing solutes like surfactants, humic acids, and dissolved salts that can inhibit or outcompete the target dyes for active adsorption sites. Consequently, the performance of AC under practical operating conditions often falls short of its idealised laboratory results, particularly in systems involving complex dye mixtures or variable ionic strengths.

Although activated carbon remains the gold standard among adsorbents for wastewater treatment due to its proven efficacy, operational reliability, and mature commercialization, the associated high production and regeneration costs, sustainability concerns, and practical limitations under real-world conditions have collectively fuelled the ongoing exploration of next-generation materials. Recent research efforts are increasingly directed toward developing cost-effective, renewable, and environmentally benign alternatives, including biochar, waste-derived carbons, inorganic-organic hybrid composites, and other advanced porous materials (Tran et al., 2017). The overarching goal is to achieve comparable or superior adsorption performance while addressing the environmental and economic trade-offs associated with conventional AC-based treatment systems.

1.7.1.2 Bio-char:

A substantial solution that emerged in the recent years is the production of a material similar to AC starting from agricultural waste, which is called biochar. It involves a cost-effective and environmentally friendly adsorbents created by heating the materials like corn cobs, rice husks, sawdust, bagasse, or coconut shells. A considerable attention from scientific community was given to biochar due to its impressive characteristics such as numerous beneficial surface functional groups, high porosity and high surface area. These characteristics make them remarkably effective not only in removing heavy metals such as chromium, lead and cadmium but also the industrial dyes like methylene blue. Type of feedstock, the conditions for pyrolysis, and any activation treatments all play a vital role in the ultimate adsorption performance. To get the maximum performance output, surface modification techniques, such as acid or base activation, are often necessary, which can add a layer of complexity to the process. Albeit all the advantages, the path isn't smooth entirely, many inconsistencies in the adsorption behaviour have been reported from variable feedstock, differing ash content and potential competition from natural organic matter (Wang et al., 2020).

1.7.1.3 Metal Organic Frameworks:

Metal-organic frameworks (MOFs) represent a newer generation of crystalline adsorbents, or MOFs. These crystalline hybrid materials, built from a precise arrangement of metal ions and organic ligands,

represent a new generation of adsorbents. Their exceptionally high surface areas, customizable pore sizes, and tuneable chemical functionalities are truly impressive. MOFs like MIL-101(Cr) and ZIF-8 have shown tremendous promise in removing organic dyes, arsenic, lead, and other toxic ions from water. Their highly ordered structure allows for high adsorption capacities and notable selectivity under controlled conditions. Despite these strong laboratory-scale results, MOFs still face significant hurdles in real-world applications. Many frameworks struggle with limited hydrothermal stability, degrading under the harsh conditions of real wastewater. Furthermore, their high synthesis costs currently stand in the way of large-scale deployment (Uddin et al., 2021). Nevertheless, research continues to push boundaries, focusing on composite formation and greener synthesis methods to overcome these limitations.

1.7.1.4 Zeolites:

Zeolites are both naturally occurring and synthetically produced and they continue to play a pivotal role, especially when it comes to heavy metal ion removal. Their distinctive ion-exchange capabilities, well-defined microporous structures, and chemical stability even in challenging environments make them invaluable. Natural zeolites like clinoptilolite and synthetic variants have a proven track record of successfully adsorbing metal ions like copper, arsenic, lead, mercury, nickel and cadmium from industrial wastewater streams, particularly from electroplating and mining operations. Their abundance and relatively low cost make them appealing for large-scale applications. However, they do have their limitations, including moderate surface areas compared to activated carbon, a susceptibility to pore blockage, and reduced selectivity when competing ions are present. This often means that zeolites require modification or hybridization to truly shine in the intricate world of complex industrial wastewater matrices (Velarde et al., 2023).

1.7.1.5 Graphene Oxide:

Another fascinating class of advanced adsorbents comes in the form of graphene oxide (GO) and other carbon nanomaterials. Researchers have extensively explored these materials due to their notable surface area, specific layered structure, and high density of oxygen-containing functional groups. These features translate into rapid adsorption kinetics and strong interactions with a diverse range of organic dyes, pharmaceuticals, and metal ions. Studies have shown that GO composites, especially when modified with magnetic nanoparticles or metal oxides, can significantly boost selectivity, reusability, and the ease with which they can be separated from treated water. Despite these impressive properties, the high cost of production, potential ecotoxicity of the nanomaterials

themselves, and regulatory concerns regarding their safe disposal or recovery once spent currently limit their widespread use (Priyadharshini et al., 2022).

The quest for sustainable and efficient wastewater treatment has become a critical global challenge, driving extensive research into innovative adsorbent materials. While the range of available adsorbent materials is broad and continually expanding, no single material satisfies all performance, cost, scalability, and sustainability criteria simultaneously. Each presents specific trade-offs that must be assessed in the context of the target application. The objective, therefore, is not to identify the highest-performing adsorbent in isolation, but to identify materials that deliver adequate performance within practical operational and economic constraints. Instead, the focus must shift to achieving a delicate balance between adsorption performance, economic feasibility, scalability, and genuine long-term sustainability under real-world operating conditions. This imperative is increasingly driving researchers and industries to explore more unconventional sources, including industrial by-products and electronic waste, in pursuit of more integrated and holistic solutions.

1.7.1.6 Industrial Waste Valorisation:

Most recently, there's been a surge of interest in adsorbents derived from industrial waste such as fly ash, red mud, metallurgical slag, and foundry sand. This growing focus aligns with integrated waste valorisation strategies. For instance, modified fly ash has shown commendable adsorption performance for both cationic dyes and heavy metals, offering a truly cost-effective way to transform an industrial by-product into a valuable functional material (Jadaa, 2024). Utilizing these wastes not only embodies the principles of a circular economy but also helps reduce disposal costs and alleviate the burden on landfills. However, a crucial consideration that still remains is the potential for secondary contamination due to the leaching of residual heavy metals from these adsorbents. Therefore, robust pre-treatment and stabilization methods are absolutely essential to ensure their safe and effective use in large-scale applications.

1.7.1.7 Silica:

Among the many pathways explored within this framework, one particularly promising direction involves the utilization of inorganic waste derivatives and earth-abundant compounds for environmental remediation applications. Silica-based materials have attracted considerable attention due to their inherent abundance, structural versatility, and ability to be derived from both natural and secondary sources, including agricultural residues and electronic waste by-products such as processed printed circuit board (PCB) glass fibres. The conversion of such waste-derived silica not only

addresses the growing challenge of e-waste management but also provides a sustainable feedstock for advanced adsorbents with high environmental utility. By transforming what was once considered an environmental burden into a valuable resource, this approach is consistent with circular economy principles and provides a route for converting e-waste into materials with high environmental utility.

Among candidate adsorbent materials, silica is notable for its structural versatility, tuneable surface chemistry, and wide availability from both natural and waste-derived sources. These properties make it a practical and sustainably sourced platform for environmental applications, well-suited to integration within circular economy frameworks.



Figure 14: Silica

Silica as an adsorbent:

Silica, one of the most abundant inorganic materials in the Earth's crust, has long been recognised for its versatility in environmental applications. While it is widely used in catalysis, filtration, and as an industrial filler, its application as an adsorbent for wastewater treatment continues to gain traction, especially in contexts where cost-effectiveness and sustainability are critical.

Furthermore, silica is far more than a static chemical compound; it serves as a highly tuneable, versatile inorganic platform that can be precisely sculpted at the nanoscale. Through controlled synthetic pathways, researchers can orchestrate its porous topology, effectively engineering high-surface-area internal networks with customised pore sizes tailored to trap specific molecular dimensions. Beyond geometric confinement, silica exhibits a highly reactive surface chemistry dominated by native hydroxyl (silanol, -Si-OH) groups.

In widespread environmental literature, these silanol groups are frequently exploited as anchoring sites for chemical functionalisation, the covalent grafting of specific organic moieties or chelating agents that act as selective molecular vectors to capture heavy metals or complex contaminants.

However, an equally powerful and more sustainable paradigm relies on pure topological and charge-driven engineering. By maximising the specific surface area and modifying the structural porosity of

the silica matrix without external chemical functionalisation, the density and spatial distribution of deprotonated, negatively charged silanol sites ($-\text{Si}-\text{O}$) can be highly optimised. These native structural configurations generate intense, localised electrostatic fields capable of rapidly sequestering oppositely charged species, such as cationic organic dyes, with significant kinetic rates and capacities that rival heavily modified composites. This dual capability, functioning either as an inherently active, charge-selective matrix or as a scaffold for chemical functionalisation makes silica a versatile platform for wastewater remediation, enabling both direct electrostatic dye capture and targeted surface modification.

Naturally occurring silica, such as diatomaceous earth, sand, and opaline silica deposits, has been applied for contaminant removal due to its inherent porosity, inertness, and broad availability. Diatomaceous earth (DE), for example, is a siliceous sedimentary material formed from fossilised diatom skeletons. DE has a high natural porosity, low density, and a moderately high surface area (typically 20–65 m²/g) that make it suitable for adsorbing pollutants from water. Research by Al-Ghouti et al. (2003) showed that DE can effectively remove metal ions like boron, lead and copper and organic dyes when used either in raw form or after mild modification. However, its adsorption capacity is often limited by the lack of active functional groups on its surface, which means chemical treatment, such as acid washing or surface activation is often necessary to enhance its binding sites (Bhatnagar & Sillanpää, 2010).

Rice husk ash (RHA) is another well-documented source of low-cost amorphous silica. Rice husk is one of the world's largest agricultural residues, and burning it under controlled conditions generates ash containing up to 90% silica by weight. This ash, when properly purified and treated, can yield high-quality amorphous silica with significant surface area and active silanol groups (Salavati-Niasari et al., 2013). Numerous studies have shown that RHA-derived silica, especially after functionalization with amine, thiol, or carboxyl groups, is highly effective for removing heavy metals like lead, cadmium, and chromium from aqueous solutions. The reuse of rice husk ash also contributes to waste valorisation and reduces open-field burning, aligning with sustainable waste management goals (Kenechi et al., 2016).

Fly ash, a by-product of coal combustion in thermal power plants, is another abundant industrial residue that has been explored as a silica-rich adsorbent. Although raw fly ash typically contains alumina and other oxides along with silica, controlled extraction processes can separate amorphous silica from its matrix. Extracted fly ash silica, when modified or used as a filler in composite adsorbents, has shown notable performance for dye and metal removal (Sharma et al., 2023).

However, the presence of trace heavy metals in raw fly ash poses a risk of secondary contamination if the material is not adequately treated and stabilised.

Other natural and agro-waste-derived silica sources, including bagasse ash (from sugarcane processing) and geothermal sludge, have also been studied for water purification. Patel (2020) demonstrated that bagasse ash can be converted into silica gel or functional powders that effectively adsorb dyes and metal ions, offering a promising circular economy route in sugar-producing regions. The silica content of such ashes varies depending on combustion conditions and feedstock origin, so consistent production quality remains a practical challenge that must be addressed through standardised processing protocols.

Even though silica has proved to be a great adsorber however, the practical use of natural silica and waste silica is not free from challenges. The physical form of natural and waste silica, which often comes as fine powders, requires considerable effort to manage in a safe manner to prevent inhalation. Additionally, spent silica adsorbents require safe disposal, which contributes to secondary pollution. Some purification and extraction methods rely on acid leaching which must be controlled to minimise chemical waste, therefore increasing overall operational cost.

Naturally and agro-industrially derived silica waste have provided a low-cost locally available option for the treatment of water and wastewater. Such materials are designed to help support resource recovery and minimisation of waste by solving the problem of value-adding to agricultural or industrial by-products which are otherwise seen as burdens. In order to improve the usefulness of these materials in real life, subsequent studies need to be directed towards safe handling and regeneration procedures, green extraction techniques, and scale up treatment processes that keep the high efficiency of adsorption while lowering the environmental impact.

Within this broader context, the repurposing of processed printed circuit board (PCB) residues as functional adsorbents stands out as particularly innovative and pragmatic. By transforming the non-metallic fractions of discarded PCBs, which are typically challenging to recycle and manage due to their complex composite nature, into silica-based materials for wastewater remediation, we address two pressing global issues simultaneously that is the escalating volume of electronic waste and the urgent demand for accessible, high-performing water treatment technologies. This approach symbolises the principles of a circular economy, translating an abstract concept into a tangible, impactful strategy that delivers real-world benefits. It directly links waste stream valorisation, where discarded materials gain new purpose, with resource recovery and environmental protection, integrating them into a cohesive and mutually beneficial solution.

The repurposing of PCB non-metallic residues as functional adsorbents represents a practical application of circular economy principles: rather than treating the leached residue as a disposal liability, it is redirected as a feedstock for water treatment materials, simultaneously addressing two distinct waste streams without generating new resource demands.

While keeping into account the safety of the modified materials, their production efficiency and their environmental impact and how they are developed and implemented responsibly, this approach holds great promise for closing material loops within industrial systems. It can substantially reduce dependence on non-renewable raw materials while simultaneously minimising waste generation. This approach converts an end-of-life waste fraction into a functional material for environmental remediation, exemplifying the cascade-use strategy at the core of the circular economy.

1.8 Adsorption Kinetics: Mechanisms and Dynamics:

Adsorption kinetics is a critical aspect of understanding the efficiency and effectiveness of adsorption processes. It describes the rate at which adsorbate molecules or ions are transferred from the bulk solution to the surface of the adsorbent. This rate directly influences the design of adsorption systems and their practical applications, especially in water treatment and environmental remediation. Following are the important factors that are responsible in influencing the adsorption kinetics.

Nature of the Adsorbate and Adsorbent:

The size, shape, and charge of the adsorbate molecules impact their interaction with the adsorbent surface. The surface area, pore size distribution, and functional groups on the adsorbent determine the accessibility and availability of active sites.

Concentration Gradient:

A higher concentration gradient between the bulk solution and the adsorbent surface accelerates the diffusion process, enhancing the adsorption rate and vice versa.

Temperature:

Increasing temperature often improves molecular motion, enhancing diffusion rates. For exothermic adsorption processes, higher temperatures can reduce adsorption efficiency by shifting equilibrium away from adsorption, the opposite occurs for endothermic processes.

Agitation:

Stirring or mixing reduces boundary layer resistance, promoting faster mass transfer and improving the adsorption rate.

1.8.1 Adsorption Kinetic Models:

To understand and predict adsorption behaviour, several kinetic models are commonly applied:

Pseudo-First-Order Model:

It assumes the adsorption rate is directly proportional to the difference between the equilibrium concentration and the amount of adsorbate adsorbed at a given time. The model is expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (1)$$

Where:

q_e = Amount adsorbed at equilibrium (mg/g)

q_t = Amount adsorbed at time t (mg/g)

k_1 = Rate constant of pseudo-first-order adsorption (1/min)

Pseudo-Second-Order Model:

The pseudo-second-order (PSO) model was originally proposed under the assumption that chemisorption is the rate-limiting step involving valence forces through the sharing or exchange of electrons. However, it has since been extensively demonstrated in the literature that PSO kinetics are equally consistent with physisorption-dominated systems in which the overall rate is governed by the occupation velocity of available active surface sites rather than by formal electron exchange (Azizian, 2004). The equation is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

Whereas,

k_2 = Rate constant of pseudo-second-order adsorption (g/mg/min)

This model is widely used due to its ability to fit many experimental datasets. This model accounts for adsorbate-adsorbent interactions more effectively than the pseudo-first-order model, particularly for heterogeneous systems or systems with strong chemical bonding.

Intraparticle Diffusion Model:

Describes the diffusion of adsorbate molecules into the pores of the adsorbent as a rate-limiting step. The equation is:

$$q_t = k_i t^{0.5} + C \quad (3)$$

Where:

- k_i : Intraparticle diffusion rate constant
- C : Boundary layer effect constant

This model is often used alongside others to determine whether diffusion within the pores or external film resistance governs the adsorption process. If the plot of q_t versus $t^{0.5}$ is linear and passes through the origin, intraparticle diffusion is the sole rate-limiting step. Otherwise, other mechanisms are also at play.

Elovich Equation:

The Elovich equation is primarily used to describe adsorption processes occurring on heterogeneous surfaces with non-uniform energy distribution. It is particularly effective for systems involving chemisorption, where the rate of adsorption decreases exponentially with increasing surface coverage. The model is expressed as:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (4)$$

Where:

- q_t : Amount adsorbed at time t (mg/g)
- α : Initial adsorption rate (mg/g/min)
- β : Desorption constant related to the extent of surface coverage and activation energy (g/mg)

The Elovich model assumes that the adsorption sites decrease exponentially in their adsorption potential as they become saturated. It is particularly suitable for systems with heterogeneous adsorbent surfaces, such as activated carbon or functionalised materials.

Boyd Model:

The Boyd model is used to distinguish between external mass transfer (film diffusion) and intraparticle diffusion as the rate-limiting step in adsorption processes. This model provides a

quantitative framework to assess whether the adsorption kinetics are controlled by the boundary layer or internal diffusion. The Boyd function is expressed as:

$$\beta_t = -0.4977 - \ln(1 - F_t) \quad (5)$$

Where:

- β_t : Boyd function, related to time t and fractional adsorption (F_t)
- F_t : Fractional adsorption at time t , calculated as $F = \frac{q_t}{q_e}$

The Boyd plot (β_t vs t) is analysed to determine the dominant mechanism:

A linear plot passing through the origin suggests that film diffusion controls the process.

A non-linear plot indicates intraparticle diffusion as the rate-limiting step.

Application to Environmental Remediation:

Understanding the kinetics of adsorption is paramount for optimising the removal of pollutants, such as dyes, from industrial wastewater. The rate at which pollutants are removed from solution directly influences the efficiency and feasibility of the adsorption process for real-world applications.

Key considerations for optimising adsorption processes based on kinetic studies:

Achieving Rapid Pollutant Removal: Fast adsorption kinetics are highly desirable for real-time treatment applications, especially in industries where continuous wastewater streams require immediate treatment.

Identifying Rate-Limiting Steps: By analysing the kinetics of adsorption, it is possible to identify the rate-limiting steps in the process. This could involve diffusion of the pollutant within the adsorbent particles (intraparticle diffusion), mass transfer limitations in the bulk solution, or even the rate of the adsorption reaction itself.

Optimising Adsorbent Materials: Understanding the rate-limiting steps allows for the targeted design and modification of adsorbent materials to enhance their performance. For instance, if intraparticle diffusion is the rate-limiting step, increasing porosity of the adsorbent can significantly improve the adsorption rate.

Optimising Process Parameters: Kinetic studies can provide valuable insights into the influence of various process parameters, such as contact time, initial pollutant concentration, temperature, and pH,

on the adsorption rate. This information can be used to optimise operating conditions for maximum removal efficiency and minimise treatment costs.

By analysing the kinetics of adsorption, this research aims to enhance our understanding of how specific factors, such as the nature of the adsorbent, the characteristics of the pollutant, and the operating conditions, influence the rate of pollutant removal. This knowledge will be instrumental in developing more efficient and scalable adsorption systems for the effective treatment of contaminated water and the protection of the environment.

1.9 Research Objectives and Thesis Structure:

1.9.1 Research Objectives:

The growing accumulation of electronic waste (e-waste), particularly printed circuit boards (PCBs), represents a significant environmental and technological challenge. While metallic recovery from PCBs has been extensively investigated, the non-metallic fraction remains underutilised despite its high silica and glass fibre content. The present thesis addresses this gap by exploring the valorisation of PCB-derived non-metallic residues as functional materials for wastewater treatment.

The central premise of this work is that PCB-derived residues, when subjected to controlled mechanical, chemical, and structural modification processes, can be transformed into effective and reusable adsorbent materials.

The specific objectives of this thesis are:

1. **To prepare** metal-free PCB-derived materials through three distinct treatment routes; microwave-assisted acid digestion (MA-CT-PCB), sequential buffered leaching (BL-PCB), and reagent-free mechanical and electrostatic processing (MP-PCB) and to comprehensively characterise their physicochemical properties using X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS), BET surface area and nitrogen physisorption analysis, and surface charge measurements. Within this objective, the adsorption performance of all three material families toward methylene blue (MB) as a model organic dye is evaluated under controlled batch conditions; the effects of particle size, adsorbent dosage, and surface functionalisation with biopolymers (chitosan and alginate) and polydopamine (PDA) are investigated; and the photo-assisted degradation activity of the materials under simulated solar irradiation is thoroughly assessed.

2. **To synthesise** ordered mesoporous silica ($m - SiO_2$) from mechanically processed PCB-derived silica precursors via cetyltrimethylammonium bromide (CTAB)-templated hydrothermal methods, to evaluate the structural development of the mesoporous framework through BET surface area analysis, pore volume determination, and low-angle XRD, and to assess the adsorption performance of the synthesised material toward cationic and anionic model dyes. This objective also encompasses the evaluation of material stability and reusability through repeated adsorption–desorption cycles using sodium dodecyl sulphate (SDS) as a regenerant, and comparison of regeneration efficiency with commercial activated carbon.
3. **To validate** the adsorption performance of PCB-derived adsorbent materials at volumetrically scaled-up conditions (100mL and 500 mL), and to assess whether equilibrium adsorption capacity remains effectively independent of solution volume, providing mechanistic evidence consistent with a surface-controlled adsorption mechanism and supporting the prospect of industrial translation.
4. **To contextualise** the developed materials and processes within a circular economy framework, discussing their environmental relevance, sustainability profile, regulatory alignment, and industrial applicability.

Through these objectives, the thesis aims to provide a systematic evaluation of PCB-derived non-metallic fractions as value-added materials for environmental remediation.

1.9.2 Thesis Structure

The research presented in this dissertation is organised into six chapters, tracing the process from material synthesis and characterisation to operational testing and sustainability analysis:

- **Chapter 1 – Introduction:** Establishes the socio-economic and environmental context of electronic waste generation, focusing on the processing challenges and recycling potentials of non-metallic printed circuit board fractions. This chapter reviews the circular economy principles underlying the SMaRT-PCBs project, examines the impact of water pollution caused by synthetic organic dyes like methylene blue, and details the theoretical frameworks governing adsorption mechanisms, transport kinetics, and surface charge thermodynamics. The chapter concludes with the specific research objectives and the structural outline of the thesis.
- **Chapter 2 – Materials and Methods:** Documents the source materials, processing histories, and theoretical operating principles of the analytical instrumentation used throughout the

study. It details the preparation routes for the Microwave-Assisted Chemically Treated Printed Circuit Board matrix, the Buffered Chemically Leached PCB residue, the Mechanically Processed PCB matrix, and the scaled-up configuration designated as the Buffered Chemically Leached PCB Scale-Up sample. Additionally, the chapter outlines the fundamental physics and parameters for Ultraviolet-Visible Spectrophotometry, Micro-Raman Spectroscopy, X-Ray Diffraction, Surface Charge/Zeta Potential analysis, and Scanning Electron Microscopy coupled with Energy Dispersive X-Ray Spectroscopy.

- **Chapter 3 – Experimental Section:** Details the step-by-step laboratory procedures implemented during the experimental phases without incorporating resulting data or findings. It outlines the protocols used for particle size standardization, physicochemical measurements, and batch fluid-phase adsorption runs. This section also describes the hydrothermal workflows used to synthesise high-surface-area mesoporous silica platform materials using CTAB templates, alongside surface functionalisation methods using Alginate and Chitosan biopolymer slurries or Polydopamine coatings. It concludes with the operational parameters used for simulated solar photodegradation, multi-cycle desorption and reusability tests, and the volumetric scale-up experimental conditions.
- **Chapter 4 – Results and Discussion:** Presents the experimental data and mechanistic interpretations for all investigated material systems, structured to mirror the modification chronology of the waste matrices. The chapter begins with the characterisation, adsorption behaviours, and kinetic modelling of the Microwave-Assisted Chemically Treated series, followed by the structural properties, equilibrium isotherms, and solar photodegradation kinetics of the Buffered Chemically Leached materials. The discussion then details the physical characteristics, adsorption parameters, and photocatalytic performance of the Mechanically Processed matrices, specifically focusing on their conversion into functional mesoporous silica platforms. The chapter concludes by analysing the cyclic reusability profiles of the mesoporous silica master-platform and evaluating the volumetric scalability of the scaled-up chemical leaching stream.
- **Chapter 5 – Sustainability and Industrial Relevance:** Evaluates the laboratory benchmarks within broader economic, ecological, and industrial frameworks. This chapter positions the PCB-derived mesoporous silica architectures within circular economy models, reviews life-cycle environmental considerations, and demonstrates regulatory alignment with European REACH regulations and the European Union Water Framework Directive. The analysis assesses overall industrial feasibility, notes techno-economic translation barriers, presents

scale-up evidence, and maps potential commercialisation pathways for transitioning these waste-derived matrices toward higher Technology Readiness Levels.

- **Chapter 6 – Conclusions and Future Perspectives:** Summarises the primary findings and original contributions established throughout the research program. This final chapter addresses the boundary constraints and limitations of the current datasets before proposing a technical roadmap for future work. Suggested directions include continuous-flow pilot-scale validations, heavy-metal leaching environmental assays, long-term multi-cycle reusability assessments, and testing the general applicability of these extraction protocols on alternative industrial and electronic waste silica sources.

CHAPTER 2: MATERIALS AND METHODS

2.1 Sample Description and Origin:

As previously mentioned, this thesis is part of the **Sustainable Materials Recycling Technology for Printed Circuit Boards (SMaRT-PCBs)** project, which is an initiative aimed at developing environmentally sustainable solutions for the recycling and reuse of materials from electronic waste, particularly printed circuit boards (PCBs). The project is a multidisciplinary collaboration involving several stakeholders, with the University of Brescia playing a pivotal role in investigating adsorption-based wastewater treatment methods.

In support of these objectives, experimental samples were provided through the SMaRT-PCBs consortium. These samples were processed PCB materials, categorised into four distinct batches, each representing a unique treatment methodology. The following sections describe the treatment procedure and characterisation of all the different batches, the first microwave assisted and chemically treated PCB residue which was specifically designed to isolate the non-metallic glass fibre fraction from electronic waste, the second sample bunch was buffered chemically leached and the third batch samples was only treated mechanically and electrostatically.

2.2 Microwave Assisted Chemically Treated PCB Residue (MA-CT-PCB):

The first batch consisted of samples derived from the non-metallic fraction of Random-Access Memory (RAM) printed circuit boards. These samples were obtained as a solid residue after undergoing acidic digestion, and they represent approximately 40 wt.% of the original material. The primary aim of this batch preparation was to remove metallic constituents, isolating the glass fibre matrix for subsequent adsorption studies. This work was performed by the University of Cagliari.

For this batch MA-CT-PCB, about 200 g of assorted RAM boards, collected from mixed origins, were initially subjected to mechanical milling. The milling was carried out for 24 hours using a four-stage Retsch planetary ball mill operating at 300 rpm, with stainless steel jars containing 1.4 kg of hard metal balls of 6 mm diameter. To improve the uniformity of the grinding process and prevent particle aggregation, a solvent medium, Carbsyn 110 (250 mL), was used. After milling, the slurry obtained was separated from the milling media using 4 mm grating sieves, and the solvent was recovered by distillation. The solid fraction was then air-dried to remove any remaining traces of the solvent and prepared for acid digestion.

The metallic components were removed through microwave-assisted acid digestion. Accurately weighed portions of the dried milled material were treated with a reagent mixture composed of nitric acid (HNO₃, 65%), hydrochloric acid (HCl, 37%), and hydrogen peroxide (H₂O₂, 30%) in the proportions of 2 mL, 6 mL, and 0.5 mL, respectively. The digestion was performed using a Milestone Ethos 1 microwave digester equipped with a HPR1000/10S high-pressure segmented rotor and ATC-400CE temperature controller and Terminal 640 software. The procedure was carried out in two steps (10 mins and 20 mins) at 220 °C with a maximum power of 1000 W, ensuring complete dissolution of the metallic components.

The final residue obtained after digestion consisted mainly of silicon (Si) and glass fibres. As hydrofluoric acid (HF) was not used in this treatment, the silicon-based materials were preserved, resulting in a stable and inert matrix. This aspect was particularly beneficial, as it maintained the structural integrity of the glass fibres and ensured the suitability of the residue for reuse in adsorption and surface modification studies.

The samples were named as MA-CT-PCB 1 and 2.

Table 6: MA-CT-PCB Samples

Sample ID	Description
MA-CT-PCB-1	Glass fibre sample from Treatment 1, Sample 1
MA-CT-PCB-2	Glass fibre sample from Treatment 1, Sample 2

These materials were later used for morphological characterisation, verification of residual metal content, and adsorption experiments involving model pollutants such as methylene blue (MB) and methyl orange (MO). The outcome of this process was a high-purity, non-metallic solid with excellent chemical stability, forming a reliable foundation for subsequent comparative studies with later batches prepared using milder and more sustainable leaching treatments.

2.3 Buffered Chemically Leached PCB Residue (BL-PCB):

In contrast to the strong acid digestion procedure of the first type of samples, the second series of samples were subjected to a more environmentally friendly leaching method. Again, this experimental work was performed by the University of Cagliari. This alternative method was employed to recover metallic constituents from waste printed circuit boards (PCBs) using milder and less hazardous reagents to reduce secondary waste and produce less corrosive or toxic by-products. This method indicates a transition toward greener hydrometallurgical techniques consistent with

sustainable resource recovery and circular systems for materials. The leaching provided a three-step sequential treatment, with each step focusing on reducing different classes of metals and chemical bonds from the composite PCB structure while decreasing the metallic burden at each step.

1. Lactic Acid Buffer (0.5 M):

The first phase of the leaching method employed a mild lactic acid buffer (0.5 M) to initiate the breakdown of the PCBs epoxy and fibreglass matrix. As a weak organic acid, lactic acid exchanges protons at the material surface and begins to dissolve metal oxides as the acid complexes, without aggressively assaulting either the siliceous or polymeric fraction of the PCB. This initial phase encapsulates to both loosening the metal interfaces and preparing them for oxidation in subsequent phases of the leaching treatment.

2. Ammoniacal Buffer:

For the second step, the samples underwent the ammoniacal buffer leaching leverage containing hydrogen peroxide (H_2O_2). The addition of H_2O_2 introduces an oxidative environment capable of dissolving transition metals such as Cu, Ni, and Fe by forming their respective ammine complexes under mildly alkaline conditions. This reaction promotes selective oxidation while avoiding the excessive degradation of the composite's polymeric backbone, maintaining the material's mechanical integrity for potential reuse.

3. Aqueous Iodine/Iodide (I^-/I_2) Solution:

The final step of the material treatment involved a mild, environmentally conscious oxidation-leaching sequence utilising an aqueous iodine/iodide solution. This system was specifically chosen as a potent yet gentle oxidizing agent to dissolve any residual noble or base metals remaining after the initial two stages. The I^-/I_2 redox couple significantly enhances metal solubilization by promoting the formation of highly stable metal-iodide complexes (e.g., CuI_2^-). This strategic approach ensured the maximum recovery of residual metals while simultaneously minimising the need for highly toxic reagents, thereby reducing environmental risk.

Upon completion of the leaching sequence, all treated samples were subjected to a thorough washing procedure. They were thoroughly washed with both deionised water and acetone to effectively eliminate any residual leachate or reagent traces. The materials were then air-dried at ambient temperature. This final preparation process yielded a clean, solid non-metallic residue, which

primarily comprised the inert matrix components: glass fibres, resin fragments, and trace inorganic inclusions.

The resulting PCB residues were classified according to particle size and labelled using a standardised nomenclature to facilitate comparative testing. The sample codes (BL-PCB) correspond to Treatment of printed circuit boards that was buffered and leached, and the number indicating increasing particle size.

Table 7: BL-PCB Samples

Sample ID	Granulometry (mm)
BL-PCB-1	0.5 mm
BL-PCB-2	2 mm
BL-PCB-3	4 mm

This classification was essential for subsequent adsorption and characterisation experiments, as particle size strongly influences surface area availability, adsorption kinetics, and diffusion mechanisms during dye removal tests.

Residual Metal Characterisation:

To evaluate the effectiveness of the green leaching process, quantitative elemental analysis was performed on all three samples. The table below summarises the residual metal content (in % w/w) along with standard deviations, according to the results shared by the University of Cagliari.

Table 8: Residual metal content in BL-PCB Samples

Element	BL-PCB-1 (% w/w)	Std. Dev.	BL-PCB-2 (% w/w)	Std. Dev.	BL-PCB-3 (% w/w)	Std. Dev.
Pb	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.00	0.00	0.40	0.10	0.02	0.01
Cu	0.01	0.00	0.01	0.00	0.17	0.08
Fe	0.01	0.00	0.52	0.14	0.03	0.00
Ag	0.00	0.00	0.00	0.00	0.00	0.00
Al	0.22	0.01	0.23	0.03	0.19	0.02
Sn	0.03	0.00	0.21	0.06	0.01	0.00
Au	0.00	0.00	0.00	0.00	0.00	0.00

Observations and Discussion:

Unlike the MA-CT-PCB, which predominantly yielded glass-fibre-rich residues due to aggressive acid digestion, this second batch BL-PCB retained small traces of metals within the composite structure. The presence of metals such as; Fe, Cu, Ni, and Sn, although minimal, suggests that the milder leaching agents did not achieve full metal extraction. However, this trade-off offers substantial environmental and operational advantages, including reduced reagent hazards and better material preservation. Furthermore, in this series of samples the organic/polymeric component should remain.

The differences in particle sizes allow comparative analysis of adsorption efficiency, surface area interactions, and dye removal kinetics which are critical parameters for assessing the suitability of PCB-derived residues in water purification systems. The low residual metal content, particularly the near absence of toxic elements such as Pb, Cr, and Mn, highlights the safety and environmental compatibility of the treated materials, making them suitable for subsequent adsorption experiments involving organic pollutants such as Methylene Blue (MB) and Methyl Orange (MO).

2.4 Mechanically Processed PCB Residue (MP-PCB):

In line with the overarching objective of the SMaRT-PCBs (Sustainable Materials Recycling Technology for Printed Circuit Boards) project to develop environmentally friendly and low-impact recycling strategies for e-waste, the third batch of samples was processed exclusively through mechanical means (MP-PCB), entirely avoiding chemical leaching, including even mild acids, performed by Politecnico di Milano, as described in the following.

Unlike chemical leaching, which relies on selective dissolution, the mechanical approach aimed to recover the siliceous and polymeric components intact, thus enabling their direct application as potential adsorbent materials for dye removal. The MP-PCB batch therefore represented a crucial step toward achieving a fully circular, reagent-free, and scalable method for converting electronic waste into functional materials suitable for environmental remediation.

MP-PCB exemplifies the most sustainable and non-invasive treatment strategy among the three, aiming to assess the potential of mechanical recovery alone as a viable pre-treatment or separation technique for printed circuit board (PCB) waste.

The PCBs were sourced from a mixture of end-of-life electronic components, including server and computer motherboards, hard disk drives, and memory (RAM) modules. Two different representative categories were identified:

- **RAM modules** (Samples: MP-PCB-1 to MP-PCB-6): More homogeneous in composition, offering a consistent basis for evaluating fragmentation efficiency
- **Mixed PCBs/ Schede Miste** (Samples: MP-PCB-7 to MP-PCB-12): Heterogeneous composition, containing multiple component types and solder alloys.

Each category was initially subjected to primary coarse shredding using an Erdwich M600 single-shaft shredder. This step reduced the boards into fragments of manageable size, typically between 20–40 mm, while ensuring the preliminary detachment of mounted components. The shredder operated under low rotational speed and high torque, employing shear forces to minimise the generation of excessive fines while maintaining structural liberation of metallic and resinous phases.

The coarse-shredded material was then processed through a Retsch SM300 knife mill for fine comminution. This stage was critical in achieving particle liberation suitable for downstream separation. The SM300 operates at adjustable rotational speeds (1000–3000 rpm), with fragmentation controlled by interchangeable grid sieves of 0.5 mm, 1 mm, 2 mm, and 4 mm.

For this batch, processing was conducted primarily at 2000 rpm, with 1 mm and 2 mm grids selected to obtain optimal liberation between metallic and non-metallic phases while minimising material loss. Each milling cycle lasted approximately 5 minutes, ensuring uniform particle distribution. The resulting product exhibited particle sizes typically below 2 mm, facilitating efficient separation and characterisation.

During processing, it was observed that RAM boards produced more uniform and finer particulates due to their consistent composition, while mixed PCBs generated broader particle-size distributions, often with metallic fragments remaining partially attached to the resin matrix. A small quantity of metallic residues was noted to remain within the milling chamber after processing, primarily due to their ductility and higher density compared to the resin components.

After the fine milling process, the ground material underwent electrostatic separation using a Hemos Corona-type separator to isolate metallic, non-metallic, and mixed (partially liberated) fractions. This system operates on the principle of differential electrical conductivity and the particles are segregated in three different chambers:

- Conductive particles (primarily copper, aluminium, and other metals) discharge rapidly and are collected as the metallic fraction.

- Nonconductive particles (fibreglass, epoxy resin) retain charge longer, adhering to the rotating drum and forming the non-metallic fraction.
- The intermediate fraction consists of incompletely liberated particles containing both metallic and polymeric constituents.

For the 1 mm grid runs, the separation yielded approximately 32% metallic fraction, 24–26% mixed fraction, and 43–45% nonmetallic fraction. When the 2 mm grid was employed, the metallic fraction increased to ~36–38%, indicating improved liberation and conductive separation efficiency. The 2 mm configuration was therefore selected as the most effective condition, balancing material recovery and purity without excessive fine generation.

Table 9: Operational and Sample details of MP-PCB Samples

Sample ID	Run	Grid (mm)	Speed (RPM)	Avg. Time in Chamber (s)	Mass In (g)	Mass Out (g)	Loss (g)	Loss (%)
MP-PCB-1	1	1	2000	480	758	680.8	77.2	10%
MP-PCB-2	1	1	2000	495	765	681.7	83.3	11%
MP-PCB-3	1	1	2000	496	755	679.2	75.8	10%
Average (Run 1)	—	—	—	—	—	—	—	10%
MP-PCB-4	2	2	2000	336	756.8	694.3	62.5	8%
MP-PCB-5	2	2	2000	345	750	680.3	69.7	9%
MP-PCB-6	2	2	2000	312	562	528.7	33.3	6%
Average (Run 2)	—	—	—	—	—	—	—	8%

Total Mass (RAM Category):

- **Input:** 4346.8 g
- **Output:** 3945.0 g
- **Average Loss:** ~10%

Table 10: Operational and Sample details of MP-PCB Samples

Sample ID	Run	Grid (mm)	Speed (RPM)	Avg. Time in Chamber (s)	Mass In (g)	Mass Out (g)	Loss (g)	Loss (%)
MP-PCB-7	1	1	2000	900	762	659	103	14%
MP-PCB-8	1	1	2000	915	749.2	665	84.2	11%
MP-PCB-9	1	1	2000	927	768	666.1	101.9	13%
Average (Run 1)	—	—	—	—	—	—	—	13%
MP-PCB-10	2	2	2000	710	761	693.6	67.4	9%
MP-PCB-11	2	2	2000	715	768	688	80	10%
MP-PCB-12	2	2	2000	715	750.4	664	86.4	12%
Average (Run 2)	—	—	—	—	—	—	—	10%

Total Mass (Mixed PCBs Category):

- **Input:** 4558.6 g
- **Output:** 4035.7 g
- **Average Loss:** ~11.5%

The mass losses recorded during mechanical treatment likely result from fine particulate matter (dust), volatile plastic fragments, or adsorbed humidity due to temperature changes during shredding. As no chemical reagents were involved, the materials recovered from this batch retained most of their original constituents, making them ideal for further dry separation techniques such as magnetic or density-based sorting. The variance in residence time within the chamber across samples allows for future correlation with parameters like fragmentation efficiency, material liberation, and suitability for downstream reuse.

2.5 Buffered Chemically Leached PCB Residue-Scale Up (BL-PCB-SU):

To bridge the gap between bench-scale batch kinetics and continuous engineering translation, a dedicated large-batch sample was prepared from an independent secondary PCB feedstock batch which resembled BL-PCB samples. Designated as BL-PCB-SU (Scale-Up), this material was processed by subjecting a significantly larger feedstock mass (100.3g) to the sequential buffered leaching chemistry before being mechanically sieved to isolate a standardised fraction ($\leq 300\mu\text{m}$).

The physical and elemental composition of this specialised scale-up material is summarised below in the tables respectively.

Table 11: Physical Processing Yield of the Scale-Up (BL-PCB-SU) Matrix

Sample ID	Granulometry (mm)	Initial PCB Feed Mass (g)	Recovered Solid Residue (g)	Net Mass Loss (%)
BL-PCB-SU	0.3	100.3	69.1	31.1

A critical comparative analysis between the scale-up matrix and the baseline series reveals a higher retention of residual metals within the BL-PCB-SU structure. The composite exhibits elevated concentrations of iron (3.70% w/w), tin (2.60% w/w), copper (1.60% w/w), and aluminium (1.50% w/w), alongside measurable micro-traces of silver and gold. This chemical signature reflects a distinct, partial metal retention profile that diverges from the highly demetallized baseline fractions shown in Table 12.

Table 12: Quantitative Elemental Profile of the BL-PCB-SU Composite

Element	Residual Content (% w/w)	Standard Deviation ($\pm$)
Pb	0.13	0.03
Ni	0.70	0.10
Cu	1.60	0.20
Fe	3.70	0.60
Ag	0.20	0.04
Al	1.50	0.20
Sn	2.60	0.70
Au	0.14	0.07

This variance is structurally rationalised by a combination of macroscopic scaling effects and localised processing optimisations conducted during the batch synthesis. When scaling the leaching mass to over 100g, mass-transport limitations, local concentration gradients of the organic acid chelators, and the complex interlocking nature of the multi-layered glass-reinforced polymer resin can shield micro-metallic veins from complete chemical dissolution. Additionally, the fine

granulometry of this sample $\leq 300\mu\text{m}$ was achieved through controlled post-leaching mechanical milling rather than pre-leaching micronation, which partially locks internal metallic segments within the consolidated matrix.

Despite this higher metallic background, the structural integrity of the active organic resin and glass-fibre surface boundaries remains entirely intact. The presence of these encapsulated, zero-valent or oxidised metal inclusions does not compromise the environmental safety of the material, as they are securely bound within the vitrified polymer network. This unique multiphase architecture was excluded from subsequent surface modifications or advanced mesoporous transformations; instead, its deployment was strictly restricted to large-volume fluid systems (100 mL and 500 mL). This focused application serves to directly test whether the high surface accessibility of the $\leq 300\mu\text{m}$ geometry can maintain strict volumetric kinetic invariance, validating the raw e-waste composite's industrial viability under scaled, hydrodynamic conditions.

2.6 Samples Comparison:

Table 13: Sample comparison between all three Batches

Aspect	MA-CT-PCB	BL-PCB	MP-PCB
Treatment Type	Strong acid digestion	Mild acid leaching (buffered)	Mechanical shredding only
Chemical Reagents Used	HNO ₃ , HCl, H ₂ O ₂	Lactic buffer, ammonia buffer, I ⁻ /I ₂	None
Metal Removal Efficiency	High (metal-free residue)	Moderate (partial metal content retained)	Mechanical Separation
Environmental Impact	High (acid waste generation)	Medium (sustainable acids used)	Low (greenest method)
Sample Output	Fine glass fibres	Granular solids (0.5–4 mm)	Shredded PCB fragments (2 mm grid)

2.7 Characterisation Techniques:

Following the preparation of the treated PCB-derived samples across the three treatment categories, a comprehensive series of analytical characterisations was conducted to evaluate their physicochemical, morphological, and structural properties. These analyses were essential to establish a clear understanding of the modifications induced by each treatment process and to assess the suitability of the resulting materials as potential adsorbents for pollutant removal.

The characterisation techniques applied in this work were selected based on their ability to provide complementary insights into the samples' composition, surface chemistry, crystallinity, morphology and activity. Together, these analyses enabled a systematic comparison between the three batches and helped to correlate structural and chemical attributes with adsorption performance.

The main instruments employed in this research included **Ultraviolet–Visible Spectrophotometry (UV–Vis)** for monitoring the adsorption experiments and determining the variation of dye concentrations over adsorption time, **Scanning Electron Microscopy (SEM)** for material morphology and microstructural evaluation, **X-ray Diffraction (XRD)** for crystalline phase determination, **Energy Dispersive X-ray Spectroscopy (EDS)** for elemental analysis and **Raman Spectroscopy** for chemical analysis and material characterisation.

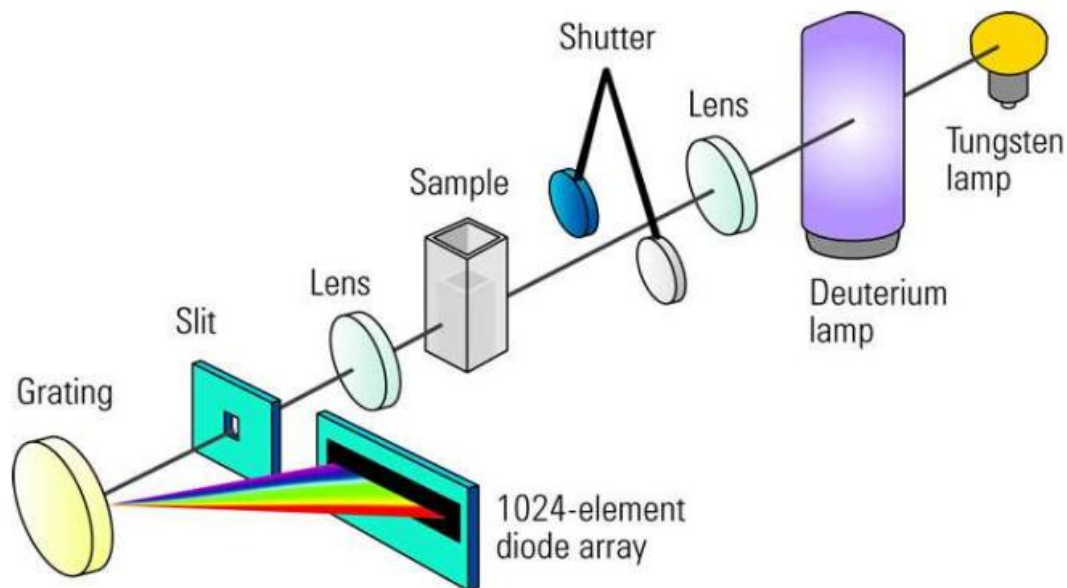
2.8 Ultraviolet-Visible Spectrophotometer:

For the adsorption experiments conducted in this study, the concentration of methylene blue in aqueous solution was analysed using a QE65000 Ocean Optics ultraviolet–visible (UV–Vis) spectrophotometer. UV–Vis spectrophotometry is an analytical technique based on the interaction of electromagnetic radiation with matter, specifically the ability of chemical species to absorb light at characteristic wavelengths. When a beam of light passes through a solution, part of the incident radiation is absorbed by the dissolved analyte, while the remaining portion is transmitted to the detector. The instrument subsequently measures the intensity difference between the incident and transmitted light, enabling quantitative determination of the analyte concentration.

The spectrophotometer employed in this work is equipped with two light sources: a tungsten lamp for the visible region (400–800 nm) and a deuterium lamp for the ultraviolet region (100–400 nm). Different chemical compounds exhibit distinct absorption behaviours depending on their molecular structure and electronic transitions, thereby allowing both qualitative identification and quantitative analysis. Liquid samples were analysed using cuvettes manufactured from optically transparent

materials such as plastic or quartz. Quartz cuvettes, although more expensive, provide superior optical performance due to their negligible absorption across a wider wavelength range.

Block Diagram:



http://www.chem.agilent.com/en-US/products-services/instruments-systems/molecular-spectroscopy/8453-uv-vis-diode-array-system/Pages/photodiode_array_benefits.aspx

Figure 15: UV-Vis Block Diagram

Prior to each experimental run, the spectrophotometer was calibrated using a blank solution consisting of the solvent employed during the adsorption experiments. In this study, “Acqua Norda” mineral water was selected as the blank medium, as it was the solvent used for the preparation of all the dyes solutions in order to simulate realistic water conditions. Calibration with an appropriate blank is essential to eliminate background absorbance and ensure the accuracy of concentration measurements. UV–Vis spectrophotometry is widely utilised in environmental and analytical chemistry because the absorbance intensity of a solution is directly related to the concentration of the absorbing species through the Lambert–Beer Law.

2.8.1 Lambert Beer Law:

The Lambert–Beer Law, constitutes one of the fundamental principles of spectrophotometric analysis in analytical and environmental chemistry. The law establishes a direct relationship between the absorbance of light by a solution, and the concentration of the absorbing species present within that solution. (Harris, 2015).

In its modern form, the Lambert–Beer Law states that when light passes through a homogeneous solution, the reduction in light intensity is proportional to both the concentration of the absorbing species and the optical path length of the sample. The relationship is mathematically expressed as:

$$A = \epsilon bC \quad (6)$$

where:

- A represents the absorbance (dimensionless);
- ϵ is the molar absorptivity coefficient ($Lmol^{-1}cm^{-1}$) of the absorbing specie. It is a parameter which is typical for each chemical substance and it varies as a function of λ ;
- b is the optical path length of the cuvette (cm);
- C is the concentration of the analyte ($molL^{-1}$).

This linear relationship forms the basis for the preparation of calibration curves used in quantitative analysis. Standard solutions of known concentrations are prepared and their absorbance values measured at a selected wavelength, typically corresponding to the maximum absorption wavelength (λ_{max}) of the analyte. The resulting calibration curve enables accurate determination of unknown concentrations by interpolation. For methylene blue, the maximum absorption wavelength in aqueous solution occurs at approximately 664 nm, which provides high analytical sensitivity while minimising spectral interferences (Senthilkumaar et al., 2005).

In the present research, the Lambert–Beer Law played a central role in evaluating the adsorption performance of PCB-derived adsorbent materials for methylene blue removal from water. Since the primary objective of this study is to investigate the feasibility of converting non-metallic printed circuit board waste into functional adsorbents, accurate quantification of dye concentration before and after treatment is essential for assessing adsorption efficiency.

The reliability of all calculated adsorption parameters depends fundamentally on the correct application of the Lambert–Beer Law. Any deviation from ideal analytical conditions, including turbidity, suspended solids, or instrumental instability, can introduce substantial inaccuracies into concentration measurements and compromise the validity of the experimental results. Consequently, rigorous calibration procedures, careful sample preparation, and repeated experimental measurements were implemented throughout this work to minimise analytical errors and ensure reproducibility.

Beyond its analytical importance, the application of the Lambert–Beer Law in this research also supports the broader objective of validating e-waste valorisation as a sustainable environmental strategy. Accurate spectrophotometric measurements provide the quantitative evidence required to demonstrate that processed PCB waste can function as an effective and low-cost adsorbent for dye-contaminated wastewater. The ability to generate precise and reproducible adsorption data also enables direct comparison with conventional adsorbents such as activated carbon and other biochar-based materials reported in the literature.

Overall, the Lambert–Beer Law forms the analytical foundation of this study. Its application enables the rigorous evaluation of dye adsorption by PCB-derived materials and provides the scientific basis for assessing the feasibility of integrating e-waste recycling with sustainable wastewater treatment technologies.

2.9 Raman Spectroscopy:

Raman spectroscopy was employed to investigate the chemical composition and structural features of the PCB-derived materials before and after the applied treatments, as well as to evaluate possible changes occurring after adsorption experiments. Raman spectra were collected using a microRaman LabRAM HR-800 spectrometer (Horiba Jobin Yvon®, France) coupled to an Olympus BX41 optical microscope. The system was equipped with a He–Ne laser operating at a wavelength of 632.8 nm and a CCD detector for spectral acquisition.

All measurements were performed in backscattering geometry. The laser beam was focused onto the sample surface through microscope objectives of appropriate magnification, and the scattered radiation

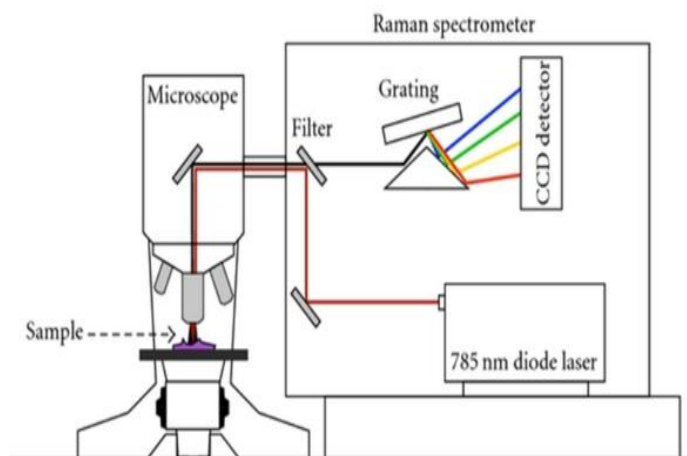


Figure 16: Raman Spectroscopy

was collected along the same optical path. Instrumental parameters, including laser power, acquisition time, grating, and objective magnification, were optimised for each sample to obtain an adequate signal-to-noise ratio while avoiding thermal or photochemical degradation. Raman spectra were acquired from multiple regions of each sample to ensure reproducibility and to account for surface heterogeneity.

Raman spectroscopy provided molecular-level information on the chemical structure of the PCB-derived materials, enabling identification of polymeric, carbonaceous, and inorganic components. The technique was particularly useful for detecting functional groups, assessing the structural integrity of resinous and glass fibre phases, and monitoring chemical modifications induced by different processing routes.

In addition, Raman analysis was used to evaluate potential structural changes occurring after adsorption experiments, offering insights into possible interactions between the adsorbent surface and the adsorbed species. The non-destructive nature and high spatial resolution of micro-Raman spectroscopy make it especially suitable for characterising heterogeneous materials such as PCB waste and for correlating chemical structure with adsorption performance.

2.10 X-Ray Diffraction:

To elucidate the crystallographic architecture and phase composition of the PCB-derived materials, X-ray diffraction (XRD) analysis was conducted. This characterisation is fundamental for identifying the long-range atomic order within the synthesised adsorbents and distinguishing between the amorphous glass-reinforced polymer matrices and the crystalline mineral or metallic inclusions.

Measurements were executed using a PANalytical X'Pert PRO diffractometer (Malvern Panalytical, The Netherlands), utilizing a Cu K α radiation source ($\lambda = 1.5406 \text{ \AA}$). The generator was operated at an accelerating voltage of 40 kV and an emission current of 40 mA. To ensure statistical representativeness and minimise preferred orientation effects, the samples were pulverised to a uniform granulometry and mounted on low-background sample holders. Diffraction patterns were systematically acquired over a 2θ angular range of 10° to 90° , employing a precise step size of 0.02° and a dwell time equivalent to 1° per 20 seconds.

Data acquisition and subsequent post-processing, including background subtraction and peak smoothing were performed using the X'Pert Pro software suite. Phase identification was achieved through a rigorous cross-referencing protocol,



Figure 17: PANalytical X'Pert PRO diffractometer (Malvern Panalytical)

matching the experimental Bragg reflections against standard reference patterns within international crystallographic databases. The XRD analysis facilitated a comprehensive qualitative and semi-quantitative assessment of the crystalline and amorphous constituents within the untreated and treated PCB-derived materials. Specifically, the technique was instrumental in identifying silica-based phases (originating from the e-glass fibre reinforcement), detecting residual metallic or metal oxide species, and monitoring structural phase transitions induced by the various chemical or thermal treatment routes.

2.11 Surface Charge:

The surface charge properties of the PCB-derived materials were evaluated by means of a dynamic light scattering (DLS) instrument equipped with electrophoretic mobility capability (Nanolink S900, Linkoptik, Zhuhai, China).

For each measurement, a known amount of powdered sample was dispersed in deionised water to obtain a dilute and stable suspension suitable

for electrophoretic analysis. The suspensions were gently stirred and allowed to equilibrate prior to measurement to ensure homogeneous particle dispersion and to minimise aggregation effects. No additional electrolytes or pH-adjusting agents were added, unless otherwise specified, in order to preserve conditions comparable to those adopted during adsorption experiments.

Surface charge values were determined by measuring the electrophoretic mobility of the particles under an applied electric field and converting the mobility values into zeta potential using the Smoluchowski approximation, which is appropriate for aqueous systems with moderate ionic strength. Each sample was measured at least three times, and the reported values represent the average of the independent measurements.

surface charge is particularly relevant for adsorption studies involving ionic organic pollutants, as electrostatic interactions between the adsorbent surface and the adsorbate can strongly influence adsorption capacity and kinetics.

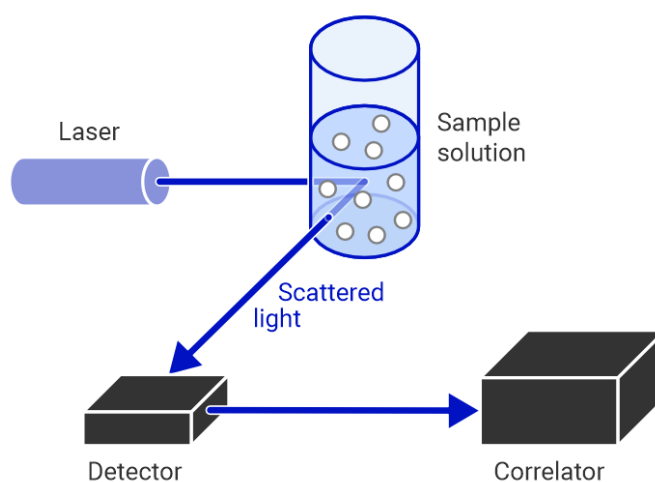


Figure 18: Simplified DLS Mechanism

In the present work, surface charge measurements were used to support the interpretation of adsorption results obtained with oppositely charged dyes, such as methylene blue (cationic) and methyl orange (anionic). The surface charge data allowed qualitative assessment of electrostatic attraction or repulsion phenomena and contributed to a more comprehensive understanding of the adsorption mechanisms governing dye removal by the PCB-derived materials.

2.12 Scanning Electron Microscope (SEM):

The surface morphology and microstructural features of the PCB-derived materials were investigated using a scanning electron microscope (SEM, ZEISS EVO MA10, Carl Zeiss, Germany) equipped with an energy-dispersive X-ray spectroscopy (EDS) detector (Oxford Instruments). SEM imaging was performed to evaluate surface texture, particle morphology, and phase distribution, while EDS analysis was used to determine the elemental composition of selected regions.

The SEM was operated under high-vacuum conditions with an accelerating voltage in the range of 10–20 kV, depending on sample conductivity and imaging requirements. Both secondary electron (SE) and backscattered electron (BSE) detectors were employed to obtain topographical and compositional contrast images. The working distance was maintained between 8 and 10 mm, and imaging parameters were optimised to achieve adequate resolution and signal-to-noise ratio.

Prior to analysis, the samples were dried and mounted on aluminium stubs using conductive carbon tape. To minimise charging effects arising from the presence of non-conductive resin and glass fibre phases, the samples were sputter-coated with a thin gold layer (approximately 10 nm) using a Quorum Q150R ES sputter coater.

EDS analyses, including point analysis and elemental mapping, were conducted on selected surface regions to identify and semi-quantitatively assess the distribution of major and minor elements. The acquired spectra and maps were processed using Oxford INCA software.

SEM–EDS analysis provided critical information on surface morphology, phase heterogeneity, and elemental distribution in the untreated and treated PCB-derived materials. These observations supported the interpretation of structural changes induced by different processing routes and contributed to understanding the role of surface features and composition in the adsorption behaviour of the developed materials.

CHAPTER 3: Experimental Section:

The experimental procedures described below were applied to all PCB-derived materials prepared according to the protocols detailed in the Materials and Methods section. All PCB-derived materials, irrespective of the treatment route used for their preparation, were subjected to a final mechanical conditioning step prior to characterisation and adsorption experiments. This step was introduced to ensure comparable particle size distribution and experimental reproducibility across all batches.

3.1 Particle Size Standardisation:

Preliminary batch trials were executed using the large, unground bulk composite matrices to assess their baseline, macro-scale interfacial behaviour. Later, all samples were subjected to a controlled mechanical conditioning step to ensure comparable particle size distribution and experimental reproducibility across all batches.

PCB-derived materials with initial particle sizes ranging from approximately 4 mm to 0.5 mm were mechanically processed using a high-frequency mixer mill (Retsch MM400). Milling was carried out in 10 mL stainless steel jars loaded with seven stainless steel balls, each with a diameter of 7 mm. The milling frequency was set to 25 Hz.

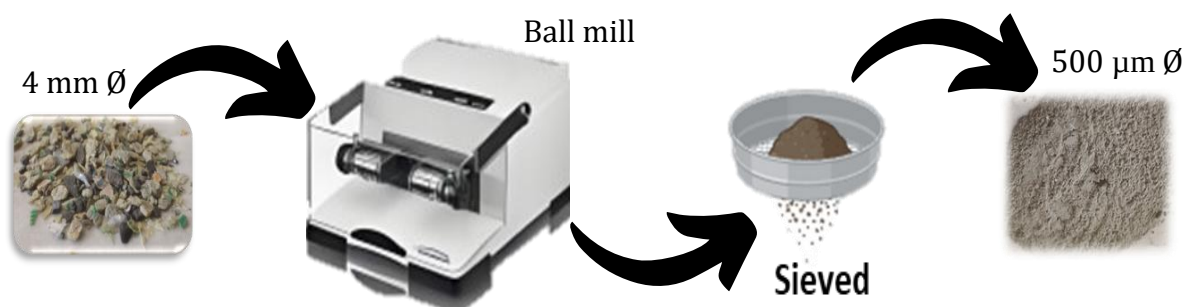


Figure 19: Ball Milling and Sieving

For samples obtained via microwave-assisted acidic digestion (first batch), the dried non-metallic residue was milled for 3 min, reflecting the reduced mechanical resistance of the treated material. In contrast, samples obtained through buffered leaching and purely mechanical treatment (second and third batches) were milled for 9 min to account for their higher structural heterogeneity and mechanical stability.

After milling, all samples were manually sieved using a 500 µm stainless steel mesh for approximately 30–40 s to remove coarse fractions and obtain a uniform powder suitable for

subsequent experiments. The sieved powders were homogenised and stored in airtight containers prior to use.

For adsorption experiments, a fixed adsorbent mass of 6.00 ± 0.02 mg was used unless otherwise stated. In a typical batch test, the adsorbent was contacted with 5 mL of dye solution, corresponding to an adsorbent dosage of 1.2 mg mL^{-1} . This standardised dosage enabled direct comparison between samples produced through different processing routes and ensured consistency with previously published experimental work.

3.2 Physicochemical Characterisation Experiment:

Physicochemical characterisation was performed to assess the structural, morphological, and surface properties of the PCB-derived materials prior to and after adsorption experiments. Characterisation protocols and instrumental conditions were kept constant for all samples to ensure comparability.

3.2.1 Crystallographic Analysis:

X-ray diffraction (XRD) analysis was conducted to identify crystalline and amorphous phases present in the samples and to evaluate structural changes induced by the different treatment routes. Diffraction patterns were collected using a PANalytical X'Pert PRO diffractometer equipped with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), operating at 40 kV and 40 mA. Data were acquired over a 2θ range of 10° – 90° with a step size of 0.02° . Phase identification was performed by comparison with reference database patterns using the instrument software.

3.2.2 Raman Spectroscopic Analysis:

Raman spectroscopy was employed to investigate the chemical composition and structural features of the PCB-derived materials, with particular attention to carbonaceous, polymeric, and inorganic components. Spectra were recorded using a LabRam HR-800 micro-Raman spectrometer (Horiba Jobin Yvon) equipped with a He–Ne laser ($\lambda = 632.8 \text{ nm}$). The laser power was attenuated to 0.3 mW, and the acquisition time was set to 10 s. Measurements were collected from multiple regions of each sample to ensure representativeness and reproducibility.

3.2.3 Morphological and Elemental Analysis:

Surface morphology and microstructural features were examined using optical microscopy and scanning electron microscopy (SEM). SEM observations were carried out using a ZEISS EVO MA10, Carl Zeiss, microscope to evaluate particle morphology, fibre exposure, and surface texture. Elemental composition was qualitatively assessed by energy-dispersive X-ray spectroscopy (EDS)

on selected regions, providing confirmation of the removal or retention of metallic elements depending on the treatment route.

3.2.4 Surface Charge Measurements:

The electrokinetic properties of the PCB-derived materials were evaluated through zeta potential measurements. Analyses were performed using a dynamic light scattering instrument (Nanolink S900, Linkoptik). Dilute aqueous suspensions were prepared using deionised water, and measurements were conducted at room temperature. Each sample was analysed in triplicate, and average zeta potential values were reported. These measurements provided information on surface charge behaviour relevant to adsorption mechanisms involving ionic dyes.

3.3 Adsorption Experiments:

Adsorption experiments were conducted to evaluate the ability of the PCB-derived materials to remove organic dyes from aqueous solutions under controlled batch conditions. Methylene blue (MB) was selected as the primary model cationic dye; methyl orange (MO) as an anionic probe; and crystal violet (CV) and rhodamine 6G (R6G) as supplementary cationic probes evaluated for $m\text{-SiO}_2$ selectivity studies (Section 4.3.4). Dye solutions of known initial concentration were prepared using mineral water without pH adjustment (measured $\text{pH} \approx 7.5$).

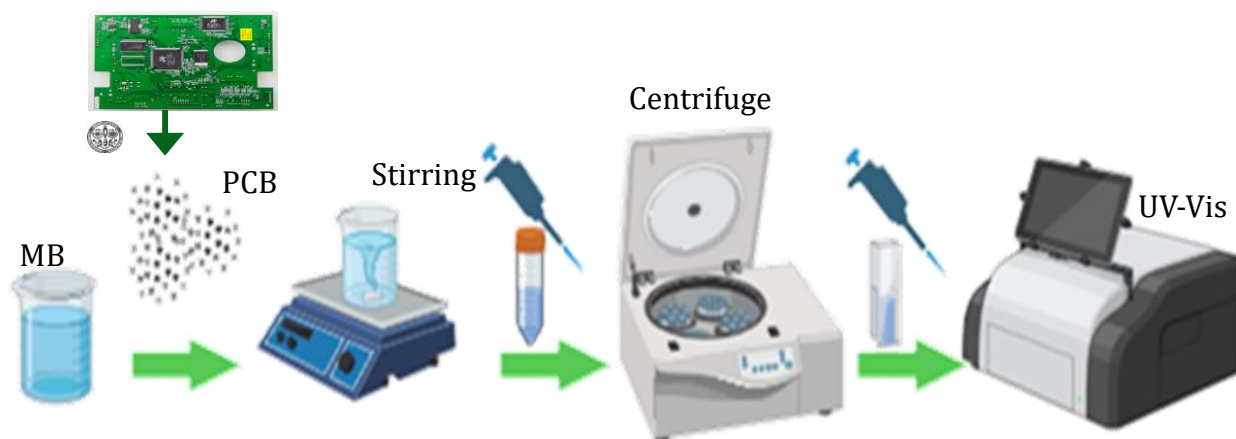


Figure 20: Example of an Adsorption experiment

In a typical experiment, a known mass of adsorbent (generally 6 mg) was added to 5 mL of dye solution and magnetically stirred at 700 rpm at room temperature (25 °C). Adsorption experiments were performed in the dark to avoid photodegradation effects unless otherwise stated for photo-assisted studies. The adsorbent dosage and operational parameters were systematically varied depending on the specific experimental objective.

To investigate adsorption kinetics, samples were collected at predetermined contact times ranging from 1 min to 1440 min. At each time interval, the suspensions were centrifuged at 9000 rpm for 4 min to separate the solid and liquid phases and to eliminate optical interference during spectrophotometric analysis. The supernatant was subsequently analysed using a QE65000 Ocean Optics UV–Visible spectrophotometer.

Residual dye concentrations were determined from absorbance measurements recorded at the characteristic maximum absorption wavelengths (λ_{max}) of each dye: 664 nm for MB, 590 nm for CV, 460 nm for MO, and 526 nm for R6G. Concentrations were calculated using Beer–Lambert calibration relationships within the validated linear response range.

The percentage removal efficiency (%) was determined according to the following equation:

$$\% \text{ Adsorbed} = \frac{A_0 - A_t}{A_0} * 100 \quad (7)$$

Where A_0 is the initial value of absorbance of the analyte (proportional to the value of its initial concentration) and A_t is the value of absorbance measured at time t after the mixing with the adsorbent in the dark. The obtained data were used for the calculation of q_t , which represents the amount of adsorbed pollutant per gram of adsorbent (mg g^{-1}) at any time t (min), and for the calculation of q_e (mg g^{-1}), which corresponds to the amount of adsorbed pollutant per gram of adsorbent after the reaching of the equilibrium between the processes of dye adsorption and desorption (equilibrium adsorption capacity).

$$q_t = \frac{(C_0 - C_t) * V}{m} \quad (8)$$

Where C_0 and C_t are the initial and time-dependent dye concentrations ($\text{mg} * \text{L}^{-1}$), respectively, V is the solution volume (L), and m is the dry mass of adsorbent (g). At equilibrium ($t \rightarrow \infty$), C_t becomes the equilibrium concentration (C_e), allowing determination of the equilibrium adsorption capacity (q_e).

The experimental kinetic data were analysed using non-linear forms of the pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models. Non-linear regression analysis was performed using the Solver add-in in Microsoft Excel to minimise residual errors without applying linearised transformations that may introduce statistical bias (Wang & Guo, 2020). Goodness-of-fit was evaluated using the coefficient of determination (R^2) together with error analysis parameters, including root-mean-square error (RMSE).

For benchmarking purposes, adsorption experiments were also performed using commercial activated carbon (DARCO, Sigma-Aldrich), untreated PCB powders, glass substrates, and silica sand under identical operating conditions. All experiments were conducted in triplicate, and the reported values represent mean results with standard deviation analysis used to evaluate experimental reproducibility.

3.4 Photo-Assisted Degradation under Simulated Solar Irradiation:

Photo-assisted degradation experiments were carried out to evaluate the behaviour of PCB-derived materials under simulated solar irradiation following adsorption treatments. These experiments were designed to investigate the combined effect of adsorption and light exposure under controlled laboratory conditions, by assessing the response of dye-loaded systems to simulated solar light.

Photodegradation experiments were performed using a solar simulator equipped with a xenon arc lamp providing a continuous spectrum representative of natural sunlight. The system was operated under AM 1.5G spectral conditions, reproducing the solar irradiation reaching the Earth's surface. The light intensity at the sample position was adjusted to 1 sun ($\approx 100 \text{ mW cm}^{-2}$) and verified using a calibrated reference photodiode.

The irradiation setup consisted of a fixed lamp-sample configuration, with samples placed at a constant distance from the light source to ensure uniform exposure. All experiments were conducted at ambient temperature, and no external temperature control was applied during irradiation.

Photodegradation tests were conducted in transparent glass vials to allow full transmission of visible light. In a typical experiment, 5 mL of aqueous dye solution was placed in the vial, either alone or in the presence of the PCB-derived material previously subjected to adsorption treatment, depending on the experimental condition.

Prior to light exposure, samples containing adsorbent materials were kept under dark conditions for a defined period of 24 hours to ensure adsorption equilibrium. After this step, the vials were positioned under the solar simulator and exposed to continuous irradiation for the selected duration.

During irradiation, the samples were maintained under continuous magnetic stirring to prevent particle sedimentation and to replicate realistic post-adsorption treatment scenarios. Control experiments were performed under identical irradiation conditions in the absence of adsorbent material to isolate the effect of light exposure alone.

At predefined irradiation times usually 60minutes, samples were withdrawn and centrifuged at 9000 rpm for 4 min to separate the solid phase from the liquid phase. The supernatant was collected and

analyzed by UV–Visible spectroscopy using the same instrumental setup and calibration procedures adopted for adsorption experiments.

Absorbance spectra were recorded over the visible range, and concentration changes were monitored at the characteristic absorption maxima of the target dyes. All measurements were performed at room temperature, and experiments were carried out in triplicate to ensure reproducibility. The photo-assisted degradation experiments were conducted for both cationic and anionic model dyes.

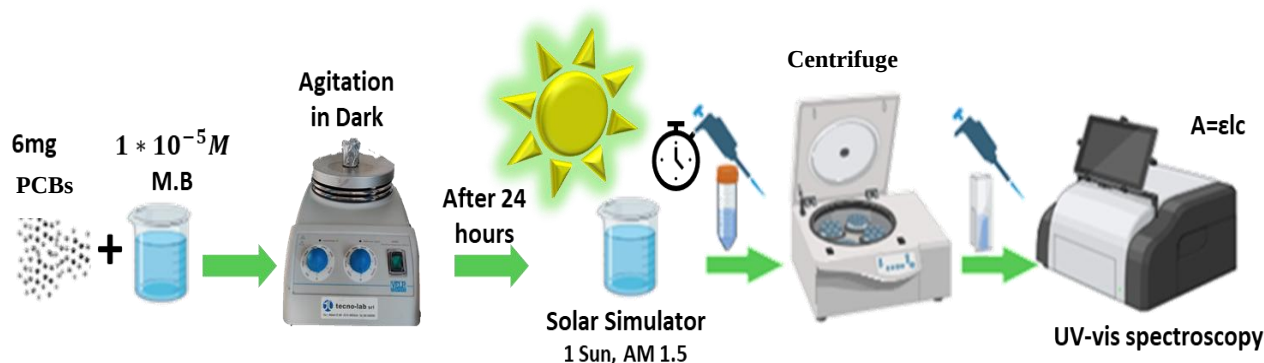


Figure 21: Solar Degradation

A schematic representation of the experimental workflow is shown in the figure to illustrate the overall experimental sequence.

3.5 Conversion of PCB-Derived Materials into Mesoporous Silica and Surface-Modified Adsorbents:

3.5.1 Rationale and Scope:

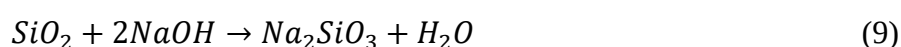
As shown in Chapter 4, BL-PCB and MP-PCB materials showed lower adsorption performance than MA-CT-PCB. For this reason, innovative strategies to maximise their decontamination activity against MB were investigated. On one hand surface functionalisation using naturally derived biopolymers was explored; on the other the conversion into mesoporous silica ($m\text{-SiO}_2$). The first strategy was investigated to assess the potential enhancement of adsorption efficiency through the introduction of additional functional groups on the PCB-derived material. In particular, chitosan, alginate and dopamine were selected as starting point for functionalization due to their environmental compatibility and known affinity for organic pollutants.

In addition, the conversion into mesoporous silica instead could be a productive approach, enabling a significant increase in accessible surface area and porosity.

3.5.2 Synthesis of Mesoporous Silica from PCB-Derived Materials:

Mesoporous silica (m- SiO_2) was synthesised following a procedure adapted from Liou and Jheng (2018), using a silica precursor extracted from MP-PCB samples.

The ground non-metallic fraction deriving from MP-PCBs was subjected to alkaline leaching with concentrated NaOH to extract the Si-contents in the form of sodium silicate, for resin wastes. In particular, 5 g was added to 32.5 mL of NaOH 4M and they were left under agitation and boiling at 100°C for 6h. Then, the solution was chilled at room temperature and filtered, to separate the sodium silicate solution from the residual MP-PCB powder. The extraction process follows the well-established reaction:



The sodium silicate solution was used as precursor for the synthesis of m- SiO_2 . A CTAB solution was prepared by dissolving 210 mg of cetyltrimethylammonium bromide (CTAB; $\geq 98\%$, Sigma-Aldrich) in 3.2 mL of deionised water under gentle stirring until complete dissolution. It was mixed with the 10.4 mL of the sodium silicate solution. The pH of the final solution was acidified thanks to addition of incremental amount of H_2SO_4 (approximately, 9mL of H_2SO_4 1M and 6.5 mL of concentrated H_2SO_4 96%) until a stable pH=11 was achieved measured through the pH-meter). The resulting gelling solution was transferred inside a PTFE-lined stainless-steel autoclave (volume 125 mL) and heated inside an electric oven at 100°C for 48 h. The obtained powder was recovered through centrifugation at 9000 rpm for 4 minutes and the solid was dried at ambient temperature for 24 hours. Finally, it was annealed at 550°C for 6 hours in a tubular oven (heating rate: 5°C min⁻¹).

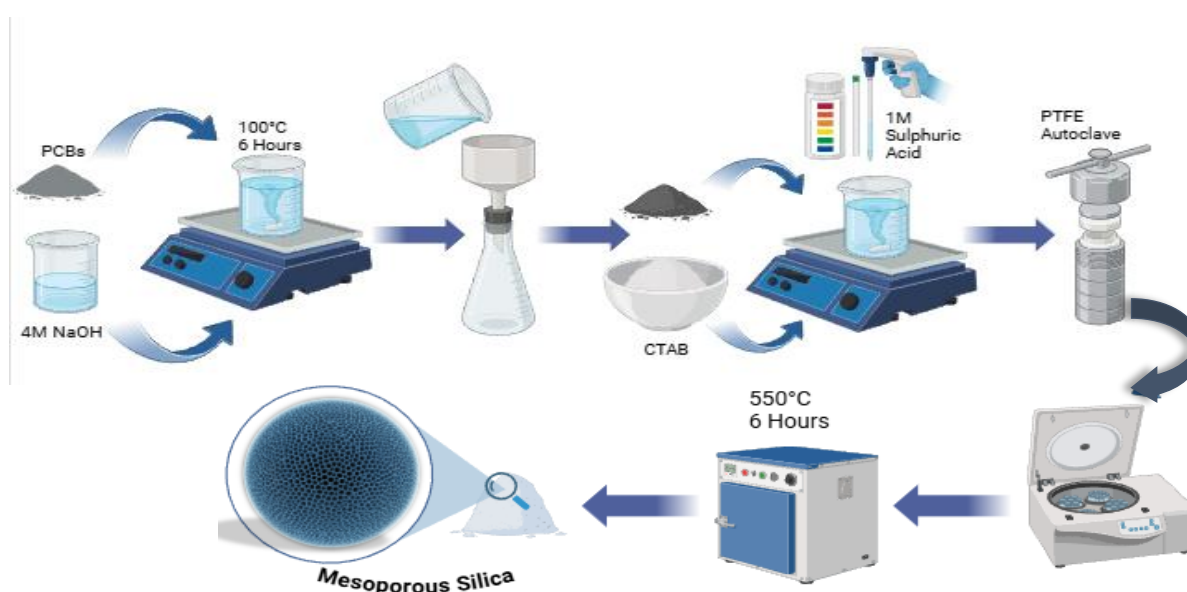


Figure 22: Mesoporous Silica Synthesis

These mesoporous silica samples were characterised to assess their structural and surface properties: conventional and low-angle X-ray diffraction (XRD) analysis was performed to verify the formation of ordered mesoporous structures and to evaluate the amorphous or crystalline nature of the silica framework. DLS measurements were conducted to determine surface charge characteristics in aqueous suspension, electron microscopy was performed for morphological analysis (courtesy of prof. Casula, University of Cagliari) and BET analysis was performed for surface area and porosity characterisation (courtesy of prof. Casula, University of Cagliari). The adsorption behaviour of the materials was further assessed through UV–Visible spectroscopy during dye removal experiments.

3.5.3 Surface Functionalisation with Biopolymers:

To optimise the e-waste-derived materials for specific environmental applications, surface modification was employed using natural biopolymers. The high density of reactive sites such as hydroxyl, amino, and carboxyl groups, inherent in biopolymeric chains allows for the creation of a hybrid organic-inorganic interface. By utilising thermal digestion and controlled agitation, the biopolymers are anchored onto the adsorbent surface, significantly increasing the theoretical number of binding sites available for ion exchange and complexation during the adsorption process.

3.5.3.1 Alginate Functionalisation:

Sodium alginate functionalisation of BL-PCB samples was performed to introduce additional surface functional groups and enhance adsorption affinity of the PCB-derived materials. An alginate solution was prepared by dissolving 45 mg of sodium alginate in 50 mL of Milli-Q water, and the solution was sonicated to ensure complete dissolution and homogeneity.

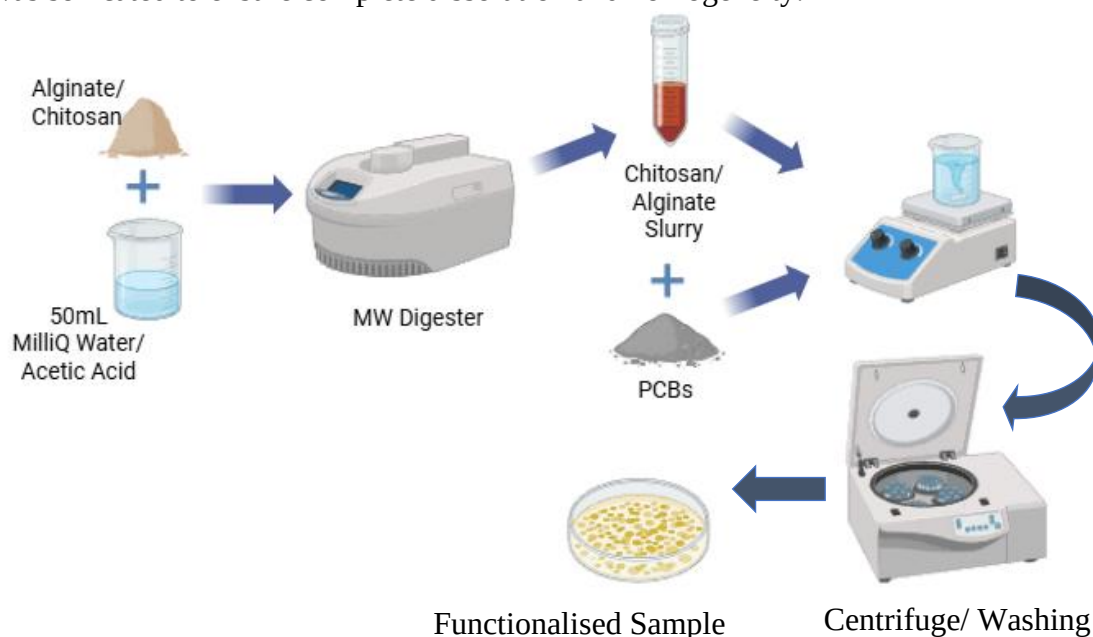


Figure 23: Alginate and Chitosan Functionalisation

Subsequently, 15 mL of the alginate solution was subjected to digestion under the following conditions: namely a digestion temperature of 200 °C, 5 min ramp time, 15 min holding time, 200 psi pressure, and 150 W power. This treatment produced, as reported by Vassalini et al., (2020), a slurry composed of a mixture of C-Dots, alginate and mixed organic acids which is capable to increase the adsorption of different oxides materials against MB.

The functionalisation process involved mixing 100 mg of the BL-PCB powder with 1 mL of the digested alginate solution, followed by agitation at 700 rpm for 60 minutes. The suspension was then centrifuged at 9000 rpm for 4 min, the liquid phase was removed, and the solid material was dried under ambient conditions for 24 hours to obtain the alginate-functionalised adsorbent.

3.5.3.2 Chitosan Functionalisation:

Chitosan functionalization of BL-PCBs was performed to introduce additional surface functional groups and enhance adsorption affinity. A chitosan solution was prepared by dissolving 45 mg of chitosan in 50 mL of 5% (v/v) acetic acid (CH_3COOH) aqueous solution. The mixture was initially treated in an ultrasonic bath to promote complete dissolution and homogenization of the biopolymer.

Following sonication, 15 mL of the chitosan solution was transferred into a digestion vessel and subjected to thermal treatment using a microwave digestion system. The digestion was conducted at 200 °C, with a ramp time of 5 min and a holding time of 15 min, under an applied pressure of approximately 200 psi and a power input of 150 W. This step ensured proper activation and molecular dispersion of the chitosan prior to immobilisation.

For the functionalisation step, 100 mg of the BL-PCB batch adsorbent material was mixed with 1 mL of the digested chitosan solution. The suspension was agitated at 700 rpm for 60 min to allow uniform coating and interaction between the adsorbent surface and the biopolymer. After agitation, the mixture was centrifuged at 9000 rpm for 4 min, and the supernatant was carefully decanted.

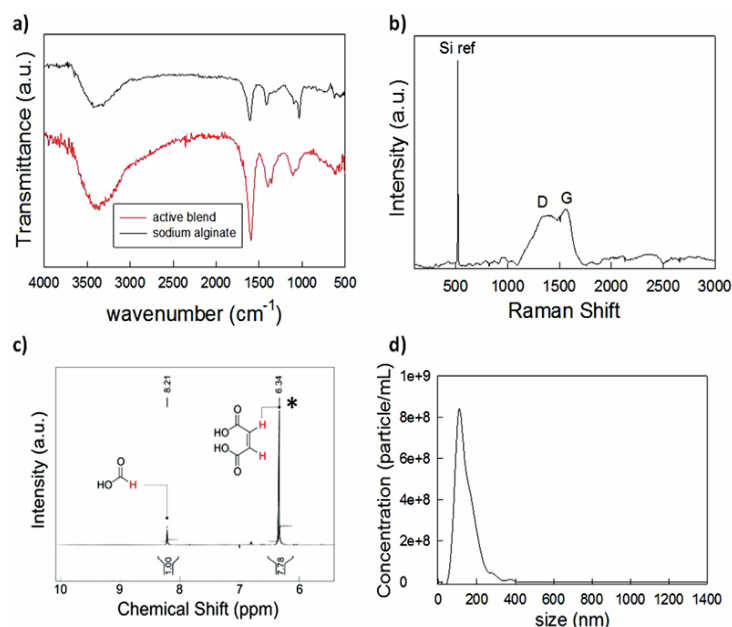


Figure 24: Characterisation of Alginate derived blend. a) IR Spectrum. b) Raman Spectrum. c) NMR Spectrum d) Hydrodynamic radius of contained C-NPs

The resulting solid was collected and dried under ambient conditions for 24 hours, yielding the chitosan-functionalised adsorbent.

3.5.3.3 Polydopamine Functionalisation:

Polydopamine (PDA) functionalisation was performed to enhance the surface chemistry of the PCB-derived adsorbent and introduce additional oxygen- and nitrogen-containing functional groups capable of improving dye adsorption performance. The functionalization procedure was adapted from dopamine self-polymerization methods under mildly alkaline conditions.

In a typical synthesis, approximately 0.16 g of the PCB-derived adsorbent material was dispersed in 38 mL of Milli-Q water. Subsequently, 0.20 g of hexamethylenetetramine (HMTA) and 15 mg of dopamine hydrochloride (DA) were added to the suspension. The resulting mixture was magnetically stirred at room temperature for 2 hours to promote the oxidative self-polymerisation of dopamine and the formation of a conformal PDA coating on the adsorbent surface.

Following functionalisation, the suspension was centrifuged to recover the solid material, which was subsequently washed several times with Milli-Q water and ethanol to remove unreacted species and weakly adsorbed residues. Each washing step was followed by centrifugation to ensure efficient phase separation and purification of the coated material.

The purified PDA-functionalised adsorbent was then dried under ambient atmospheric conditions for 48 hours prior to further characterisation and adsorption experiments.

Adsorption experiments using mesoporous silica and biopolymer-functionalised samples were carried out under the same experimental conditions adopted for the unmodified PCB-derived materials. Methylene blue was used as the model pollutant. Dye concentration, solution volume, adsorbent dosage, stirring rate, and contact time were kept constant to enable direct comparison of adsorption performance.

Residual dye concentrations were determined by UV–Visible spectroscopy, and adsorption capacities were calculated using standard mass balance equations.

3.5.4 Reusability and Stability Tests:

The reusability of the $m\text{-SiO}_2$ materials derived from MP-PCB residues was evaluated through consecutive adsorption–desorption cycles under identical experimental conditions. The experimental protocol for evaluating the cyclic stability of PCBs was designed to simulate the rigorous conditions of industrial wastewater treatment, where material longevity is as critical as initial capacity. For this purpose, synthesised mesoporous silica sample (MP-PCB-MS) was selected. This setup focuses on

the iterative restoration of active sites, ensuring that the waste-derived silica framework can function as a high-performance, multi-use reagent.

After completion of each adsorption experiment, the adsorbent was separated from the solution by centrifugation at 9000 rpm for 4 min. The recovered solid was subjected to a regeneration treatment using 0.1 M sodium dodecyl sulphate (SDS) aqueous solution as a desorbing agent. The adsorbent was dispersed in the SDS solution at a concentration higher than its critical micellar concentration and maintained under agitation for several hours to promote desorption of the previously adsorbed dye molecules.

Following the desorption step, the material was centrifuged and thoroughly washed multiple times with deionised water to remove residual surfactant and loosely bound species. The regenerated material was then dried at ambient conditions prior to reuse.

The regenerated mesoporous silica was subsequently reused in a new adsorption experiment under the same operational parameters (adsorbent mass, solution volume, initial dye concentration, and contact time) as the original test. This regeneration and reuse procedure (schematically summarised in Figure 25) was repeated for four consecutive cycles to evaluate the structural stability and operational durability of the material.

All adsorption and regeneration experiments were performed under the same and reproducible laboratory conditions to ensure comparability between cycles.

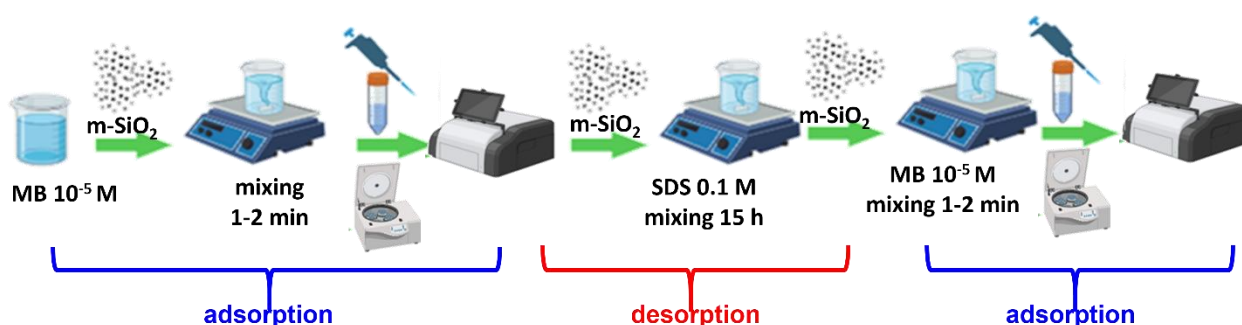


Figure 25: Schematic of the Reusability Workflow: It details the cyclic process including the addition of the pollutant, magnetic stirring, centrifugal recovery, and the subsequent desorption/washing steps required for regeneration.

The evaluation of reusability was conducted to assess the long-term applicability of the synthesised materials in realistic water treatment scenarios. Demonstrating stable performance over multiple adsorption–desorption cycles is essential to reduce material consumption, minimise secondary waste generation, and improve process sustainability. The ability to regenerate PCB-derived mesoporous silica supports its potential integration into circular economy strategies, where electronic waste is valorised into functional materials for environmental remediation.

3.6 Volumetric Scale-Up Adsorption Experiments:

Adsorption experiments at increased reaction volumes were conducted using the BL-PCB-SU material to evaluate the volumetric invariance of the adsorption system. Two scaled configurations were tested: 100 mL and 500 mL, representing 20-fold and 100-fold increases relative to the standard 5 mL bench protocol. The adsorbent mass was scaled proportionally to maintain a constant dosage of 1.2 mg mL^{-1} (0.12 g at 100 mL; 0.60 g at 500 mL). Methylene blue solutions at $1 \times 10^{-5} \text{ M}$ were prepared in mineral water without pH adjustment ($\text{pH} \approx 7.5$). Experiments were performed in borosilicate glass vessels under magnetic stirring at 700 rpm at ambient temperature ($25 \pm 1^\circ\text{C}$). Aliquots of 1.5 mL were withdrawn by syringe at contact times of 1, 15, 30, 60, 240, 480, 1440, and 4320 minutes. Each aliquot was centrifuged at 9000 rpm for 4 minutes to separate suspended adsorbent, and the absorbance of the supernatant was measured at 664 nm against a mineral water blank. Adsorption parameters (q_t , q_e , % removal) were calculated using the equations defined in Section 3.3.

CHAPTER 4: RESULTS AND DISCUSSION

This chapter presents a comprehensive analysis of the physicochemical properties and adsorption performance of PCB-derived materials obtained through three distinct processing routes: microwave-assisted chemical treatment (MA-CT-PCB), buffered leaching (BL-PCB), and mechanical processing (MP-PCB) and their modifications according to what reported in Chapter 3.

A comparative approach is adopted to evaluate the influence of treatment methodology on material properties and functional performance. Particular emphasis is placed on correlating structural features with adsorption efficiency and understanding the mechanisms governing dye removal under both dark and irradiated conditions.

4.1 Microwave Assisted Chemically Treated Printed Circuit Board (MA-CT-PCB):

4.1.1 Structural and Morphological Characterisation:

The structural and compositional properties of the MA-CT-PCB materials were investigated using X-ray diffraction (XRD), Raman spectroscopy, and microscopic techniques in order to evaluate the effects of microwave-assisted acidic treatment on the original PCB matrix.

The XRD pattern (Figure 26 a) revealed that the material is predominantly composed of an amorphous phase, evidenced by the presence of a broad diffraction halo, which can be attributed to amorphous $m\text{-SiO}_2$ originating from the fibreglass substrate. In addition to the amorphous contribution, distinct diffraction peaks were observed at $2\theta \approx 28.4^\circ$, 47.3° , and 56.1° , corresponding to crystalline silicon. A minor peak centred at $2\theta \approx 26.6^\circ$ was also detected and assigned to quartz (crystalline $m\text{-SiO}_2$). The presence of these phases confirms that the microwave-assisted acidic treatment described in Chapter 2 and performed by the University of Cagliari effectively removed the majority of metallic and polymeric components while preserving the silica-based framework.

Raman spectroscopy (Figure 26b) further supported these findings, showing a characteristic peak at approximately 520 cm^{-1} associated with crystalline silicon. The absence of additional Raman bands corresponding to polymeric or organic components indicates the effective removal of epoxy resin during the microwave-assisted acidic digestion process.

The elimination of metals such as Cu, Fe, Al, Ni, Zn, Pb, and others, together with the removal of epoxy resin, suggests that the applied treatment significantly altered the chemical composition of the original PCB material. The persistence of crystalline silicon is attributed to the absence of hydrofluoric acid in the leaching process, which would otherwise dissolve silica phases.

Morphological analysis using optical microscopy and SEM (Figure 26 c, d) revealed irregular particle geometries and the presence of fibrous structures characteristic of glass fibres. These fibres exhibited microstructural defects and surface irregularities, which are expected to enhance adsorption by increasing surface accessibility and providing additional active sites.

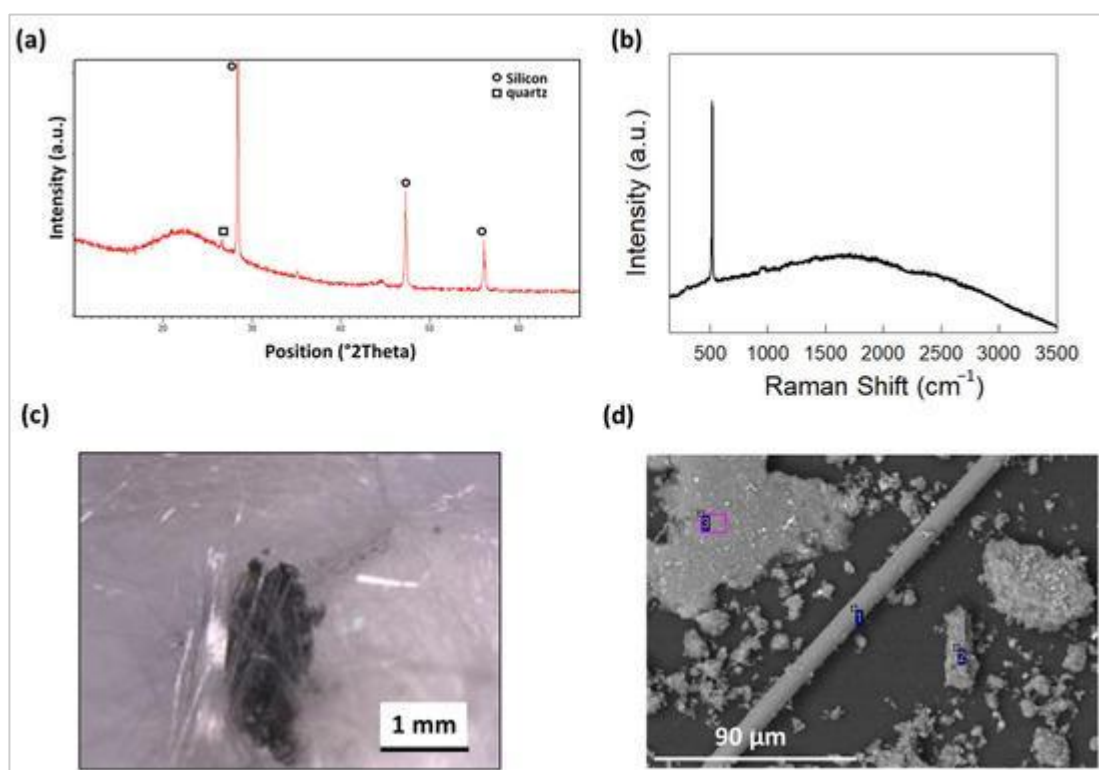


Figure 26:(a) XRD pattern, (b) Raman spectrum, (c) Optical microscopy, (d) SEM images of MA-CT-PCB

4.1.2 Adsorption Behaviour:

The adsorption performance of MA-CT-PCB materials was systematically evaluated using methylene blue as a model organic contaminant under environmentally relevant conditions (pH = 7.5, no buffering, room temperature, and simple magnetic stirring), in order to assess their applicability in realistic water treatment scenarios.

The adsorption process (Figure 20: Example of an Adsorption experiment) exhibited a rapid initial uptake followed by a slower approach to equilibrium, indicating the presence of highly accessible active sites at the early stages of contact. This behaviour is characteristic of adsorption systems in

which surface interactions dominate the initial phase, followed by progressive site saturation and equilibrium establishment.

A critical parameter influencing adsorption efficiency was the granulometry of the adsorbent. As shown in Figure 27, coarse MA-CT-PCB fragments ($\sim 0.3 \text{ cm}^2$) exhibited very limited adsorption performance, achieving only $\sim 16\%$ MB removal after 24 h. In contrast, finely ground powder ($< 500 \text{ }\mu\text{m}$) displayed a dramatic enhancement in adsorption, reaching $\sim 89\%$ removal under identical conditions. Notably, the pulverised material achieved $\sim 38.7\%$ removal within the first minute, already exceeding the 24-hour performance of coarse samples.

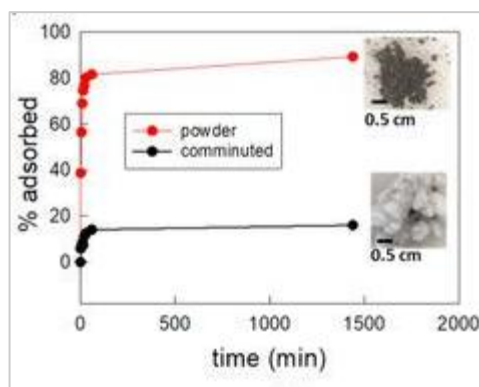


Figure 27: Effect of granulometry on MB adsorption

This pronounced improvement can be attributed to the increase in specific surface area and the exposure of previously inaccessible adsorption sites upon particle size reduction. The results clearly demonstrate that post-treatment grinding is not merely beneficial but essential to activate the adsorption potential of the material.

The influence of adsorbent dosage was further investigated. Increasing the adsorbent concentration from 0.6 mg mL^{-1} to 1.2 mg mL^{-1} resulted in a significant increase in adsorption efficiency. However, further increases in dosage (up to 2.4 mg mL^{-1}) produced only marginal improvements, particularly at equilibrium, where MB removal

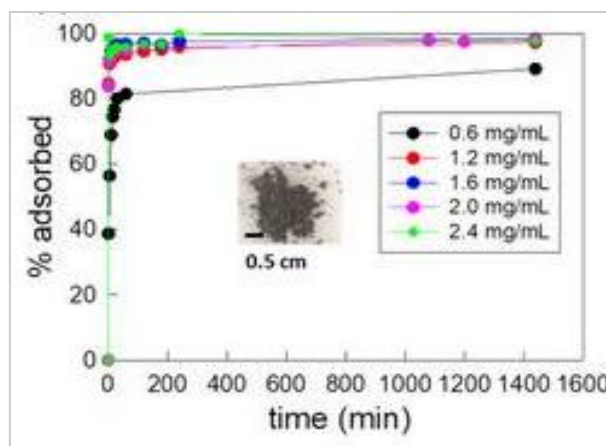


Figure 28: Effect of adsorbent dosage on MB Adsorption

remained approximately constant at $\sim 98\%$. This indicates that above a threshold concentration, the system becomes limited by dye availability rather than adsorption site density. Consequently, an adsorbent dosage of 1.2 mg mL^{-1} was identified as the optimal operating condition and was used for all subsequent experiments (regarding also the other PCB-derived materials).

The adsorption capacity (q_t) as a function of contact time further confirmed the rapid kinetics of the system. A substantial fraction of MB uptake occurred within the first 5 minutes, after which q_t approached a plateau, indicating the establishment of a dynamic equilibrium between adsorption and desorption processes.

Under these optimised conditions, the MA-CT-PCB material achieved near-complete MB removal (~97–98%) without the need for pH adjustment, chemical additives, or thermal input, highlighting its potential for low-cost and sustainable water treatment applications.

The adsorption performance was further evaluated at a higher dye concentration (2×10^{-5} M). Even under these more demanding conditions, the material maintained excellent efficiency, achieving 77.5% removal within 1 min, increasing to 89.9% at 5 min, and reaching 98.9% at equilibrium (24 hours). Notably, the equilibrium adsorption capacity increased to 5.27 ± 0.007 mg g⁻¹, which is more than double the value obtained at 10^{-5} M (2.59 mg g⁻¹), indicating that the material possesses additional available adsorption sites and does not operate near saturation under lower concentration conditions.

This behaviour suggests that MA-CT-PCB materials can effectively accommodate higher pollutant loads, further supporting their applicability in real wastewater treatment scenarios.

4.1.3 Kinetic Modelling and Mechanistic Interpretation:

The adsorption kinetics of methylene blue onto MA-CT-PCB were quantitatively analysed in order to identify the rate-limiting mechanism and to extract the parameters that govern the dye–surface interaction. Four kinetic models, widely employed in the adsorption literature (Wang & Guo, 2020) were fitted to the experimental q_t versus t data using the non-linearised forms of their respective equations through the Solver routine of Microsoft Excel: (i) the pseudo-first-order (PFO) model, (ii) the pseudo-second-order (PSO) model, (iii) the Elovich model, and (iv) the intraparticle diffusion model.

Table 14:Pseudo Second Order model (highlighted) provides the optimal description of the system

Statistical Parameter	PFO	PSO (best fit)	Elovich	Intraparticle Diffusion
R²	0.9919	0.9975	0.7955	0.1256
MSE	0.0036	0.0011	0.0042	0.3864

The Boyd model, which distinguishes film diffusion from intraparticle diffusion, was not applied as the low R^2 of the intraparticle diffusion model (0.1256) already indicates that boundary-layer film diffusion is not the dominant rate-limiting mechanism in this system.

The full kinetic dataset, spanning 1 to 1440 minutes of contact time at $MB = 1 \times 10^{-5}$ M, adsorbent dosage = 1.2 mg mL^{-1} , mineral water matrix, ambient temperature, and magnetic stirring at 700 rpm, was used for the fitting. The corresponding model fits are reported in Figure 30. The statistical analysis identifies the pseudo-second-order (PSO) model as the optimal kinetic descriptor of the MB / MA-CT-PCB system. The PSO model returns the

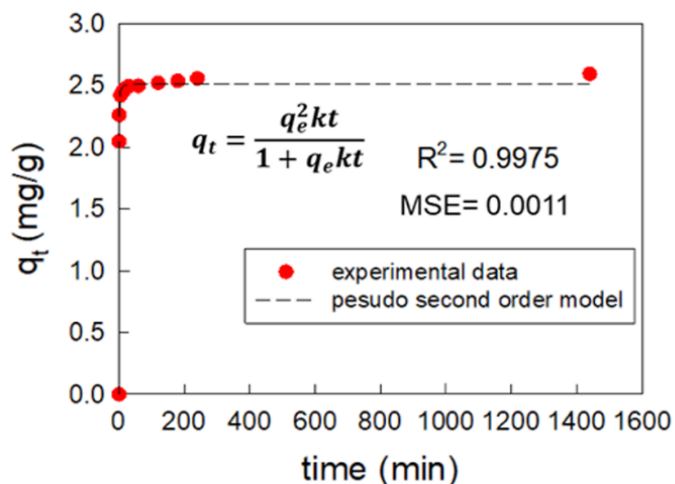


Figure 29: Points represent the experimental data; dashed lines represent the results of the fitting using the non-linearised form of pseudo-second-order model.

highest R^2 (0.9975) and the lowest value of MSE (0.0011) among the four models evaluated. In quantitative terms, the PSO MSE is 3.3-fold lower than that of the PFO model, 3.8-fold lower than that of the Elovich model, and over two orders of magnitude lower than that of the intraparticle diffusion model.

This conclusion is mechanistically consistent with the morphological characterisation reported in figure 26 that MA-CT-PCB consists predominantly of glass-fibre filaments with low intraparticle pore volume, which provides a limited internal diffusion length and consequently shifts the rate control to surface-site occupation kinetics. The close correspondence between experimental and calculated adsorption capacities suggests the suitability of this model in describing the system. The pseudo-second-order behaviour suggests that the adsorption process is predominantly controlled by the electrostatic interactions between the adsorbent surface and the dye molecules. This is consistent with the rapid initial uptake observed experimentally, followed by a slower approach to equilibrium due to progressive occupation of active sites.

The kinetic profile can be divided into two distinct regions:

- i. An initial fast adsorption phase, dominated by surface interactions and external mass transfer, and
- ii. A slower stage governed by site saturation and possible intraparticle diffusion limitations.

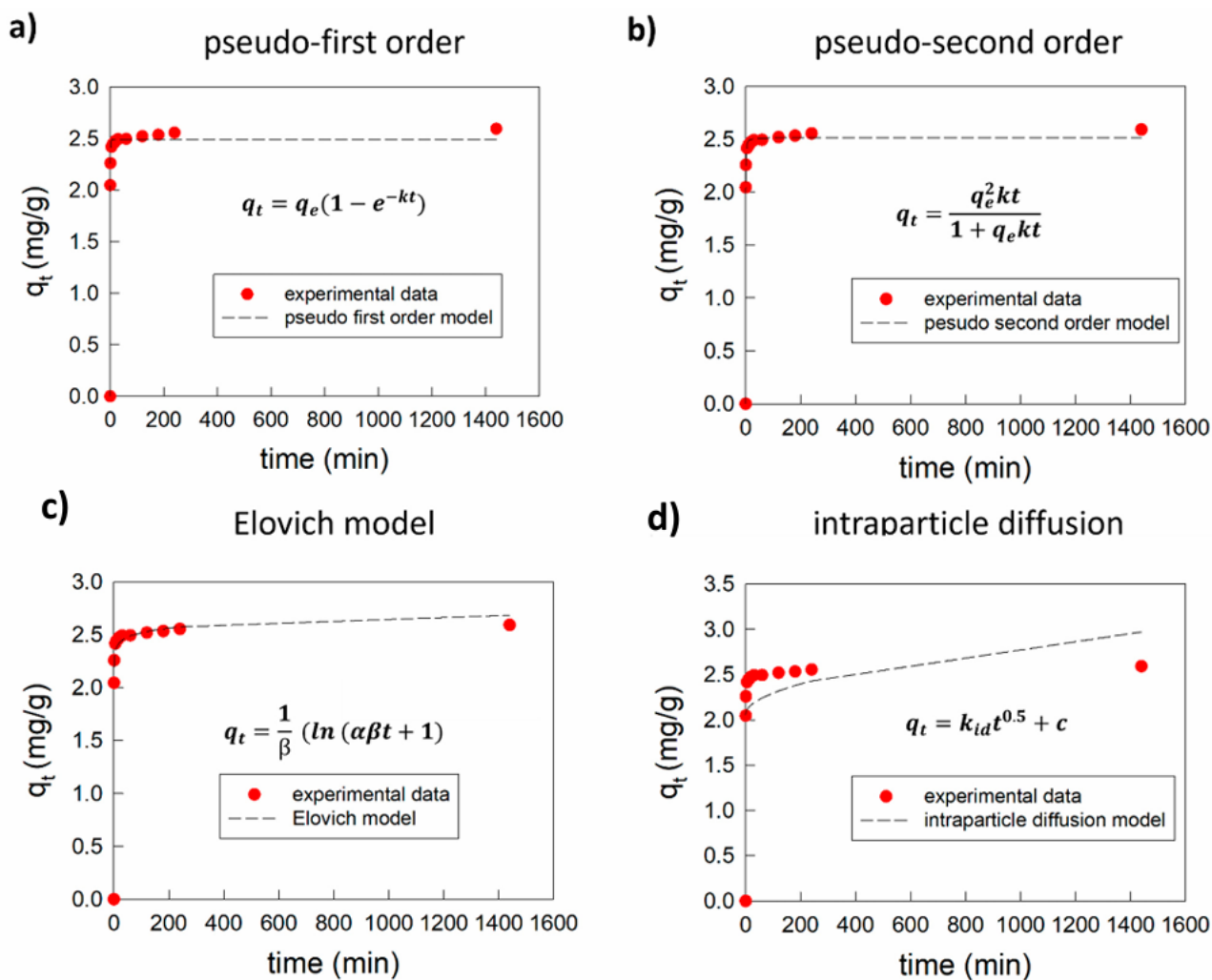


Figure 30: Fitting of the experimental adsorption data of MA-CT-PCB (red points) for MB at 1×10^{-5} M using the non-linearised forms of four kinetic models (black dashed lines): (a) pseudo-first-order (b) pseudo-second-order; (c) Elovich; (d) intraparticle diffusion. The model equation is reported within each panel.

The validity of the pseudo-second-order model across different dye concentrations further approves that the adsorption mechanism remains consistent even under increased pollutant load, indicating the robustness of the system.

4.1.3.1 Comparative Adsorption Experiments with reference materials:

To contextualise the MB adsorption performance of MA-CT-PCB within the broader adsorbent landscape, comparative batch experiments were carried out under identical experimental conditions (MB = 1×10^{-5} M; adsorbent dosage = 1.2 mg mL^{-1} ; mineral water matrix; $\text{pH} \approx 7.5$; ambient temperature; magnetic stirring at 700 rpm) using three reference materials, each selected for a specific mechanistic purpose:

- i. Commercial activated carbon (AC; DARCO, Sigma Aldrich, St. Louis, MO, USA), the industry-standard adsorbent for organic dye removal, providing the upper performance benchmark for microporous carbonaceous adsorbents;
- ii. Powder derived from untreated PCB substrates (denoted PCBs), included to verify whether the microwave-assisted acidic leaching step responsible for the transformation of raw PCB into MA-CT-PCB confers a quantifiable adsorption advantage over the unprocessed source material;
- iii. Powder derived from glass slides (denoted glass), included as a chemical compositional analogue of MA-CT-PCB, in which the amorphous $m\text{-SiO}_2$ framework is retained but the residual carbonaceous and metal-oxide phases preserved in the PCB-derived material are absent.

The reference powders were prepared by an analogous mechanical-comminution protocol to the one applied to the MA-CT-PCB material. Approximately 2 mL (≈ 100 mg) of either glass slide or untreated PCB substrate was placed into a stainless-steel jar (10 mL total volume) loaded with seven steel balls ($\varnothing$ 7 mm) and milled at 25 Hz; milling time was set at 3 minutes for glass and 9 minutes for untreated PCB, the longer time reflecting the greater mechanical resistance of the multilayer PCB composite. The resulting powders were sieved through a 500 μm mesh the same granulometric specification used for MA-CT-PCB and stored under ambient conditions prior to use. The commercial activated carbon (DARCO) was used as received without further processing.

Each reference material was physiochemically characterised using the same suite of techniques applied to MA-CT-PCB X-ray diffraction (XRD), Raman spectroscopy, and scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS). The full characterisation dataset is reported by Javaid et al., (2024) and is summarised below:

- Activated carbon (AC): the XRD pattern shows a broad amorphous halo centred at $2\theta \approx 22\text{--}25^\circ$, characteristic of a disordered carbonaceous framework. The Raman spectrum exhibits the

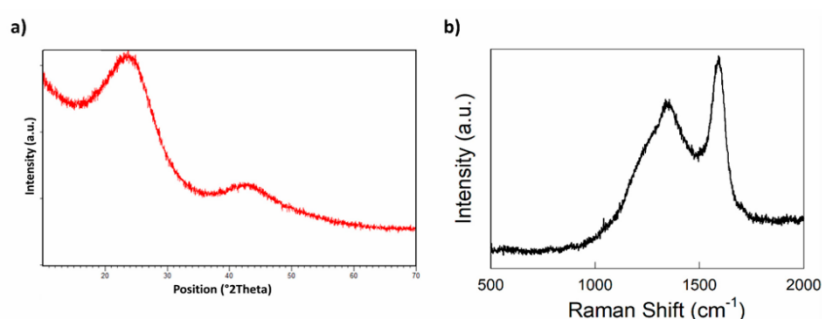


Figure 31: a) X-ray Diffractogram. b) Raman spectrum of ACs.

canonical D-band at $\sim 1350\text{ cm}^{-1}$ and G-band at $\sim 1580\text{ cm}^{-1}$, attributable to sp^3 -defective and sp^2 graphitic carbon domains respectively, confirming the activated-carbon nature of the material.

• Untreated PCB powder: the XRD pattern is dominated by sharp reflections of metallic copper, alongside quartz (low and high polymorphs), aluminium silicate, and an FeAl_2 phase, reflecting the multilayer architecture of the source PCB. The Raman spectrum displays the D- and G-bands of the residual carbonaceous

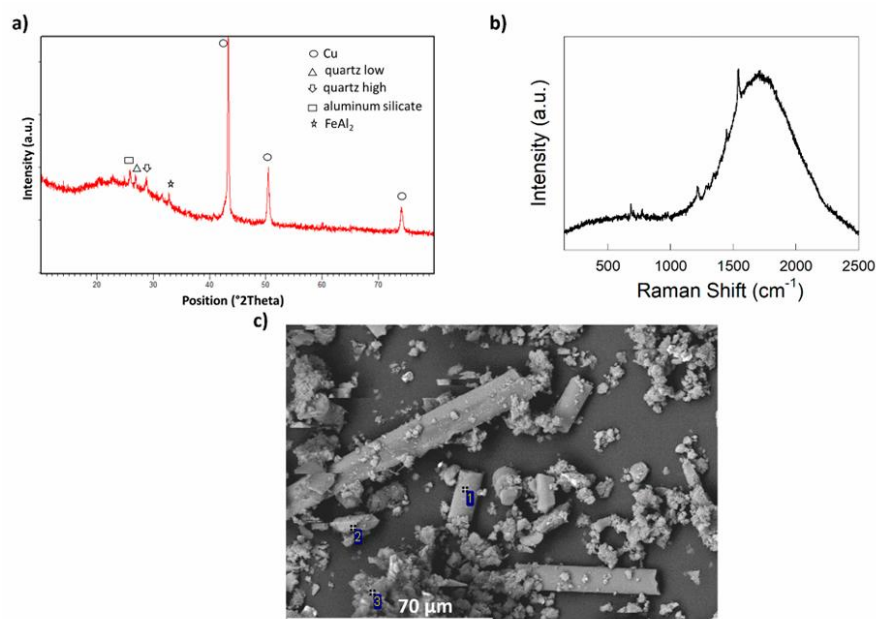


Figure 32: a) X-Ray Diffractogram of untreated PCBs; b) Raman spectrum of untreated PCBs, c) SEM image and related EDS analysis

component derived from the epoxy resin. SEM–EDS confirms a heterogeneous morphology in which glass-fibre filaments are inter-dispersed with metallic and resinous matrix domains; the detected elemental composition includes Si, Al, Ca, and Cu in varying proportions across the analysed regions.

• Glass powder: the material is compositionally simple, consisting essentially of an amorphous SiO_2 network and lacking the carbonaceous and metallic phases retained in the PCB-derived powders.

The comparative kinetic and temporal adsorption datasets across the experimental series demonstrate a significant, processing-dependent difference in both Methylene Blue (MB) remediation efficiencies and underlying mass-transfer mechanisms. Commercial activated carbon establishes the upper operational boundary of the series,

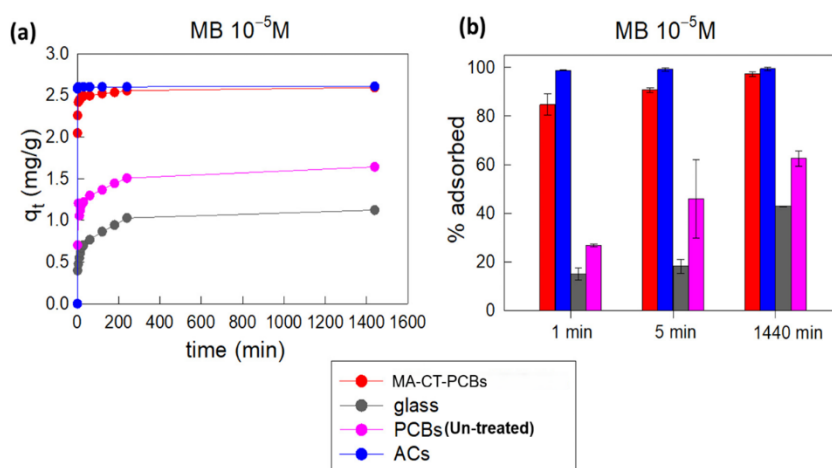


Figure 33: Comparative MB adsorption performance of MA-CT-PCB and three reference materials (AC, untreated PCB, glass powder) at $\text{MB} = 1 \times 10^{-5}$ M. (Left) Adsorption capacity q_t as a function of contact time. (Right) Percentage MB adsorbed at selected contact times

achieving instantaneous, near-quantitative decolourisation ($\approx 100\%$) within the initial minute of

contact due to its highly developed microporous network and low mass-transport resistance. Notably MA-CT-PCB material functions in close alignment with this industrial benchmark under identical unbuffered mineral-water parameters, delivering rapid removal efficiencies of $\approx 85\%$ at 1min and $\approx 90\%$ at 5min, before reaching an equilibrium ceiling of 97-98% at 1440 minutes. This contrasts with the raw, untreated PCB powder, which reaches a modest $\approx 57\%$ removal at equilibrium, and the pure glass powder control, which exhibits the lowest performance of the series (42% at 1440 minutes). The comparative results confirm that the microwave-assisted acidic leaching step is essential for activating the adsorption potential of the electronic waste matrix, removing surface-passivating metallic residues and chemical impurities that otherwise systematically suppress dye uptake.

Mathematically, the fundamental transition from Elovich kinetics observed in both the untreated PCB ($R^2 = 0.925$) and the control glass powder ($R^2 = 0.972$) to a pseudo-second-order (PSO) kinetic model in the MA-CT-PCB matrix ($R^2 > 0.995$) serves as the kinetic signature of this surface transformation. While the Elovich profiles mathematically register a highly heterogeneous, fragmented surface architecture governed by multi-phase diffusion barriers, the PSO alignment of the treated matrix confirms a transition to a surface-controlled, site-occupation rate-limiting mechanism operating across a highly uniform, chemically uniform surface. This optimisation is driven by three mutually reinforcing effects induced during hydrometallurgical processing: mechanical particle-size reduction that minimises internal pore diffusion lengths; the generation of localised micro-porosity via microwave-assisted thermal stress; and the un-shielding of a dense network of highly active, native silanol ($-\text{Si}-\text{OH}$) groups. Upon exposure to the aqueous background, these sites deprotonate into negatively charged silanolate ($-\text{Si}-\text{O}$) centres, which engage in cooperative electrostatic attraction with the cationic MB^+ chromophores alongside supplementary π - π stacking interactions at preserved carbonaceous patches. Ultimately, these kinetic results confirm that the microwave-assisted treatment converts the PCB non-metallic fraction into an effective, predictable, surface-controlled adsorbent that directly matches the equilibrium efficacy of premium commercial activated carbons.

In view of these promising results, we investigated the possibility of using MA-CT-PCB powder for the adsorption of methyl orange (MO), and we compared its activity with that of ACs, glass powder, and not-treated PCB powder. When subjected to the anionic dye under identical parameters ($\text{pH}=7.5$) and equivalent mass dosages, the MA-CT-PCB exhibits a complete reversal in performance compared to its high cationic affinity, capturing a minimal dye removal efficiency of only $\approx 5\%$ at equilibrium.

This severe suppression is electrostatically rationalised by its net surface potential of -23 ± 6 mV (measured via Dynamic Light Scattering), which closely mirrors pristine waste fibreglass. At operational pH levels, the deprotonated, native silanolate ($-\text{Si}-\text{O}$) sites dominating the clean

inorganic skeleton of the MA-CT-PCB exert a strong Coulombic repulsion against the incoming negatively charged MO chromophores, heavily inhibiting active site occupation.

Conversely, the reference commercial activated carbon (AC) completely overrides these electrostatic repulsion boundaries despite carrying a similar negative surface charge of -26 ± 1 mV achieving rapid, near-quantitative MO capture. As confirmed by its turbo-

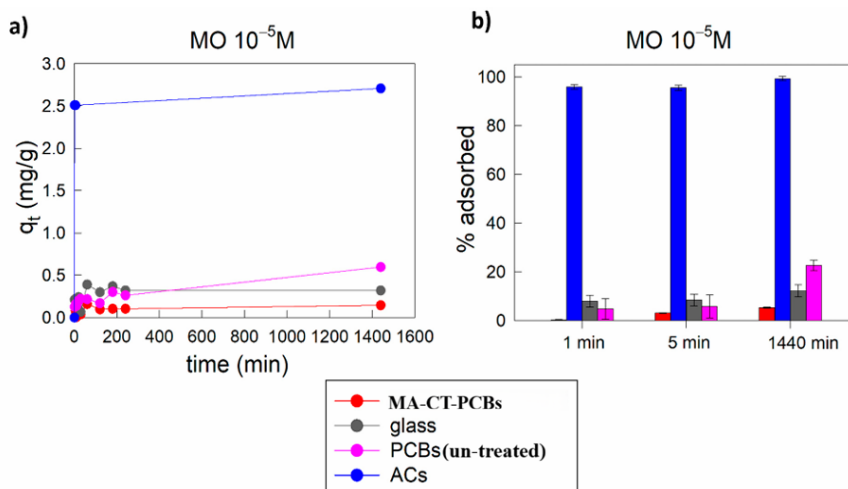


Figure 34: Comparison between the adsorption capacity of MA-CT-PCB & those of reference materials (ACs, glass powder and untreated PCBs) during the adsorption of MO. a) variation of adsorption capacities as a function of time; b) comparison between the percentage of adsorbed MO 10⁻⁵ M at selected time intervals.

Raman D and G bands (1350 cm^{-1} and 1600 cm^{-1}), the AC framework consists of dense, piled aromatic stacks that facilitate intense, charge-independent π - π stacking interactions with the aromatic rings of various organic pollutants.

Notably, both the raw glass powder and the untreated PCB powder outperformed the optimised MA-CT-PCB matrix toward the anionic contaminant, yielding equilibrium MO removal efficiencies of $\approx 12\%$ and $\approx 23\%$, respectively. Characterisation profiles (XRD, SEM-EDS) reveal that the untreated PCB retains high background concentrations of crystalline copper, aluminium silicates, and metallic $FeAl_2$ phases.

More critically, Raman spectroscopy of the untreated PCB resolves intense organic bands at 690 cm^{-1} , 770 cm^{-1} , 1220 cm^{-1} , 1290 cm^{-1} , and 1550 cm^{-1} , tracking the chemical footprint of the intact epoxy resin matrix wrapping the fibreglass core. While the aggressive microwave-assisted acidic leaching step is necessary to strip away this resin layer and expose a highly active silicate interface for cationic capture, it simultaneously eradicates these hydrophobic aromatic domains. In the untreated PCB powder, the survival of this epoxy resin layer preserves accessible graphitic patch boundaries that enable localised π - π interactions with the dissolved MO molecules.

Ultimately, this comparative synthesis demonstrates that while clean, inorganic e-waste silanol networks dictate highly efficient, electrostatically driven cationic remediation, the strategic retention

or post-synthetic grafting of hydrophobic organic domains is mandatory to extend the capabilities of electronic waste-derived materials to include anionic aquatic contaminants.

Limitations:

Although its adsorption performance was limited to cationic dye, it was able to match the activity of commercial activated carbons during MB removal, significantly outperforming similar powders obtained from the grinding of glass slides or un-treated PCB samples. The MA-CT-PCB adsorbent developed in this work was characterised by low raw material cost, since it was obtained through the valorisation of wastes, limiting not only the costs of raw materials but also those of the disposal of the original waste, with clear advantages in comparison to commercial activated carbons (~250 EUR/kg). The €250/kg is the Sigma-Aldrich DARCO laboratory catalogue price for small quantities.

Despite the highly promising adsorption performance of MA-CT-PCB materials, several limitations should be critically acknowledged. Firstly, the adsorption efficiency was found to be strongly dependent on particle size reduction, requiring an additional mechanical milling step to achieve optimal performance. While effective, this step introduces additional energy consumption and processing time, which may influence large-scale applicability. Secondly, the adsorption mechanism appears to be primarily driven by electrostatic interactions between the negatively charged surface and cationic dye molecules. This inherently limits the versatility of the material, as evidenced by its reduced affinity toward anionic contaminants, suggesting that further surface modification strategies would be required to broaden its applicability.

Additionally, although the material demonstrated adsorption capacities comparable to commercial activated carbon, its performance under more complex water matrices (e.g., presence of competing ions, organic matter, or variable pH conditions) remains to be fully explored. The long-term structural stability and regeneration efficiency of the material also require further systematic investigation to assess its practical durability over multiple use cycles.

From a process perspective, the adsorption experiments were intentionally conducted under simplified and non-optimised conditions to simulate realistic scenarios. While this strengthens the practical relevance of the results, it also implies that further optimisation such as pH control, temperature variation, or surface functionalization could potentially enhance the adsorption performance even further.

Overall, these considerations highlight that, while MA-CT-PCB materials represent a highly promising low-cost and sustainable alternative to conventional adsorbents, additional studies are

necessary to fully establish their scalability, versatility, and long-term operational performance in real-world water treatment systems.

4.2 Buffered Chemically Leached PCB Residue (BL-PCB):

Following the characterisation and adsorption evaluation of microwave-assisted chemically treated PCB residues (MA-CT-PCB), this section presents the results obtained from the second class of PCB-derived materials: Buffered Chemically Leached PCB residues (BL-PCB). In contrast to the aggressive acidic digestion employed in the first treatment route, the BL-PCB materials were prepared through a sequential, environmentally conscious leaching process comprising lactic acid buffer, ammoniacal buffer with hydrogen peroxide, and an aqueous iodine/iodide (I^-/I_2) solution, as described in detail in [Section 2.3](#).

This greener leaching strategy was designed to achieve selective metal removal while preserving the structural integrity of the non-metallic PCB matrix, thereby enabling a more sustainable approach to e-waste valorisation. Furthermore, the organic component should not be removed. The three particle size fractions obtained BL-PCB-1 (0.5 mm), BL-PCB-2 (2 mm), and BL-PCB-3 (4 mm), allow for a systematic investigation of granulometry effects on adsorption behaviour, complementing and extending the findings from MA-CT-PCBs.

The majority of the experimental work reported in this chapter was conducted using BL-PCB-1 (0.5 mm fraction). This selection was based on the significantly higher adsorption efficiency exhibited by BL-PCB-1 in initial screening experiments, consistent with its smaller particle size and correspondingly greater specific surface area. BL-PCB-1 was therefore the subject of the full experimental programme, including kinetic modelling, photo-assisted degradation under simulated solar irradiation, surface functionalization with biopolymers, and mesoporous silica synthesis. The results are presented following the same structural framework as before. This comparison is central to evaluating the trade-offs between chemical processing intensity, metal removal efficiency, and adsorption performance.

4.2.1 Structural and Morphological Characterisation:

To minimise the effect of granulometry during the physio-chemical characterisation step, a portion of the BL-PCB-2 (2 mm) and BL-PCB-3 (4 mm) fractions were ball-milled to a final granulometry of 0.5 mm, matching the native size of BL-PCB-1. Consequently, the X-ray diffraction (XRD) analysis represents the structural fingerprints of materials with identical particle sizes but distinct chemical processing histories. Raman spectra revealed a heterogeneous surface. Scanning Electron Microscopy combined with Energy Dispersive X-ray Spectroscopy (SEM-EDS) observations were

conducted across multiple surface regions for each sample, providing spatially resolved information on morphology, phase heterogeneity, and elemental distribution that directly contextualises and extends the bulk spectroscopic findings.

4.2.1.1 X-Ray Diffraction Analysis:

The diffractograms for the BL-PCB series are defined by a broad scattering halo centred at $2\theta \approx 22^\circ$, characteristic of the amorphous $m\text{-SiO}_2$ framework from the fibreglass reinforcement. A significant observation is the variation in halo intensity despite all samples being ball-milled to 0.5 mm prior to analysis.

BL-PCB-1 exhibits the highest relative intensity for the silica halo, indicating that its original 0.5 mm granulometry during the leaching process allowed for exhaustive reagent penetration and removal of

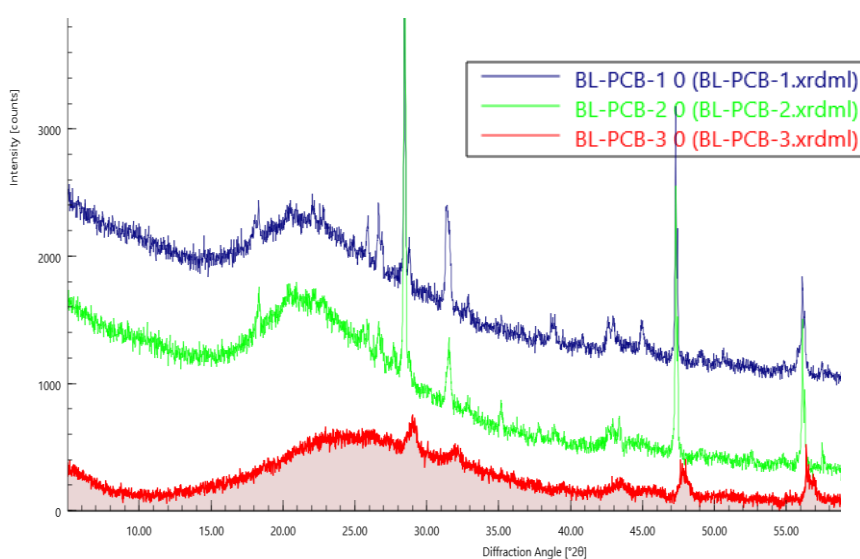


Figure 35: XRD Analysis of BL-PCB Samples

surface masking agents. In contrast, BL-PCB-2 and BL-PCB-3 show a broader amorphous shoulder at lower angles ($12\text{--}18^\circ$ 2θ), revealing the presence of residual epoxy resin that remained "shielded" within the core of the larger fragments during the leaching phase. The sharp reflection at $2\theta \approx 26.6^\circ$ confirms the presence of quartz, while the absence of crystalline Si peaks in the XRD patterns, despite localised detection in Raman, suggests that crystalline silicon fragments are present only as trace surface micro-inclusions below the detection threshold of bulk diffractometry highlights the structural preservation afforded by the green, buffered leaching route.

4.2.1.2 Raman Spectroscopic Interpretation:

The Raman spectroscopy was employed to characterise the surface chemistry of the waste PCB samples post-leaching. The spectra reveal a heterogeneous surface composed of a fibreglass-reinforced epoxy matrix and residual chemical complexes from the buffering and leaching process.

- **Silicon and Polymer Matrix:** A sharp, high-intensity peak at 524 cm^{-1} is observed, which is the clear signature of crystalline silicon (c-Si). This indicates the presence of residual micro-component fragments or semi-conductor die remnants on the PCB surface. The peaks in

the 1585–1610 cm^{-1} region correspond to the aromatic $\text{C}=\text{C}$ stretching vibrations, characteristic of the bisphenol-A epoxy resin (DGEBA) backbone used in the PCB construction.

- **Carboxylate Coordination:** A prominent diagnostic peak at 1417 cm^{-1} is assigned to the symmetric stretching of carboxylate (COO^-) groups. This suggests the retention of the lactic acid buffer and its successful coordination with the substrate, likely through the formation of stable metal-lactate complexes during the leaching phase.
- **Halogen Interaction:** Significant vibrational activity in the low-frequency region (110–180 cm^{-1}) is attributed to metal-iodide ($M\text{-I}$) vibrations. This provides evidence that the aqueous I^-/I_2 leaching solution leaves detectable halide residues tethered to the surface, contributing to the chemical complexity of the substrate.

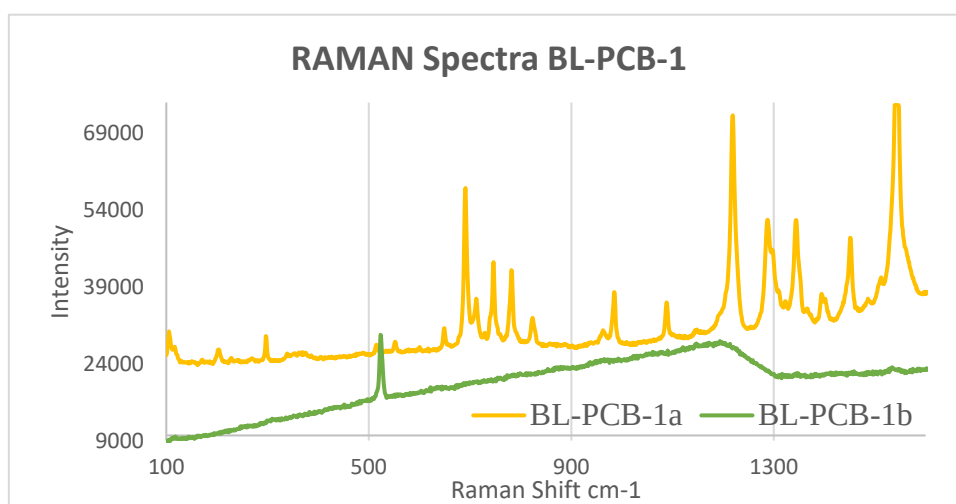


Figure 36: Micro-Raman spectra of BL-PCB surface showing chemical heterogeneity between a resin-rich region (a) and an exposed substrate region (b)

The multi-panel spectra documented in Figure 36 highlight a pronounced spatial variation across the sample surface, mapping the micro-heterogeneity of the e-waste-derived composite. In a critical diagnostic correlation, the high-intensity spectral profile recorded in the resin-rich domain (region a) does not merely reflect generic polymer bands, but matches the precise vibrational footprint of copper phthalocyanine green, the industry-standard pigment embedded within commercial PCB solder masks. The clear resolution of these pigment-specific modes provides experimental confirmation of the structural preservation of the native epoxy resin matrix following the green, buffered leaching procedure.

Conversely, transitioning to the exposed substrate domain (region b) reveals a drastic suppression of these organic and pigmented features, accompanied by a dominant resurgence of the 524 cm^{-1} crystalline silicon peak. This spatial shift confirms that the milder chemical leaching agent

selectively extracts base metals while leaving the underlying glass-reinforced resin core intact, generating a heterogeneous surface where regions of high organic occlusion alternate with raw, exposed inorganic fragments.

Ultimately, the identification of these diverse surface moieties specifically the carboxylate, aromatic epoxy, phthalocyanine green, and halide patches confirms that the recovered BL-PCB matrix is not a simple, inert siliceous waste. Instead, it functions as a highly complex, self-functionalised hybrid composite.

4.2.1.3 Scanning Electron Microscope (SEM) Analysis:

The morphological and elemental characterisation of the BL-PCB series via SEM-EDS reported in Figure 37 reveals a pronounced microscale heterogeneity that is intrinsic to the complex multilayer architecture of the original BL-PCB glass-fibre epoxy substrates. This spatial irregularity persists across all treatment variants, manifesting as a mosaic of organic epoxy-resin domains, amorphous silica phases, and calcium aluminosilicate glass-fibres and trace metallic inclusions (Cu, Sn, Fe, Ni).

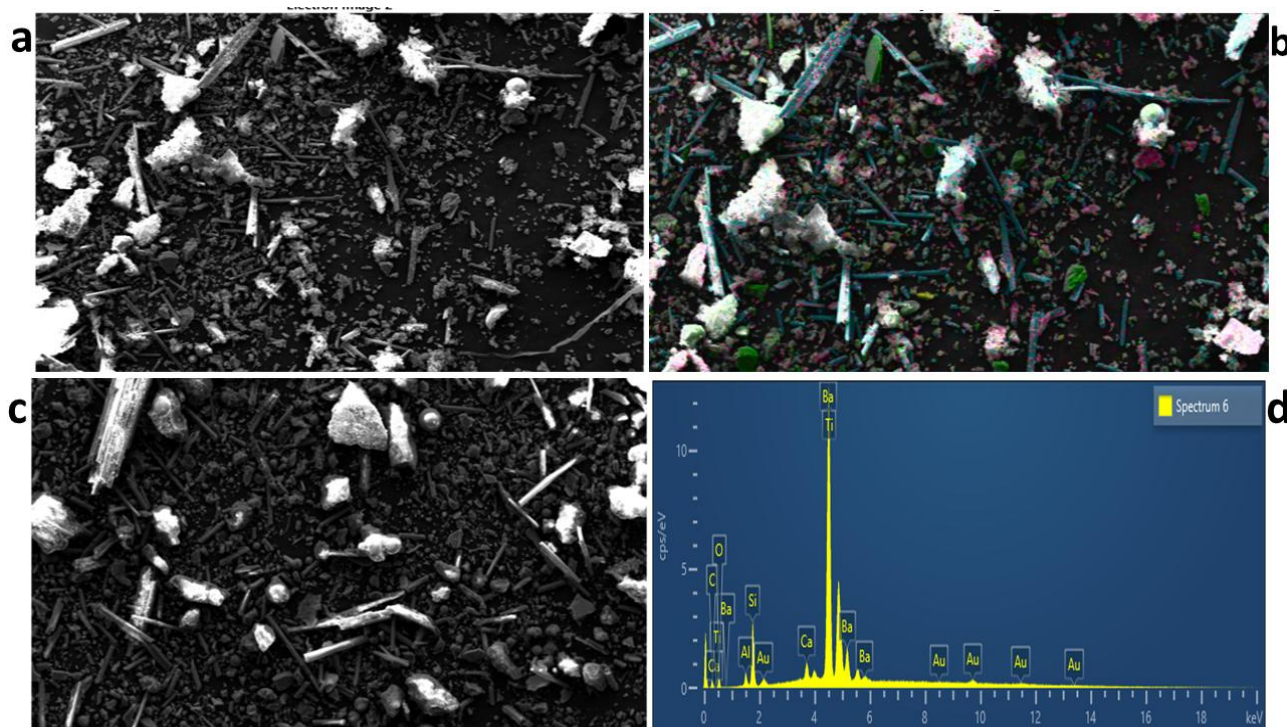


Figure 37: Morphological & elemental analysis of BL-PCBs. (a) Liberated fibreglass in BL-PCB-1; (b) Fractured resins in ball-milled BL-PCB-3; (c) Elemental mapping illustrating the heterogeneous distribution of Si & C phases; (d) Point spectrum identifying BaTiO₃

Bulk elemental mapping confirms that carbon remains the dominant fraction in BL-PCB-1 and BL-PCB-2 (ranging from 44 to 62 wt%), representing the polymeric matrix, while silicon signals (7–13 wt%) trace the distribution of the fibreglass reinforcement. Localised point spectra expose an extreme

compositional span, ranging from near-pure organic polymer to inorganic dielectric clusters, underscoring the challenge of treating these residues as chemically homogeneous adsorbents.

The impact of mechanical processing is highly visible in the morpho-chemical profile of BL-PCB-3, where high-energy ball milling and subsequent sieving preferentially fractured the cross-linked polymeric matrix along the rigid glass-fibre boundaries. This localised structural delamination resulted in an increased exposure of silicon and oxygen at the particle exterior, shifting the apparent surface chemistry toward a more inorganic-rich profile. However, this intense mechanical reduction also liberated encapsulated metallic segments, introducing trace background levels of iron and nickel from the milling media and exposing previously isolated internal copper track fragments, which consequently modified the local surface energy distribution.

The inconsistency in performance improvement observed following mechanical processing is most likely attributable to the intrinsic compositional heterogeneity of the BL-PCB materials. Individual particle fractions sampled from these mechanically processed residues may contain variable proportions of carbonaceous, siliceous, and ceramic phases, reflecting the complex multilayer architecture of the substrate. As a result, surface area increase through particle size reduction does not translate linearly into adsorption improvement, as the chemical nature of the newly exposed surfaces and therefore their affinity for cationic dye species, varies from particle to particle.

As summarised in Table 15, the elemental profile of BL-PCB-3 displays a ~33% increase in silicon relative to BL-PCB-2. While this trend aligns with the qualitative SEM observations showing an exposed internal inorganic fibreglass core, this numerical variance must be interpreted as a combined effect of mechanical matrix exposure and the intrinsic micro-heterogeneity characteristic of these multi-phase secondary composites. Because EDS acts as a localised surface probe, these stoichiometric fluctuations reflect the stochastic distribution of resin and glass phases across

individual fractured particulates rather than a uniform chemical transformation. Conversely, the exclusive detection of Iodine (I) within the finest BL-PCB-1 fraction provides a definitive chemical footprint, confirming the retention of residual tri-iodide complex phases from the sequential leaching regime.

Table 15: Representative SEM–EDS elemental composition of the BL-PCB fractions.

Sample	Carbon (wt%)	Oxygen (wt%)	Silicon (wt%)	Notable Minor Elements
BL-PCB-1	58.60	21.01	8.99	Br (1.82%), I (0.77%)
BL-PCB-2	62.05	24.16	7.09	Br (1.27%), Sn (0.17%)
BL-PCB-3	49.84	31.18	13.13	Cu (0.28%), Fe (0.16%)

Note: Elemental weight percentages are normalised to 100% excluding the Gold (Au) sputter-coating artifact required for SEM conductivity.

Collectively, this profound surface heterogeneity carries significant mechanistic implications for the material's performance. The coexistence of energetically non-equivalent active sites, ranging from silanol-bearing glass surfaces to carboxylate-rich resin fragments, explains the high standard deviations observed in subsequent adsorption experiments. Ultimately, the SEM-EDS data established that while leaching and functionalization modify the surface, the underlying complexity of the e-waste precursor remained a defining characteristic that governs the material's interaction with organic pollutants.

The combined XRD and Raman analysis revealed a clear structural pattern. Although the mechanical ball-milling standardised the particle size to 0.5 mm for all tests, it could not equalise the chemical history of the samples.

BL-PCB-1 is the most surface activated material in the series. Its dominant XRD amorphous silica halo, lowest Raman epoxy peak intensities, highest observed Si content in point EDS spectra, and most extensively exposed glass fibre morphology collectively indicate that the buffered leaching effectively unlocked the glass fibre surface, exposing a high density of silanol (Si–OH) groups that carry a net negative surface charge at $\text{pH} > 2\text{--}4$. This surface charge is the primary electrostatic driver for cationic methylene blue adsorption, directly explaining BL-PCB-1's superior adsorption performance relative to BL-PCB-2 and BL-PCB-3.

4.2.2 Adsorption Results:

MB removal efficiency across the BL-PCB series was strongly dependent on particle size, chemical processing history, and surface heterogeneity. The kinetic trajectories and steady-state

decolourisation percentages across the various matrices compiled under standard unbuffered batch conditions ($\text{pH} \approx 7.5$) at an adsorbent dosage of 1.2 mg mL^{-1} reveal a clear hierarchy in remediation performance, as systematically documented in Figure 38.

4.2.2.1 Effect of granulometry and contact time on adsorption:

When isolating the three unmodified, as-produced samples characterised by different granulometries, a distinct trend emerged regarding mass-transport resistance and accessible surface boundaries. The finest sieved fraction, designated as BL-PCB-1 (0.5mm), consistently exhibits the highest baseline adsorption efficiency among the non-functionalised series, delivering a maximum MB removal of approximately 55% at the 1440 min equilibrium limit.

As the native particle size threshold increases to the intermediate range in BL-PCB-2 (2mm) and the coarsest matrix in BL-PCB-3 (4mm), the maximum dye removal values drop systematically to roughly 19% and 33%, respectively. This geometric size-dependence is entirely consistent with the well-established relationship between particle size and mass-transfer kinetics; the smaller macro-scale profiles of BL-PCB-1 minimise intraparticle diffusion lengths, maximizing the immediate exposure of interfacial active sites to the bulk solution per unit mass.

To decouple chemical processing history from geometric particle size effects, the coarser fractions BL-PCB-2 and BL-PCB-3 were subjected to ball-milling and sieving to generate standardised 0.5 mm fractions matching the native diameter of BL-PCB-1. This produced two mechanically processed sub-series, a ground-only fraction and a ground-and-sieved fraction each of which reveals distinct behaviour. For BL-PCB-2, ball-milling alone (BL-PCB-2 Ground) yields $34.2 \pm 8.4\%$ removal, representing a substantial improvement over the native BL-PCB-2 (19.9%), but still well below BL-PCB-1. Sieving the ground BL-PCB-2 to the 0.5 mm fraction (BL-PCB-2 Sieved) increases performance further to $53.5 \pm 13.8\%$, closely approaching the native BL-PCB-1 value of 54.6%. For BL-PCB-3, ball-milling alone (BL-PCB-3 Ground) raises performance dramatically to $52.8 \pm 11.6\%$, nearly matching the BL-PCB-1 baseline, while the sieved BL-PCB-3 fraction reaches $46.6 \pm 9.6\%$, slightly lower than the ground-only value, suggesting that the sieving step removes some of the most reactive, finest particles generated during milling. The critical observation across this same-granulometry comparison is that, despite achieving nominally identical particle sizes, none of the mechanically processed variants consistently surpasses the native BL-PCB-1 performance, confirming that chemical leaching history, specifically the degree of surface activation achieved during the buffered leaching protocol confers an intrinsic surface chemistry advantage to BL-PCB-1 that mechanical size reduction alone cannot fully replicate.

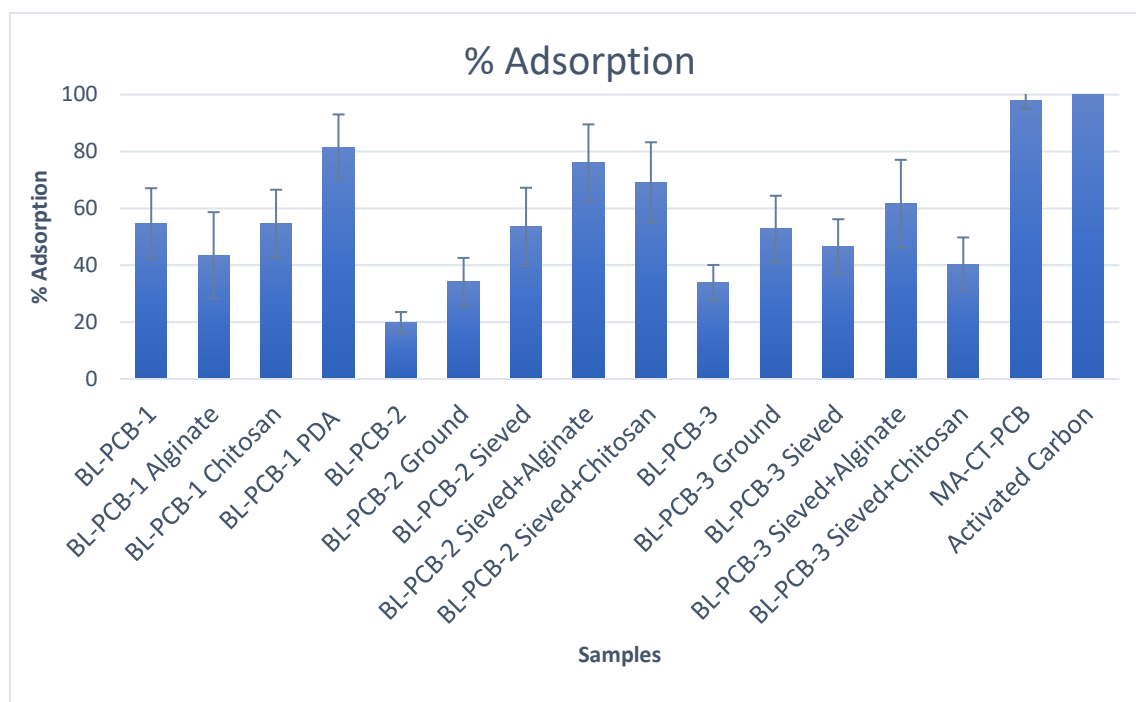


Figure 38: Adsorption Results for BL-PCB Samples

When benchmarked against the commercial activated carbon (AC) reference standard (DARCO, Sigma-Aldrich), which routinely achieves rapid, near-quantitative decolourisation exceeding 99% within the first minutes of contact, all unmodified BL-PCB matrices exhibit a lower absolute thermodynamic capacity. This operational gap reflects the non-porous nature of raw fibreglass fragments compared to the ultra-dense micro- and mesoporous architectures inherent to activated carbons. When compared to fibreglass samples MA-CT-PCB (98-99%) the adsorption is less for buffered and leached samples.

However, the fact that the native BL-PCB-1 fraction can adsorb 55% of the dissolved dye without any chemical adjustments or pH modification confirms the inherent adsorption potential of these green-leached residues.

This performance hierarchy can be rationalised based on the localised surface composition and morphological heterogeneity of the independent fractions, as verified by scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) diagnostics. The native BL-PCB-1 fraction contains a significantly higher fraction of accessible, exposed carbonaceous domains derived from the fractured epoxy resin matrix. These regions play a critical role in the immobilisation of cationic dyes by enabling strong, long-range π - π stacking interactions between the aromatic, conjugated rings of the MB molecule and the graphitic or disordered carbon networks of the resin substrate. These hydrophobic forces operate in parallel with localised electrostatic attractions

facilitated by residual oxygen-containing functional groups (including deprotonated hydroxyl, carboxyl, and carbonyl boundaries, $-\text{OH}$, $-\text{COOH}$, $\text{C}=\text{O}$) present at the resin exterior.

4.2.2.2 Surface Functionalisation with Biopolymers and Polydopamine

To overcome the limitations imposed by the chemical heterogeneity of the raw e-waste fragments and deliberately introduce high-density, uniform binding sites, surface modification of the BL-PCB matrices was executed utilizing two distinct biopolymers (Chitosan and Alginate) alongside a bio-inspired Polydopamine (PDA) coating architecture.

The application of Chitosan was designed to anchor abundant amino ($-\text{NH}_2$) and hydroxyl ($-\text{OH}$) functionalities across the substrate exterior. However, the experimental results for the Chitosan-functionalised variants failed to yield a statistically significant trend or a reliable performance enhancement. This lack of clear improvement is rationalised by the protonation state of the biopolymer relative to the fluid background.

In contrast, Alginate functionalisation characterised by the introduction of highly dense, negatively charged carboxylate ($-\text{COO}^-$) networks revealed a distinct performance divergence that was heavily dependent on the chemical history of the targeted sample. For the initially coarser fractions, BL-PCB-2 and BL-PCB-3, the deposition of the Alginate coating forced a notable, systematic increase in the final adsorption percentage. Here, the dissolved biopolymer successfully macromolecularly "bridged" the inert or resin-occluded areas identified during characterisation, effectively masking the dead structural zones with a fresh, uniform layer of dense negative charge that dramatically accelerated the electrostatic capture of the cationic dye, matching the trends reported by Vassalini et al. (2020).

Conversely, an unexpected "masking effect" was observed for the finest fraction, where Alginate-coated BL-PCB-1 exhibited a slight decrease in net adsorption efficiency compared to its raw state. This behaviour indicates that the thick Alginate macromolecular envelope occluded the highly active, native silanol and carboxylate sites that were already optimally exposed in the un-functionalised BL-PCB-1 matrix. In this specific case, the biopolymer overlayer acted as a mass-transfer barrier rather than a performance enhancer, proving that for highly active, finely ground fractions, additional biopolymer encapsulation can be counterproductive.

Distinct from the variable performance of the biopolymer treatments, Polydopamine (PDA) functionalisation demonstrated a significant, consistent, and superior improvement in adsorption performance across the series, specifically optimising the native BL-PCB-1 matrix. PDA undergoes self-polymerisation to form a robust, highly adhesive, and conformal nano-layered coating that uniformly blankets the multi-phase (glass fibre/resin/metal) topography of the e-waste residue.

PDA enhancement in performance, driving the total equilibrium MB removal of the PDA-modified BL-PCB-1 from its modest 52% baseline up into 80%+. This performance effectively bridges the operational gap and matches the remediation performance of premium commercial activated carbons. The success of PDA is rooted in its multifunctional chemical nature, enabling three simultaneous interaction pathways:

1. **π - π Interactions:** Between the aromatic catechol rings of the PDA and the MB dye structure.
2. **Hydrogen Bonding:** Facilitated by the abundant hydroxyl and amine groups.
3. **Electrostatic Attraction:** Driven by the deprotonated phenolic groups.

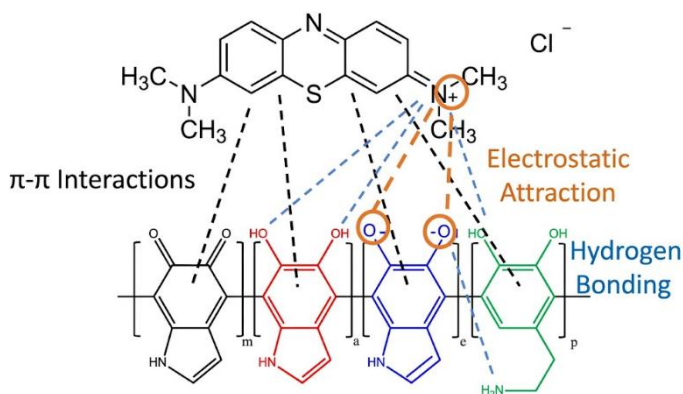


Figure 39: Schematic visualization of three synergistic & parallel adsorption pathways governing sequestration of cationic MB by functionalised Polydopamine.

The synergistic effect of these pathways led to a marked increase in MB removal for BL-PCB-1, reaching the highest adsorption values in the functionalised series. The superior performance of PDA suggests that its bio-inspired adhesion is better suited for the complex, multi-phase (glass fibre/resin/metal) surface of PCB residues than traditional biopolymers. These adsorption results were compared to activated carbon which shows 100% adsorption of MB and is commercially used for this purpose.

While the traditional biopolymers are highly sensitive to the underlying phase distribution and topography of the e-waste, the bio-inspired adhesion mechanism of PDA successfully homogenises the complex surface. converts the heterogeneous waste residue into a reproducible, effective adsorbent.

4.2.3 Methylene Blue Photodegradation:

In order to increase the MB removal, we tested the BL-PCB samples also as photocatalyst to induce the MB degradation under solar illumination. For the experiments we followed the procedures reported in [section 3.4](#). The transition from purely adsorptive sequestration to solar-driven remediation represents a critical evolution in the treatment of wastewater using waste-derived frameworks. While the preceding sections established the material ability to sequester Methylene Blue (MB) transferring the contaminant from the aqueous phase to the solid surface, in this case,

utilizing solar energy, the adsorbed organic molecules can be degraded *in situ*. In this way the material effectively circumvents the saturation ceiling, regenerating its active sites.

After the sequestration phase has reached the equilibrium, the intact suspension, comprising both the solid adsorbent and the supernatant was placed under a solar simulator and the MB absorbance was monitored at regular time intervals. In particular, the ratio A_t/A_0 . (Where A_0 corresponds to the solution absorbance at the end of the adsorption in dark step, while A_t corresponds to the absorbance value of the solution under illumination) was evaluated over time, being representative of the C_t/C_0 ratio, where C represents the MB concentration remaining in the liquid phase. A photolysis control was conducted in parallel to account for the measurable self-photolysis of MB, which reached $C/C_0 = 0.35$ at 360 minutes and $C/C_0 = 0.02$ at 1440 minutes in the absence of any adsorbent. Consequently, the efficacy of each material is evaluated by its ability to accelerate the degradation kinetics beyond this photolysis baseline, providing a rigorous assessment of material-mediated photocatalysis.

Prior to solar simulator activation, a critical 24-hour dark pre-equilibration step was maintained to decouple early surface phase adsorption from purely photo-induced pathways. During this dark phase, the configurations achieved comparable pre-concentration profiles, yielding baseline MB removals ranging from 77.1%

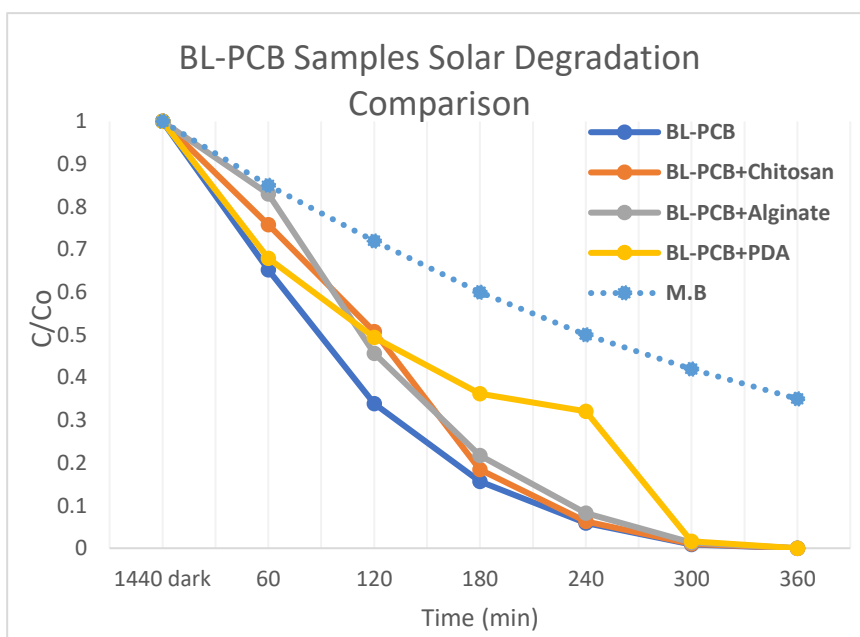


Figure 40: Direct comparison of solar degradation profiles for BL-PCB and its bi-polymers

Specifically, the unmodified BL-PCB reached the highest dark absorption ceiling (86.7%), while the Chitosan (82.6%), PDA (81.1%), and Alginate (77.1%) variants modulated the dark uptake incrementally without shifting the order of magnitude of initial solute concentration. This convergence is methodologically essential; it ensures that the subsequent solar-driven reaction trajectories originate from nearly uniform surface boundaries, allowing a direct comparison of the intrinsic photocatalytic reaction rates.

Following dark equilibration, the batch adsorption phase concentration profiles were normalised ($C/C_0 = 1$) at the immediate zero-minute boundary of illumination. Upon initiation of the simulated solar flux, the materials diverged rapidly in their decolourisation behaviours, as shown in the kinetic degradation vectors in Figure 40.

A mechanistic evaluation of the degradation kinetics revealed that the unmodified BL-PCB material exhibited the highest intrinsic photocatalytic activity among all investigated samples. Upon solar irradiation, the normalised concentration ratio (C/C_0) decreased rapidly from 1.00 to 0.652 at 60 min, 0.339 at 120 min, and 0.157 at 180 min, reaching complete dye degradation ($C/C_0 = 0$) after 360 min of irradiation. In contrast, the photolysis control experiment, consisting of methylene blue solution exposed to identical irradiation conditions in the absence of adsorbent, retained a significant residual concentration ($C/C_0 = 0.35$) after 360 min, confirming that direct photolysis alone was insufficient to achieve complete degradation.

The pronounced photocatalytic activity of the BL-PCB matrix can be attributed to the preservation of photoactive inorganic and carbonaceous domains following the mild organic-acid leaching treatment. The partially preserved disordered carbonaceous structures originating from the epoxy resin fraction act as conductive electron-transfer pathways. These graphitic domains facilitate charge separation by suppressing electron-hole recombination, thereby promoting the formation of reactive oxygen species. The generated radicals subsequently drive oxidative degradation of the chromophore structure of methylene blue, resulting in rapid decolourisation and mineralisation of the dye molecules.

4.2.3.1 Influence of Surface Functionalisation on Photocatalytic Behaviour:

Although all functionalised materials retained photocatalytic activity, surface modification with biopolymers and polydopamine introduced measurable changes in degradation kinetics. Importantly, all modified systems still outperformed the blank photolysis control, demonstrating that the underlying BL-PCB substrate remained photoactive after functionalisation.

Among the modified samples, the PDA-functionalised material showed the highest retention of photocatalytic efficiency. The BL-PCB+PDA system followed a degradation profile relatively close to that of the unmodified material during the initial irradiation period, reaching $C/C_0 = 0$ after 120 min compared with 0.339 for pristine BL-PCB. A temporary kinetic plateau was observed between 180 and 240 min; however, complete degradation was still achieved after 360 min of irradiation.

The favourable photocatalytic behaviour of the PDA-coated material is attributed to the conjugated aromatic structure of polydopamine. The catechol-rich polymeric layer can participate in photo-

induced charge transfer processes while maintaining photon accessibility to the underlying semiconductor domains. Consequently, PDA acts not only as a surface functionalisation layer enhancing adsorption properties, but also as a partially photoactive interfacial coating that preserves the catalytic behaviour of the substrate.

In contrast, chitosan- and alginate-functionalised samples exhibited slower degradation kinetics during the early stages of irradiation. The chitosan-coated material showed a delayed concentration decay, while the alginate-functionalised sample displayed the slowest initial degradation profile, particularly within the first 120 min of treatment. Nevertheless, both systems ultimately achieved complete dye removal after 360 min of irradiation.

The reduced photocatalytic rate observed for the polysaccharide-functionalised materials is primarily associated with two concurrent effects. First, the polymeric coating forms a diffusion barrier around the active surface sites, limiting the transport of dissolved oxygen and reactive oxygen species between the catalyst surface and the surrounding solution. Second, the biopolymer layers partially attenuate incident light through absorption and scattering phenomena, thereby reducing photon penetration and lowering the rate of electron-hole pair generation within the underlying semiconductor domains.

4.2.3.2 Implications for Water Remediation Applications:

The obtained results demonstrate that PCB-derived materials can simultaneously exhibit strong adsorption capability and intrinsic photocatalytic activity, providing a multifunctional platform for water remediation applications. The unmodified BL-PCB material showed excellent solar-assisted degradation performance due to the preservation of photoactive inorganic and conductive carbonaceous phases within the composite structure.

Surface functionalisation improved adsorption-related surface properties but introduced moderate kinetic limitations during photocatalytic degradation. Among the investigated modifications, PDA functionalisation provided the most balanced performance by combining enhanced adsorption behaviour with preservation of photocatalytic activity.

These findings suggest that PCB-derived materials may be strategically implemented in integrated or multi-stage treatment systems. Functionalised materials may be employed during the initial adsorption stage to rapidly immobilise pollutants from aqueous streams, while highly photoactive unmodified BL-PCB matrices may subsequently be used for efficient solar-assisted degradation and mineralisation of the concentrated contaminants.

4.3 Mechanically Processed Printed Circuit Board (MP-PCB):

The third and final class of PCB-derived materials investigated in this thesis comprises the mechanically processed residues obtained through shredding and electrostatic separation as described in [section 2.4](#). They encompass 12 samples which differs for the shredding time and the type of starting waste-PCBs, as described in Table 9 and Table 10, but the here-reported physiochemical characterisation focused on MP-PCB-1, which exhibited the highest MB adsorption performance as shown in Figure below.

Upon the identification of MP-PCB-1 as one of the best-performing raw material in the MP-PCB series, it was subjected to alkaline leaching and controlled sol-gel and templated condensation process to synthesise mesoporous silica (designated MP-PCB-MS, or $m\text{-SiO}_2$ throughout this section) following the experimental procedure reported in [section 3.5.2](#).

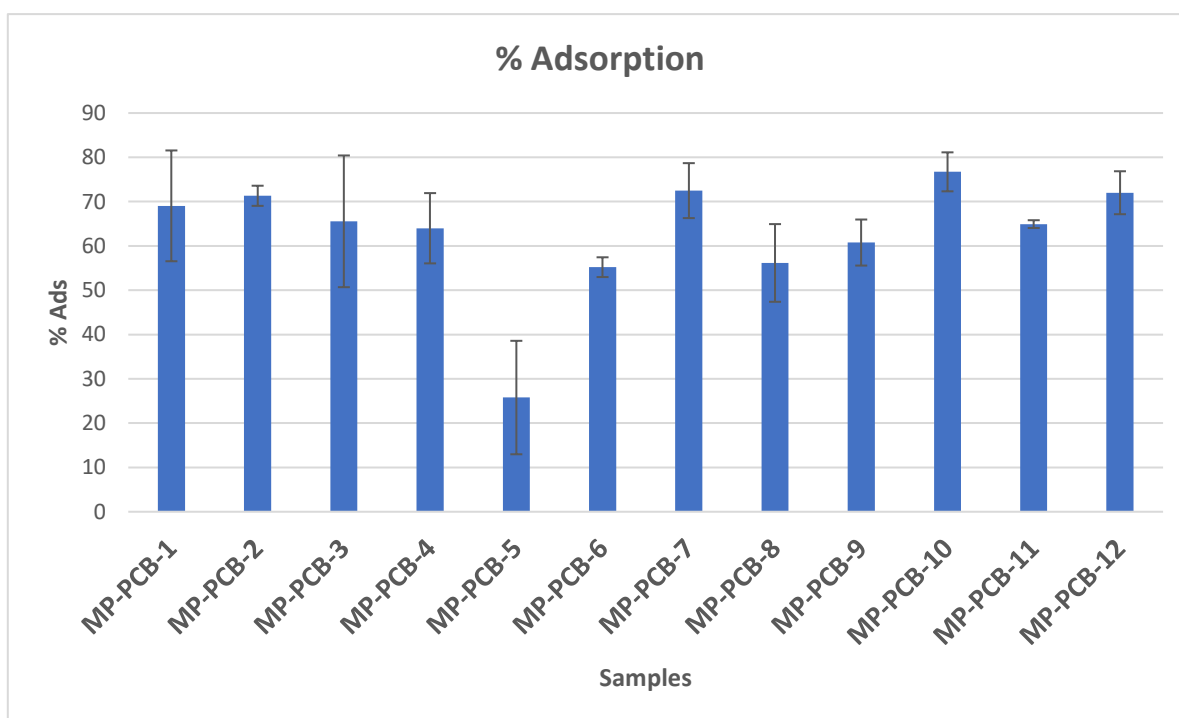


Figure 41: Adsorption % for MP-PCB samples.

4.3.1 Physicochemical and Structural Characteristics:

To elucidate the structural and elemental variability among the MP-PCB series, a multi-technique approach was employed. Micro-morphology and phase composition were assessed via SEM and XRD, while functional groups were identified through Raman spectroscopy. Furthermore, textural properties and electrostatic surface charge were also measured. Collectively, these analyses were essential for understanding how mechanical and chemical processing governed the availability of active adsorption sites.

4.3.1.1 XRD Analysis:

X-ray diffraction (XRD) analysis of MP-PCB-1 reveals a predominantly amorphous profile, characterised by a broad scattering halo centred at $2\theta \approx 22^\circ$ from the glass-fibre-derived SiO_2 framework. Superimposed on this halo, sharp reflections at $2\theta \approx 28.4^\circ$, 47.3° and 56.1° confirm the presence of crystalline silicon (c-Si), originating from residual semiconductor die fragments. This is further supported by the identification of quartz and cristobalite phases, representing the crystalline fraction of the silica matrix. The diffractogram also confirms the presence of metallic copper (Cu) and its oxidation products (CuO , Cu_2O).

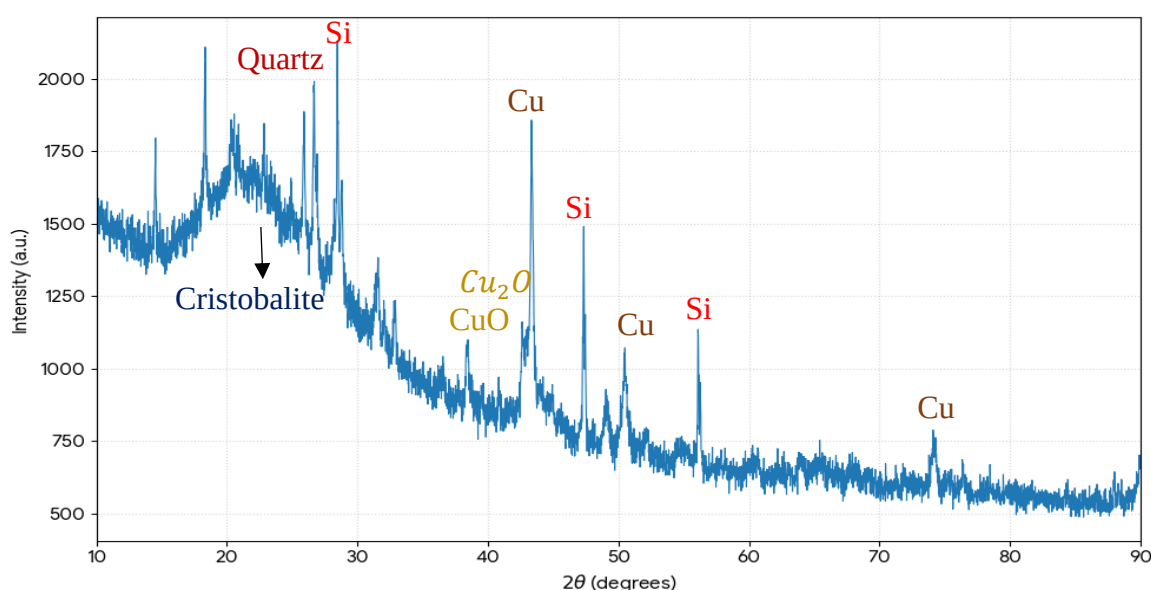


Figure 42: XRD Pattern of MP-PCB-1

This complex mineralogical profile demonstrates that while the mechanical route (MP-PCB) preserves the structural integrity of the silica, it retains a distinct metallic and semiconductor 'fingerprint' compared to more aggressive chemical leaching routes.

4.3.1.2 Raman Analysis:

The surface chemistry and phase heterogeneity of MP-PCB-1 were investigated using spatially resolved Raman spectroscopy revealing a complex multi-component structure arising from the mechanical pulverization of the substrate and its embedded electronic components.

Distinct regions of the sample exhibit a sharp, intense peak at $\sim 521 \text{ cm}^{-1}$, corresponding to crystalline silicon (c-Si). This confirms the successful integration of pulverised semiconductor fragments originating from silicon-based micro-components during the milling process. The spectra also display prominent features at $\sim 1350 \text{ cm}^{-1}$ (D-band) and $\sim 1585 \text{ cm}^{-1}$ (G-band), characteristic of disordered carbon. These bands indicate the presence of defect-rich carbonaceous domains, likely generated

through the localised thermal and mechanical degradation of the polymeric resin matrix during high-energy shredding.

Additional vibrations observed near 1608 cm^{-1} are assigned to aromatic $C = C$ skeletal stretching, consistent with the bisphenol-A (DGEBA) epoxy resin backbone. A diagnostic band at 1417 cm^{-1} is associated with the symmetric stretching of carboxylate (COO^-) groups, suggesting mechanochemical surface oxidation or the liberation of encapsulated organic additives. In the mid-wavenumber region ($500\text{--}1000\text{ cm}^{-1}$), broad contributions from inorganic silicate phases are evident, correlating to the amorphous SiO_2 network of the glass-fibre reinforcement. In addition, distinct spectral features identified in selected regions of the samples are

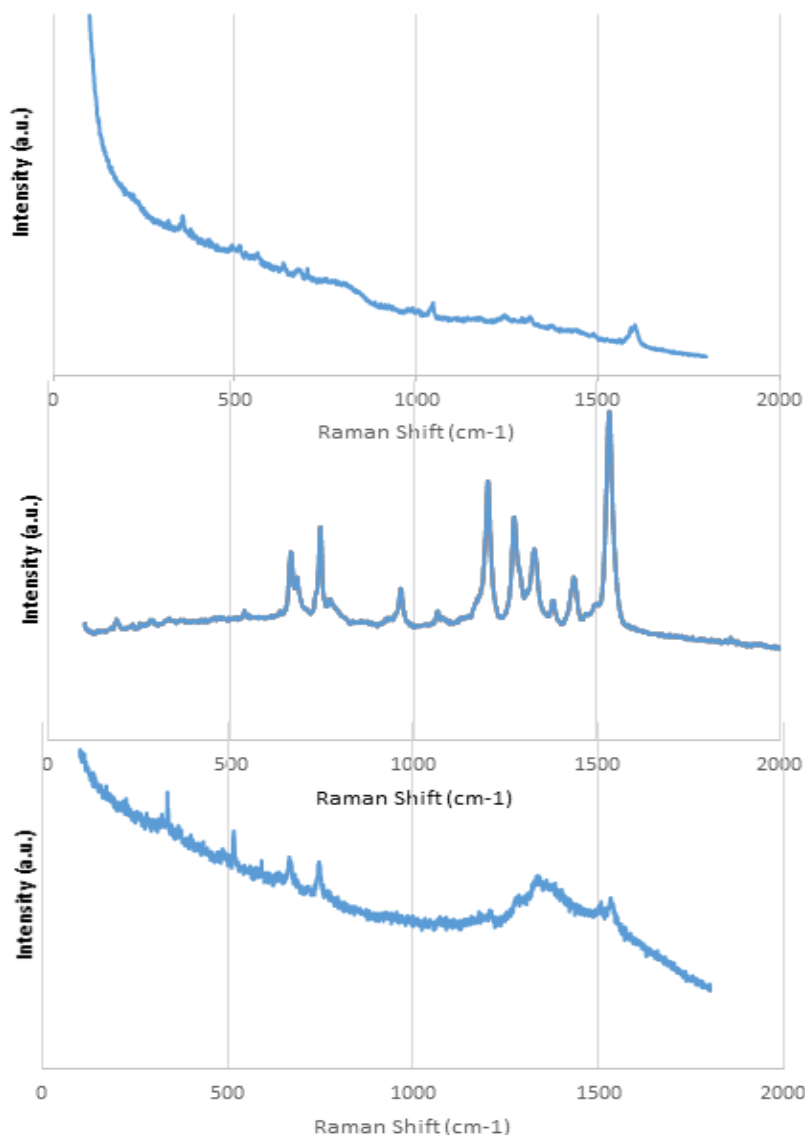


Figure 43: Raman spectra of MP-PCB-1 and its constituent phases. High-energy milling process successfully integrates crystalline silicon (521 cm^{-1}) and generates an active surface featuring carboxylate groups (1417 cm^{-1}) and aromatic epoxy domains (1608 cm^{-1}).

consistent with the characteristic Raman fingerprint of copper phthalocyanine (CuPc), a pigment widely employed in green solder mask coatings. The detection of these Cu phthalocyanine-related bands further suggests the preservation of residual epoxy/solder-mask-derived organic components within the PCB-derived non-metallic fraction and explains the characteristic green coloration observed in portions of the material.

The Raman findings are highly consistent with SEM-EDS observations, which confirm a heterogeneous inorganic-organic matrix dominated by Si, O, Al, and Ca from the fibreglass

components, alongside trace metallic impurities such as Cu, Fe, Mg, and Ba. Collectively, the coexistence of silanol groups, oxygenated moieties, and aromatic domains establishes a chemically heterogeneous surface. This surface heterogeneity indicates multiple potential interaction pathways for organic molecules, including electrostatic attraction and π - π stacking, which are expected to significantly influence the material's adsorption performance.

4.3.1.3 Textural Properties and Pore Architecture of $m - SiO_2$ (BET and Low-Angle XRD):

The structural transformation from the raw PCB waste to the engineered adsorbent was quantified via N_2 physisorption and low-angle X-ray diffraction (XRD). While the as-prepared MP-PCB-1 is a dense composite with modest surface area, the synthesised and derived MP-PCB-MS Mesoporous Silica ($m - SiO_2$) exhibits a fundamentally reorganised framework. The N_2 adsorption-desorption isotherm follows a Type IV profile with a distinct H3-type hysteresis loop. This behaviour is characteristic of a mesoporous material featuring slit-shaped pores, likely formed by the hierarchical assembly of silica fragments. The specific surface area is $S_{BET} = 331 \text{ m}^2/\text{g}$ with a total pore volume of $V_p = 0.67 \text{ cm}^3/\text{g}$.

Crucially, the low-angle XRD analysis provides evidence of a structurally ordered meso-structure. The presence of a well-defined reflection at $2\theta \approx 1.5^\circ$ indicates a periodic arrangement of pores with long-range order, similar to that observed in disordered or worm-like mesoporous silicas.

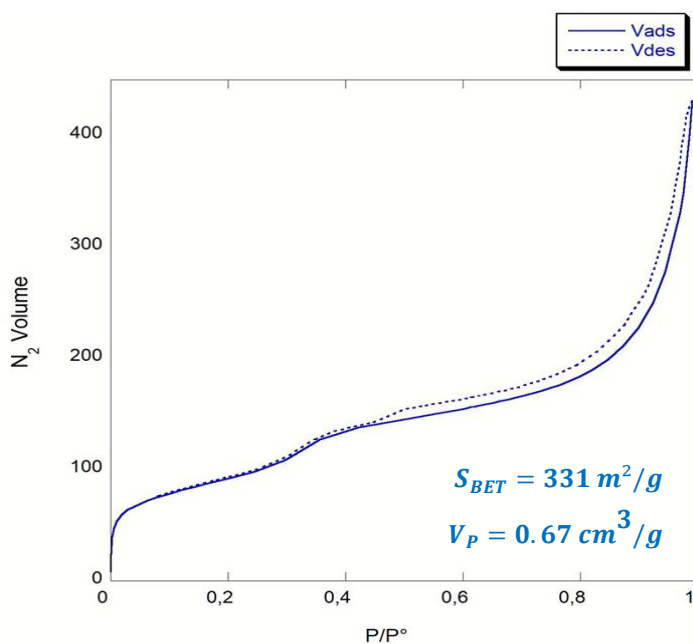


Figure 44: Nitrogen adsorption-desorption isotherm for $m-SiO_2$. The Type IV isotherm and H3 hysteresis loop suggests a well-developed mesoporous architecture.

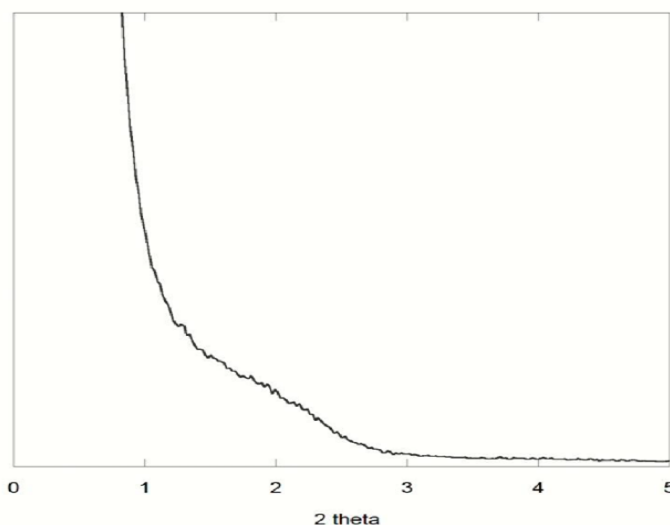


Figure 45: Low Angle XRD of MP-PCB-MS

4.3.1.4 Morphological and Microstructural Analysis (SEM and TEM):

The transition from a heterogeneous waste to a refined nanomaterial is further evidenced by electron microscopy. Scanning electron microscopy (SEM) of the raw MP-PCB-1 (a) reveals a typical comminuted composite morphology, characterised by angular fractured surfaces, protruding glass-fibre filaments, and metallic micro-inclusions.

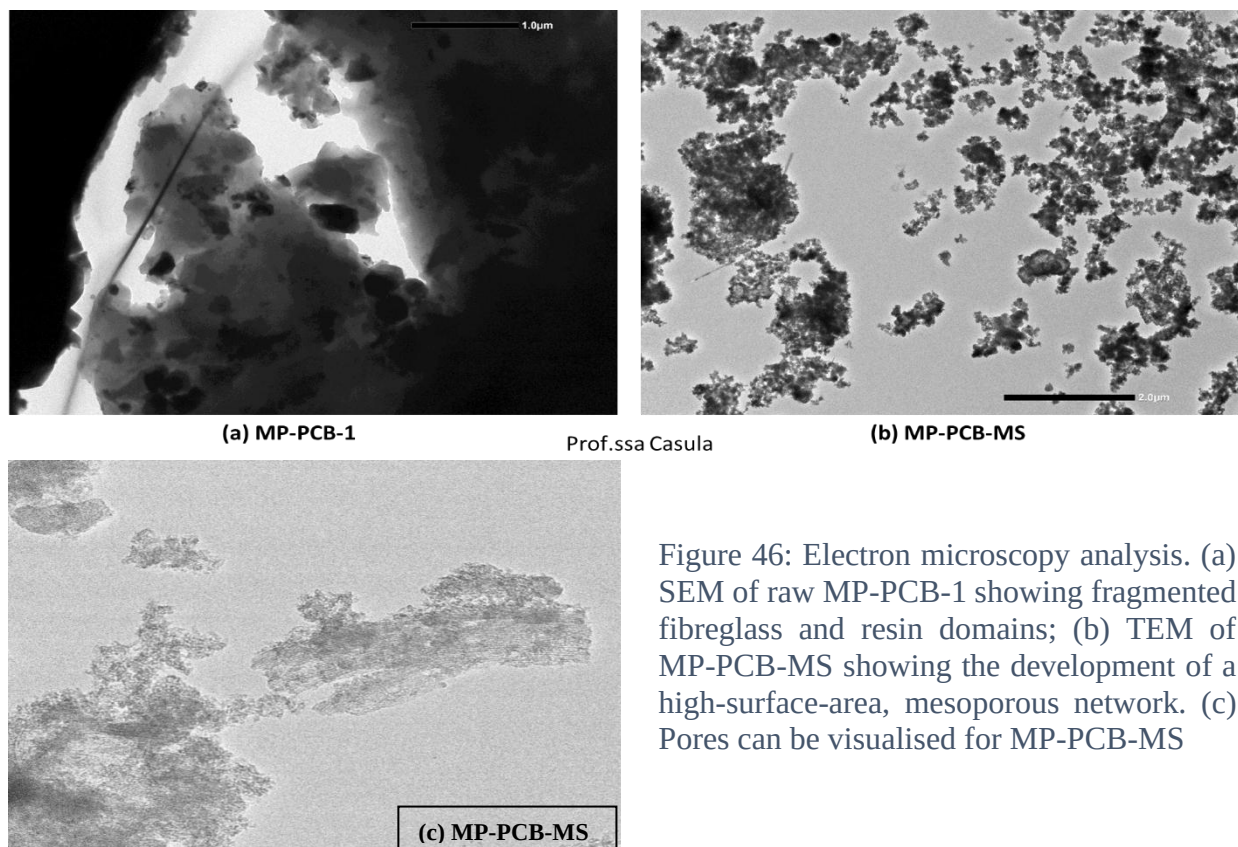


Figure 46: Electron microscopy analysis. (a) SEM of raw MP-PCB-1 showing fragmented fibreglass and resin domains; (b) TEM of MP-PCB-MS showing the development of a high-surface-area, mesoporous network. (c) Pores can be visualised for MP-PCB-MS

By contrast, the MP-PCB-MS presents a complete morphological reorganization. Transmission Electron Microscopy (TEM) (b) reveals a mesostructured framework composed of uniform particles. The micrographs clearly show the internal pore network and the absence of the large, dense glass-fibre bundles seen in the precursor, confirming the effectiveness of the sol-gel condensation process in reorganizing the siliceous precursor into an accessible porous architecture.

4.3.1.5 Electrostatic Surface Charge:

The surface charge and colloidal stability of the MP-PCB derived materials were evaluated via DLS measurements conducted in mineral water (NORDA, pH $\approx$ 7). These results were essential for interpreting the electrostatic behaviour governing adsorption of ionic species, such as the cationic Methylene Blue (MB^+) dye.

Table 16: Zeta potential and conductivity data for MP-PCB-derived materials.

Sample	Zeta Potential (mV)	Conductivity (mS/cm)	Note
MP-PCB-1	-27.57 ± 2.1	0.258	Mechanically processed E-waste
MP-PCB-MS (m- SiO_2)	-20.50 ± 1.0	0.264	Stable silanol-terminated surface
Sabbia Silica	-24.90 ± 1.4	0.260	Natural silica (benchmark)

The raw mechanically processed powder, MP-PCB-1, exhibited the most strongly negative surface charge (-27.57 mV). At near-neutral pH, this value exceeds the threshold for colloidal stability (± 25 mV), indicating a high degree of electrostatic repulsion that promotes dispersion in aqueous media. This intense negative charge is attributed to the deprotonation of silanol groups ($Si - OH \rightarrow Si - O^-$) from the glass-fibre fraction.

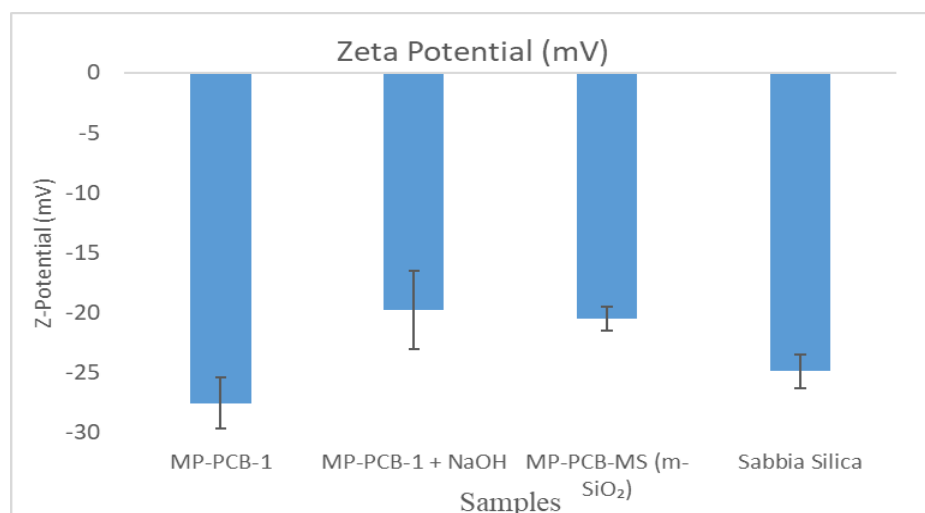


Figure 47: The strong negative potential of MP-PCB-1 (-27.57 mV) indicates a high density of ionisable silanol and carboxylate groups, while the stabilised potential of m- SiO_2 (-20.50 mV) reflects a chemically uniform, mesoporous silica surface.

Alkaline pre-treatment (MP-PCB-1 + NaOH) and the subsequent sol-gel synthesis of m- SiO_2 resulted in a stabilised potential of approximately -20.50 mV. While this represents a slight reduction in absolute charge density compared to the raw waste, the synthesised MP-PCB-MS provides a chemically uniform, silanol-terminated surface with significantly higher accessibility. The surface charge of m- SiO_2 is comparable to the natural Sabbia Silica benchmark (-24.90 mV). This suggests that the synthesis successfully replicates the surface properties of purified natural silicates while providing the added advantage of a tailored mesoporous architecture.

The combination of high specific surface area ($331\text{ m}^2/\text{g}$) and stable negative surface charge establishes MP-PCB-MS as an effective adsorbent. The following sections will demonstrate how these physicochemical properties translate into superior adsorption kinetics and capacity for organic pollutants.

4.3.2 Adsorption Performance:

The practical utility of the PCB-derived materials was evaluated through Methylene Blue (MB) $1 \times 10^{-5}\text{ M}$ adsorption studies.

A preliminary screening of the 12 mechanically processed PCB fractions identified MP-PCB-1 as the most promising precursor due to its consistent surface properties. The raw MP-PCB-1 powder exhibits a significant innate adsorption capacity, reaching a removal efficiency of $69 \pm 12.5\%$ after 24 hours of contact $1 \times 10^{-5}\text{ M}$ MB.

This baseline activity is a direct consequence of the material's surface chemistry, as the high negative Zeta Potential ($\zeta = -27.57\text{ mV}$) and the presence of silanol and carboxylate groups (confirmed via Raman) provide active sites for electrostatic attraction with the cationic dye. However, the adsorption process is notably slow and displays high variance; this is mechanistically consistent with a surface-limited process where active sites are confined to the external faces of dense fibreglass and resin particles, severely limiting the rate of mass transfer.

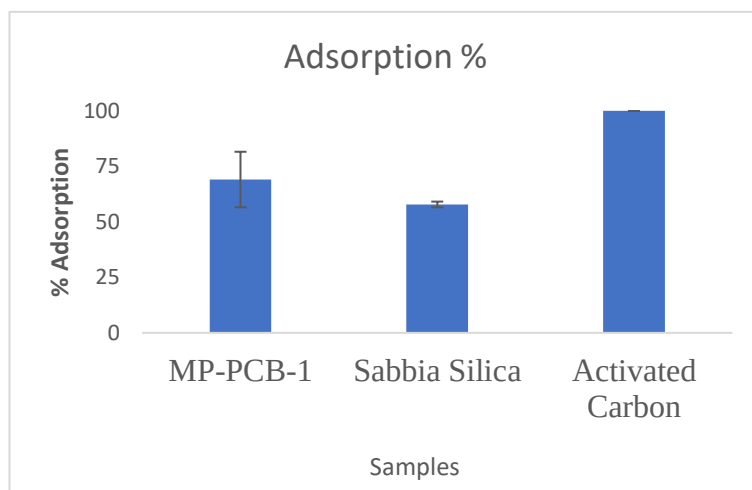


Figure 48: Adsorption Percentage Comparison

MP-PCB-1 outperforms sabia silica but falls well short when compared to activated carbon. This shortfall was the driving force for the synthesis of MP-PCB-MS and functionalization with PDA.

To increase the removal performances of MP-PCB-1 against MB we followed three parallel routes: functionalisation with PDA (since it resulted the most promising treatments operate on BL-PCB samples, testing of its photodegradation activity, and its conversion into $m - \text{SiO}_2$).

4.3.2.1 Functionalisation of MP-PCB-1 with Polydopamine (PDA):

Polydopamine (PDA) functionalization of MP-PCB-1 yielded a meaningful improvement in adsorption performance relative to the unmodified material. The equilibrium adsorption capacity increased from 1.81 mg g^{-1} to 2.23 mg g^{-1} (+23.3%), while MB removal at 24 hours rose from 69.05% to 85.1%. More notably, the relative standard deviation in removal efficiency collapsed from 12.1% to just 0.005%, a ~99% reduction, indicating that the PDA overlayer acts as a chemically uniform coating that homogenises the otherwise heterogeneous PCB surface, suppressing the batch-to-batch variability inherent to raw e-waste-derived materials. By masking the inconsistent resinous and metallic patches of the raw e-waste with a uniform coating of catechol and amine groups, the functionalization homogenises the surface, effectively transforming a heterogeneous waste residue into a standardised adsorbent. This shift is driven by the multifunctional nature of PDA, which introduces $\pi - \pi$ stacking and hydrogen bonding pathways that the bare siliceous/resinous surface lacks. However, performances are still far away from those of AC which is capable to adsorb 100% MB in 10 minutes.

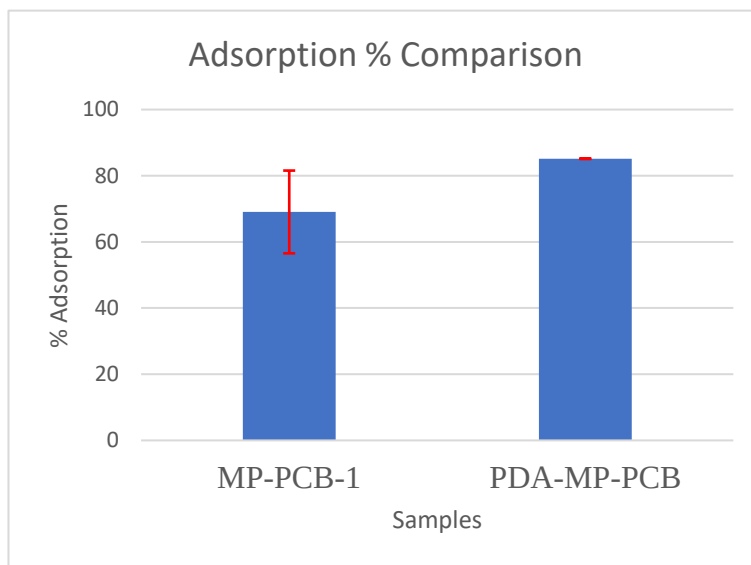


Figure 49: Adsorption performance and statistical reliability of raw vs. functionalised MP-PCB-1. The PDA overlayer increases removal efficiency to 85.1% and suppresses variability, providing a chemically uniform surface for consistent pollutant sequestration.

4.3.3 MP-PCB Samples Photocatalytic Activity:

This section details the degradation efficiency of these materials under simulated solar irradiation, following the established 24-hour dark-phase sequestration protocol. photocatalytic performance of the samples from Random-Access Memory (MP-PCBs-1-6) and Printed Circuit Boards (MP-PCBs-7-12) waste. The analysis also evaluates the photocatalytic performance of the engineered mesoporous silica (MS) framework.

The MP-PCB (1 through 6 RAM samples) series demonstrated notable kinetic consistency and high-load robustness. For the standard $1 \times 10^{-5} M$ system, the baseline sample (MP-PCB-1) achieved a dark-adsorption removal of 69.6%.

Upon activation of the solar simulator, the normalised concentration (C/C_0) fell sharply, reaching $C/C_0 = 0.443$ at 180 minutes and achieving 100% mineralization within 360 minutes. The broader MP-PCB series (MP-PCB-2 through MP-PCB-6) exhibited a tightly clustered degradation profile, with most samples reaching near-zero residual concentrations ($C/C_0 < 0.05$) between 480 and 600 minutes.

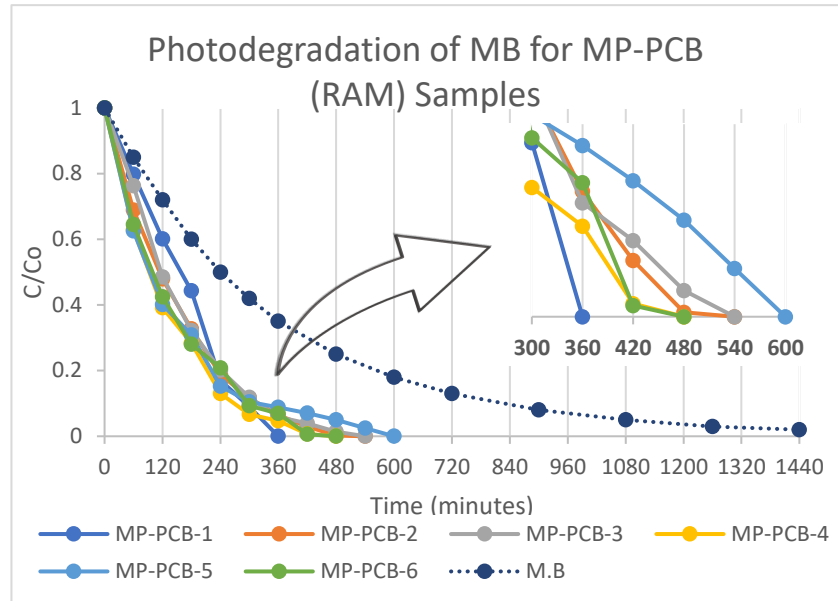


Figure 50: Comparative photocatalytic mineralisation profiles for MP-PCB Samples 1 to 6

The MP-PCB (7 through 12) series, derived from mixed printed circuit boards residues, exhibited a similarly aggressive degradation trajectory. Samples MP-PCB-7 and MP-PCB-8 reached total elimination by 420 minutes, while MP-PCB-9, MP-PCB-10 and MP-PCB-12 showcased kinetics, achieving $C/C_0 = 0$ within 480 minutes. The slight kinetic advantage observed in specific PCB batches may be attributed to trace metallic dopants (such as

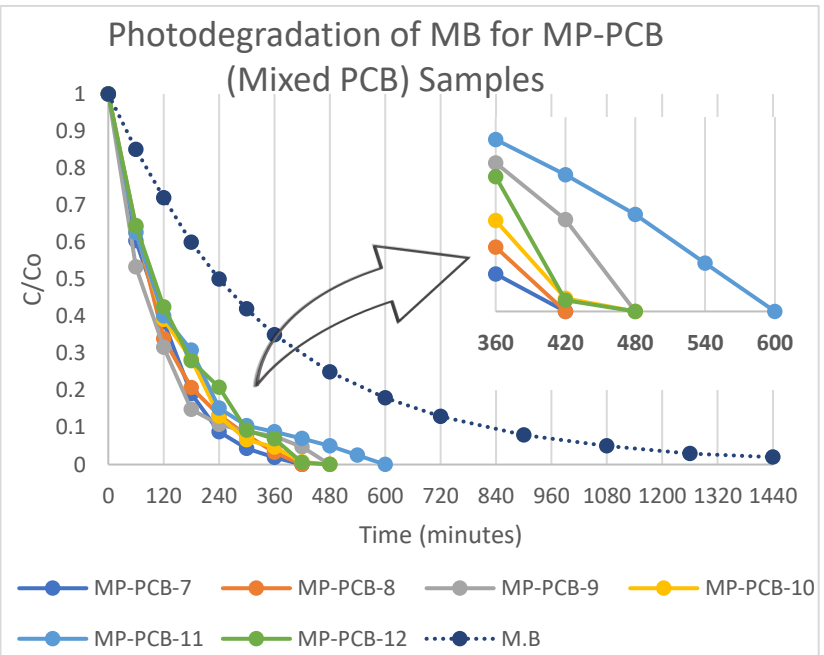


Figure 51: Comparative photocatalytic mineralisation profiles for MP-PCB Samples 7 to 12

gold or silver common in PCB contacts) that remained in the sample, acting as localised electron traps that suppress charge-carrier recombination.

4.3.4 Conversion into $m-SiO_2$:

The synthesis of mesoporous silica ($m-SiO_2$) from the PCB precursor triggers a fundamental shift in performance. In contrast to the 24-hour equilibration required by the raw powder and PDA-functionalised sample, the MP-PCB-MS ($m-SiO_2$) achieves essentially complete adsorption (98–100%) within the first 1–2 minutes of contact with the MB $10^{-5}M$ solution.

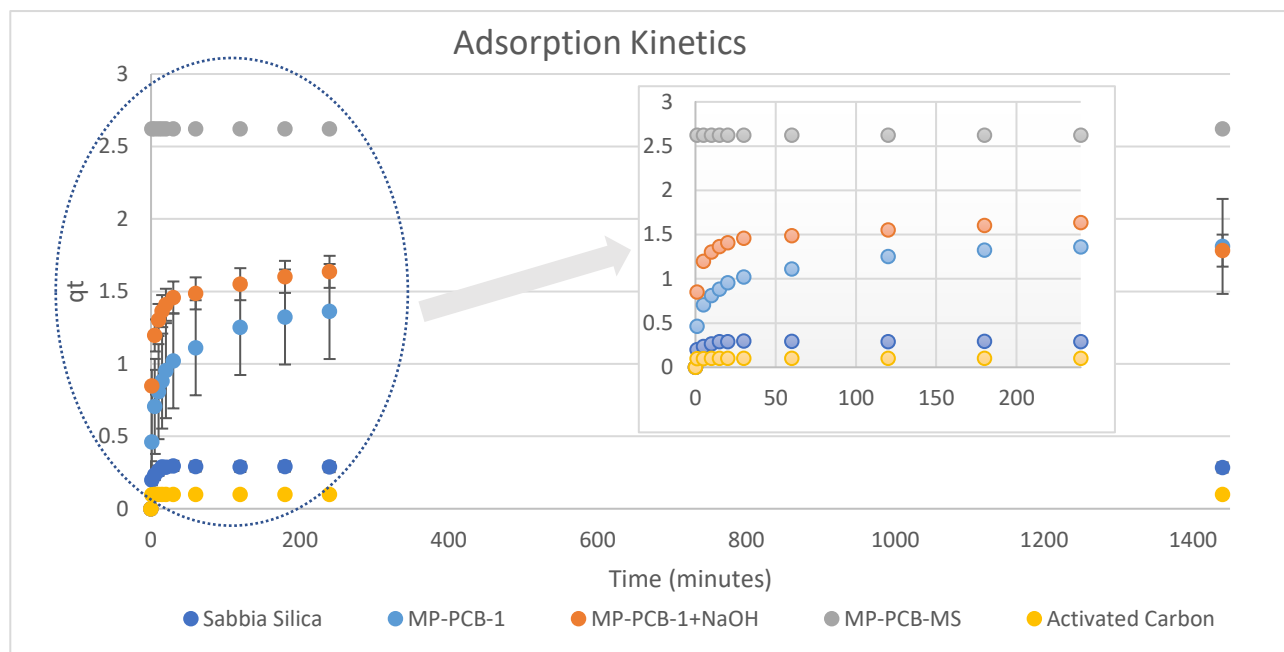


Figure 52: The main plot shows the long-term stability of the q_e plateau up to 24 hours. Inset: Detail of the first 240 minutes, highlighting the exceptional kinetic response where 98-100% of the total capacity is realised within the initial contact phase.

As shown, the kinetic profile of MP-PCB-MS was qualitatively indistinguishable from commercial activated carbon, the industrial gold standard for water treatment. The graph clearly shows a Pseudo-second-order behaviour where the curve is almost vertical at $t \rightarrow 0$ minutes, indicating that the active sites are not just present, but immediately accessible. Furthermore, it significantly outperforms the Sabbia Silica (natural sand) benchmark, which achieved only 57.8% removal under the same 24-hour conditions. This comparison highlights that the synthesis does not merely recover silica; it transforms it into a high-performance adsorbent framework. The rapid kinetics are the direct result of the structural reorganization detailed in previous sections: the high specific surface area ($331 \text{ m}^2/\text{g}$) and the ordered mesoporous channels allow for immediate intraparticle diffusion, making every active silanol site instantly accessible to the pollutant.

During the synthesis of $m-SiO_2$, at the end of the alkaline leaching step, we obtained a new type of solid waste consisting of Si-free MP-PCB-1, which was similarly tested for the removal of MB ($10^{-5} M$). Interestingly, its removal performance after 24 hour was identical to that of the original MP-PCB-1. These results confirm that Si extraction from waste-PCBs is an effective strategy to generate

two distinct but efficient adsorbents: a Si-deprived solid waste, whose removal efficiency remained comparable to the pristine waste, with no decrease associated with Si removal, and $m\text{-SiO}_2$ whose removal capabilities were significantly enhanced compared to the original material, leading to very fast adsorption. The superior performances of $m\text{-SiO}_2$ were ascribed to its modified morphology, specifically the increased specific surface area and porosity

4.3.4.1 Influence of Concentration and Isotherm Modelling:

The sequestration capacity of $m\text{-SiO}_2$ was evaluated across a concentration gradient from $1 \times 10^{-5}M$ to $4 \times 10^{-4}M$. As the initial concentration increases, the equilibrium capacity (q_e) scales proportionally, rising from 2.6 mg/g at $1 \times 10^{-5}M$ to a maximum of 76.7 mg/g at $3 \times 10^{-4}M$.

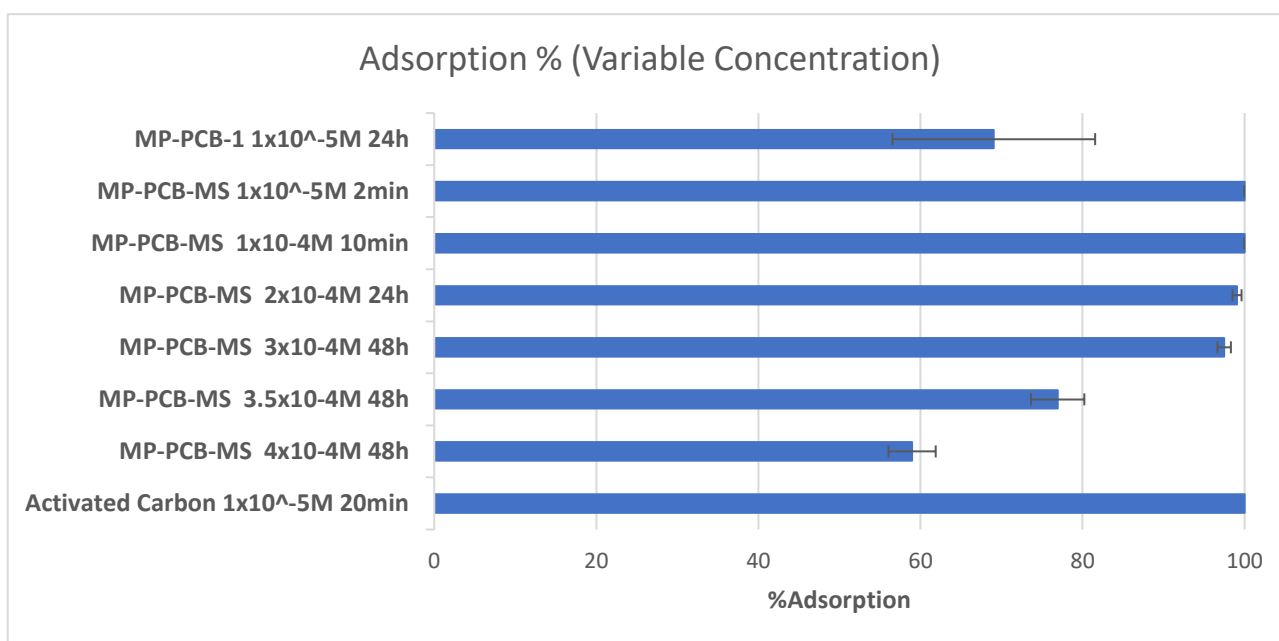


Figure 53: Comparing removal % for MB at different concentrations.

At the higher threshold of $4 \times 10^{-4}M$, the removal efficiency stabilises at approximately 77% after 48 hours of agitation. This behaviour is rigorously described by the Langmuir Adsorption Isotherm, indicating that adsorption occurs via monolayer formation on a finite population of energetically equivalent silanolate sites ($Si - O^-$). This quantitative scaling behaviour demonstrates a typical saturation-limited framework. At lower initial dye boundaries, the abundance of unshielded functional sites drives high fractional removal. Conversely, at elevated initial concentrations, the absolute mass of immobilised solute increases due to the steeper concentration gradient that provides the driving force to overcome solid-liquid mass transfer resistance, eventually flattening as site saturation is reached. The saturation plateau confirmed by the data implies that once the internal mesopore surface ($331 m^2/g$) is occupied, the geometric constraints of the 3.5–5 nm channels prevent further multi-layer accumulation.

This structural limitation mathematically validates the Langmuir assumption of a finite active site landscape. Because the underlying matrix consists of fractured glass-fibre silicate planes interlocked with epoxy boundaries as resolved in our preceding Micro-Raman analyses the physical boundary constraints of these exposed inorganic-organic cleavage planes restrict any further phase accumulation or vertical molecular stacking beyond the primary chemisorbed monolayer.

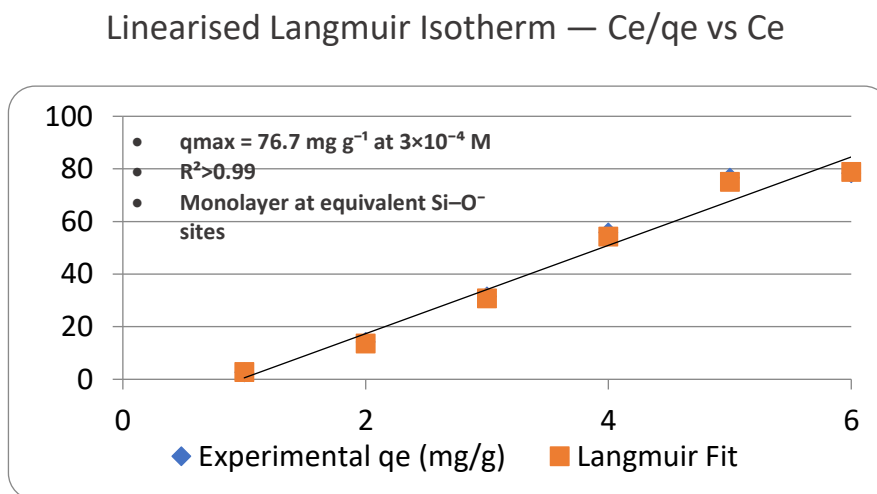


Figure 54: Linearised Langmuir adsorption isotherm C_e/q_e vs C_e for Methylene Blue immobilisation on the MP-PCB-MS samples

4.3.4.2 Influence of Temperature:

The effect of thermal energy on MB adsorption by $m - SiO_2$ was investigated at room temperature (25°C), 45°C and 65°C for high-concentration system of $3.5 \times 10^{-4} M$. An increase of temperature to 45°C yielded a distinct enhancement in the adsorption percentage, reaching 88% compared to lower values at ambient temperature of 76%. Temperature of 65°C further increased the adsorption slightly to 89.3%, suggesting that the system effectively approaches its maximum thermodynamic capacity at these elevated temperatures. The UV-Vis absorption spectra for the $3.5 \times 10^{-4} M$ and $4 \times 10^{-4} M$ systems exhibit a characteristic blue-shift (hypso-chromic shift) and changes in peak intensity. This behaviour suggests that the MB adsorption is an endothermic process, however it is to underline that during the heating of the system we observed a blueshift of MB-characteristic peak (as reported in Figure 55), which limit our possibility to perform a real thermodynamic analysis. In particular, the $3.5 \times 10^{-4} M$ MB solution absorption spectrum at ambient temperature is characterised by the copresence of 2 peaks: one at

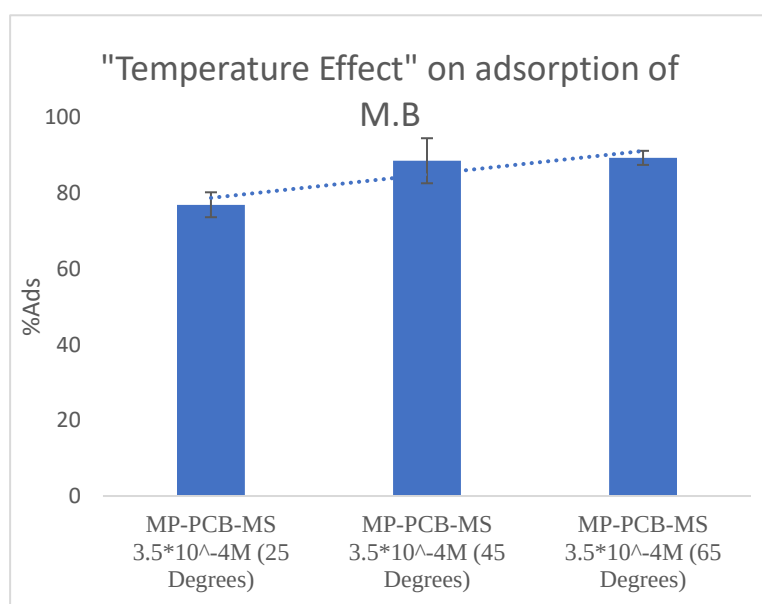


Figure 55: Increasing the temperature has significant impact on the adsorption of MB.

~664 nm, due to monomeric molecules in solution, and one (a lower intensity shoulder) at ~612 nm due to H-type dimers or aggregates. All these chemical species are in equilibrium in solution, and they are characterised by a different cross-section. By heating the m- SiO_2 MB system we observed not a real lowering of these two MB peaks, which can likely be ascribed to a decrease of MB molecules in solution, but we observed a broadening-blue shifting- lowering of the absorbance peaks. This behaviour could be due also to a change of the type of the molecular forms of MB in solution: for instance, heating could favour the formation of MB dimers instead of its adsorption on m- SiO_2 .

These observations are consistent with previous spectroscopic studies reporting the coexistence of monomeric and aggregated methylene blue species in aqueous environments, where the principal absorption band near 664 nm is attributed to monomeric MB, while the lower-wavelength shoulder around 610–620 nm originates from H-type dimers or higher-order aggregates. Temperature variations are known to modify the equilibrium between these species, producing spectral broadening and shifts in the absorption maxima.

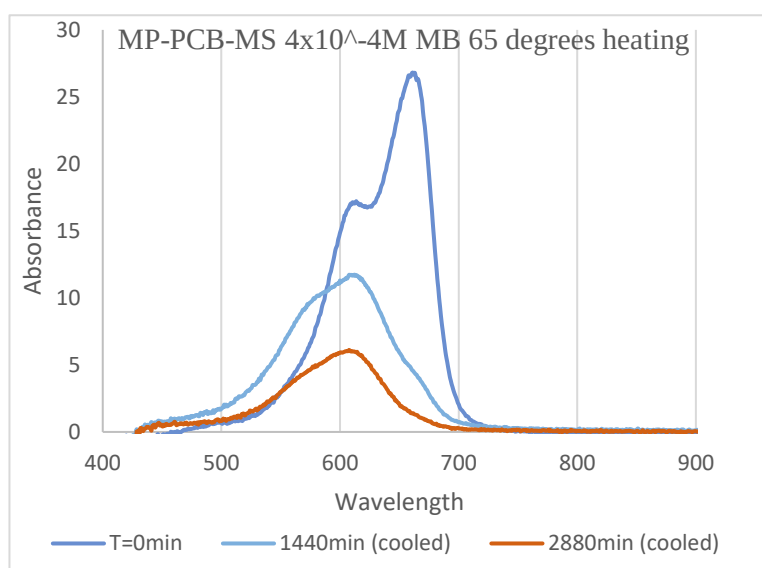


Figure 56: Temperature-dependent UV-Vis absorption spectra. The spectral changes reflect the combined influence of adsorption-related concentration decrease and temperature-induced reorganisation of MB monomer–dimer equilibria in solution.

Therefore, the thermal response observed in the present system likely results from the combined influence of adsorption phenomena and temperature-induced reorganization of MB aggregation states in solution, rather than from adsorption effects alone. (Heger et al., 2005).

4.3.4.3 Dye Selectivity: Beyond Methylene Blue:

To evaluate the universality of the electrostatic mechanism, MP-PCB-MS (m- SiO_2) was tested against a suite of probe molecules with varying charges and sizes. Cationic dyes including Crystal Violet (100% removal) and Rhodamine 6G (73% removal) were successfully sequestered in 24 hours. The slightly lower uptake of Rh6G is attributable to steric hindrance; its larger xanthene ring system experiences increased resistance when diffusing into the 3.5–5 nm mesopore channels compared to the more planar MB molecule.

Conversely, the anionic dye Methyl Orange (MO) showed negligible adsorption (<3%) on the synthesised $m\text{-SiO}_2$. This provides definitive functional proof of the surface charge results (-20.5 mV); the deprotonated silanol surface on $m\text{-SiO}_2$ creates an electrostatic repulsion field that excludes anionic species. Interestingly, MP-PCB-MS ($m\text{-SiO}_2$) was tested in a binary equimolar mixture of Methylene Blue (MB) and Methyl Orange (MO). The total solution volume was maintained at 5 mL, comprised of 2.5 mL of each dye $2 \times 10^{-5} M$, resulting in an equimolar competitive environment with an initial concentration of $1 \times 10^{-5} M$ per species.

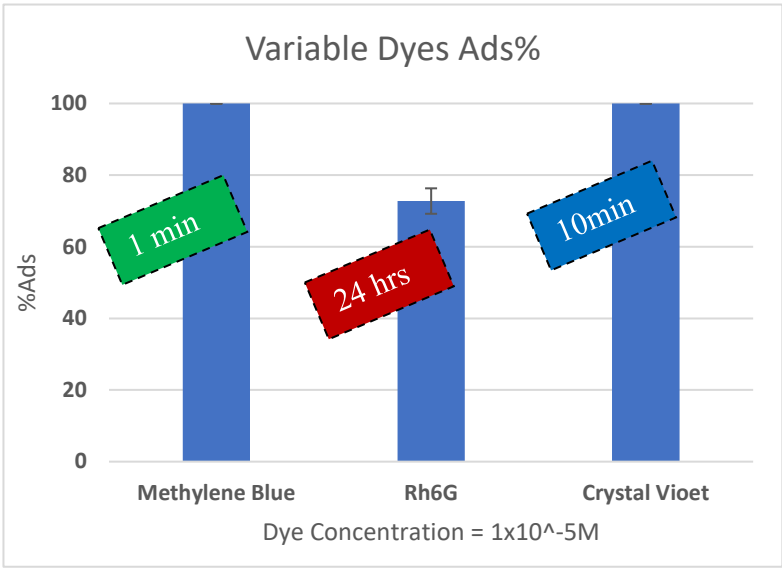


Figure 57: MP-PCB-MS tested for variable dyes for Adsorption

In single-component systems ($1 \times 10^{-5} M$), MB removal is instantaneous (<2 min). While, in the binary mixture, the time required for 100% MB sequestration increases to only 5–10 minutes. This kinetic delay is probably a result of competitive bulk-phase interference. The electrostatic attraction between cationic MB^+ and anionic MO^- molecules can facilitate the formation of MB–MO ion pairs. These molecular aggregates possess a larger hydrodynamic radius than free MB^+ monomers, significantly increasing the mass transfer resistance. However, it is noteworthy that MO ions do not hinder MB adsorption.

MIX MO + MB $10^{-5} M$

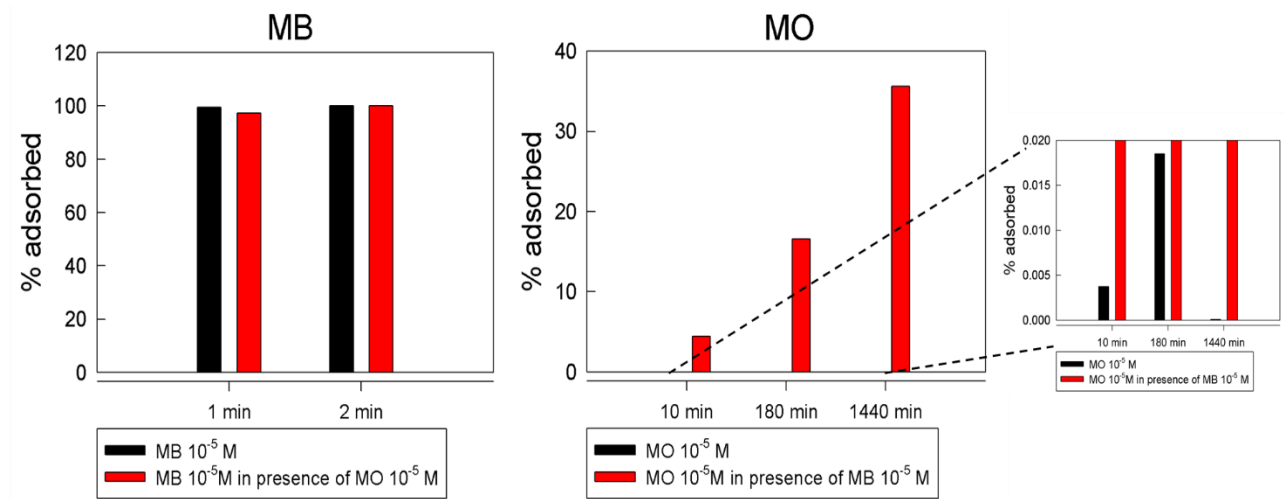


Figure 58: MO and MB mix co-adsorption

The most significant finding is the "forced" adsorption of methyl orange. While MO alone is excluded by the negative silica surface (<3% removal), its removal in the presence of MB increases to values ranging from 5% to 35%.

This phenomenon is explained by 'ion-pair co-adsorption' the formation of cationic MB⁺–anionic MO[−] ion pairs in solution reduces the net charge of the MB–MO complex, lowering the electrostatic repulsion between the MO sulphonate group and the negatively charged silanol surface. Alternatively, an initial partial MB adsorption on the m-SiO₂ surface can reduce the negative surface charge, lowering MO repulsion. The final result is the enabling partial co-adsorption of the otherwise electrostatically excluded anionic dye. The high variability in MO uptake (5% vs. 35%) is a hallmark of aggregate-driven processes, which are highly sensitive to the orientation of molecular assembly at the pore entrances.

Table 17: Comparison of Single-Component and Equimolar Binary Systems

System Type	Dye	Concentration	Removal Efficiency	Time to Equilibrium	Mechanism
Single	MB	$1 \times 10^{-5} M$	~100%	< 2 min	Electrostatic Attraction
Single	MO	$1 \times 10^{-5} M$	< 3%	24 hours	Electrostatic Repulsion
Binary	MB (+ MO)	$1 \times 10^{-5} M$	100%	5–10 min	Electrostatic Attraction
Binary	MO (+ MB)	$1 \times 10^{-5} M$	5% – 35%	24 hours	ion-pair co-adsorption

4.4 Cyclic Reusability of MP-PCB-MS:

For an adsorbent derived from waste to be genuinely viable, it must demonstrate not only high single-use performance but the capacity for repeated recycling, a requirement that governs both the economic and environmental credibility of the technology (Gupta & Suhas, 2009). MP-PCB-MS (m-SiO₂) was therefore subjected to four consecutive adsorption–desorption cycles against MB ($1 \times 10^{-5} M$) using 0.1 M sodium dodecyl sulphate (SDS) as the regenerant. Furthermore, its behaviour was benchmarked directly against commercial activated carbon (AC, DARCO, Sigma-Aldrich) under identical conditions.

SDS was selected because its anionic sulphonate head group (SO₃[−]) competitively displaces adsorbed cationic MB⁺ from the negatively charged silanolate surface, while its high concentration leads to the

formation of micelles in water that can host and stabilise MB, preventing its re-adsorption. The entire procedure is performed at ambient temperature without any thermal treatment, acid washing, or organic solvent, just water was used for cleaning.

The reusability results are presented in Figure 59, In cycle 1, MP-PCB-MS (m-SiO₂) achieves 99.55% MB removal at one minute and 100% at two minutes. After SDS regeneration, cycle 2 returns 97.55% at one minute, recovering to 100% by five minutes. Cycles 3 and 4 achieve 98.48% and 99.12% at one minute respectively,

both reaching 100% by two minutes. The equilibrium adsorption capacity q_t at the two-minute endpoint spans only 2.610–2.621 mg g⁻¹ across all four cycles, a total variation of 0.46%, indistinguishable from measurement uncertainty, confirming that the adsorption capacity of MP-PCB-MS (m-SiO₂) is quantitatively invariant across the regeneration sequence. The minor

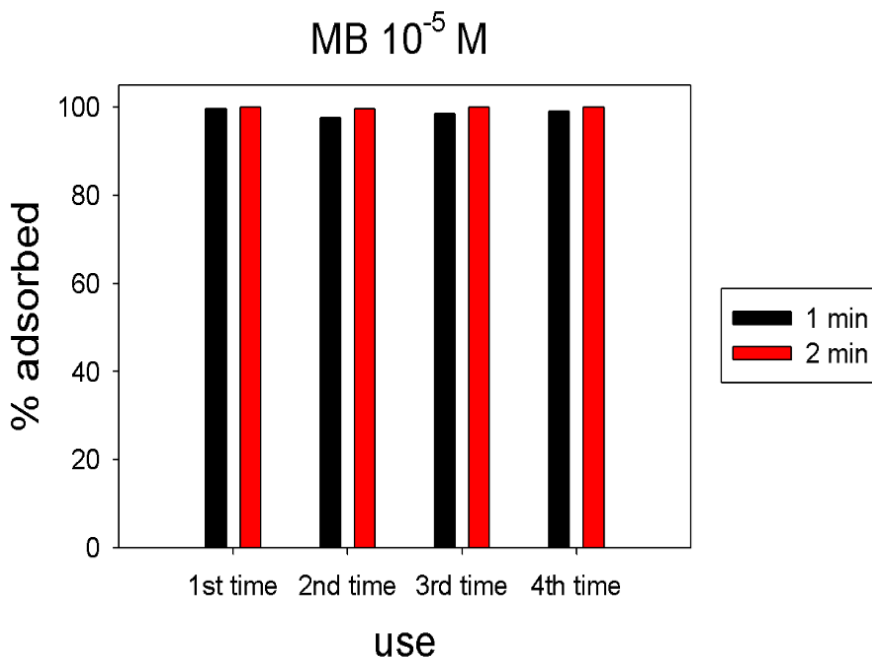


Figure 59: Cyclic reusability of MP-PCB-MS over four consecutive SDS-regeneration cycles (MB: 1×10^{-5} M, adsorbent dosage: 1.2 mg mL⁻¹, pH $\approx$ 7.5, ambient temperature).

reduction in one-minute uptake in cycle 2, which stabilises from cycle 3 onward, is consistent with transient residual SDS in pore-interior positions following the first washing step, a phenomenon well-documented for mesoporous silica systems and without consequence for equilibrium performance (Zhuravlev, 2000). The four cycles tested here do not represent the operational limit of the material and the 0.46% capacity variation suggests that the material's operational lifespan extends well beyond the four cycles tested here.

In parallel, MB desorption was followed spectroscopically via UV-vis by evaluating the increase of the intensity of the peak at 664 nm in the SDS solution over the time. Complete MB recovery is confirmed in every cycle. Cycle 1 desorbs 87.54% within one minute and reaches completion within approximately two minutes, the fastest desorption observed. Cycle 2 achieves 78.15% at one minute, 98.03% by thirty minutes, and is confirmed complete at three hours. Cycles 3 and 4 follow the same

alternating fast–slow pattern at one minute (88.38% and 78.75% respectively) before reaching full desorption in both cases within 60 minutes.

Comparison with activated carbon:

Activated carbon achieves 99.2% MB removal at 5-10 minutes, nominally equivalent to MP-PCB-MS, consistent with its established position as the benchmark adsorbent for organic dye removal (Rafatullah et al., 2010). However, SDS desorption of MB-loaded AC yields only 4.2% recovery after 48 hours of continuous exposure. The adsorption performance of AC arises predominantly from micropores with diameters of 0.5–2.0 nm (Tran et al., 2017), within which MB is physically confined. The SDS micelle in aqueous solution has a hydrodynamic diameter of approximately 4–5 nm, two to ten times larger than these micropores, and is geometrically excluded from the sites where MB is held. Desorption therefore cannot occur regardless of contact time.

In MP-PCB-MS (m-SiO₂), MB is adsorbed electrostatically at silanolate sites (Si–O[−]) within ordered mesopore channels of 3.5–5 nm, a diameter that is geometrically commensurate with the SDS micelle. This compatibility is a direct consequence of the CTAB-templated synthesis: the mesopore diameter is set by the CTAB micellar geometry during sol-gel condensation (Kresge et al., 1992), and the same micellar dimensions that defined the pore during synthesis enable the SDS regenerant to access and reverse the adsorption in operation. The silanolate groups are not chemically altered by SDS exposure, they are transiently occupied then vacated, leaving surface identical to its pre-adsorption state and ready for next cycle.

Considering only adsorption efficiency and kinetics, AC and the synthesised m-SiO₂ could be considered equivalent single-use adsorbent, but AC requires thermal regeneration at 700–900°C per industry standard, energy-intensive, structurally damaging to the carbon framework, and incompatible with decentralised treatment. On the contrary, MP-PCB-MS is completely regenerated by ambient-temperature surfactant washing and retains its full adsorption capacity across repeated cycles. For a material derived from electronic waste at zero feedstock cost, this re-generability profile constitutes a decisive operational advantage.

Table 18: Adsorption & Desorption Summary

Material / Cycle	Adsorption at 1 min (%)	Adsorption at 2 min (%)	Equilibrium Capacity (qe)	SDS Desorption Efficiency (%)	Time to Eq. Desorption (min)
Cycle 1	99.55	100.00	2.622	100.0 ²	2
Cycle 2	97.55	99.54	2.622	100.0	180
Cycle 3	98.48	100.00	2.622	99.39	180
Cycle 4	99.12	100.00	2.622	99.24	60
(AC)	~99.2	~99.8	~2.6	4.2	>2880 (48 h)

Critical Discussion and Operational Limits:

The transformation of MP-PCB-1 into MP-PCB-MS (m-SiO₂) represents a successful "upcycling" of electronic waste into a high-performance material that matches industrial benchmarks. However, the parametric studies reveal specific operational limits:

1. **Concentration Thresholds:** The adherence to the **Langmuir model** suggests that performance is surface-area limited. At extremely high loads, pore blockage or site saturation occurs, reducing the speed of the "instantaneous" kinetics observed at lower concentrations.
2. **Charge Sensitivity:** While the material is a significant cation exchanger, its repulsion of anions like MO requires careful consideration when treating mixed-charge wastewater, though the co-adsorption effect noted in binary mixtures offers a potential workaround.
3. **Synthesis Consistency:** The high specific surface area is the primary driver of performance. Any deviation in the sol-gel process that leads to a less ordered meso-structure will directly impact the intraparticle diffusion rates

4.5 Industrial Scalability of BL-PCB-SU:

Following the validation of the material's reusability, the final stage of performance evaluation of PCB-derived materials addresses the industrial scalability of the upcycling process. Transitioning

² Efficiency corrected for standard blank measurement artifacts; original raw value 104.3%.

from small-batch laboratory trials to larger volumes is the ultimate test of an engineered adsorbent's viability. For this evaluation, the BL-PCB-SU (Scale-Up) series was used: it represents an analogue of the previously tested BL-PCB samples, provided by University of Cagliari after having performed an optimised green leaching on waste ground PCBs.

To assess the robustness of the BL-PCB-SU mechanism, the adsorption system was scaled from the standard 5 mL batch to 100 mL and 500 mL volumes, maintaining a constant adsorbent-to-pollutant dosage (1.2 mg/mL). This experiment is critical for identifying potential mass-transfer limitations or "scale-down" effects that typically constraints the waste-derived catalysts when moved beyond microliter environments.

The BL-PCB-SU sample was tested for MB 10^{-5} M adsorption as it was received and after having being sieved in order to obtain a powder granulometry lower than 300 μm . The initial comparison between the raw BL-PCB-SU sample and the BL-PCB-SU Sieved (300 μm) variant highlights again the importance of particle size and feedstock preprocessing. The sieved BL-PCB-SU achieved an equilibrium removal of 98.20% ($q_t = 2.6\text{mg/g}$), significantly outperforming the non-sieved counterpart (76.45%). By limiting

particle size to $\leq 300\text{ }\mu\text{m}$ through mechanical sieving, the accessible surface area per unit mass is maximised, the intraparticle diffusion path length within individual particles is reduced, and the heterogeneous glass-fibre and resin domains are more uniformly exposed to the bulk solution.

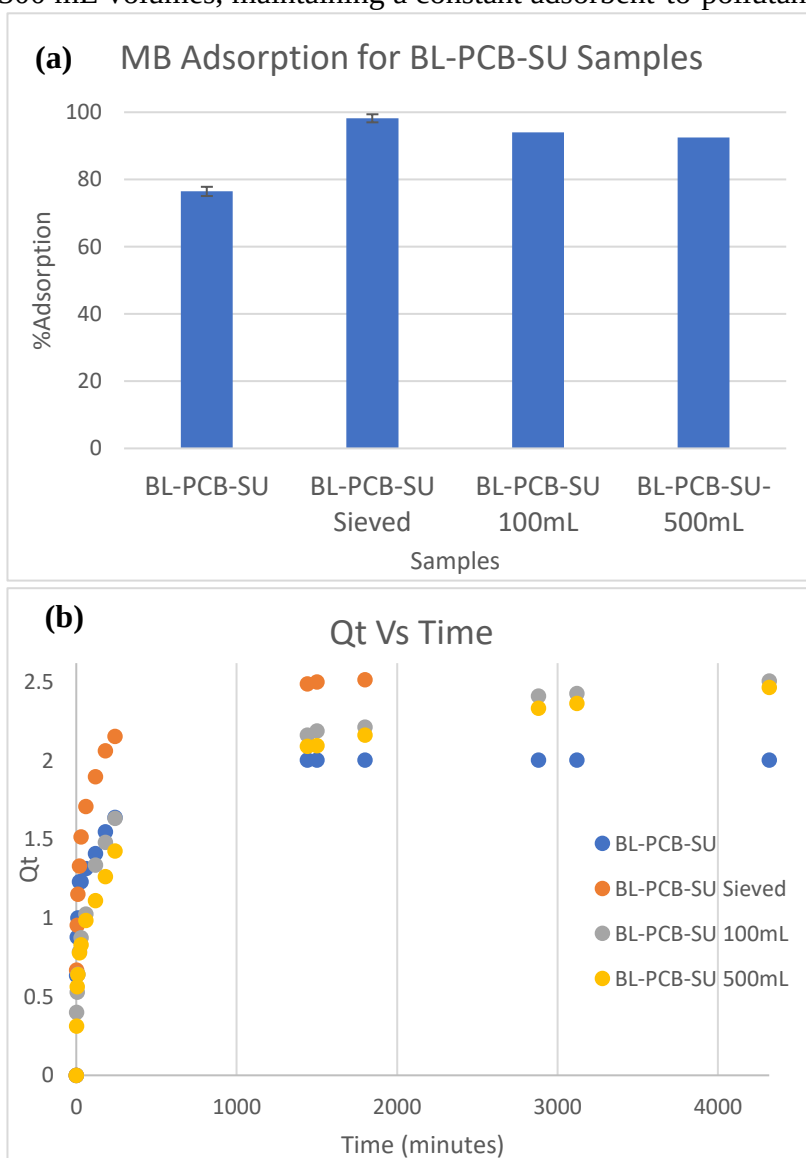


Figure 60: Performance metrics for the BL-PCB-SU scale-up series. Sieving is a critical parameter for optimising the adsorption kinetics and total removal efficiency.

So, the BL-PCB-SU Sieved (300 μm) variant was selected to test the possibility of performing efficiently at a bigger scale. The scalability trials demonstrate a remarkable preservation of adsorption performance across a 100-fold volume increase from the initial pilot tests:

- **100 mL Trial:** Reached a final removal efficiency of 94.04%, achieving a $q_t = 2.51\text{mg/g}$.
- **500 mL Trial:** Maintained high efficiency with a final removal of 92.52% and $q_t = 2.5\text{mg/g}$.

The data reveals that the equilibrium capacity remains virtually constant (2.51mg/g) regardless of the reactor volume. The slight divergence in kinetics observed in the first 120 minutes, where the 500 mL system exhibited a marginal lag compared to the 100 mL system, is a standard hydrodynamic effect related to the stirring efficiency and boundary layer thickness in larger vessels. However, the convergence of both systems at the same thermodynamic endpoint confirms that the BL-PCB-SU mechanism is not volume-sensitive, a high-value characteristic for industrial reactor design.

The consistency of the q_t values across the scale-up series proves that the adsorbent derived from the non-metallic fraction of waste PCBs possesses the structural integrity required for large-scale wastewater remediation. The ability of the material to maintain over 92% removal at half-liter scales without requiring complex modifications suggests that the production process is inherently scalable. This results in an outcome consistent with circular economy principles and with the requirements for deployment in decentralised treatment systems.

CHAPTER 5: SUSTAINABILITY AND INDUSTRIAL RELEVANCE

5.1 Introduction: From Laboratory Discovery to Systemic Value:

The experimental work presented in the preceding chapters demonstrates that the non-metallic residues of printed circuit boards can be transformed into high-performance adsorbents and photocatalytic materials through a hierarchy of processing routes, culminating in the synthesis of ordered mesoporous silica. Evaluated in their broader context, however, they represent something of broader significance a practical demonstration that one of the fastest-growing solid waste streams globally like electronic waste, can be redirected into the solution architecture for another equally pressing global challenge like water pollution by industrial organic contaminants.

This chapter situates the experimental findings within the overlapping frameworks of circular economy theory, life cycle thinking, regulatory compliance, and industrial water treatment practice. The objective is not to claim immediate commercial readiness, but to provide a rigorous and evidence-based assessment of where this work sits on the practical pathway from laboratory concept to deployed technology, and to identify the specific conditions under which its value proposition becomes economically and environmentally promising. Particular emphasis is placed on the mesoporous silica MP-PCB-MS ($m\text{-SiO}_2$), which emerged from the experimental programme as the system with the highest remediation performance and the most promising industrial profile; the MA-CT-PCB and BL-PCB material families are considered where they sharpen the broader argument.

5.2 Circular Economy Positioning: Closing the Loop on Electronic Waste:

The circular economy framework, as articulated in the European Union's Circular Economy Action Plan (2020) and the wider academic literature (Stahel, 2016), proposes a fundamental reorientation of industrial systems away from the linear "take-make-dispose" paradigm toward closed-loop models in which the end of one material's service life becomes the beginning of another's. Within this framework, value retention is hierarchical: the preferred strategies are reuse and remanufacturing, followed by recycling of material streams, with energy recovery as a last resort before disposal (Waste framework Directive, 2008).

Electronic waste occupies an especially complex position within this hierarchy. As documented in Chapter 1, global e-waste generation reached 62 million tonnes in 2022, representing the fastest-growing solid waste stream worldwide, with formal recycling rates stagnating below 25% (Hagelüken, 2006; Baldé et al., 2024). The predominant focus of e-waste recycling, both in industrial practice and in the academic literature has been the recovery of economically valuable metallic fractions: gold, silver, palladium, and copper (Tuncuk et al., 2012) and (Li et al., 2004). The non-metallic residue, which constitutes approximately 30% of a PCB by mass and is composed primarily of glass-fibre-reinforced epoxy resin, is routinely treated as a processing liability rather than a resource stream. It is incinerated, landfilled, or at best downcycled into construction aggregates, losing the structural and chemical complexity that makes it potentially valuable (Hekkert et al., 2010).

The approach demonstrated in this thesis inverts this hierarchy of value for the non-metallic fraction. Rather than accepting the residue as a waste management problem to be minimised, it treats the siliceous glass-fibre matrix as a functional precursor for advanced adsorbent materials. This constitutes what the circular economy literature terms a "cascade use" strategy: the material passes through a primary function (structural support in a circuit board), then through a secondary function (adsorption of industrial dye pollutants from water), with each stage retaining more value than simple incineration or landfill would allow. Crucially, this cascade is enabled not by the introduction of expensive new materials but by the exploitation of properties such as high silica content, residual metal oxide phases, mechanical processability, already inherent in the waste stream (Kresge et al., 1992).

The three treatment routes investigated in this thesis represent three distinct points on the circular economy spectrum. Microwave-assisted chemical treatment (MA-CT-PCB) achieves the highest material purity but requires concentrated acid inputs and generates hazardous leachate, incurring a chemical processing footprint that must be weighed against the performance advantage. Buffered chemical leaching (BL-PCB) occupies a more favourable position, using environmentally benign lactic acid and ammoniacal buffers that generate less hazardous effluent while retaining sufficient surface functionality for effective adsorption. Mechanical processing (MP-PCB) is the most compelling from a circular economy standpoint: it requires no chemical reagents whatsoever, relies entirely on physical size reduction and separation, and as demonstrated in Results and Discussion chapter yields a precursor of sufficient quality to produce mesoporous silica through subsequent sol-gel synthesis (Wan & Zhao, 2007). Furthermore, the m-SiO₂ synthesis led to a waste, MP-PCB-NaOH, which was demonstrated to be capable of adsorbing MB as efficiently as the starting MP-PCB sample, suggesting the possibility of producing to efficient systems for MB removal starting from the

same waste. The MP-PCB route therefore satisfies the circular economy principle of minimum process intensity while maximising functional output.

A critical determinant of a material's sustainability profile in water treatment applications is not its single-use performance but its capacity for repeated regeneration without significant loss of function. An adsorbent that achieves high removal efficiency but must be landfilled after a single use generates a secondary waste problem that partially offsets its remediation benefit. The reusability evaluation of MP-PCB-MS, described in detail previously, demonstrates that the mesoporous silica framework retains its adsorptive function across at least four consecutive adsorption-desorption cycles when regenerated with 0.1 M sodium dodecyl sulphate (SDS) solution, so this constitutes an additional operational strength of the material.

The sol-gel synthesis step that converts MP-PCB-1 into MP-PCB-MS ($m\text{-SiO}_2$) does require chemical inputs sodium hydroxide, CTAB surfactant, and sulphuric acid and an energy-intensive hydrothermal step at 100°C for 48 hours followed by calcination at 550°C. These inputs represent the primary environmental cost of the synthesis route and must be acknowledged in any sustainability assessment. However, they are not specific to this process; they are standard reagents and conditions for mesoporous silica synthesis from any silica source, including high-purity commercial TEOS (Tran et al., 2019). The distinguishing feature of the present work is that the silica precursor is derived from electronic waste at zero raw material cost, replacing a virgin petrochemical feedstock with a recovered waste stream. The environmental and economic implications of this substitution are examined in later sections.

5.3 Life Cycle Considerations and Environmental Footprint:

A rigorous life cycle assessment (LCA) of the MP-PCB-MS synthesis and deployment pathway is beyond the scope of this thesis, as it would require detailed inventory data on the PCB collection logistics, energy consumption at each processing stage, and end-of-life handling of the spent adsorbent, data that are not yet available for the specific process configuration studied here. However, a qualitative life cycle framing is both possible and necessary to situate the work appropriately within the sustainability literature, and several comparative observations can be made with confidence based on the available evidence.

The functional unit for comparison is the removal of one gram of methylene blue from aqueous solution. For commercial activated carbon, the production of this quantity of adsorbent at laboratory characterised performance ($q_{\text{max}} \approx 225\text{--}900$ mg/g depending on source material and activation conditions (Tran et al., 2017) requires the processing of lignocellulosic biomass or coal through

carbonisation and chemical activation, consuming approximately 3–10 MJ/kg of AC produced and generating CO₂, volatile organic compounds, and acidic effluent depending on the activation agent used (Gupta et al., 2012). For MP-PCB-MS, the silica precursor is obtained as a by-product of PCB metal recovery at no additional resource extraction cost: the glass fibre and epoxy resin that would otherwise require disposal energy (typically 12–18 MJ/kg for incineration of fibre-reinforced polymer composites (Job, 2013)) instead become the feedstock for a value-added material. Life cycle assessment of hydrometallurgical Waste from Electrical and Electronic Equipment (WEEE) residue processing indicates that metal-extraction stages remain a major environmental burden, reinforcing the value of downstream residue valorisation strategies (Rocchetti et al., 2013).

The sol–gel synthesis stage nevertheless introduces additional material and energy demands associated with surfactant-assisted hydrothermal processing, including the consumption of chemical reagents, water, and thermal energy during stirring, drying, and heat-treatment steps. A rigorous quantitative life cycle assessment (LCA) of these contributions would require complete process inventory data, including reagent consumption, electricity demand, process yield, and emissions associated with laboratory-scale synthesis operations, which were beyond the scope of the present study. However, despite these additional inputs, the environmental burden of the MP-PCB-MS route is partially offset by the avoidance of virgin silica extraction and by the diversion of non-metallic PCB residues from conventional disposal pathways such as incineration or landfilling. Consequently, the process remains consistent with the core principles of circular resource valorisation and waste-to-material conversion.

The most significant life cycle advantage of the MP-PCB route, however, lies in the avoided burden category. Current PCB non-metallic residue management in Europe predominantly involves co-incineration in cement kilns, construction materials or direct landfilling, which carry associated CO₂ emissions, leachate risks, and loss of material value (Widmer et al., 2005). By diverting this fraction into a functional adsorbent, the present approach simultaneously avoids the incineration burden and replaces a portion of the commercial adsorbent market, a double dividend that is characteristic of high-quality circular economy interventions (Ardente & Mathieux, 2014). This structure is analogous to the avoided burden logic applied to recovered fly ash in cement production, or to recycled polyethylene terephthalate (rPET) in textile manufacture, both of which are now considered best-practice circular economy implementations by the European Environment Agency (2016).

Life cycle assessment of hydrometallurgical WEEE residue processing indicates that metal-extraction stages remain a major environmental burden, reinforcing the value of downstream residue valorisation strategies (Rocchetti et al., 2013). The one life cycle stage that requires critical

transparency is the calcination step, which at 550°C for 480 minutes represents the most energy-intensive single step in the MP-PCB-MS synthesis. In the current laboratory configuration, this step is performed in an electric muffle furnace, the energy source for which depends on the grid mix of the country of use. In a renewable-heavy grid context (such as northern Italy or Norway), the carbon intensity of this step would be substantially lower than in a fossil-fuel-heavy grid. In a scaled industrial context, alternative calcination approaches including microwave-assisted calcination, which has been demonstrated to reduce processing time and energy consumption by 60–80% for mesoporous silica systems (Cai et al., 2010) or direct surfactant extraction with ethanol could replace thermal calcination entirely, reducing the energy footprint of the synthesis while maintaining the mesoporous architecture (Sayari & Hamoudi, 2001).

5.4 Regulatory Alignment and Policy Context:

The operational deployment of any new water treatment material in Europe is conditioned on compliance with a network of regulatory frameworks that govern both the material itself and the treatment process. An assessment of the regulatory landscape suggests that the MP-PCB-MS adsorbent pathway is well-aligned with existing and emerging policy direction, with no fundamental barriers to regulatory approval identified at this stage of development.

The European Union Water Framework Directive (WFD, 2000/60/EC) establishes the requirement for achieving good chemical and ecological status of water bodies through the implementation of effective pollution-control and wastewater-treatment strategies. In parallel, the Best Available Techniques (BAT) conclusions for the textile sector emphasise the reduction of colour, organic contaminants, and recalcitrant dye species in industrial effluents through advanced treatment technologies, including adsorption-based approaches (European Commission, 2016).

Within this regulatory framework, the adsorption behaviour demonstrated by the MP-PCB-MS (m-SiO₂) material highlights its potential relevance for sustainable wastewater remediation applications. In particular, complete removal of methylene blue was achieved for dilute aqueous systems (1×10^{-5} M MB, corresponding to approximately 3.2 mg/L) under ambient operating conditions and near-neutral pH, without the need for additional chemical oxidants, pH adjustment, or pre-treatment steps. Although direct comparison with BAT-associated colour emission limits is not straightforward, since BAT colour values are commonly expressed in Pt/Co colorimetric units rather than as specific dye mass concentrations, the obtained results nevertheless demonstrate the capability of the developed adsorbent to efficiently eliminate dissolved organic dye species from water under environmentally mild conditions.

Furthermore, the adsorption process was achieved using a secondary raw material derived from waste printed circuit boards, thereby integrating wastewater remediation with waste valorisation and circular economy principles. This dual environmental functionality aligns closely with current European sustainability strategies focused on resource efficiency, waste minimisation, and the development of low-impact treatment technologies for industrial water management.

The REACH Regulation (EC No. 1907/2006), which governs the registration, evaluation, authorisation, and restriction of chemical substances in Europe, would apply to MP-PCB-MS (m-SiO₂) as a substance manufactured or imported in quantities exceeding one tonne per year (ECHA, 2022). Key requirements would include characterisation of the substance's physicochemical properties (already partially met by the BET, XRD, surface charge, SEM-EDS, and Raman data reported in Chapter 4), assessment of its ecotoxicological profile, and evaluation of leaching potential under service conditions. The trace metallic content of MP-PCB-MS (m-SiO₂) principally residual copper co-incorporated from the PCB precursor represents the primary REACH concern, as copper is an aquatic eco-toxin subject to priority substance monitoring under the WFD Environmental Quality Standards Directive (2008). However, the surface charge data (−20.50 mV) suggests that these metal phases are deeply embedded within the silica framework rather than surface-exposed, limiting their leaching potential. A dedicated leaching study under simulated service conditions (acidic, neutral, and alkaline pH, contact times representative of multiple adsorption cycles) would be required to quantify this risk before regulatory submission, and constitutes a clearly identified direction for future work.

The WEEE Directive (2012/19/EU), provides legislative framework for e-waste collection and treatment in Europe, establishes that PCB residues from authorised treatment facilities may be transferred to approved downstream processors. The use of these residues as precursors for functional materials rather than incineration or landfill, is consistent with the Directive's stated preference for preparation for reuse and recycling over energy recovery, and is explicitly supported by the EU's Critical Raw Materials Act (2024), which identifies the recovery of strategic materials from e-waste as a policy priority. A commercial operation for MP-PCB-MS pathway could in principle be structured as a downstream treatment activity within the WEEE authorisation framework, receiving pre-processed PCB non-metallic residues from certified dismantlers rather than handling the boards.

5.5 Volumetric Scale-Up and Translational Feasibility:

All adsorption and photocatalytic experiments described in the preceding chapters were conducted at a bench-microvolume scale of 5 mL reaction volume, optimised for mechanistic precision, statistical

reproducibility, and conservation of material during the characterisation phase. The transition from this microvolume configuration to a practical treatment system requires that the adsorption performance demonstrated at 5 mL be validated at volumetrically significant scales, a step that is too often omitted from laboratory-focused adsorption studies, and one that has been specifically addressed in this thesis.

To evaluate the practical robustness of PCB-derived adsorbents under scaled conditions, a buffered-leached PCB composite (designated BL-PCB-SU) was processed through mechanical sieving to a standardised particle size of $\leq 300\ \mu\text{m}$ and tested at two volumetric scales: 100 mL and 500 mL, representing 20-fold and 100-fold increases in reaction volume respectively. BL-PCB-SU was prepared by subjecting a 100.3 g PCB feedstock to the same sequential buffered leaching chemistry lactic acid buffer, ammoniacal buffer with H_2O_2 , and aqueous iodine/iodide solution, as the laboratory-characterised BL-PCB series, followed by post-leaching sieving to $\leq 300\ \mu\text{m}$. It is important to note explicitly that BL-PCB-SU is a heterogeneous leached PCB composite comprising amorphous silica glass fibres, residual epoxy resin domains, and encapsulated metal phases. The synthesis scale-up of the structural mesoporous silica platform (MP-PCB-MS) remains outside the scope of this investigation. In both scale-up trials, the adsorbent mass was scaled proportionally to maintain a constant dosage of $1.2\ \text{mg mL}^{-1}$ (0.12 g at 100 mL; 0.60 g at 500 mL), preserving the adsorbent-to-solution ratio that governs equilibrium performance.

The results demonstrate a notable consistency of adsorption performance across a 100-fold increase in reactor volume. At 100 mL, MB removal reached 38.5% at 60 minutes, 61.3% at 4 hours, 81.1% at 24 hours, and 94.04% at 72 hours ($q_e = 2.51\ \text{mg g}^{-1}$). At 500 mL, the corresponding values were 37.0% at 60 minutes, 53.5% at 4 hours, 78.4% at 24 hours, and 92.52% at 72 hours ($q_e = 2.51\ \text{mg g}^{-1}$). The 72-hour equilibrium adsorption capacities of both scaled systems are numerically identical ($q_e = 2.51\ \text{mg g}^{-1}$), and the 72-hour removal efficiencies of 94.0% and 92.5% for the 100 mL and 500 mL systems respectively are within 1.5 percentage points of each other despite a fivefold difference in reaction volume between the two scaled experiments and a hundredfold difference from the bench reference.

This convergence of equilibrium performance confirms that the adsorption capacity of BL-PCB-SU is governed primarily by the adsorbent-to-solution dosage ratio, as expected for a surface-controlled adsorption process operating below site saturation, and is independent of absolute reactor volume. The adsorption mechanism of BL-PCB-SU is governed by a combination of electrostatic attraction at surface silanolate and carboxylate groups and π - π stacking interactions at residual carbonaceous resin domains, surface sites whose density is set by the adsorbent mass loaded, not by the solution

volume. The scale-independence of the equilibrium capacity is therefore a thermodynamic consequence of this surface-controlled mechanism and is consistent with Langmuir adsorption theory (Ruthven, 1984). These results demonstrate that the equilibrium adsorption behaviour of the BL-PCB-SU system remains effectively independent of reaction volume under the investigated batch conditions, supporting the scalability of the adsorption mechanism beyond the laboratory microvolume regime. The scale-up campaign was conducted on BL-PCB-SU and not on the synthesised $m\text{-SiO}_2$ platform; the direct volumetric validation of MP-PCB-MS adsorption at scale is identified as the most immediate experimental priority and is discussed in detail in Section 6.4.

The kinetic profile at scale was modestly slower than the very rapid adsorption kinetics of the optimised laboratory MP-PCB-MS material: MB removal at 1 minute is 15.0% at 100 mL and 11.7% at 500 mL, compared to the 98–100% one-minute uptake of MP-PCB-MS. This kinetic offset reflects two factors operating in combination. First, BL-PCB-SU is an independent PCB source batch with a different leaching history, milling sequence, and particle size distribution from MP-PCB-1; as established throughout Chapter 4, inter-batch variability in e-waste-derived materials produces measurable differences in adsorption rate at the same nominal particle size. Second, at larger reaction volumes the ratio of adsorbent surface area to bulk solution volume decreases at any fixed impeller speed, increasing boundary layer thickness and extending the time required for mass transfer to the adsorbent surface, a well-understood consequence of volumetric scaling in stirred batch systems (Ruthven, 1984). Critically, this kinetic offset does not affect equilibrium performance: the system reaches the same final removal efficiency regardless of volume, given sufficient contact time. In a continuous-flow or semi-batch industrial configuration, contact time is a design variable controlled by the hydraulic retention time of the treatment unit, and would be set to accommodate the kinetic profile of the scaled material.

The scale-up results demonstrate the practical feasibility of the BL-PCB-SU system under expanded batch conditions: a treatment system processing 500 mL of dye-contaminated water with 0.6 g of BL-PCB-SU achieves 92.5% MB removal within 72 hours at ambient temperature, neutral pH, and without chemical additives. At 24 hours MB removal reaches 78.4%, rising to 87.5% at 48 hours. These removal rates, while lower than the near-instantaneous performance of the optimised MP-PCB-MS material, are consistent with the treatment performance targets for dye removal in semi-batch industrial configurations, where contact times of 24–72 hours are standard for secondary adsorption polishing stages (Ruthven, 1984; McKay et al., 1982).

The 500 mL configuration represents a meaningful intermediate scale between laboratory microvolume experiments and future continuous-flow pilot-scale systems. The 0.6 g of adsorbent

used could reasonably be obtained from a few grams of raw PCB feedstock through the buffered leaching and sieving protocol described in Chapter 3. Extrapolating to a 1-litre batch at a dosage of 1.2 mg mL^{-1} (1.2 g adsorbent), performance is expected to follow the same kinetic and equilibrium profile as the 500 mL system, based on the demonstrated volumetric invariance of the equilibrium capacity.

5.6 Industrial Feasibility and Comparative Economic Context:

The translation of a laboratory adsorbent into an industrial water treatment material requires favourable positioning across three simultaneously evaluated dimensions: technical performance relative to existing solutions, synthesis cost relative to alternatives, and operational compatibility with existing treatment infrastructure. Each of these is assessed below in the context of the experimental data generated in this thesis.

On technical performance, the benchmark against which any new adsorbent must be assessed is activated carbon, which remains the dominant commercial adsorbent for organic dye removal globally, with an installed market estimated at USD 5.8 billion in 2023 and projected to reach USD 8.4 billion by 2028 (Marketsandmarkets research, 2023). Patent literature shows that PCB recycling is a multi-route technological field rather than a single standardised process, and that non-metal fraction exploitation remains an active area of innovation (Rocchetti et al., 2018). As established in Chapter 4, MP-PCB-MS achieves adsorption kinetics that are qualitatively indistinguishable from commercial DARCO activated carbon. Both materials achieve 98–100% removal within one to two minutes, while offering a substantially superior regeneration profile (>99% SDS desorption vs 4.2% for AC). At higher concentrations ($3 \times 10^{-4} \text{ M}$), MP-PCB-MS achieves a maximum adsorption capacity of $q_e = 76.7 \text{ mg g}^{-1}$, which, while lower than the highest literature values for premium-grade activated carbons ($\sim 225\text{--}900 \text{ mg/g}$) (Velarde et al., 2023), is comparable to or exceeds many commercially relevant and more economically accessible adsorbents including zeolites (typically 10–80 mg/g for MB, raw silica materials (5–30 mg/g) (Al-Ghouti & Da'ana, 2020), and several classes of biochar (20–150 mg/g depending on feedstock) (Wang & Wang, 2019). Crucially, the q_{max} of MP-PCB-MS is obtained from a zero-cost waste feedstock rather than from a virgin petroleum-derived or biomass-derived precursor, a unique distinction with significant implications for the cost analysis.

Table 19: Economic comparison between TEOS based commercial Mesoporous Silica, MP-PCB-MS & AC benchmarks. Initial synthesis cost of MP-PCB-MS is higher but ambient-temperature regenerability and zero-cost e-waste feedstock offer significant long-term sustainability and economic advantages. All costs denote bulk industrial scales

Parameter	Commercial Mesoporous Silica (TEOS-based)	MP-PCB-MS	Commercial Activated Carbon
Feedstock precursor	Virgin TEOS alkoxide chemicals	Non-metallic PCB fraction (zero-cost co-product)	Coal or lignocellulosic biomass
Feedstock cost	€ 20–80 kg ⁻¹ (2)	Zero (waste by-product of WEEE chain)	€ 0.15–0.55 kg ⁻¹
Estimated production cost	€ 15–30 kg ⁻¹ (est) ⁽²⁾	€ 8–25 kg ⁻¹ (pilot scale) / € 3.5–5.5 kg ⁻¹ (industrial minimum)	€ 1.30–3.20 kg ⁻¹
Typical market price	€ 45–120 kg ⁻¹ 3	Not commercially available (projected € 15–35 kg ⁻¹)	€ 3–8 kg ⁻¹
Regeneration mechanism	Solvent extraction or thermal calcination	Ambient-temperature SDS washing	Thermal reactivation, 700–900°C
Capacity loss over 4 cycles	Not reported	0.46%	Not recoverable by SDS
Estimated CO ₂ footprint	~25–32 kg CO ₂ -eq kg ⁻¹ (est.) ⁴	~4.5–7.0 kg CO ₂ -eq kg ⁻¹ (est.) ⁵	~10–15 kg CO ₂ -eq kg ⁻¹ (coal-based) ⁶
Optimal operating pH	Variable (3.0–9.0)	7.5 — neutral	Variable (4.0–8.5)
Target pollutant profile	Specialised organics and catalysis	Cationic dyes; reactive textile streams	Broad-spectrum dissolved organics ^g
Circular economy alignment	Linear (virgin resource depletion)	Circular (zero-cost waste feedstock + ambient sorbent)	Open-loop (structural loss during reactivation) ⁷

On synthesis cost, the primary economic driver of the MP-PCB-MS synthesis is the sol-gel reagent set (NaOH, CTAB, H₂SO₄) and the energy cost of the hydrothermal and calcination steps (Diez et al., 2021). These are standard industrial chemicals available at bulk commodity prices; CTAB, the most

³ TEOS industrial bulk pricing estimated from chemical commodity market data; mesoporous silica market value consistent with specialty chemical pricing for MCM-41/SBA-15 type materials (Wan & Zhao, 2007; Beck et al., 1992). No peer-reviewed LCA specifically for TEOS-based mesoporous silica.

⁴ CO₂ footprint for TEOS-based mesoporous silica is a process-based estimate. No peer-reviewed LCA for this material class is available; indicative value.

⁵ Process based estimate: zero burden for waste feedstock + CTAB synthesis (~0.75–1.25 kg CO₂) + NaOH/H₂SO₄ (~0.50–1.00 kg CO₂) + hydrothermal synthesis and calcination energy (~1.5–3.0 kg CO₂), offset by avoided incineration burden of the FRP composite (~12–18 MJ kg⁻¹). This estimate has not been validated by formal life cycle assessment. A dedicated LCA is required.

⁶ coal feedstock processing (~3 kg coal per kg AC × ~2.5 kg CO₂ per kg coal = ~7.5 kg CO₂) plus high-temperature activation energy (~3–6 kWh kg⁻¹ × emission factor). Biomass-based AC yields lower values (~3–7 kg CO₂-eq kg⁻¹). The stated range applies to coal-derived product (Rocchetti et al., 2013; Tran et al., 2017; Ahmaruzzaman, 2010).

⁷ All values and estimates are reported through: (Rocchetti et al., 2013; Tran et al., 2017; Ahmaruzzaman, 2010, Wan & Zhao, 2007; Beck et al., 1992; Diez et al., 2021; Gupta & Suhas, 2009)

expensive input, is commercially available at bulk commodity prices (approximately €3–8/kg) from major chemical suppliers, and the hydrothermal autoclave is a standard chemical engineering unit operation. The silica precursor (MP-PCB residue) is obtained at negative net cost when considered within the WEEE recycling value chain: the metal recovery step that generates the non-metallic residue as a by-product is already economically justified by the precious metal revenues, meaning that the non-metallic fraction is effectively a co-product generated at zero marginal extraction cost.

A preliminary and conservative economic analysis was conducted by benchmarking the process against agricultural silica synthesis literature (Ahmaruzzaman, 2010). While commercial mesoporous silica prices typically range from €45 to €120/kg, the un-optimised synthesis and processing cost of MP-PCB-MS was calculated to fall within €15–35/kg. This preliminary estimate is based on laboratory-scale reagent quantities (NaOH, CTAB, HMTA) at industrial bulk pricing and does not account for process optimisation, energy recovery, or economies of scale; a rigorous techno-economic analysis at pilot scale is required to validate this figure. While this is higher than the €3–8/kg bulk price of granular activated carbon (Gupta & Suhas, 2009), the gap is substantially offset by the zero-cost waste feedstock and superior regeneration efficiency, which minimises replacement frequency.

Operational compatibility was validated by conducting experiments under conditions mirroring secondary textile effluent treatment: neutral pH (7.5) without buffering, ambient temperature, and mineral water solvents (Yaseen & Scholz, 2019). These structures have high selectivity for cationic dyes aligns with the primary waste streams of reactive dye processes (European Commission, 2014). Furthermore, the cationic bridging observed in mixed-dye systems suggests that MP-PCB-MS remains effective in complex, multi-charge wastewater streams, broadening its applicability beyond single-dye scenarios.

5.7 Commercialisation Pathway and Technology Readiness

The positioning of MP-PCB-MS within the Technology Readiness Level (TRL) structure, as defined by the European Commission (2014), is currently at TRL 3–4. Laboratory experiments have established a robust proof-of-concept, while initial volume expansions from 100 mL to 500 mL have confirmed performance consistency across a 100-fold range. Advancing to TRL 5/6 requires pilot-scale demonstrations (1–10 L level) using continuous-flow packed bed columns and authentic textile effluent matrices to test resilience against competing organic compounds and ionic fluctuations.

Regulatory integration remains a critical hurdle; dedicated leaching studies under service conditions are necessary to establish REACH compliance and potential alignment with the German Drinking Water Ordinance or Italian Legislative Decree 31/2001.

From a commercial perspective, the most viable model involves vertical integration within WEEE authorised treatment facilities. By redirecting non-metallic PCB residue, currently a disposal liability into on-site synthesis units, logistics costs are eliminated. Such ventures may qualify for EPR (Extended Producer Responsibility) scheme revenue under the WEEE Directive. The competitive edge of MP-PCB-MS rests not on direct cost competition with bulk activated carbon, but on its alignment with regulatory-driven demand for green chemistry (e.g., EU Green Deal and CSRD) and the superior performance of selective, regenerable adsorbents for high-value effluent streams in the textile, leather, and paper sectors (Paźdźor et al., 2019; EU Directive 2464, 2022).

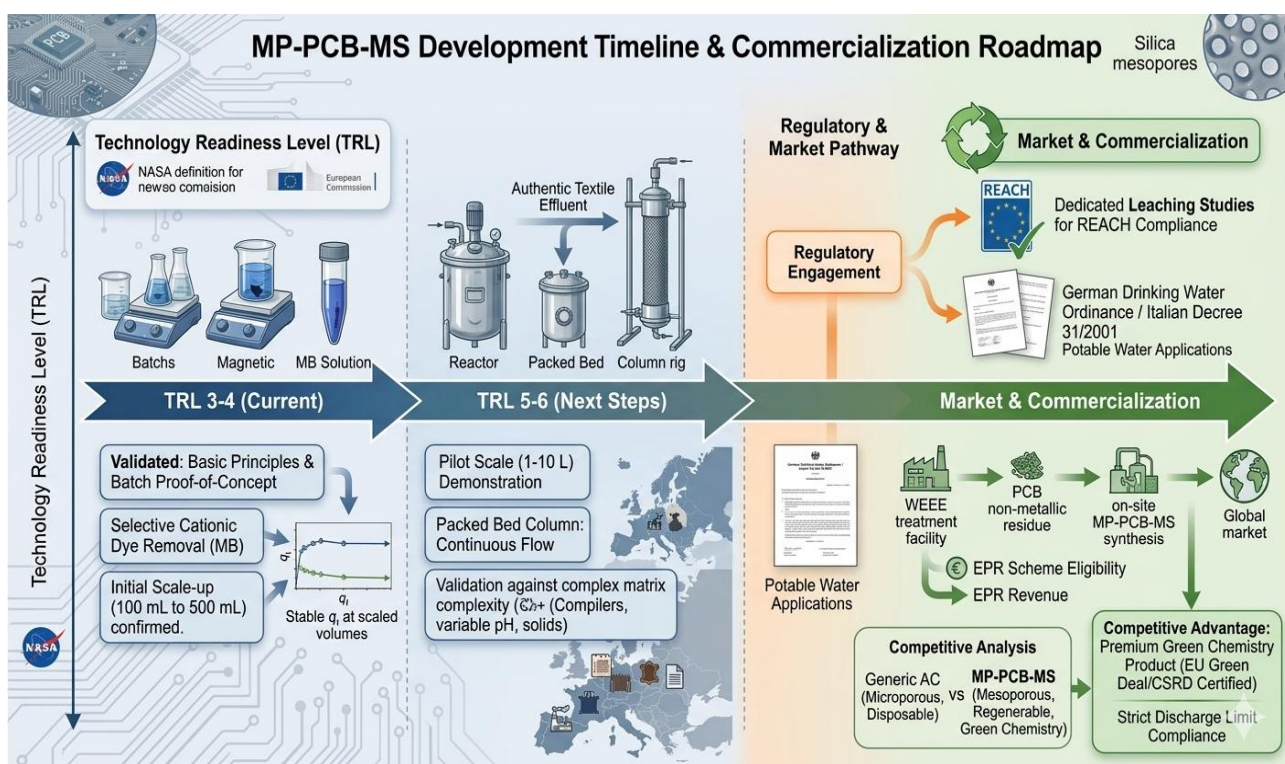


Figure 61: Strategic Development and Commercialization Roadmap for MP-PCB-MS. This integrated infographic maps the current technical maturity of the adsorbent technology against the required pathways for industrial implementation

This analysis has demonstrated that the experimental findings of this thesis are not merely of laboratory scientific interest but carry credible and substantiated relevance to the interconnected challenges of electronic waste management, industrial water pollution, and the transition to a circular economy. The principal conclusions are described in figure 61.

The conversion of PCB non-metallic residues into mesoporous silica adsorbents represents a genuine cascade use strategy that simultaneously addresses two of the most pressing material-cycle challenges of the 21st century: the growing accumulation of electronic waste and the inadequate treatment of organic contaminant-bearing industrial wastewater. By exploiting properties already inherent in the waste stream, silica content, residual photocatalytic metal phases, mechanical processability rather than introducing new materials, the approach minimises the environmental footprint of the remediation solution while maximising material value retention consistent with the principles of the circular economy.

The operational sustainability of the technology is underwritten by the demonstrated SDS regenerability of MP-PCB-MS ($m\text{-SiO}_2$) across four use cycles without loss of kinetic performance or mesopore integrity, a regeneration efficiency that compares favourably with the principal commercial alternative. The scale-up data at 100 mL and 500 mL suggests that adsorption capacity is volumetrically invariant across a 100-fold volume range, establishing the mechanistic basis for further scale-up with confidence. The regulatory landscape, particularly under the WEEE Directive, REACH, and the WFD, is well-aligned with the proposed technology pathway, with no fundamental barriers identified at this stage of development. A patent landscape analysis by Rocchetti et al. (2018) confirms that while mechanical treatment and metal recovery from PCBs are mature, well-patented domains, the exploitation of non-metallic PCB fractions for functional applications including water treatment remains largely absent from the commercial patent record. This gap represents an identifiable space for intellectual property development and commercialisation, reinforcing novelty and practical relevance of present work.

The technology is assessed at TRL 3–4, with a clearly defined and scientifically grounded pathway to TRL 5–6 through pilot-scale demonstration in continuous-flow configuration using real wastewater matrices. The combination of zero-cost feedstock, ambient-condition operation, surfactant regeneration, and solar-assisted photocatalytic mineralisation capacity positions MP-PCB-MS as a distinct contribution to the adsorbent materials landscape, whose most compelling value proposition is not its performance in isolation but the systemic efficiency it enables by converting a waste problem into a remediation solution.

While the present results demonstrate strong proof-of-concept potential for PCB-derived adsorbent materials, full industrial implementation would require integrated pilot-scale validation, comprehensive techno-economic assessment, long-term leaching analysis, and complete life cycle assessment under realistic wastewater operating conditions.

Table 20: Path to market for MP-PCB-MS technology. The strategic transition from laboratory validation to industrial implementation requires pilot-scale testing and rigorous regulatory alignment to capitalise on emerging "green chemistry" market premiums.

Milestone	Current Status	Required Action	Regulatory/Market Driver
Maturity (TRL)	3–4	Pilot scale (1–10 L) in continuous flow	TRL 5–6 Advancement
Validation	Model Solutions	Real textile wastewater matrices	Performance reliability
Safety	Laboratory Bench	Service-condition leaching studies	REACH Compliance
Business Model	Research-led	Vertical integration with WEEE facilities	Circular Economy / EPR
Competitive Edge	Selective/Regenerable	Market as a "Certified Circular Product"	EU Green Deal / CSRD

CHAPTER 6: CONCLUSIONS AND FUTURE PERSPECTIVES

6.1 Research Context:

This doctoral research was conducted within the Sustainable Materials Recycling Technology for Printed Circuit Boards (SMaRT-PCBs) project, a multi-institutional initiative developed through a partnership between the University of Cagliari, the University of Brescia, and industrial consortium members including Gold Fixing Srl, Vesti Solidale, and the Lombardy Energy Cleantech Cluster. The project's core ambition was to develop an integrated, low-environmental-impact technology for the sustainable valorisation of both metallic and non-metallic fractions from end-of-life PCBs, moving beyond the selective recovery of precious metals to engage with the full material composition of the waste stream.

Partner institutions directed their efforts toward innovative metal recovery through hydrometallurgical and electrochemical routes. The contribution described in this thesis addressed the complementary and historically neglected challenge: the non-metallic residue, predominantly glass-fibre-reinforced epoxy resin that constitutes approximately 30% of a PCB by mass and is routinely consigned to incineration or landfill once metals have been extracted. The objective was not simply to find an alternative use for this fraction, but to demonstrate that it could be transformed into a high-performance functional material capable of addressing an entirely separate and urgent environmental problem: the contamination of industrial wastewater by organic dyes.

Three processing routes were investigated, each representing a distinct position on the spectrum between chemical intensity and process sustainability: microwave-assisted chemical treatment (MA-CT-PCB), buffered chemical leaching (BL-PCB), and reagent-free mechanical processing (MP-PCB). A central finding of this thesis is that these routes do not simply rank by adsorption performance, they define fundamentally different relationships between processing chemistry, material character, and functional outcome, and together they establish a systematic profile of the adsorption potential of the PCB non-metallic fraction.

MA-CT-PCB demonstrated that strong acid digestion produces a chemically clean silica-rich residue with meaningful adsorption potential, but one whose performance is entirely contingent on post-treatment particle size reduction and whose preparation generates concentrated acid waste that partially undermines its sustainability rationale. Although its adsorption performance was limited to cationic dye, it was able to match the activity of commercial activated carbons during MB removal, significantly outperforming similar powders obtained from the grinding of glass slides or un-treated PCB samples.

BL-PCB materials, prepared through sequential environmentally benign leaching with organic acid and ammoniacal buffers, showed that milder processing routes preserve sufficient surface functionality for effective adsorption of MB while generating substantially less hazardous effluent, a more sustainable preparation but it leads to a lowering of the adsorption performances (98% for MA-CT-PCB and 52% for BL-PCB-1). This limit, as well as the high inter-sample variability across the BL-PCB series reflecting the compositional heterogeneity of the e-waste source itself, pushed us to test the surface modification functionalisation with MW- treated alginate or chitosan solution or polydopamine, in order to increase the affinity towards organic molecules or induce a photodegradation activity under solar illumination.

MP-PCB, processed without any chemical reagents through controlled shredding, sieving and electrostatic separation, yielded a material that was not only capable of adsorbing MB with an efficiency higher than BL-PCB samples, but, more importantly, it resulted to be the suitable precursor for the synthesis of mesoporous silica. The progression from aggressive to the mild, to reagent-free mirrors the hierarchy that responsible materials engineering requires, and the conclusion it supports is important: chemical complexity is not a prerequisite for functional performance when the subsequent processing strategy is appropriately designed.

6.2 The Mesoporous Silica Platform:

The conversion of the mechanically processed PCB residue into mesoporous silica through CTAB-templated sol-gel synthesis is the principal contribution of this thesis and its most significant contribution to the field of waste-derived functional materials (Beck et al., 1992). The synthesis, dissolving the PCB silica fraction in sodium hydroxide to form a sodium silicate precursor, then condensing it hydrothermally around cetyltrimethylammonium bromide micelles before calcination to remove the surfactant template, is well-established for purified silica sources (Kresge et al., 1992),

but its application to heterogeneous e-waste precursors had not previously been demonstrated with structural and functional characterisation of this depth.

The outcome was a material with a specific surface area of $331 \text{ m}^2 \text{ g}^{-1}$ and a well-developed mesoporous architecture confirmed by Type IV nitrogen adsorption isotherm, H3-type hysteresis, and low-angle XRD periodic ordering. The observed increase in accessible surface relative to the raw precursor confirmed that the sol-gel process successfully re-organised a compositionally heterogeneous industrial waste into a chemically uniform and reproducible adsorbent platform (Zhuravlev, 2000).

The practical consequence of this targeted engineering strategy was a marked improvement in adsorption kinetics. In contrast to the raw precursor, which approaches a restricted equilibrium plateau within the first few hours of contact while retaining a significant residual dye fraction in solution the optimised MP-PCB-MS matrix achieves near-instantaneous methylene blue removal of 98–100% within a narrow 1–2 minutes window. This near-instantaneous adsorption profile is functionally equivalent to the performance benchmarks of commercial premium activated carbons evaluated under identical operating parameters (Tran et al., 2017).

When benchmarked against natural silica sand, which achieved a modest 57.8% removal only after a prolonged 24-hour equilibration period, the performance improvement is substantial and clearly demonstrated. The notable kinetic acceleration and saturation capacity of the MP-PCB-MS sample are not merely passive consequences of silica phases being present in the electronic waste residue. Instead, they are directly driven by the mechanically amplified external surface area and the optimised pore architecture generated during processing. This spatial configuration renders every native silanolate ($\text{Si}-\text{O}^-$) binding site immediately accessible to the incoming dye molecules, avoiding the intraparticle diffusion limitations that restrict adsorption in raw or non-templated materials.

Consequently, this system does not simply recover secondary silica from an electronic waste stream; it transforms it into a high-performance adsorbent mechanism that unmodified natural silica cannot match.

The synthesis does not introduce new surface chemistry: the silanolate groups responsible for cationic dye adsorption were present in the raw PCB material throughout, constrained within a dense and poorly accessible glass-fibre matrix. The sol-gel process reorganises the same silicon and oxygen atoms into an architecture that liberates that latent chemistry. It is a structural transformation, not a

chemical one, and it is this distinction that makes the approach both scientifically coherent and practically promising.

The parametric investigations conducted across the full operational range of MP-PCB-MS established both the breadth of the material's function and the mechanistic consistency that underlies it. Adsorption capacity scales predictably with dye concentration, following Langmuir monolayer behaviour, confirming electrostatic, site-specific uptake at silanolate groups (Zhuravlev, 2000) with a maximum capacity of 76.7 mg g^{-1} , a value that compares favourably with zeolites, raw silica materials, and many biochar-based adsorbents reported in the literature (Tran et al., 2017).

The dye selectivity experiments were among the most instructive in the programme. The complete electrostatic exclusion of anionic methyl orange (<3% removal) alongside the efficient capture of all cationic species tested, crystal violet at 100%, rhodamine 6G at 73%, and methylene blue at 100% confirmed that charge-specific selectivity is a robust, reproducible, and geometry-sensitive property of the mesoporous silica surface. The reduced uptake of rhodamine 6G, attributable to its bulkier xanthene ring system experiencing steric resistance in the 3.5–5 nm mesopore channels, is direct structural evidence that the pore geometry actively participates in selectivity, a feature that would be absent from a non-templated or macro-porous material.

The binary methylene blue and methyl orange system produced the most mechanistically novel observation of the parametric programme. In equimolar mixed solutions, MO completely excluded in single-component systems, underwent partial co-adsorption through an ion-pair co-adsorption mechanism: adsorbed MB^+ cations at the silanolate surface neutralise the local negative charge and create electrostatic anchoring points that enable associated MO^- anions to be co-adsorbed through π – π stacking and localised charge-patch interactions. This observation has practical significance for the treatment of real mixed-charge effluents, where exclusive cationic selectivity would otherwise constrain applicability, and it represents a mechanistically novel contribution to the adsorption literature on charged surfaces.

The reusability study produced the most industrially consequential comparative finding of the thesis. MP-PCB-MS (m-SiO_2) maintains an essentially constant equilibrium adsorption capacity across four consecutive SDS-regeneration cycles, with a total variation of just 0.46%, a degree of stability that reflects the chemical inertness of the silica framework toward ambient-temperature surfactant washing and the reversible, non-destructive character of the electrostatic adsorption mechanism. The contrast with commercial activated carbon is mechanistically fundamental rather than merely

quantitative. Activated carbon achieves nominally equivalent single-use adsorption performance but yields only 4.2% SDS recovery after 48 hours of continuous contact, because its micropores are geometrically narrower than the SDS micelle and physically exclude the regenerant (Tran et al., 2017). The ordered mesopores of MP-PCB-MS, sized by the CTAB micellar template during synthesis, are dimensionally commensurate with the SDS micelle, making the pore and the regenerant structurally compatible (Kresge et al., 1992). This is a designed consequence of templated synthesis, and it is the single most important functional advantage of this material over activated carbon in a practical treatment context. Industrial regeneration of activated carbon requires thermal treatment at 700–900°C with associated energy consumption and progressive structural degradation (Tran et al., 2017); regeneration of MP-PCB-MS requires dilute aqueous surfactant at ambient temperature. For a material derived at zero feedstock cost from electronic waste, this represents an important operational and environmental advantage

Finally, we performed a scale-up study on BL-PCB-SU sample confirmed that equilibrium adsorption capacity is volumetrically invariant across a 100-fold increase in reactor volume, from the bench-scale 5 mL system to 100 mL and 500 mL, with less than 1.5 percentage points difference in 72-hour removal efficiency between the two scaled systems. This invariance is the expected behaviour of a thermodynamically controlled, surface-limited Langmuir process, but its demonstration for an e-waste-derived material, characterised by inherent batch variability and structural heterogeneity is an empirically significant validation. It establishes that the adsorption mechanism of PCB-derived waste is governed entirely by the surface properties and the adsorbent-to-solution dosage ratio, not by any artefact of small-volume experimental conditions, and it provides the mechanistic foundation on which further scale-up can be planned with confidence.

6.3 Limitations:

These conclusions must be bounded by honest acknowledgement of what was not demonstrated. All experiments were conducted in model dye solutions prepared in mineral water at controlled conditions. The performance of these materials in the compositionally complex environment of a real industrial effluent, containing competing organics, ionic surfactants, variable pH, and suspended solids simultaneously has not been established, and extrapolation from model to real systems requires experimental validation rather than assumption.

The reusability dataset spans four cycles, which establishes proof-of-concept regenerability but cannot predict behaviour over the operational lifetimes of 50–100 cycles or more that an industrial

adsorbent must sustain. The trace metal phases that confer photocatalytic activity, residual copper, iron, and associated oxide phases retained from the PCB matrix may leach into treated water under service conditions. A dedicated leaching study under simulated service conditions is the single most important safety and regulatory prerequisite before any water treatment deployment, and it is the primary knowledge gap this thesis leaves open. The life cycle assessment presented in this thesis, while evidence-based and directionally sound, remains qualitative; quantitative LCA with full inventory data is required to substantiate the sustainability argument numerically.

6.4 Future Perspectives:

The experimental programme presented in this thesis establishes the scientific foundation for a practical pathway whose next stages can now be defined with precision. The directions outlined below are not generic research aspirations but specific experimental campaigns, each ordered by its capacity to convert the present TRL 3–4 demonstration into an industrially deployable technology.

The most immediate experimental priority is the direct volumetric scale-up of MP-PCB-MS itself. The present thesis demonstrated, on BL-PCB-SU (a buffered-leached PCB composite), that equilibrium adsorption capacity remains consistent across a 100-fold volume increase (5 mL to 500 mL), and this finding provides a strong mechanistic precedent: if a heterogeneous, structurally complex leached composite maintains its equilibrium capacity across a 100-fold volume range, a structurally uniform and well-characterised mesoporous silica system governed predominantly by surface-controlled adsorption mechanisms may reasonably be expected to exhibit similar behaviour. This expectation cannot substitute for direct empirical validation, however, and such validation was not performed within this thesis. A dedicated scale-up campaign should be conducted on MP-PCB-MS at constant adsorbent-to-solution dosage (1.2 mg mL^{-1}) across 100 mL, 500 mL, and 1 L volumes under continuous-flow conditions. The campaign should address three specific questions sequentially:

1. whether the sol-gel synthesis is linearly scalable from the current gram-scale batch to 50–100 g while maintaining the ordered mesoporous architecture suggested by low-angle XRD;
2. whether the equilibrium Langmuir capacity ($q_{max} = 76.7 \text{ mg g}^{-1}$; $q_e = 2.6 \text{ mg g}^{-1}$ at $1 \times 10^{-5} \text{ M}$) remains invariant at constant dosage across the volume range; and
3. whether the near-instantaneous kinetics observed at 5 mL are preserved at scale or attenuated by increased boundary layer thickness, and if attenuated, whether this is recoverable through increased stirring speed or transition to a continuous-flow packed-bed configuration.

The second priority is the pilot-scale validation of MP-PCB-MS in a continuous-flow packed-bed configuration at the 1–10 L scale using authentic textile effluent. This step would advance the technology to the readiness level at which regulatory pre-engagement under REACH and the EU Water Framework Directive becomes meaningful, and would expose the material to the matrix complexity; surfactants, salts, residual auxiliary chemicals, and competing organic species that model solutions cannot replicate. The leaching study must be conducted in parallel: its outcome either confirms regulatory compatibility or defines the specific passivation treatment steps required prior to deployment.

A particularly promising direction enabled by the dual functionality of the PCB-derived materials is the demonstration of a fully integrated adsorption–regeneration–photodegradation closed-loop process. In a continuous-flow packed-bed configuration, MP-PCB-MS would be contacted with the dye-laden effluent in a fixed column, with periodic in-situ regeneration by an SDS surfactant wash; the SDS regenerant stream, now containing the desorbed and concentrated dye, would in turn be subjected to solar-assisted photocatalytic dye degradation using a PCB-derived photocatalyst potentially the unmodified BL-PCB or MP-PCB material shown in Chapter 4 to possess intrinsic photocatalytic activity. The end-state of such an integrated configuration would be complete dye destruction with no secondary contaminated waste stream, aligning the operational outcome with the zero-waste objective of the SMaRT-PCBs project mechanism. This integrated scheme was not experimentally validated within the present thesis, and several open questions must be addressed before its deployment: the photocatalytic activity of MP-PCB-MS in the presence of micellar SDS, the kinetic compatibility of the adsorption and photodegradation steps, and the long-term stability of the photocatalyst in the regenerant stream. These constitute the principal experimental targets of the next phase of work.

Beyond these system-level directions, three further mechanistic and operational investigations remain. Extended cycle validation, assessing MP-PCB-MS ($m\text{-SiO}_2$) performance across 20–50 SDS-regeneration cycles with periodic structural characterisation, is required to convert the current proof-of-concept into an industrially credible operational lifespan. The photocatalytic mechanism warrants deeper investigation through phase-specific in-situ spectroscopic studies, which would allow quantitative attribution of the photocatalytic activity to specific elemental phases copper oxide, iron oxide, graphitic carbon and enable deliberate optimisation of the sol-gel synthesis to retain or concentrate those phases. Thermodynamic characterisation of the adsorption process determination of ΔG° , ΔH° , and ΔS° from temperature-dependent isotherms acquired in a concentration regime that suppresses the monomer–dimer speciation effect identified in Chapter 4 would provide the

quantitative thermodynamic structure that the qualitative endothermic behaviour already demonstrated in this thesis.

Looking further outward, the methodology of CTAB-templated sol-gel synthesis from e-waste silica precursors should be extended to other silica-containing waste streams: LCD screen glass, photovoltaic (PV) panel encapsulants, and glass substrates from obsolete electronics. Extending the approach to these feedstocks would test the generality of the methodology, identify the e-waste fractions that yield the highest structural quality, and substantially amplify the impact of the work as the volume and compositional diversity of electronic waste continues to grow. In parallel, and within the continuing structure of the SMaRT-PCBs project, the developed materials should be tested against pollutant classes beyond cationic dyes pharmaceutical compounds, pesticides, and endocrine disruptors to define the operational envelope of MP-PCB-MS as a broad-spectrum waste-derived adsorbent.

Taken together, these directions outline a coherent practical programme that would advance the present TRL 3–4 demonstration toward a meaningful TRL 5–6 pilot demonstration within a two-to-three-year experimental horizon, and would establish electronic waste valorisation through structurally engineered adsorbents as a viable contribution to the broader portfolio of circular-economy water-treatment technologies.

APPENDIX A:

List of Abbreviations:

Abbreviation	Full Form
AC	activated carbon
AOP	advanced oxidation process
ATC-400CE	automatic temperature controller (model designation)
BAT	Best Available Techniques
BET	Brunauer–Emmett–Teller (surface area analysis)
BL-PCB	Buffered Chemically Leached Printed Circuit Board residue
BL-PCB-SU	Buffered Chemically Leached PCB Scale-Up
BSE	backscattered electron (SEM detector mode)
CAPEX	capital expenditure
CFL	compact fluorescent lamp
CE	circular economy
COD	chemical oxygen demand
CRM	critical raw material
CRT	cathode ray tube
c-Si	crystalline silicon
CSRD	Corporate Sustainability Reporting Directive
CTAB	cetyltrimethylammonium bromide

C-NPs	carbon nanoparticles
CV	crystal violet
DA	dopamine hydrochloride
DE	diatomaceous earth
DGEBA	diglycidyl ether of bisphenol A (epoxy resin monomer)
DLS	dynamic light scattering
EPR	Extended Producer Responsibility
EU	European Union
GO	graphene oxide
HMTA	hexamethylenetetramine
IPD	intraparticle diffusion
IR	infrared spectroscopy
KL	Langmuir adsorption constant ($L\text{ mg}^{-1}$)
LCA	life cycle assessment
LE2C	Lombardy Energy Cleantech Cluster
MA-CT-PCB	Microwave-Assisted Chemically Treated Printed Circuit Board
MB	methylene blue
MO	methyl orange
MOF	Metal organic framework
MP-PCB	Mechanically Processed Printed Circuit Board residue

MP-PCB-MS / m-SiO₂	mesoporous silica synthesised from mechanically processed PCB precursor
NIR	near-infrared spectroscopy
NMR	nuclear magnetic resonance spectroscopy
OPEX	operating expenditure
PCB	printed circuit board
PDA	polydopamine
PEDOT	poly(3,4-ethylenedioxythiophene)
PET	polyethylene terephthalate
PFO	pseudo-first-order (kinetic model)
PLS	pregnant leach solution
POP	persistent organic pollutant
PSO	pseudo-second-order (kinetic model)
PTFE	polytetrafluoroethylene
PV	photovoltaic
PVDF	polyvinylidene fluoride
q_e	equilibrium adsorption (mg g ⁻¹)
q_{max}	maximum Langmuir monolayer adsorption capacity (mg g ⁻¹)
q_t	adsorption capacity at time t (mg g ⁻¹)
R6G	rhodamine 6G
RAM	random-access memory

REACH	Registration, Evaluation, Authorisation, and Restriction of Chemicals (EU Regulation)
RHA	rice husk ash
RL	dimensionless separation factor (Langmuir isotherm)
SE	secondary electron (SEM detector mode)
SDS	sodium dodecyl sulphate
SEM	scanning electron microscopy
SEM-EDS	scanning electron microscopy with energy-dispersive X-ray spectroscopy
SMaRT-PCBs	Sustainable Materials Recycling Technology for Printed Circuit Boards (project)
TEM	transmission electron microscopy
TEOS	tetraethyl orthosilicate
TRL	Technology Readiness Level
UV-Vis	ultraviolet-visible spectroscopy
WEEE	Waste Electrical and Electronic Equipment
WFD	Water Framework Directive (EU Directive 2000/60/EC)
WHO	World Health Organization
XRD	X-ray diffraction
λ_{max}	maximum absorption wavelength

APPENDIX B:

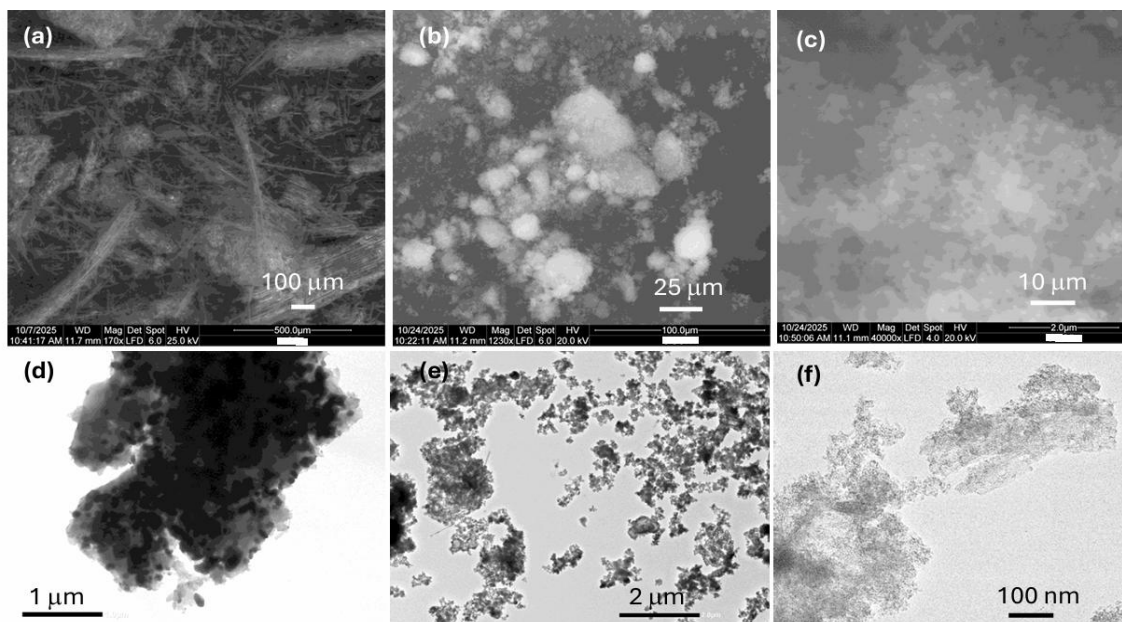


Figure . Scanning electron microscopy (top) and Transmission electron microscopy (bottom) images of MP-PCB(a, d) and m-SiO₂ MP-PCB- (b, c, e, f)

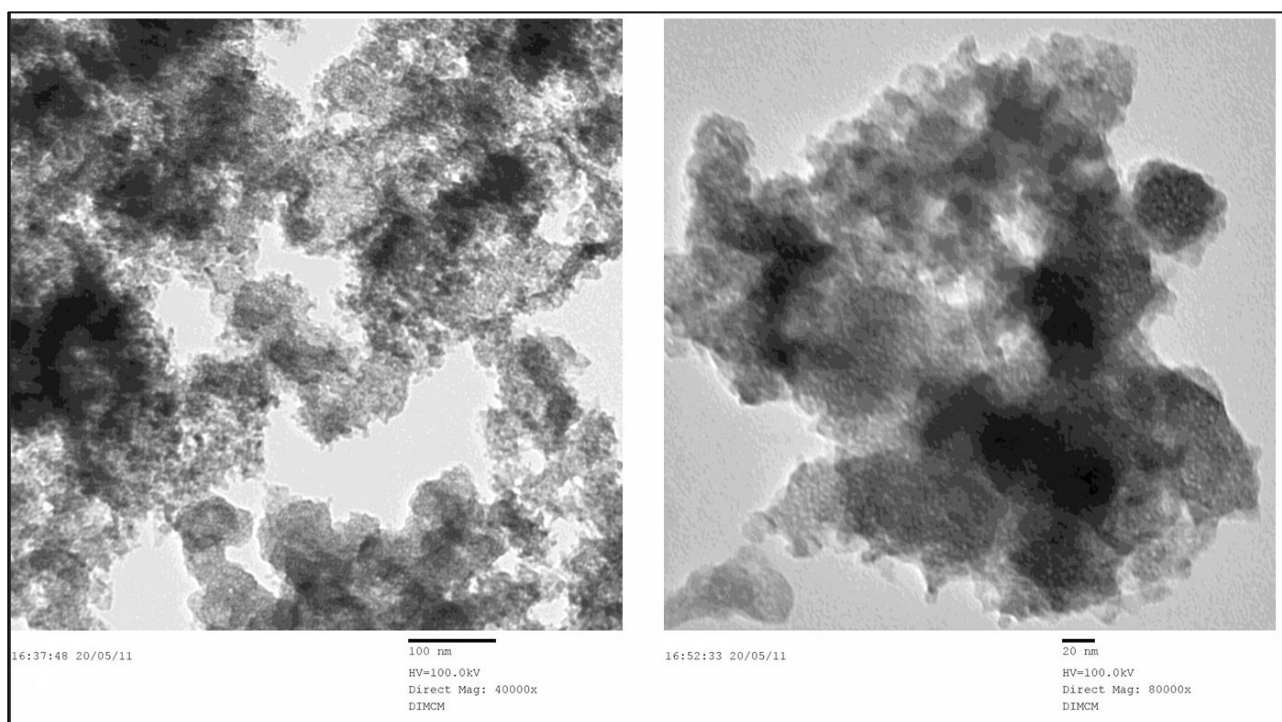


Table 21: Elemental composition (in atom percentage) as obtained by SEM -EDS analysis. Carbon was not accounted for in data analysis. The MP-PCB-1 data refer to the whole scanned area; the $m - SiO_2$ data were calculated as the average values among the analysis of five scanned areas

Element	MP-PCB Atom %	$m - SiO_2$ Atom %
O	63.7	74.67
Si	21.68	18.25
Ca	5.65	
Al	4.76	2.31
Cu	0.92	1.88
Br	1.69	
Fe	0.44	
S	0.23	0.2
Mo		0.03
Mg	0.21	
P	0.33	
Ba	0.33	
Cl	0.07	
Na		2.65

Glossary:

AC: Activated Carbon. A highly porous carbonaceous material widely used as a commercial reference adsorbent in industrial wastewater treatment due to its extensive internal surface area.

at%: Atomic Percentage. The relative fraction of a specific atom type within a multi-element matrix, calculated as a percentage of the total number of atoms present.

BET: Brunauer-Emmett-Teller. A theoretical mathematical model describing the multi-layer physical adsorption of inert gas molecules (typically nitrogen) onto a solid material surface, used to calculate specific surface area (expressed in $m^2 g^{-1}$).

BL-PCB: Buffered Chemical Leaching of Printed Circuit Boards. An environmental processing route utilizing chemical extraction systems under stabilised pH buffers to isolate and treat target structural fractions of electronic waste.

CeSAR: Centro Servizi Ricerca d'Ateneo. The centralised core scientific research instrumentation facility at the University of Cagliari, housing advanced TEM, SEM, and XRD analytical platforms.

CUP: Codice Unico di Progetto. The unique alphanumeric project identifier code assigned to public research grants and infrastructure investments by the Italian government.

EDX / EDS: Energy-Dispersive X-ray Spectroscopy. An analytical microanalysis technique used in conjunction with electron microscopy, where characteristic X-rays emitted from a sample under electron bombardment are measured to identify and quantify elemental composition.

ESEM: Environmental Scanning Electron Microscopy. An advanced variation of scanning electron microscopy that permits the structural imaging of specimens under controlled gaseous atmospheres and pressures.

E-waste / WEEE: Waste Electrical and Electronic Equipment. A rapidly growing global post-consumer waste stream comprising discarded electrical devices, circuitry, and complex multi-material printed board assemblies.

HEC: Higher Education Commission of Pakistan. The primary national statutory institution responsible for funding, regulating, and overseeing higher education development and international scholarship operations in Pakistan.

MA-CT-PCB: Microwave-Assisted Chemical Treatment of Printed Circuit Boards. An accelerated multi-phase digestion and processing technique using targeted microwave irradiation alongside chemical agents to process electronic waste substrates.

MASE: Ministero dell'Ambiente e della Sicurezza Energetica. The Italian Ministry of Environment and Energy Security, responsible for funding national circular economy projects and waste electronics valorisation calls.

MB: Methylene Blue. A heterocyclic aromatic compound widely utilised as a standard model cationic dye analyte in liquid-phase adsorption kinetics and capacity benchmarking experiments.

MP-PCB: Mechanically Processed Printed Circuit Boards. A clean, reagent-free processing sequence relying exclusively on physical shredding, sizing screens, and density milling to isolate non-metallic vitreous-plastic fractions from raw e-waste.

MP-PCB-MS / m-SiO₂: Mechanically Processed Printed Circuit Board-Derived Mesoporous Silica. The primary synthetic material developed in this thesis, featuring an ordered porous silicate network with engineered channels, exhibiting a surface area of approximately 331 m² g⁻¹.

PCB / WPCB: Waste Printed Circuit Board. The structural, multi-layered foundation of modern electronic architecture, containing glass-fibre-reinforced epoxy polymers intertwined with conductive precious and base metallic tracks.

RAM: Random Access Memory. A specific sub-classification of computerised circuit boards characterised by highly uniform layouts, evaluated within mechanical processing logs for physical recovery assessments.

RPM: Revolutions Per Minute. A standardised engineering unit describing the rotational velocity of mechanical components, specifically applied to describe the kinetic processing intensity of industrial milling rotors.

SDS: Sodium Dodecyl Sulphate. An anionic surfactant compound utilised as an ambient elution wash agent to remove adsorbed molecules from internal mesopores during circular regeneration evaluations.

SEM: Scanning Electron Microscopy. A high-resolution imaging method that builds detailed surface topology maps of a solid sample by scanning it with a focused high-energy electron beam.

SMaRT-PCBs: Sustainable Materials Recycling Technology for Printed Circuit Boards. The collaborative industrial-academic research framework dedicated to establishing closed-loop recovery methodologies for electronic components.

TEM: Transmission Electron Microscopy. An analytical imaging technique where an electron beam is transmitted through an ultra-thin sample slice to map its crystalline morphology and internal structural characteristics.

TEOS: Tetraethyl Orthosilicate. A traditional, highly purified liquid alkoxide chemical compound commonly used as the reference synthetic precursor for commercial mesoporous silica production.

UNIBS: Università degli Studi di Brescia. The host academic institution providing the primary doctoral research framework within the Department of Information Engineering.

wt%: Weight Percentage. The relative mass fraction of a specific component or chemical element expressed as a percentage of the total mass of the compiled material matrix.

XRD: X-ray Diffraction. A non-destructive analytical method used to identify the structural characteristics, phase purity, and crystal organization of long-range atomic structures.

2 θ (Two-Theta): The standard angular expression denoting the diffraction angle measured between the direct un-scattered X-ray beam path and the trajectory of the deflected diffracted signal.

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