



# Recycling lithium-ion battery graphite: Synthesis of adsorbent materials for highly efficient removal of dye and metal ions from wastewater

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## ABSTRACT

The fate of residual graphite derived from hydrometallurgical treatment of spent Lithium-ion batteries remains uncertain. This study dwells on the aim of identifying the potentialities of recycling residual graphite for wastewater treatment. Graphite was recovered hydrometallurgically, and new adsorption materials: graphite oxide (GO) and graphene oxide (GrO) were synthesized from the residual graphite using the chemical oxidation method. Synthesized materials showed higher interlayer spacings (GO = 0.81 nm, GrO = 0.78 nm) than the commercially available similar materials. Adsorption studies revealed higher adsorption capacities for both dye (>550 mg/g in all cases) and metal ions (highest ~93 mg/g for Ni<sup>2+</sup> and lowest ~68 mg/g for Zn<sup>2+</sup>). GrO showed superior results than GO due to its high surface area and porosity despite GO having more functional groups. Moreover, produced materials showed about 97 % removal of dye and about 94 % removal of contaminated metals which are higher performance than existing commercial or similar materials. These findings highlight the promising recycling capabilities of waste graphite and suggest its potential as a substitute for natural graphite.

## 1. Introduction

Since the first application in portable devices in early 90's, the demand of lithium-ion batteries (LIBs) grew rapidly. LIBs are now commonly used in various devices like electric vehicles, light machinery, mobile electronic devices, medical devices, recreational devices, due to their cycling efficacy, energy density and optimal capability. LIBs world market value was USD 29.86 billion in 2017 and is predicted to reach USD 139.36 billion by 2029 [1,2]. However, the increasing demand for LIBs also brings challenges, particularly in managing spent batteries. Disposing of spent LIBs irresponsibly could harm the environment and human health as they contain toxic organic solvents, metals, and flammable plastics. Moreover, these batteries are composed of critical raw materials that have risk of supply interruption in the short and medium-term. Therefore, it is crucial to recycle spent LIBs to achieve the circular economy [3].

Recycling of LIBs is currently an attractive topic in industrial environments, national research institutes and among academic professionals. The elements obtained from recycled LIBs range from poor to

high quality materials based on the extracting methods. There are three categories of recycling processes based on the final recovered materials: pyrometallurgical, hydrometallurgical, and direct physical recycling. Direct recycling, recover materials mainly through physical methods, as an example; Shi et al. developed a non-invasive method to reconstruct LiCoO<sub>2</sub> using combination of brief heat treatments [4]. Though the authors reported promising results with recovery of graphite, in overall direct recycling was not yet succeeded in restoring the full potential of the cathode material [5]. Pyrometallurgical process involves smelting battery components at temperatures above 1000 °C to obtain alloys such as Co, Ni, and Cu. Nevertheless, materials like graphite and organic electrolytes will be burnt in this process limiting their recovery, while Li is present in slag phase. Lee and the collaborators also identified a joint process (hydrometallurgy and calcination) to recycle LiCoO<sub>2</sub> type batteries followed by shredding and separation procedures. The method produced LiCoO<sub>2</sub> powder from the used cathode materials that can be used as a new cathode. Though the produced cathode materials show better performance in charge and discharge cycles, materials including graphite and electrolytes were lost during the smelting steps and was not

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recovered [6].

Hydrometallurgical methods involve chemical processes in aqueous media that may include extraction through solvents, purification/precipitation steps, redox reactions, or reaction with acid-alkali solutions. Compared to pyrometallurgy, hydrometallurgy is a highly effective method that can recover nearly all materials present in LIBs, including cathodes, anodes, separators, and electrolytes. Also, Lithium may recover as a high-pure product. Most hydrometallurgical-based recycling methods follow a similar process with slight adjustments, such as using different synthesizing methods, reactants, and recycling channels [7–10].

Cathode recovery was the spotlight in current LIBs recycling scenarios due to the economic importance, and low attention is given to graphite recovery. Currently, graphite, which is responsible for 10–15 % of the total economic worth of the battery, ranges from minimum of 8 USD to maximum of 13 USD per kilogram of anode material. Furthermore, spent LIBs contain approximately 12–21 wt% graphite [11,12]. With the high utilization of LIBs, the quantity of disposed graphite accumulates rapidly and soon the total would become an intolerable amount for easy disposal [13]. Hence, it is imperative and essential to incorporate recycled graphite anodes in a closed-loop or open-loop system.

During the use of graphite in LIBs, its structure is subjected to various deformities. For an example, changes in crystalline structure, changes in interlayer distances and defects due to repeated cycles of charging and discharging [2]. It is widely reported that novel methods for graphite recovery need to be developed to reuse the graphite in new battery cells [14]. Though extraction or separation of graphite from active materials is challenging, enhancing the graphite properties to be reused in new battery materials is even more problematic. This is mainly due to the high cost of treatment methods identified such as leaching, surface modification, and pyrolysis [2]. Hence, closed loop recycling of graphite is still to be fully developed to make it economical. However, separating defected graphite from the cathode active material by physical means is experimented. Kepper and the collaborators reported that filtration-based separation of graphite from mixture of carbon coated LFP ( $\text{LiFePO}_4$ ) and graphite resulted in a low separation efficiency around 1–15 % [15]. Moreover, an attempt made by Mennik et al. (2023) to separate metals from spent LIBs through flotation and magnetic separation resulted in graphite ending up with the critical metals available in the cathodic part [16]. These findings suggest that hydrometallurgical methods are much more convincing in extracting the graphite available in the active materials. However, impurities accumulated throughout the hydrometallurgical methods along with structural deformities of graphite prevent recycled graphite from being used in new LIB applications. Instead, recovered graphite can be used in secondary applications such as reducing agents, negative electrodes, synthesis of graphene or derivatives, graphite-based materials, or functional materials [2]. Among those options, synthesis of graphene or derivatives is likely to be more convenient as it can be used as adsorbents for wastewater treatments.

On the other hand, wastewater treatment chemicals and processes that are used for treatment of dye wastewater or metallic ions contaminated water are at high cost [17]. However, most of these materials act as adsorbent materials with higher adsorption capacities. For an instant, scholars assessed the adsorption of malachite green using activated carbon, manufactured through gasification of waste. It is assessed that the material has the adsorbent capacity of 226.06 mg/g against malachite green [18]. Xu et al., presented methylene blue removal from distillers' grains hydro-char with an adsorption capacity of 340.3 mg/g [19]. Nevertheless,  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  removal was studied by a group of scientists using cherry kernels biochar. It was identified that adsorption capacities of these adsorbents to be 92.42 and 66.22 mg/g respectively [20]. Also, rice straw biochar was used to remove  $\text{Zn}^{2+}$  by Sakhiya et al. It was identified that the adsorption capacity for this to be 35.71 mg/g [21]. All these materials have considerably high adsorption capacity

hence a higher cost is expected. Ighalo et al. (2022) demonstrated that the costs of the adsorption treatment are highly dependent upon the adsorption capacity and the use of virgin raw materials. They also concluded that cost of adsorption treatments can vary from USD 1–200 per mol [22]. On the positive side, it is evident that most of these adsorbent materials listed above are made from carbon-based materials which resulted in comparably higher adsorption capacities. However, bio-based carbon products such as bio char needs to be treated at very high temperatures (300–1000 °C) prior to wastewater treatment application, utilizing higher energy for production [23]. This can lower the overall sustainability of such materials. Accordingly, the high cost of production and less sustainable synthesizing methods can be the main drawbacks of existing adsorbent materials. Hence a competitive adsorbent material would be made from recycled, carbon-based material through less energy intensive synthesis. Hence the idea of using recycled graphite-based derivatives to replace existing adsorbents was generated.

Examining these challenges, the objective of the study is set; to assess the reusability of waste graphite derived from end-of-life (EoL) LIBs in effective pollutant removal from wastewaters. In achieving so, this manuscript describes a potential utilization of residual graphite that resulted as a waste from a real-life hydrometallurgical metal extraction route. The fate of this waste product is not yet explored in the existing literature. Moreover, modification of residual graphite was carried out to synthesis Graphene oxide (GrO) and graphite oxide (GO). Enhanced properties of graphite derivatives (GO and GrO) such as higher surface area, increased pore spaces and higher adsorption capacities were expected to address the objectives of the study. We examined and identified the performances, capacities, and adsorption mechanisms of the produced graphite derivatives (adsorbent materials) through various analysis and calculations.

As organic pollutants Methylene blue (MB) and Malachite green (MG) were used. As per the metallic pollutants  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  were used. MB and MG dyes are being used extensively in paper, leather, and textile industries. Moreover, these two dye types are extensively studied in literature, which makes it easier for comparative studies to understand the adsorption capacities of the newly made adsorbents. In the case of metallic adsorbates, they also have wide range of applications and subject to accumulate in the wastewaters. Hence, these adsorbates also studied well in laboratory studies making it easier for the comparison studies.

## 2. Methodology

### 2.1. Graphite recovery

Twenty cylindrical batteries of NMC 811 were discharged completely using Ni–Cr wire (4Ω). Subsequently, the discharged modules were milled and sieved to gain the particle fraction <9 mm. Following this, another sieving step (>5 mm) was utilized to remove the non-metallic fraction from the mixture. The coarser fraction here contained the separator materials and plastics. Later, the finer fraction was left under the fume hood for 1 day at ambient temperature to evaporate organic solvents and electrolytics. After, the dried material is subjected into another milling and sieving step >2 mm. This step removed most of the copper and aluminum in the mixture leaving only active materials for the leaching steps. 1 M  $\text{H}_2\text{SO}_4$  was used for the leaching step of the active materials. Conditions were set to 90 °C, at atmospheric pressure for 90 min of leaching with the condenser. The residue material, known as waste graphite (WG), was filtered, washed with deionized water, and dried for 24 h at 60 °C [24]. The leach residue derived from this step was then dried at 60 °C for 1 day and taken for the next steps of the experiment.

### 2.2. Characterization of WG

WG recovered from hydrometallurgical leaching was analyzed using X-ray diffraction (Miniflex instrument, Rigaku), Raman spectroscopy

(InVia R.M. instrument Renishaw), X-ray fluorescence-energy dispersive spectroscopy (XRF-EDX, EDX-7000 Shimadzu), particle size analysis (Mastersizer 2000 instrument Malvern), scanning electron microscopy (SEM-EDS, Phenom ProX instrument Thermo Fisher), and carbon content analysis (Elementrac CS instrument ELTRA GmbH).

### 2.3. Adsorption material synthesis

Chemical oxidation (Hummer's method) was utilized to prepare the graphite derivatives; GrO and GO [25]. This method was incorporated as it is most widely accepted oxidation method to produce graphite-based derivatives industrially as the process itself is safer and convenient compared to other existing methods [26]. To prepare GO, 230 mL of concentrated (98 %)  $\text{H}_2\text{SO}_4$  was mixed with WG in an ice bath ( $5^\circ\text{C}$ ) in 1:23 (g/mL) ratio. The materials were kept in suspension using a mechanical stirrer (180 rpm) for 1 h. Sudden temperature elevation was avoided while adding  $\text{KMnO}_4$  (99 %) slowly in the ratio of 3:1 ( $\text{KMnO}_4$ : WG) to the mixture. Ice baths were further used to keep the temperature less than  $40^\circ\text{C}$  during the addition of  $\text{KMnO}_4$ . Stirring continued for another 3 h with the mentioned conditions. The dropping funnel method was used to add DI water dropwise in the ratio of 1:2 ( $\text{H}_2\text{SO}_4$ : DI water). This step elevated the temperature up to  $90^\circ\text{C}$  and taken around 3 h to complete. After another 30 min, more DI water was added to dilute the slurry (1:1 ratio of  $\text{H}_2\text{SO}_4$ : DI water) using the same method. Finally, the oxidation reaction was stopped by adding 30 % of  $\text{H}_2\text{O}_2$  in the ratio of 1:1 with graphite added (1 mL/g of graphite). The mixture was kept in suspension with stirring for another 15 min and then the slurry was filtered to be taken into further steps.

Excess of diluted (10 %) HCl was used to wash the residue derived from the filtration of the above mixture. After further washing of the residue was carried out first by excess of 99 % ethanol and second by DI water until the pH of the effluent water becomes 5.5. The remaining material was dried at  $50^\circ\text{C}$  for 24 h, and then ground with a pestle and mortar. The resulting material was 13 g of GO.

Ultrasonication was utilized to prepare GrO through the exfoliation of a portion of GO that had been prepared [27]. Specifically, produced GO and DI water was inserted to a polypropylene tube with solid to liquid ratio of 2 g/L. The charged material underwent sonication (using an Ultrasonic Bath made of solid steel and 100 W) for a period of 30 min. The 30 min sonication has been done using 6 cycles, where each cycle included 5 min sonication followed by 5 min centrifugation. The centrifugation was carried out at 3000 rpm. After the last centrifugation step, the sediment was recovered and was then dried for 24 h at  $50^\circ\text{C}$  in a furnace before being ground using a pestle and mortar. Using 2 g of GO in total, the resulting sample was 1.4 g of GrO [24].

Chemical analysis for the adsorption materials prepared was carried out by using Raman spectroscopy, XRD, and SEM. Other than that, active functional groups of the prepared materials were evaluated through Fourier-transform infrared spectroscopy (FTIR) with a diamond plate and Smart iTR technology (Nicolet, Madison, WI, USA) before and after the adsorption processes.

### 2.4. Batch adsorption tests for spiked dye wastewater

A magnetic stirrer at 300 rpm was used to carry out the dye adsorption experiments. Initially, concentrations of dye solutions were set in the range 30–100 ppm with 50 mL of volume each. Typical dye concentration in textile effluents can vary from 50 to 2500 ppm. However, many authors used the effective concentration range of 30–100 ppm (as an average) for synthetic dye waste in laboratory studies [28]. Adsorption dosage was determined to be 10 mg for dye adsorption experiments. This was determined by analyzing the dye removal percentages at different GO and GrO dosages varied from 2 to 25 mg with 50 ppm initial dye concentration. The adsorption experiments were carried out for 10 min, and samples were taken for UV–vis spectroscopy (Shimadzu AA-7000, Japan) analysis. These steps were carried out at

room temperature ( $25^\circ\text{C}$ ) and at pH of 5.5. Previous workings that have been done for similar materials (graphite derivatives) with MB and MG dye types showed the best effective temperature range for the maximum adsorption to be  $20\text{--}29^\circ\text{C}$  and the pH at around 5–6 [29–31]. Hence, the temperature and the pH values for the adsorption processes were pre-decided to be  $25^\circ\text{C}$  and pH to be 5.5 respectively. Moreover, decided values are closer to ambient temperature and pH of the waters, confirming that the process can be carried out without adjusting the values prior to the adsorption, confirming the lowest cost of treatment.

The adsorption percentage and the equilibrium capacity of adsorption ( $q_{e,\text{cal}}$ ) (mg/g) were evaluated using Equations (1) and (2), respectively.  $C_0$  and  $C_e$  denote the starting concentration and the concentration at equilibrium in mg/L respectively. The volume of the effluent is given by 'v' and the 'm' stands for the adsorbent mass added in g.

$$\text{adsorption \%} = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$q_{e,\text{cal}} = (C_0 - C_e) \times \frac{v}{m} \quad (2)$$

### 2.5. Batch adsorption tests for spiked metal ion contaminated wastewater

Stock solutions in the range 30–150 ppm from each metallic ion were prepared. Metal ion concentrations in industrial wastewater are dependent on various applications. For an instant, in plating industry wastewater, metal ion concentration can be up to 200 ppm for Nickel [32]. However, in the textile industry this can be lower as 60 ppm [28]. In order to cover up a higher range of concentrations this study utilizes the metal ion concentration of 30–150 ppm. Moreover, initial dosage optimization (2–25 mg with 50 ppm initial metal ion concentration) confirmed that 20 mg of adsorbent material dosage will be a good compromise between the removal percentage and the cost of treatment. Hence, 20 mg from each adsorbent materials were mixed with 20 mL of solution at room temperature ( $25^\circ\text{C}$ ) under magnetic stirring. Experiments were performed within 24 h and at each 2 h intervals samples were taken out. Extracted solution samples were subjected for centrifugation for 5 min at 3000 rpm before analyzing in the Inductively Coupled Plasma (ICP-OES) spectroscopy. At the end of the 24 h, metallic ions concentrations were also determined using AAS.

The adsorption percentage and the adsorption capacity ( $q_{e,\text{cal}}$ ) (mg/g) of metallic ions in each of the adsorbent were identified using equations (1) and (2) respectively.

## 3. Results

### 3.1. Characterization

The initial characterization of the WG was done to determine the particle size distribution, specific surface area and carbon content. The particle size analysis showed that the WG has a uniformity index of 0.546, which suggests that the particles vary from  $d(0.1)$  at  $7.727\ \mu\text{m}$  to  $d(0.9)$  at  $32.705\ \mu\text{m}$  with the mean at  $16.348\ \mu\text{m}$ . Moreover, the specific surface area of the particles is at  $0.461\ \text{m}^2/\text{g}$ . Additionally, carbon content of the sample was 96.6 %.

To determine the impurities, present in the WG, chemical and physical characterizations were also done. Accordingly, XRD, XRF and SEM analysis were carried out. The sample contains graphite from anode and cathode materials mostly, other than that minor amount of aluminum oxide (where Al - 0.38 %), undissolved cathode active materials (Ni-1.05 %, Co-0.38 %, Mn-0.32 %), case (Fe-0.05 %) and electrolyte (where Cl-1.98 %) were present. The source of  $\text{Al}_2\text{O}_3$  should be from cathode and anode or the  $\text{Al}_2\text{O}_3$  coated separators. Though these materials along with other metals supposed to be leached and dissolved completely during the leaching steps, due to the inertness of  $\text{Al}_2\text{O}_3$  and the incomplete reactions between the leaching solution and the metals,

some of these materials can be present at the end of the leaching process. These results agree with the previous results obtained by Ma et al. (2019) [33].

XRD results presented in Fig. 1-a suggest that the crystalline structure of the WG is well preserved as the (002) peak is the strongest. Further, the interlayer spacing of the recovered graphite is identified to be 0.336 nm through the attributed peak at  $2\theta = 26.5^\circ$ . This is slightly higher than the standard graphite materials or fresh cell graphite materials reported (0.334 nm) by Maher and Yazami (2014) [34]. This suggests that the recovering technique used in the study is somewhat better in preserving the crystal structure of graphite for future applications. Also, structural deformities of WG reported [2] was not found in the graphite recovered.

After the oxidation (preparation of GO) of WG, the XRD pattern changed. Accordingly,  $26.50^\circ$  peak is no longer to be seen, instead a

peak appeared at  $2\theta = 10.90^\circ$  resulting an interlayer spacing of 0.81 nm. When producing graphite oxide, interlayer spacing would be enhanced due to the introduction of functional groups (hydroxyl and epoxy groups) between the layers and due to their repulsive forces. This confirms a better oxidation of graphite according to the literature [35, 36].

In the case of GrO prepared through ultra-sonication of GO,  $2\theta$ -theta peak shifted to  $11.2^\circ$  giving an interlayer spacing of 0.78 nm. This reduction shows separation or exfoliation of layers in GO hence reducing the interlayer spacing. This can be due to the GO layers that experience localized forces created by ultrasonication which cause their separation or exfoliation. The weak van der Waals forces that hold these layers together are disrupted by the shear forces and turbulence generated through ultrasonic cavitation. This leads to a reduction in the interlayer spacing. Moreover, ultrasonication has the potential to induce

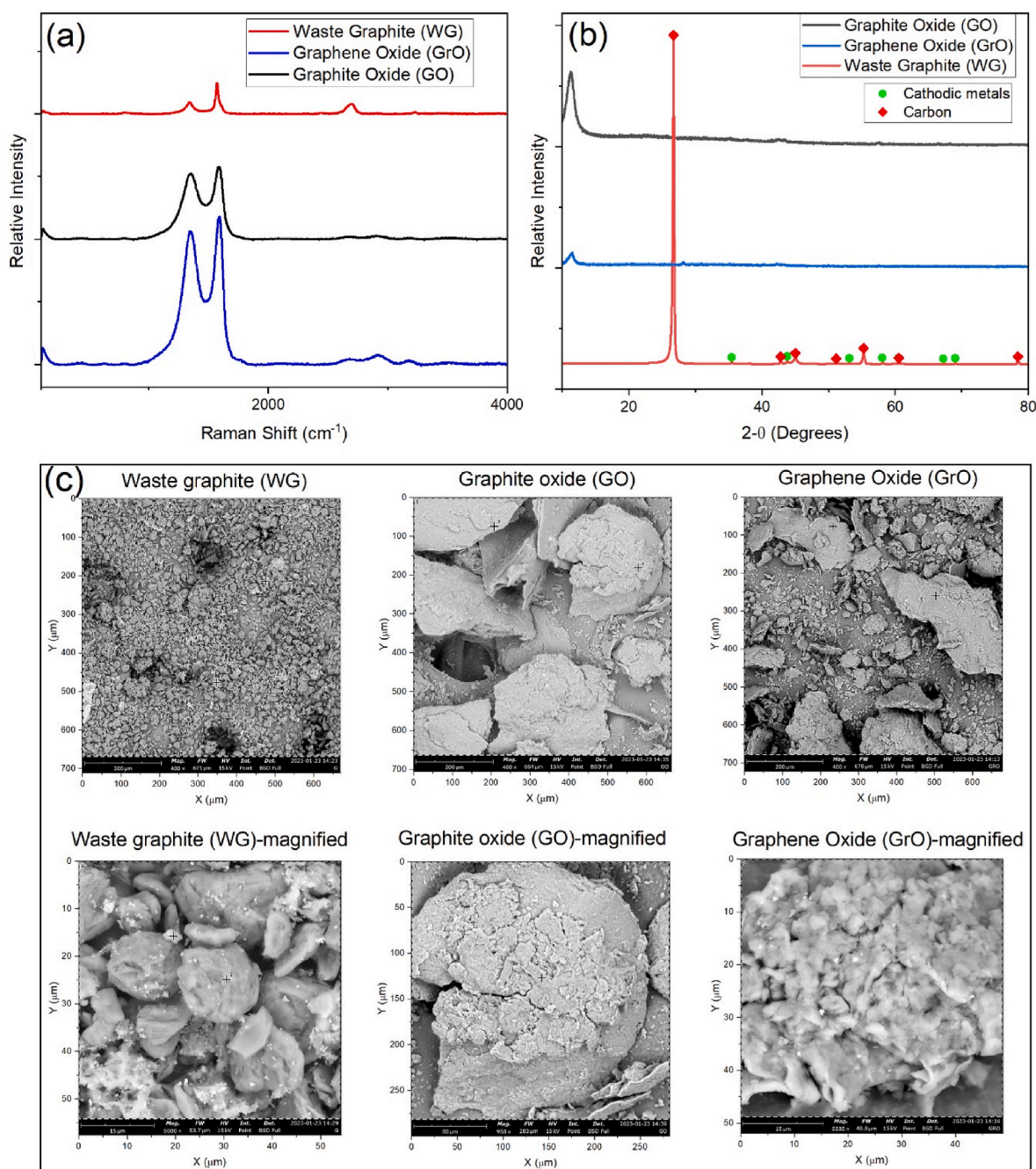


Fig. 1. Characterization of waste graphite (WG), graphite oxide (GO) and graphene oxide (GrO) a) XRD results b) Raman spectra c) SEM images.

dispersion and fragmentation of the graphite oxide sheets into smaller sizes. The mechanical energy that ultrasonic waves impart promotes the breakup of larger graphite oxide flakes or aggregates into smaller particles. In addition, the mechanical energy caused by ultrasonication can break some of the functional groups that already bonded to GrO layers, making the repulsive forces between layers to be lower. This, in turn, can contribute further to the decrease in the interlayer spacing while increasing the total surface area [37]. In both GO and GrO, XRD patterns peaks corresponding to cathodic metals are completely disappearing confirming a complete reaction between the metals and the acids used in preparing the materials [38].

According to the Raman spectra of graphite, D-band and the G-band appeared at  $1344.6\text{ cm}^{-1}$  and  $1572.56\text{ cm}^{-1}$  respectively (Fig. 1-b). G-band in graphite Raman Spectra corresponds to the vibrations of carbons atoms in a  $sp^2$  configuration and provide details about the graphitic order (stacking of layers) while the D-band corresponds to the vacant or disordered carbon atoms (activated by single phonon scattering process) and provide details about structural deformities of the material [34,39]. Relative high intensity of G-band ( $I(D)/I(G) = 0.38$ ) of recovered graphite confirms the presence of well structured graphitic order with well stacked graphite layers. Here, low intense D-band cannot be taken as a structural deformity as similar d-band was reported by Maher & Yazami (2014) in a fresh cell graphite structure as well [34]. Moreover, the presence of such characteristic (low intense D-band) does not contradict with the potential of augmented stacking arrangement of the layers of graphene during repetitive lithium intercalation and de-intercalation. Throughout this process, the layers of graphene slide against each other, ultimately forming AA stacking in  $LiC_6$  after initially exhibiting ABAB and ABCABC stacking in hexagonal and rhombohedral graphite, respectively. During repetitive layer movement during cycling, the potential for the resolution of stacking defects in the initial graphite anode material arises, thus resulting in an improvement in crystallinity [38].

In addition, the shoulder like structure appeared in G-band of the graphite Raman Spectra is known as the  $D'$ -band which is a result by a second order band activated by double phonon scattering effect [40]. Accordingly,  $D'$ -band also implies a possible deformity available in the graphite structure ( $I(D')/I(G) = 0.25$ ). As the  $D'$ -band corresponds to  $sp^2$  defects mostly, the reasons for this deformity can be caused by the adsorption of foreign atoms or chemical functionalization occurred during the chemical reactions took place during the metal leaching [41, 42].

GO and GrO Raman Spectra (Fig. 1-b) shows a significant difference than WG as expected. Moreover, it is vital to discuss even 2D bands appear in the Raman Spectra of these structures which corresponds to stacking of graphene layers. 2D region (entire region) can detect any modification in the graphitic layers. Basically, it would appear 2 peak profiles in 2D region in  $2500\text{ cm}^{-1}$  to  $3000\text{ cm}^{-1}$  range if it's a multi-layer formation and only one peak profile very close to  $2500\text{ cm}^{-1}$  if it's monolayer stacking [43]. In the Raman Spectra of GO, intense bands of D and G ( $I(D)/I(G) = 0.90$ ) are observed with mostly flat part in 2D region. This suggests that during the oxidation of graphite, a higher number of functional groups have attached the graphene layers making the graphitic structures disturbed highly. This can be further convinced through comparing the 2D band region of graphite and GO. Relative intensity of the 2D region has considerably reduced in GO, which is highly sensitive to the number of layers available. As a matter of fact, it is possible to conclude that oxygen containing functional groups prevents stacking graphene layers in GO. In contrast, GrO shows further increase in the relative intensities of D and G bands ( $I(D)/I(G) = 0.88$ ) while G band been slight increased than D band than GO. Moreover, an identical 2 peak profile can also be seen in the GrO Raman Spectra in  $2648\text{ cm}^{-1}$  and  $2912\text{ cm}^{-1}$ . These details provide the information that exfoliation of GO causes partial healing of graphite basal plains by removing some of its functional groups attached previously. Broader D and G peaks of both GO and GrO are due to the availability of  $D'$ -bands as

the graphitic structure is heavily disturbed. However, through the intensity enhancement of D and G bands of GrO, than the GO confirms that the exfoliation has occurred successfully. Similar results for Raman spectra of GO and GrO has reported by Refs. [43,44].

The effect of the recovery method used on the graphite was also examined by SEM-EDS presented in Fig. 1-c. Some agglomerations and impurities can be seen on the surface of the graphite recovered. As suggested by EDS results, the agglomerations on the graphite surface are  $Al_2O_3$  and small fraction of Cl. However, the morphology of the graphite did not show damage, giving credit to the recovery method used. Moreover, the SEI layer was not detected, which suggests that the recycling route removed it from the surface of the graphite. In contrast, GO shows a higher degree of oxidation giving that atomic ratio between C:O is at 3:2 confirming the availability of high number of functional groups attached. The morphology of the GO showed wrinkled and layered flakes with rough appearance. This confirms the full oxidations of graphite layers available in its structure. A similar SEM image for GO was reported by Refs. [45,46]. As reported by Yan et al. (2014), GrO should show exfoliations of stacked layers of GO under sonication. Accordingly, the SEM image of GrO shows a degree of exfoliation under the magnification examined. The morphology of GrO appears to be rougher than GO with much smaller fragments under the same magnification. This is due to the shear stresses applied by the sonication. Also, under the higher magnification it shows expansion of layers making empty spaces appear. This further confirms the production of GrO [47]. Also, it is vital to note that in GrO, C:O ratio is slightly affected by the sonication, accordingly, C:O ratio has reduced to 7:3. This could be due to the intense localized forces created by sonication making the functional groups detached or degrade during the processing.

### 3.2. Dye adsorption studies

The conditions were set for the initial dye solution at ambient temperature ( $25^\circ\text{C}$ ) with pH of 5.5 for batch adsorption experiments. To ensure proper mixing and homogenous sample, magnetic stirrer was utilized with 300 rpm stirring. Initial concentration was set to 30 mg/L of each dye solution with 50 mL of volume and 10 mg of adsorption materials. Dye removal capacities by each adsorbent was studied in 2 min interval for 10 min period of time. Fig. 2-a,b shows time dependant dye removal efficiency by GrO and GO.

According to Fig. 2-a,b, GrO absorbed relatively higher amount (94 % for MB and 91 % for MG) of dye waste than GO (90 % for MB and 87.5 % for MG) within 10 min time. However, in adsorbing MB, GO has a faster adsorption rate than GrO at the beginning. A possible reason for this observation could be the large number of functional groups in GO structure than GrO. So, it is possible to adsorb many pollutants at the beginning. As the time passes the surface-active groups cover and hence declining of the speed. In the case of GrO, though it has a lower number of functional groups than GO, the number of accessible functional groups is larger than GO given its exfoliated nature [48]. Fig. 2-c, d shows dye removal percentage by each of the adsorbents at different initial dye concentrations.

According to Fig. 2-c,d it is visible that GrO has a quite higher adsorption capacity than GO at different dye concentrations. However, it can be noted that increase of initial dye concentration reduces the dye removal percentage in both GO and GrO. Nevertheless, in GO this reduction is lower than GrO. This could be a result of having more surface-active sites in GO. Specifically, at high concentration of dye pollutant particles are pressurized to access more functional groups that are difficult to access at lower dye concentrations in GO. However, overall GrO shows the highest adsorption efficiency. This is because GrO has oxygen-containing functional groups that offer stability, antifouling, and hydrophilicity, which can interact with pollutants through hydrogen bonding, van der Waals forces, and  $\pi$ - $\pi$  stacking interactions easily than GO [48]. The probability of participating in these bonding mechanisms increased in GrO due to its high surface area compared to

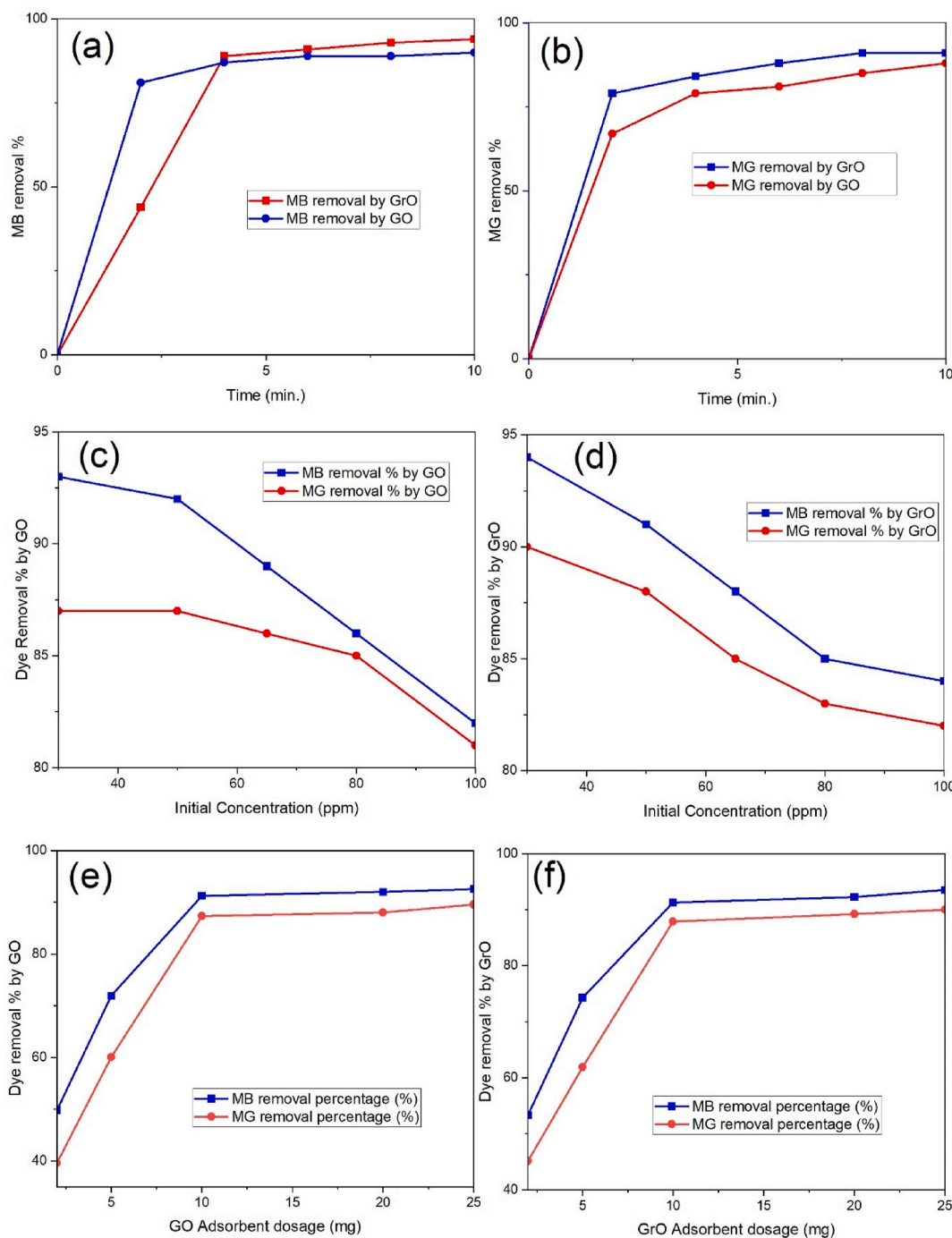


**Fig. 2.** Dye adsorption experiment results a) Time dependent adsorption of MB dye to different adsorbents, b) Time dependent adsorption of MG dye to different adsorbents, c) Dye removal percentage by GO at different initial dye concentrations, d) Dye removal percentage by GrO at different initial dye concentrations, e) Dye removal percentage at different dosages of GO and f) Dye removal percentage at different dosages of GrO.

GO.

As per Fig. 2-e, f, it is evident that increasing of adsorbent material dosage increases the dye removal percentage as more adsorbent material provides more functional groups and void spaces that dye pollutants can be trapped. However, 10 mg of adsorbent dosage seems to be a good compromise between the removal percentage and the adsorbent mass used. Further increase of adsorbent materials does not cause a significant increase of dye removal percentage. It suggests that though more functional groups and void spaces are provided for the adsorption, the pollutant concentration is too low to pressurize themselves into the available sites. Nevertheless, GrO shows higher adsorption (~93 %, ~90 %)

of dye pollutants (MB and MG) than GO (~92 %, ~89 %) at different dosages due to its increased surface area and wide accessibility of functional groups.

Compared to literature values, these removal efficiencies are higher. For an instant, Liu et al. (2012) recorded <85 % removal of MB under neutral pH levels using aqueous solution of graphene [49]. Also, around 85 % removal efficiency of MB by graphene oxide/calcium alginate composites was reported by Li and others at neutral pH levels [50]. In the case of MG, 90 % removal was reported by Sykam et al. using exfoliated graphite [51]. Also, it is important to note that these materials are derived from virgin materials while materials produced in this study

comes from recovered graphite. In depth comparison of adsorption capacities is provided under adsorption capacity studies.

### 3.2.1. Dye adsorption kinetics

Time dependent adsorption of dye with different adsorbents was used to determine the adsorption kinetics. Liquid film diffusion (LFD), Elovich, Weber-Morris intra-particle diffusion (IPD) and frequently used Pseudo-first order (PFO) and second order (PSO) kinetic models were used to calculate the rate of the adsorption and adsorption mechanisms. The linear equations and parameter values obtained for each of the models studied were reported in Table 1 along with the experimental conditions<sup>1</sup>.

The PFO model (equation 3) developed based on the assumption that adsorption rate is proportional to the difference between initial and adsorbate surface concentration of the dye in an aqueous medium [52]. To evaluate the current study according to the PFO model, the linearized PFO model equation (3) was used.

The initial rate constant for adsorption,  $K_1$ , and the calculated equilibrium adsorption capacity,  $q_{e,cal}$ , were determined through the interception and slope of  $\ln(q_e - q_t)$  vs.  $t$  graph. The plotted graphs were given in supplementary materials Figs. S1–a while the parameter values were shown in Table 1. High  $R^2$  values were obtained for all the adsorption processes ( $R^2 > 0.92$ ), suggests that the processes could follow PFO model. Accordingly,  $K_1$  and  $q_{e,cal}$  was calculated. Calculated  $q_e$  values for each adsorption is significantly different to the experimented  $q_e$  values ( $q_{e,exp} = 129.5$  mg/g for MB with GrO, 143.5 mg/g for MG with GrO, 129.92 mg/g for MB with GO and 129.98 mg/g for MG with GO). Having inconsistencies with calculated and experimented  $q_e$  values limits the PFO model applicability to the current adsorption process.

The PSO model assumes that rate of the adsorption process depends on chemisorption [52]. To understand the applicability of the PSO model to the current study, equation 4 mentioned on the Table 1 under PSO model was used.

The second order rate constant for adsorption,  $K_{obs}$ , and the equilibrium adsorption capacity were obtained by analyzing the intercept and slope of the  $t/q_t$  vs.  $t$  graph. The parameter values obtained were reported in Table 1 and the graphs were given in Figs. S1–b. According to the higher coefficient of correlation obtained, it is safe to assume that the adsorption processes follow PSO model concluding that rate determining factor of the adsorption process is chemisorption of the heterogeneous mixture. Moreover, calculated  $q_{e,cal}$  (169.89, 150.65, 133.49, 139.36 mg/g) are somewhat similar to the experimental  $q_{e,exp}$  values (129.5, 143.5, 129.92 mg/g and 129.98 mg/g). However, slight discrepancy between the  $q_e$  values can be due to the other rate determining factors (such as decreasing dye concentration and decreasing number of unoccupied active sites) involved in with adsorption process.

Though Elovich model (equation 5) originally designed for the assessment of gas adsorption into solid adsorbents, it has been used frequently in assessing aqueous media adsorption mechanisms [52]. The Elovich model also determines the second order kinetics based on the assumption that the surface of the adsorbent materials is heterogeneous and has non uniform adsorption energies. Moreover, it also provides information on the effect of pore sizes in the adsorption process. The equation 5 was adapted to evaluate the Elovich model for this study.

The preliminary adsorption rate;  $\alpha$  and activation energy/surface coverage coefficient;  $\beta$  were calculated using the interception and the slope of the graph between the  $q_t$  vs.  $\ln t$ . Figs. S1–c shows the linear plot of the adsorption while Table 1 shows the important parameter data of the process. Higher correlation coefficients (above 0.9 except the case of GrO with MB) confirms that the adsorption processes may follow the Elovich model as well. Nevertheless, high values received for the adsorption rate constant ( $\alpha$ ) suggests that chemisorption occurred fast for MB adsorption to GO followed by MG into GrO. Also, the model suggests that there is a high surface coverage ( $\beta$ ) by each adsorbate with higher adsorption rate ( $\alpha$ ). According to the model values, the slowest adsorption was shown by the MB with GrO. More importantly, considering the ending of the adsorption process, the process is much more likely to follow Elovich model with higher  $R^2$  values (0.95 for GrO + MB, 0.85 for GrO + MB, 0.98 for GO + MB and 1.00 for GO + MG). Further, this suggests that pore diffusion plays a significant role in the adsorption process [53].

LFD model (equation 6) uses the assumption that the adsorption rate depends on the rate that the adsorbate particles diffuse in the liquid film and the rate of the direct adsorption onto the adsorbent active sites [52]. Which means that the rate determining factor of the adsorption process is the spread of particles of the adsorbate within the liquid film surrounding the absorbent surface.

Liquid film diffusion rate factor  $K_{fd}$  was determined through the graph between  $\ln(1 - \frac{q_t}{q_e})$  vs.  $t$ . The high  $R^2$  value obtained suggests that the adsorption process can also follow the LFD model. However, as per Figs. S1–d the graph does not go through the origin point of the graph (though it's very close to zero in most cases). This suggests that LFD model cannot describe the adsorption process alone and there is a contribution of other processes for the total rate of adsorption. This finding correlates with the suggestion received by Elovich and PSO models. Moreover, liquid film diffusion rate factor ( $K_{fd}$ ) suggests that the highest diffusion rate received from MG adsorption to GrO ( $0.73 \text{ min}^{-1}$ ) followed by MB adsorption into GrO ( $0.62 \text{ min}^{-1}$ ). Adsorption of dye into GO is comparably slower as per the model diffusion rate values ( $0.59 \text{ min}^{-1}$  for MB and  $0.39 \text{ min}^{-1}$  for MG).

Finally, IPD model (equation 7) assumes that the diffusion mechanism determines the total rate of the adsorption process [52]. To evaluate this hypothesis and the corresponding diffusion mechanism for the

**Table 1**  
Parameter values calculated for different adsorption kinetic models.

| Model   | Linear Function                                                           | Parameter (Units)                                                                | GrO + MB                            | GrO + MG                            | GO + MB                             | GO + MG                             |
|---------|---------------------------------------------------------------------------|----------------------------------------------------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| PFO     | $\ln(q_e - q_t) = \ln q_{e,cal} - k_1 t$ (3)                              | $q_{e,cal}$ (mg/g)<br>$k_1$ (g/mg.min)<br>$R^2$                                  | 147.70<br>0.62<br>0.96              | 143.91<br>0.73<br>0.92              | 70.34<br>0.59<br>0.92               | 88.99<br>0.39<br>0.93               |
| PSO     | $\frac{t}{q_t} = \frac{1}{k_{obs} q_{e,cal}^2} + \frac{t}{q_{e,cal}}$ (4) | $q_{e,cal}$ (mg/g)<br>$k_2$ (g/mg.min)<br>$R^2$                                  | 169.89<br>0.002<br>0.94             | 150.65<br>0.01<br>1.00              | 133.49<br>0.03<br>1.00              | 139.36<br>0.01<br>1.00              |
| Elovich | $q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$ (5)      | $\alpha$ (mg/g.min)<br>$\beta$ (g/mg)<br>$R^2$                                   | $1.22 \times 10^2$<br>0.024<br>0.79 | $9.90 \times 10^4$<br>0.078<br>0.98 | $7.77 \times 10^6$<br>0.123<br>0.93 | $2.64 \times 10^3$<br>0.056<br>0.96 |
| LFD     | $\ln(1 - \frac{q_t}{q_e}) = -k_{fd} t$ (6)                                | $k_{fd}$ (1/min)<br>$R^2$                                                        | 0.62<br>0.96                        | 0.73<br>0.92                        | 0.59<br>0.93                        | 0.39<br>0.93                        |
| IPD     | $q_t = k_{id} \times t^{0.5} + C$ (7)                                     | $K_{id}$ (mg/g.min <sup>0.5</sup> )<br>$C$ (mg/g)<br>$R^2$<br>$q_{e,exp}$ (mg/g) | 44.32<br>6.76<br>0.91<br>129.5      | 44.36<br>26.07<br>0.82<br>143.5     | 39.87<br>26.07<br>0.79<br>129.92    | 40.25<br>19.26<br>0.87<br>129.98    |

<sup>a</sup>Experimental condition: pH = 5.5, Temperature = 25 °C, L/S = 5 L/g, Initial concentration of dye = 30 ppm.

current study the linear equation of the model was used.

The  $k_{id}$ ; the initial rate of intra-particle diffusion controlled adsorption was determined using the linear graph between  $q_t$  vs.  $t^{0.5}$ . The values obtained for  $k_{id}$  for each adsorption process are given in Table 1 and the corresponding figure is given in Figs. S1–e. The relatively low coefficient of correlation values limit the use of IPD model to describe the adsorption process alone. However, intercept (C) values received for the IPD model provide information about the thickness of the boundary layer [53,54]. As per the higher values received for C in IPD model suggests that effect of the boundary layer is higher in each adsorption process. Moreover, it can be concluded that the boundary layer in GrO is thinner than the GO as per the relatively lower C values received for the GrO systems. Which suggests that more mass transfer or more adsorptions can occur in GrO than GO.

From the evaluated kinetics models, to describe the rate determining factor of the adsorption process, PSO model matches perfectly well with significantly higher  $R^2$  value. So, it is safe to say that chemisorption is the main rate determining factor of the adsorption process. However, in the order of highest coefficient of correlation except PSO, Elovich > LFD > PFO models also describe the adsorption mechanism with relatively higher  $R^2$  values. Which can be interpreted as the rate of the adsorption mechanism also depends on the amount of adsorbate over time, variation of the maximum adsorption concentration of the adsorbents, and the rate of diffusion of adsorbate in the liquid film. However, identification of Elovich model applicability with higher  $R^2$  values for the ending part of the adsorption process suggests that the adsorption process, turns to second order adsorption as the dye concentration in the aqueous solution reduces. In conclusion, the dye adsorption to the considered adsorbents initially controlled by multiple mechanisms such as the chemisorption, variation of dye concentrations in liquid phase and the adsorbent phase, and the diffusion of the adsorbate in the liquid film. Nevertheless, to the ending, the adsorption process mainly controlled by chemisorption and liquid film diffusion rate (second order processes).

### 3.2.2. Dye adsorption isotherms

The Langmuir (LI), Freundlich (FI), Temkin (TI), Halsey (HI) and Harkins-Jura (HJI) isotherms were employed to investigate the interactions of the adsorbent particles on the adsorbent surface once the adsorption process reached equilibrium. Consequently, the adsorption experiments were carried out at pH of 5.5, with stirring speed of 300 rpm in the ambient temperature, using a liquid-to-solid ratio of 5. The initial concentrations of the dye waste were changed from 30 ppm to 100 ppm to attain the maximum adsorption capacity at each initial dye concentration. The linear equations and parameter values obtained for each of the models studied were reported in Table 2.

The Langmuir isotherm model (equation 8) was established assuming that binding sites are homogeneous, and the adsorption energies of the binding sites are identical. Furthermore, it assumes that there are no intermolecular interactions between adsorbents [52]. The linearized model of the Langmuir isotherm was used for the calculation of parameters and plotting of the graph.

Theoretical maximum adsorption capacity  $q_{max}$ , and Langmuir constant  $K_L$  determine the maximum adsorption capacity of the adsorbent and the affinity of the sites that bind respectively. These parameters were calculated through the graph  $C_e/q_e$  vs.  $C_e$ . Here,  $C_e$ ; dye concentration in the solution at equilibrium,  $C_0$ ; initial dye concentration in the solution,  $q_e$ ; adsorption capacity at equilibrium. The values obtained were depicted in Table 2 and the corresponding graph can be found in Figs. S2–a. Moreover, the unitless separation factor,  $R_L$  provides the validity of the Langmuir isotherm, which can be calculated through equation (9).

$$R_L = \frac{1}{1 + K_L C_0} \quad (9)$$

When  $R_L > 1$ , the adsorption becomes adverse, if  $R_L < 1$ , it shows a desirable adsorption. For  $R_L = 0$ , shows an irrevocable adsorption and for  $R_L = 1$ , means a linear adsorption [52]. As per the results obtained, it can be deduced that both adsorbent materials interactions with two different dyes follow a linear pattern at different initial concentrations. This can be confirmed by the high  $R^2$  values obtained (0.96–1.00). Moreover, the  $q_{max}$  values obtained for GrO/MB, GrO/MG, GO/MB and GO/MG are 546.7, 640.68, 527.87, 813.14 mg/g respectively. These values obtained are somewhat like the evaluated experimented values except for the GO/MG adsorption (421.5, 410.55, 410.15, 406.2 mg/g). Nevertheless, the separation factor ( $R_L$ ) values obtained also suggests a favorable adsorption, being all the values less than 1 (0.16, 0.27, 0.15, 0.37). Also, it is observed that,  $R_L$  value for the adsorption of MB is less than MG with both GO and GrO, indicating that, there is a higher inclination towards adsorbing MB dye by the adsorbent materials produced.

Freundlich model (equation 10) describes that energy distribution in surface sites are not uniform and hence, multilayer adsorption can be taken place [52]. To understand the applicability of multilayer adsorption, the linear form of Freundlich isotherm model was considered (equation 10).

The graph  $\ln q_e$  vs.  $C_e$  was utilized to determine Freundlich rate constant,  $K_F$  and unit less heterogeneity factor,  $1/n$ . Freundlich rate constant indicates the adsorbents maximum adsorption capacity and heterogeneity factor describes the desirability of the adsorption process. Also, heterogeneity factor can predict the heterogeneity of the surface of

**Table 2**  
Different isotherm models used for the evaluation along with main parameters, units and calculated values.

| Model | Linear Function                                                                           | Parameter (Units)                                          | GrO + MB                                     | GrO + MG                                     | GO + MB                                      | GO + MG                                      |
|-------|-------------------------------------------------------------------------------------------|------------------------------------------------------------|----------------------------------------------|----------------------------------------------|----------------------------------------------|----------------------------------------------|
| LI    | $\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}}$ (8)                       | $q_{max}$ (mg/g)<br>$K_L$ (L/mg)<br>$R^2$<br>$R_L$         | 546.77<br>0.17<br>0.97<br>0.16               | 640.68<br>0.09<br>0.98<br>0.27               | 527.87<br>0.19<br>1.00<br>0.15               | 813.14<br>0.06<br>0.96<br>0.37               |
| FI    | $\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$ (10)                                            | $K_F$ (mg/L)<br>$1/n$<br>$R^2$                             | 112.44<br>0.47<br>1.00                       | 76.32<br>0.58<br>0.99                        | 111.89<br>0.47<br>0.97                       | 56.56<br>0.70<br>0.97                        |
| TI    | $q_e = B_T \ln k_T + B_T \ln C_e$ (11)                                                    | $q_{max}$ (mg/g)<br>$B_T$ (J/mol)<br>$K_T$ (L/mg)<br>$R^2$ | 557.59<br>118.06<br>1.78<br>0.96             | 554.50<br>142.92<br>0.85<br>0.98             | 558.49<br>119.72<br>1.71<br>1.00             | 616.99<br>172.58<br>0.57<br>1.00             |
| HI    | $\ln q_e = \frac{1}{n_H} \ln k_H - \frac{1}{n_H} \ln C_e$ (13)                            | $n_H$<br>$K_H$<br>$R^2$                                    | −2.12<br>$2.27 \times 10^4$<br>1.00          | −1.72<br>$2.16 \times 10^3$<br>0.99          | −2.12<br>$2.16 \times 10^4$<br>0.97          | −1.42<br>$3.12 \times 10^8$<br>0.97          |
| HJI   | $\frac{1}{q_e^2} = \frac{B_{HJ}}{A_{HJ}} - \left( \frac{1}{A_{HJ}} \right) \log C_e$ (14) | $A_{HJ}$<br>$B_{HJ}$<br>$R^2$<br>$q_{e,exp}$ (mg/g)        | $2.25 \times 10^4$<br>1.22<br>0.92<br>421.50 | $1.72 \times 10^4$<br>1.26<br>0.88<br>410.55 | $2.28 \times 10^4$<br>1.23<br>0.82<br>410.15 | $1.40 \times 10^4$<br>1.23<br>0.81<br>406.10 |

<sup>a</sup> Experimental conditions: pH = 5.5, Temperature = 25 °C, L/S = 5 L/g, Initial concentration of dye = 30–100 ppm.

the adsorbent materials. For an instant, if the value of  $1/n$  becomes zero or very close to zero, it indicates that the adsorption is much desirable [52]. On the other hand, “ $n$ ” closer to 1 shows a more homogeneous structure and deviations to the higher than 1 indicates more heterogeneous structure [55]. Hence, the logarithmic graph of  $q_e$  vs.  $C_e$  was used to determine KF and  $1/n$  parameters. The important parameters of the adsorption indicated in Table 2, and the graphs can be found in Figs. S2–b. Higher correlation coefficients ( $R^2 = 0.97$  to  $1.00$ ) suggest that adsorption processes adhered to Freundlich isotherm as well. Moreover, heterogeneity factor ( $1/n$ ) for each adsorption, are closer to zero (varies 0.4 to 0.7) indicating that a better adsorption and heterogeneous structure of the GO and GrO surfaces. The highest Freundlich rate constants were shown by GrO with MB ( $112.44$  mg/L) followed by GO with MB ( $111.90$  mg/L). Rate constant for the adsorption of MG by each adsorbent material is lower than MB (GrO showed  $76.33$  mg/L, GO showed  $56.56$  mg/L with MG). Accordingly, it is possible to understand that MB has a higher inclination for the adsorption process than MG. Focusing on the  $R^2$  at higher concentrations (mostly  $\approx 1.00$ ) (depicted on the graph) illustrates that 2nd order isotherms are much adhered to the adsorption process at higher concentrations better than considering the whole range of concentrations.

The Temkin isotherm model (equation 11) is developed taking “heat of adsorption produced by the indirect interaction between adsorbent and adsorbate” into consideration. It is assumed that heat of adsorption of the adsorption sites decline linearly as the coverage increases. The linear model of Temkin isotherm (equation 11) was used to determine the applicability of the model.

A graph was plotted between  $q_e$  and  $\ln C_e$  to determine the important parameters of the model. Accordingly, the graph can be seen in Figs. S2–c and the parameters calculated are shown in Table 2.  $B_T$  in the model is the Temkin constant and it provides information about the heat of adsorption.  $K_T$  is the equilibrium binding constant [52]. Further,  $B_T$  is related to  $b_T$ , Temkin isotherm exponent through.

$$B_T = \frac{RT}{b_T} \quad (12)$$

Here,  $R$  stands for the universal gas constant ( $8.314$  J/K.mol), and  $T$  the temperature in Kelvin ( $298$  K).  $b_T$ , the Temkin isotherm exponent provides details about the favorability of the adsorption being close to 1. Significant lower values of  $b_T$ , indicates negative cooperativity in binding [56]. As per the high coefficient of correlation, it is possible to consider that the adsorption follows the Temkin model as well. However, values obtained for  $b_T$  exceeds 1 in all the cases. Higher values of  $b_T$  implies that the rate of linear reduction of the heat of adsorption is much lower than the standard Temkin model rate, limiting the applicability of the model to the adsorption system. However, this suggests the surface of the adsorbates are more heterogeneous as higher  $b_T$  can reduce the  $B_T$  (heat of adsorption) significantly [53,57]. Nevertheless, comparably lower values of  $B_T$  for MB adsorption ( $118.06$  and  $119.72$  J/mol) suggest that adsorption requires lower energy, hence favorable adsorption than MG into the adsorbent materials [56].

The Halsey isotherm model (Equation 13) assumes a multilayer adsorption with heterogeneous sites available in the adsorbent which is like the assumptions made in Freundlich model. However, there are distinguishable differences between the two empirical models. Moreover, Halsey focuses specifically on the heterogeneity of the adsorbent surface while the Freundlich considers heterogeneous adsorption energy distribution on the surface and affinities.

Parameters such as  $k_H$ , and  $n_H$ ; were obtained through the graph between  $\ln q_e$  vs.  $\ln C_e$ . Parameter values obtained were shown in Table 2 and the plotted graphs are shown in Figs. S2–d. Halsey isotherm constant ( $k_H$ ) provides information about the adsorption capacity and Halsey equilibrium exponent ( $n_H$ ) provides an insight of the heterogeneity of the surface and related to the energy distribution of the adsorption sites available. Higher values of  $n_H$  indicates a greater heterogeneity [56].  $R^2$  values obtained for each of the adsorption

mechanisms suggests that the adsorption process follows the Halsey model as well. Accordingly, very high adsorption capacities can be identified for GrO with MB ( $2.24 \times 10^4$ ) and GO with MB ( $2.16 \times 10^4$ ). For GrO with MG and GO with MG, the adsorption values are still high ( $1.69 \times 10^3$  and  $3.12 \times 10^2$  respectively) but lower than that of MB. In contrast,  $n_H$  values obtained for each adsorption is negative, which indicates that the model does not correctly explain the adsorption reaction alone [56,58].

Harkins-Jura isotherm model (Equation 14) can predict both monolayer and multilayer adsorption between the adsorbent and the adsorbate. It built on the assumption of availability of varied pore sizes in the adsorbent materials which implies the heterogeneity of the surface [52,56]. The linear equation of the model was used to evaluate the model applicability.

A linear graph was plotted between  $\frac{1}{q_e}$  vs.  $\log C_e$  to obtain the parameter values for  $B_{HJ}$  and  $A_{HJ}$ , Harkins-Jura isotherm parameter and constant respectively. Table 2 denotes the values calculated for the model parameters whereas the graph can be found in Figs. S2–e. Goodness of fit of the obtain values to the model shows a strong negative relationship which suggest that the adsorption processes follow the Harkins-Jura’s model. Higher Harkins-Jura heterogeneity constant ( $A_{HJ}$ ) received for adsorbents with MB ( $2.25 \times 10^4$ ,  $2.28 \times 10^4$ ) shows higher surface area and heterogeneity than with MG ( $1.72 \times 10^4$ ,  $1.40 \times 10^4$ ). This further confirms the high affinity of MB dye to the adsorption materials studied. Further, monolayer heat of adsorption constants ( $1.22$ ,  $1.26$ ,  $1.23$  and  $1.23$  for MB and MG with GrO and MB, MG with GO respectively) values reported are slightly higher in GrO than GO in average. This indicates that physisorption can be involved in the adsorption process of GrO more than GO. The reason for this could be the availability of pore spaces in GrO than GO.

The coefficient of correlation ( $R^2$ ) values for each isotherm models can be listed as follows from the highest to lowest, Freundlich > Halsey > Temkin > Langmuir > Harkins-Jura. Taking this order and the analysis done above into consideration we can conclude that the adsorbent materials follow Freundlich Isotherm (2nd order isotherm) with cationic dyes studied at higher concentrations with acceptable parameter values. Also, it’s possible to deduce that adsorption can follow 1st order adsorptions at lower concentrations. It is reasonable to think that at higher concentrations, interactions between pores, functional groups and adsorbates are much more complex and hence can be fit into different isotherms as studied. Though Halsey and Temkin also have very high coefficient of correlation, it is not ideal to use these isotherms due to unacceptable parameter values obtained as discussed above. Hence, maximum adsorption capacities ( $q_{max}$ ) of GrO and GO for corresponding dye waste were calculated according to the Freundlich isotherm parameters using equation (15) for the comparison with recent studies [59].

$$q_{max} = K_F C_0^{\frac{1}{n}} \quad (15)$$

Where,  $K_F$  represents the Freundlich constant and  $C_0$  is the initial concentration of adsorbate used. Calculated  $q_{max}$  values are present in Table 2 and a comparison of  $q_{max}$  with recent study values were listed in Table S1 in the supplementary materials. Accordingly, high maximum adsorption capacities can be observed for the material synthesized in this study (GO =  $558.49$  mg/g with MB,  $616.99$  mg/g with MG and GrO =  $557.59$  mg/g with MB &  $554.5$  mg/g with MG for a dose of  $0.2$  g/L). It is proven that the adsorption capacity is influenced by various factors such as available functional groups, pore space structure and surface area. These factors mainly governed by the material modification method and the degree of oxidization of the graphite material [60]. Hence, we can deduce that extracted graphite from LIBs can be easily oxidized to a higher degree with mild oxidization like Hummer’s method. The reason behind this easy oxidization can be the slightly enhanced interlayer spacings of the spent graphite occurred due to

repetitive charging and discharging cycles of the LIBs as discussed in section 3.1. This can be further justified by the higher maximum adsorption capacity obtained by Nataraja et al. (2016) (to be around 1000 mg/g with 5 g/L dosage). Nataraja and the collaborators also utilized graphite derived from spent LIBs for their study [36]. However, different modification and recovery methods resulted a higher maximum adsorption capacity for the current study compared to the used adsorbent dosage.

### 3.3. Metallic ions adsorption experiments

Adsorption experiments of metallic ions were carried separately for each metal ion type at room temperature (25 °C) with the pH of 5.5. 30

mg/L Initial metal ion concentration was used for each stock solution with 20 mL of volume. After 20 mg of adsorption materials were added into each solution. Metallic ions removal capacities by each adsorbent was studied in 4 h interval for 24 h. Fig. 3-a,b shows the time dependant metallic ion removal efficiency by GO and GrO for each ion studied respectively. GrO has the highest removal efficiency compared to GO. This is mainly due to the availability of more accessible sites in GrO. GO, on the other hand, has more surface sites, but accessibility is limited due to the compacted nature. Further, it can be identified that,  $\text{Ni}^{2+}$  has the highest kinetics in adsorbing into each adsorbent material studied.  $\text{Zn}^{2+}$  showed the slowest kinetics among all the metal ions studied.

Fig. 3-b and 3-c presents the removal efficiency of considered adsorbates at different initial concentrations using the two adsorbent

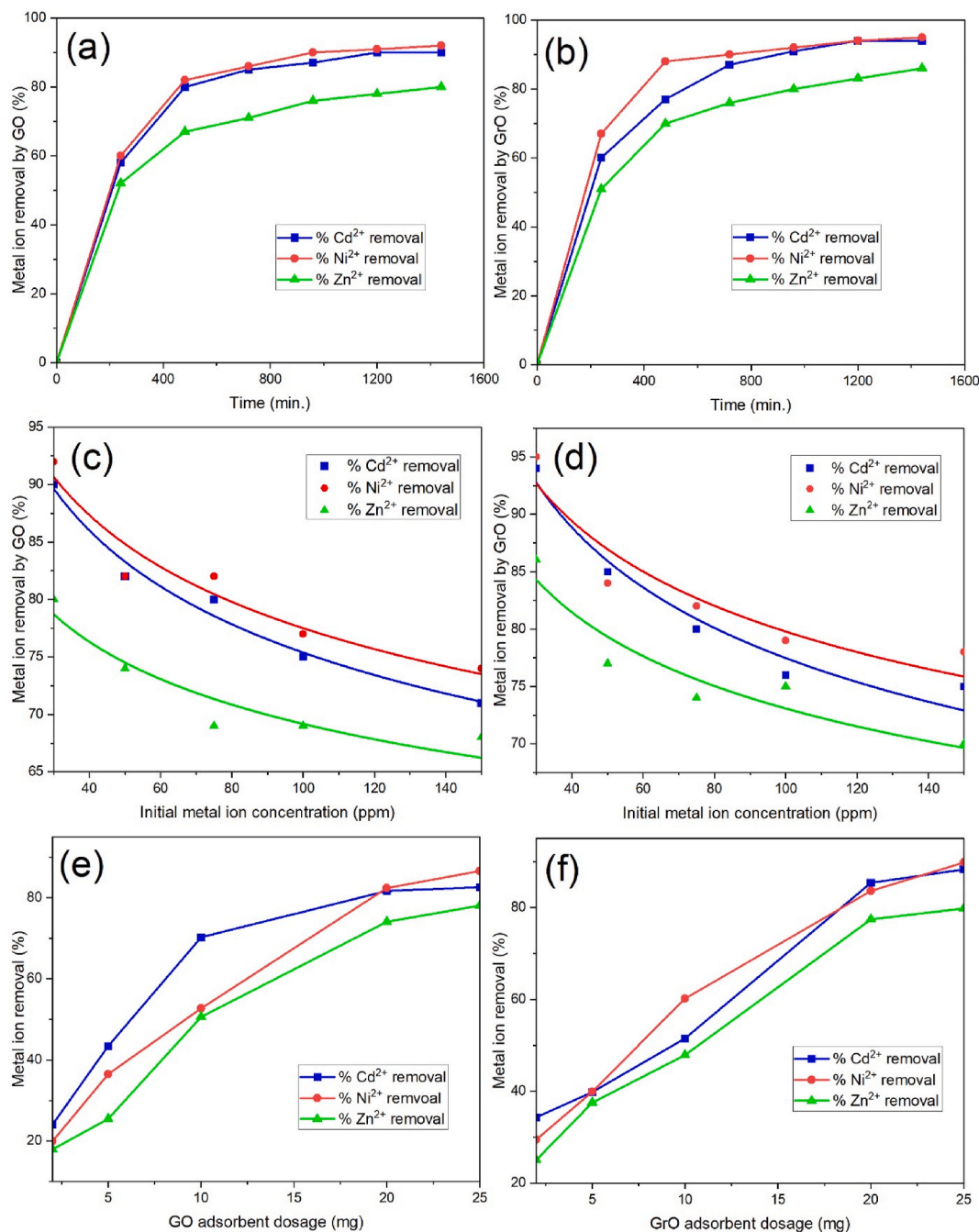


**Fig. 3.** Metal ion adsorption experiment results a) Time dependent adsorption of metal ions to GO, b) Time dependent adsorption of metal ions to GrO, c) Metal ion removal percentage by GO at different initial dye concentrations, d) Metal ion removal percentage by GrO at different initial dye concentrations, e) Metal ion removal percentage by GO at different dosages, f) Metal ion removal percentages by GrO at different dosages.

materials. The observation received for the final concentrations were non-monotonic, hence the mean value used to calculate the percentage removal also shows a fluctuating nature. Hence, trending line of the observations were considered to make the comparison between the adsorbent materials. Generally, all metal adsorption capacities decrease along with the increasing of initial metal concentrations in the aqueous media. Moreover, It is clear that GrO performance is better at different metallic ion concentrations for  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$ . Moreover,  $\text{Ni}^{2+}$  has the highest removal efficiency (95 % with GrO, 92 % with GO with 30 ppm initial concentration) with both the adsorbents and  $\text{Zn}^{2+}$  is the least adsorbed metal ion (86 % removal with GrO and 80 % removal with GO).  $\text{Cd}^{2+}$  adsorption was at 90 % with GO at 30 ppm of initial  $\text{Cd}^{2+}$  concentration and GrO showed 94 % adsorption at the same initial metal concentration.

Metal ion removal percentages were studied with varying adsorbent dosages (2–25 mg) at 50 ppm initial metal ion concentrations. Fig. 3-e,f shows the results obtained through the experimental studies. Accordingly, increase of adsorbent material dosage of both GO and GrO increase the metal ion removal percentage. As explained before, this is mainly due to the availability of more functional groups and void spaces. Nevertheless, adsorption of metal ions are higher in GrO at different dosages than GO. This can be explained by the availability of more accessible sites in GrO than GO as per the exfoliated nature of GrO. Moreover, it can be predicted that, metal ion may be trapped inbetween the layers of GrO enhancing its total adsorption capacity. In addition, affinity of  $\text{Ni}^{2+}$  seems to be higher towards both of the adsorbent materials than  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$ .  $\text{Zn}^{2+}$  reported the lowest adsorption efficiency compared to the rest.

Guo et al., in 2018 reported similar results for the dye removal efficiency using carbon based adsorption materials. According to the study, adsorption material longan hull, could remove 92 % of  $\text{Ni}^{2+}$  and 87 % of  $\text{Cd}^{2+}$  available in the wastewater with an adsorbent dosage of 1.2 g and 1.5 g respectively [61]. In another recent study done by, Dhauadi et al. (2021), also reported that among the metal ion studied,  $\text{Ni}^{2+}$  has the highest adsorption followed by  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$ . Authors used pyrolyzed carbon based materials for the adsorption of these metals at 30 °C and pH of 5 [62]. A detail comparison of adsorption capacities is provided under adsorption capacity studies.

### 3.3.1. Metal ion adsorption kinetics

To analyze the adsorption kinetics and mechanisms, PFO, PSO, Elovich, LFD, and IPD kinetic models were employed. The linear equations and parameter values obtained for each of the models studied were reported in Table 3 along with the experimental conditions<sup>2</sup>.

As shown under section 3.2.1, equation 3 explains the PFO model's linear equation along with the assumptions used in the model and the

important parameters. Accordingly, a graph was plotted between  $\ln(q_e - q_t)$  vs.  $t$  to understand the applicability of the corresponding model to the adsorption process experimented with metal ions. The graph received is shown under Figs. S3-a and the corresponding parameter values have been demonstrated in Table 3. Coefficient of correlation for each adsorption process are very high ranging from 0.94 to 0.99 suggesting that, adsorption rate may be proportional to the variation of the dye concentration in the solution. Moreover, adsorption capacity at equilibrium ( $q_e$ ) calculated using the PFO model (27.56, 19.47, 31.84 mg/g) close to the experimented values in the case of GO with  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ , and GrO with  $\text{Cd}^{2+}$  (27.00, 23.97, 28.20 mg/g) respectively. However, the rest of the values are not consistent with experimented  $q_e$  values. This inconsistency reduces the applicability of PFO model to the adsorption process entirely. In addition, it is worth noting that, coefficient of correlation is much higher (>0.99) for the PFO model during the initial part of the adsorption process suggesting that initial rate determining factor could be the concentration variation of the metal ions in the liquid and the adsorbent phase (physisorption).

The PSO model assumes that adsorbent consist of heterogeneous functional groups is responsible for the adsorption while chemisorption being the rate determining factor. This was previously explained under equation 3. To understand the applicability of the model to the current study of metal ion adsorption, a graph was plotted between  $t/q_t$  and  $t$ . The parameter values calculated are shown in Table 3 and the graphs are in Figs. S3-b. Coefficient of correlation received the highest value of 1.00 to the nearest two decimal places suggesting that chemisorption is the rate determining factor. Moreover, calculated  $q_e$  values using the model (30.08, 30.32, 26.72, 32.03, 30.56, 29.68 mg/g) have much consistency with the experimented values (27, 27.5, 23.97, 28.2, 28.5, 25.9 mg/g) for each adsorption process. Having higher consistency with experimented and calculated  $q_e$  values in PSO model, supports the idea that the PSO model can explain the rate determining step better than PFO model. However, the discrepancy between the values could be due to the other rate determining factors such as variation of dye concentration and unoccupied active site availability that involved with the process as suggested by Mosaffa and collaborators [52].

The Elovich model developed assuming that functional groups in the adsorbent surface are heterogeneous and contain different adsorption energies. Moreover, diffusion of pore spaces and their effect on the adsorption can be understood using the Elovich model. The model explained above under equation 5, and it determines the second order kinetics. As per the results obtained through the graph  $q_t$  vs.  $\ln t$  (given in Figs. S3-c), Elovich model also suggests that the adsorptions follow second order kinetics with higher  $R^2$  values (above 0.9 except GrO adsorption with  $\text{Ni}^{2+}$ ). On the other hand, adsorption rate constant ( $\alpha$ ) determined through the Elovich model explains the rate of the

**Table 3**

Linearized kinetic models, parameter values and units calculated for different adsorption kinetic models.

| Model   | Linear Function                                                       | Parameter (Units)                   | GO                    |                       |                       | GrO                   |                       |                       |
|---------|-----------------------------------------------------------------------|-------------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
|         |                                                                       |                                     | $\text{Cd}^{2+}$      | $\text{Ni}^{2+}$      | $\text{Zn}^{2+}$      | $\text{Cd}^{2+}$      | $\text{Ni}^{2+}$      | $\text{Zn}^{2+}$      |
| PFO     | $\ln(q_e - q_t) = \ln q_{e,cal} - k_1 t$                              | $q_{e,cal}$ (mg/g)                  | 27.56                 | 23.18                 | 19.47                 | 31.84                 | 18.72                 | 21.68                 |
|         |                                                                       | $k_1$ (g/mg.min)                    | $4.20 \times 10^{-3}$ | $3.71 \times 10^{-3}$ | $2.94 \times 10^{-3}$ | $4.13 \times 10^{-3}$ | $3.34 \times 10^{-3}$ | $2.66 \times 10^{-3}$ |
|         |                                                                       | $R^2$                               | 0.98                  | 0.99                  | 0.99                  | 0.98                  | 0.94                  | 0.99                  |
| PSO     | $\frac{t}{q_t} = \frac{1}{k_{obs} q_{e,cal}^2} + \frac{t}{q_{e,cal}}$ | $q_{e,cal}$ (mg/g)                  | 30.08                 | 30.32                 | 26.72                 | 32.03                 | 30.56                 | 29.68                 |
|         |                                                                       | $k_2$ (g/mg.min)                    | $2.27 \times 10^{-4}$ | $2.44 \times 10^{-4}$ | $2.23 \times 10^{-4}$ | $1.76 \times 10^{-4}$ | $3.24 \times 10^{-4}$ | $1.55 \times 10^{-4}$ |
|         |                                                                       | $R^2$                               | 1.00                  | 1.00                  | 1.00                  | 1.00                  | 1.00                  | 1.00                  |
| Elovich | $q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$      | $\alpha$ (mg/g.min)                 | 0.75                  | 0.97                  | 0.65                  | 0.59                  | 2.48                  | 0.38                  |
|         |                                                                       | $\beta$ (g/mg)                      | 0.19                  | 0.20                  | 0.22                  | 0.17                  | 0.23                  | 0.17                  |
|         |                                                                       | $R^2$                               | 0.90                  | 0.90                  | 0.98                  | 0.96                  | 0.85                  | 0.97                  |
| LFD     | $\ln\left(1 - \frac{q_t}{q_e}\right) = -k_{fd} t$                     | $k_{fd}$ (1/min)                    | $4.23 \times 10^{-3}$ | $3.50 \times 10^{-3}$ | $2.68 \times 10^{-3}$ | $4.28 \times 10^{-3}$ | $2.81 \times 10^{-3}$ | $2.44 \times 10^{-3}$ |
|         |                                                                       | $R^2$                               | 0.96                  | 0.99                  | 0.99                  | 0.97                  | 0.93                  | 0.99                  |
| IPD     | $q_t = k_{id} \times t^{0.5} + C$                                     | $K_{id}$ (mg/g.min <sup>0.5</sup> ) | 0.40                  | 0.38                  | 0.35                  | 0.45                  | 0.33                  | 0.45                  |
|         |                                                                       | $C$ (mg/g)                          | 13.29                 | 14.27                 | 11.29                 | 12.49                 | 17.13                 | 9.82                  |
|         |                                                                       | $R^2$                               | 0.81                  | 0.81                  | 0.93                  | 0.90                  | 0.75                  | 0.92                  |
|         |                                                                       | $Q_{e,exp}$ (mg/g)                  | 27.00                 | 27.50                 | 23.97                 | 28.20                 | 28.50                 | 25.90                 |

<sup>a</sup>Experimental conditions: pH = 5.5, Temperature = 25 °C, L/S = 1 L/g, Initial concentration of metal ions = 30 ppm.

adsorption process (parameters given in Table 3). It is possible to observe that  $\text{Ni}^{2+}$  adsorption into GrO is quite faster (2.48 mg/g.min. while the rest is  $< 1.00$  mg/g.min.) than the rest of the adsorption. This fast adsorption could be a reason for the less coefficient of correlation received for the adsorption process with Elovich model. However, considering the ending part of the adsorption process, coefficient of the correlation is above 0.93 in all the cases (even reached 1.00 in the case of GrO with  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$ ). This suggests that the rate can be due to the second order adsorption during the later part of the adsorption process. This suggests that physisorption may start the adsorption process due to the pore spaces at the starting and later, when adsorbates attract to active sites turns the process into the second order adsorption (chemisorption).

Equation 6 in section 3.2.1 explains the LFD model. As per the model, it is assumed that the rate of the adsorption determined by both by the speed of liquid film diffusion around the solid adsorbent and the adsorption of the adsorbates onto the active groups of the adsorptive material. To understand the applicability of the model, the graph was drawn between  $\ln\left(1 - \frac{q_t}{q_e}\right)$  vs.  $t$ . Table 3 contains the parameter values received for the model while Figs. S3–d shows the graph plotted. High  $R^2$  values ( $>0.93$ ) received for the model suggests that the interaction between the liquid film and the adsorbent can also determine the rate of the adsorption. Moreover, Liquid diffusion rate for  $\text{Cd}^{2+}$  is higher with both GO and GrO ( $4.23 \times 10^{-3} \text{ min}^{-1}$  and  $4.28 \times 10^{-3} \text{ min}^{-1}$  respectively) suggesting that higher adsorption rate of  $\text{Cd}^{2+}$  into the adsorbents. The second highest diffusion rate reported by  $\text{Ni}^{2+}$  and the  $\text{Zn}^{2+}$  ( $3.50 \times 10^{-3} \text{ min}^{-1}$ ,  $2.68 \times 10^{-3} \text{ min}^{-1}$  respectively with GO and  $2.81 \times 10^{-3} \text{ min}^{-1}$  and  $2.44 \times 10^{-3} \text{ min}^{-1}$  respectively with GrO). This suggests that  $\text{Cd}^{2+}$  has a higher affinity towards the adsorbents studied followed by  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$ .

Finally, equation 7 explained above deals with IPD model, which suggests the diffusion mechanism can determine the rate limiting factor. A linear graph was drawn ( $q_t$  vs.  $t^{0.5}$ ) to determine the compatibility of the process with the IPD model. Table 3 consist with the important parameters worked out for the model while the graph is given in Figs. S3–e. The low  $R^2$  values received for the graphs compared to the initially studied models, suggest that incompatibility of the IPD model to the adsorption process studied. Nevertheless, close monitoring of the last part of the adsorption process suggest that the  $R^2$  value enhanced. This suggest that intra particle diffusion can be a part of the rate determination of the process at the ending part of the adsorption mechanism. Moreover, higher intercept values received for the model values, suggests that comparably lower thickness of the layers in GrO increasing the mass transfer of the same than the GO [54].

Referring to the graph demonstrated in Fig. S3, it is possible to see that initially adsorption processes are much more likely to follow the PFO model and later it's much adhered to second order graphs like PSO and Elovich models. This suggests that rate of the adsorption process initially controlled by saturation of dye particles in the liquid and the adsorbate. However, when the time passes the rate would be controlled by several other factors like chemisorption and liquid film diffusion rather than the concentration of the metal ions. In physical meaning, initially, as the concentration of the metal ion particles are higher and there is more availability of unoccupied active sites, the concentration variation can undertake a fast adsorption which adhered with the first order adsorption. Nevertheless, as the unoccupied sites and concentration of metal ions is diminishing over time, adsorption rate will be determined by the diffusion of the adsorbate in the liquid film surrounded the functional groups and bonds that involve interactions between molecules [53,54]. This explains the findings of the adsorption kinetic evaluation.

### 3.3.2. Metal ion adsorption isotherms

Five different isotherms; Langmuir (LI), Freundlich (FI), Temkin (TI), Halsey (HI) and Harkins-Jura (HJI) were employed to investigate the

interface correlation between the metal ions;  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  with the two adsorbents (GO and GrO) under equilibrium conditions. Consequently, experimental conditions were set to pH of 5.5, liquid-to-solid ratio of 1 (L/g), stirring speed of 300 rpm at ambient temperature of 25 °C. Initial metal ion concentrations were changed from 30 to 150 ppm to evaluate the highest adsorption capacities as a function of changing initial concentrations. Table 4 reports the linear equations and parameter values obtained for each of the models studied along with the experimental conditions used<sup>4</sup>.

The Langmuir isotherm was built based on monolayer adsorption with sites that have uniform adsorption energies as explained under equation 8. Moreover, it rejects the idea of having intermolecular interactions. To evaluate the applicability of the model to the current metal ion adsorption process, equation 8 was utilized. Accordingly, a graph was drawn using the ratio between equilibrium concentration and adsorption capacity vs. the equilibrium concentration. The obtain graph was reported in Figs. S4–a and the parameter values obtained were reported in Table 4. The  $R^2$  values recorded for the adsorption processes are comparably lower for most of processes. The maximum coefficient of correlation was given by GO with  $\text{Cd}^{2+}$  (0.91) and the minimum coefficient of correlation was reported by GO with  $\text{Zn}^{2+}$  and GrO with  $\text{Ni}^{2+}$  (0.77). However, it is worth understanding that, at lower metal ion concentrations, the adsorption follows the Langmuir model better with higher coefficient of correlation ( $>0.90$  in all cases). For an instant, GO with  $\text{Zn}^{2+}$ , the  $R^2$  was 0.98, and GrO with  $\text{Cd}^{2+}$  the coefficient of correlation was 0.97. Hence, it is possible to assume that the adsorption processes follow the Langmuir model at lower concentrations. Moreover, Considering the separation factor  $R_L$ , it is possible deduce that, the adsorption is much favorable for  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  with both the adsorbents ( $R_L \sim 0.39$  with GO and 0.33 with GrO). However,  $\text{Zn}^{2+}$  adsorption  $R_L$  much closer to 1 (0.65 with GO and 0.52 with GrO) showing less favorability than the other two metal ions considered. Nevertheless,  $\text{Zn}^{2+}$  adsorption is more favorable with GrO than GO given the slightly less  $R_L$  value received. Maximum adsorption capacities (146.41, 154.54, 204.80, 138.54, 152.32, and 171.86 mg/g) modeled by the Langmuir isotherm is not similar to the experimented adsorption capacities (106.77, 111.02, 101.91, 113.15, 116.63, and 104.66 mg/g), limiting the further application of the model fully to the current metal ion adsorption process. Though Langmuir model assumes a monolayer adsorption with uniform adsorption energies, real application could be much more complex than that. Specifically, heterogeneity of the adsorbent sites, variations in the adsorption energies, interactions between adsorbates can influence the experimental maximum adsorption capacities to deviate from the model values. Moreover, ideal conditions assumed by the model do not exist in real life applications influencing the experimental values to be deviated from the expected model values. Further, this suggests that other adsorption mechanisms can be incorporated in the studied sorption process.

Freundlich Isotherm on the other hand hypothesis multilayer adsorption with non-uniform adsorption sites as described under equation 10. The applicability of Freundlich model was also tested with the current adsorption using the graph depicted in Figs. S4–b. The graph resulting from  $\ln q_e$  vs.  $\ln C_e$  was used to work out the important parameters that are given under Table 4. Freundlich isotherm model fitted well with the processes with higher  $R^2$  values. For an instant,  $R^2$  values are 0.98, 0.97, 0.99, 0.95, 0.91, and 0.97 for  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  with GO and  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  respectively. Moreover, it is possible to observe that, the  $R^2$  is much higher if only higher concentrations were considered (0.98, 0.99, 1.00, 0.98, 0.98, and 0.96). This suggests that multilayer adsorption is much preferable for medium to higher concentrations mostly. Heterogeneity factor  $1/n$ , shows that, the adsorption is favorable for all the metal ions considered given the value of  $1/n$  less than 1. Moreover, it is possible to assume that the affinity decreases in the order of  $\text{Ni}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$  ( $1/n = 0.52, 0.51$ , and 0.69 with GO and 0.44, 0.44, and 0.60 with GrO respectively). Also, the affinity of metal ions towards the GrO is higher than GO as the  $1/n$  values

**Table 4**

Different isotherm models used to evaluate along with main parameters, units and calculated parameter values of metal ion adsorption.

| Model | Linear Function                                                                      | Parameter (Units)         | GO               |                  |                  | GrO              |                  |                  |
|-------|--------------------------------------------------------------------------------------|---------------------------|------------------|------------------|------------------|------------------|------------------|------------------|
|       |                                                                                      |                           | Cd <sup>2+</sup> | Ni <sup>2+</sup> | Zn <sup>2+</sup> | Cd <sup>2+</sup> | Ni <sup>2+</sup> | Zn <sup>2+</sup> |
| LI    | $\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}}$                      | q <sub>max</sub> (mg/g)   | 146.41           | 154.54           | 204.80           | 138.54           | 152.32           | 171.86           |
|       |                                                                                      | K <sub>L</sub> (L/mg)     | 0.05             | 0.05             | 0.02             | 0.07             | 0.06             | 0.03             |
|       |                                                                                      | R <sup>2</sup>            | 0.91             | 0.87             | 0.77             | 0.83             | 0.77             | 0.84             |
|       |                                                                                      | R <sub>L</sub>            | 0.40             | 0.39             | 0.65             | 0.32             | 0.34             | 0.52             |
| FI    | $\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$                                            | K <sub>F</sub> (mg/L)     | 14.48            | 15.85            | 6.60             | 19.90            | 21.07            | 10.34            |
|       |                                                                                      | 1/n                       | 0.52             | 0.51             | 0.69             | 0.44             | 0.44             | 0.60             |
|       |                                                                                      | R <sup>2</sup>            | 0.98             | 0.97             | 0.99             | 0.95             | 0.91             | 0.97             |
|       |                                                                                      | q <sub>max</sub> (mg/g)   | 83.99            | 89.85            | 68.30            | 88.03            | 93.19            | 78.29            |
| TI    | $q_e = B_T \ln k_T + B_T \ln C_e$                                                    | B <sub>T</sub> (J/mol)    | 28.92            | 29.17            | 35.51            | 25.03            | 25.42            | 32.33            |
|       |                                                                                      | K <sub>T</sub> (L/mg)     | 0.63             | 0.72             | 0.26             | 1.14             | 1.28             | 0.40             |
|       |                                                                                      | R <sup>2</sup>            | 0.91             | 0.88             | 0.89             | 0.82             | 0.78             | 0.89             |
|       |                                                                                      | n <sub>H</sub>            | -1.93            | -1.96            | -1.46            | -2.29            | -2.29            | -1.68            |
| HI    | $\ln q_e = \frac{1}{n_H} \ln k_H - \frac{1}{n_H} \ln C_e$                            | K <sub>H</sub>            | 175.96           | 225.19           | 15.59            | 934.94           | 1068.08          | 50.61            |
|       |                                                                                      | R <sup>2</sup>            | 0.98             | 0.97             | 0.99             | 0.95             | 0.91             | 0.97             |
|       |                                                                                      | A <sub>HJ</sub>           | 883.78           | 924.62           | 547.03           | 1097.85          | 1114.35          | 711.98           |
|       |                                                                                      | B <sub>HJ</sub>           | 1.57             | 1.54             | 1.63             | 1.56             | 1.52             | 1.59             |
| HJI   | $\frac{1}{q_e^2} = \frac{B_{HJ}}{A_{HJ}} - \left( \frac{1}{A_{HJ}} \right) \log C_e$ | R <sup>2</sup>            | 0.92             | 0.94             | 0.92             | 0.97             | 0.98             | 0.94             |
|       |                                                                                      | q <sub>esmax</sub> (mg/g) | 106.77           | 111.02           | 101.91           | 113.15           | 116.63           | 104.66           |

<sup>a</sup>Experimental conditions: pH = 5.5, Temperature = 25 °C, L/S = 1 L/g, Initial concentration of metal ions = 30–150 ppm.

received are comparably lower for GrO with metal ions. This further confirms by the Freundlich rate constant received for each metal ion adsorption with the adsorbents. Further, analysis of the value of “n” can provide information about the heterogeneity of the surface [55]. The higher values (n > 1) received for the heterogeneity factor “n” suggests that the functional groups available in the adsorbent surfaces are heterogeneous and contains different adsorption energies.

Temkin’s model is described under equation 11, section 3.2.2. According to Temkin’s model, indirect coordination of the adsorbate and the adsorbent produce the heat of adsorption which linearly decreases as the coverage of the adsorption sites increases. Figs. S4–c was developed based on the linear equation of the Temkin’s model taking q<sub>e</sub> on the y-axis and ln C<sub>e</sub> on the x-axis. The parameters calculated for Temkin’s model were depicted under Table 4. Though R<sup>2</sup> values received for the model (varies from 0.78 to 0.91) are not very high like Freundlich model, it is possible to observe that for higher concentrations the R<sup>2</sup> value is comparably higher (varies from 0.94 to 0.99). This suggests that there is a possibility of linear decline of heat of energy of the adsorption process at higher concentrations, elevating the adsorption. Moreover, Lower values received for the BT (heat of adsorption) suggest that the adsorption process is favorable. In fact, the favorability of the adsorption decreases in the order of, Cd<sup>2+</sup> > Ni<sup>2+</sup> > Zn<sup>2+</sup> in both the cases of GO and GrO. Moreover, the favorability of metal adsorption towards the GrO is higher than that of GO according to the BT values received. Though the model provides useful information about the adsorption process under many aspects, the values received for the b<sub>T</sub> (Temkin isotherm exponent) according to the equation (12) are higher than 1 in all cases. This limits the applicability of the model alone to the current metal ion adsorption.

The Halsey isotherm model, which is built upon the base of heterogeneous functional groups availability in the adsorbents as explained under section 3.2.2, equation 13 was also employed to assess the adsorption process in question. It further assumes that heterogeneity of functional groups supports multilayer adsorption of adsorbates on to the adsorbent surface. The graph ln q<sub>e</sub> vs. ln C<sub>e</sub> was used to determine the Halsey isotherm constant (k<sub>H</sub>) and Halsey equilibrium exponent (n<sub>H</sub>) as per Figs. S4–d. Table 4 shows the parameters calculated for the model. High coefficient of correlations (>0.91 in all cases) received for each of the graphs confirms the applicability of the Halsey model to the metal adsorption mechanism confirming a greater heterogeneity of adsorption sites. The Halsey Isotherm constant values received confirms that the affinity of Ni<sup>2+</sup> is significantly higher towards GrO (k<sub>H</sub> = 1068.08) than the other metals. Zn<sup>2+</sup> affinity to GO (k<sub>H</sub> = 15.59) is the lowest among.

Comparing the two adsorbents, GrO (k<sub>Hcd</sub> = 934.94, k<sub>Hni</sub> = 1068.96, k<sub>Hzn</sub> = 50.61) seems to be more efficient in adsorbing metal ions than GO (k<sub>Hcd</sub> = 175.96, k<sub>Hni</sub> = 225.19, k<sub>Hzn</sub> = 15.59) with significantly high k<sub>H</sub> values received. However, values calculated for n<sub>H</sub> become negative as the slope of the graph shows a positive relationship which limits the applicability of the model to adsorption mechanism.

Applicability of Harkins-Jura’s Isotherm model was also examined using the graph between  $\frac{1}{q_e^2}$  and log C<sub>e</sub> according to equation 14. The model assumes a heterogeneous adsorption with different affinity towards multi sized pore spaces. Moreover, the model is able to predict both monolayer and multilayer adsorptions through its parameter. The parameter values received for the model were given in Table 4, while the graph is shown in Figs. S4–e. High R<sup>2</sup> values (>0.92) received for the model confirms the applicability of the model to the current adsorption mechanism. Accordingly, parameter A<sub>HJ</sub> gives an implication on the heterogeneity and the surface area of the adsorbent and B<sub>HJ</sub> shows the affinity of the adsorption via monolayer heat of adsorption [56,63]. GrO shows very high surface areas with the highest heterogeneity as per the high values received for the heterogeneity factor (for GrO with Cd<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup> A<sub>HJ</sub> = 1097.85, 1114.35, 711.98 while for GO, A<sub>HJ</sub> = 883.78, 924.62, 547.03 respectively). Among the metal ions, higher adsorption can be seen from Ni<sup>2+</sup> given the high A<sub>HJ</sub> values received. On the other hand, low monolayer heat of adsorption values reported for the model indicates that monolayer adsorptions are also possible. The monolayer heat of adsorption is lowest in GrO with different metal ions (For GrO B<sub>HJ</sub> = 1.56, 1.52 and 1.59 for Cd<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup> respectively, For GO B<sub>HJ</sub> = 1.57, 1.54 and 1.63 for Cd<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup> respectively). However, observed slight changes in B<sub>HJ</sub> values indicate that the heat of monolayer adsorption is the same for both the adsorbent materials. Hence, considering both the parameters it is safe to say that the adsorption is mainly governed by heterogeneity of the active sites and pore sizes which leads to multilayer adsorption of metal ions.

Considering the coefficient of correlation values obtained for the different isotherms studied, it is possible to order the isotherms that best describes the adsorption of metal ions to the adsorbents. Accordingly, Freundlich > Halsey > Harkins-Jura > Temkin > Langmuir explains the adsorption in the decreasing order. Hence, authors are confident enough to conclude that, the adsorption follows the Freundlich model (2nd order) isotherms the best. However, with the other findings and partial analysis of R<sup>2</sup> values indicate that, it is possible for the metal ion adsorption to follow physisorption at lower concentrations.

Table 4 has given the maximum adsorption values for each metal ion with each adsorbent according to the Freundlich model calculated

through equation (15). Further, Table S2 compares the maximum adsorption capacities of other similar carbon-based materials with the current study values. As per the results reported by other authors, the adsorption materials synthesized in this study shows a competitive adsorption capacity (for GO = 88.03, 93.19, 78.29 mg/g while GrO = 83.99, 89.85, 68.30 mg/g with  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  respectively). Maximum adsorption capacities for metal ion adsorption are comparably lower than dye waste adsorption values. This is due to the size of the ionic radii of the metal ions and their comparably high charge density [64]. Moreover, the affinity of functional groups for the dye waste can be higher than that of metal ions [65]. However, comparing metal ion adsorption of this study with existing studies, the reported values for the maximum adsorption capacities varies in a very high range. For instance, Murphy et al. (2023) reported 76.3, 45.5, and 32.6 mg/g ( $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  respectively) maximum adsorption capacities for a dosage of 0.025 g/L which is 40 times lower than the dosage used in this study [63]. Moreover, Chen et al. (2020) reported only 3.25 mg/g maximum adsorption capacity with  $\text{Ni}^{2+}$  for a dose of 0.25 g/L [66]. However, the maximum adsorption values we received in this study consist within the average values found in literature. Nevertheless, considering the maximum adsorption capacity with dye waste and metal ions in the current study, it is safe to say that the modified materials have a higher affinity towards the dye waste rather than metal ion adsorption. Key findings of the kinetic and isotherm analysis for each adsorbent across pollutants were briefly given in Table 5.

### 3.4. Evaluation of adsorption mechanism

The study was carried out using mono-elementary synthetic solutions to evaluate the performance and mechanisms of the adsorption process of the newly modified adsorbent materials. It is important to note that, if used multi-elementary solutions, it would be difficult to assess the mechanisms of the adsorption due to complexity arise according to the many elements contain in the solution.

According to the FTIR analysis (Fig. 4) (4000–400  $\text{cm}^{-1}$  range at 4  $\text{cm}^{-1}$  resolutions) of the adsorbent materials, it is possible to understand that the availability of functional groups such like epoxide (C–O–C) at 1065–1226  $\text{cm}^{-1}$ , hydroxyl (–OH) at 3254–3420  $\text{cm}^{-1}$ , carbonyl (–C=O) at 1622–1739  $\text{cm}^{-1}$  and carboxyl (–C–OH) at 951–1015  $\text{cm}^{-1}$  which are readily disperse in aqueous solution and make the solution negatively charged. This finding is also in line with the latest publication by Fauziyah et al. (2023) [67]. Hence, cationic dyes and the cations which act as positively charged ions can easily absorb onto adsorbents through electrostatic bonding. Moreover, Pi–Pi bonding is another key factor that

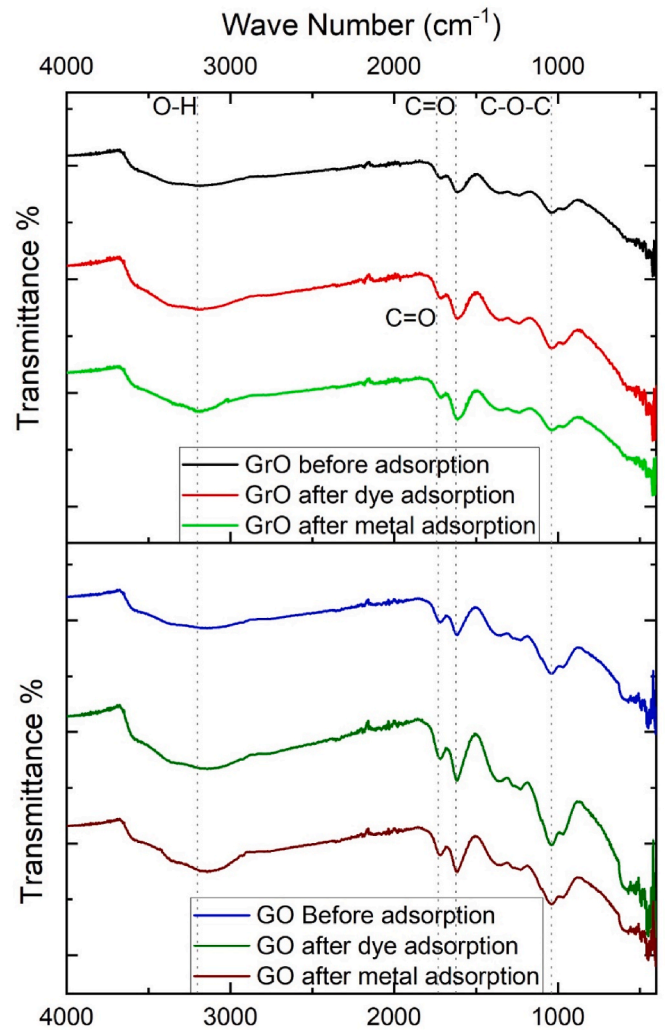


Fig. 4. FTIR analysis of the two adsorbent materials GrO and GO before and after the adsorption of dye and metal ions.

enhances the adsorption capacity of the considered graphite-based adsorbents. Aromatic rings of the dye and the adsorbent materials can interact with each other through Pi–Pi bonding. Nevertheless, Pi–Pi

Table 5

Key findings of the adsorbent materials across pollutants.

| Pollutant type | GrO                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | GO                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |
|----------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Dye pollutants | <ul style="list-style-type: none"> <li>Initial rate determinant governs by multiple mechanisms (both physisorption and chemisorption)</li> <li>Chemisorption and liquid film diffusion responsible for the rate determination at the ending</li> <li>Multilayer adsorption is highly probable at higher concentrations as the surface of the adsorbent is heterogeneous.</li> <li>Both functional groups and pore spaces distribution are responsible for the adsorption.</li> <li>Lower layer thickness.</li> <li>Very high adsorption.</li> <li>Higher affinity towards MB.</li> </ul> | <ul style="list-style-type: none"> <li>Rate determination mainly governs by second order kinetics throughout the process (Chemisorption and liquid film diffusion).</li> <li>Fast adsorption than GrO in the first few minutes.</li> <li>Multilayer adsorption is prominent, active sites have considerable differences and adsorption energies.</li> <li>Availability of functional groups mainly responsible for the adsorption.</li> <li>The thickness of the layer is higher than GrO.</li> <li>Relatively lower adsorption than GrO.</li> <li>Higher affinity towards MB</li> </ul> |
| Metal ions     | <ul style="list-style-type: none"> <li>Overall rate of adsorption is determined by Chemisorption.</li> <li>Initially, physisorption can make the adsorption faster.</li> <li>Multilayer adsorption is observed.</li> <li>Both functional groups and pore spaces are responsible for the absorption.</li> <li>Low adsorption than dye pollutants govern by the size of the atomic radii, changes in the charge and affinity.</li> <li>Relatively higher affinity towards <math>\text{Ni}^{2+}</math>.</li> </ul>                                                                          | <ul style="list-style-type: none"> <li>Initial fast adsorption due to multiple mechanisms, mainly physisorption and chemisorption.</li> <li>As per the ending, the influence of chemisorption and liquid film diffusion is higher.</li> <li>Multilayer adsorption.</li> <li>Functional groups are responsible for the adsorption.</li> <li>Low affinity towards the metal ion than dye pollutants.</li> <li>Relatively higher affinity towards <math>\text{Ni}^{2+}</math>.</li> </ul>                                                                                                   |

interactions can also occur between aromatic rings of the metal ions and the surface of the adsorbents. Also, all the adsorbents contain H containing hydroxyl groups on their surfaces which can induce H-bonding with the cationic dyes.

Mostly, N and S atoms in MB and MG cationic dyes may act as H-bonding acceptors. Another main reason to have higher adsorption between metallic ions with adsorbents is coordination bonding. Since, adsorbent surface contains more O containing functional groups, coordination bonding can occur through the donation of electron pairs from O atoms to the metal ions forming a stable complex. This is also visible through the differences between the intensities of each functional group before and after the adsorption processes. In addition, given the structure of the graphite materials, interplanar Vander-walls forces can also interact with dye particles that can also affect absorbing the dye particles. Another important factor for the observed high adsorption of modified materials is the pore size distribution. The approximate size of dye particles is 1.2–1.8 nm and for metals it is even less. The pore size of meso-porous materials such like graphite derivatives vary between 2 and 50 nm [68]. Hence, dye particles and metal ions can trap inside the pores of adsorbents making the adsorption of the same very high. These mechanisms are also validated by previous studies [36,51,69,70].

GrO has a slightly lower number of adsorption sites compared to GO as per the intensities of the FTIR analysis. However, GrO showed very high adsorption towards cationic dyes and metallic ions, even though it has lower number of active sites than GO. The main reasons for this

observation could be the larger surface area and high porosity of GrO. It has a relatively higher surface area giving a higher number of accessible sites for organic dye and metals owing to the exfoliated structure. This can be further convinced by the adsorption isotherm (Harkins-Jura isotherm findings) studies carried out previously. Also, expanded nature provides more pores that can trap pollutants inside enhancing the adsorption capacity. Moreover, it is studied that the reactivity of the GrO is higher than GO due to its high oxygen contain monolayer structure and can contribute to its high hydrophilic nature and excellent ion-exchange capacity [71].

Fig. 5 depicts a possible adsorption mechanism that explains the arguments made above. In figure D' stands for cationic dye while M' stands for the metallic ion and the red dot represents metal or dye pollutants.

The results and the discussion support the idea that the waste graphite recovered from spent LiBs are a better source to synthesis of adsorption materials such as graphite oxide or graphene oxide. Also, better results can be expected from such prepared materials than the commercially available ones as the interlayer spacings have a slight expansion than natural graphite leading to easy oxidation. The adsorption material can be used for dye waste removal more efficiently than the metal ion removal due to high maximum adsorption capacities received with dye pollutants. The adsorption will be mainly governed by chemisorption. However, the effect of physisorption also provides considerable support for the process.

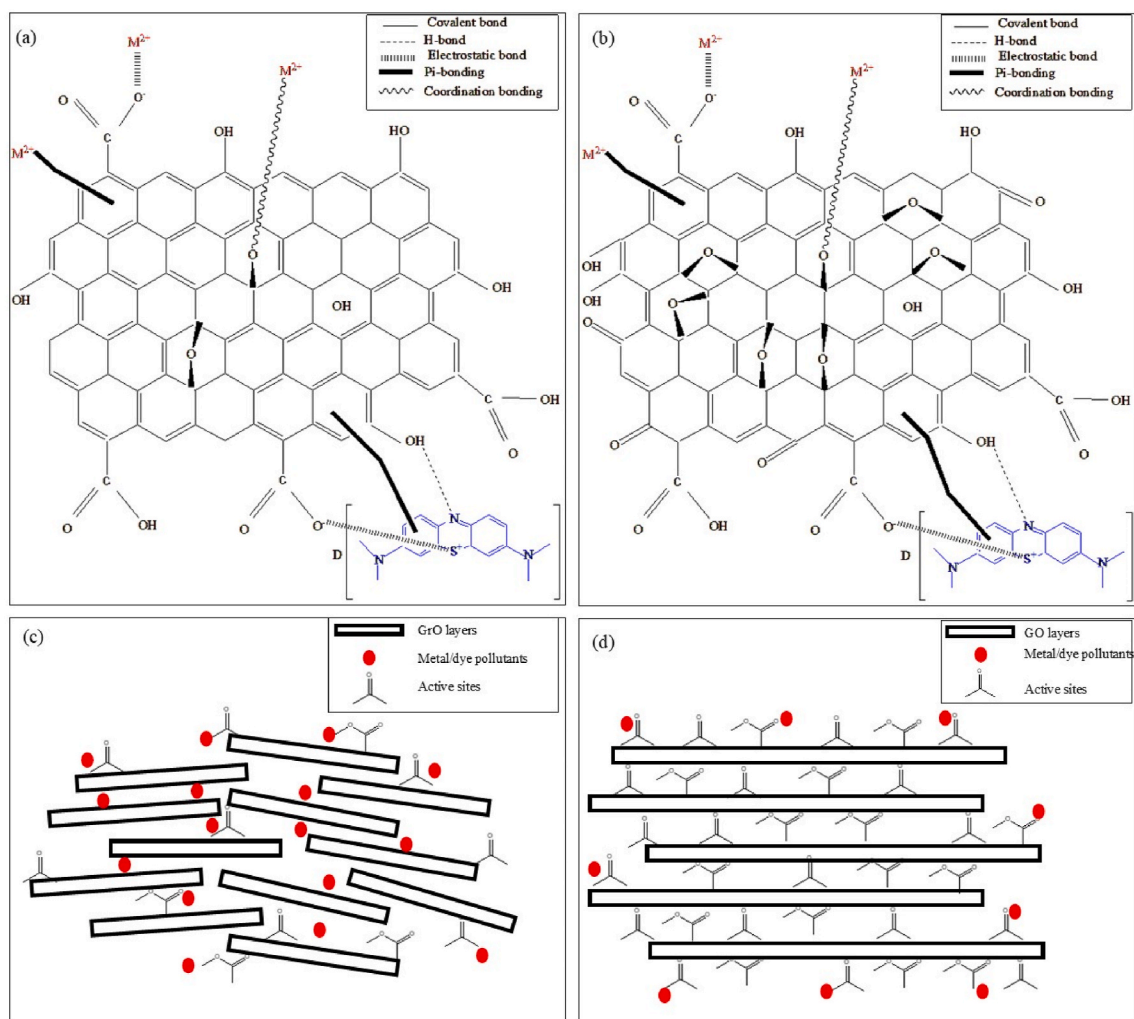


**Fig. 5.** Possible adsorption mechanisms by (a) Graphene oxide surface active sites (b) Graphite oxide surface active sites with cationic dyes (as D) and metallic ions (as  $M^{2+}$ ) (c) graphene oxide adsorption through cross section (d) graphite oxide adsorption through cross section.

#### 4. Conclusions

The graphite was recovered from spent LiBs through a real-life hydrometallurgical route. Graphite was modified using chemical oxidation, to produce value-added materials such as graphite oxide and graphene oxide. Characterization of the produced adsorbents showed synthesis of desired materials with higher quality than the commercially available substances. The main reason for better synthesis is identified to be the expanded nature of the used-up graphite as it was subjected to continuous charge and discharge cycles. Graphite oxide showed high oxidization and higher number of functional groups further identified through the FTIR analysis. Graphene oxide was shown to be having less functional groups but higher surface area with high porosity due to the ultrasonic vibration. The best adsorption was shown by GrO and in the case of dye waste, the adsorption rate was at around 95 % with 30 ppm dye concentration, and for metallic ions around 94 % at 30 ppm concentration. Kinetic analysis revealed, rate determinant factor of the overall process is chemisorption. However, initial, high concentration of dye or metal ion can lead to physisorption during the first few minutes. Dye adsorption of the adsorbents occurred in 10 min; nevertheless, metal ion adsorption took around 24 h to complete. Isotherm analysis showed that, adsorbent contain heterogenous structure with different adsorption energies. Multilayer adsorption was shown by graphene oxide due to the availability of functional groups and pore spaces. Graphite oxide seems to have different functional groups that drive it to show multilayer adsorption. High affinity towards the dye adsorption was shown by the adsorbents with the best adsorption between methylene blue and graphene oxide.  $\text{Ni}^{2+}$  absorbed the best to graphene oxide than other metal ions. The highest adsorption capacity with dye waste was shown by GO at 616.99 mg/g for MG and 558.49 mg/g for MG. In the case of metallic ions, the highest adsorption capacities were shown by GrO with  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$ ; 88.03, 93.19, 78.29 mg/g respectively. Compared to existing maximum adsorption materials, the synthesized material showed higher capacities, attributed to the possibility of preparing high quality adsorption material from spent graphite. This is mainly because waste graphite from spent LiBs shows slightly exfoliated nature than natural graphite making it easier to generate value-added materials like graphite oxide and graphene oxide.

##### 4.1. Future perspectives

Synthesis of the adsorption materials using chemical oxidation is convenient over the other existing processes. However, it is vital to understand the scalability of production of such materials in industrial applications. In doing so, economic criteria, and production efficiency compared to natural graphite need to be considered.

The current study evaluates the reusability of the waste graphite that derived from EoL LiBs using single component systems. In real life, wastewater contains multi-component systems. However, most dye adsorption experiments that are undertaken for multi-component systems show synergistic effect with various carbon-based adsorbents [72, 73]. Nevertheless, it would be better to understand experimentally, how the modified adsorbent materials in this study would behave with multi-component systems with possible synergistic or antagonistic effects.

Reusability and recyclability of the materials synthesized is also an important practical consideration. It would be beneficial to understand the performance of the adsorbent materials studied here with possible cost-effective regeneration methods as a future study.

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#### CRediT authorship contribution statement

**Dilshan Sandaruwan Premathilake:** Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. **Francesca Colombi:** Investigation. **Amilton Barbosa Botelho Junior:** Writing – review & editing, Validation, Resources. **Jorge Alberto Soares Tenório:** Supervision, Funding acquisition. **Denise Croce Romano Espinosa:** Supervision, Funding acquisition. **Mentore Vaccari:** Supervision, Funding acquisition.

#### Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Mentore Vaccari reports financial support was provided by Italian Ministry of Foreign Affairs and International Cooperation. Jorge Alberto Soares Tenorio reports financial support was provided by Fundação de Amparo à Pesquisa do Estado de São Paulo and Capes. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.rineng.2024.102232>.

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