

## Article

# Decoloration of Waste Cooking Oil by Maghnia Algerian Clays via Ion Exchange and Surface Adsorption

Abdelhak Serouri <sup>1</sup>, Zoubida Taleb <sup>1,\*</sup>, Alberto Mannu <sup>2,3,\*</sup>, Chahineze Nawel Kedir <sup>4,5</sup>, Cherifa Hakima Memou <sup>6</sup>, Sebastiano Garroni <sup>7</sup>, Andrea Mele <sup>8</sup>, Oussama Zinai <sup>1</sup> and Safia Taleb <sup>9</sup>

- <sup>1</sup> Laboratory of Materials & Catalysis, Faculty of Exact Sciences, Djillali Liabes University, Sidi Bel Abbès W-22000, Algeria; serouriabdelhak@gmail.com (A.S.); ouss.zinai48@gmail.com (O.Z.)
- <sup>2</sup> Chemistry for Technologies Laboratory, University of Brescia, 25123 Brescia, Italy
- <sup>3</sup> INSTM and Chemistry for Technologies Laboratory, University of Brescia, Via Branze 38, 25123 Brescia, Italy
- <sup>4</sup> Department of Chemical and Physical Sciences, Materials Institute, University of Alicante (UA), 03080 Alicante, Spain; kedir.nawel@hotmail.fr
- <sup>5</sup> LSTE Laboratory, University of Mustapha Stambouli Mascara, Mascara W-29000, Algeria
- <sup>6</sup> Laboratory of Physical and Macromolecular Organic Chemistry, Faculty of Exact Sciences, Djillali Liabes University, Sidi Bel Abbès W-22000, Algeria; cherifa\_h1996@yahoo.fr
- <sup>7</sup> Department of Chemical, Physics, Mathematics and Natural Science, INSTM, University of Sassari, Via Vienna 2, 07100 Sassari, Italy; sgarroni@uniss.it
- <sup>8</sup> Department of Chemistry, Politecnico di Milano, Materials and Chemical Engineering “Giulio Natta”, 20133 Milan, Italy; andrea.mele@polimi.it
- <sup>9</sup> Water Academy, 1 Street Miollis, 75015 Paris, France; safiatat@yahoo.fr
- \* Correspondence: zoubidataleb@yahoo.fr (Z.T.); alberto.mannu@unibs.it (A.M.)

Academic Editor: George Z. Papageorgiou

Received: 15 March 2025

Revised: 20 April 2025

Accepted: 12 May 2025

Published: 16 May 2025

**Citation:** Serouri, A.; Taleb, Z.; Mannu, A.; Kedir, C.N.; Memou, C.H.; Garroni, S.; Mele, A.; Zinai, O.; Taleb, S. Decoloration of Waste Cooking Oil by Maghnia Algerian Clays via Ion Exchange and Surface Adsorption. *ChemEngineering* **2025**, *9*, 50. <https://doi.org/10.3390/chemengineering9030050>

**Copyright:** © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

**Abstract:** The purification of waste cooking oils (WCOs) through clay-based adsorption is an established recycling method, yet the relationship between clay composition and adsorption efficiency remains an area of active research. The aim of the present research work was to assess the performance of Maghnia bentonite in WCO decoloration and to gain information about the specific refining process. Thus, natural bentonite from the Maghnia region (Algeria) was investigated as an adsorbent for WCO refining for biolubricant production. The adsorption efficiency was evaluated under different conditions, achieving up to 70% decolorization at 10 wt% clay after 4 h of treatment. Structural characterization of the bentonite before and after adsorption was conducted using FT-IR spectroscopy, powder X-ray diffraction (XRD), and X-ray fluorescence (XRF) to assess compositional and morphological changes. FT-IR analysis confirmed the adsorption of organic compounds, XRD indicated minor alterations in interlayer spacing, and XRF revealed ion exchange mechanisms, including a reduction in sodium and magnesium and an increase in calcium and potassium. Adsorption kinetics followed a pseudo-second-order model, with desorption effects observed at prolonged contact times. The pHPZC of 8.3 suggested that bentonite adsorption efficiency is enhanced under acidic conditions. The high decoloration capacity of Maghnia bentonite, combined with the availability and the low cost of the material, suggests a possible industrial application of this material for WCO refinement, especially in lubricant production.

**Keywords:** waste cooking oil; decoloration; bentonite; adsorption; ion exchange

## 1. Introduction

The increasing consumption of fried foods in households and the food industry has led to a significant rise in the production of waste cooking oils (WCOs). Improper disposal of WCOs can cause severe environmental pollution, particularly by contaminating water sources and contributing to soil degradation. However, their recycling offers an opportunity to integrate these waste materials into a circular economy, reducing environmental impact while generating valuable by-products. WCOs are mainly composed of triglycerides, along with varying amounts of free fatty acids (FFAs), oxidation products, volatile organic compounds, and contaminants such as metals and food residues [1,2]. Their purification is crucial for repurposing them in industrial applications, including biofuels, lubricants, and chemical feedstocks [3–6]. Among the various purification methods, adsorption using natural and modified clays has gained significant attention due to its efficiency, cost-effectiveness, and environmental sustainability [7].

Among the various purification methods, adsorption using natural and modified clays has emerged as a highly effective and sustainable approach [8]. Bentonite, in particular, has been widely used for decolorization and impurity removal in vegetable oil refining due to its high surface area, cation exchange capacity, and controllable adsorption properties [9,10]. Several studies have demonstrated that the adsorption efficiency of bentonites depends on their structural and textural characteristics, which influence their ability to retain specific organic molecules [11,12]. Different bentonites, depending on their composition and activation treatments, exhibit selective affinities for various impurities, making them versatile materials for (waste) oil purification [13–16]. For example, bentonite clay was used at different concentrations to treat mustard oil, which was used in the continuous frying of potato chips. Response surface methodology was employed to optimize the effects of process parameters (contact time, heating time, and adsorbent concentration) on residual free fatty acid (FFA) levels. The optimized conditions were determined as 10 h for contact time and heating time, and 0.4 g/L for adsorbent concentration, which helped maintain FFA levels below the permissible limit. The results indicated that FFA adsorption followed a pseudo-second-order model, with strong agreement between the calculated and experimental data. The Langmuir adsorption model was found to be suitable for correlating the equilibrium data in this study [17]. Egbuna et al. [18] reported an investigation of the adsorption mechanism involved in the bleaching of palm oil using activated clay. A locally sourced clay from Inyi, Oji River Province, in Enugu State was activated with Tetraoxosulphate (VI) acid. Based on the obtained results, a mechanism for the bleaching of palm oil using the activated clay was developed, and the stability of the oil was assessed through various parameters, including a free fatty acid (FFA) content of 0.12%, peroxide value (PV) of 3.0 meq/kg, anisidine value (AV) of 4.55 meq/kg, iodine value (IV) of 48, iron (Fe) content of  $4.3 \times 10^3$  ppm, and phosphorus content of 0.015 ppm. The findings indicated that the acid activation enhanced the bleaching efficiency of the activated clay [19].

Despite these advances, most studies have focused on synthetic modified bentonites, often requiring complex activation procedures that may limit their industrial applicability. Moreover, the correlation between the morphological properties of bentonite and its adsorption efficiency remains an area of active research. In this context, the present study investigates, for the first time, the purification potential of a commercially available Algerian bentonite from the Maghnia region for WCO treatment. The adsorption performance of this natural clay is evaluated under different conditions, using oil decolorization as a key performance indicator. A comprehensive characterization of the bentonite before and after adsorption is conducted using Fourier transform infrared (FT-IR) spectroscopy, powder X-ray diffraction (XRD), and X-ray fluorescence (XRF). The structural and compositional changes are analyzed to better understand the adsorption mechanisms

involved, providing insights into the industrial feasibility of using commercial Algerian bentonite for large-scale WCO purification. Thus, this study aims to evaluate the adsorption efficiency and structural behavior of natural Maghnia bentonite as a low-cost and sustainable clarifying agent for the purification of waste cooking oils, with a focus on decolorization performance and the underlying physicochemical interactions.

## 2. Materials and Methods

### 2.1. Raw Materials

Edible frying oil under the commercial brand “Elio” (Algerian market) and composed of a blend of 80% soya and 20% sunflower oils was used for the present study. The oil was used for at least ten cycles of deep frying. A natural bentonite clay extracted from a natural cave in the Maghnia region in western Algeria and commercialized by National Company of Non-Ferrous Mining Products (ENOF) was used for the present study.

### 2.2. Adsorption Protocol

An amount of 100 g of waste cooking oil was placed in a glass beaker (for typical experiments, a 250 mL beaker volume was sufficient). Then, the mixture was stirred using a Lab Tech® Daihan Labtech Co., Ltd. (HTDS, USA) equipped with a magnetic bar. The experiments were conducted at room temperature. After processing, the mixture was centrifuged with an Apogee Swing-3000 Horizontal Centrifuge (HTDS, USA) at 2700 rpm for 15 min.

### 2.3. UV-VIS Color Analysis

For UV-VIS analyses, a Perkin-Elmer spectrophotometer (model Lambda 45) (HTDS, USA) dual beam, operating over a range of 200–700 nm, was used. The samples were analyzed in a cuvette with 1 cm of path length.

The adsorption performance of the bentonite was measured by decoloration yield, which was calculated according to Equation (1) [20].

$$\text{Yields (\%)} = \frac{A_0 - A}{A_0} \times 100 \quad (1)$$

In Equation (1), the terms  $A$  and  $A_0$  represent, respectively, the absorbance of the treated and untreated oil at  $\lambda_{\text{max}} = 269.05$  nm. The value of  $A_0$  corresponds to 0.744 nm.

### 2.4. FT-IR Analysis

A Perkin Elmer Frontier FT-IR spectrometer was used across a range of 4000–400  $\text{cm}^{-1}$  with a resolution of 1  $\text{cm}^{-1}$  (Model SPECTRUM 100, from the USA manufacturer represented, in Algeria, by the commercial company HTDS), for the spectroscopic characterization of the bentonite prior to and after processing.

### 2.5. X-Ray Diffraction (XRD) Analysis

Powder XRD (PXRD) analyses were conducted using a PROTO diffractometer (HTDS, USA) equipped with a CuK radiation source ( $\lambda = 1.540593$ ) at various angles of incidence at a voltage of 30 kV and an intensity of 20 mA (scan time 2 h and 36 min.).

Data were collected at room temperature (25 °C), from 5.00° to 80° in  $2\theta$  with a step size of 0.05°.

### 2.6. X-Ray Fluorescence Analysis

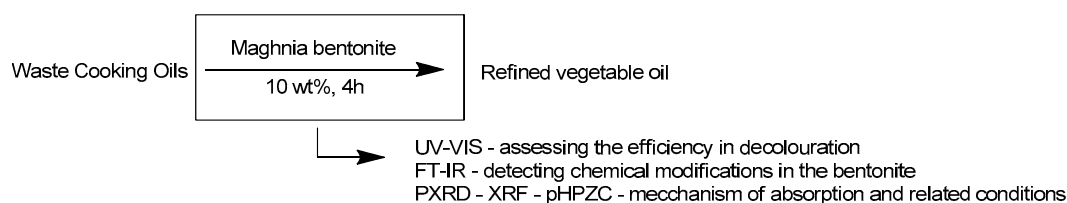
Elemental chemical analyses of the clay samples (before and after oil processing) were carried out using a BRUKER M4 TORNADO micro-XRF benchtop instrument

(HTDS, USA), with a 50 KV wavelength dispersion equipped with a Rh X-ray tube and a polycapillary lens with a 20  $\mu\text{m}$  spot.

### 2.7. pH at Point of Zero Charge (pHPZC) Determination

The pHPZC of the pristine and exhausted bentonite samples was determined to evaluate changes in surface charge properties due to the adsorption of waste cooking oil (WCO). The pHPZC was measured using the drift method, where bentonite samples were suspended in 0.01 M NaCl solutions with initial pH values ranging from 2 to 12. The suspensions were stirred for 24 h, and the final pH was recorded.

A general summary of the process herein studied and the related analytical techniques involved is reported in Scheme 1.

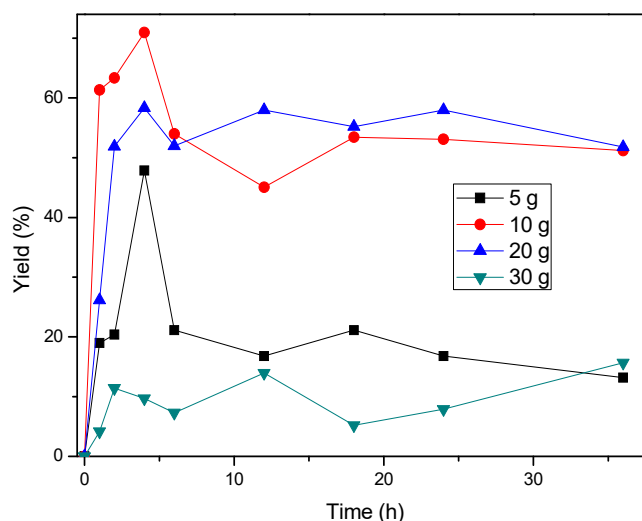


**Scheme 1.** General workflow.

## 3. Results

### 3.1. Adsorption Kinetics Assessment

Adsorption experiments were conducted using four different bentonite concentrations (5 wt%, 10 wt%, 20 wt%, and 30 wt% relative to the WCO mass). The variation in oil color over time was monitored using UV-VIS spectroscopy for up to 36 h. The results are presented in Figure 1.



**Figure 1.** Decoloration yields over time during the processing of WCO with different amounts of clay.

As shown in Figure 1, a similar adsorption behavior was observed over time for the 5 wt%, 10 wt%, and 20 wt% bentonite treatments. In all three cases, maximum decolorization was achieved after 4 h of stirring, with the highest decolorization yield (71%) obtained

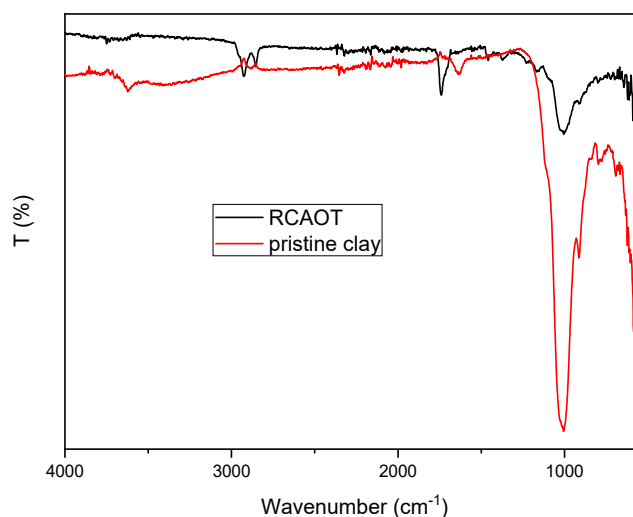
at 10 wt% bentonite. However, beyond this point, adsorption efficiency declined, likely due to particle agglomeration, which reduces the available surface area for adsorption. Additionally, these agglomerates may create diffusion barriers, preventing oil impurities from reaching active sites on the clay particles, thus diminishing the overall adsorption capacity [20–22]. Between 4 and 12 h, a noticeable decrease in adsorption efficiency was observed, suggesting desorption phenomena or complex interactions between the oil components and the clay surface. This behavior indicates that the adsorption mechanism is likely physical and reversible, with prolonged stirring leading to the release of previously adsorbed molecules. However, for extended contact times (>12 h), a secondary increase in adsorption efficiency was observed for the 5 wt%, 10 wt%, and 20 wt% samples. This could be attributed to the reintroduction of oil impurities into the interlayer spaces and external surfaces of the clay.

When 30 wt% of bentonite loading was used, the kinetic profile differed significantly. The maximum decolorization yield was only achieved after 11 h of contact time, with oscillatory adsorption–desorption kinetics observed between 0 and 25 h. This result suggests that excessive clay loading may lead to particle clustering, reducing adsorption efficiency in the early stages of treatment.

Overall, these findings confirm that bentonite is an effective adsorbent for WCO treatment, with optimal decolorization occurring at 10 wt% clay concentration within 4 h of treatment. However, prolonged contact times and excessive clay dosages may negatively affect adsorption efficiency due to agglomeration and potential desorption mechanisms.

### 3.2. Chemical Modification Investigation Through FTIR

The structural characteristics of both pristine and exhausted bentonite samples were analyzed using Fourier transform infrared (FT-IR) spectroscopy, as shown in Figure 2.



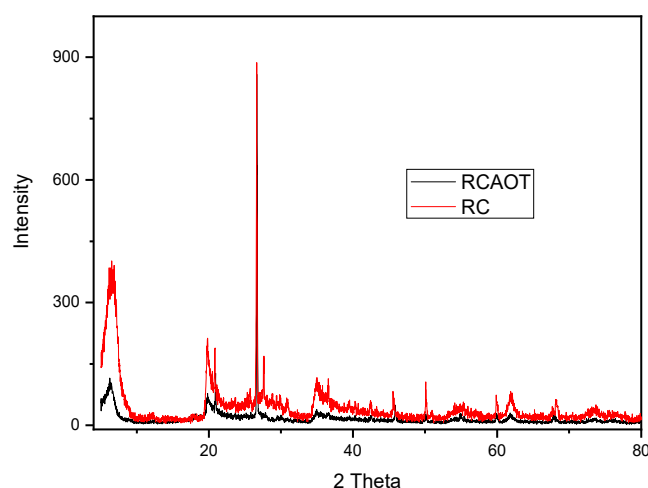
**Figure 2.** FTIR spectra of pristine clay (red line) and after oil processing (exhausted clay, black line) between 400 and 4000  $\text{cm}^{-1}$ .

The absorption profiles before and after waste oil processing are in line with the same analysis reported for similar bentonites [23,24]. In particular, the most relevant bands were attributed to O-H and Si-O bonds: stretching vibrations of the structural OH groups of montmorillonite show typical bands between 3700 and 3200  $\text{cm}^{-1}$ , the bending vibration of adsorbed water (-OH) is observed at 1640  $\text{cm}^{-1}$ , and, finally, the perpendicular Si-O

vibrations are observed near  $1100\text{ cm}^{-1}$ . Comparison of the FT-IR spectra of the samples before and after oil processing (pristine and exhausted clay) indicates a decrease in the Si-O intensity and disappearance of the two O-H bands. On the other hand, new absorption bands appear at  $2925$  and  $2855\text{ cm}^{-1}$ , which can be attributed to the asymmetric and symmetric stretching of the  $-\text{CH}_2$  moiety. An additional band, situated at  $1740\text{ cm}^{-1}$ , is characteristic of C=O stretching. These spectral modifications suggest that the adsorption process involves strong interactions between the clay's surface functional groups and the organic compounds in WCO, leading to structural changes in the bentonite. The presence of hydrocarbon and carbonyl bands in the exhausted clay confirms the retention of oil-derived impurities, reinforcing the clay's effectiveness as an adsorbent.

### 3.3. Structural Investigation by Powder X-Ray Analysis

Powder X-ray diffraction (PXRD) analysis was conducted to investigate the crystallographic structure of the bentonite before and after adsorption. The corresponding diffractograms are shown in Figure 3, while the major identified phases and their respective diffraction angles ( $2\theta$ ) are summarized in Table 1.



**Figure 3.** PXRD diffractograms of pristine (red line) and exhausted (black line) clays.

**Table 1.** PXRD phase attribution for pristine and exhausted clays.

| Identified Phase       | Plane [hkl] | Pristine ( $2\theta$ ) | Exhausted ( $2\theta$ ) |
|------------------------|-------------|------------------------|-------------------------|
| Montmorillonite        | (001)       | 6.67                   | 6.35                    |
| Illite                 | (002)       | 19.85                  | 19.89                   |
| Montmorillonite/Illite | (110)       | 20.79                  | 20.91                   |
| Quartz/Illite          | (020)       | 26.63                  | 26.69                   |
| Calcite/Illite         | (002)       | 27.59                  | /*                      |
| Illite                 | (110)       | 34.99                  | 34.89                   |
| Quartz/Illite          | (200)       | 36.51                  | /*                      |
| Quartz/Illite          | /           | 45.55                  | 45.89                   |
| Quartz/Illite          | /           | 50.15                  | 50.11                   |
| Montmorillonite/Illite | (060)       | 61.86                  | 61.82                   |

\* Not detected.

The PXRD pattern of the pristine bentonite confirmed the presence of montmorillonite, the dominant mineral phase, with its characteristic peak at  $6.67^\circ$  (001). This phase is

responsible for the clay's high cation exchange capacity and large interlayer spacing, which facilitate the adsorption of organic molecules. Additional peaks corresponding to illite ( $19.85^\circ$  and  $34.99^\circ$ ), quartz ( $26.63^\circ$ ), and calcite ( $27.59^\circ$ ) were also detected, consistent with the typical composition of natural bentonite [23,25]. After the adsorption process, no major phase transformations were observed, indicating that the bentonite's fundamental crystalline structure remained stable. However, notable changes in peak intensity and slight shifts in diffraction angles were detected, particularly for the montmorillonite (001) reflection, which shifted from  $6.67^\circ$  to  $6.35^\circ$ . The d-spacing change, calculated by Bragg's law, corresponded to  $0.67 \text{ \AA}$  (from  $d = 13.24 \text{ \AA}$  to  $d = 13.91 \text{ \AA}$  after oil adsorption). This appears to indicate the intercalation of organic molecules contained in waste oils (fatty acids, oxidized polymers, etc.) between the clay layers. This intercalation causes the layers to swell, increasing the interlayer distance and thus shifting the  $2\theta$  angles toward smaller values (because  $d$  and  $2\theta$  are inversely proportional according to Bragg's law) [26,27].

The increase in d-spacing after adsorption onto bentonite clay of large molecules such as diuron or cresol was previously studied, and the observed results confirm the incorporation of molecules in the interfoliar space during adsorption. This shift suggests a reduction in interlayer spacing, likely due to the incorporation of organic molecules within the clay's layered structure [28]. Additionally, a slight increase in the intensity of montmorillonite and illite peaks suggests that oil adsorption may have influenced crystal packing and surface interactions, leading to partial reorganization of the clay layers. The disappearance of certain calcite and quartz peaks in the exhausted clay suggests that these minor phases may have been involved in secondary adsorption mechanisms, such as chemical interactions with oil impurities [29].

The observed structural modifications support the hypothesis that WCO adsorption occurs primarily through surface adsorption, in which organic impurities contained in the oil attach to external clay surfaces, reducing the peak intensity [30]. Then, some organic compounds may penetrate the interlayer spaces, altering the basal spacing. Also, peak shifts and intensity changes can be promoted by exchange mechanisms between organic molecules and interlayer cations (e.g.,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ). These findings align with previous studies on clay-based oil refining, where bentonite adsorption is primarily a physical process, with limited structural damage to the crystalline framework.

### 3.4. Structural Investigation Through XRF Analysis

X-ray fluorescence (XRF) analysis was conducted to determine the elemental composition of the bentonite before and after the adsorption of waste cooking oil (WCO). The results, summarized in Table 2, reveal notable changes in the concentrations of key elements, providing insights into the adsorption mechanism and the interaction between the clay and oil impurities.

**Table 2.** Element compositions of pristine and exhausted clays.

| Elements | Pristine Clay (wt%) * | Exhausted Clay (wt%) * |
|----------|-----------------------|------------------------|
| Na       | 1.88                  | n.d.                   |
| Mg       | 4.57                  | 3.03                   |
| Al       | 20.50                 | 17.65                  |
| Si       | 53.39                 | 48.87                  |
| S        | 0.54                  | 0.64                   |
| K        | 2.95                  | 3.68                   |
| Ca       | 1.63                  | 5.42                   |
| Sc       | 0.00                  | 0.00                   |
| Ti       | 0.85                  | 1.09                   |
| V        | 0.03                  | 0.04                   |

|              |       |       |
|--------------|-------|-------|
| <b>Mn</b>    | 0.22  | 0.29  |
| <b>Fe</b>    | 10.02 | 12.30 |
| <b>Zn</b>    | 0.02  | 0.03  |
| <b>Rb</b>    | 0.03  | 0.04  |
| <b>Sr</b>    | 0.11  | 0.11  |
| <b>Y</b>     | 0.01  | --    |
| <b>Zr</b>    | 0.05  | 0.04  |
| <b>Ru</b>    | 0.73  | 1.60  |
| <b>Rh</b>    | 1.92  | 3.20  |
| <b>Pd</b>    | 0.56  | 1.96  |
| <b>Ga</b>    | --    | 0.01  |
| <b>Total</b> | 100   | 100   |

\* Standard deviation =  $\pm 0.02\%$ ; n.d. stands for not detected.

The pristine bentonite was primarily composed of silicon (Si) and aluminum (Al), which are characteristic of montmorillonite's aluminosilicate framework. Other significant elements included Fe, Mg, Ca, Na, and K, which are commonly found in natural bentonites [31–34]. The presence of minor elements such as Ti, S, and transition metals (Ru, Rh, Pd) suggests that the clay contains traces of accessory minerals such as quartz, feldspars, and iron oxides [35]. Following the adsorption process, notable shifts in the elemental composition were observed, indicating ion exchange, surface interactions, and possible structural modifications, confirming the XRD analysis. Looking at the variation in the elements' amounts, a reduction in Si, Al, and Mg content was observed. Silicon decreased from 53.39% to 48.87%, while aluminum dropped from 20.50% to 17.65%, suggesting a partial dissolution of the clay matrix due to prolonged interaction with WCO, leading to the displacement of aluminosilicate units or their coverage by organic molecules [30]. The decrease in magnesium (Mg) from 4.57% to 3.03% further supports the hypothesis of cation exchange and leaching effects, as  $Mg^{2+}$  is a common exchangeable cation in montmorillonite. The increase in Ca and K content suggests that cation exchange between clay interlayer sites and oil-derived species may occur, replacing leached  $Mg^{2+}$  and  $Na^+$  ions. The rise in the Fe amount (10.02% to 12.30%) could indicate oxidation reactions or the adsorption of metal-containing impurities from the oil. In fact, the observed increase in iron content may partially stem from the oxidation of structural  $Fe^{2+}$  to  $Fe^{3+}$  within the montmorillonite layers, induced by interaction with oxidized oil components or oxygen exposure during treatment. Additionally, peroxides and aldehydes formed during the degradation of triglycerides in WCO may promote redox reactions with Fe species in the clay, leading to increased surface retention and possible complexation. This may be linked to the mobilization of Fe from structural sites followed by surface re-precipitation as iron oxides or hydroxides, consistent with the increase detected by XRF. The adsorption process can disrupt the metal–oxygen bonds in clay, leading to the release of structural cations such as Fe. This is particularly relevant when oils contain complexing agents that can interact with these metals [36].

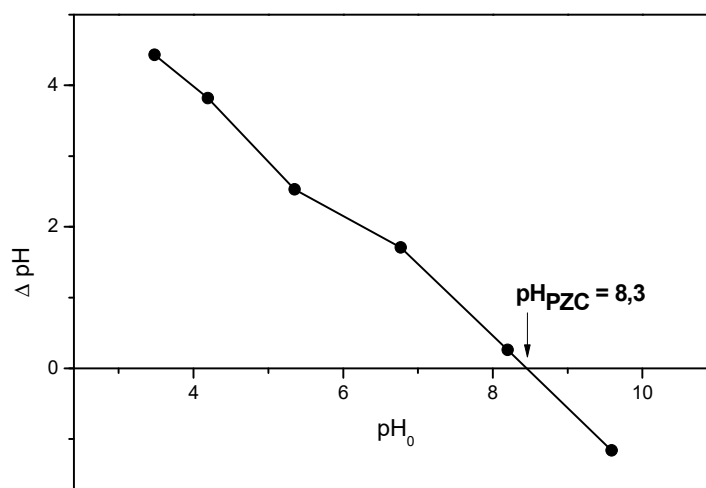
It is also worth highlighting the disappearance of Na, likely due to its high mobility and tendency to be replaced by larger cations ( $Ca^{2+}$ ,  $K^+$ ) during the adsorption process. A cation exchange capacity (CEC) of 59.27 meq/100 g was determined using the methylene blue (MB) method. Finally, the appearance of Ga, albeit in trace amounts, suggests possible contamination or selective adsorption of trace metals from WCO, which may be present due to cooking vessel interactions or residual food processing [37].

The observed elemental variations support three primary adsorption mechanisms: (I) ion exchange, (II) surface precipitation and complexation, (III) physical entrapment and diffusion-limited adsorption [38,39].

- (I) The loss of Na and Mg, coupled with an increase in Ca and K, suggests that interlayer cations in the clay were replaced by metal-containing organic species from WCO. This mechanism is common in bentonites used for oil purification.
- (II) The increase in Fe, Rh, and Pd content implies that clay surface sites interacted with oil impurities, leading to the retention of transition metals and possibly oxidation processes.
- (III) The reduction in Si and Al suggests that some oil components penetrated the clay structure, covering active sites and altering the elemental composition.

### 3.5. Adsorption Investigation: pH at Point of Zero Charge (pHPZC)

The point of zero charge (pHPZC) is a critical parameter in adsorption studies, as it defines the pH at which the net surface charge of the adsorbent is neutral. Below this pH, the surface is positively charged, favoring the adsorption of anionic species, whereas above this pH, the surface becomes negatively charged, promoting cationic adsorption [40]. The pHPZC value corresponds to the pH where the final pH equals the initial pH (i.e., where the surface exhibits zero net charge). The results are plotted in Figure 4, showing the intersection of the curve with the neutral charge axis at pH 8.3.



**Figure 4.** Zero load point plot.

The pHPZC value of 8.3 is consistent with values reported for natural montmorillonite-rich clays, which typically range between 6.4 and 8.5, depending on the mineral composition and exchangeable cations. This suggests that the pristine bentonite primarily exhibits negatively charged sites at neutral to slightly alkaline pH, making it favorable for cationic adsorption under these conditions. After WCO adsorption, no significant shift in pHPZC was observed, indicating that the adsorption process primarily involved physical interactions rather than strong chemisorption or ion exchange mechanisms. However, minor changes in surface charge distribution could be inferred from the altered adsorption kinetics observed in other sections.

The adsorption of WCO, which contains neutral and slightly polar compounds, did not significantly alter the charge properties of bentonite. Since oil impurities do not strongly ionize in aqueous media, electrostatic attraction was not the dominant adsorption mechanism, supporting the idea that van der Waals forces and hydrophobic interactions

played a more significant role. At  $\text{pH} < 8.3$ , the surface is positively charged, which could enhance interactions with anionic contaminants (e.g., fatty acid residues from WCO). At  $\text{pH} > 8.3$ , the bentonite surface is negatively charged, meaning that the adsorption of additional anionic species would be hindered due to electrostatic repulsion.

The relatively high pHPZC suggests that bentonite can be an effective adsorbent for polar organic contaminants in neutral to acidic conditions, but its efficiency may decrease in highly alkaline environments. Studies on acid-activated bentonites often report a shift in pHPZC to lower values (e.g.,  $\text{pH} 4\text{--}6$ ) due to increased surface acidity and enhanced cation exchange capacity. The lack of pHPZC shift in this study confirms that the commercial Maghnia bentonite retains its natural charge properties and does not undergo significant structural modification during WCO adsorption. The high pHPZC (8.3) suggests that this bentonite is best suited for treating WCO with acidic or neutral impurities, such as free fatty acids and oxidized compounds [41–46].

The summary of the main results of the present study is reported in Table 3.

**Table 3.** Summary of main findings.

| Category               | Parameter/Observation                                  | Key Findings  |
|------------------------|--|---|
| Adsorption Performance | Optimal bentonite dosage                               | 10 wt%  |
|                        | Optimal contact time                                   | 4 h   |
|                        | Maximum decolorization yield                           | 70–71%  |
|                        | Adsorption kinetics model                              | Pseudo-second-order   |
|                        | High clay loading effect                               | Agglomeration → reduced efficiency; oscillatory kinetics at 30 wt% clay                   |
| Structural Changes     | FT-IR: Functional group interactions                   | Disappearance of OH bands, appearance of -CH <sub>2</sub> and C=O bands in exhausted clay |
|                        | FT-IR implication                                      | Adsorption of hydrocarbon impurities confirmed  |
|                        | PXRD: Montmorillonite (001) peak shift                 | From 6.67° to 6.35° → suggests interlayer incorporation of organics                       |
|                        | PXRD: General structural stability                     | No major phase changes; slight reorganization   |
| Elemental Composition  | XRF: Decrease in Si, Al, Mg                            | Indicates surface coverage and leaching   |
|                        | XRF: Disappearance of Na                               | Suggests ion exchange with oil-borne cations  |
|                        | XRF: Increase in Ca, K, Fe, transition metals (Rh, Pd) | Confirms ion exchange, surface adsorption, and possible oxidation                         |
|                        | Adsorption mechanisms (from XRF + PXRD + FTIR)         | (I) Ion exchange, (II) surface adsorption, (III) physical entrapment                      |
| Surface Properties     | pHPZC  | 8.3—favors adsorption under acidic/neutral conditions                                     |
|                        | pHPZC shift post-adsorption                            | Negligible—implies predominantly physical adsorption                                      |

## 4. Conclusions

This study evaluated the potential of Maghnia Algerian bentonite as an effective adsorbent for refining waste cooking oils (WCOs). The results demonstrated that the clay achieved up to 70% decolorization under optimal conditions (10 wt% bentonite, 4 h of treatment). The adsorption efficiency was influenced by the clay concentration, contact time, and structural properties, with excessive bentonite loading leading to agglomeration effects.

Structural characterization provided key insights into the adsorption mechanism. FT-IR analysis confirmed the retention of oil-derived impurities, the XRD data suggested minimal crystalline changes, and the XRF results highlighted shifts in the elemental composition, supporting ion exchange and surface adsorption mechanisms. Adsorption kinetics followed a pseudo-second-order model, indicating strong interactions between the oil and the clay surface. Additionally, the pHPZC of 8.3 suggested that adsorption is pH-dependent, with enhanced efficiency in acidic conditions.

These findings demonstrate the viability of Maghnia bentonite as a natural, cost-effective adsorbent for WCO purification, offering an environmentally friendly alternative to chemical refining processes. Future studies should explore strategies to improve adsorption efficiency, including clay modification techniques (e.g., acid activation or surfactant functionalization) and regeneration methods to enhance reusability in industrial applications. In the context of the continuous search for sustainable alternatives to the current state of the art, the employment of natural clay, such as the Maghnia one, without any particular activation (such as classic acidic bentonite activation) represents an interesting solution for industry. However, despite the easiness of the process, the recyclability of the material should be explored to consistently increase the performance in terms of sustainability. Regarding the scalability of the process, as the employment of bentonites is an already assessed methodology, even in small industrial productions, it would not represent an issue.

**Author Contributions:** Conceptualization, Z.T., A.M. (Alberto Mannu) and S.T.; methodology, A.S., Z.T., C.N.K., C.H.M. and O.Z.; validation, Z.T. and A.M. (Alberto Mannu); formal analysis, Z.T., A.M. (Alberto Mannu), S.T. and A.M. (Andrea Mele); investigation, A.S., C.N.K., C.H.M. and O.Z.; resources, data curation, S.G.; writing—original draft preparation, A.S., Z.T., C.N.K., C.H.M. and O.Z.; writing—review and editing, A.M. (Alberto Mannu), A.M. (Andrea Mele) and S.G.; supervision, Z.T., S.T., S.G. and A.M. (Andrea Mele); project administration, Z.T., S.T. and A.M. (Andrea Mele); funding acquisition, Z.T., S.T., A.M. (Andrea Mele) and S.G. All authors have read and agreed to the published version of the manuscript.

**Funding:** The present work was funded by WORLD Project-RISE, a project that has received funding from the European Union's Horizon 2020 research and innovation programme, under the Marie Skłodowska-Curie, Grant Agreement No. 873005.

**Data Availability Statement:** Additional data will be provided if requested.

**Acknowledgments:** The authors acknowledge the support of the Platform of Industrial Technologies (UDL). Also, the Algerian Directorate General of Scientific Research and Technological Development (DGRSDT) and the Algerian Ministry of Higher Education and Scientific Research (MESRS) are greatly thanked for their financial support.

**Conflicts of Interest:** The authors declare no conflicts of interest.

## References

1. Andrikopoulos, N.K.; Boskou, G.; Dedoussis, G.V.Z.; Chiou, A.; Tzamtzis, V.A.; Papathanasiou, A. Quality assessment of frying oils and fats from 63 restaurants in Athens, Greece. *Food Serv. Technol.* **2003**, *3*, 49–59.
2. Ziaifar, A.M.; Achir, N.; Courtois, F.; Trezzani, I.; Trystram, G. Review of mechanisms, conditions, and factors involved in the oil uptake phenomenon during the deep-fat frying process. *Int. J. Food Sci. Technol.* **2008**, *43*, 1410–1423.
3. Mannu, A.; Almendras Flores, P.; Briatico Vangosa, F.; Di Pietro, M.E.; Mele, A. Sustainable production of raw materials from waste cooking oils. *RSC Sustain.* **2025**, *3*, 300–310.
4. Foo, W.H.; Koay, S.S.N.; Chia, S.R.; Chia, W.Y.; Tang, D.Y.Y. Saifuddin Nomanbhay, Kit Wayne Chew, Recent advances in the conversion of waste cooking oil into value-added products: A review. *Fuel* **2022**, *324*, 124539.
5. Dangal, A.; Tahergorabi, R.; Acharya, D.R.; Timsina, P.; Rai, K.; Dahal, S.; Acharya, P.; Giuffrè, A.M. Review on deep-fat fried foods: Physical and chemical attributes, and consequences of high consumption. *Eur. Food Res. Technol.* **2024**, *250*, 1537–1550.
6. Mannu, A.; Ferro, M.; Di Pietro, M.E.; Mele, A. Innovative applications of waste cooking oil as raw material. *Sci. Prog.* **2019**, *102*, 153–160.
7. Awad, A.M.; Shaikh, S.M.R.; Jalab, R.; Gulied, M.H.; Nasser, M.S.; Benamor, A.; Adham, S. Adsorption of organic pollutants by natural and modified clays: A comprehensive review, *Sep. Purif. Technol.* **2019**, *228*, 115719.
8. Kaushik, S.; Sati, V.; Kanojia, N.; Mehra, K.S.; Malkani, H.; Pant, H.; Gupta, H.; Singh, A.P.; Kumar, A.; Paul, A.R.; et al. Biodiesel a Substitution for Conventional Diesel Fuel: A Comprehensive Review. In *Advances in Mechanical Engineering; Lecture Notes in Mechanical Engineering*; Springer: Singapore, 2021. [https://doi.org/10.1007/978-981-16-0942-8\\_10](https://doi.org/10.1007/978-981-16-0942-8_10).
9. Panadare, D.C.; Rathod, V.K. Applications of Waste Cooking Oil Other Than Biodiesel. *Iran. J. Chem. Eng.* **2015**, *12*, 55.
10. Mannu, A.; Garroni, S.; Ibanez Porras, J.; Mele, A. Available Technologies and Materials for Waste Cooking Oil Recycling. *Processes* **2020**, *8*, 366.
11. Komadel, P. Acid activated clays: Materials in continuous demand. *Appl. Clay Sci.* **2016**, *131*, 84–99.
12. Hymore, F.K. Effects of some additives on the performance of acidactivated clays in the bleaching of palm oil. *Appl. Clay Sci.* **1996**, *10*, 379–385.
13. Mannu, A.; Poddighe, M.; Mureddu, M.; Castia, S.; Mulas, G.; Murgia, F.; Di Pietro, M.E.; Mele, A.; Garroni, S. Impact of morphology of hydrophilic and hydrophobic bentonites on improving the pour point in the recycling of waste cooking oils. *Appl. Clay Sci.* **2024**, *262*, 107607.
14. Mannu, A.; Vlahopoulou, G.; Urgeghe, P.; Ferro, M.; Del Caro, A.; Taras, A.; Garroni, S.; Rourke, J.P.; Cabizza, R.; Petretto, G.L. Variation of the Chemical Composition of Waste Cooking Oils upon Bentonite Filtration. *Resources* **2019**, *8*, 108.
15. Makhoukhi, B.; Didi, M.A.; Villemin, D.; Azzouz, A. Acid activation of Bentonite for use as a vegetable oil bleaching agent. *Grasas Aceites* **2009**, *60*, 343–349.
16. Avelino Ratkiewicz, L.; Vieira Da Cunha Filho, F.J.; De Barros Neto, E.L.; Santanna, V.C. Modification of bentonite clay by a cationic surfactant to be used as a viscosity enhancer in vegetable-oil-based drilling fluid. *Appl. Clay Sci.* **2017**, *135*, 307–312.
17. Önal, M.; Sarıkaya, Y. Maximum Bleaching of Vegetable Oils by Acid-Activated Bentonite: Influence of Nanopore Radius. *Adsorpt. Sci. Technol.* **2012**, *30*, 97–104.
18. Egbuna, S.O. Development of kinetic model for adsorption of carotenoids on activated clay in the bleaching of PalmOil. *Int. J. Res. Eng. Technol.* **2014**, *3*, 371–380.
19. Ifa, L.; Wiyania, L.; Nurdjannah, N.; Muhammad, A.; Ghaliba, T.; Ramadhaniara, S.; Kusuma, H.S. Analysis of bentonite performance on the quality of refined crude palm oil's color, free fatty acid and carotene: The effect of bentonite concentration and contact time. *Heliyon* **2021**, *7*, e07230.
20. Nayak, P.K.; Dash, U.; Radha Krishnan, K.; Mishra, B.K.; Rayaguru, K. Process optimization for minimizing residual free fatty acid levels in fried mustard oil: Isotherm and kinetics studies. *J. Food Process Eng.* **2017**, *40*, e12426.
21. Foletto, E.L.; Volzone, C.; Porto, L.M. Clarification of cottonseed oil: How structural properties of treated bentonites by acid affect bleaching efficiency. *Lat. Am. Appl. Res.* **2006**, *36*, 37–40.
22. Yan, N.; Masliyah, J.H. Adsorption and desorption of clay particles at the oil-water interface. *J. Colloid Interface Sci.* **1994**, *168*, 386–392.
23. Vogt, E.; Pacura, W. Hydrophobization of bleaching clay used for purification of waste frying oils. *IOP Conf. Ser. Earth Environ. Sci.* **2019**, *214*, 012009.
24. Luo, J.; Liu, M.; Xing, Y.; Gui, X.; Li, J. Investigating agglomeration of kaolinite particles in the presence of dodecylamine by force testing and molecular dynamics simulation. *Colloids Surf. A Physicochem. Eng. Asp.* **2022**, *645*, 128930.

25. Serouri, A.; Taleb, Z.; Mannu, A.; Garroni, S.; Senes, N.; Taleb, S.; Brini, S.; Abdoun, S.K. Variation of Used Vegetable Oils Composition upon Treatment with Algerian Clays. *Recycling* **2021**, *6*, 68.
26. Tlemsani, S.; Taleb, Z.; Piraúlt-Roy, L.; Taleb, S. Temperature and pH influence on diuron adsorption by Algerian Mont-Na clay. *Int. J. Environ. Anal. Chem.* **2024**, *104*, 2316–2333.
27. Taleb, Z.; Ramdani, A.; Berenguer, R.; Ramdani, N.; Adjir, M.; Taleb, S.; Morallón, E.; Nemnich, S.; Tilmatine, A. Combined ozonation process and adsorption onto bentonite natural adsorbent for the o-cresol elimination. *Int. J. Environ. Anal. Chem.* **2023**, *103*, 977–994.
28. Mannu, A.; Vlahopoulou, G.; Sireus, V.; Petretto, G.L.; Mulas, G.; Garroni, S. Bentonite as refining agent in waste cooking oils recycling: Flash point, density and color evaluation. *Nat. Prod. Commun.* **2018**, *12*, 1–2.
29. Moore, D.M.; Reynolds, R.J. *X-Ray Diffraction and the Identification and Analysis of Clay Minerals*; Oxford University Press: New York, NY, USA, 1989; p. 332.
30. Parolo, M.E.; Pettinari, G.R.; Musso, T.B.; Sánchez-Izquierdo, M.P.; Fernández, L.G. Characterization of organo-modified bentonite sorbents: The effect of modification conditions on adsorption performance. *Appl. Surf. Sci.* **2014**, *320*, 356–363.
31. Zhu, R.; Chen, Q.; Zhou, Q.; Xi, Y.; Zhu, J.; He, H. Adsorbents based on montmorillonite for contaminant removal from water: A review. *Appl. Clay Sci.* **2016**, *123*, 239–258.
32. Maged, A.; Kharbish, S.; Ismael, I.S.; Bhatnagar, A. Characterization of activated bentonite clay mineral and the mechanisms underlying its sorption for ciprofloxacin from aqueous solution. *Environ. Sci. Pollut. Res.* **2020**, *27*, 32980–32997.
33. Angar, Y.; Djelali, N.E.; Kebbouche-Gana, S. Study of the Effect of the Bentonite Modification Treatments on the Adsorption Removal of Ammonium Ions from Aqueous Solution. *Fresenius Environ. Bull.* **2016**, *25*, 3646–3653.
34. Boufatit, M.; Ait-Amar, H.; McWhinnie, W.R. Development of an Algerian material montmorillonite clay. Adsorption of phenol, 2-dichlorophenol and 2, 4, 6-trichlorophenol from aqueous solutions onto montmorillonite exchanged with transition metal complexes. *Desalination* **2007**, *206*, 394–406.
35. Mohammed-Azizi, F.; Dib, S.; Boufatit, M. Removal of heavy metals from aqueous solutions by Algerian bentonite. *Desalin. Water Treat.* **2013**, *51*, 4447–4458.
36. Abdullahi, S.L.; Audu, A.A. Comparative analysis on chemical composition of bentonite clays obtained from Ashaka and tango deposits in Gombe State, Nigeria. *ChemSearch J.* **2017**, *8*, 35–40.
37. Aljlil, S.A.; Alsewailam, F.D. Adsorption of Cu & Ni on bentonite clay from waste water. *Athens J. Sci.* **2014**, *1*, 21–30.
38. Liu, X.; Tournassat, C.; Grangeon, S.; Kalinichev, A.G.; Takahashi, Y.; Marques Fernandes, M. Molecular-level understanding of metal ion retention in clay-rich materials. *Nat. Rev. Earth Environ.* **2022**, *3*, 461–476.
39. Pavlov, D.I.; Yu, X.; Ryadun, A.A.; Samsonenko, D.G.; Dorovatovskii, P.V.; Lazarenko, V.A.; Sun, N.; Sun, Y.; Fedin, V.P.; Potapov, A.S. Multiresponsive luminescent metal–organic framework for cooking oil adulteration detection and gallium(III) sensing. *Food Chem.* **2024**, *445*, 138747.
40. Apeiranthitis, N.; Greenwell, H.C.; Carteret, C. Far-and mid-infrared examination of nontronite-1 clay mineral–Redox and cation saturation effects. *Appl. Clay Sci.* **2022**, *228*, 106628.
41. Pavan Korf, E.; Lange Salvia, A.; Larisse Scopel, S.; Marques Prietto, P.D.; Thomé, A. Competitive Sorption of Metallic Species under Different pH in a Residual Clayey Soil. *J. Environ. Eng.* **2017**, *143*, 06017009.
42. Sposito, G. On Points of Zero Charge. *Environ. Sci. Technol.* **1998**, *32*, 2815–2819.
43. Mudzielwana, R.; Gitari, M.W.; Akinyemi, S.A.; Msagati, T.A. Performance of Mn<sup>2+</sup>-modified bentonite clay for the removal of fluoride from aqueous solution. *S. Afr. J. Chem.* **2018**, *71*, 15–23.
44. Kallay, N.; Žalac, S. Charged surfaces and interfacial ions. *J. Colloid Interface Sci.* **2020**, *230*, 1–11.
45. de Souza, T.R.P.; Olenka, L.; Peternella, W.S. A study of degradation in vegetable oils by exposure to sunlight using fourier transform infrared spectroscopy. *Mater. Sci. Appl.* **2020**, *11*, 678–691.
46. Tlemsani, S.; Taleb, Z.; Pirault-Roy, L.; Taleb, S. Heterogeneous Catalytic Degradation of Diuron Using Algerian Sodium Montmorillonite. *Clean-Soil Air Water* **2022**, *50*, 2000468.

**Disclaimer/Publisher’s Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.