

Article

Synthesis and Application of FeMg-Modified Hydrochar for Efficient Removal of Lead Ions from Aqueous Solution

Jelena Petrović ^{1,*}, Marija Koprivica ¹, Marija Ercegović ¹, Marija Simić ¹, Jelena Dimitrijević ¹, Mladen Bugarčić ¹ and Snežana Trifunović ²

¹ Institute for Technology of Nuclear and Other Raw Mineral Materials, 11000 Belgrade, Serbia; m.koprivica@itnms.ac.rs (M.K.); m.ercegovic@itnms.ac.rs (M.E.); m.petrovic@itnms.ac.rs (M.S.); j.dimitrijevic@itnms.ac.rs (J.D.); m.bugarcic@itnms.ac.rs (M.B.)

² Faculty of Chemistry, University of Belgrade, 11000 Belgrade, Serbia; snezanat@chem.bg.ac.rs

* Correspondence: j.petrovic@itnms.ac.rs

Abstract

This study explores the utilization of waste grape pomace-derived hydrochar as an efficient adsorbent for lead (Pb^{2+}) removal from aqueous solutions. Hydrochar was produced via hydrothermal carbonization (HTC) at 220 °C, followed by doping with magnesium and iron salts, and subsequent pyrolysis at 300 °C to obtain Fe/Mg-pyro-hydrochar (FeMg-PHC). The material's structural and morphological changes after Pb^{2+} adsorption were examined using FTIR. FTIR revealed chemisorption and ion exchange as key mechanisms, shown by decreased hydroxyl, carbonyl, and metal–oxygen peaks after Pb^{2+} adsorption. Adsorption tests under varying pH, contact time, and initial Pb^{2+} concentrations revealed optimal removal at pH 5. Kinetic modeling indicated that the process follows a pseudo-second-order model, suggesting chemisorption as the dominant mechanism. Isotherm analysis showed that the Sips model best describes the equilibrium, with a maximum theoretical adsorption capacity of 157.24 mg/g. Overall, the simple two-step synthesis—HTC followed by pyrolysis—combined with metal doping yields a highly effective and sustainable adsorbent for Pb^{2+} ion removal from wastewater.

Keywords: Fe/Mg-doped hydrochar; lead adsorption; grape valorization; hydrothermal carbonization



Academic Editor: Anna Wołowicz

Received: 30 May 2025

Revised: 19 June 2025

Accepted: 26 June 2025

Published: 29 June 2025

Citation: Petrović, J.; Koprivica, M.; Ercegović, M.; Simić, M.; Dimitrijević, J.; Bugarčić, M.; Trifunović, S. Synthesis and Application of FeMg-Modified Hydrochar for Efficient Removal of Lead Ions from Aqueous Solution. *Processes* **2025**, *13*, 2060. <https://doi.org/10.3390/pr13072060>

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/>).

1. Introduction

In recent decades, the expansion of industrial, agricultural, and domestic activities has led to the accumulation of large quantities of waste biomass. Its inadequate management has resulted in considerable environmental degradation and associated economic losses [1–3]. Although currently considered waste, biomass represents a valuable and renewable resource that, if properly utilized, can contribute to the circular economy and sustainable environmental practices. However, its direct application is often limited due to poor physicochemical stability, low energy density, and complex handling requirements [1–3]. To address these limitations, recent research has focused on biomass conversion into valuable products such as biofuels, fertilizers, and especially functional materials for environmental remediation [4,5]. Among the most promising technologies for this purpose is hydrothermal carbonization (HTC), a thermochemical process that converts biomass into carbon-rich hydrochars in an aqueous medium under moderate temperatures (typically 180–260 °C) and autogenous pressure [4,5]. HTC offers several advantages over conventional dry pyrolysis, including the use of wet feedstocks without

the need for energy-intensive drying, lower operational costs, and reduced greenhouse gas emissions [6,7].

Hydrochars produced via HTC are structurally stable, chemically active materials enriched with oxygen-containing functional groups such as hydroxyl, carboxyl, and carbonyl, which facilitate pollutant adsorption through electrostatic interactions, ion exchange, chelation, and surface complexation [8–10]. Their favorable porosity, hydrophobicity, and surface area contribute to efficient adsorption under various environmental conditions [8,9]. However, unmodified hydrochars often lack sufficient capacity for practical heavy metal removal. To enhance their performance, modification techniques such as oxidative treatments, alkali activation, and incorporation of metal salts or nanoparticles have been applied, improving surface reactivity, binding site density, and pore accessibility [5,7,9,11].

To address the limitations of unmodified hydrochars, various modification strategies have been developed to enhance their adsorption capacity, especially for toxic heavy metals. Among these contaminants, lead (Pb^{2+}) stands out as one of the most hazardous due to its toxicity, bioaccumulation, and widespread presence in industrial effluents from sources such as battery manufacturing, metal plating, and mining industries. Effective and economical treatment methods are crucial to mitigate its environmental and health impacts [12–16]. Recent studies have demonstrated the potential of modified hydrochars derived from agro-industrial residues in Pb^{2+} removal. For instance, rice husk-derived hydrochars [14] and sugarcane bagasse hydrochars [11] have shown promising adsorption capacities. Moreover, Petrović et al. reported a fivefold increase in Pb^{2+} adsorption for alkali-modified grape pomace hydrochar compared to the untreated counterpart [17]. Additional research highlights the effectiveness of activation treatments in improving Pb^{2+} sorption by alkali and H_2O_2 -modified hydrochars [7,8], further emphasizing the role of surface functionalization in enhancing adsorption performance.

Despite growing interest in biomass valorization, research on Fe/Mg-doped hydrochars derived from grape pomace, an abundant by-product of the wine industry, remains limited. Grape pomace is generated globally in vast quantities, as 20–30% of the fruit's weight remains as pomace, resulting in an estimated 13 million tons produced annually by the global wine industry [18]. Its improper management contributes significantly to greenhouse gas emissions and environmental degradation [4,9]. Valorization of grape pomace into functional materials not only addresses waste disposal challenges but also promotes sustainable resource recovery and aligns with circular economy principles.

Moreover, unlike previous studies focusing mainly on single-step HTC or direct pyrolysis, our work employs a unique two-step synthesis combining hydrothermal carbonization followed by pyrolysis. This approach enhances the physicochemical properties of the Fe/Mg-doped hydrochars, resulting in improved stability, porosity, and active site availability, advantages that have not been comprehensively reported in earlier research.

This study aims to fill this knowledge gap by introducing a novel two-stage Fe/Mg-doping strategy applied to grape pomace-derived pyro-hydrochar, a modification approach not previously explored for this biomass. Combining hydrothermal carbonization, metal salt impregnation, and subsequent pyrolysis, we seek to develop a highly efficient adsorbent for Pb^{2+} removal. The objectives are: (1) to synthesize and thoroughly characterize Fe/Mg-doped pyro-hydrochar from grape pomace; (2) to evaluate its Pb^{2+} adsorption performance under varying conditions such as pH, contact time, and initial concentration; and (3) to elucidate the adsorption mechanisms using FTIR spectroscopy, and kinetic and isotherm modeling. This comprehensive approach provides new insights into the design of cost-effective metal-doped carbonaceous adsorbents and highlights the potential of agricultural waste valorization for advanced water treatment applications.

2. Materials and Methods

2.1. Reagents and Chemicals

All the chemicals and reagents used in the present study were of analytical grade. The primary standard solution of Pb (1000 mg/L) was prepared by dissolving the weighed amount of Pb (Sigma-Aldrich, Steinheim, Germany) in ultra-distilled water. Solutions of various Pb concentrations used in experiments were prepared by diluting the primary stock solution with ultra-distilled water. For modification treatment, 0.2 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.4 M $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ solutions were prepared from solid chemicals (Sigma-Aldrich, Steinheim, Germany).

2.2. Preparation and Modification of Hydrochar

Hydrothermal carbonization of waste grape pomace at 220 °C is detailed and explained in our previous research [9]. Briefly, pomace collected from an open landfill after grape processing was air-dried, ground for homogeneity, and carbonized. The biomass was treated hydrothermally in water (1:15 *m/v*) at 220 °C for 1 h in an autoclave (Carl Roth, model II). After the reaction, the suspension was filtered, and the obtained hydrochar (GPHC) was dried at 105 °C for further use. The impregnation with MgO and FeO includes a two-step co-precipitation procedure. First, 1 g of the hydrochar was stirred with 0.2 M and 0.4 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ solutions, followed by the addition of 1 M NaOH to adjust the pH to 12. The mixture was continuously stirred for 1 h under these conditions to facilitate co-precipitation. Afterward, the resulting material was filtered and thoroughly washed. During the second step, the material was pyrolyzed at 300 °C in an inert atmosphere (Nabertherm 30–3000 °C, Germany) for 1 h, with a heating rate of 10 °C/min and an inert gas flow rate of 80 mL/min. During the second step, the material was pyrolyzed at 300 °C (Nabertherm 30–3000 °C, Germany) in an inert atmosphere, within 1 h. The obtained FeMg-PHC was rinsed, dried until constant weight, and utilized in adsorption experiments.

2.3. Adsorption Tests

To optimize experimental conditions, the effects of initial solution pH (2.0–5.0), contact time (10–700 min), and Pb^{2+} concentration (100–600 mg/L) were investigated. The pH of the solutions was adjusted by adding small amounts of 0.1 M HNO_3 and 0.1 M NaOH, and continuously monitored using a calibrated pH meter. For each test, 25 mL of Pb^{2+} solution was mixed with 1.0 g/L of FeMg-PHC and stirred for 24 h at room temperature (298 ± 0.5 K). Adsorption experiments were conducted in 100 mL flasks placed on a Heidolph Unimax1010 orbital shaker at 250 rpm. The residual Pb^{2+} concentration in the filtrates was measured by atomic absorption spectrophotometry (Perkin Elmer PinAAcle 900T, Perkin Elmer, Waltham, MA, USA). All experiments were performed in triplicate, and average values were reported. The amounts of Pb^{2+} removed by tested FeMg-PHC were calculated by following the equation:

$$q_{eq} = \left(\frac{C_0 - C_{eq}}{m} \right) \times V \quad (1)$$

where C_0 and C_{eq} are the initial and equilibrium concentrations of the Pb^{2+} solution (mg/L); V represents the volume of the Pb^{2+} solution (L), m is the amount of adsorbent (FeMg-PHC) (g), respectively.

To assess the material's performance under realistic conditions, FeMg-PHC was tested with untreated wastewater from an accumulator factory. The effluent contained various heavy metals, and adsorption was performed without pH or concentration adjustment. Metal levels were quantified via AAS before and after treatment.

2.4. Characterization of FeMg-PHC Before and After Pb²⁺ Removal

Spectroscopic measurements were carried out using a Thermo Scientific Nicolet iS50 FT-IR spectrometer to investigate the functional groups and molecular vibrations present in the FeMg-PHC sample before and after Pb²⁺ adsorption. The samples, prepared by mixing 0.8 mg of powdered FeMg-PHC with 80 mg of KBr, were analyzed in transmission mode over a spectral range of 4000 to 400 cm^{−1} to gain insights into the chemical composition and of the involvement of surface functional groups in the adsorption of the selected pollutant. The surface structures of FeMg-PHC before and after Pb²⁺ adsorption were examined using a JSM-7001F SEM-EDS system (JEOL Inc., Akishima, Japan) to evaluate morphological changes and elemental distribution. Prior to imaging, all samples were sputter-coated with a thin layer of gold and mounted onto conductive carbon adhesive tabs to ensure optimal imaging quality and signal detection. Bulk density of the hydrochar was determined by gently filling a 10 mL graduated cylinder with oven-dried (105 °C) FeMg-hydrochar without compaction. The sample was leveled carefully and its mass was measured. Bulk density (g/cm³) was then calculated as the ratio of sample mass (M) to its occupied volume (V), using the equation [19]:

$$\rho_{\text{bulk}} = M/V \quad (2)$$

Linear and non-linear regression analyses of adsorption kinetics and isotherms were conducted using Origin 9.0 software.

3. Results and Discussion

3.1. Characterization Before and After Pb²⁺ Adsorption Using FeMg-PHC

The FTIR spectrum of the FeMg-PHC reveals several important features that provide insights into surface functionality and possible adsorption properties (Figure 1). A broad absorption band between 3200–3600 cm^{−1} is attributed to O-H stretching vibrations, originating from hydroxyl and carboxyl groups on the surface [17]. The peaks observed in the 2800–3000 cm^{−1} range correspond to C-H stretching in aliphatic structures, indicating the presence of residual organic matter [9]. A prominent band near 1600 cm^{−1} is assigned to the C=O stretching of carboxylic and/or carbonyl groups, which play a crucial role in metal ion binding. The peak around 1400 cm^{−1} is linked to C-H bending or aromatic C=C stretching, suggesting the presence of aromatic domains within the hydrochar matrix [9]. Vibrations in the 1000–1100 cm^{−1} region are associated with C-O stretching from alcohols or phenolic compounds [6]. Importantly, bands in the 500–800 cm^{−1} region are assigned to Fe-O and Mg-O vibrations, confirming the successful incorporation of metal species during modification [9].

Notable spectral changes were observed following Pb²⁺ adsorption (Figure 1). The broad O-H band (3200–3600 cm^{−1}) significantly decreased, indicating the interaction of Pb²⁺ ions with hydroxyl groups via chemisorption or surface complexation [1]. Likewise, the reduced intensity and slight shift of the carbonyl peak near 1600 cm^{−1} suggest the involvement of C=O and carboxyl groups in metal binding, likely through coordination mechanisms [16,17]. The weakened intensity of aromatic C=C and C-H bending vibrations implies the participation of aromatic structures in the adsorption process, possibly through alterations in their electronic environment; however, π - π interactions are unlikely to be the primary binding mechanism for Pb²⁺ ions [17]. Furthermore, decreases in Fe-O and Mg-O bands after adsorption point toward partial ion exchange or changes in the metal-oxygen bonding environment [9,16]. Collectively, these findings indicate that Pb²⁺ removal occurs via a combination of surface complexation, ion exchange, and chemisorption facilitated by Fe and Mg active sites. The presence of hydroxyl, carboxyl, and metal-oxygen functional

groups provides multiple synergistic binding sites, significantly enhancing the adsorption efficiency of FeMg-PHC.

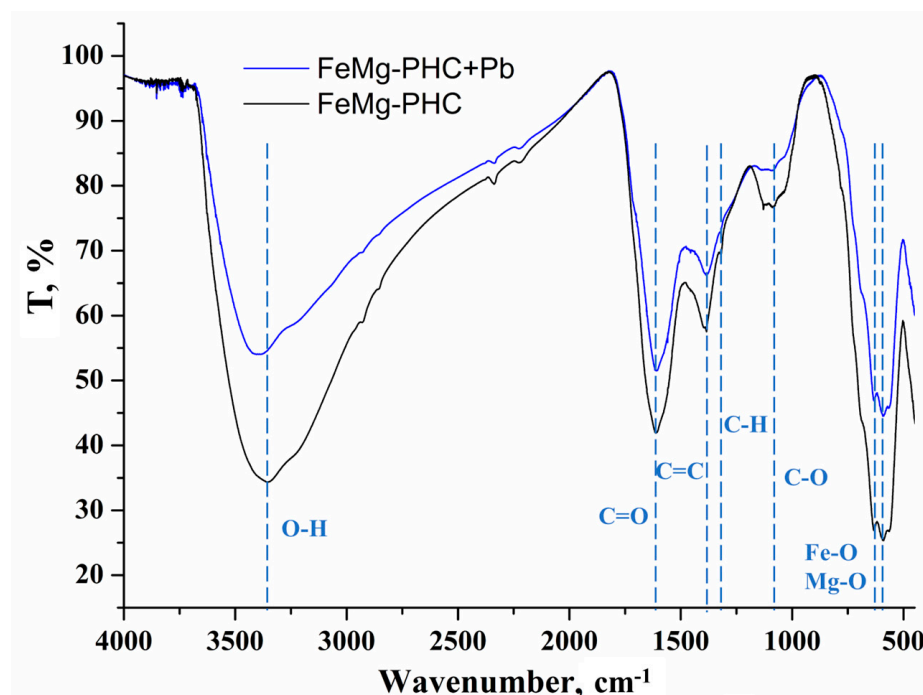


Figure 1. FTIR spectra of FeMg-PHC before and after Pb^{2+} ions removal.

Quantitative FTIR analysis revealed significant reductions in peak areas after Pb^{2+} adsorption, supporting functional group involvement. The O-H stretching band ($\sim 3300\text{ cm}^{-1}$) decreased from 45,526.5 to 34,629.6 $\text{a.u.}\cdot\text{cm}^{-1}$, indicating hydrogen bonding or ion exchange. Carboxyl-associated bands (~ 1600 and $\sim 1400\text{ cm}^{-1}$) declined from 12,070.0 to 10,241.9 and from 6799.7 to 6097.6 $\text{a.u.}\cdot\text{cm}^{-1}$, respectively, suggesting Pb^{2+} coordination. Additional decreases at 1100 cm^{-1} (C-O stretch: 8258.0 to 7734.7) and 600 cm^{-1} (M-O: 10,888.2 to 7174.9) confirm contributions of both organic and inorganic surface functionalities to metal binding.

Figure 2a,b present the surface morphology and elemental composition of the FeMg-PHC material before and after exposure to Pb^{2+} , respectively. The SEM image of the pristine sample (a) reveals a heterogeneous, porous structure characteristic of Fe- and Mg-enriched hydrochar [9]. After adsorption (b), no significant morphological alterations are observed; however, a slight reduction in pore visibility suggests partial filling by adsorbed species. The EDS spectrum of the sample after adsorption confirms the successful binding of Pb^{2+} on the surface. Simultaneously, a noticeable decrease in the intensity of Fe and Mg peaks is observed, indicating a potential ion exchange mechanism between the introduced Pb^{2+} ions and the native Fe/Mg species present on the hydrochar surface.

The bulk density of the prepared hydrochar was determined to be 0.3744 g/cm^3 , which falls within the broader range reported for biochars ($0.08\text{--}1.7\text{ g/cm}^3$) [20], yet remains higher than typical values for unmodified hydrochars derived from agricultural biomass ($0.189\text{--}0.276\text{ g/cm}^3$) [21]. This increase is likely due to the effects of Mg-Fe doping and post-treatment (pyrolysis), which promote a more compact structure. The resulting denser material facilitates better handling and packing in adsorption systems and may also contribute to improved Pb^{2+} removal.

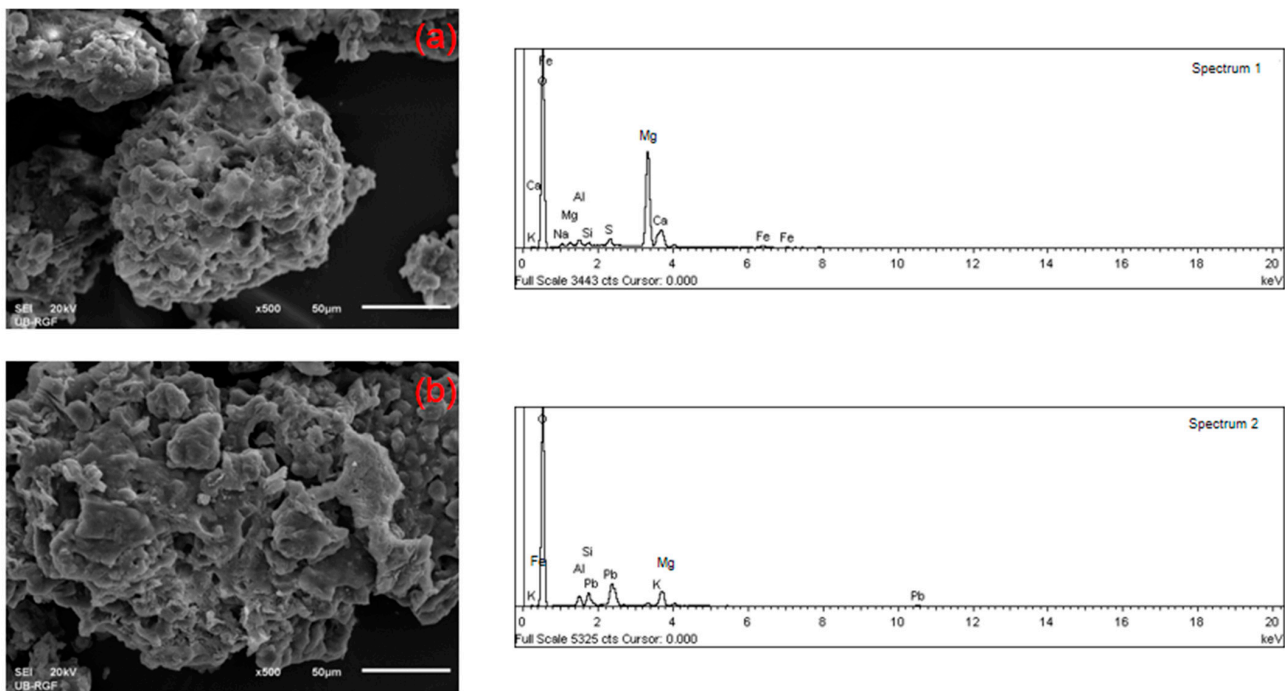


Figure 2. SEM-EDS analysis of FeMg-PHC before (a) and after (b) Pb(II) adsorption.

3.2. Influence of Initial pH

The pH of the initial metal solution has a significant impact on the adsorption capacity of FeMg-PHC by influencing both the surface charge of the material and the speciation of Pb^{2+} ions in the solution. Increasing the pH from 2.0 to 5.0 enhances the adsorption capacity for Pb^{2+} (Figure 3), as the deprotonation of surface functional groups, primarily carboxylic ($-\text{COOH}$) and hydroxyl ($-\text{OH}$), leads to the formation of negatively charged sites ($-\text{COO}^-$, $-\text{O}^-$). These negatively charged groups exhibit strong electrostatic attraction toward Pb^{2+} ions, facilitating their binding to the adsorbent surface [6,9,22]. This interaction may also include complexation or coordination mechanisms, contributing further to the efficient removal of metal ions from the solution. At pH 5.0, the adsorption capacity reaches a maximum of 139.6 mg/g.

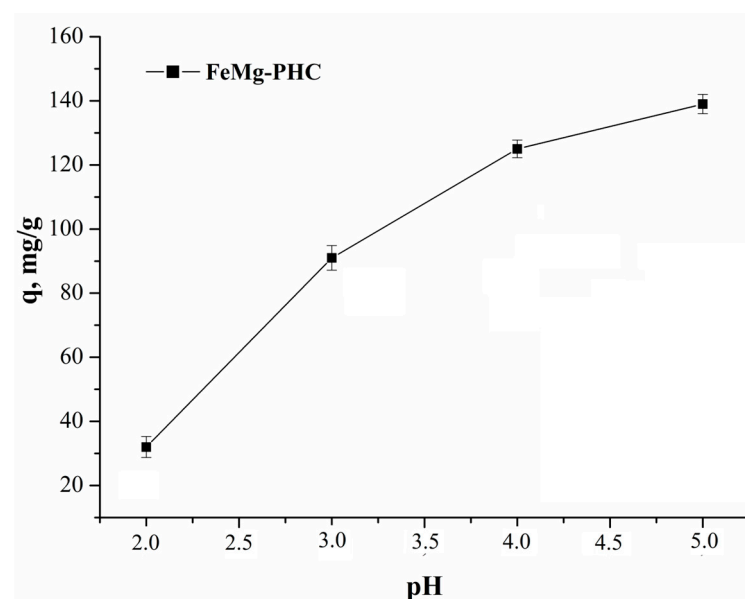


Figure 3. Influence of initial pH solution on adsorption capacity.

Further, an increase in pH above 5.0 was intentionally avoided in order to prevent the precipitation of Pb^{2+} ions in the form of lead hydroxide $\text{Pb}(\text{OH})_2$, which would interfere with the adsorption process and result in overestimation of the material's adsorption capacity [7,16,17].

3.3. Influence of Contact Time and Kinetic Study

The effect of contact time on the adsorption capacity of the FeMg-PHC adsorbent is shown in Figure 4. As depicted, the removal of Pb^{2+} ions follows a typical adsorption pattern, starting with a rapid increase in capacity that slows down over time. In the first 30 min, the adsorption rate is high, with nearly 50% of the total removal achieved. This indicates that a large number of binding sites on the material's surface are available and become quickly occupied [17,22]. Between 30 and 60 min, the adsorption rate decreases as the available sites become increasingly filled, leading to a slower rise in adsorption capacity. After 200 min, the rate of adsorption continues to decline and the system reaches equilibrium, with the remaining sites becoming progressively less available for further adsorption. Similar observations reported by Koprivica et al., during their investigation of Pb^{2+} removal using alkali-modified hydrochar derived from Paulownia leaves [7]. The maximum achieved removal capacity was 139.6 mg/g. This kinetic profile highlights the initial rapid adsorption followed by a slow approach to equilibrium as the available binding sites are filled.

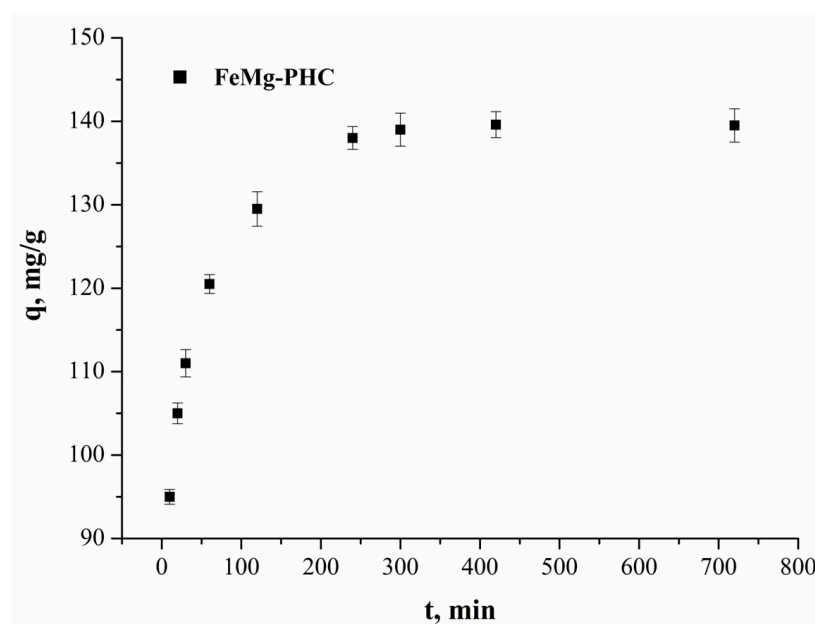


Figure 4. Influence of contact time on Pb^{2+} ions removal using FeMg-PHC ($C_{\text{Pb}} = 200 \text{ mg/L}$, $\text{pH} = 5$, dose = 1 g/L).

To gain deeper insights into the Pb^{2+} binding mechanism, kinetic models such as the Lagergren pseudo-first-order model (PFO) [23], the pseudo-second-order model (PSO) [24], and the Weber–Morris intra-particle diffusion model [25] were employed for analyzing the experimental data. To prevent incorrect conclusions and limitations that may result from using only linear or non-linear kinetic models [26], we interpreted the experimental results through both approaches, summarizing the obtained parameters in Table 1.

Table 1. Kinetic parameters of linear and non-linear models for Pb²⁺ adsorption onto FeMg-PHC, C_{Pb} = 200 mg/L.

Adsorbent FeMg-PHC	
q _{eq,exp} (mg/g)	139.6 ± 1.25
Pseudo-First-Order Linear Model	
q _{eq,cal} (mg/g)	136.61 ± 1.08
k ₁ (1/min)	4.93 ± 0.37
χ ²	7.01
R ²	0.9235
Pseudo-Second-Order Linear Model	
q _{eq,cal} (mg/g)	142.05 ± 2.17
k ₂ (g/mg·min)	0.00087 ± 0.00003
χ ²	5.27
R ²	0.9998
Pseudo-First-Order Non-Linear Model	
q _{eq,cal} (mg/g)	132.44 ± 0.75
k ₁ (1/min)	0.10 ± 0.03
χ ²	10.87
R ²	0.6742
Pseudo-Second-Order Non-Linear Model	
q _{eq,cal} (mg/g)	138.73 ± 1.13
k ₂ (g/mg·min)	0.0013 ± 0.0001
χ ²	2.26
R ²	0.9323
Weber–Morris Diffusion Model	
K _{id1} (mg/g·min ^{1/2})	4.27 ± 0.15
C ₁ (mg/g)	85.02 ± 1.33
R ²	0.9568
K _{id2} (mg/g·min ^{1/2})	0.16 ± 0.01
C ₂ (mg/g)	136.02 ± 2.21
R ²	0.7987

The linear (3) and non-linear (4) form of the Lagergren pseudo-first-order kinetic equation is expressed as:

$$1/q_t = (k_1/q_{eq}) (1/t) + (1/q_{eq}) \quad (3)$$

$$q_t = q_{eq} \times (1 + e^{-k_1 t}) \quad (4)$$

Similarly, the pseudo-second-order kinetic model is represented in its linear (5) and non-linear (6) forms as:

$$t/q_t = (1 + k_2 q_{eq}^2) + (1/q_{eq})t \quad (5)$$

$$q_t = q_{eq}^2 k_2 t / (1 + k_2 q_{eq}^2 t) \quad (6)$$

In these equations, q_{eq} and q_t denote the quantities of Pb²⁺ adsorbed onto the FeMg-PHC (mg/g) at equilibrium and at a given time t , respectively, as determined by the kinetic models. The constants k_1 (1/min) and k_2 (g/mg·min) correspond to the pseudo-first-order and pseudo-second-order rate constants, respectively.

Additionally, the intra-particle diffusion model is described by the following equation:

$$q = K_{id} t^{0.5} + C \quad (7)$$

Here, q (mg/g) represents the amount of Pb²⁺ adsorbed at time t (min), K_{id} (mg/g·min^{1/2}) is the rate constant for intra-particle diffusion, and C is the intercept. The

slope of the linear plot of q versus $t^{0.5}$ is utilized to determine K_{id} , providing insight into the contribution of intra-particle diffusion to the overall adsorption process.

Figure 5 displays the results of the non-linear fitting (Figure 5a) and the linearized plots of the applied pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models (Figure 5b,c), along with the intra-particle diffusion model (Figure 5d). Additionally, Table 1 summarizes the calculated kinetic parameters and adsorption capacities for each model.

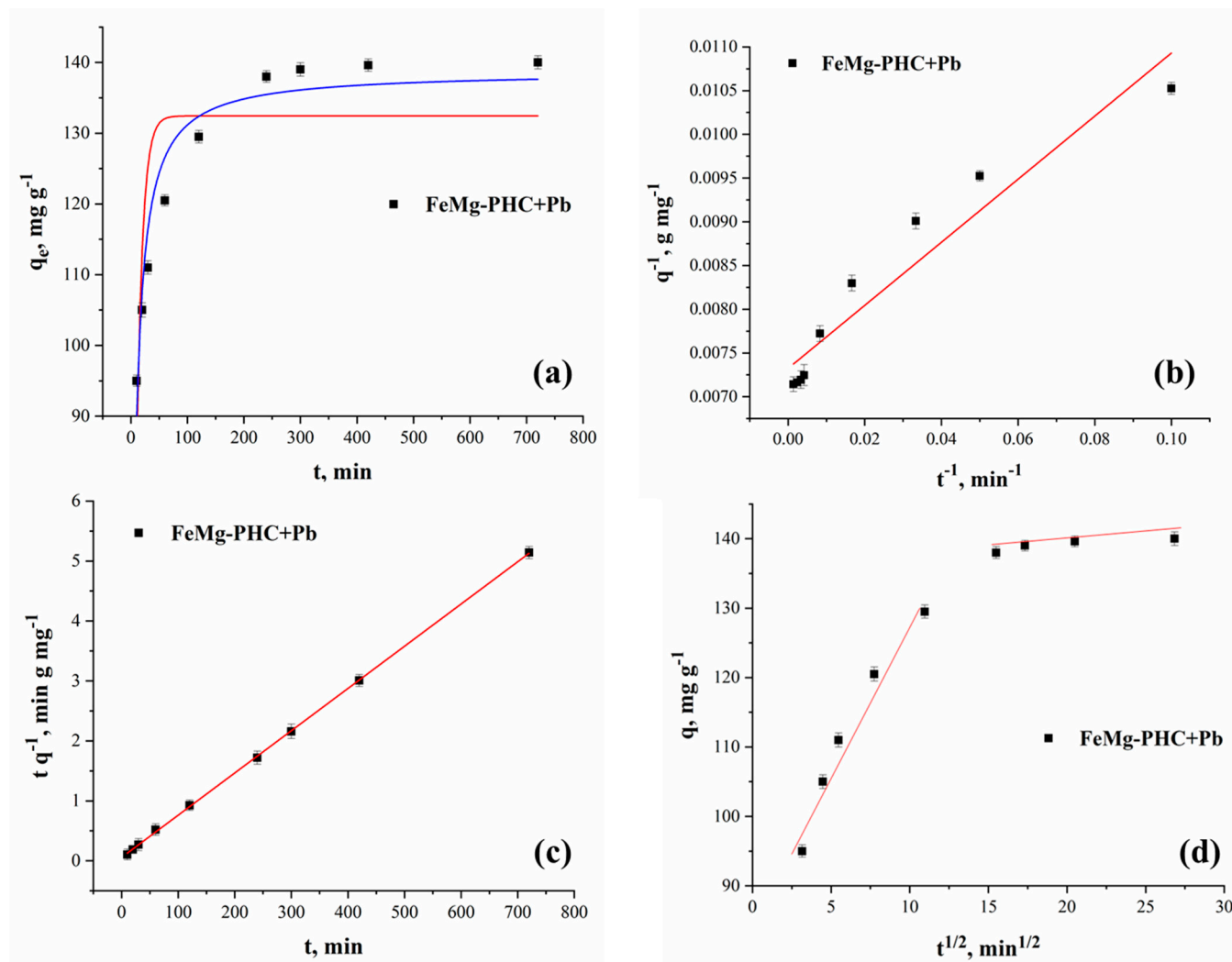


Figure 5. Non-linear (a), linear PFO (b), linear PSO (c), and intra-particle diffusion (d) kinetic models.

Based on the kinetic parameters presented in Table 1, it can be concluded that the adsorption of Pb²⁺ ions onto FeMg-PHC followed the linear PSO model most closely, with a correlation coefficient of $R^2 = 0.9998$. Moreover, the adsorption capacity predicted by the linear PSO model ($q_e = 142.05 \text{ mg/g}$) is in excellent agreement with the experimentally obtained value ($q_{e,\text{exp}} = 139.6 \text{ mg/g}$). This strong correlation supports the hypothesis that chemisorption is the dominant mechanism governing Pb²⁺ removal, involving chemical interactions such as covalent bonding and electron sharing between Pb²⁺ ions and surface functional groups on the hydrochar [7,9,27].

To further validate this conclusion, the experimental data were also fitted using the non-linear forms of the PFO and PSO models (Figure 5a, Table 1). Although the correlation coefficients were slightly lower compared to their linear counterparts, the non-linear PSO model still showed good agreement ($R^2 = 0.9323$), further supporting the proposed adsorption mechanism. Similar trends have been reported in previous studies on heavy metal adsorption using comparable modified biochars and hydrochars [7,16].

Application of the Weber–Morris intra-particle diffusion model (Figure 5d) revealed a multi-linear trend with two distinct phases, indicating that intra-particle diffusion was not the sole rate-limiting step. The initial sharper slope corresponds to the rapid external surface adsorption of Pb^{2+} ions, while the second, more gradual phase represents intra-particle diffusion into the interior pores of the FeMg-PHC material [1,9,16]. Overall, the kinetic analysis reveals that Pb^{2+} adsorption onto FeMg-PHC follows a dual-stage mechanism, involving fast external adsorption followed by slower intra-particle diffusion. This synergistic adsorption behavior demonstrates both the high affinity of the material for Pb^{2+} ions and its efficient porous structure, highlighting the material's potential for advanced heavy metal remediation applications. The kinetic behavior is in agreement with the FTIR analysis, which showed changes in hydroxyl, carbonyl, and metal–oxygen bands after Pb^{2+} adsorption. These spectral shifts support the chemisorption mechanism indicated by the pseudo-second-order model, confirming that chemical interactions play a dominant role in the adsorption process. These results are consistent with previous studies on modified hydrochars from spent mushroom substrate and Paulownia leaves, which also reported pseudo-second-order kinetics and FTIR evidence of functional group involvement in Pb^{2+} chemisorption [7,16].

3.4. Influence of Initial Pb^{2+} Concentration and Isothermal Assay

Figure 6 illustrates that, as the initial concentration of the tested ions in the solution increases, the amount of adsorbed Pb^{2+} also rises until it reaches equilibrium. Once equilibrium is attained, further increases in concentration do not affect the adsorption capacity. This is because a higher pollutant concentration reduces the number of available active sites on the adsorbent's surface, as these sites become occupied through interaction. Equilibrium is reached when all active sites are filled [1,27,28].

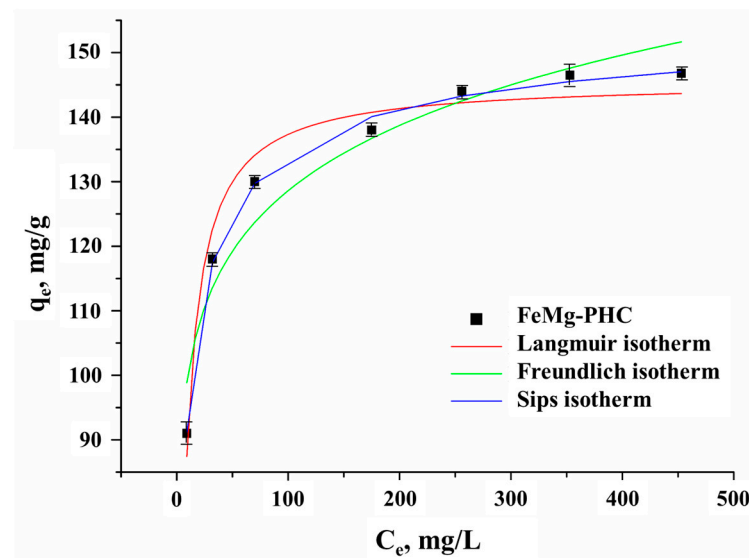


Figure 6. Non-linear fits of isotherm models to the Pb^{2+} adsorption using FeMg-PHC (pH = 5.0, dose 1 g/L, $t = 24$ h).

To understand how Pb^{2+} ions interact with the FeMg-PHC surface and to determine the maximum adsorption capacity, the experimental results were analyzed using three isotherm models [1,9].

The Langmuir isotherm model:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (8)$$

The Freundlich isotherm:

$$q_e = K_F C_e^{1/n} \quad (9)$$

The Sips isotherm model (hybrid form of the Langmuir and Freundlich models):

$$q_e = q_m \frac{K_S C_e^{n_s}}{1 + K_S C_e^{n_s}} \quad (10)$$

where C_e represents the equilibrium concentration (mg/L), q_m is the maximum quantity of adsorbed Pb^{2+} ions (mg/g), K_L , K_F , and K_S are model constants, $1/n$ adsorption intensity, n_s is the Sips model exponent.

The results are displayed in Figure 6, and the calculated parameters are summarized in Table 2.

Table 2. Parameters and determination coefficients of the isotherm models for Pb^{2+} removal.

Models	Parameters	Value
Langmuir	q_m (mg g ⁻¹)	145.55 ± 301
	K_L (L/mg)	0.16 ± 0.03
	R^2	0.9665
Freundlich	K_F (mg/g)(L/mg) ^{1/n}	77.77 ± 0.98
	$1/n$	10
	R^2	0.9393
Sips	q_m (mg/g)	157.24 ± 2.45
	K_S (L/mg)	0.37 ± 0.02
	n_s	0.59
	R^2	0.9974

The adsorption data presented in Table 2 demonstrate that the Sips isotherm model provides the best fit for describing the interaction between Pb^{2+} ions and the FeMg-PHC adsorbent in aqueous solution, with a correlation coefficient (R^2) of 0.9974. This superior fit suggests that the adsorption process occurs on a heterogeneous surface with sites of varying affinity and involves characteristics of both Langmuir and Freundlich models, consistent with a multilayer adsorption mechanism. The Sips model combines the Langmuir assumption of monolayer adsorption on uniform sites with the Freundlich model's description of heterogeneous sites with different affinities, making it suitable for complex adsorption processes like multilayer formation on diverse surfaces. The maximum adsorption capacity (q_m) predicted by the Sips model is 157.24 mg/g. Additionally, the Sips constant ($K_S = 0.37$ L/mg) and heterogeneity index ($n_s = 0.59$) further support the notion of a heterogeneous adsorption surface. Analysis of isotherm parameters—including the Langmuir constant ($K_L = 0.16$ L/mg), the Freundlich heterogeneity factor ($1/n = 0.10$), and high R^2 values across models—indicates that the adsorption of Pb^{2+} onto FeMg-PHC is not only favorable but also efficient under the tested conditions [7,9,12]. These observations are in line with previously published results for Pb^{2+} adsorption using Ca-impregnated spent mushroom substrate [16]. These findings confirm the strong potential of FeMg-PHC as an effective and promising adsorbent for the removal of Pb^{2+} ions from aqueous media.

Table 2 shows that FeMg-PHC exhibits strong adsorption performance, achieving a maximum adsorption capacity of 157.24 mg/g. This impressive capacity underscores the material's significant potential as an effective adsorbent for pollutant removal under mild experimental conditions. As shown in Table 3, this performance positions FeMg-PHC among the leading adsorbents reported in the literature. The relatively high adsorption capacity reflects the effective surface properties and the presence of abundant active sites, which facilitate the adsorption process. These enhanced characteristics can be attributed

to the successful doping with Mg and Fe, as well as the applied pyrolysis treatment. These modifications significantly improve the adsorptive properties of the hydrochar compared to its non-modified counterparts. In fact, the non-modified hydrochar derived from grape pomace treated solely by hydrothermal carbonization at 220 °C for 1 h exhibited an adsorption capacity of only 27.8 mg/g, highlighting the considerable enhancement achieved through the applied modification strategy [17]. Given the simplicity and efficiency of the synthesis method, the FeMg-PHC composite presents a promising balance between performance and potential for practical applicability. Therefore, based on the available data for various materials and their adsorption capacities, using FeMg-PHC as an adsorbent is well justified. Its favorable adsorption characteristics strongly suggest it can serve as an effective and reliable material for contaminant removal in environmental applications.

Table 3. Comparison of adsorption capacities of various adsorbents.

Used Material	Preparation Method	pH	q (mg/g)	Ref.
Cactus hydrochar	Microwave-magnetic HTC	5.0	139.34	[29]
Corn straw biochar/rGO composite	HTC	5.5	34.02	[30]
<i>Prosopis africana</i> shell	Pyrolysis + HTC	5.0	45.3	[31]
Paulownia leaves	HTC	5.0	49.62	[7]
Pine wood	Oxone-modified hydrochar	5.0	46.7	[32]
Wheat straw	HTC	5.0	64.97	[33]
Spent mushroom substrate	HTC + Ca pyrolysis	5.0	297	[16]
Chicken feathers	Mg-modified hydrochar	5.0	70.41	[34]
Tea residues	Magnetic hydrochar	5.6	328.2	[35]
Corn stalk	Pyrolysis	5.0	20.8	[36]
Sawdust	H ₂ O ₂ modified hydrochar	5.0	92.8	[37]
Poplar sawdust	Phosphate-modified hydrochar	5.0	119.61	[38]
Sewage sludge	MgAl-layered	5.0	62.41	[39]
Grape pomace	HTC	5.0	27.8	[17]
FeMg-PHC	HTC + Fe/Mg pyrolysis	5.0	157.24	This study

The sorption efficiency of FeMg-PHC was evaluated using untreated industrial wastewater from an accumulator factory (AFW), which contained multiple heavy metals. The experimental results before and after adsorption using FeMg-PHC are presented in Table 4. Although the overall removal efficiency was lower compared to single-metal systems—likely due to the low pH of the solution (pH ≈ 2) and the presence of competing ions—FeMg-PHC still exhibited good potential for Pb²⁺ and coexisting metal ion removal under realistic conditions.

Table 4. Pb²⁺ removal efficiency from accumulator factory wastewater using FeMg-PHC.

Sample	Pb (mg/L)	Cu (mg/L)	Zn (mg/L)	Cd (mg/L)	Ni (mg/L)
AFW	6.05	9.23	3.98	0.98	4.99
FeMg-PHC	2.98	6.53	2.12	0.52	3.28

3.5. Potential Mechanism of Pb²⁺ Adsorption

Figure 7 summarizes the potential mechanism of the adsorption of Pb²⁺ ions from aqueous solution utilizing FeMg-PHC. The strong agreement between the Sips isotherm model and the experimental data, along with the excellent fit of the PSO kinetic model, suggests that Pb²⁺ adsorption onto FeMg-PHC is primarily governed by chemisorption occurring on a heterogeneous surface. The observed dual-stage adsorption process is marked by an initial rapid removal of Pb²⁺, followed by a slower rate of intra-particle diffusion. This behavior reflects the high surface reactivity and the well-developed porous structure

of the material. Notably, the surface modification achieved through the incorporation of Fe and Mg ions during the pyrolysis process resulted in the creation of additional binding sites. These metal ions, which are anchored to the hydrochar surface, engage in ion exchange interactions with Pb^{2+} from the solution, further enhancing the adsorption performance. Furthermore, the presence of aromatic and oxygen-containing functional groups facilitates π - π interactions and promotes specific chemical bonding with Pb^{2+} ions. FTIR analysis indicated significant shifts in the aromatic, hydroxyl, carbonyl, and metal-oxygen bands following adsorption, providing additional evidence for the chemisorptive mechanism. In summary, these findings confirm that the synergistic effects of surface heterogeneity, metal-assisted ion exchange, and strong chemical affinity contribute to the high adsorption capacity and selectivity of FeMg-PHC. This underscores its potential as an efficient and sustainable adsorbent for the removal of Pb^{2+} from contaminated water.

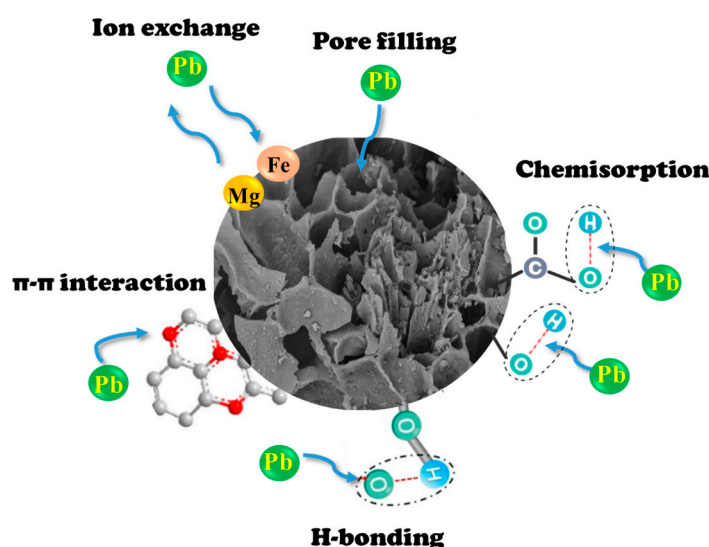


Figure 7. Potential mechanism of Pb^{2+} adsorption using FeMg-PHC.

4. Conclusions

This study demonstrated that Fe- and Mg-modified hydrochar derived from grape pomace (FeMg-PHC) is an efficient adsorbent for Pb^{2+} removal from aqueous solutions. Adsorption followed the pseudo-second-order kinetic model and the Sips isotherm, indicating chemisorption on a heterogeneous surface with a maximum capacity of 157.24 mg/g. The process involved rapid surface binding and slower intra-particle diffusion, supported by FTIR evidence of interactions with hydroxyl, carbonyl, and metal-oxygen groups. SEM and FTIR analyses suggest that ion exchange plays a significant role in Pb^{2+} uptake, facilitated by metal doping that introduces additional active sites and enhances ion exchange interactions. The synergy of surface heterogeneity, functional group reactivity, and metal-assisted binding contributed to the material's high capacity and selectivity.

Nevertheless, challenges such as the scalability of the pyrolysis process and potential interference from competitive ions in real wastewater must be addressed for practical applications. Future studies should focus on scaling up the synthesis, evaluating adsorbent performance in complex wastewater matrices, investigating regeneration and reuse cycles, and conducting column adsorption experiments to bridge the gap between laboratory research and industrial deployment.

Overall, this work highlights grape pomace as a sustainable and low-cost precursor for producing high-performance adsorbents, offering a promising approach for heavy metal removal and wastewater treatment within a circular economy framework.

Author Contributions: Conceptualization, J.P.; methodology, J.P. and M.S.; software, M.K.; validation, M.E.; formal analysis, S.T. and J.D.; investigation, M.B.; resources, J.P.; data curation, M.S. and M.K.; writing—original draft preparation, J.P. and M.S.; writing—review and editing, M.E.; visualization, J.D. and M.B.; supervision, J.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Acknowledgments: The authors are grateful to the Ministry of Science, Technological Development and Innovation of the Republic of Serbia for its financial support (contract no. 451-03-136/2025-03/200023 and 451-03-136/2025-03/200168).

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

References

1. Simić, M.; Petrović, J.; Šoštarić, T.; Ercegović, M.; Milojković, J.; Lopičić, J.; Kojić, M. Mechanism assessment and differences of cadmium adsorption on raw and alkali-modified agricultural waste. *Processes* **2022**, *10*, 1957. [\[CrossRef\]](#)
2. Fernández, L.A.G.; Castillo, N.A.M.; Polo, M.S.; Frómeta, A.E.N.; Cadre, J.E.V. Algal-Based Carbonaceous Materials for Environmental Remediation: Advances in Wastewater Treatment, Carbon Sequestration, and Biofuel Applications. *Processes* **2025**, *13*, 556. [\[CrossRef\]](#)
3. Noor, A.; Ali Khan, S. Agricultural Wastes as Renewable Biomass to Remediate Water Pollution. *Sustainability* **2023**, *15*, 4246. [\[CrossRef\]](#)
4. Pan, T.; Guo, Z.; Zhang, X.; Feng, L. Hydrothermal carbonization of biomass waste and application of produced hydrochar in organic pollutants removal. *J. Clean. Prod.* **2024**, *457*, 142386. [\[CrossRef\]](#)
5. Petrović, J.; Ercegović, M.; Simić, M.; Koprivica, M.; Dimitrijević, J.; Jovanović, A.; Pantić, J.J. Hydrothermal carbonization of waste biomass: A review of hydrochar preparation and environmental application. *Processes* **2024**, *12*, 207. [\[CrossRef\]](#)
6. Li, B.; Lv, J.Q.; Guo, J.Z.; Fu, S.Y.; Guo, M.; Yang, P. The polyaminocarboxylated modified hydrochar for efficient capturing methylene blue and Cu(II) from water. *Bioresour. Technol.* **2019**, *275*, 360–367. [\[CrossRef\]](#)
7. Koprivica, M.; Simić, M.; Petrović, J.; Ercegović, M.; Dimitrijević, J. Evaluation of Adsorption Efficiency on Pb(II) Ions Removal Using Alkali-Modified Hydrochar from Paulownia Leaves. *Processes* **2023**, *11*, 1327. [\[CrossRef\]](#)
8. Hammud, H.H.; Karnati, R.K.; Al Shafee, M.; Fawaz, Y.; Holail, H. Activated hydrochar from palm leaves as efficient lead adsorbent. *Chem. Eng. Commun.* **2019**, *208*, 197–209. [\[CrossRef\]](#)
9. Petrović, J.; Ercegović, M.; Simić, M.; Kalderis, D.; Koprivica, M.; Milojković, J.; Radulović, D. Novel Mg-doped pyro-hydrochars as methylene blue adsorbents: Adsorption behavior and mechanism. *J. Mol. Liq.* **2023**, *376*, 121424. [\[CrossRef\]](#)
10. Yang, X.; Wan, Y.; Zheng, Y.; He, F.; Yu, Z.; Huang, J.; Wang, H.; Ok, Y.S.; Jiang, Y.; Gao, B. Surface functional groups of carbon-based adsorbents and their roles in the removal of heavy metals from aqueous solutions: A critical review. *Chem. Eng. J.* **2019**, *366*, 608–621. [\[CrossRef\]](#)
11. Azzaz, A.A.; Khiari, B.; Jellali, S.; Ghimbeu, C.M.; Jeguirim, M. Hydrochars production, characterization and application for wastewater treatment: A review. *Renew. Sustain. Energy Rev.* **2020**, *127*, 109882. [\[CrossRef\]](#)
12. Li, B.; Guo, J.Z.; Liu, J.L.; Fang, L.; Lv, J.Q.; Lv, K. Removal of aqueous-phase lead ions by dithiocarbamate-modified hydrochar. *Sci. Total Environ.* **2020**, *714*, 136897. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Khanzada, A.K.; Al-Hazmi, H.; Kurniawan, T.A.; Majtacz, J.; Piechota, G.; Kumar, G.; Ezzati, P.; Saeb, M.S.; Rabiee, N.; Karimi-Maleh, H.; et al. Hydrochar as a bio-based adsorbent for heavy metals removal: A review of production processes, adsorption mechanisms, kinetic models, regeneration and reusability. *Sci. Total Environ.* **2024**, *945*, 173972. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Nadarajah, K.; Bandala, E.; Zhang, Z.; Mundree, S.; Goonetilleke, A. Removal of heavy metals from water using engineered hydrochar: Kinetics and mechanistic approach. *J. Water Process Eng.* **2021**, *40*, 101929. [\[CrossRef\]](#)
15. Khan, M.A.; Alqadami, A.A.; Otero, M.; Siddiqui, M.R.; Alothman, Z.A.; Alsohaimi, I.; Rafatullah, M.; Hamedelnieh, A.E. Heteroatom-doped magnetic hydrochar to remove post-transition and transition metals from water: Synthesis, characterization, and adsorption studies. *Chemosphere* **2019**, *218*, 1089–1099. [\[CrossRef\]](#)
16. Kojić, M.; Mihajlović, M.; Marinović-Cincović, M.; Petrović, J.; Katanić, Đ.; Krstić, A.; Butulija, S.; Onjia, A. Calcium-pyro-hydrochar derived from the spent mushroom substrate as a functional sorbent of Pb²⁺ and Cd²⁺ from aqueous solutions. *Waste Manag. Res.* **2022**, *40*, 1629–1636. [\[CrossRef\]](#)

17. Petrović, J.; Stojanović, M.; Milojković, J.; Petrović, M.; Šošćarić, T.; Laušević, M.; Mihajlović, M. Alkali modified hydrochar of grape pomace as a perspective adsorbent of Pb²⁺ from aqueous solution. *J. Environ. Manag.* **2016**, *182*, 292–300. [\[CrossRef\]](#)
18. Sodhi, G.K.; Kaur, G.; George, N.; Walia, H.K.; Sillu, D.; Rath, S.K.; Saxena, S.; Rios-Solis, L.; Dwibedi, V. Waste to wealth: Microbial-based valorization of grape pomace for nutraceutical, cosmetic, and therapeutic applications to promote circular economy. *Process Saf. Environ. Prot.* **2024**, *188*, 1464–1478. [\[CrossRef\]](#)
19. Eisenbies, M.H.; Volk, T.A.; Therasme, O.; Hallen, K. Three bulk density measurement methods provide different results for commercial scale harvests of willow biomass chips. *Biomass Bioenergy* **2019**, *124*, 64–73. [\[CrossRef\]](#)
20. Abel, S.; Peters, A.; Trinks, S.; Schonsky, H.; Facklam, M.; Wessolek, G. Impact of biochar and hydrochar addition on water retention and water repellency of sandy soil. *Geoderma* **2013**, *202–203*, 183–191. [\[CrossRef\]](#)
21. Pavkov, I.; Radojčin, M.; Stamenković, Z.; Bikić, S.; Tomić, M.; Bukurov, M.; Despotović, B. Hydrothermal Carbonization of Agricultural Biomass: Characterization of Hydrochar for Energy Production. *Solid. Fuel Chem.* **2022**, *56*, 225–235. [\[CrossRef\]](#)
22. Hu, X.; Dai, L.; Ma, Q.; Xu, J.; Ma, J.; Liu, X. One-pot synthesis of iron oxides decorated bamboo hydrochar for lead and copper flash removal. *Ind. Crop Prod.* **2022**, *187*, 115396. [\[CrossRef\]](#)
23. Lagergren, S. Zur Theorie der Sogenannten Adsorption Gelöster Stoffe. *K. Sven. Vetensk. Handl.* **1898**, *24*, 1–39. [\[CrossRef\]](#)
24. Ho, Y.S.; McKay, G. Pseudo-second order model for sorption processes. *Process Biochem.* **1999**, *34*, 451–465. [\[CrossRef\]](#)
25. Weber, W.; Morris, J. Kinetics of adsorption on carbon from solution. *J. Sanit. Eng. Div.* **1963**, *89*, 31–60. [\[CrossRef\]](#)
26. Obradović, B. Guidelines for general adsorption kinetics modeling. *Hem. Ind.* **2020**, *74*, 65–70. [\[CrossRef\]](#)
27. Ercegović, M.; Petrović, J.; Koprivica, M.; Simić, M.; Grubišić, M.; Vuković, N.; Krstić, J. Efficient adsorption of pollutants from aqueous solutions by hydrochar-based hierarchical porous carbons. *Water* **2024**, *16*, 2177. [\[CrossRef\]](#)
28. Meili, L.; Lins, P.V.; Zanta, C.L.P.S.; Soletti, J.I.; Ribeiro, L.M.O.; Dornelas, C.B.; Silva, T.L.; Vieira, M.G.A. MgAl-LDH/biochar composites for methylene blue removal by adsorption. *Appl. Clay Sci.* **2019**, *168*, 11–20. [\[CrossRef\]](#)
29. Qu, J.; Du, Z.; Lei, Y.; Li, M.; Peng, W.; Wang, M.; Liu, J.; Hu, Q.; Wang, L.; Wang, Y.; et al. Microwave-assisted one-pot preparation of magnetic cactus-derived hydrochar for efficient removal of lead(II) and phenol from water: Performance and mechanism exploration. *Bioresour. Technol.* **2023**, *388*, 129789. [\[CrossRef\]](#)
30. Zhang, Y.; Wan, Y.; Zheng, Y.; Yang, Y.; Huang, J.; Chen, H.; Chen, J.; Mosa, A.; Gao, B. Hydrochar loaded with nitrogen-containing functional groups for versatile removal of cationic and anionic dyes and aqueous heavy metals. *Water* **2024**, *16*, 3387. [\[CrossRef\]](#)
31. Elaigwu, S.E.; Rocher, V.; Kyriakou, G.; Greenway, G.M. Removal of Pb²⁺ and Cd²⁺ from aqueous solution using chars from pyrolysis and microwave-assisted hydrothermal carbonization of *Prosopis africana* shell. *J. Ind. Eng. Chem.* **2014**, *20*, 3467–3473. [\[CrossRef\]](#)
32. Madduri, S.; Elsayed, I.; Hassan, E.B. Novel oxone-treated hydrochar for the removal of Pb(II) and methylene blue (MB) dye from aqueous solutions. *Chemosphere* **2020**, *260*, 127683. [\[CrossRef\]](#) [\[PubMed\]](#)
33. Su, Y.; Liao, Q.; Xia, S.; Shen, X.; Zhu, J.; Liao, Y.; Wang, W.; Fang, Z.; Liu, D. Adsorption of heavy metal Pb(II) in dredged sediment using different biochar materials. *Processes* **2025**, *13*, 957. [\[CrossRef\]](#)
34. Deng, W.; Kuang, X.; Xu, Z.; Li, D.; Li, Y.; Zhang, Y. Adsorption of Cadmium and Lead Capacity and Environmental Stability of Magnesium-Modified High-Sulfur Hydrochar: Greenly Utilizing Chicken Feather. *Toxics* **2024**, *12*, 356. [\[CrossRef\]](#)
35. Yang, X.; Yu, J.; Liu, Y.; Duan, R.; Tang, Q.; Tian, L.; Xu, R.; Wang, H.; Xiang, T. Lead and antimony removal from wastewater via tea residue derived hydrochar: Immobilization capacity and industrial practicality. *Ind. Crops Prod.* **2025**, *231*, 121158. [\[CrossRef\]](#)
36. Yang, W.; Lu, C.; Liang, B.; Yin, C.; Lei, G.; Wang, B.; Zhou, X.; Zhen, J.; Quan, S.; Jing, Y. Removal of Pb(II) from Aqueous Solution and Adsorption Kinetics of Corn Stalk Biochar. *Separations* **2023**, *10*, 438. [\[CrossRef\]](#)
37. Xia, Y.; Yang, T.; Zhu, N.; Li, D.; Chen, Z.; Lang, Q.; Liu, Z.; Jiao, W. Enhanced adsorption of Pb(II) onto modified hydrochar: Modeling and mechanism analysis. *Bioresour. Technol.* **2019**, *288*, 121593. [\[CrossRef\]](#)
38. Qin, X.; Meng, W.; Cheng, S.; Xing, B.; Shi, C.; Nie, Y.; Wang, Q.; Xia, H. Efficient removal of heavy metal and antibiotics from wastewater by phosphate-modified hydrochar. *Chemosphere* **2023**, *345*, 140484. [\[CrossRef\]](#)
39. Luo, X.; Huang, Z.; Lin, J.; Li, X.; Qui, J.; Liu, J.; Mao, X. Hydrothermal carbonization of sewage sludge and in-situ preparation of hydrochar/MgAl-layered double hydroxides composites for adsorption of Pb(II). *J. Clean. Prod.* **2020**, *258*, 120991. [\[CrossRef\]](#)

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.