

Article

Converting Pine Cone Waste into Sustainable Biosorbent for Fe^{II} Removal: A Comprehensive Equilibrium, Thermodynamic, Kinetic, and Mechanistic Study

Marius Gheju ^{1,*}  and Ionel Balcu ² 

¹ Faculty of Chemical Engineering, Biotechnologies and Environmental Protection, Politehnica University Timisoara, Bd. V. Parvan Nr. 6, 300223 Timisoara, Romania

² National Institute for Research and Development in Electrochemistry and Condensed Matter, Str. Dr. Aurel Paunescu Podeanu Nr. 144, 300587 Timisoara, Romania; ionel_balcu@yahoo.com

* Correspondence: marius.gheju@upt.ro

Abstract

This study advances sustainable wastewater management by investigating the efficacy of untreated pine cone powder (PCP), an abundant and renewable forest byproduct, for Fe^{II} removal from aqueous solutions. The surface morphology and composition of PCP was characterized by performing SEM-EDX, FTIR, point of zero charge, and total specific surface area analysis. Investigation of experimental factors revealed that equilibrium adsorption capacity increases with higher pH and temperature but decreases with elevated initial Fe^{II} concentration and ionic strength. The experimental kinetic and equilibrium data were best fitted to the pseudo first-order and Freundlich models, respectively. Thermodynamic analysis further indicated that the adsorption process was spontaneous and endothermic in nature, accompanied by an increase of randomness at the solid–liquid interface. Low activation and Temkin bonding energies suggest that physical adsorption is the dominant removal mechanism. With a maximum Langmuir adsorption capacity of 12.7 mg g^{−1}, PCP represents a promising eco-friendly adsorbent for the removal of Fe^{II}. By transitioning from conventional, high-footprint water treatments to such low-impact, eco-friendly alternatives, this research supports the circular valorization of biomass as a viable solution for the sustainable mitigation of industrial heavy metal pollution.

Keywords: heavy metal pollution; adsorption; sustainable water treatment; renewable biosorbent



Academic Editor: Andrea G. Capodaglio

Received: 4 May 2026

Revised: 7 June 2026

Accepted: 8 July 2026

Published: 10 July 2026

Copyright: © 2026 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 \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

1. Introduction

While industrialization has been traditionally seen as a sign of advancement, it has also led to a rise in environmental pollution. The continuously increasing number of industrial activities release numerous harmful pollutants, including heavy metals, polluting ecosystems and causing them to degrade [1]. Unlike most organic pollutants, which eventually break down in the environment, metal contaminants are more persistent because they do not biodegrade; this allows them to build up in living organisms, becoming more concentrated as they move up the food chain [2–4]. Essential heavy metals like zinc, copper, iron, manganese, and cobalt are required as micronutrients for organism growth in low quantities; however, they may exert toxic effects at higher concentrations. In addition, most other heavy metals have no biological function, and their environmental presence is detrimental to a wide range of living organisms, including humans [5,6]. Numerous

industrial sectors contribute to the environmental release of heavy metals by failing to properly treat gaseous/aqueous emissions, neglecting necessary precautions, or experiencing accidental spills. These include iron and steel production, metal finishing and power station industries, electroplating, mining processing, wood preservation, pigment manufacturing, etc.; in addition, fossil fuel combustion and the use of pesticides and chemical fertilizers in agriculture substantially increase environmental heavy metal accumulation [2,6–8].

Iron is a critical heavy metal utilized across a wide range of industrial applications, being the primary constituent of ferrous alloys and steels used for fabrication of a variety of metal products (industrial machinery, transportation equipment, construction equipment, electronics, instruments, automotive parts, sports goods, etc.). Within natural aqueous environments, iron predominantly exists as Fe^{II} and Fe^{III} , two oxidation states that exhibit stability across a broad spectrum of environmental conditions; however, while Fe^{II} predominates in anoxic waters, Fe^{III} is the most stable oxidation state in well oxygenated waters [9]. Under circumneutral conditions, the dominant species of Fe^{III} is the solid $\text{Fe}(\text{OH})_3$, which frequently confines Fe^{III} to the particulate phase. Conversely, Fe^{II} remains predominantly in the form of a simple hydrated ion up to pH 8, rendering it the iron species with highest solubility and mobility [10,11].

In aerobic river waters, the dissolved iron concentration is typically below 1 mg L^{-1} , though values can reach up to 6 mg L^{-1} [12–14]. Significantly higher levels occur in anaerobic groundwaters, where concentrations usually range from 0.5 to 10 mg L^{-1} and can escalate up to or beyond 50 mg L^{-1} under strongly reducing conditions [14,15]. An even more extreme scenario is observed in mine drainage waters; characterized by high acidity and low dissolved oxygen, these systems can harbor massive iron loads, with reported concentrations as high as 1940 mg L^{-1} [16].

Owing to its redox activity, iron readily undergoes electron transfer processes, which are fundamental to various metabolic processes in most living cells; therefore, as an essential micronutrient, iron is indispensable to the metabolic frameworks of nearly all living organisms, driving vital physiological processes that include molecular oxygen transport, storage, and activation, as well as the reduction of dinitrogen and ribonucleotides, oxidative pathways, and cellular proliferation [17–20].

However, the very same ability of iron to gain or lose electrons, which is crucial for life, can also turn toxic when iron builds up excessively inside cells. The toxicological effects and environmental hazards associated with iron contamination are primarily driven by its divalent form for two key reasons. First, Fe^{II} represents the most bioavailable species in aquatic ecosystems. Second, it acts as the biologically active form of the element, as intracellular iron metabolism utilizes Fe^{II} rather than Fe^{III} . The toxicological effects of Fe^{II} are driven by its capacity to induce the formation of highly reactive free radicals within biological tissues via three main mechanisms [19]: (1) Fe-catalyzed reduction of oxygen, yielding toxic hydroxyl radicals; (2) Fenton reaction, which similarly generates hydroxyl radicals; and (3) decomposition of lipid peroxides, producing alkoxyl and peroxy radicals. Subsequently, all these generated free radicals may attack cellular membranes, proteins, and DNA [18,21]. Disorders of iron metabolism may include microbial infections or tissue damage; furthermore, evidence suggests that elevated levels of free iron might contribute to carcinogenesis, as well as to neurodegenerative pathologies like Alzheimer's and Parkinson's diseases [9,22].

Consequently, Fe^{II} removal is an essential remediation step that must be implemented across all iron-bearing aqueous effluents to mitigate potential public health risks. Several techniques can be used for heavy metal ion removal from contaminated waters, including chemical precipitation, chemical coagulation and flocculation, electrochemical methods, membrane filtration, ion exchange, bioremediation, and adsorption [2,6,23]. Among these,

chemical precipitation is the conventional process most extensively used due to its straightforward controllability; however, this technology has some important drawbacks, such as the requirement of high quantities of chemicals, slow metal precipitation, the generation of toxic sludge needing additional processing, associated increased operational costs, and the potential for long-term environmental consequences [2,24].

On the other hand, adsorption has emerged over the last decades as a promising alternative for the treatment of heavy-metal-contaminated water; this approach owes its success to a simple design, flexible operation under various conditions, high selectivity, and excellent efficiency [2,25]. Adsorption is the process in which a dissolved substance transfers from a liquid to a solid surface, binding via physical (physisorption) or chemical (chemisorption) interactions [7,24]. Adsorption-based water treatment processes rely on two different adsorbent classes, conventional and novel, each with their own advantages and limitations [26]. Activated carbon stands out as the preferred conventional adsorbent, thanks to its exceptional combination of large surface area, extensive porosity, ease of surface functionalization, high chemical reactivity, and excellent adsorption capacity; however, relatively high costs associated with acquiring and regenerating activated carbons often prohibited their use in low-income developing countries [27,28]. Recently, biosorption techniques have garnered considerable attention for their ability to retain heavy metals from contaminated waters; these include the use of a wide range of low-cost vegetal materials as a replacement for costly activated carbons, owing to their abundance, physiochemical properties, availability in large quantities, and low cost [8]. Utilizing biomass in its raw state eliminates the energy-intensive chemical and thermal treatments associated with synthetic adsorbents; it also promotes a sustainable circular economy, offering an environmentally responsible alternative to conventional water purification methodologies [4,6,8,24–26,29–31].

Over the last two decades, pine cone biomass has attracted great interest for its adsorptive removal of various heavy metals and metalloids (Pb^{II} , Cu^{II} , Co^{II} , Ni^{II} , Cd^{II} , Cr^{VI} , Sb^{V} , As^{III}) from aqueous effluents, owing to its [32–51]: (1) worldwide availability in large amounts as forestry waste, (2) excellent physicochemical properties, and (3) content of various functional groups (hydroxyl, carbonyl, carboxyl, lactone, sulfhydryl, sulfonate, thioether, amine, alcohols, phenols, and esters) capable of binding contaminants through different mechanisms. While efforts have predominantly focused on the potential of pine cones as a precursor for activated carbons and biochars [32–46], only a few works attempted to minimize operational expenses and the complexity of the adsorptive removal process by simply using unmodified (i.e., no physical/chemical activation) milled pine cone powder [47–51]. Similarly, with respect to the removal of Fe^{II} , while the use of bioadsorbents has been a topic of some research interest [52–60], only a few studies have been devoted to the cost-effective and straightforward approach of using unmodified vegetal precursors [55,58]. In addition, to our knowledge, no prior studies have investigated pristine or engineered pine cone biomass for the elimination of this metallic ion. Therefore, this study aimed to investigate the effectiveness of Fe^{II} removal from aqueous media by adsorption onto raw pine cone powder (PCP). First, the adsorbent's physicochemical properties were investigated to understand how they relate to its ability to adsorb ferrous ions. We subsequently evaluated how pH, initial iron ion concentration, ionic strength, and temperature influenced the overall adsorption performance. Finally, adsorption kinetics, equilibrium, and thermodynamics were systematically investigated to model and predict the overall sorption behavior of Fe^{II} onto PCP.

2. Materials and Methods

2.1. Materials

Analytical reagent-grade $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, H_2SO_4 98%, 1,10-phenanthroline, and NaCl were used as supplied. The pine cones were collected from pine trees (*Pinus sylvestris*) located in proximity to our faculty. After being harvested, the cones were thoroughly rinsed with distilled water, ambiently air-dried for one week, and then pulverized with an electric grinder. The obtained pine cone powder (PCP) was washed repeatedly with distilled water until there was no longer a brown tint to the rinse water and subsequently dried in an oven at 60 °C for 24 h. After cooling, the biomass cake was ground using a mortar and pestle and fractioned to particles sized < 0.5 mm. The resulting PCP was further used without any other treatment in the experiments described below.

2.2. Experimental Procedure

A 1000 mg L^{−1} Fe^{II} stock solution was prepared by dissolving the calculated amount of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in distilled water. This solution was sequentially diluted with distilled water to yield target Fe^{II} concentrations for the adsorption experiments. The pH of the solution was adjusted with 1 M of H_2SO_4 solution. Batch kinetic experiments were performed by mixing 5 g of PCP with 500 mL of working Fe^{II} solution in a Berzelius beaker. Agitation was maintained at 200 rpm via a jar test apparatus (Ovan, Badalona, Spain); solution aliquots were collected at predetermined intervals, filtered through a 0.45 µm syringe filter, and subsequently analyzed for Fe^{II}. The influence of solution pH, Fe^{II} concentration, ionic strength, and temperature on the adsorption process was systematically evaluated, as summarized in Table S1. For the equilibrium studies, different amounts of the adsorbent were suspended in Erlenmeyer flasks containing 50 mL of 10 mg/L Fe^{II} solution at pH 3.2. Flasks were sealed and stirred at 100 strokes per minute using a Julabo SW22 (Seelbach, Germany) apparatus for 24 h to allow the adsorption to reach the equilibrium (Table S2); subsequently, the solutions were filtered, and the resulting filtrates were analyzed to determine the residual Fe^{II} concentration.

2.3. Analytical Procedure

The residual Fe^{II} in the filtrate was determined spectrophotometrically at 510 nm following the 1,10-phenanthroline method [61], using a Specord 200 PLUS (Analytik Jena, Jena, Germany) spectrophotometer. Solution pH values were determined using a pH meter (WTW Inolab 7320, Frankfurt, Germany), calibrated across the operational range using standard buffers (pH 4.0, 7.0, and 10.0). The pH drift method was applied to determine the PCP's point of zero charge (pH_{pzc}) [62]. The PCP's total specific surface area (SSA) was determined via the EGME method [63]. The surface morphology and chemical composition of fresh and exhausted adsorbent were investigated via scanning electron microscopy (SEM—Inspect S, FEI, Eindhoven, The Netherlands) equipped with energy dispersive X-ray spectroscopy (EDX—GENESIS XM 2i, Eindhoven, The Netherlands), complemented by Fourier transform infrared spectrometry (FTIR—VERTEX 70, Bruker, Germany).

2.4. Experimental Data Processing

Five kinetic models (pseudo-first-order, pseudo-second-order, pseudo-nth-order, Elovich, Weber–Morris intraparticle diffusion [64–75]) and five isotherm models (Langmuir, Freundlich, Langmuir–Freundlich, Temkin, Redlich–Peterson [67,68,72,76–85]) were employed to evaluate the kinetics and equilibrium aspects of the adsorption; they were chosen based on their widespread validation and prevalence in contemporary adsorption literature, which ensures comparability with existing datasets. Models were analyzed using nonlinear equations, in line with numerous recent reports revealing that linear regression fitting fails

to provide accurate model parameters [68,73,78,84,86–88]. Detailed descriptions of these models are given in Tables S3 and S4. The Solver tool in Microsoft Excel (Microsoft 365) was used for fitting experimental data to model equations [89]. To assess the validity of our models, in addition to R^2 , several other statistical parameters were used, including χ^2 , SSE, RMSE, and HYBRID, as recommended by previous researchers [65,78,88–90].

Results of the kinetic modelling at three temperatures were applied to calculate the adsorption activation energy (E_a) using the Arrhenius equation [72] (Table S5).

To predict the sorption behavior of Fe^{II} onto PCP (spontaneity, favorability for the given experimental conditions, thermal feasibility, nature of the adsorption reaction), standard Gibbs free energy (ΔG°), standard enthalpy (ΔH°), and standard entropy (ΔS°) changes were derived from the equilibrium datasets acquired at three temperatures, according to equations listed in Table S6 [77,78,88,91–98].

All experimental data are presented as the mean of two independent replicates, with a relative error of less than 5%. Statistical evaluations were carried out using Microsoft Excel software (Microsoft 365).

3. Results and Discussion

3.1. Adsorbent Characterization

FTIR spectra of fresh and metal-loaded biomass were recorded in the wavenumber range of 400–4000 cm^{-1} at a spectral resolution of 4 cm^{-1} . The Essential FTIR software (3.50 free trial version) was used for analyzing the obtained FTIR spectra. Figures S1 and S2 show several absorption peaks typical for a lignocellulosic structure, highlighting the complexity of the PCP biomass. The strong wide absorption band with maximum intensity centered around 3448 cm^{-1} corresponds to the O-H stretching vibrations of hydroxyl groups originating from alcoholic and phenolic structures [38,41,51,53]. The high intensity peak at 2922 cm^{-1} can be assigned to the C-H bonds stretch in the methylene group [47,51,99]. The strong band with two peaks at around 1736 cm^{-1} and 1645 cm^{-1} was assigned to the C = O stretching vibration of ketone and carbonyl groups [42,100]. The band observed at 1514 cm^{-1} corresponded to the aromatic skeletal vibration of the C = C bond [45,101]. The peaks located around 1458 cm^{-1} and 1377 cm^{-1} are indicative for the C-H bending in CH_3 and CH_2 [51,102,103]. The absorption band at approximately 1269 cm^{-1} can be attributed to the presence of carboxylic and phenolic groups, associated with characteristic C–O stretching vibrations [47], and/or C–N stretching with amine [104]. The strong band located at about 1032 cm^{-1} corresponds to C–O groups stretching vibration in primary alcohol groups [39,48]; furthermore, shoulders around 1057, 1111, and 1163 cm^{-1} correspond to C–O stretch in primary, secondary, and tertiary alcohol, respectively [74,105]. The minor peak observed at approximately 897 cm^{-1} belongs to the glycosidic C1–H deformation [100,106]. Absorption bands below 800 cm^{-1} correspond to complex vibrational modes that typically originate from aromatic compounds. A comparison of Figures S1 and S2 reveals that both fresh and Fe-loaded biomass samples showed similar peaks; furthermore, no peaks disappeared, and no supplementary peaks emerged after the adsorption process. However, slight changes in the peaks' positions were noticed in the surface structure of PCP upon metal adsorption, as revealed in Table S7 [42,45,47,48,51,99–101,104,107]. These alterations in the FTIR spectrum confirm the direct involvement of the PCP functional groups in binding Fe^{2+} during adsorption. The fact that all major characteristic peaks of the biomass remained intact after metal loading, with no new peaks appearing or any existing ones disappearing, indicates that the core structural framework of the PCP biomass remains stable during the process.

The surface and textural morphology of the fresh and Fe-loaded PCP are depicted in Figures S3 and S4, respectively. Visual examination of the SEM images revealed

the particles to be needle-shaped, with a rough surface and pores of consistent size (~2–5 micrometers) distributed uniformly; a non-uniform surface morphology is advantageous for the adsorption process, as it provides a greater number of accessible sites for adsorbate molecules to bind [107]. However, SEM micrographs showed no significant changes in the adsorbent's surface after the adsorption process; additionally, no visible contaminant buildup was observed on the exhausted adsorbent, likely because of the minimal amount of retained metal on its surface.

The EDX spectra of fresh and Fe-loaded adsorbent (PCP-Fe) are shown in Figures S5 and S6, respectively. Examination of this data reveals that additional signals corresponding to Fe appeared in the EDX spectra of PCP-Fe in comparison to the pristine PCP, indicating the retention of Fe at the surface of the adsorbent.

The determination of PCP's point of zero charge yielded a value of 6.0, which falls within the range reported in previous studies for pine cone biomass (5.62–7.49) [42,45,47,49] and is also close to the values (5.5–6.6) determined for other untreated agricultural waste biosorbents, such as walnut shell, sour cherry leaves, sour cherry stones, and avocado kernel seeds [55,108,109]. The PCP's SSA was found to be $163.9 \text{ m}^2 \text{ g}^{-1}$; a comparison of the SSA values reported in the literature for different raw agricultural waste bioadsorbents is provided in Table S8 [109–114].

3.2. Influence of Parameter Variability on Fe^{II} Removal Performance

3.2.1. Influence of pH

The aqueous medium pH represents a well-documented fundamental variable governing the biosorption of metal ions; by determining both the protonation state of the adsorbent functional groups and the speciation of the metal ions, pH fundamentally dictates the interfacial interaction mechanisms between the adsorbent and the metal ions, thereby controlling the overall adsorption capacity [47,52]. To investigate the influence of pH on Fe^{II} removal, the metal ion solution pH varied across a range from 2.1 to 4.1. This low pH range was chosen to prevent precipitation of Fe^{II} as well as its oxidation to Fe^{III} ; it is representative of acid mine drainages, where iron is often the main heavy metal present [115,116]. The dependence of Fe^{II} adsorption onto PCP as a function of solution pH is illustrated in Figures 1 and 2.

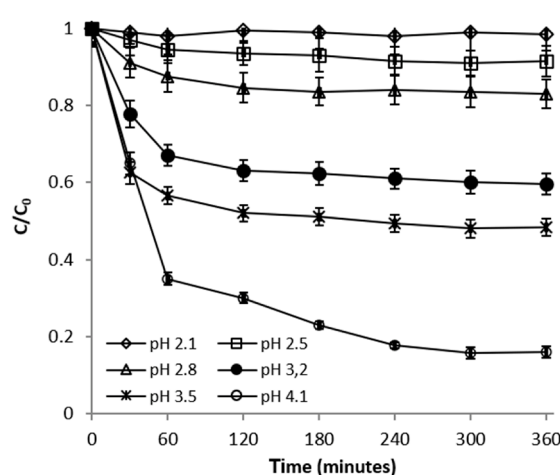


Figure 1. Influence of initial solution pH on Fe^{II} adsorption by PCP. Experimental conditions: $C_0 = 50 \text{ mg L}^{-1}$; temperature = 22°C ; mixing intensity: 200 rpm; PCP dose = 10 g L^{-1} ; ionic strength = 0 M NaCl; contact time = 360 min.

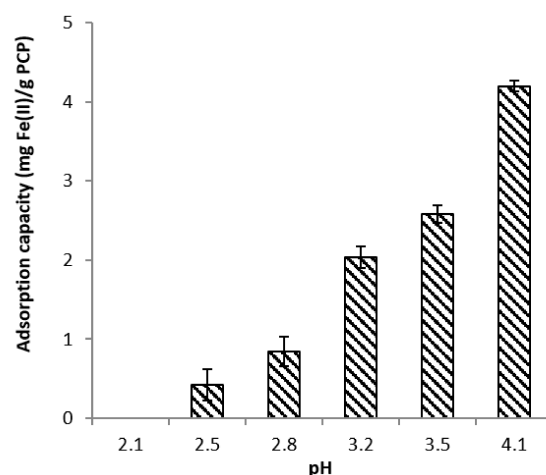


Figure 2. Influence of initial solution pH on Fe^{II} adsorption capacity of PCP. Experimental conditions: $C_0 = 50 \text{ mg L}^{-1}$; temperature = 22°C ; mixing intensity: 200 rpm; PCP dose = 10 g L^{-1} ; ionic strength = 0 M NaCl; contact time = 360 min.

As can be seen, no Fe^{II} removal was observed at pH 2.1, while only limited adsorption was noticed at pH 2.5. However, as the pH increased towards 4.1, both the efficiency of Fe^{II} retention and the adsorption capacity of PCP were significantly improved. This is consistent with previous studies on Fe^{II} adsorption using different waste biomass-based adsorbents (walnut shell, orange peels, jamun seeds, aloe vera leaves, crownflower roots), which also documented a similar increase in removal efficiency with an increase in aqueous phase pH [52–57].

The findings reported here most likely result from the electrostatic coulombic interactions between the cationic ferrous species and the localized surface charges on the PCP matrix. At pH values lower than pH_{pzc} (i.e., <6.0), the PCP surface acquires a net positive charge; conversely, when the solution pH exceeds the pH_{pzc} , deprotonation occurs, causing the PCP surface to acquire a net negative charge. Thus, it is evident that, over the entire studied pH range, the PCP surface will carry a net positive charge. Hence, throughout the investigated pH range, repulsion forces will generally make adsorption onto PCP unfavorable. Accordingly, the complete prevention of adsorption at pH 2.1 can be explained by the high abundance of H_3O^+ ions, which protonate the PCP surface functionalities, establishing a strong positive charge density that prevents metal binding. Nevertheless, increasing the solution pH to 4.1 causes the PCP surface to develop more negative charges and loses positive charges, which explains why adsorption is initiated at pH greater than 2.1, and its effectiveness increases as the pH rises. In addition, higher pH values also contribute to increased Fe^{II} cation removal by decreasing the H_3O^+ ion concentration, thereby enhancing metal accessibility to the negatively charged binding functional sites on the PCP matrix. However, it must be noted that, at pH 4.1, Fe^{II} precipitation and/or oxidation to Fe^{III} already had a small but distinct contribution to removal of the metal, as can be seen from the control experiments (no PCP added) depicted in Figure S7. Therefore, to guarantee that Fe^{II} elimination was governed exclusively by surface adsorption rather than precipitation, all further experiments were conducted at a controlled pH of 3.2.

The pH-dependent behavior observed in the batch adsorption experiments correlates strongly with FTIR spectral shifts in the carbonyl, carboxyl, and phenolic regions (Table S7). At higher pH values, the deprotonation of these groups reduces electrostatic repulsion and provides negatively charged sites, facilitating enhanced surface complexation and ion exchange with the positively charged Fe^{2+} .

3.2.2. Influence of Fe^{II} Initial Concentration

Another important parameter influencing sorption efficiency is the initial metal concentration; in this work, it was investigated across a range spanning from 10 to 90 mg L⁻¹. The temporal evolution of Fe^{II} concentration as a function of its initial load, presented in Figure 3, reveals that the higher the concentration of Fe^{II}, the less efficiently PCP can take it up. At low initial adsorbate loadings, a high ratio exists between the number of PCP adsorption sites and the concentration of Fe^{II} ions in the solution; therefore, this abundance of binding sites facilitated the efficient removal of Fe^{II} ions through adsorption. However, as illustrated in Figure 3, the kinetic profile of Fe^{II} uptake onto PCP exhibits a distinct biphasic behavior rather than a uniform progression. During the primary phase, a steep decrease in solution concentration is observed; this behavior arises because the initial density of unoccupied surface functionalities is vastly superior to the concentration of the Fe^{II} ions, minimizing competitive effects. The time span of this stage decreased with increasing Fe^{II} concentration; the first step lasted about 60 min for the 10–50 mg L⁻¹ concentration, and only approximately 30 min for the 70 and 90 mg L⁻¹ concentrations (Figure 3). The second stage exhibited a significant decline in adsorption rates, ascribed to an increasing degree of adsorption site saturation and diminished accessibility of the remaining adsorption-active sites.

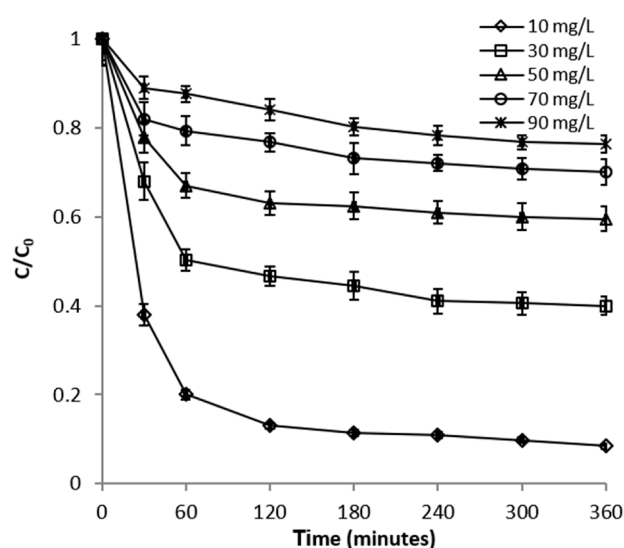


Figure 3. Influence of initial Fe^{II} concentration on Fe^{II} adsorption by PCP. Experimental conditions: pH = 3.2; temperature = 22 °C; mixing intensity: 200 rpm; PCP dose = 10 g L⁻¹; ionic strength = 0 M NaCl; contact time = 360 min.

In contrast, as the initial Fe^{II} concentration was elevated, the mass-dependent adsorption capacity of PCP increased correspondingly until a saturation steady-state was attained (Figure 4). The PCP surface reached saturation only for Fe^{II} concentrations starting with 50 mg/L, when the experimental maximal adsorption capacity tended towards a constant value of about 2.1 mg g⁻¹. The increased adsorption capacity observed at higher initial Fe^{II} concentrations is driven by an enhanced concentration gradient between the aqueous phase and the solid–liquid interface, which [53,117]: (1) increased the probability of metal ion collision with the biosorbent surface, (2) counteracted any mass transfer limitations that might hinder the Fe^{II} ions from reaching the surface of the PCP, and (3) enhanced the rate of metal ions mass transfer into the biosorbent pore. These results align consistently with findings presented by previous researchers for Fe^{II} sequestration utilizing alternative waste biomass-derived adsorbents (walnut shell, orange peels, jamun seeds, pine bark, coir fibre, crownflower roots) [53,55–59].

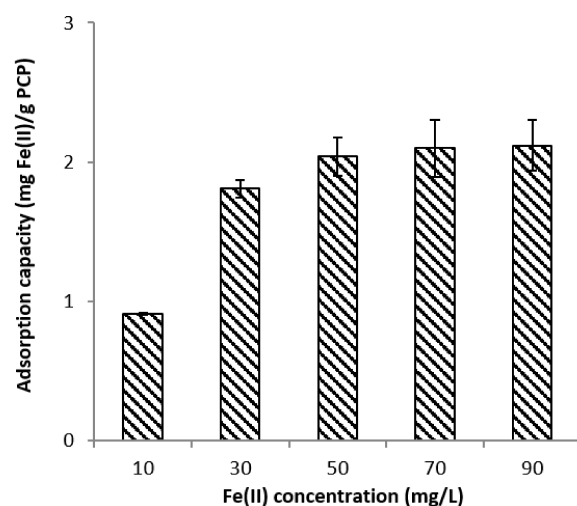


Figure 4. Influence of initial Fe^{II} concentration on Fe^{II} adsorption capacity of PCP. Experimental conditions: pH = 3.2; temperature = 22 °C; mixing intensity: 200 rpm; PCP dose = 10 g L⁻¹; ionic strength = 0 M NaCl; contact time = 360 min.

3.2.3. Influence of Temperature

Temperature represents another key operational parameter in adsorption processes, as it simultaneously governs the mass transport and solubility of the adsorbate, while shifting the thermodynamic equilibrium capacity [118]; thus, temperature can affect the adsorption process from both a kinetic and thermodynamic perspective. The influence of temperature on the system was systematically evaluated across a thermal range of 10–32 °C; the resulting data sets are presented in Figures 5 and 6.

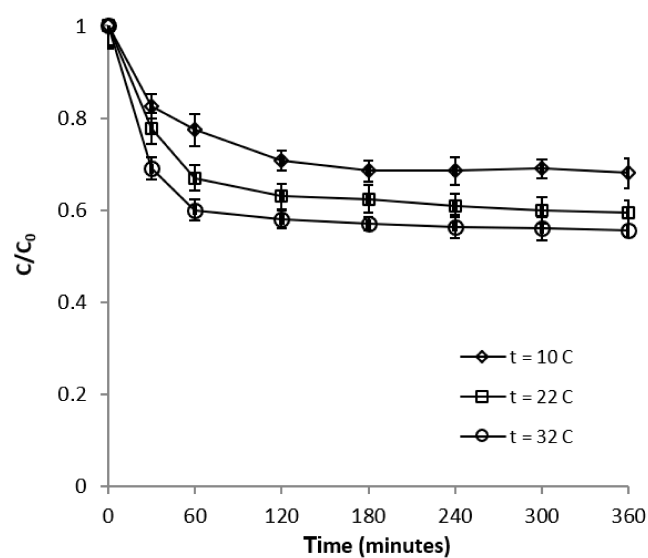


Figure 5. Influence of temperature on Fe^{II} adsorption by PCP. Experimental conditions: pH = 3.2; C_0 = 50 mg L⁻¹; mixing intensity: 200 rpm; PCP dose = 10 g L⁻¹; ionic strength = 0 M NaCl; contact time = 360 min.

Both the removal efficiency and equilibrium adsorption capacity of the PCP matrix exhibited a strong positive correlation with temperature across the entire investigated range. Notably, the most important improvement was exhibited when the operating temperature was raised from 10 to 22 °C. Further increasing the temperature to 32 °C offered some benefit for the Fe^{II} uptake, but the improvement was less significant compared to previous increases. This suggests that higher temperatures would not be cost-effective for the

adsorptive sequestration process. The positive correlation between elevated temperature and Fe^{II} binding may be attributed to [38,51]: (1) an increase in the number of adsorption sites; (2) higher thermal energy of the adsorbing species, which increases their speed and frequency of collisions with PCP; and (3) desolvation of incoming adsorbing species, along with a compression of the boundary layer surrounding the PCP matrix; this decreases mass transfer resistance in the boundary layer, leading to increased rates of intraparticle adsorbate diffusion in PCP pores. The observed relationship between temperature and adsorption capacity indicates the process is endothermic. A comparable positive thermal effect on removal efficiency has been documented in earlier literature examining Fe^{II} adsorption on agro-waste adsorbents (walnut shell, orange peels, jamun seeds) [53,55,56]. However, when utilizing acid-modified aloe vera leaves for Fe^{II} adsorption, it was reported that as temperature increased, the elimination percentage decreased [52].

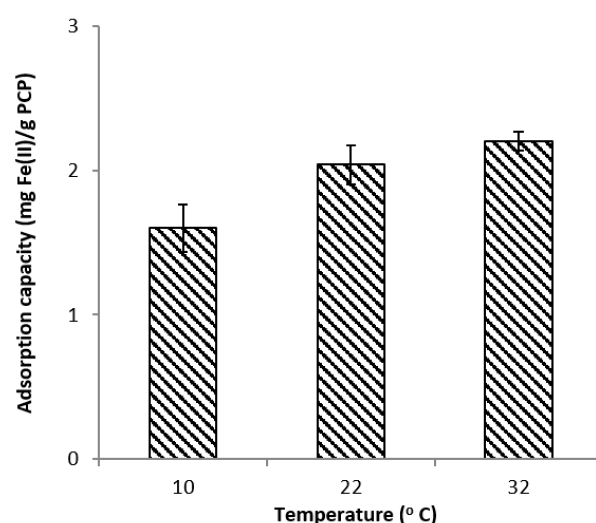


Figure 6. Influence of temperature on Fe^{II} adsorption capacity of PCP. Experimental conditions: pH = 3.2; $C_0 = 50 \text{ mg L}^{-1}$; mixing intensity: 200 rpm; PCP dose = 10 g L^{-1} ; ionic strength = 0 M NaCl; contact time = 360 min.

3.2.4. Influence of Ionic Strength

Ionic strength is another important parameter to be studied because both natural water bodies and wastewater effluents usually contain various concentrations of dissolved salts, which could affect adsorption performance [119]. In addition, by analyzing how metal adsorption changes with increasing ionic strength, we can distinguish between the two main mechanisms by which ions bind to minerals: physical adsorption (weak, non-specific) and chemical adsorption (strong, specific). In the present work, the influence of ionic strength on Fe^{II} adsorption was systematically evaluated by varying the concentration of a background electrolyte between 0 and 0.05 M. NaCl was selected as an indifferent electrolyte because its chemically inert behavior isolates ionic strength effects without pH interference or competitive reactions, while its ubiquity realistically models natural and industrial aquatic matrices. As illustrated in Figures 7 and 8, it resulted that higher ionic strength values gradually slow down the adsorption of Fe^{II} . The observed influence of ionic strength is likely driven by electrostatic competition between sodium and iron cations for the available binding functional groups on the biosorbent surface [120]. This finding indicates that adsorption occurs predominantly by the formation of outer sphere complexes involving weak, non-specific interactions, characteristic of physisorption [121–123].

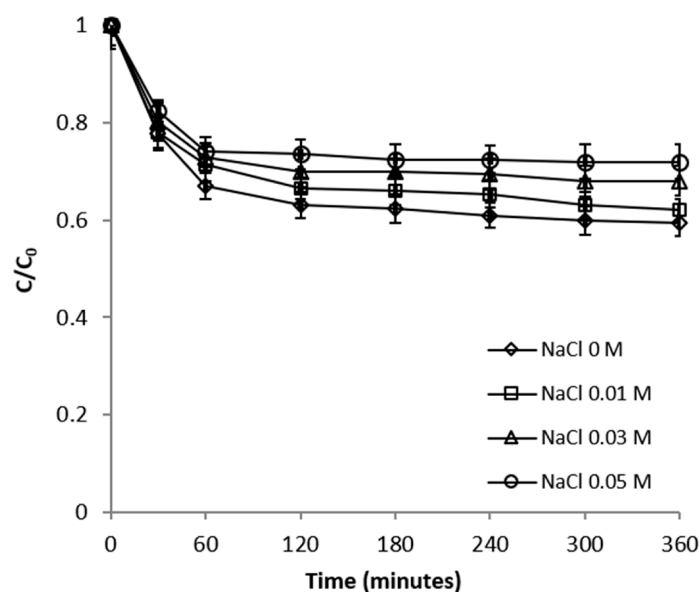


Figure 7. Influence of ionic strength on Fe^{II} adsorption by PCP. Experimental conditions: $\text{pH} = 3.2$; $C_0 = 50 \text{ mg L}^{-1}$; mixing intensity: 200 rpm; PCP dose = 10 g L^{-1} ; temperature = 22°C ; contact time = 360 min.

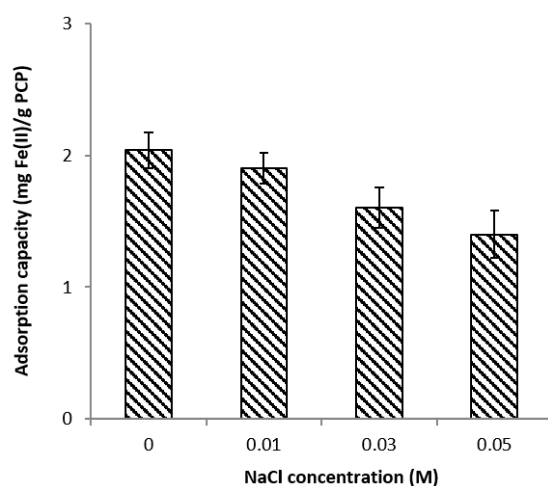


Figure 8. Influence of ionic strength on Fe^{II} adsorption capacity of PCP. Experimental conditions: $\text{pH} = 3.2$; $C_0 = 50 \text{ mg L}^{-1}$; mixing intensity: 200 rpm; PCP dose = 10 g L^{-1} ; temperature = 22°C ; contact time = 360 min.

3.3. Kinetic Studies

3.3.1. Kinetic Modelling

The fitted curves of the studied kinetic models and the parameter values with their statistical fits are given in Figures S8–S13 and Table 1, respectively. According to the parameters listed in Table 1, the high coefficients (R^2) indicate that both the pseudo-first-order and pseudo-second-order kinetic models correlate strongly with the experimental data, exhibiting only marginal variations in their regression values. Hence, this is a clear example of why calculating R^2 alone is not enough in evaluating how well models represent the experimental data; as confirmed by previous studies, other error functions must be determined and used as criteria for assessing the fitting quality of the investigated models [78,84,88,90]. Accordingly, a further comparison of the error functions summarized in Table 1 (lower values mean a better fit of the model) established the pseudo-first-order framework as the more accurate representation of the empirical kinetic profile. The validity of this mechanism is verified by the striking proximity between the empirically determined

uptake capacity ($q_e^{\text{exp}} = 2.02$) and the theoretical value predicted by the pseudo-first-order model ($q_e^{\text{calc}} = 1.96$). This is consistent with previous reports on Fe^{II} adsorption using pine bark, jamun seeds, and aloe vera leaves as waste biomass-based adsorbents [52,56,58]; the kinetic parameters derived from the pseudo-first-order model across various investigations are compiled for comparative analysis in Table S9 [52,56,58]. Instead, other studies employing orange peels, walnut shells, and pomegranate peels as adsorbent biomaterials demonstrated that the sequestration process conformed closely to pseudo-second-order kinetics [53,55,60].

Table 1. Results of Fe^{II} adsorption kinetic modeling.

Kinetic Model	Parameters and Error Functions	Value
Pseudo-first-order	k_1 (min^{-1})	$2.83 \cdot 10^{-2}$
	q_e (mg g^{-1})	1.96
	R^2	0.9950
	χ^2	0.0090
	SSE	0.0169
	RMSE	0.0492
	HYBRID	0.1802
Pseudo-second-order	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	$1.86 \cdot 10^{-2}$
	q_e (mg g^{-1})	2.17
	R^2	0.9933
	χ^2	0.0155
	SSE	0.0225
	RMSE	0.0567
	HYBRID	0.3111
Pseudo-nth-order	k_n ($\text{g}^{(n-1)} \text{mg}^{(-1)} \text{min}^{-1}$)	$7.86 \cdot 10^{-3}$
	q_e (mg g^{-1})	2.47
	n	3.0
	R^2	0.9897
	χ^2	0.0241
	SSE	0.0349
	RMSE	0.0706
Elovich	HYBRID	0.6074
	α ($\text{mg g}^{-1} \text{min}^{-1}$)	0.47
	β (g mg^{-1})	2.96
	R^2	0.9801
	χ^2	0.0459
	SSE	0.0677
	RMSE	0.0984
Weber–Morris	HYBRID	0.9438
	k_d ($\text{mg g}^{-1} \text{min}^{-0.5}$)	$9.77 \cdot 10^{-2}$
	C (mg g^{-1})	0.46
	R^2	0.8166
	χ^2	0.7424
	SSE	0.6247
	RMSE	0.2987
	HYBRID	4.59

From a physicochemical perspective, first-order models are typically applicable when adsorption is limited by film diffusion or when transport has negligible impact on the overall adsorption rate [124]. At the same time, a pseudo-first order kinetics implies that adsorption is fast and adsorbent equilibrium is more rapidly attained, knowing that the saturation time exponentially increases with the rate order [66].

To elucidate the primary rate-controlling steps governing the Fe^{II} uptake, the Weber–Morris intraparticle diffusion model was applied to the kinetic experimental data. Generally, the process of contaminant removal via adsorption can be separated into four stages [67,89,125]: (1) transport of the contaminant through the bulk aqueous phase, (2) film diffusion of the contaminant across the stagnant liquid film surrounding the particle to reach its external periphery, (3) contaminant intraparticle diffusion from the external surface into the internal porous matrix of the adsorbent, and (4) contaminant immobilization onto the active functional groups. However, since a well mixed batch system was employed in this study, stage 1 cannot become a rate-limiting step [126]. Furthermore, stage 4 is typically also a fast process and does not usually limit the overall rate of adsorption [127]. Thus, only the film diffusion (stage 2) and intraparticle diffusion (stage 3) resistances may act as the potential rate-limiting steps during the solute immobilization process. According to the Weber–Morris framework, intraparticle diffusion governs the overall adsorption velocity, provided that the regression of q_t against $t^{0.5}$ yields a linear relationship that intersects the origin [67]. However, the profile displayed in Figure S13 exhibits a distinct segmented linearity, indicating that the adsorption process proceeds via two separate, successive mass transfer stages. As illustrated by the high slope of the first segment, the early kinetic phase is governed predominantly by mass transfer boundary layer diffusion effects (i.e., film diffusion). The subsequent segment, characterized by a markedly reduced slope, corresponds to a kinetic regime predominantly governed by the gradual adsorption inside the pores (i.e., intraparticle diffusion). Hence, it can be concluded that intraparticle diffusion does not act as the exclusive kinetic bottleneck during the sequestration of Fe^{II} onto PCP [67,128]. In addition, the Weber–Morris k_d and C parameters can provide further information regarding transport resistances. Specifically, the intraparticle diffusion rate coefficient k_d serves as an indicator of internal mass transfer resistance, where lower values signify heightened diffusional limitations within the pore architecture. Concurrently, the intercept C correlates directly with the boundary layer thickness; an elevated C value denotes a thicker stagnant fluid film, thereby imposing a greater hindrance on solute transport [129,130]. Similar Weber–Morris profiles characterized by deviation from the origin and the presence of segmented linearity have been documented in prior literature analyzing Fe^{II} sequestration on biosorbents based on pine bark, walnut shell, jamun fruit seeds, and aloe vera leaves [52,55,56,58]; a comparison of the Weber–Morris parameters reported in these studies is provided in Table S10 [55,56,58].

3.3.2. Energy of Activation

To evaluate the activation energy governing the adsorption process, the linearized Arrhenius relationship [72] was applied (Table S5). Utilizing kinetic coefficients determined at 283, 295, and 305 °K, the activation energy of the adsorption process was calculated to be 17.8 kJ mol^{-1} from the linear slope representing $\ln k_1$ versus $1/T$ (Figure S14). The numeric value of the activation energy provides a clear diagnostic criterion to distinguish between the domination of weaker physisorption or stronger chemisorption processes. An activation energy below 40 kJ mol^{-1} confirms physisorption as the dominant process [118,131]. This is in line with previous results ($E_a = 12.9 \text{ kJ mol}^{-1}$) reported for adsorption of Fe^{II} by pine bark biomass [58].

3.4. Equilibrium Isotherm Studies

The five studied equilibrium isotherms are depicted in Figures S15–S19, while their parameters and error functions are outlined in Table 2. The experimental results were best described by the Freundlich and Redlich–Peterson isotherms, which have identical R^2 coefficients. This can be ascribed to the fact that, at elevated adsorbate concentrations,

the Redlich–Peterson model converges toward the Freundlich isotherm [132]. However, the lower error function values calculated for the Freundlich model confirm its superior fit to the experimental data. The assumptions underlying the empirical Freundlich model include [78,84,133]: (1) adsorption takes place across heterogeneous surfaces, featuring multiple distinct sites; (2) ion retention is reversible and can occur in multiple layers; and (3) the value of the adsorption energy is not constant for all adsorption sites. Similar best fitting of the Freundlich isotherm was previously reported for Fe^{II} adsorption on pine bark, orange peels, jamun seeds, and crownflower roots as waste biomass-based adsorbents [53,56–58].

Table 2. Results of Fe^{II} adsorption equilibrium modeling.

Thermodynamic Model	Parameters and Error Functions	Value
Langmuir	$q_{\max}$ (mg g ^{−1})	12.7
	K_L (L mg ^{−1})	$1.54 \cdot 10^{-1}$
	R_L	0.39
	R^2	0.9886
	χ^2	0.7133
	SSE	0.4652
	RMSE	0.2157
	HYBRID	3.89
Freundlich	K_F ((mg g ^{−1}) (mg L) ^{−1/n})	1.74
	$1/n_F$	0.70
	R^2	0.9989
	χ^2	0.0427
	SSE	0.448
	RMSE	0.0638
	HYBRID	0.5005
Langmuir–Freundlich	$q_{\max}$ (mg g ^{−1})	649.7
	K_{LF} (L mg ^{−1})	$2.83 \cdot 10^{-4}$
	n	0.76
	R^2	0.9894
	χ^2	0.0780
	SSE	0.0652
	RMSE	0.0808
	HYBRID	0.8380
Temkin	K_T (L mg ^{−1})	4.58
	b (kJ mol ^{−1})	1.50
	R^2	0.9083
	χ^2	3.88
	SSE	3.79
	RMSE	0.6161
	HYBRID	27.2
Redlich–Peterson	K_{RP} (L mg ^{−1})	1938.0
	a (L mg ^{−1}) ^g	1113.4
	g	0.29
	R^2	0.9989
	χ^2	0.0428
	SSE	0.0448
	RMSE	0.0669
	HYBRID	0.5725

The Freundlich constant $1/n_F$ quantifies the process favorability; adsorption is considered favorable if $0 < 1/n_F < 1$ and unfavorable if $1/n_F > 1$. Furthermore, the Freundlich constant $1/n_F$ can also give information on the heterogeneity of the adsorbent surface. If

$1/n_F = 1$, the adsorbent surface is homogeneous, with equal adsorption energies for all sites, resulting in linear adsorption. Instead, values of $1/n_F < 1$ signify surface heterogeneity and varied site energies, leading to isotherm nonlinearity; the closer the $1/n_F$ value to 0, the higher the surface heterogeneity and the broader the distribution of binding energies on the adsorbent surface. In this last case, the binding sites with the highest energy are occupied first and, as these sites become occupied, adsorption continues on sites with progressively lower energies [88,134]. In this study, we determined a value of $1/n_F = 0.70$ (Table 2), indicating that adsorption of Fe^{II} on PCP was favorable. This is in accord with the Langmuir R_L separation factor (determined as detailed in Supplementary Material) having a value of 0.39 (Table 2); given that this parameter falls between 0 and 1, it reveals the favorability of the adsorption system [88].

Because the Freundlich model assumes a multilayer retention of adsorbate on adsorbent, it could suggest that physisorption is the primary mechanism [62,68]. However, as with kinetic models, the successful fit of an adsorption isotherm model offers limited insight into the specific mechanism governing the adsorption process; other analyses may be needed to fully understand the adsorption process [68,128].

Since the Temkin bonding energy b value (Table 2) is below 8 kJ mol^{-1} , weak physical interactions can be designated as the primary force governing the uptake process [131]; this conclusion is consistent with the recorded activation energy (see Section 3.3.2), which also identifies physisorption as the dominant process involved in the retention of Fe^{II} by PCP.

3.5. Thermodynamic Studies

To evaluate the thermodynamic nature of the adsorption process, the standard Gibbs free energy (ΔG°), standard enthalpy (ΔH°), and standard entropy (ΔS°) changes were determined. These parameters were calculated utilizing equilibrium data gathered across a temperature range of 283, 295, and 305 °K. Because using equilibrium constant values with dimensions for the calculation of ΔG° , ΔH° , and ΔS° thermodynamic parameters is mathematically incorrect [94], we first calculated the dimensionless standard adsorption equilibrium constants K° at temperatures of 283, 295, and 305 °K, from the K_L Langmuir constants obtained at the same temperatures, as presented in Table S6 [91]. Then, based on the linearized van 't Hoff relationship (Table S6), the values for ΔS° and ΔH° were derived from the resulting intercept and slope of the linear regression of $\ln K^\circ$ against $1/T$ (Figure S20). Finally, the variations in ΔG° values across the investigated temperature range were determined from the equation describing the relationship of ΔG° with ΔH° and ΔS° (Table S6) [68,92]. As indicated by the negative ΔG° values (Table 3), adsorption is a favorable process at all examined temperatures; the more negative ΔG° is, the more favorable the adsorption [96]. The endothermic character of the adsorption process is confirmed by the positive ΔH° (Table 3) [62]. This aligns with experimental results, which demonstrated that increasing the temperature has a beneficial impact on overall adsorption capacity. Furthermore, the magnitude of ΔH° can be used to infer the main pathway by which the adsorbent and adsorbate interact [73]; a physisorption-dominated removal mechanism is indicated by the fact that the obtained ΔH° was under 40 kJ mol^{-1} in this study [94]. Lastly, the positive ΔS° value reflects an enhanced degree of disorder at the solid–liquid interface during the adsorption process, along with a good affinity of the PCP adsorbent towards Fe^{II} [88].

Table 3. Thermodynamic parameters of Fe^{II} adsorption on PCP.

$\Delta G^\circ (\text{kJ mol}^{-1})$			$\Delta H^\circ (\text{kJ mol}^{-1})$	$\Delta S^\circ (\text{J mol}^{-1} \text{K}^{-1})$
T = 283 °K	T = 295 °K	T = 305 °K		
−20.5	−22.1	−23.5	19.0	139.5

3.6. Fate of the Spent Adsorbent

While the regeneration and reusability of traditional, high-cost synthetic adsorbents are essential to balance process economics [2], the system investigated here relies on abundant, low-cost vegetal waste. From a technoeconomic standpoint, the chemical and energetic expenditure required for desorption surpasses the value of the precursor material, rendering regeneration economically unviable. Furthermore, because of the relatively low Fe^{II} toxicity, the disposal challenges associated with other hazardous heavy metals are largely averted. Therefore, instead of being subject to discarding or regeneration, the exhausted adsorbent can be valorized in several circular economy applications including iron-rich agricultural soil amendment, low-cost stabilizing filler in construction materials, and reactive material for other water treatment processes [2,55]. Nevertheless, it is worth noting that a reliable regeneration profile cannot be fully represented by simplified synthetic aqueous Fe^{II} systems. Real-world Fe^{II} bearing effluents (e.g., acid mine drainage or industrial wastewater) feature complex co-existing ions and organic matter that can trigger surface fouling, irreversible competitive binding, and altered desorption behavior. Consequently, meaningful evaluation of regeneration and longevity metrics will be targeted in future work under such realistic conditions.

4. Conclusions

This study reported the successful use of pine cone lignocellulosic material as a sustainable bioadsorbent utilized for the remediation of Fe^{II} -contaminated aqueous phases. Heavy metal adsorption correlated positively with temperature and pH but showed an inverse relationship with increasing ionic strength and initial Fe^{II} concentration. To evaluate the adsorption process, the reaction kinetics and equilibrium behavior were characterized using five distinct kinetic models and five isotherm equations, respectively. An analysis utilizing four error functions revealed that the pseudo-first-order model approach offered the best fit for the kinetic data, while the Freundlich isotherm successfully characterized the adsorption equilibrium. Thermodynamic parameters ΔG° , ΔH° , and ΔS° for Fe^{II} adsorption on PCP have been evaluated.

The positive ΔH° reflects that the sorption process is endothermic. The negative ΔG° implies that adsorption was favorable over the studied temperature spectrum. This is in line with the R_L Langmuir separation factor and $1/n_F$ Freundlich constant, which consistently point towards favorable adsorption conditions. Similarly, the positive ΔS° value implies a good affinity of the PCP for Fe^{II} , reflecting a higher state of disorder at the adsorbent–solution boundary. The combined kinetic and thermodynamic analysis points towards physisorption as the main mechanism for binding Fe^{II} onto PCP. Furthermore, both intraparticle diffusion and boundary layer (film) diffusion were found to control the kinetics of the process, as revealed by the Weber–Morris plot. The maximum Langmuir adsorption capacity of PCP reached 12.7 mg g^{-1} . Compared to the single untreated waste-derived adsorbent found in the literature (2.02 mg g^{-1} for pine bark, [58]), PCP demonstrates superior performance, establishing it as an efficient and economical alternative to commercial activated carbons. The findings demonstrate that PCP serves as an effective, low-cost alternative to traditional water treatment media. By repurposing biological waste into a functional resource, this research provides a scalable, eco-friendly solution for industrial heavy metal mitigation. This “waste-to-resource” strategy aligns with green chemistry principles, offering a cost-effective pathway to mitigate environmental pollution while minimizing the ecological footprint of water purification technologies. To further advance the significance and practical application of this work, future research directions should focus on: (1) continuous-flow fixed-bed column studies to transition from batch scales to realistic industrial configurations, (2) testing the adsorbent against complex multi-metal matrices

and real effluents to validate its robustness in real-world environmental remediation, and (3) evaluating the desorption behavior and reusability profiles of the spent PCP biomass to ensure process economy. Addressing these aspects will bridge the gap between laboratory findings and field-scale applications, further establishing PCP as a viable, eco-friendly technology for heavy metal remediation.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su18147064/s1>, Figure S1: FTIR spectra of fresh PCP; Figure S2: FTIR spectra of fresh PCP-Fe; Figure S3: SEM micrograph of PCP; Figure S4: SEM micrograph of PCP-Fe; Figure S5: EDX pattern of PCP; Figure S6: EDX pattern of PCP-Fe; Figure S7: Effect of pH on Fe^{II} concentration in control experiments; Figure S8: Fitting results of the pseudo-first-order kinetic model; Figure S9: Fitting results of the pseudo-second-order kinetic model; Figure S10: Fitting results of the pseudo-nth-order kinetic model; Figure S11: Fitting results of the Elovich kinetic model; Figure S12: Fitting results of the Weber–Morris kinetic model (qt vs. time); Figure S13: Fitting results of the Weber–Morris kinetic model (qt vs. $\text{time}^{0.5}$); Figure S14: Arrhenius plot of $\ln k_1$ versus $1/T$ for the determination of the activation energy; Figure S15: Fitting results of the Langmuir isotherm model; Figure S16: Fitting results of the Freundlich isotherm model; Figure S17: Fitting results of the Langmuir–Freundlich isotherm model; Figure S18: Fitting results of the Temkin isotherm model; Figure S19: Fitting results of the Redlich–Peterson isotherm model; Figure S20: Plot of $\ln K^\circ$ versus $1/T$ for the determination of the ΔH° and ΔS° ; Table S1: Setup design of batch kinetic experiments; Table S2: Setup design of batch equilibrium experiments; Table S3: Kinetic models applied for the evaluation of the adsorption process; Table S4: Thermodynamic models applied for the evaluation of the adsorption process; Table S5: Arrhenius equation used for the evaluation of activation energy; Table S6: Equations used for the evaluation of thermodynamic parameters; Table S7: Assignments in the FTIR spectrum of fresh and exhausted PCP; Table S8: Comparison of specific surface area reported in the literature for various agricultural waste bioadsorbents; Table S9: Comparison of pseudo-first-order kinetic parameters reported in the literature for the adsorption of Fe^{II} on various agricultural waste bioadsorbents; Table S10: Comparison of Weber–Morris kinetic parameters reported in the literature for the adsorption of Fe^{II} on various bioadsorbents.

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

Funding: This research was funded by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI—UEFISCDI, through the project Center of Excellence in water management, materials, by-products and waste valorisation for circular bioeconomy implementation, proposal number PN-IV-P6-6.1-CoEx-2024-0056, contract 6 CoEx/02.06.2026.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Material.

Acknowledgments: We sincerely thank the four anonymous reviewers whose insightful comments and suggestions provided on earlier version of this manuscript helped improve and clarify this study.

Conflicts of Interest: The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

Abbreviations

The following abbreviations are used in this manuscript:

PCP	Fresh pine cone powder
PCP-Fe	Fe-loaded exhausted pine cone powder

References

- Mingelgrin, U.; Nasser, A. Diagnosis and prognosis of the distribution of contaminants in the Geosphere. In *Soil and Water Pollution Monitoring, Protection and Remediation*; Twardowska, I., Allen, H.E., Haggblom, M.H., Eds.; Springer: Dordrecht, The Netherlands, 2006; pp. 3–23.
- Fouda-Mbanga, B.G.; Velepini, T.; Pillay, K.; Tywabi-Ngeva, Z. Heavy metals removals from wastewater and reuse of the metal loaded adsorbents in various applications: A review. *Hybrid Adv.* **2024**, *6*, 100193. [[CrossRef](#)]
- Shrivastava, R.; Upreti, R.K.; Chaturvedi, U.C. Various cells of the immune system and intestine differ in their capacity to reduce hexavalent chromium. *FEMS Immunol. Med. Microbiol.* **2003**, *38*, 65–70. [[CrossRef](#)] [[PubMed](#)]
- Corda, N.; Kini, M.S. Recent studies in adsorption of Pb(II), Zn(II) and Co(II) using conventional and modified materials: A review. *Sep. Sci. Technol.* **2020**, *55*, 2679–2698.
- Rehman, K.; Fatima, F.; Waheed, I.; Akash, M.S.H. Prevalence of exposure of heavy metals and their impact on health consequences. *J. Cell. Biochem.* **2018**, *119*, 157–184.
- Vardhan, K.H.; Kumar, P.S.; Panda, R.C. A review on heavy metal pollution, toxicity and remedial measures: Current trends and future perspectives. *J. Mol. Liq.* **2019**, *290*, 111197. [[CrossRef](#)]
- Dhokpande, S.R.; Deshmukh, S.M.; Khandekar, A.; Sankhe, A. A review outlook on methods for removal of heavy metal ions from wastewater. *Sep. Purif. Technol.* **2024**, *350*, 127868. [[CrossRef](#)]
- Yaashika, P.R.; Palanivelu, J.; Hemavathy, R.V. Sustainable approaches for removing toxic heavy metal from contaminated water: A comprehensive review of bioremediation and biosorption techniques. *Chemosphere* **2024**, *357*, 141933. [[CrossRef](#)]
- Stefansson, A.; Seward, T. A spectrophotometric study of iron(III) hydrolysis in aqueous solutions to 200 °C. *Chem. Geol.* **2008**, *249*, 227–235. [[CrossRef](#)]
- Davison, W.; Seed, G. The kinetics of the oxidation of ferrous iron in synthetic and natural waters. *Geochim. Cosmochim. Acta* **1983**, *47*, 67–79. [[CrossRef](#)]
- Davison, W. Iron and manganese in lakes. *Earth Sci. Rev.* **1993**, *34*, 119–163. [[CrossRef](#)]
- Khatri, N.; Tyagi, S.; Rawtani, D. Recent strategies for the removal of iron from water: A review. *J. Water Process Eng.* **2017**, *19*, 291–304. [[CrossRef](#)]
- Ekstrom, S.M.; Regnell, O.; Reader, H.E.; Nilsson, P.A.; Lofgren, S.; Kritzbeg, E.S. Increasing concentrations of iron in surface waters as a consequence of reducing conditions in the catchment area. *J. Geophys. Res. Biogeosci.* **2016**, *121*, 479–493. [[CrossRef](#)]
- World Health Organization. Iron. In *Guidelines for Drinking-Water Quality. Vol. 2. Health Criteria and Other Supporting Information*, 2nd ed.; Mastercom/Wiener Verlag: Wien, Austria, 1996; pp. 248–253.
- Jensen, D.L.; Boddum, J.K.; Redemann, S.; Christensen, T.H. Speciation of dissolved iron(II) and manganese(II) in a groundwater pollution plume. *Environ. Sci. Technol.* **1998**, *32*, 2657–2664. [[CrossRef](#)]
- Espana, J.S.; Pamo, E.L.; Pastor, E.S. The oxidation of ferrous iron in acidic mine effluents from the Iberian Pyrite Belt (Odiel Basin, Huelva, Spain): Field and laboratory rates. *J. Geochem. Explor.* **2007**, *92*, 120–132. [[CrossRef](#)]
- Lieu, P.; Heiskala, M.; Peterson, P.; Yang, Y. The roles of iron in health and disease. *Mol. Asp. Med.* **2001**, *22*, 1–87. [[CrossRef](#)]
- Nair, M.; Iyengar, V. Iron content, bioavailability & factors affecting iron status of Indians. *Indian J. Med. Res.* **2009**, *130*, 634–645. [[PubMed](#)]
- Fontecave, M.; Pierre, J.L. Iron: Metabolism, toxicity and therapy. *Biochimie* **1993**, *75*, 767–773. [[CrossRef](#)] [[PubMed](#)]
- Abbaspour, N.; Hurrell, R.; Kelishadi, R. Review on iron and its importance for human health. *J. Res. Med. Sci.* **2014**, *19*, 164–174. [[PubMed](#)]
- Andrews, N.C. Iron metabolism: Iron deficiency and iron overload. *Annu. Rev. Genom. Hum. Genet.* **2000**, *1*, 75–98. [[CrossRef](#)]
- Oliveira, F.; Rocha, S.; Fernandes, R. Iron metabolism: From health to disease. *J. Clin. Lab. Anal.* **2014**, *28*, 210–218. [[CrossRef](#)] [[PubMed](#)]
- Mortadi, A.; El Hafidi, E.M.; El Moznine, R. Monitoring the coagulation mechanism and aluminum sulfate impact on textile wastewater treatment: Insights from impedance spectroscopy. *J. Indian Chem. Soc.* **2025**, *102*, 101501. [[CrossRef](#)]
- Barakat, M.A. New trends in removing heavy metals from industrial wastewater. *Arab. J. Chem.* **2011**, *4*, 361–377. [[CrossRef](#)]
- Chai, W.S.; Cheun, J.Y.; Kumar, P.S.; Mubashir, M.; Majeed, Z.; Banat, F.; Ho, S.H.; Show, P.L. A review on conventional and novel materials towards heavy metal adsorption in wastewater treatment application. *J. Clean. Prod.* **2021**, *296*, 126589. [[CrossRef](#)]

26. Wibowo, Y.G.; Taher, T.; Khairurrijal, K.; Ramadan, B.S.; Safitri, H.; Sudibyo, S.; Yuliansyah, A.T.; Petrus, H.T.B.M. Recent advances in the adsorptive removal of heavy metals from acid mine drainage by conventional and novel materials: A review. *Bioresour. Technol. Rep.* **2024**, *25*, 101797. [\[CrossRef\]](#)
27. Ghosh, S.; Debsarkar, A.; Dutta, A. Technology alternatives for decontamination of arsenic-rich groundwater—A critical review. *Environ. Technol. Innov.* **2019**, *13*, 277–303. [\[CrossRef\]](#)
28. Deliyanni, E.A.; Kyzas, G.Z.; Triantafyllidis, K.S.; Matis, K.A. Activated carbons for the removal of heavy metal ions: A systematic review of recent literature focused on lead and arsenic ions. *Open Chem.* **2015**, *13*, 699–708. [\[CrossRef\]](#)
29. Bailey, S.E.; Olin, T.J.; Brick, R.M.; Adrian, D.D. A review of potentially low-cost sorbents for heavy metals. *Water Res.* **1999**, *33*, 2469–2479. [\[CrossRef\]](#)
30. Joshi, N.C.; Joshi, A.; Mitra, D.; Gururani, P.; Kumar, N.; Joshi, H.K. Removal of heavy metals using cellulose-based materials: A mini-review. *Environ. Nanotechnol. Monit. Manag.* **2024**, *21*, 100942. [\[CrossRef\]](#)
31. El Hafidi, E.M.; Mortadi, A.; Lizoul, B.; Hairch, Y.; Mghaiouini, R.; Sabor, A.; Mnaouer, K.; Chahid, G.; Jebbari, S.; El Moznine, R.; et al. Assessment of sand and hearth ash filtration for wastewater treatment and novel monitoring via complex conductivity. *Euro-Mediterr. J. Environ. Integr.* **2025**, *10*, 1137–1148. [\[CrossRef\]](#)
32. Zafar, M.; Van Vinh, N.; Behera, S.K.; Park, H.S. Ethanol mediated As(III) adsorption onto Zn-loaded pinecone biochar: Experimental investigation, modeling, and optimization using hybrid artificial neural network-genetic algorithm approach. *J. Environ. Sci.* **2017**, *54*, 114–125. [\[CrossRef\]](#)
33. Yu, H.; Miksik, F.; Thu, K.; Miyazaki, T. Characterization and optimization of pore structure and water adsorption capacity in pinecone-derived activated carbon by steam activation. *Powder Technol.* **2024**, *431*, 119084. [\[CrossRef\]](#)
34. Teng, D.; Zhang, B.; Xu, G.; Wang, B.; Mao, K.; Wang, J.; Sun, J.; Feng, X.; Yang, Z.; Zhang, H. Efficient removal of Cd(II) from aqueous solution by pinecone biochar: Sorption performance and governing mechanisms. *Environ. Pollut.* **2020**, *265*, 115001. [\[CrossRef\]](#) [\[PubMed\]](#)
35. Muslim, A. Optimization of Pb(II) adsorption onto Australian pine cones-based activated carbon by pulsed microwave heating activation. *Iran. J. Chem. Chem. Eng.* **2017**, *36*, 115–127.
36. Muslim, A. Australian pine cones-based activated carbon for adsorption of copper in aqueous solution. *J. Eng. Sci. Technol.* **2017**, *12*, 280–295.
37. Huang, W.H.; Chang, Y.J.; Lee, D.J. Layered double hydroxide loaded pinecone biochar as adsorbent for heavy metals and phosphate ion removal from water. *Bioresour. Technol.* **2024**, *39*, 129984. [\[CrossRef\]](#)
38. Huong, P.T.; Lee, B.K.; Kim, J.; Lee, C.H.; Chong, M.N. Acid activation pine cone waste at differences temperature and selective removal of Pb²⁺ ions in water. *Proc. Saf. Environ. Prot.* **2016**, *100*, 80–90. [\[CrossRef\]](#)
39. Khan, B.A.; Ahmad, M.; Iqbal, S.; Ullah, F.; Bolan, N.; Solaiman, Z.M.; Shafique, M.A.; Siddique, K.H.M. Adsorption and immobilization performance of pine-cone pristine and engineered biochars for antimony in aqueous solution and military shooting range soil: An integrated novel approach. *Environ. Pollut.* **2023**, *317*, 120723. [\[CrossRef\]](#) [\[PubMed\]](#)
40. Masuku, M.; Nure, J.F.; Atagana, H.I.; Hlongwa, N.; Nkambule, T.T.I. Advancing the development of nanocomposite adsorbent through zinc-doped nickel ferrite-pinecone biochar for removal of chromium (VI) from wastewater. *Sci. Total Environ.* **2024**, *908*, 168136. [\[CrossRef\]](#) [\[PubMed\]](#)
41. Momcilovic, M.; Purenovic, M.; Bojic, A.; Zarubica, A.; Randelovic, M. Removal of lead(II) ions from aqueous solutions by adsorption onto pine cone activated carbon. *Desalination* **2011**, *276*, 53–59. [\[CrossRef\]](#)
42. Ofomaja, A.; Naidoo, E.; Modise, S. Removal of copper (II) from aqueous solution by pine and base modified pine cone powder as biosorbent. *J. Hazard. Mater.* **2009**, *168*, 909–917. [\[CrossRef\]](#) [\[PubMed\]](#)
43. Ofomaja, A.E.; Naidoo, E.B. Biosorption of lead(II) onto pine cone powder: Studies on biosorption performance and process design to minimize biosorbent mass. *Carbohydr. Polym.* **2010**, *82*, 1031–1042. [\[CrossRef\]](#)
44. Ofomaja, A.; Naidoo, E.; Modise, S. Biosorption of copper (II) and lead (II) onto potassium hydroxide treated pine cone powder. *J. Environ. Manag.* **2010**, *91*, 1674–1685. [\[CrossRef\]](#)
45. Pholosi, A.; Naidoo, E.B.; Ofomaja, A.E. Enhanced Arsenic (III) adsorption from aqueous solution by magnetic pine cone biomass. *Mat. Chem. Phys.* **2019**, *222*, 20–30. [\[CrossRef\]](#)
46. Zhang, Y.; Qu, J.; Yuan, Y.; Song, H.; Liu, Y.; Wang, S.; Tao, Y.; Zhao, Y.; Li, Z. Simultaneous scavenging of Cd(II) and Pb(II) from water by sulfide-modified magnetic pinecone-derived hydrochar. *J. Clean. Prod.* **2022**, *341*, 130758. [\[CrossRef\]](#)
47. Amar, M.B.; Walha, K.; Salvado, V. Valorisation of pine cone as an efficient biosorbent for the removal of Pb(II), Cd(II), Cu(II), and Cr(VI). *Ads. Sci. Technol.* **2021**, *2021*, 6678530. [\[CrossRef\]](#)
48. Amar, M.B.; Mallek, M.; Valverde, A.; Monclus, H.; Myers, T.G.; Salvado, V.; Cabrera-Codony, A. Competitive heavy metal adsorption on pinecone shells: Mathematical modelling of fixed-bed column and surface interaction insights. *Sci. Total Environ.* **2024**, *917*, 170398. [\[CrossRef\]](#) [\[PubMed\]](#)
49. Ouafi, R.; Omor, A.; Gaga, Y.; Akhazzane, M.; Taleb, M.; Rais, Z. Pine cone powder for the adsorptive removal of copper ions from water. *Chem. Ind. Chem. Eng. Q.* **2021**, *27*, 341–354. [\[CrossRef\]](#)

50. Uçun, H.; Bayhan, Y.K.; Kaya, Y.; Çakıcı, A.; Algur, O.F. Biosorption of lead (II) from aqueous solution by cone biomass of *Pinus sylvestris*. *Desalination* **2003**, *154*, 233–238. [\[CrossRef\]](#)
51. Malkoc, E. Ni(II) removal from aqueous solutions using cone biomass of *Thuja orientalis*. *J. Hazard. Mater.* **2006**, *B137*, 899–908. [\[CrossRef\]](#)
52. Sivalingam, S.; Gopal, V. Low-cost adsorbent from biomass for removal of Fe(II) and Mn(II) for water treatment: Batch and column adsorption study. *Chem. Pap.* **2024**, *78*, 4891–4908. [\[CrossRef\]](#)
53. Adebayo, G.B.; Mohammed, A.A.; Sokoya, S.O. Biosorption of Fe(II) and Cd(II) ions from aqueous solution using a low cost adsorbent from orange peels. *J. Appl. Sci. Environ. Manag.* **2016**, *20*, 702–714. [\[CrossRef\]](#)
54. Ghasemi, M.; Ghoreyshi, A.A.; Younesi, H.; Khoshhal, S. Synthesis of a high characteristics activated carbon from walnut shell for the removal of Cr(VI) and Fe(II) from aqueous solution: Single and binary solutes adsorption. *Iran. J. Chem. Eng.* **2015**, *12*, 28–51.
55. Gheju, M.; Balcu, I. Sequential abatement of Fe^{II} and Cr^{VI} water pollution by use of walnut shell-based adsorbents. *Processes* **2021**, *9*, 218. [\[CrossRef\]](#)
56. Nilavazhagi, A.; Felixkala, T. Adsorptive removal of Fe(II) ions from water using carbon derived from thermal/chemical treatment of agricultural waste biomass: Application in groundwater contamination. *Chemosphere* **2021**, *282*, 131060. [\[CrossRef\]](#) [\[PubMed\]](#)
57. Verma, Y.; Pandey, P.; Choubey, S. Removal of Fe (II) from aqueous solution by Calotropis Procera: Kinetics, isotherm studies, and measurement of competitive adsorption with UV-Visible spectrophotometer. *Anal. Met. Environ. Chem. J.* **2023**, *6*, 18–30. [\[CrossRef\]](#)
58. Acemioglu, B. Removal of Fe(II) ions from aqueous solution by Calabrian pine bark wastes. *Bioresour. Technol.* **2004**, *93*, 99–102. [\[CrossRef\]](#) [\[PubMed\]](#)
59. Shukla, S.R.; Pai, R.S.; Shendarkar, A.D. Adsorption of Ni(II), Zn(II) and Fe(II) on modified coir fibres. *Sep. Purif. Technol.* **2006**, *47*, 141–147. [\[CrossRef\]](#)
60. Moghadam, M.R.; Nasirizadeh, N.; Dashti, Z.; Babanezhad, E. Removal of Fe(II) from aqueous solution using pomegranate peel carbon: Equilibrium and kinetic studies. *Int. J. Ind. Chem.* **2013**, *4*, 19. [\[CrossRef\]](#)
61. American Public Health Association (APHA); American Water Works Association (AWWA); Water Environment Federation (WEF). 3500-Fe B. Phenanthroline method. In *Standard Methods for the Examination of Water and Wastewater*, 21st ed.; Eaton, A.D., Clesceri, L.S., Rice, E.W., Greenberg, A.E., Franson, M.A.H., Eds.; American Public Health Association: Washington, DC, USA, 2005; pp. 3.77–3.78.
62. Zach-Maor, A.; Semiat, R.; Shemer, H. Synthesis, performance, and modeling of immobilized nano-sized magnetite layer for phosphate removal. *J. Colloid Interface Sci.* **2011**, *357*, 440–446. [\[CrossRef\]](#) [\[PubMed\]](#)
63. Cerato, A.B.; Lutenecker, A.J. Determination of surface area of fine-grained soils by the ethylene glycol monoethyl ether (EGME) method. *Geotech. Test. J.* **2002**, *25*, 314–320. [\[CrossRef\]](#)
64. Lagergren, S. Zur theorie der sogenannten adsorption gelöster stoffe. *K. Sven. Vetenskapsakademiens Handl.* **1898**, *24*, 1–39.
65. Wang, J.; Guo, X. Adsorption kinetic models: Physical meanings, applications, and solving methods. *J. Hazard. Mat.* **2020**, *390*, 122156. [\[CrossRef\]](#)
66. Huang, J.; Liu, F.; Zhang, J. Insights into adsorption rate constants and rate laws of preset and arbitrary orders. *Sep. Purif. Technol.* **2021**, *255*, 117713. [\[CrossRef\]](#)
67. Opotu, L.A.; Inuwa, I.M.; Wong, S.; Ngadi, N.; Razmi, F.A. Errors and inconsistencies in scientific reporting of aqueous phase adsorption of contaminants: A bibliometric study. *Clean. Mater.* **2022**, *5*, 100100. [\[CrossRef\]](#)
68. Tran, H.N.; You, S.J.; Hosseini-Bandegharai, A.; Chao, H.P. Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: A critical review. *Water Res.* **2017**, *120*, 88–116. [\[CrossRef\]](#) [\[PubMed\]](#)
69. Ho, Y.S.; McKay, G. Pseudo-second order model for sorption processes. *Process Biochem.* **1999**, *34*, 451–465. [\[CrossRef\]](#)
70. Ozer, A. Removal of Pb(II) ions from aqueous solutions by sulphuric acid-treated wheat bran. *J. Hazard. Mater.* **2007**, *14*, 753–761. [\[CrossRef\]](#)
71. Tseng, R.L.; Wu, P.H.; Wu, F.C.; Juang, R.S. A convenient method to determine kinetic parameters of adsorption processes by nonlinear regression of pseudo-nth order equation. *Chem. Eng. J.* **2014**, *237*, 153–161. [\[CrossRef\]](#)
72. Lima, E.C.; Adebayo, M.A.; Machado, F.M. Kinetic and equilibrium models of adsorption. In *Carbon Nanomaterials as Adsorbents for Environmental and Biological Applications*; Bergmann, C., Machado, F., Eds.; Springer: Cham, Switzerland, 2015; pp. 33–69.
73. Vareda, J.P. On validity, physical meaning, mechanism insights and regression of adsorption kinetic models. *J. Mol. Liq.* **2023**, *376*, 121416. [\[CrossRef\]](#)
74. Weber, W.J., Jr.; Morris, J.C. Kinetics of adsorption on carbon from solution. *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.* **1963**, *89*, 31–59. [\[CrossRef\]](#)
75. Obradovic, B. Guidelines for general adsorption kinetics modeling. *Hem. Ind.* **2020**, *74*, 65–70. [\[CrossRef\]](#)
76. Langmuir, I. The adsorption of gases on plane surface of glasses, mica and platinum. *J. Am. Chem. Soc.* **1918**, *40*, 1361–1403. [\[CrossRef\]](#)

77. Azizian, S.; Eris, S.; Wilson, L.D. Re-evaluation of the century-old Langmuir isotherm for modeling adsorption phenomena in solution. *Chem. Phys.* **2018**, *513*, 99–104. [\[CrossRef\]](#)
78. Chen, X.; Hossain, M.F.; Duan, C.; Lu, J.; Tsang, Y.F.; Islam, M.S.; Zhou, Y. Isotherm models for adsorption of heavy metals from water—A review. *Chemosphere* **2022**, *307*, 135545. [\[CrossRef\]](#) [\[PubMed\]](#)
79. Foo, K.Y.; Hameed, B.H. Insights into the modeling of adsorption isotherm systems. *Chem. Eng. J.* **2010**, *156*, 2–10. [\[CrossRef\]](#)
80. Freundlich, H. Über die adsorption in Lösungen. *Z. Phys. Chem.* **1907**, *57*, 385–470. [\[CrossRef\]](#)
81. Jeppu, G.P.; Clement, T.P. A modified Langmuir-Freundlich isotherm model for simulating pH-dependent adsorption effects. *J. Contam. Hydrol.* **2012**, *129–130*, 46–53. [\[CrossRef\]](#) [\[PubMed\]](#)
82. de Vargas Briao, G.; Hashim, M.A.; Chu, K.H. The Sips isotherm equation: Often used and sometimes misused. *Sep. Sci. Technol.* **2023**, *58*, 884–892. [\[CrossRef\]](#)
83. Temkin, M.I. Adsorption equilibrium and the kinetics of processes on nonhomogeneous surfaces and in the interaction between adsorbed molecules. *Zhurnal Fiz. Khimii* **1941**, *15*, 296–332.
84. Hu, Q.; Lan, R.; He, L.; Liu, H.; Pei, X. A critical review of adsorption isotherm models for aqueous contaminants: Curve characteristics, site energy distribution and common controversies. *J. Environ. Manag.* **2023**, *329*, 117104. [\[CrossRef\]](#)
85. Redlich, O.; Peterson, D.L. A useful adsorption isotherm. *J. Phys. Chem.* **1959**, *63*, 1024–1026. [\[CrossRef\]](#)
86. Lima, E.C.; Sher, F.; Guleria, A.; Saeb, M.R.; Anastopoulos, I.; Tran, H.N.; Hosseini-Bandegharai, A. Is one performing the treatment data of adsorption kinetics correctly? *J. Environ. Chem. Eng.* **2021**, *9*, 104813. [\[CrossRef\]](#)
87. Moussout, H.; Ahlafi, H.; Aazza, M.; Maghat, H. Critical of linear and nonlinear equations of pseudo-first order and pseudo-second order kinetic models. *Karbala Int. J. Mod. Sci.* **2018**, *4*, 244–254. [\[CrossRef\]](#)
88. Al-Ghouti, M.A.; Da'ana, D.A. Guidelines for the use and interpretation of adsorption isotherm models: A review. *J. Hazard. Mater.* **2020**, *393*, 122383. [\[CrossRef\]](#) [\[PubMed\]](#)
89. Suwannahong, K.; Wongcharee, S.; Kreetachart, T.; Sirilamduan, C.; Rioyo, J.; Wongphat, A. Evaluation of the microsoft excel solver spreadsheet-based program for nonlinear expressions of adsorption isotherm models onto magnetic nanosorbent. *Appl. Sci.* **2021**, *11*, 7432. [\[CrossRef\]](#)
90. Benmessaoud, A.; Nibou, D.; Mekatel, E.H.; Amokrane, S. A comparative study of the linear and non-linear methods for determination of the optimum equilibrium isotherm for adsorption of Pb²⁺ ions onto Algerian treated clay. *Iran. J. Chem. Chem. Eng.* **2020**, *39*, 153–171.
91. Zhou, X.; Yu, X.; Hao, J.; Liu, H. Comments on the calculation of the standard equilibrium constant using the Langmuir model in Journal of Hazardous Materials 422 (2022) 126863. *J. Hazard. Mater.* **2022**, *429*, 128407. [\[CrossRef\]](#) [\[PubMed\]](#)
92. Lima, E.C.; Sher, F.; Saeb, M.R.; Abatal, M.; Seliem, M.K. Comments on “Reasonable calculation of the thermodynamic parameters from adsorption equilibrium constant, Journal of Molecular Liquids 322 (2021) 114980.”. *J. Mol. Liq.* **2021**, *334*, 116542. [\[CrossRef\]](#)
93. Tran, H.N.; Lima, E.C.; Juang, R.S.; Bollinger, J.C.; Chao, H.P. Thermodynamic parameters of liquid–phase adsorption process calculated from different equilibrium constants related to adsorption isotherms: A comparison study. *J. Environ. Chem. Eng.* **2021**, *9*, 106674. [\[CrossRef\]](#)
94. Tran, H.N. Improper estimation of thermodynamic parameters in adsorption studies with distribution coefficient K_d (q_e/c_e) or Freundlich constant (KF): Considerations from the derivation of dimensionless thermodynamic equilibrium constant and suggestions. *Ads. Sci. Technol.* **2022**, *2022*, 5553212. [\[CrossRef\]](#)
95. Chen, T.; Da, T.; Ma, Y. Reasonable calculation of the thermodynamic parameters from adsorption equilibrium constant. *J. Mol. Liq.* **2021**, *322*, 114980. [\[CrossRef\]](#)
96. Salvestrini, S.; Bollinger, J.C. Revisiting the extended van't Hoff equation: Comments on “Highly-efficient nitrogen self-doped biochar for versatile dyes' removal prepared from soybean cake via a simple dual-templating approach and associated thermodynamics”. *J. Clean. Prod.* **2022**, *373*, 133632. [\[CrossRef\]](#)
97. Salvestrini, S.; Ambrosone, L.; Kopinke, F.-D. Some mistakes and misinterpretations in the analysis of thermodynamic adsorption data. *J. Mol. Liq.* **2022**, *352*, 118762. [\[CrossRef\]](#)
98. Zhou, X.; Yu, X.; Maimaitiniyazi, R.; Zhang, X.; Qu, Q. Discussion on the thermodynamic calculation and adsorption spontaneity re Ofudje et al. (2023). *Heliyon* **2024**, *10*, e28188. [\[CrossRef\]](#) [\[PubMed\]](#)
99. Coates, J. Interpretation of infrared spectra, a practical approach. In *Encyclopedia of Analytical Chemistry*; Meyers, R.A., Ed.; John Wiley & Sons: Chichester, UK, 2000; pp. 10815–10837.
100. Shi, J.; Xing, D.; Lia, J. FTIR studies of the changes in wood chemistry from wood forming tissue under inclined treatment. *Energy Proc.* **2012**, *16*, 758–762. [\[CrossRef\]](#)
101. Bykov, I. Characterization of Natural and Technical Lignins Using FTIR Spectroscopy. Master's Thesis, Lulea University of Technology, Lulea, Sweden, 2008.
102. He, L.; Hu, W. Lignocellulose determination and categorization analysis for biofuel pellets based on FT-IR Spectra. *Spectrosc. Suppl.* **2022**, *37*, 14–22. [\[CrossRef\]](#)

103. Bai, R.S.; Abraham, T.E. Studies on enhancement of Cr(VI) biosorption by chemically modified biomass of *Rhizopus nigricans*. *Water Res.* **2002**, *36*, 1224–1236. [[CrossRef](#)] [[PubMed](#)]
104. Sen, T.K.; Afroze, S.; Ang, H.M. Equilibrium, kinetics and mechanism of removal of methylene blue from aqueous solution by adsorption onto pine cone biomass of *Pinus radiata*. *Water Air Soil Pollut.* **2011**, *218*, 499–515.
105. Mahmoodi, N.M.; Hayati, B.; Arami, M.; Lan, C. Adsorption of textile dyes on pine cone from colored wastewater: Kinetic, equilibrium and thermodynamic studies. *Desalination* **2011**, *268*, 117–125. [[CrossRef](#)]
106. Javier-Astete, R.; Jimenez-Davalos, J.; Zolla, G. Determination of hemicellulose, cellulose, holocellulose and lignin content using FTIR in *Calycophyllum spruceanum* (Benth.) K. Schum. and *Guazuma crinita* Lam. *PLoS ONE* **2021**, *16*, e0256559. [[CrossRef](#)] [[PubMed](#)]
107. Cheng, F.; Luo, H.; Hu, L.; Yu, B.; Luo, Z.; Fidalgo de Cortalezzi, M. Sludge carbonization and activation: From hazardous waste to functional materials for water treatment. *J. Environ. Chem. Eng.* **2016**, *4*, 4574–4586. [[CrossRef](#)]
108. Mosoarca, G.; Vancea, C.; Popa, S.; Dan, M.; Boran, S. A novel high-efficiency natural biosorbent material obtained from sour cherry (*Prunus cerasus*) leaf biomass for cationic dyes adsorption. *Materials* **2023**, *16*, 4252. [[CrossRef](#)] [[PubMed](#)]
109. Mekonnen, E.; Yitbarek, M.; Soreta, T.R. Kinetic and thermodynamic studies of the adsorption of Cr(VI) onto some selected local adsorbents. *S. Afr. J. Chem.* **2015**, *68*, 45–52. [[CrossRef](#)]
110. Popoola, L.T. Taguchi parametric optimization and cost analysis of hexavalent chromium sequestration from aqueous solution by NaOH-modified *Garcinia kola* hull particles. *Environ. Health Insights* **2023**, *17*, 11786302231200867. [[CrossRef](#)] [[PubMed](#)]
111. Gheju, M.; Balcu, I.; Jurchescu, P. Removal of hexavalent chromium from aqueous solutions by use of chemically modified sour cherry stones. *Desalin. Water Treat.* **2016**, *57*, 10776–10789. [[CrossRef](#)]
112. Sarin, V.; Pant, K.K. Removal of chromium from industrial waste by using eucalyptus bark. *Bioresour. Technol.* **2006**, *97*, 15–20. [[CrossRef](#)] [[PubMed](#)]
113. Rangabhashiyam, S.; Selvaraju, N. Adsorptive remediation of hexavalent chromium from synthetic wastewater by a natural and ZnCl₂ activated *Sterculia guttata* shell. *J. Mol. Liq.* **2015**, *207*, 39–49. [[CrossRef](#)]
114. Albadarin, A.B.; Mangwandi, C.; Walker, G.M.; Allen, S.J.; Ahmad, M.N.M.; Khraisheh, M. Influence of solution chemistry on Cr(VI) reduction and complexation onto date-pits/tea-waste biomaterials. *J. Environ. Manag.* **2013**, *114*, 190–201. [[CrossRef](#)]
115. Rakotonimaro, T.V.; Neculita, C.M.; Bussiere, B.; Zagury, G.J. Comparative column testing of three reactive mixtures for the bio-chemical treatment of iron-rich acid mine drainage. *Miner. Eng.* **2017**, *111*, 79–89. [[CrossRef](#)]
116. Blodau, C. A review of acidity generation and consumption in acidic coal mine lakes and their watersheds. *Sci. Total Environ.* **2006**, *369*, 307–332. [[CrossRef](#)] [[PubMed](#)]
117. Baral, S.S.; Das, S.N.; Rath, P. Hexavalent chromium removal from aqueous solution by adsorption on treated sawdust. *Biochem. Eng. J.* **2006**, *31*, 216–222. [[CrossRef](#)]
118. Brahma, D.; Saikia, H. Synthesis of ZrO₂/MgAl-LDH composites and evaluation of its isotherm, kinetics and thermodynamic properties in the adsorption of congo red dye. *Chem. Thermodyn. Therm. Anal.* **2022**, *7*, 100067. [[CrossRef](#)]
119. Bernal, V.; Giraldo, L.; Moreno-Pirajan, J.C. Thermodynamic analysis of acetaminophen and salicylic acid adsorption onto granular activated carbon: Importance of chemical surface and effect of ionic strength. *Thermochim. Acta* **2020**, *683*, 178467. [[CrossRef](#)]
120. Schiewer, S.; Wong, M.H. Ionic strength effects in biosorption of metals by marine algae. *Chemosphere* **2000**, *41*, 271–282. [[CrossRef](#)] [[PubMed](#)]
121. Wang, L.; Zhang, J.; Zhao, R.; Li, Y.; Li, C.; Zhang, C. Adsorption of Pb(II) on activated carbon prepared from *Polygonum orientale* Linn.: Kinetics, isotherms, pH, and ionic strength studies. *Bioresour. Technol.* **2010**, *101*, 5808–5814. [[CrossRef](#)] [[PubMed](#)]
122. McBride, M.B. A critique of diffuse double layer models applied to colloid and surface chemistry. *Clays Clay Miner.* **1997**, *45*, 598–608. [[CrossRef](#)]
123. Brown, G., Jr.; Parks, G. Sorption of trace elements on mineral surfaces: Modern perspectives from spectroscopic studies, and comments on sorption in the marine environment. *Int. Geol. Rev.* **2001**, *43*, 963–1073. [[CrossRef](#)]
124. Douven, S.; Paez, C.A.; Gommers, C.J. The range of validity of sorption kinetic models. *J. Colloid Interface Sci.* **2015**, *448*, 437–450. [[CrossRef](#)] [[PubMed](#)]
125. Benmahdi, F.; Semra, S.; Haddad, D.; Mandin, P.; Kolli, M.; Bouhelassa, M. Breakthrough curves analysis and statistical design of phenol adsorption on activated carbon. *Chem. Eng. Technol.* **2019**, *42*, 355–369.
126. Ho, Y.S.; Ng, J.C.Y.; McKay, G. Kinetics of pollutant sorption by biosorbents: Review. *Sep. Purif. Methods* **2000**, *29*, 189–232. [[CrossRef](#)]
127. Mohan, D.; Pittman, C.U., Jr. Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water. *J. Hazard. Mater.* **2006**, *B137*, 762–811. [[CrossRef](#)]
128. Mudhoo, A.; Pittman, C.U., Jr. Adsorption data modeling and analysis under scrutiny: A clarion call to redress recently found troubling flaws. *Chem. Eng. Res. Des.* **2023**, *192*, 371–388. [[CrossRef](#)]

129. Mortazavian, S.; An, H.; Chun, D.; Moon, J. Activated carbon impregnated by zero-valent iron nanoparticles (AC/nZVI) optimized for simultaneous adsorption and reduction of aqueous hexavalent chromium: Material characterizations and kinetic studies. *Chem. Eng. J.* **2018**, *353*, 781–795. [[CrossRef](#)]
130. Valderrama, C.; Cortina, J.L.; Farran, A.; Gamisans, X.; de las Heras, F.X. Kinetic study of acid red “dye” removal by activated carbon and hyper-cross-linked polymeric sorbents Macronet Hypersol MN200 and MN300. *React. Funct. Polym.* **2008**, *68*, 718–731. [[CrossRef](#)]
131. Inglezakis, V.J.; Zorpas, A.A. Heat of adsorption, adsorption energy and activation energy in adsorption and ion exchange systems. *Desalin. Water Treat.* **2012**, *39*, 149–157. [[CrossRef](#)]
132. Serafin, J.; Dziejarski, B. Application of isotherms models and error functions in activated carbon CO₂ sorption processes. *Microporous Mesoporous Mater.* **2023**, *354*, 112513. [[CrossRef](#)]
133. Kalam, S.; Abu-Khamsin, S.A.; Kamal, M.S.; Patil, S. Surfactant adsorption isotherms: A review. *ACS Omega* **2021**, *6*, 32342–32348. [[CrossRef](#)] [[PubMed](#)]
134. Farrell, J.; Reinhard, M. Desorption of halogenated organics from model solids, sediments, and soil under unsaturated conditions. 1. Isotherms. *Environ. Sci. Technol.* **1994**, *28*, 53–62. [[CrossRef](#)] [[PubMed](#)]

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.