

Article Removal of Pb(II) by Adsorption of HCO–(Fe₃O₄)_x Composite Adsorbent: Efficacy and Mechanism

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Abstract: With the development of industry, the concentration of lead (Pb) in water bodies is gradually increasing, the forms of Pb pollution in water are becoming increasingly diversified, and the environmental and human health hazards caused by Pb pollution are receiving increasing attention. A HCO-(Fe₃O₄)_x composite adsorbent prepared by the coprecipitation method of Fe₃O₄ mixed in cerium-rich grinding and polishing sludge was used to remove Pb from water. The effects of Ce/Fe molar ratio, pH, dosing amount, and time on the adsorption of $HCO-(Fe_3O_4)_x$ for Pb removal were investigated and the adsorption isotherm model, adsorption kinetics, and adsorption mechanism were studied. The results showed that the maximum adsorption capacity of HCO– $(Fe_3O_4)_x$ on Pb(II) was 35.93 mg·g⁻¹ at a Ce/Fe molar ratio of 1.5:1, pH 4–5, and temperature of 25 $^{\circ}$ C, and the removal rate could reach 96.05%; the process of Pb(II) adsorption by $HCO-(Fe_3O_4)_x$ was in accordance with the Langmuir isothermal adsorption model and the pseudo-second-order reaction kinetic model; chemisorption was dominant. Characterization results, such as EDS, XRD, and XPS, showed that the composite preparation of HCO with Fe₃O₄ increased the specific surface area of HCO-(Fe₃O₄)_x and generated amorphous iron oxides, such as FeCe₂O₄, FeOOH, Fe₃O₄, and Fe₂O₃, which provided conditions for the formation of Fe-O-Pb and Ce-O-Pb complexes during the adsorption process, thus facilitating the adsorption removal of Pb(II).

Keywords: HCO-(Fe₃O₄)_x adsorbent; Pb(II); Ce/Fe molar ratio; adsorption mechanism

1. Introduction

In recent years, the adverse health effects of the heavy metal lead (Pb) have attracted widespread attention from scholars at home and abroad [1,2]. Acute Pb poisoning or long-term chronic Pb exposure can harm all systems of the body [3–5]. As a result, Pb poisoning has become a recognized and important health problem [2,3,6,7]. Pb is widely used in the production of lead–acid batteries, electroplating, construction, paper making, textiles, guns, and other materials, and is also emitted in the nonferrous metal smelting, extractive, and chemical industry [8–12]. This led the Pb(II) concentration in nearby bodies of water to rise gradually, and the situation of Pb pollution in the water environment is now very serious. Therefore, Pb emission control should be taken seriously and removing Pb from aqueous solutions should be considered as an important part of wastewater treatment in heavy industries [4,8,13–16].

The current methods for the removal of Pb(II) from solution mainly include chemical precipitation [17–19], electrolysis [20], biotechnology [21,22], electrodialysis [23,24], and adsorption [21]. Among these, the adsorption method is the most widely used, owing to the advantages of low cost, simple operation, and a vast source of raw materials [25,26]. Moreover, Fe_3O_4 is a commonly used adsorbent for removing Pb(II) [27,28], due to its advantages such as short adsorption time, low cost, wide pH adaptation range, and high renewable utilization efficiency [18,29–32]. However, the capacity of conventional Fe_3O_4 to adsorb Pb(II) is low. Therefore, the preparation of iron-loaded composite adsorbent with



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Copyright: © 2023 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/). high adsorption capacity has become the key for current adsorption technology innovation and breakthroughs [26,33]. In this study, based on the ideas of resource recycling and treating waste with waste, Fe₃O₄ and cerium oxide-rich grinding and polishing sludge (hydrous ceric oxide: CeO₂–nH₂O, abbreviated as HCO) were used as raw materials and the Fe₃O₄/HCO composite adsorbent was prepared according to the literature [30,32]. HCO–Fe₃O₄ composite adsorbents with different Ce/Fe molar ratios (abbreviated as: HCO– (Fe₃O₄)_x) were prepared by a modified coprecipitation method and the influencing factors (Ce/Fe molar ratio, pH, reaction time and coexisting anions), attachment properties, isothermal adsorption model, and adsorption kinetic processes of HCO–(Fe₃O₄)_x adsorption for the removal of Pb(II) from water were investigated. Meanwhile, the surface morphology, crystal structure, and Pb(II) valence of HCO–(Fe₃O₄)_x, both before and after Pb(II) adsorption, were characterized by modern testing techniques to elucidate the adsorption mechanism of Pb(II) by HCO–(Fe₃O₄)_x with different Ce/Fe molar ratios, providing a technical reference for the adsorption and removal of Pb(II) from bodies of water.

2. Materials and Methods

2.1. Preparation and Characterization of $HCO-(Fe_3O_4)_x$ Composite Adsorbent

The raw material for the production of HCO– $(Fe_3O_4)_x$ is grinding and polishing sludge (HCO) which was collected from the wastewater treatment plant of LSKJ Co. The sludge contained some waste impurities; the main components were water (78.10%), cerium oxide (7.80%), silica (4.50%), alumina (3.80%), and calcium oxide (2.80%), etc. HCO– $(Fe_3O_4)_x$ was prepared using the coprecipitation method using HCO and Fe3O4 [1,34]; the Ce/Fe molar ratios were 1:0 (raw sludge), 0:1 (Fe₃O₄), 1:2 (HCO– $(Fe_3O_4)_{0.5}$), 1:1 (HCO– $(Fe_3O_4)_{1.5}$) by controlling the dosing amount. The details of the preparation procedure are described in the literature [30,32,35].

2.2. Adsorption and Desorption Experiments

2.2.1. Batch Adsorption Experiments

(1) The effect of Ce/Fe molar ratio: batch adsorption experiments were conducted in 250 mL glass bottles under different conditions. HCO– $(Fe_3O_4)_x$ (2000 mg·L⁻¹) and Pb(II) (20 mg·L⁻¹) [17,36] were combined in the bottles; the mixture was then shaken at 150 rpm at a constant temperature ((25 ± 1) °C) for up to 300 min. Aqueous solutions of 0.1 mol·L⁻¹ hydrochloric acid or sodium hydroxide were used to adjust the pH of the solution. During the reaction, the solution was sampled at different times; a clear solution was obtained by filtration through a 0.45 µm membrane for testing. The removal performance and adsorption capacity were calculated (Equations (1) and (2)) [18,29,31]. All tests were performed in three parallel trials. Based on the removal rate and adsorption capacity of Pb(II), the best Ce/Fe molar ratio HCO–(Fe₃O₄)_x adsorbent was selected for the following studies.

$$\eta = (C_0 - C_t) / C_0 \times 100\% \tag{1}$$

$$q_e = V(C_0 - C_t)/m \tag{2}$$

In the equation, η is the removal rate at adsorption equilibrium, expressed in %; C_0 , C_t , and C_e are initial, moment t, and equilibrium concentration of Pb(II), respectively, expressed in mg·L⁻¹; q_e is the adsorption capacity of the adsorbent for Pb(II) at equilibrium, expressed in mg·g⁻¹; V is the volume of the solution after fixing, expressed in L; and m is the mass of HCO–(Fe₃O₄)_x, expressed in g.

- (2) pH effect experiment: under the conditions of 2000 mg·L⁻¹ of HCO–(Fe₃O₄)_x, 2.0 h of reaction time, and (25 ± 1) °C, the effects of initial solution pH (2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, and 9.0) on the adsorption of Pb(II) by HCO–(Fe₃O₄)_x were investigated to determine the optimal pH for adsorption.
- (3) Adsorption time effect experiment: under the conditions of 2000 mg·L⁻¹ of HCO– $(Fe_3O_4)_x$, the initial pH of 4.0, and temperature of (25 ± 1) °C, the effects of adsorption

time on the adsorption of Pb(II) by HCO– $(Fe_3O_4)_x$ were investigated to determine the optimal adsorption time for adsorption.

- (4) Experiment on the effect of coexisting anions: the wastewater of lead-zinc ore dressing often contains a large amount of anions [36,37] such as chloride ions (Cl⁻), sulphate ions (SO₄²⁻), phosphate ions (PO₄³⁻), and silicate ions (SiO₃²⁻). Therefore, the effect of these coexisting anions on the adsorption of Pb(II) by HCO–(Fe₃O₄)_x was investigated under the conditions of HCO–(Fe₃O₄)_x dosage of 2000 mg·L⁻¹, initial pH of the solution of 4, and temperature of (25 ± 1) °C. The concentration of all coexisting anions was 1.0 mol·L⁻¹.
- (5) Desorption experiments: according to the conclusion reached in the literature [30,32], the Pb(II) adsorbed by HCO–(Fe₃O₄)_x was desorbed and regenerated using ultrapure water (H₂O) and 0.1 mol·L⁻¹ hydrochloric acid (HCl), sodium hydroxide (NaOH), and ethylenediaminetetraacetic acid (EDTA); the desorbed and regenerated HCO–(Fe₃O₄)_x was filtered and dried, and then Pb(II) adsorption experiments were performed to determine its optimal desorbent and evaluate its regeneration capacity [32].

2.2.2. Adsorption Isotherm Experiment

After preparing 100 mL of Pb(II) solution with concentrations ranging from 0 to $100 \text{ mg} \cdot \text{L}^{-1}$ and adding 0.2 g of HCO–(Fe₃O₄)_x at 25 °C with constant temperature shaking for 6 h, the supernatant was passed over a 0.45 µm membrane to determine the residual concentration of Pb(II) and calculate its equilibrium adsorption amount. The data were fitted using Langmuir (Equation (3)), Freundlich (Equation (4)), and Dubinin–Radushkevich (D–R) (Equations (5)–(7)) adsorption isotherm models [26,31,38].

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}} \tag{3}$$

$$\lg(q_e) = \lg\left(K_f\right) + \frac{1}{n} \lg(C_e) \tag{4}$$

$$\ln(q_e) = \ln(q_s) - \beta \varepsilon^2 \tag{5}$$

$$\varepsilon = RTln\left(1 + \frac{1}{C_e}\right) \tag{6}$$

$$E = (-2\beta)^{-1/2}$$
(7)

In the equation: C_e is the concentration of Pb(II) in solution at adsorption equilibrium, expressed in mg·L⁻¹; q_e and q_{max} are the equilibrium adsorption capacity and maximum adsorption capacity, expressed in mg·g⁻¹, respectively; *b* is the Langmuir adsorption constant, expressed in L·mg⁻¹; K_f and 1/n are the Freundlich adsorption constants; β is constant of D–R isotherm, expressed in mol²·kJ⁻²; qs is the theoretical isothermal saturation ability, expressed in mg·g⁻¹; ε is polanyi adsorption potential; *R* is the universal gas constant of 8.314J.molK⁻¹; *T* is the absolute temperature, expressed in *K*; and *E* is adsorption energy, expressed in KJ·mol⁻¹.

2.2.3. Adsorption Kinetics Experiments

A 100 mL solution of Pb(II) at a concentration of 100 mg·L⁻¹ was prepared [17,36], 0.2 g of adsorbent was added and shaken in a constant temperature shaker at 25 °C, and the residual concentration of Pb(II) was measured after taking the supernatant of different reaction times over a 0.45 μ m membrane; the removal rate and adsorption amount of Pb(II) were calculated. Then, the data were fitted using a pseudo-first-order model (Equation (8)), pseudo-second-order model (Equation (9)), Elovich model (Equation (10)), and intraparticle diffusion model (Equation (11)) [26,31,38]:

$$q_t = q_e(1 - \exp(k_1 t)) \tag{8}$$

$$q_t = q_e - q_e(k_2 q_e t + 1)$$
(9)

$$q_t = \frac{\ln(\alpha\beta)}{\beta} + \frac{1}{\beta}lnt \tag{10}$$

$$q_t = \alpha_l + k_{4i} t^{0.5} \tag{11}$$

In the equation, *t* is the adsorption time, expressed in min; q_t is the adsorption capacity at time *t* (min), expressed in mg·g⁻¹; k_1 is the pseudo-first-order model rate, expressed in min⁻¹; k_2 is the pseudo-second-order model rate, expressed in g·(mg·min)⁻¹, q_e is the adsorption equilibrium amount at moment *t*, expressed in mg·g⁻¹; q_t is the adsorption capacity at time t (min), expressed in mg·g⁻¹; α is the adsorption constant of Elovich model, expressed in mg·mg⁻¹·min⁻¹; β is related to the surface area and chemical activation energy of the adsorbent, expressed in g·mg⁻¹; k_{4i} is the adsorption rate constant at a particular stage of adsorption, expressed in mg·g⁻¹·min^{-0.5}; and α_i is the intraparticle diffusion model constant for a particular stage of adsorption.

2.3. Analysis Method

The experimental reagents were all superior purity, and the experimental water was all deionized water. In the test, 1.5986 g of Pb(NO₃)₂ was weighed, dissolved in ultrapure water, transferred to a 1L volumetric flask, fixed, and shaken well to obtain 1.0 g·L⁻¹ of Pb(II) standard reserve solution; the desired concentration of Pb(II) solution was obtained by diluting the appropriate amount of Pb standard reserve solution [30]. The concentration of Pb(II) was measured using a flame atomic absorption spectrometer (AA-7002A, Beijing East-West Analytical Instruments Co., Ltd., Peking, China) [12,32].

2.4. Characterization Analysis Method

The residues of HCO–(Fe₃O₄)_x before and after the adsorption of Pb(II) were characterized using a scanning electron microscopy (SEM, JSM-6380LV, JEOL Ltd., Tokyo, Japan) with an operating voltage of 5.0 KV; the elemental species and content of HCO–(Fe₃O₄)_x before and after Pb adsorption were determined using energy-dispersive spectroscopy (EDS, Bruker XFlash 5010, Karlsruhe, Germany). Analysis of the compounds involved in the adsorption process and the remaining compounds after the adsorption of Pb(II) was conducted using X-ray diffraction (XRD, D8 Advance, Brook AXS Ltd., Karlsruhe, Germany) with a scanning range of 10–90° and a scanning speed of $6 \cdot \min^{-1}$. Analysis of the functional groups and bond composition before and after adsorption was conducted using FTIR (Nicolet 6700, Thermo Fisher, Waltham, MA, USA) with a scan range of 4000–500 cm⁻¹. The valence states of Fe, Ce, and Pb before and after adsorption were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Scientific: Esala 250Xi, Waltham, MA, USA) with all binding energies (B.E) using the carbon peak C1s at 285.1 eV as a reference value and the analysis software XPS Peak.

3. Results and Discussion

3.1. The Influence of Ce/Fe Molar Ratio

The Ce/Fe molar ratio affects the structure and properties of HCO–(Fe₃O₄)_x [26,30,32], which, in turn, affect its effect on Pb(II) adsorption. The removal of Pb(II) by adsorption of HCO–(Fe₃O₄)_x with Ce/Fe molar ratios of 1:0 (HCO), 0:1 (Fe₃O₄), 1:2, 1:1, and 1.5:1, respectively, is provided in Figure 1. The adsorption of HCO–(Fe₃O₄)_x for the removal of Pb(II) was better than that of pure HCO or Fe₃O₄, indicating that the composite preparation of HCO–(Fe₃O₄)_x can improve the removal of Pb(II) ions from aqueous solutions. As shown in Figure 1, the removal rate of Pb(II) increased from 32.84% to 96.45% when the Ce/Fe molar ratio increased from 0:1 to 1.5:1, and its removal rate increased with the increase in the Ce/Fe molar ratio. This occurred because Fe₃O₄ loaded onto HCO formed HCO–(Fe₃O₄)_x adsorbent with porous and multiple active sites, which was also supported by the specific surface area (SBET) parameters determined by the nitrogen adsorption–desorption method

(Table A1). For example, the SBET at the Ce/Fe molar ratio of 1:2 is 104.64 m²·g⁻¹, which is 3.5 times higher than that of the Ce/Fe molar ratio 1:0 sample (29.63 m²·g⁻¹)—which is close to 132.2 m²·g⁻¹ of the maximum specific surface area (SBET) obtained by Qi et al. [39] using cerium-doped Fe₃O₄. The specific surface area (SBET) increased from 104.64 m²·g⁻¹ to 108.57 m²·g⁻¹ when the Ce/Fe molar ratio increased from 1:2 to 1.5:1, implying that the specific surface area of HCO–(Fe₃O₄)_x increased with the increase in the x value. This is in agreement with the conclusion of Qi et al. [39] that when increasing the molar ratio of Ce, the increase in the specific surface area of HCO–(Fe₃O₄)_x provides more active sites [39], which provides a good basis for the adsorption of Pb(II). Overall, HCO–(Fe₃O₄)_x with a Ce/Fe molar ratio of 1.5:1 had the best adsorption and removal effect on Pb(II). Therefore, follow–up studies were conducted with HCO–(Fe₃O₄)_x adsorbent with the Ce/Fe molar ratio of 1.5:1.



Figure 1. Removal rates of HCO–(Fe₃O₄)_x with different Ce/Fe molar ratios on Pb(II): initial concentration Pb(II) = 20 mg·L⁻¹, adsorbent dosage = 2.0 g·L⁻¹, pH = 5 \pm 0.1, reaction time = 4.0 h.

3.2. The Influence of pH

The effects of initial pH on the adsorption of Pb(II) onto HCO– $(Fe_3O_4)_x$ are shown in Figure 2a. As shown in Figure 2a, when the pH increased from 2 to 4, the Pb(II) removal rate increased rapidly from 59.74% to 96.05% and reached the maximum; when the pH continued to increase to 9, the rate decreased slowly to 86.41%. Therefore, the adsorption efficiency increased first and then slightly decreased with the increase in pH. When pH < 4, Pb(II) in the solution are mainly present as Pb^{2+} and $Pb(OH)^{2+}$ [40], and the large amount of H^+ present in the solution at this time adheres to the surface of $HCO-(Fe_3O_4)_x$ and protonates it, resulting in few available heavy active sites for Pb(II). However, the adsorption efficiency increased significantly with the initial pH of 4–5 and became stable at $pH = 4.0 \times 5.0$. This implies that the increased pH greatly weakened the competition of H⁺ and increased the adsorption efficiency. To further explain this result, the point of zero charge (pH_{pzc}) was tested (Figure 2b). When $pH > pH_{pzc}$, the HCO–(Fe_3O_4)_x was negatively charged; otherwise, it was positively charged. The pH_{pzc} of HCO–(Fe₃O₄)_x was 4.08, which is consistent with previous studies [39,41]. At pH < 4.08, the positively charged surface of HCO-(Fe₃O₄)_x will electrostatically repulse with cations. This result is not conducive to the adsorption of Pb(II). At pH > 4.08, the surface of HCO–(Fe₃O₄)_x is dominated by negative charge, which provides more active sites and promotes the adsorption of Pb(II). Therefore, a large amount of Pb(II) was adsorbed onto the surface of $HCO-(Fe_3O_4)_x$ at high pH, which is consistent with previous studies [17]. When the pH increases to 6–9, Pb ions in solution mainly exist in various forms, such as Pb^{2+} , $Pb(OH)^+$, and Pb(OH)₂ [42], and some Pb(II) is removed by Pb(OH)₂ precipitation. Overall, the suitable pH values for Pb(II) adsorption by HCO– $(Fe_3O_4)_x$ are 4–5.



Figure 2. The influence of pH on adsorption efficiency (**a**) and pH_{pzc} (**b**): initial concentration Pb(II) = 20 mg·L⁻¹, Ce:Fe molar ratio = 1.5:1, adsorbent dosage = 2.0 g·L⁻¹, reaction time = 4.0 h.

3.3. The Influence of Adsorption Time

Different adsorption times will directly affect the adsorption effect, and the adsorption equilibrium time can reflect the performance of the adsorbent to a certain extent [18,29,31]. As can be seen from the black line in Figure 3, the reaction of HCO–(Fe₃O₄)_x on the removal of Pb(II) reached 90.07% removal of Pb(II) by 240 min, and the reaction continued until 480 min, when the removal rate only increased to 92.00%. Therefore, the reaction equilibrium time for the adsorption of Pb(II) was 4 h. In addition, the red line in Figure 3 shows that in the initial stage of adsorption, there are a large number of active sites on the adsorbent surface and the reaction can proceed rapidly; after 20 min, as time passes, the active sites are gradually occupied by Pb(II) ions until the adsorption is saturated and the reaction gradually declines and stops.



Figure 3. Influence of adsorption time on adsorption of Pb(II): the initial concentration Pb(II) = 20 mg·L⁻¹, Ce:Fe molar ratio = 1.5:1, adsorbent dosage = 2.0 g·L⁻¹, reaction time = 4.0 h, pH = 5 \pm 0.1.

3.4. The Influence of Coexisting Anions

In natural waters, a wide variety of anions are usually present, which affect the removal of heavy metals by adsorption through physicochemical reactions such as competition, promotion, and complexation [11,18,19,43]. The effects of four anions, Cl^- , SO_4^{2-} , PO_4^{3-} , and SiO_3^{2-} , on the removal of Pb(II) by adsorption of HCO–(Fe₃O₄)_x are provided in Figure 4. As can be seen from Figure 4, the removal rates of Pb(II) were 73.85% and 75.23% when the concentrations of Cl^- and SiO_3^{2-} were 1 mol·L⁻¹, respectively, which were lower than those of the blank experimental group (96.05%). It can be seen that Cl^- and SiO_3^{2-} had a negative effect on the adsorption and removal of Pb(II); the reason for this needs to

be studied further. When the concentration of PO_4^{3-} was 1 mol·L⁻¹, the removal rate of Pb(II) was 99.77%, which was higher than that of the blank experimental group (96.05%), indicating that PO_4^{3-} could promote the adsorption of Pb(II) by HCO–(Fe₃O₄)_x. It may be that PO_4^{3-} and Pb(II) generate precipitates with very low solubility, leading to the increase in the removal rate of Pb(II) [44]. In addition, SO_4^{2-} had no effect on the adsorption of HCO–(Fe₃O₄)_x onto the Pb(II) group.



Figure 4. Influence of coexisting anions on HCO–(Fe₃O₄)_x adsorption of Pb(II): the initial concentration Pb(II) = 20 mg·L⁻¹, Ce:Fe molar ratio = 1.5:1, adsorbent dosage = 2.0 g·L^{-1} , reaction time = 4.0 h, pH = 5 ± 0.1 .

3.5. Regeneration of Adsorbent

The effects of four eluents, pure water (H₂O), and 0.1 mol·L⁻¹ HCl, NaOH, and EDTA on the desorption and readsorption of Pb(II) from HCO–(Fe₃O₄)_x are provided in Figure 5. As shown in Figure 5a, the highest efficiency (80.41%) of Pb(II) adsorption by HCO–(Fe₃O₄)_x was obtained after 2 desorptions of NaOH solution, which shows that NaOH solution is the best eluent; this is consistent with the findings of Deng et al. [32,35]. As shown in Figure 4b, the adsorption and removal of Pb(II) by HCO–(Fe₃O₄)_x can still reach 70.08% after 5 adsorption/desorptions by NaOH solution, which is close to the regenerative use performance of Ce–Fe₃O₄, reflecting the good regeneration performance and laying a good foundation for the reuse of HCO–(Fe₃O₄)_x and the recovery of Pb, with potential economic use value.



Figure 5. Influence of number of adsorption/desorption cycles on $HCO-(Fe_3O_4)_x$ adsorption of Pb(II): (a) different eluents; (b) adsorption/desorptions by NaOH solution.

3.6. Adsorption Isotherm

The adsorption isothermal model was used to fit the process of Pb(II) adsorption on HCO– $(Fe_3O_4)_x$. The results are shown in Figure 6 and Table 1. As shown in Tables 1 and 2, the correlation coefficient R^2 of Pb(II) adsorption by the Freundlich model at each temperature is higher than that of the Langmuir model and the D-R model, which indicates that the Freundlich model can better describe the process of Pb(II) adsorption on HCO– $(Fe_3O_4)_x$. Considering the empirical adsorption model, in which the Freundlich model assumes whether its ion-binding sites are occupied or not, the adsorption of Pb(II) by HCO– $(Fe_3O_4)_x$ is introduced as mainly multilayer adsorption [45]. The $K_{\rm f}$ constant of the Freundlich model gradually increases and 1/n gradually decreases as the temperature increases (Table 1), which indicates that the adsorption process of HCO-(Fe₃O₄)_x for Pb(II) is a heat absorption reaction [46], and 1/n is between 0.1 and 0.5 (Table 1), implying that Pb(II) is easily adsorbed by HCO–(Fe₃O₄)_x [9]. Furthermore, the correlation coefficient R^2 for Pb(II) adsorption by the Langmuir model at temperature is only slightly lower than that of the Freundlich model, implying that the process of Pb(II) adsorption by HCO-(Fe₃O₄)_{1.5} contains both monolayer (chemical) and multilayer (physical) adsorption [46]. Moreover, whether the adsorption of Pb(II) on HCO– $(Fe_3O_4)_x$ belongs to a physical adsorption process or a chemical adsorption process can be determined based on the E value of the D-R model. When the *E* value is between 1–8 KJ·mo⁻¹, it belongs to physical adsorption; when the *E* value is between 9–16 KJ·mo⁻¹ it belongs to ion exchange; when the *E* value is greater than 16 KJ·mo⁻¹, it belongs to chemical adsorption [30,47]. As shown in Table 1, the *E* value is between 20.926 and 28.845 KJ·mo⁻¹; therefore, HCO-(Fe₃O₄)_x adsorption Pb(II) belongs to chemical adsorption.



Figure 6. Adsorption isothermal model of Pb(II) on HCO–(Fe₃O₄)_x:(**a**) Langmuir and Freundlich model, (**b**) D–R model.

Table 1. Parameters of adso	ption isothermal	model o	of Pb(II).
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Model		Langmuir]	Freundlic	ı		D-R		
Temperature °C	q_m	b	R^2	K _f	1/n	R^2	β	qs	Ε	R^2
20	33.93	0.051	0.947	3.824	0.482	0.973	$-1.1 imes 10^{-8}$	20.926	68.810	0.889
25	28.27	0.169	0.965	6.632	0.371	0.991	$-9.9 imes10^{-9}$	26.154	70.992	0.966
30	35.93	0.174	0.963	8.667	0.376	0.985	-7.54×10^{-9}	28.845	81.417	0.947

Parameters	$q_e/(\mathrm{mg}\cdot\mathrm{g}^{-1})$	$k_1/(\min^{-1})$	R^2
Pseudo-first-order	30.85	0.018	0.946
Pseudo-second-order	35.34	0.001	0.962
Parameters	$a/(\text{mg}\cdot\text{mg}^{-1}\cdot\text{min}^{-1})$	$\beta/(g \cdot mg^{-1})$	R^2
Elovich	2.103	0.159	0.928

Table 2. Dynamics model parameter of HCO– $(Fe_3O_4)_x$ adsorption of Pb(II).

3.7. Adsorption Dynamical Model

The pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion dynamics models were used to fit the experimental data (Figure 7) and the relevant data parameters were listed in Tables 2 and 3. The fitting coefficient of the pseudo-second-order model ($\mathbb{R}^2 = 0.962$) is larger than that of the other three models. Moreover, the q_e value $(35.34 \text{ mg} \cdot \text{g}^{-1})$ calculated by the pseudo-second-order model is close to the experimental value (35.93 mg·g⁻¹), further supporting that the kinetic process of Pb(II) adsorption by HCO– $(Fe_3O_4)_x$ follows the pseudo-second-order kinetic model [21]. The result also implied that the whole process of Pb(II) adsorption by $HCO-(Fe_3O_4)_x$ is controlled by the chemical reaction at the solid–liquid interface [48]. In a word, the kinetic process of $HCO-(Fe_3O_4)_x$ adsorption of Pb(II) is appropriate for fitting by the pseudo-second-order model, which suggests that electron sharing or electron transfer is the main source of adsorption kinetics [48,49] and chemisorption is dominant, which is also consistent with the results of Deng [35] and Zhu [9,50] et al. The limiting factor in the adsorption process was further studied by using the intraparticle diffusion model and the results are shown in Figure 7b and Table 3. As shown in Figure 7b, the adsorption process is divided into two parts: the first stage is the fast diffusion process on the surface and the second stage is the slow diffusion process inside the particle [17]. The two stages have the following relationship: $k_{41} > k_{42}$, which is because the adsorption sites on HCO–(Fe₃O₄)_x decrease with the increase in reaction time [17,30]. Meanwhile, the value of k_{42} becomes lower, which also reflects the decrease of the diffusion rate and the equilibrium of chemical adsorption. Moreover, the larger the liquid film thickness constant a_i , the greater the boundary layer effect of the diffusion process [17,30].



Figure 7. Kinetic model of Pb(II) adsorption on HCO– $(Fe_3O_4)_x$: (a) pseudo-first-order, pseudo-second-order, Elovich model, (b) intraparticle diffusion model.

Table 3.	Intraparticle	diffusion	dynamics	model parameter.
	1			1

Parameters -	Intraparticle Diffusion							
	$a_1/(\mathrm{mg}\cdot\mathrm{g}^{-1})$	$k_1/({ m mg~g^{-1}.h^{-0.5}})$	R^2	<i>a</i> ₂ /(mg/g)	$k_2/(\text{mg g}^{-1}.\text{h}^{-0.5})$	<i>R</i> ²		
Pb(II)	4.086	1.950	0.959	30.398	0.0361	0.858		

3.8. Adsorption Mechanism

3.8.1. Apparent Morphological Analysis of the Sample

The SEM was used to characterize the morphological structure of HCO–(Fe₃O₄)_x before and after the adsorption of Pb(II) (Figure 8). The surface of the unmodified treated polished sludge was relatively smooth and demonstrated large porosity [28,36,51] (Figure 8a), whereas the HCO–(Fe₃O₄)_x prepared with different Ce/Fe moles had a rough surface and showed many very small pores (Figure 8b,c) with a significantly higher specific surface area (Appendix A, Table A1). At the same time, irregular spherical particles appeared on the surface of the adsorbent and, possibly, amorphous iron oxide crystals such as FeCe₂O₄, FeOOH, Fe₃O₄, and Fe₂O₃ [30,39,52]. This provides a large number of active sites for the adsorptive removal of Pb(II). Figure 8c shows an increase in surface spherical particles and roughness compared to Figure 8b, indicating that the prepared HCO–(Fe₃O₄)_x composite adsorbent increases in specific surface area with the increase in Ce/Fe molar ratio, which facilitates the adsorption and removal of Pb(II) [53]. After the adsorption of Pb(II) by HCO–(Fe₃O₄)_x (Figure 8d), a large number of smaller particles were added around HCO–(Fe₃O₄)_x and the porosity was obviously reduced, which indicates that Pb(II) occupied the active sites on the adsorbent surface.



Figure 8. SEM characterization of HCO–(Fe₃O₄)_x: (a) polished sludge; (b) Ce/Fe = 1:1; (c) Ce/Fe = 1.5:1; (d) after adsorption of Pb(II).

3.8.2. EDS Energy Spectra of HCO–(Fe₃O₄)_x before and after Adsorption

The chemical elements in the polished sludge and HCO–(Fe₃O₄)_x were analyzed by EDS, resulting in Table 4. The elements and their contents, before and after the adsorption of HCO–(Fe₃O₄)_x, can be seen in Table 3. The main components in the polished sludge were Ce ((31.92 ± 1.65) %) and O ((27.26 ± 1.34)%). HCO–(Fe₃O₄)_x is mainly composed of

Ce ((38.47 ± 1.87)%), O ((29.95 ± 2.34)%), and Fe ((26.14 ± 2.41)%), in that order. Before adsorption, the content of elemental Pb in HCO–(Fe₃O₄)_x was (0.21 ± 0.02)%, which was found to be due to the small amount of elemental Pb in the HCO polished sludge. After adsorption, the content of Pb increased to (3.74 ± 0.94)%, further confirming the feasibility of Pb adsorption by HCO–(Fe₃O₄)_x. In addition, the content of Fe changed from (26.14 ± 2.41)% to (22.8 ± 1.67)% and Ce from (38.47 ± 1.87)% to (36.32 ± 1.79)% after adsorption, probably due to the hydrolysis of Fe and Ce, resulting in a decrease in their content, while other elements also showed slight changes of varying degrees.

Table 4. Element content of HCO–(Fe₃O₄)_x before and after adsorption Pb(II) (%).

Element	0	Na	Mg	Al	Si	Cl	Ca	Fe	Ce	Pb
Before adsorption	29.95 ± 2.34	0.25 ± 0.10	0.1 ± 0.02	0.62 ± 0.23	1.87 ± 0.47	1.54 ± 0.26	0.85 ± 0.31	26.14 ± 2.41	38.47 ± 1.87	0.21 ± 0.02
After adsorption	30.95 ± 1.58	0.39 ± 0.15	0.06 ± 0.03	1.26 ± 0.18	2.51 ± 0.46	0.82 ± 0.07	0.34 ± 0.16	22.8 ± 1.67	36.32 ± 1.79	3.74 ± 0.94

3.8.3. X-ray Diffraction Analysis

The XRD technique was used to characterize the physical phases of the HCO sludge and the HCO–(Fe₃O₄)_x composite adsorbent (Figure 9). From the diffraction pattern, it can be observed that the HCO polished sludge has 9 major peaks, at 28.50°, 33.03°, 47.46°, 56.32°, 59.07°, 69.42°, 76.71°, 79.11°, and 88.8° [30]. However, in the HCO–(Fe₃O₄)_x composite adsorbent, the diffraction intensity peaks are all diminished and shifted in position, indicating that the doping of Fe₃O₄ alters the crystal structure of cerium squared in favor of the adsorption of heavy metals [40,54]. It can be assumed from the JADE software analysis that HCO–(Fe₃O₄)_x underwent a complex reaction between Fe₃O₄ and CeO₂ in HCO during the preparation process (Equation (12)) which, in turn, produced FeCe₂O₄ compounds that contributed to the adsorption of Pb(II) [55].

$$Fe_3O_4 + CeO_2.nH_2O + OH^- \rightarrow FeCe_2O_4 + H_2O$$
(12)



Figure 9. XRD analysis of Pb(II) before and after adsorption by HCO-(Fe₃O₄)_x adsorbent.

3.8.4. HCO– $(Fe_3O_4)_x$ before and after Adsorption of XPS Analysis

To further clarify the underlying mechanism of the removal process, XPS analysis was also used to detect the change of the functional groups involved in heavy metal binding (Figure 10). As shown in the full scan (Figure 10a), the main components of the HCO– $(Fe_3O_4)_x$ composite adsorbent were O, Ce and Fe, which were consistent with the EDS analysis (Table 3). A new Pb(4f) peak clearly exists after adsorption, which indicates that Pb(II) is adsorbed on the HCO– $(Fe_3O_4)_x$ [56]. As shown in Figure 10b, four characteristic peaks of the Ce 3d spectrum appeared at 882.45, 890.45, 899.61, and 916.60 eV. Related

studies concluded that 882.40, 890.40, and 900.00 eV are Ce³⁺ diffraction peaks [39] and 916.60 eV are Ce⁴⁺ diffraction peaks [54], indicating the coexistence of two valence states of Ce³⁺ and Ce⁴⁺ in HCO–(Fe₃O₄)_x [30,32,35]. Moreover, Ce³⁺ and Ce⁴⁺ ions can be hydrolyzed to carry hydroxyl groups, which is beneficial for the adsorption of Pb(II). Before reaction, characteristic peaks of Fe $2p_{3/2}$ appeared at 711.25 (Figure 10c), corresponding to the –OOH functional group (FeOOH and Fe₃O₄) [39], and characteristic peaks of Fe $2p_{1/2}$ appeared at 724.40 (Figure 10c), corresponding to Fe₂O₃ [39].Therefore, it is inferred that Fe in HCO–(Fe₃O₄)_x mainly exists in three forms: FeOOH, Fe₃O₄, and Fe₂O₃ [30,32,35,39], all of which are beneficial for the adsorption of Pb(II). After reaction, the peak area percentage of Fe²⁺ and Fe³⁺ were nearly unchanged providing strong support for a removal mechanism involving complexation without oxidation of Pb(II) [17]. Furthermore, as shown in Figure 10d, two characteristic peaks of Pb(II) [17,48]. Therefore, there was no redox reaction of Pb(II) during the adsorption process.



Figure 10. XPS analysis of HCO–(Fe₃O₄)_x before and after Pb(II) adsorption: full (**a**); Ce 3d (**b**); Fe 2p (**c**); Pb 4f (**d**).

3.8.5. Infrared Spectroscopy of HCO–(Fe₃O₄)_x before and after Adsorption

The results of the infrared spectra (FTIR) analysis before and after the adsorption of Pb(II) by HCO–(Fe₃O₄)_x are presented in Figure 11. As shown in Figure 11, multiple characteristic peaks of HCO–(Fe₃O₄)_x changed and shifted before and after the adsorption of Pb(II). The bending vibration absorption peak of 3400~3200 cm⁻¹ represents the overlapping region of the telescopic vibration absorption peaks of N-H and O-H [41], which moved from 3203 cm⁻¹ to 3379 cm⁻¹ after the adsorption of Pb(II), indicating that N-H and O-H in HCO–(Fe₃O₄)_x played a key role in the adsorption of Pb(II) [42]. The absorption peak at 1680–1620 cm⁻¹ is a C=C double bond stretching vibration peak [57], which did not change significantly after the adsorption of Pb(II), implying that the C=C bond is less likely to play a role in the adsorption peak as well as the skeletal vibration peak of the C-C bond [58] shifted from 1402 cm⁻¹ to 1382 cm⁻¹, implying that the C=O bond and the C-C single bond played an important role in the adsorption of Pb(II), as other studies have shown [58]. The C-O bond vibration peak at 1200–1000 cm⁻¹ shifted sharply from 1073 cm⁻¹ to 1033 cm⁻¹ after the adsorption of Pb(II), indicating that the peak plays a larger role in the adsorption of Pb(II). In summary, the presence of functional groups such as -COOH, -OH, C-C and N-H on the surface of HCO–(Fe₃O₄)_x forms the main active site for the adsorption of Pb(II), and these active sites are involved in the Pb(II) adsorption process through ligand exchange and complexation [52], which is consistent with the findings by Yan et al. [57].



Figure 11. FTIR analysis of Pb(II) before and after adsorption by HCO– $(Fe_3O_4)_x$ adsorbent (HCO- $(Fe_3O_4)_x$ after adsorption of Pb(II) (A) and HCO- $(Fe_3O_4)_x$ (B)).

The above analysis points to the conclusion that the main mechanism for the adsorption of Pb(II) by HCO– $(Fe_3O_4)_x$ is the following:

- (1) Adsorption kinetics and isotherm model analysis indicated that monolayer homogeneous adsorption and intraparticle diffusion played dominant roles in the removal of Pb(II) by HCO–(Fe₃O₄)_x [17]. In addition, some studies in the literature reported that the kinetic process of antimony adsorption by iron matrix adsorbents can be fitted with a variety of models, and it is hypothesized that there are different adsorption pathways for Pb(II) adsorption by HCO–(Fe₃O₄)_x [26,30,32]. The Freundlich model can better describe the adsorption of Pb(II) by HCO–(Fe₃O₄)_x, in comparison to the Langmuir model, implying that the adsorption process is mainly multilayer adsorption in a nonhomogeneous system [45]. In addition, the coefficient *K*_f increases gradually with increasing temperature, indicating that the process is heat absorption. Furthermore, HCO–(Fe₃O₄)_x has a large specific surface area, which provides more adsorption sites and facilitates the removal of Pb(II) by adsorption.
- (2) Based on research findings from the literature [17,30,59], ligand exchange and complexation reactions may play a key role in the adsorption process; this possibility requires further investigation. HCO–(Fe₃O₄)_x synthesis was prepared with the doping of Fe₃O₄ to produce the FeCe₂O₄ compound [35], which carries a more negative charge than polished sludge (Figure 2b). When HCO–(Fe₃O₄)_x adsorbs Pb(II), FeCe₂O₄ first undergoes electron transfer with water molecules during hydrolysis to form a two-electron layer structure and generates, in situ, an amorphous hydrated iron oxide, $X \equiv$ Fe-OH, with a high specific surface area. Then, the iron oxide film generates a PbFe₂O₄ precipitate through a ligand exchange reaction (Equation (13)), which results in the removal of Pb(II). At the same time, Pb is mainly present in the valence state of Pb(II) under experimental conditions, and it can be complexed with Ce₂O₃ to form Ce₂Pb₂O₆ (Equation (14)), thus enhancing the adsorption removal of Pb(II). In addition, when pH values are over 7, Pb(II) is removed by precipitation with OH- in solution (Equation (15)):

$$H^{+} + FeOOH + Pb^{2+} \rightarrow PbFe_2O_4 + H_2O$$
(13)

$$Ce_2O_3 + Pb^{2+} \rightarrow Ce_2Pb_2O_6 \tag{14}$$

$$Pb^{2+} + OH^- \rightarrow Pb(OH)_2$$
 (15)

In conclusion, the mechanism of Pb(II) adsorption by $HCO-(Fe_3O_4)_x$ mainly includes chemical reactions such as ligand exchange reaction, complexation reaction, and precipitation reaction on the surface of the adsorbent.

4. Conclusions

In this study, HCO– $(Fe_3O_4)_x$ composite adsorbent prepared from cerium-rich grinding and polishing sludge was effective for the treatment of water containing Pb, and the following conclusions were obtained: (1) the HCO– $(Fe_3O_4)_x$ was prepared by a coprecipitation method using HCO and Fe_3O_4 . The adsorption effect of Pb (II) onto HCO– $(Fe_3O_4)_x$ is influenced by the Ce/Fe molar ratio, and the optimal adsorption occurs with a Ce/Fe molar ratio of 1.5:1. (2) The initial pH of the solution has a significant impact on the adsorption of Pb(II) by HCO–(Fe₃O₄)_x, and the most suitable pH is 4–5. (3) The maximum adsorption amount of Pb(II) by HCO–(Fe₃O₄)_x at optimal adsorption conditions was $35.93 \text{ mg} \cdot \text{g}^{-1}$. ④ Coexisting anions affect the sorptive removal of Pb(II) through competitive interactions, promotion, and complexation. PO_3^{2-} and SO_4^{2-} promote the adsorption of Pb(II), while Cl^{-} and SiO_3^{2-} have an inhibitory effect. (5) The adsorption of Pb(II) by HCO–(Fe₃O₄)_x is controlled by chemical reactions, and its adsorption mechanism mainly involves ligand exchange reactions with amorphous hydrated iron oxides $X \equiv Fe$ –OH and complexation reactions with CeO₂ or Ce₂O₃, thus removing the Pb. To conclude, HCO–(Fe₃O₄)_x has a large adsorption capacity and a fast adsorption rate for Pb(II), reflecting better prospects for future application.

Author Contributions: J.L., Z.H. and R.D. further analyzed the data and wrote the manuscript. J.L. and Z.H. assessed the data, study implications and manuscript preparation. Y.C. performed the laboratory experiments. R.D. conceived the idea for the study and provided funding. Y.C. recorded experimental data and performed preliminary analyses. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: All data generated or analyzed during this study are included in the manuscript.

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

Appendix A

Table A1. Characterization parameters of the different HCO-(Fe₃O₄)_x adsorbents.

Parameters		Ce/Fe/(mol∙mo	pl^{-1})	
	1:0 (Polishing Sludge)	1:2	1:1	1.5:1
O (wt%)	27.26	17.28	26.51	26.15
Ce (wt%)	31.92	13.85	23.09	27.64
Fe (wt%)	-	45.49	20.22	16.07
S_{BET} (m ² /g)	29.63	104.64	105.12	108.57
V_{tot} (cm ³ /g)	0.109	0.115	0.123	0.214

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