Article

Removal of Cd(II) from Micro-Polluted Water by Magnetic Core-Shell Fe₃O₄@Prussian Blue

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Abstract: A novel core-shell magnetic Prussian blue-coated Fe₃O₄ composites (Fe₃O₄@PB) were designed and synthesized by in-situ replication and controlled etching of iron oxide (Fe₃O₄) to eliminate Cd (II) from micro-polluted water. The core-shell structure was confirmed by TEM, and the composites were characterized by XRD and FTIR. The pore diameter distribution from BET measurement revealed the micropore-dominated structure of Fe₃O₄@PB. The effects of adsorbents dosage, pH, and co-existing ions were investigated. Batch results revealed that the Cd (II) adsorption was very fast initially and reached equilibrium after 4 h. A pH of 6 was favorable for Cd (II) adsorption on Fe₃O₄@PB. The adsorption rate reached 98.78% at an initial Cd (II) concentration of 100 µg/L. The adsorption kinetics indicated that the pseudo-first-order and Elovich models could best describe the Cd (II) adsorption onto Fe₃O₄@PB, indicating that the sorption of Cd (II) ions on the binding sites of Fe₃O₄@PB was the main rate-limiting step of adsorption. The adsorption isotherm well fitted the Freundlich model with a maximum capacity of 9.25 mg g⁻¹ of Cd (II). The adsorption of Cd (II) on the Fe₃O₄@PB was affected by co-existing ions, including Cu (II), Ni (II), and Zn (II), due to the competitive effect of the co-adsorption of Cd (II) with other co-existing ions.

Keywords: adsorption; Prussian blue; Fe₃O₄@PB; cadmium removal; micro-polluted water

1. Introduction

Water pollution caused by heavy metals is of great concern due to their bioaccumulation, non-biodegradation, and high toxicity [1,2]. Cadmium (Cd) is extracted from zinc ore or sulfur cadmium ore as a by-product, which is widely used in paints, batteries (like nickel-cadmium batteries), pigments, and electroplating [3,4]. A growing body of evidence shows that long-term exposure to cadmium may cause adverse effects on human health [5]. The maximum carcinogenic risk of Cd was suggested at the level of 10⁻⁷ µg/L for the individual through different exposure pathways [6]. In the past few years, drinking water resources that have been subjected to heavy metal micro-pollution, such as Cd micro-polluted water, have generated various concerns. Chakrabarty and Sharma reported that higher levels of Cd (an average of 25 µg/L) in wells were caused by geogenic contamination in Assam, India [7]. Concentrations of Cd were found to be in the range of 7.1–12.3 µg/L in the rivers around Dhaka, Bangladesh [8]. Stricter legislation on pollution emissions and concentrations in the environment has been enforced. Cadmium has been classified as a
carcinogen (Group IA) by the International Agency for Research on Cancer (IARC). The US Environmental Protection Agency (EPA) has set the maximum level of cadmium to be less than 5 µg/L for drinking water [9]. As one of the listed high-priority pollutants, the Drinking Water Regulation Limit (DWRL) for Cd is also 5 µg/L [10,11]. However, as micro-polluted water treatment has mainly focused on low concentrations of nitrogen and organic pollutants in natural environments, less attention has been paid to removing heavy metals such as Cd (II) from drinking water. Since natural water bodies contain Cd (II) pollution at relatively low concentrations, the treatment of Cd (II)-polluted water should be given special consideration as micro-polluted water. Developing efficient water purification procedures for the removal of Cd from micro-polluted water is extremely urgent.

Various conventional technologies such as ion-exchange [12], adsorption [13,14], membrane filtration [15,16], chemical precipitation [17] and biological remediation [18] have been applied for Cd (II) removal from wastewater. Among these methods, the adsorption technique is an attractive approach for water treatment, especially if the adsorbent is low in cost and easy to operate, separate, and regenerate [19]. The choice of adsorbents is one of the most critical steps in the successful application of adsorption-based treatment techniques. Several materials have been previously evaluated for the removal of Cd (II) from contaminated water [20], including natural materials such as zeolites, clay [21], diatomite [22], bean-coat [23], activated carbon [24], biochar [25], mesoporous aluminosilicates [26], and nanomaterials such as nanochitosan [27], TiO$_2$ nanotubes [28], carbon-based 3D architectures [29], and Metal-organic frameworks (MOFs) [30]. However, these adsorbents are difficult to separate and recover from aqueous solutions. The commonly used recovery methods as filtration and centrifugation are time-consuming and expensive, which limits their reuse and may cause secondary pollution. Meanwhile, in studies where high initial concentrations of target pollutants were applied to evaluate the properties of adsorbents, the residual Cd concentration in solutions after treatment presents potential risks in drinking water and may exceed the DWRLs.

There is an urgent need to develop an economical and highly efficient adsorbent that can be easily prepared and separated from a solution to remove Cd from micro-polluted water. Magnetic nanoparticles that can be separated from an external magnetic field have attracted increasing research attention [31]. Unmodified Fe$_3$O$_4$ magnetic nanoparticles have been used to remove and separate heavy metals from wastewater [32,33]. The super-paramagnetic composite materials prepared by surface modification of Fe$_3$O$_4$ magnetic nanoparticles have been reported to have many applications. As a face-centered cubic lattice, Prussian blue (PB) has attracted significant attention from both theoretical and applied scientists due to its unique properties and wide applications [34]. Scientists proposed the use of magnetic Prussian blue (MPB) composites to remove toxic ions from polluted water. Sabaki et al. used the precipitation method to synthesize PB-Fe$_3$O$_4$, which could play a vital role in removing radioactive metal ions (Cs$^+$) from aqueous solutions and was found to maintain its adsorptive capacity in high ionic strength NaCl salt solution [35]. Thammawong et al. reported the development of magnetic Prussian blue nano sorbent with high sorption capacity for Cs$^+$ [36]. Uoginé et al. utilized magnetic Prussian blue nano sorbent (MPB) for the removal of Cu (II), Co (II), Ni (II), and Pb (II) from aqueous solutions [37]. Results showed that MPB was suitable for the removal processes and retained a high sorption capacity. While several authors have described the use of MPB for the sorption of radionuclides from contaminated solutions, there has been little research on the use of MPB for removing Cd (II) micro-polluted water.

The adsorption capacity of several adsorbents has been proved to be significantly improved by surface modification [38–41]. Inspired by this, this study aimed to synthesize core-shell MPB spheres (Fe$_3$O$_4$@PB) to be used as adsorbent materials to remove Cd (II) species from micro-polluted water. Fe$_3$O$_4$@PB was characterized by various methods. The effects of reaction time, dosage, co-existing ions, pH value, and initial concentration of solutions on the adsorption of Cd (II) onto Fe$_3$O$_4$@PB were explored. The possible interaction mechanisms between Cd (II) on Fe$_3$O$_4$@PB were analyzed by FT-IR and Zeta
potential, and the adsorption isotherm and kinetics were also employed to discuss the adsorption mechanisms.

2. Results and Discussion

2.1. Characterization of Fe₃O₄@PB

The micrographic features of Fe₃O₄@PB were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The exhibited SEM images of Fe₃O₄@PB in Figure 1a,b show a uniform spherical shape with a particle diameter of about 150 nm. The structures of Fe₃O₄ and Fe₃O₄@PB were further observed by TEM, as shown in Figure 1c,d, respectively. The Fe₃O₄ nanoparticles are monodispersed with a smooth surface. As exhibited in Figure 1d, Fe₃O₄ is coated by a rough layer of agglomerated PB particles, meaning that PB nanoparticles successfully adhered to the surface of Fe₃O₄. Figure 1e verifies the typical core-shell structure.

![Figure 1](image)

Figure 1. (a,b) Scanning electron microscope (SEM) images of the Fe₃O₄@PB; transmission electron microscopy (TEM) images of (c) Fe₃O₄ and (d,e) Fe₃O₄@PB nanoparticles.

The X-ray diffraction (XRD) patterns of the as-synthesized adsorbents were recorded in Figure 2a, which determined the crystalline structure and main phase of the composites. Similar peaks of Fe₃O₄ and Fe₃O₄@PB at 20° 18.29, 30.14, 35.49, 37.14, 43.13, 53.52, 57.04, and 62.64° were indexed as (111), (220), (311), (222), (400), (422), (511), and (440) planes, respectively, well-matched with the previous researches [42,43]. Besides, Fe₃O₄@PB displays four predominant 2θ peaks compared with Fe₃O₄ in the range of 17–40° corresponding to the Bragg planes of (200), (220), (400), and (420) [44], which belong to the face-centered cubic lattice structure of PB. These prove that the composites are designed by the synergistic effect between PB shell and Fe₃O₄ core, and the introduction of Fe₃O₄ did not affect the crystallinity of PB nanoparticles.

As presented in Figure 2b, FTIR was further employed to compare the functional structure of Fe₃O₄ and Fe₃O₄@PB. The peak of Fe−O locates at 594 cm⁻¹ for Fe₃O₄ [45] and shows a slight blue shift for core-shell Fe₃O₄@PB. The same typical bands revealed by FTIR indicate the introduction of Fe₃O₄ in the core-shell structure, which coincides with the result from XRD. The major peak in the vicinity of 2092 cm⁻¹ assigned to the −CN stretching vibration [46] and the stretching bands at 599 cm⁻¹ and 501 cm⁻¹ related to the formation of Fe−CN−Fe [47], demonstrating the occurrence of Fe₃O₄@PB. The coordination between the nitrogen lone electron pair of −CN in the PB and the 3p³ hybrid orbital formed by the Cd (II) 5s and 5p orbitals may have contributed to the differences shown by FTIR after adsorption. Previous studies determined that O−H groups bind to
iron cations on the surface of Fe$_3$O$_4$ in aqueous water [48,49]. However, the stretching band near 3300 cm$^{-1}$ revealed that the O–H stretching vibration was very weak, which can be attributed to vacuum desiccation in the synthesis process, making the spectrum band of O–H groups on the particle surface around 3300 cm$^{-1}$ nearly unobservable. The band at 1654 cm$^{-1}$ could be attributed to the bending vibration of O–H, indicating the existence of interstitial water in the magnetic PB nanocomposites.

![Figure 2. (a) XRD patterns; (b) FTIR spectra; (c) N$_2$ adsorption/desorption isotherms of the composites (inset figure is the pore size distribution); (d) magnetic hysteresis loops of Fe$_3$O$_4$ and Fe$_3$O$_4$@PB.](image)

The pore structure of Fe$_3$O$_4$@PB was characterized by N$_2$ adsorption/desorption analysis at 77.3 K and generated by the adsorption branch of the isotherms using the Barrett–Joyner–Halenda (BJH) method. Figure 2c displays the type II adsorption isotherm without an obvious hysteresis loop of Fe$_3$O$_4$@PB, indicating a micropore-dominated structure. In general, it was difficult for N$_2$ molecules to enter the intrinsic micropores inside due to the occupation of water molecules and other ions, which means that there are mesopores on the surface of Fe$_3$O$_4$@PB [50]. As shown in the corresponding pore size distribution curve, the pore volume of Fe$_3$O$_4$@PB is mainly contributed by pore size in the range of 1.7–5.5 nm, verifying the confounding of micropores and mesopores.

Magnetic hysteresis (M – H) curves of the Fe$_3$O$_4$ and Fe$_3$O$_4$@PB nanoparticles show a typical magnetic hysteresis loop (Figure 2d). The saturation magnetization (M$_S$) of Fe$_3$O$_4$ was 70 emu/g at room temperature. After coated by PB, the saturation magnetization decreased to 12.0 emu/g, which is similar to the M$_S$ 12.07 emu·g$^{-1}$ of the magnetic PB composites prepared by Jang et al. [51]. Despite the decreases in saturation magnetization with outer shell PB, the magnetization still could guarantee the recyclability of Fe$_3$O$_4$@PB sorbents.

The Zeta potentials of the Fe$_3$O$_4$@PB at varied pH at room temperature were collected by SOE-070 nanoparticle size and Zeta potentiometer (Delsa Nano C/Z, Beckman Coulter, Brea, CA, USA) (Figure 3). The point of zero charges (pH$_{ZPC}$) of Fe$_3$O$_4$ is approximately equal to 6.19, indicating it would be positively charged at pH below 6.19 while negatively charged at higher pHs. The Zeta potentials all had negative values within the pH range of 3–11. The negative values dramatically decreased as pH increased from 2 to 6; however, the Zeta potentials values changed only slightly as pH rose from 6 to 11. This could be
attributed to the gradual saturation of hydroxyl groups on Fe₃O₄@PB surface with the increase in solution pH. Thus, Fe₃O₄@PB was found to be negatively charged in the entire environmentally relevant pH range, which is beneficial to the adsorption of positively charged cations. The pH_{PZC} of Fe₃O₄@PB is around 2.31, much lower than that of Fe₃O₄, implying the stronger electrostatic attraction of Fe₃O₄@PB.

2.2. Effect of Fe₃O₄@PB Dosage

As shown in Figure 4a, the increasing dosage of Fe₃O₄@PB from 0.1 to 2 g·L⁻¹ significantly improved the removal efficiency of Cd (II). However, the reaction rate remained almost unchanged when the sorbent dosage was further increased to 4 g·L⁻¹. Previous studies suggested that more adsorption sites become available for metal uptake with the sorbent dosage increases [52]. At sorbent dosages >1 g·L⁻¹, the incremental Cd (II) ion removal slowed as the metal ion concentrations reached equilibrium on the surface. The decrease in q_e may have been due to the generation of unsaturated adsorption sites through the adsorption reaction when dosages increased. Another possible explanation for the decrease in q_e may have been particle interactions such as aggregation due to high dosages of sorbent, which then led to a decrease in the total surface area of the adsorbent [53]. Hence, a dosage of 1–2 g·L⁻¹ was determined to be the most suitable for Cd (II) removal in terms of efficiency and cost.

2.3. Effect of Initial pH

The pH value of aqueous solutions was one of the vital factors that significantly affected the adsorption of Cd (II) on the water-absorbent interfaces [54], the surface charge of the adsorbents, and the contaminant species [55]. Cadmium species in deionized water include Cd²⁺, Cd(OH)⁺, Cd(OH)₂⁺, and Cd(OH)₃⁺ [56]. At pH < 6, Cd²⁺ was the only ionic species present in aqueous solutions, while Cd²⁺ and Cd(OH)⁺ were the dominant cadmium species at pH < 8, and Cd(OH)₂ precipitation began to form at pH > 8. The pH of solutions influences metal ion adsorption through the competition between metal ions.
and H⁺ ions for active sorption sites [57]. In order to establish how pH affects Cd (II) ion sorption onto Fe₃O₄@PB, batch studies were conducted at different initial pH values in the range of 2 to 11.

As shown in Figure 4b, the adsorption efficiency was only 2.24% at the initial pH of 2; then, it increased from 12.53% to 98.78% as the pH increased from 3 to 6 and leveled off in the pH range of 6–9. The low metal sorption at pH of 2 was likely due to active site protonation, which led to competition between H⁺ and Cd (II) to occupy the adsorption sites [58]. The lower concentration of H⁺ weakened the competition adsorption of H⁺ and Cd (II) ions at a higher pH level [59]. Conversely, Cd (II) ions are prone to the formation of Cd(OH)⁺ and Cd(OH)₂ at pH > 6 (aggregation effect between Cd (II) with OH⁻), reducing the removal efficiency at high pH values. In alkaline conditions, precipitation plays a major role in the removal of Cd (II) due to the formation of Cd(OH)₂ precipitate. The precipitation of metal hydroxides into pores or spaces around the adsorbent particles is nearly impossible as the adsorption process is kinetically faster than precipitation. In this study, the maximum removal efficiency (98.78%) of Cd (II) was acquired at a pH of 6 for Fe₃O₄@PB. The resulting Cd (II) concentrations after adsorption were far below the 5 µg/L limit designated by the DWRL.

2.4. Effect of Coexisting Ions

Figure 5 indicates that the effect of co-existing ions on the adsorption of Cd (II) onto Fe₃O₄@PB depended on the variety of ions (Cu (II), Ni (II), and Zn (II)). As the concentration of the co-existing ions rose, competition with other heavy metal ions for the adsorption sites caused Cd (II) removal efficiency to decrease [60]. The hydrated radii of Cd (II), Cu (II), Ni (II), and Zn (II) were 4.26 Å, 4.19 Å, 4.04 Å, and 4.30 Å, respectively. Small differences in hydrated radii are a significant cause of lattice competition. Fe₃O₄@PB can remove not only Cd (II) but also Cu (II), Ni (II), and Zn (II) from wastewater. Therefore, these new insights provide valuable information for the application of Fe₃O₄@PB to remove heavy metal co-contamination from micro-polluted water.

Figure 5. Cd (II) adsorption in the presence of co-existing anions, such as Cu (II), Ni (II), and Zn (II) (from 50 to 400 µg L⁻¹) and the removal of co-existing anions by Fe₃O₄@PB.

2.5. Effect of Contact Time and Adsorption Kinetic

The Cd (II) adsorption on Fe₃O₄@PB shows two distinct phases in Figure 6a: a rapid initial phase over the first 2 h and a much slower sorption phase to reach equilibrium within 4 h. The adsorption capacity of Cd (II) on Fe₃O₄@PB increased as time passed and then reached a plateaued equilibrium. The remarkable increase in Cd (II) adsorption capacity at the initial step was due to the existence of plentiful active sites on the adsorbent surface. After that, as the majority of active surface sites were occupied by Cd (II), the
adsorption process slowed until it reached a plateaued equilibrium due to insufficient remaining binding sites for Fe₃O₄@PB to absorb Cd (II).

![Figure 6](image_url)

(Figure 6. (a) Effects of the contact time and pseudo-first-order, pseudo-second-order, intraparticle diffusion, and Elovich kinetic models for the adsorption of Cd (II) ions onto Fe₃O₄@PB; (b) Effect of initial concentration of Cd (II); the insets are equilibrium adsorption data fitted by the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich models.

To investigate the adsorption mechanism during the adsorption process, kinetic models including the pseudo-first-order, pseudo-second-order, intraparticle diffusion, and Elovich models were used to evaluate the experimental data. The parameters results are shown in Table 1. Cd (II) adsorption onto Fe₃O₄@PB followed the pseudo-first-order and Elovich models well with the correlation coefficient R² > 0.99. Moreover, the calculated adsorption capacity from the pseudo-first-order model was much closer to the experimental value. The fitness of the pseudo-first-order model indicates a surface reaction controlled process, in which the adsorption of Cd (II) onto Fe₃O₄@PB may depend on the surface active sites and the affinity between cadmium ions and the adsorbents [61]. Elovich model has been proved to describe the solid-liquid interaction in chemical adsorption processes effectively [62]. All results above indicate that the sorption of Cd (II) ions on the binding sites of Fe₃O₄@PB was the main rate-limiting step of adsorption.

| Kinetic Models                     | Constants       | Isotherm Models | Parameters       |
|-----------------------------------|-----------------|-----------------|------------------|
| Pseudo-first-order                | qₑ (µg/g)       | Langmuir        | qₑ (µg/g)        | 9243.81 |
|                                   | kₑ              |                 | K_L              | 0.0091  |
|                                   | R²              |                 | R²               | 0.9474  |
| Pseudo-second-order              | qₑ (µg/g)       | Freundlich      |                  | 2.2874  |
|                                   | k₂              |                 | K_F              | 562.1269|
|                                   | R²              |                 | R²               | 0.9939  |
| Intraparticle diffusion          | k_d             | Temkin          |                  | 1.2159  |
|                                   | C               |                 | a_T              | 2.3800  |
|                                   | R²              |                 | R²               | 0.9069  |
| Elovich                           | α               | Dubinin–Radushkevich | qₑ (µg/g)  | 5978.5921|
|                                   | β               |                 | K_DR             | 4.77 × 10⁻⁵|
|                                   | R²              |                 | R²               | 0.8627  |

### Table 1. Kinetic model and Isotherm model parameters for adsorption of Cd (II) ions by Fe₃O₄@PB.

#### 2.6. Effect of Initial Concentration and Adsorption Isotherm

The effect of Cd (II) initial concentrations on the adsorption capacity of Fe₃O₄@PB is plotted in Figure 6b. The adsorption quantity increased rapidly when the Cd(II) concentration increased from 0 to 1000 µg/L. Then, the adsorption quantity increased slower with the Cd(II) concentration increased further. At lower concentrations of Cd (II), the available sorption sites are ample with high attraction towards Cd (II), the increase in initial concentration drives the adsorption of Cd(II) from aqueous solution onto the adsorbent...
surface [63], achieving the rapid increase in equilibrium adsorption capacity. As the initial concentration continues to increase, the adsorption sites remain the same while the number of adsorbate molecules increased, leading to the competition of more Cd (II) due to the saturation effect [64].

The isotherm experiments were conducted under optimal aqueous conditions (a duration of 4 h, a pH of 6, and a temperature of 25 °C). The isotherm fitness plots and parameters are shown in insets of Figure 6b and Table 1, respectively. The Langmuir isotherm was based on reaction hypotheses and assumed that monolayer adsorption occurs on the surface sorption part without interaction among adsorbates, while the Freundlich isotherm was used to demonstrate that physicochemical adsorption on heterogeneous surfaces was related to multilayer adsorption with varying affinities [65]. Based on the higher determination coefficient ($R^2$), Cd (II) removal by Fe$_3$O$_4$@PB fitted the Freundlich model better than the Langmuir model, indicating that there were several mechanisms of Cd (II) adsorption on the surface of Fe$_3$O$_4$@PB. Integrating the results of both Zeta potential and FTIR suggested that electrostatic interaction and metal complexation may be the main adsorption mechanisms. The exponent $n$ in the Freundlich model was also an indicator for predicting whether an adsorption system is favorable. The $1/n$ value in this study was 0.4378, which fell into the range of 0.1–1, suggesting that Cd (II) was adsorbed efficiently onto Fe$_3$O$_4$@PB [66]. The maximum adsorption capacity of Fe$_3$O$_4$@PB for Cd (II) was estimated as 9.25 mg·g$^{-1}$, which provides new insight into the removal of heavy metal ions from micro-polluted water.

3. Materials and Methods

3.1. Reagents

Ferric chloride hexahydrate (FeCl$_3$·6H$_2$O), cadmium chloride (CdCl$_2$·5/2H$_2$O), potassium chloride (KCl), ferroferric oxide (Fe$_3$O$_4$), potassium ferricyanide (K$_3$Fe(CN)$_6$), and hydrochloric acid (HCl) were purchased from Macklin and Beijing Chemical Works, China.

3.2. Synthesis of Fe$_3$O$_4$@PB Magnetic Adsorbent

One-pot coordination replication and etching were used to prepare the Fe$_3$O$_4$@PB as illustrated in Scheme 1. Typically, 160 mg of Fe$_3$O$_4$, 64 mg of K$_3$Fe(CN)$_6$, and 895 mg FeCl$_3$ were added to 120 mL distilled water in a vial. After ultrasonic radiation and dispersion for 30 min, 1 M of HCl solution (120 mL) was added to the mixture. The suspension was then placed into a vapor bath and shaken under constant temperature conditions (25 °C) for 15 h. Finally, the Fe$_3$O$_4$@PB nanoparticles were separated from the solution using a permanent magnet and cleaned with ultrapure water 3 times. The product was dried overnight in a vacuum oven at 50 °C.

**Scheme 1.** Synthesis of Fe$_3$O$_4$@PB magnetic adsorbent.
3.3. Characterization and Analytical Methods

The morphology and size of Fe₃O₄@PB were observed by scanning electron microscopy (SEM, Hitachi SU-8010, Japan) and high-resolution transmission electron microscopy (TEM, JEOL JEM-2100 F). The presence of PB-modified Fe₃O₄ was confirmed by powder X-ray diffraction (XRD, Rigaku Smart Lab, Tokyo, Japan). FTIR spectra of samples were recorded by a Bruker Vertex 70 (Germany) in the wavenumber range of 400–4000 cm⁻¹ at a resolution of 4 cm⁻¹ using the KBr pellet method. The specific surface area of Fe₃O₄@PB was determined by Brunauer-Emmett-Teller (BET, Micrometrics ASAP 2460 instrument, Norcross, GA, USA) method. The magnetic properties were measured by a superconducting quantum interference device (Quantum Design SQUID-VSM, San Diego, CA, USA) in 300 K. The zeta potentials for pH values from 2 to 11 were collected on SOE-070 nanoparticle size and Zeta potentiometer (Delsa Nano C/Z, Beckman Coulter, Brea, CA, USA).

3.4. Batch Studies and Evaluation of Adsorption Ability

Batch adsorption was performed as follows: one-component metal ion solutions of Cd (II) were prepared using cadmium chloride. Samples were measured at different time intervals (0, 5, 10, 30, 60, 120, 240, 480, 720, 960, and 1440 min) to evaluate the effect of contact time. For the effect of adsorbents dosage, 5, 25, 50, 100, and 200 mg of Fe₃O₄@PB were added to polypropylene tubes containing 50 mL of 100 µg·L⁻¹ Cd (II) solution. Solution pHs were adjusted in the range of 2 to 11 to test the effect of initial pHs. To evaluate the effect of co-existing ions, 5 mg of Fe₃O₄@PB was mixed with 50 mL of 100 µg·L⁻¹ Cd (II) together with 50, 100, 200, and 400 µg·L⁻¹ of Cu (II), Ni (II), and Zn (II) mixture, respectively. Finally, to determine the effect of initial concentration, 5 mg of Fe₃O₄-FeHCF was mixed with 50 mL of Cd (II) solutions of 50, 100, 200, 500, 800, and 1000 µg·L⁻¹.

All the experiments (unless otherwise noted) were conducted in 50 mL polypropylene tubes and vigorously shaken (150 rpm) at a constant temperature of 25 ± 1 °C for 2 h. The pH of all solutions was set approximately at 6, except for the controlled experiments of pHs. Seven milliliters of all the samples were collected after being filtered using a 0.22 µm mixed cellulose ester membrane, and the concentration of Cd (II) was determined by an inductively coupled plasma mass spectrometer (ICP-MS, Thermo Fisher Scientific ICP Q, Waltham, MA, USA).

3.5. Analytical Methods

3.5.1. Calculation of Removal Efficiency and Capacity

The removal efficiency (R, %) and removal capacity (qₜ, µg·L⁻¹) of Fe₃O₄@PB for Cd (II) were calculated according to Equations (1) and (2):

\[ R = \left( C_0 - C_t \right) / C_0 \times 100, \]  
\[ q_t = \left( C_0 - C_t \right) \times V / m, \]

where \( C_0 \) and \( C_t \) (µg·L⁻¹) stand for the concentration of Cd (II) at time 0 and \( t \); \( V \) is the volume of solution in mL, and \( m \) is the mass of sorbents in g.

3.5.2. Adsorption Kinetics Study

In order to investigate the adsorption kinetics of Cd (II) by Fe₃O₄@PB, pseudo-first-order (Equation (3)), pseudo-second-order (Equation (4)), intraparticle diffusion (Equation (5)), and Elovich (Equation (6)) kinetic models were applied:

\[ \ln \left( q_e - q_t \right) = \ln q_e - k_1 \times t, \]  
\[ t / q_t = 1 / \left( k_2 \times q_e^2 \right) + t / q_e, \]  
\[ q_t = K_p \times t^{1/2} + C, \]
\[ q_t = \frac{1}{\beta} \times [\ln (\alpha \times \beta) + \ln t], \]  

where \( q_e \) and \( q_t \) represent the adsorption amounts of Cd (II) at the adsorption equilibrium time and time \( t \) in \( \mu g \cdot g^{-1} \); and \( k_1 \) and \( k_2 \) are the rate constants; \( K_p \) is the intraparticle diffusion rate constant, and \( C \) is the intercept. \( \alpha \) is the initial uptake rate (mg·g⁻¹·min⁻¹), and \( \beta \) is the degree of activation energy and surface coverage (g·mg⁻¹).

### 3.5.3. Adsorption Isotherms Study

In this paper, four adsorption isotherm models were used to express the equilibrium adsorption of Cd (II). Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherms used in this study are shown in Equations (7)–(10) respectively:

\[ \frac{C_e}{q_e} = \frac{1}{(K_L \times q_m)} + \frac{C_e}{q_m}, \]  

\[ \ln q_e = \ln K_F + \ln \frac{C_e}{n}, \]  

\[ q_e = R \times T / b_T \times (\ln a_T + \ln C_e), \]  

\[ \ln q_e = \ln q_m - K_{DR} \times \epsilon^2, \]  

where \( C_e \) is the equilibrium concentration of Cd (II) in the liquid phase in \( \mu g \cdot L^{-1} \); \( q_e \) and \( q_m \) are the equilibrium uptake amount and maximum monolayer coverage capacity of Cd (II) in \( \mu g \cdot g^{-1} \); \( K_L \) and \( K_F \) are Langmuir and Freundlich model equilibrium constants, respectively; and \( 1/n \) is the Freundlich index. \( R \) is the gas constant, 8.314 (J·mol⁻¹·K⁻¹), \( T \) (K) is the temperature, \( b_T \) (kJ·mol⁻¹) is the adsorption heat of Temkin isotherm. \( K_{DR} \) is the activity coefficient of the Dubinin–Radushkevich isotherm, and \( \epsilon \) is Polanyi potential.

### 4. Conclusions

This work described the removal of Cd (II) from micro-polluted water using novel magnetic core-shell Fe₃O₄@PB composites as adsorbents. The adsorption characteristics and mechanisms of Cd (II) on Fe₃O₄@PB were studied in detail. The formation of the PB nanoparticles on the Fe₃O₄ surface was confirmed by TEM, XRD, and FTIR. Fe₃O₄@PB was negatively charged in a wide range of solution pH > 2.31, showing significance for Cd (II) adsorption. A slight acid environment is favorable for the adsorption process, and removal efficiency of 98.78% could be achieved at low initial Cd (II) concentrations, which means a much lower remaining Cd (II) concentration than the DWRLs. The Fe₃O₄@PB adsorbents also presented an excellent adsorption efficiency for the removal of heavy metal ions in the presence of several co-existing ions. Results from the adsorption kinetic model imply a chemical-dominated adsorption process. Furthermore, Fe₃O₄@PB could be easily separated from the aqueous solution using an external magnetic field. This paper demonstrates that the as-prepared Fe₃O₄@PB can be taken as a promising adsorbent for the removal of Cd (II) from micro-polluted water, which could greatly reduce the potential risks of Cd micro-polluted effluent.

### Author Contributions:

Conceptualization, X.L. and T.H.; investigation, H.C. and T.H.; writing—original draft preparation, X.L., H.C., and T.H.; writing—review and editing, X.L., Y.Z., and R.C.; supervision, R.C., J.T., and Y.L.; funding acquisition, R.C. All authors have read and agreed to the published version of the manuscript.

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The authors declare no conflict of interest.
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References

1. Giller, K.E.; Witter, E.; Mcgrath, S.P. Toxicity of heavy metals to microorganisms and microbial processes in agricultural soils: A review. Soil Biol. Biochem. 1998, 30, 1389–1414. [CrossRef]

2. Fu, F.; Wang, Q. Removal of heavy metal ions from wastewaters: A review. J. Environ. Manag. 2011, 9, 407–418. [CrossRef]

3. Saravanan, P.S.; Kumar, D.N.V.; Swetha, S.; Ngueagani, P.T.; Karishma, S.; Jeevanantham, S.; Yaashikaa, P.R. Ultrasonic assisted agro waste biomass for rapid removal of Cd (II) ions from aquatic environment: Mechanism and modelling analysis. Chemosphere 2021, 271, 129484. [CrossRef]

4. Fu, H.; He, H.; Zhu, R.; Ling, L.; Zhang, W.; Chen, Q. Phosphate modified magnetite@ferrhydrite as an magnetic adsorbent for Cd (II) removal from water, soil, and sediment. Sci. Total Environ. 2021, 764, 124864. [CrossRef]

5. Peng, Y.; Li, Z.Y.; Yang, X.B.; Yang, L.; He, M.; Zhang, H.Y.; Wei, X.; Qin, J.; Li, X.Y.; Lu, G.D.; et al. Relation between cadmium body burden and cognitive function in older men: A cross-sectional study in China. Chemosphere 2020, 250, 126535. [CrossRef]

6. Dong, W.W.; Zhang, Y.; Quan, X. Health risk assessment of heavy metals and pesticides: A case study in the main drinking water source in Dalian, China. Chemosphere 2020, 242, 125113. [CrossRef]

7. Chakrabarty, S.; Sharma, H.P. Heavy metal contamination of drinking water in Kamrup district, Assam, India. Environ. Monit. Assess. 2011, 179, 479–486. [CrossRef]

8. Ahmad, M.K.; Islam, S.; Rahman, S.; Haque, M.R.; Islam, M.M. Heavy metals in water, sediment and some fishes of Buriganga river, Bangladesh. Int. J. Environ. Res. 2010, 4, 321–332.

9. Karunanayake, A.G.; Todd, O.A.; Crowley, M.; Ricchetti, L.; Pittman, C.U.; Anderson, R.; Mohan, D.; Mslna, T. Lead and cadmium remediation using magnetized and non-magnetized biochar from Douglas fir. Chem. Eng. J. 2018, 331, 480–491. [CrossRef]

10. European Commission. Directive 98/8/EC concerning the placing of biocidal products on the market. Off. J. Eur. Communities 1998, 23, 3–65.

11. Kokkinos, E.; Chousein, C.; Simeonidis, K.; Coles, S.; Zouboulis, A.; Mittrakas, M. Improvement of manganese ferroxyhyte’s surface charge with exchangeable Ca ions to maximize Cd and Pb uptake from water. Water Res. 2010, 13, 1762. [CrossRef]

12. Abdel-Aziz, M.H.; Amin, N.K.; El-Ashtoukhy, E.-S.Z. Removal of heavy metals from aqueous solutions by liquid cation exchanger in a jet loop contactor. Hydrometallurgy 2013, 137, 126–132. [CrossRef]

13. Chen, Z.; Liu, T.; Tang, J.J.; Zheng, Z.J.; Wang, H.M.; Shao, Q.; Chen, G.L.; Li, Z.X.; Chen, Y.Q.; Zhu, J.W.; et al. Characteristics and mechanisms of cadmium adsorption from aqueous solution using Lotus seedpod-derived biochar at two pyrolytic temperatures. Environ. Sci. Pollut. Res. 2018, 25, 11854–11866. [CrossRef] [PubMed]

14. Wysokowski, M.; Klapiszewski, L.; Moszyński, D.; Bartczak, P.; Szatkowski, T.; Majchrzak, I.; Siwińska-Stefańska, K.; Bazhenov, V.V.; Jesionowski, T. Modification of chitin with Kraft lignin and development of new biosorbents for removal of cadmium (II) and nickel (II) ions. Mar. Drugs 2014, 12, 2245–2268. [CrossRef]

15. Almasian, A.; Giahm, M.; Fard, G.C.; Dehdast, S.A.; Malekina, L. Removal of heavy metal ions by modified PAN/PANI-nylon core-shell nanofibers membrane: Filtration, antifoiling and regeneration behavior. Chem. Eng. J. 2018, 351, 1166–1178. [CrossRef]

16. Sunil, K.; Karunakaran, G.; Yadav, S.; Padaki, M.; Zadorozhnyy, V.; Pai, R.K. Al-TiO3 a mixed metal oxide based composite membrane: A unique membrane for removal of heavy metals. Chem. Eng. J. 2018, 348, 678–684. [CrossRef]

17. Chen, Q.; Luo, Z.; Hills, C.; Xue, G.; Tyner, M. Precipitation of heavy metals from wastewater using simulated flue gas: Sequential additions of fly ash, lime and carbon dioxide. Water Res. 2009, 43, 2605–2614. [CrossRef] [PubMed]

18. Suresh, K.K.; Dahms, H.U.; Won, E.J.; Lee, J.S.; Shin, K.H. Microalgae—A promising tool for heavy metal remediation. Ecotoxicol. Environ. Saf. 2015, 113, 329–352. [CrossRef] [PubMed]

19. Mohammed, F.M.; Roberts, E.P.; Hill, A.; Campen, A.K.; Brown, N.W. Continuous water treatment by adsorption and electrochemical regeneration. Water Res. 2011, 45, 3065–3074. [CrossRef]

20. Almasian, A.; Jasmine, M.; Salm, E.; Dehdast, S.A.; Malekina, L. Removal of heavy metal ions by modified PAN/PANI-nylon core-shell nanofibers membrane: Filtration, antifoiling and regeneration behavior. Chem. Eng. J. 2018, 351, 1166–1178. [CrossRef]

21. Change, J.J.; Tang, B.Q.; Wang, Q.; Liu, N.N.; Xue, Q. New insight into the removal of Cd (II) from aquatic solution by diatomite. Environ. Sci. Pollut. Res. 2020, 27, 9882–9890. [CrossRef]

22. Tian, Y.; Xie, Z.M.; Chen, M.L.; Wang, J.H. Cadmium preconcentration with bean-coat as a green adsorbent with detection by electrothermal atomic absorption spectrometry. J. Anal. Atom. Spectrom. 2011, 26, 1408–1413. [CrossRef]

23. Chang, J.J.; Liu, M.; Zhang, Y. Technology, Cd (II) removal on surface-modified activated carbon: Equilibrium, kinetics and mechanism. Water Sci. Technol. 2016, 74, 1800–1808. [CrossRef] [PubMed]

24. Li, Y.; Pei, G.; Qiao, X.; Zhu, Y.; Li, H. Remediation of cadmium contaminated water and soil using vinegar residue biochar. Environ. Sci. Pollut. Res. 2018, 25, 15754–15764. [CrossRef]
54. Chu, L.; Liu, C.B.; Zhou, G.Y.; Xu, R.; Tang, Y.H.; Zeng, Z.B.; Luo, S.L. A double network gel as low cost and easy recycle adsorbent: Highly efficient removal of Cd (II) and Pb (II) pollutants from wastewater. J. Hazard. Mater. 2015, 300, 153–160. [CrossRef]

55. Li, R.H.; Liang, W.; Huang, H.; Jiang, S.C.; Guo, D.; Li, M.L.; Zhang, Z.Q.; Ali, A.; Wang, J.J. Removal of cadmium (II) cations from an aqueous solution with aminothiourea chitosan strengthened magnetic biochar. J. Appl. Polym. Sci. 2018, 135, 46239. [CrossRef]

56. Gong, J.L.; Chen, L.; Zeng, G.M.; Long, F.; Deng, J.H.; Niu, Q.Y.; He, X. Shellac-coated iron oxide nanoparticles for removal of cadmium (II) ions from aquatic solution. J. Environ. Sci. 2012, 24, 1165–1173. [CrossRef]

57. Iqbal, M.; Saeed, A.; Zafar, S.I. FTIR spectrophotometry, kinetics and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding the mechanism of Cd\textsuperscript{2+} and Pb\textsuperscript{2+} removal by mango peel waste. J. Hazard. Mater. 2009, 164, 161–171. [CrossRef]

58. Huang, J.H.; Yuan, F.; Zeng, G.M.; Li, X.; Gu, Y.L.; Shi, L.X.; Liu, W.C.; Shi, Y.H. Influence of pH on heavy metal speciation and removal from wastewater using micellar-enhanced ultrafiltration. Chemosphere 2017, 173, 199–206. [CrossRef]

59. Yang, Z.H.; Chen, X.H.; Li, S.Y.; Ma, W.H.; Li, Y.; He, Z.D.; Hu, H.R.; Wang, T. Effective removal of Cd (II) from aqueous solution based on multifunctional nanoporous silicon derived from solar kerosene waste. J. Hazard. Mater. 2020, 385, 121522. [CrossRef] [PubMed]

60. Ding, D.H.; Lei, Z.F.; Yang, Y.N.; Feng, C.P.; Zhang, Z.Y. Selective removal of cesium from aqueous solutions with nickel (II) hexacyanoferrate (III) functionalized agricultural residue-walnut shell. J. Hazard. Mater. 2014, 270, 187–195. [CrossRef]

61. Gupta, P.L.; Jung, H.; Tiwari, D.; Kong, S.H.; Lee, S.M. Insight into the mechanism of Cd (II) and Pb (II) removal by sustainable magnetic biosorbent precursor to Chlorella vulgaris. J. Taiwan Inst. Chem. Eng. 2017, 71, 206–213. [CrossRef]

62. Guan, Q.Q.; Gao, K.X.; Ning, P.; Miao, R.R.; He, L. Value-added utilization of paper sludge: Preparing activated carbon for efficient adsorption of Cr (VI) and further hydrogenation of furfural. Sci. Total Environ. 2020, 741, 140265. [CrossRef]

63. Hayati, B.; Maleki, A.; Najafi, F.; Gharibi, F.; Gharibi, F.; McKay, G.; Gupta, V.K.; Puttaiah, S.H.; Marzban, N. Heavy metal adsorption using PAMAM/CNT nanocomposite from aqueous solution in batch and continuous fixed bed systems. Chem. Eng. J. 2018, 346, 258–270. [CrossRef]

64. Yadav, N.; Maddheshiya, D.N.; Rawat, S.; Singh, J. Adsorption and equilibrium studies of phenol and para-nitrophenol by magnetic activated carbon synthesised from cauliflower waste. Environ. Eng. Res. 2019, 25, 742–752. [CrossRef]

65. Papegowda, P.K.; Syed, A.A. Isotherm, kinetic and thermodynamic studies on the removal of methylene blue dye from aqueous solution using saw palmetto spent. Int. J. Environ. Res. 2017, 11, 91–98. [CrossRef]

66. Zhou, Q.; Liao, B.; Lin, L.; Qiu, W.; Song, Z. Adsorption of Cu (II) and Cd (II) from aqueous solutions by ferromanganese binary oxide-biochar composites. Sci. Total Environ. 2018, 615, 115–122. [CrossRef] [PubMed]