

Ionic liquid-modified magnetic nanoparticle composite for the selective adsorption of chromium ions in water

Research Article

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Abstract: Adsorption methods are widely used in the removal of heavy metals from aquatic environments, and adsorbents are crucial for adsorption efficiency. In this study, a magnetic nanoparticle composite material, $\text{Fe}_3\text{O}_4@\text{PEG@IL}$, modified with an imidazole-based ionic liquid $[\text{C}_n\text{MI}_m]\text{HCO}_3$ ($n = 2, 4, 6, 8$) was used as an adsorbent to adsorb the heavy metal chromium ($\text{Cr}(\text{VI})$) in aquatic environments, and the adsorption conditions were optimized. Moreover, the selective adsorption of $\text{Cr}(\text{VI})$ by the adsorbent was explored. The results show that when the pH value of the aqueous solution was 3.0, the solution temperature was 65°C , the amount of $\text{Fe}_3\text{O}_4@\text{PEG@IL}$ added was 25 mg, and the time of adsorption reaction was 2.5 h, a good adsorption effect would be achieved, with an adsorption rate of 99.5%. Meanwhile, $\text{Fe}_3\text{O}_4@\text{PEG@IL}$ had high adsorption selectivity for $\text{Cr}(\text{VI})$, and heavy metal cations, such as Pb^{2+} , Hg^{2+} , Cd^{2+} , and Cu^{2+} , did not interfere with the adsorption of $\text{Cr}(\text{VI})$. Moreover, the adsorbent was easy to recover and had good reusability.

Keywords: Magnetic nanoparticles • Ionic liquids • Chromium ions • Adsorption • Selectivity

1. Introduction

In recent years, the issue of heavy metal pollution in aquatic environments has become increasingly severe, gradually capturing the attention of researchers [1,2]. Among these pollutants, chromium ($\text{Cr}(\text{VI})$) has emerged as a particularly typical heavy metal contaminant due to its widespread resource and high toxicity [3]. Thus, the removal of $\text{Cr}(\text{VI})$ from water holds significant importance [4]. Adsorption methods, characterized by low cost, high efficiency, and simple operation, have been widely employed for the selective adsorption of heavy metal ions [5–7].

Nanomaterials, owing to their large specific surface area, exhibit a significant adsorption capacity for various heavy metal ions, achieving adsorption equilibrium in a relatively short time, which makes them ideal materials for adsorption [8]. Particularly, magnetic nanomaterials, possessing superparamagnetism,

can significantly shorten the enrichment time with the assistance of an external magnetic field. However, iron oxide nanoparticles have a small surface area and are susceptible to oxidation in air and erosion in acidic environments, leading to decreased adsorption effectiveness and selectivity, thereby affecting the performance of magnetic particles. Surface modification is thus required. Ionic liquids (ILs), being non-volatile, non-flammable, with tunable anion–cation structures, and possessing strong dissolution capabilities for many substances, have been widely used in the extraction of heavy metal ions. Loading ILs onto the surface of magnetic nanoparticles not only overcomes the high production cost and high viscosity of ILs but also compensates for the shortcomings of magnetic nanoparticles being prone to oxidation and aggregation. Combining the advantages of both, utilizing the excellent superparamagnetic properties of magnetic particles enables further recycling of materials. Therefore, the current focus of researchers is on modifying magnetic particles with different types of ILs. Yang et al. successfully extracted various sulfonylurea pesticide residues from soil samples using

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synthesized polymeric IL-modified magnetic nanomaterials, achieving satisfactory results [9]. Zhang *et al.* synthesized ionic liquid-modified $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ for the adsorption of trace fluoroquinolone antibiotics in food, achieving recovery rates of 85.4–105.9% for milk samples and 85.2–103.7% for pork samples [10]. Dang *et al.* used 1-octyl-3-methylimidazolium hexafluorophosphate-modified magnetic solid phase nanomaterials as extraction adsorbents to extract trace amounts of cadmium ions from environmental water samples, with spike recoveries reaching 84–100% [11]. However, these studies mostly focus on the extraction and separation in environmental analysis sample pretreatment, lacking systematic theoretical research on the application of IL-modified magnetic nanomaterials in the adsorption of heavy metals in aqueous solutions and the influence of different factors on their adsorption effectiveness. Additionally, the effect of the alkyl chain length of IL cations on their adsorption performance has not been reported to date.

Therefore, this study synthesized four imidazole-based ILs with different alkyl chain lengths to modify magnetic nanoparticles Fe_3O_4 to obtain an IL-modified magnetic nanoparticle composite material $\text{Fe}_3\text{O}_4@\text{PEG}@\text{IL}$, and applied it to the selective adsorption of $\text{Cr}(\text{VI})$ in water environments. Compared with existing studies [12,13], this study fully exploits the customizable chemical properties of IL cations through structural design, analyzes the key factors influencing their adsorption capacity for heavy metals, and possesses multiple characteristics of environmental friendliness, application diversity, and technological integration. These characteristics make supported ILs a powerful tool for addressing heavy metal pollution in water environments and are expected to play a more important role in future environmental management. This study aims to leverage the excellent performance of supported ILs to improve the adsorption efficiency of heavy metal ions in water environments, enhance adsorption selectivity, promote the reusability of adsorption materials, reduce environmental impacts and by-product generation, explore economically efficient techniques for treating heavy metal pollution in water environments, and provide new solutions for water pollution control.

2. Experimental section

2.1 Preparation of $\text{Fe}_3\text{O}_4@\text{PEG}@\text{IL}$

Four imidazole-based ILs with different alkyl chain lengths, $[\text{C}_n\text{MI}_m]\text{HCO}_3$ ($n = 2, 4, 6, 8$), were synthesized

using a two-step method, following the procedures outlined in the study of Wang *et al.* [14].

Taking 1.0 g of Fe_3O_4 (with a purity of 99.9%, carboxyl group modified, and particle size of 100 nm; supplied by Nantong Feiyu Biotechnology Co., Ltd.), magnetic separation was employed to remove the solvent from the Fe_3O_4 dispersion. Subsequently, 50 mL of deionized water was added, followed by the addition of 1.5 g of polyethylene glycol (PEG, $M_n = 4,000$, supplied by Aladdin Reagent (Shanghai) Co., Ltd.). The mixture was then stirred at room temperature under a nitrogen atmosphere for 24 h. After magnetic separation to remove the solvent, 10 mL of ultrapure water was added, and the process was repeated three times. The resulting product was vacuum dried for 8 h to obtain $\text{Fe}_3\text{O}_4@\text{PEG}$.

$\text{Fe}_3\text{O}_4@\text{PEG}@\text{IL}$ was prepared using a sonochemical-assisted impregnation method as follows: at 25°C, 0.03 g of IL and 0.07 g of $\text{Fe}_3\text{O}_4@\text{PEG}$ were added to 10 mL of acetonitrile (AR, >99%, supplied by Aladdin Reagent (Shanghai) Co., Ltd.). The mixture was mechanically stirred for 3 h and then dried at 80°C in a vacuum drying oven. Subsequently, ultrasonic treatment was performed at 200°C for 4 h to obtain the target product, $\text{Fe}_3\text{O}_4@\text{PEG}@\text{IL}$.

2.2 Material characterization

The microstructure of Fe_3O_4 microspheres and $\text{Fe}_3\text{O}_4@\text{PEG}@\text{IL}$ was characterized using transmission electron microscopy (TEM; JEOL-2010, JEOL Ltd., Japan). Copper grids (carbon-coated) were used for sample preparation, with absolute ethanol as the dispersant, and an acceleration voltage of 200 kV. Fourier transform infrared (FTIR) spectroscopy (Nicolet iS5, Thermo Fisher Scientific Inc., USA) was employed to analyze the functional group structures of Fe_3O_4 microspheres and $\text{Fe}_3\text{O}_4@\text{PEG}@\text{IL}$. Samples were prepared using powder conventional pressing, with a wavenumber range of 4,000–400 cm^{-1} and a scanning speed of 10 scans per second. Thermal stability of $\text{Fe}_3\text{O}_4@\text{PEG}@\text{IL}$ was determined using thermogravimetric analysis (TGA; 209 F1, NETZSCH-Gerätebau GmbH, Germany) under a nitrogen atmosphere. The test temperature ranged from room temperature to 1,000°C, with a heating rate of 10°C/min.

2.3 Adsorption experiments

A specified amount of the adsorbent $\text{Fe}_3\text{O}_4@\text{PEG}@\text{IL}$ was added to a 20 mL solution containing 20 mg/L $\text{Cr}(\text{VI})$ for adsorption reactions. The solution's pH was adjusted using

either 0.5 mol/L HCl or 0.05 mol/L NaOH. The temperature of the solution was controlled using a constant temperature water bath, and adsorption was carried out with oscillation. After adsorption, external magnets were used to recover the adsorbent, and the concentration of Cr(vi) in the solution was determined using inductively coupled plasma coupled with mass spectrometry. The adsorption efficiency of Cr(vi) was calculated using the following formula:

$$R\% = \frac{(C_0 - C_e)}{C_0} \times 100\%, \quad (1)$$

where $R\%$ represents the adsorption efficiency of Cr(vi), and C_0 and C_e denote the initial concentration and concentration after adsorption of Cr(vi) (mg/L), respectively.

2.4 Regeneration of the adsorbent

After adsorbing Cr(vi), the adsorbent Fe₃O₄@PEG@IL can be rapidly recovered from water under the influence of an external magnetic field. The Cr(vi) adsorbed on the surface of the adsorbent was desorbed using a reduction method. An 8% hydrazine hydrate solution was chosen as the regeneration agent, with the addition of hydrazine hydrate in excess to ensure complete reduction of Cr(vi). The regenerated adsorbent was then utilized in repeated usage experiments, following the procedures outlined in Section 2.3.

3. Results and discussion

3.1 Material characterization

3.1.1 TEM

The microstructure of pure magnetic nanoparticles Fe₃O₄ and the IL-modified magnetic nanoparticle composite material Fe₃O₄@PEG@IL was observed using TEM, and the images are depicted in Figure 1. From Figure 1a, it is evident that Fe₃O₄ microspheres exhibit good dispersion with a diameter of approximately 100 nm. A close-up observation reveals a relatively rough and non-smooth surface of Fe₃O₄ microspheres. Despite the good water dispersibility of Fe₃O₄ microspheres, a layer of PEG was coated on the surface to further enhance their dispersion [15–17]. The primary objectives of PEG coating were to prevent magnetic aggregation or uneven aggregation of

Fe₃O₄@PEG@IL post-IL modification and facilitate the binding of the IL and Fe₃O₄ microspheres. Figure 1b demonstrates that the surface of Fe₃O₄ microspheres becomes smooth after loading with the IL, indicating uniform loading of the IL on the surface of Fe₃O₄ microspheres. Furthermore, the magnetic nanoparticles composite material modified with the IL exhibits improved dispersion. By comparing the particle size of Fe₃O₄ microspheres before and after modification, it was observed that the thickness of the IL layer loaded on the surface of magnetic nanoparticles is approximately 40 nm.

3.1.2 FTIR

FTIR was employed to analyze the functional groups of pure magnetic nanoparticles Fe₃O₄ and the IL-modified magnetic nanoparticle composite material Fe₃O₄@PEG@IL, verifying the loading of the IL. As shown in Figure 2, pure magnetic nanoparticles Fe₃O₄ exhibit an O–H stretching vibration peak at 3,412 cm^{−1}, indicating the presence of hydroxyl and carboxyl groups on the surface of Fe₃O₄ prepared in this study. These active sites facilitate the modification of Fe₃O₄ by the IL. Simultaneously, the FTIR spectrum of Fe₃O₄@PEG@IL still shows a characteristic peak at 3,412 cm^{−1}, suggesting that the functional group structure of Fe₃O₄ itself remains unchanged after modification with the IL. Additionally, new characteristic peaks appear at 2,913 cm^{−1} and in the range of 1,100–1,450 cm^{−1} in the FTIR spectrum of Fe₃O₄@PEG@IL, attributed to the symmetric and antisymmetric stretching vibrations of the IL cation –CH₂– and the C–O vibration of the anion, respectively. This indicates the successful loading of the IL onto the surface of Fe₃O₄, resulting in the formation of the IL-modified magnetic nanoparticle composite material.

3.1.3 TGA

Thermal stability is a critical property of composite materials, indicating the ease with which materials undergo oxidation, reduction, decomposition, and compound formation upon heating, thereby influencing the material's overall performance. To characterize the thermal stability of the IL-modified magnetic nanoparticle composite material Fe₃O₄@PEG@IL, thermogravimetry-differential scanning calorimetry (TG-DSC) analysis was conducted, and the results are presented in Figure 3. From the graph, it can be observed that Fe₃O₄@PEG@IL undergoes two distinct weight loss stages, occurring in the range 75–100 and 250–350°C, corresponding to two pronounced endothermic peaks at 75 and 300°C in the DSC curve. This suggests that the IL undergoes partial decomposition with increasing

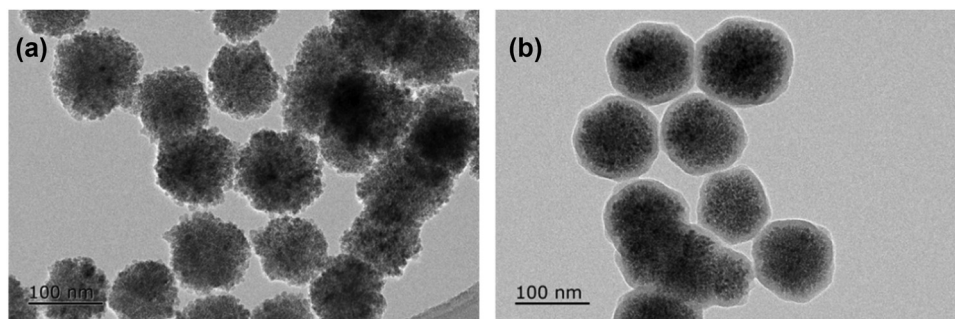


Figure 1. TEM images of (a) Fe₃O₄ and (b) Fe₃O₄@PEG@IL.

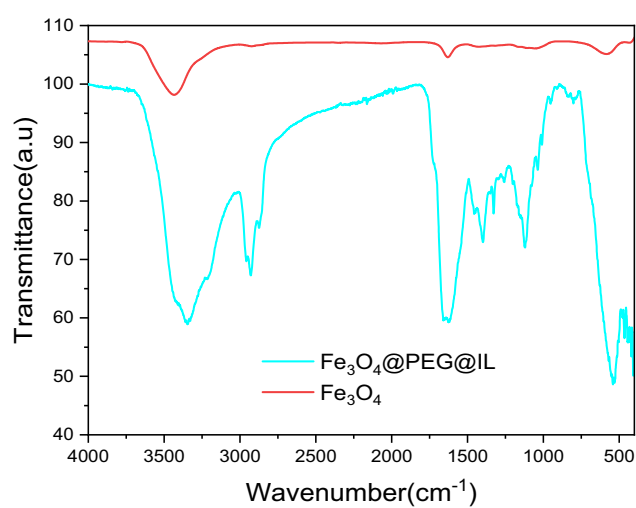


Figure 2. FTIR spectra of Fe₃O₄ and Fe₃O₄@PEG@IL.

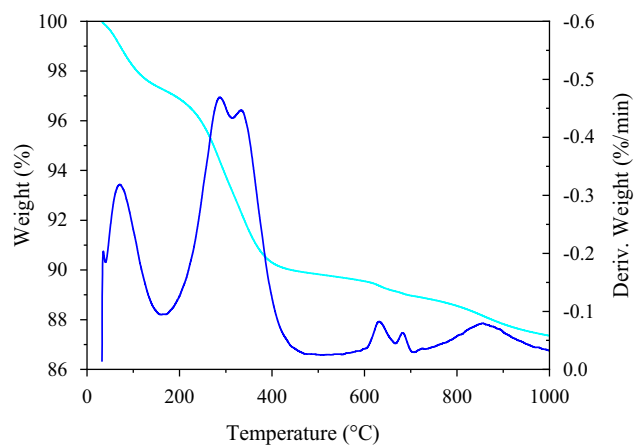


Figure 3. TGA of Fe₃O₄@PEG@IL.

temperature. Simultaneously, TG-DSC analysis confirms that $\text{Fe}_3\text{O}_4@\text{PEG@IL}$ does not experience significant weight loss below 226°C , maintaining the intact structure of the IL. Therefore, $\text{Fe}_3\text{O}_4@\text{PEG@IL}$ exhibits good thermal stability in practical applications, with a tight and stable bonding between the IL and the carrier.

3.2 Optimization of conditions for $\text{Cr}(\text{VI})$ adsorption by $\text{Fe}_3\text{O}_4@\text{PEG@IL}$

The adsorption performance of $\text{Fe}_3\text{O}_4@\text{PEG@IL}$ for $\text{Cr}(\text{VI})$ in water is influenced by various factors, such as the solution pH, temperature, dosage of $\text{Fe}_3\text{O}_4@\text{PEG@IL}$, and initial concentration of $\text{Cr}(\text{VI})$ in water. Therefore, it is essential to optimize the reaction conditions affecting the adsorption performance. This study investigated the impact of solution pH, temperature, $\text{Fe}_3\text{O}_4@\text{PEG@IL}$ dosage, and adsorption time as individual variables to determine the optimal adsorption reaction conditions.

3.2.1 Effect of solution pH on adsorption

Solution pH not only affects the existence state of heavy metal ions but also alters the surface properties of the $\text{Fe}_3\text{O}_4@\text{PEG@IL}$ adsorbent, thus playing a crucial role in the adsorption of $\text{Cr}(\text{VI})$ onto $\text{Fe}_3\text{O}_4@\text{PEG@IL}$. The results are depicted in Figure 4. When the solution is strongly acidic (pH less than 2.0), the adsorption efficiency of $\text{Fe}_3\text{O}_4@\text{PEG@IL}$ for $\text{Cr}(\text{VI})$ exceeds 99.5%. This is attributed to the abundance of H^+ in strongly acidic solutions, leading to protonation of the adsorbent surface, enhancing the

electrostatic attraction between the adsorbent and $\text{Cr}(\text{VI})$, facilitating the adsorption. As the solution acidity decreases (pH increases from 2.0 to 7.0), the adsorption efficiency of $\text{Cr}(\text{VI})$ decreases from 99.5 to 72.3%. This is primarily due to the increasing pH, reducing H^+ concentration, and diminishing protonation effects rapidly, leading to a sharp decrease in positive charges on the surface of $\text{Fe}_3\text{O}_4@\text{PEG@IL}$, resulting in a reduction in the adsorption efficiency of $\text{Cr}(\text{VI})$. As the solution pH continues to increase (from 7.0 to 11.0), the adsorption efficiency of $\text{Cr}(\text{VI})$ rapidly decreases from 72.3% to below 10.0%. This is because the OH^- ions in alkaline solutions compete with $\text{Cr}(\text{VI})$ for adsorption. Considering both the adsorption efficiency and real water conditions, a pH of 3.0 was selected as the optimal pH for the adsorption reaction.

3.2.2 Effect of solution temperature on adsorption

Solution temperature can impact the density, surface tension, and conductivity of ILs. Additionally, it can influence the dispersion of magnetic nanomaterials in solution. Therefore, solution temperature is an important factor affecting the adsorption of $\text{Cr}(\text{VI})$ by $\text{Fe}_3\text{O}_4@\text{PEG@IL}$, as illustrated in Figure 5. When the temperature is below 45°C , the adsorption rate of $\text{Cr}(\text{VI})$ is nearly unaffected by temperature, maintaining around 75%. However, as the temperature exceeds 45°C , the adsorption rate of $\text{Cr}(\text{VI})$ rapidly increases with temperature, reaching saturation at 65°C with an adsorption rate of 99.5%. This phenomenon may be attributed to the different interaction forces between the imidazole-based IL anion and $\text{Cr}(\text{VI})$ compared to the interaction between the imidazole cation in

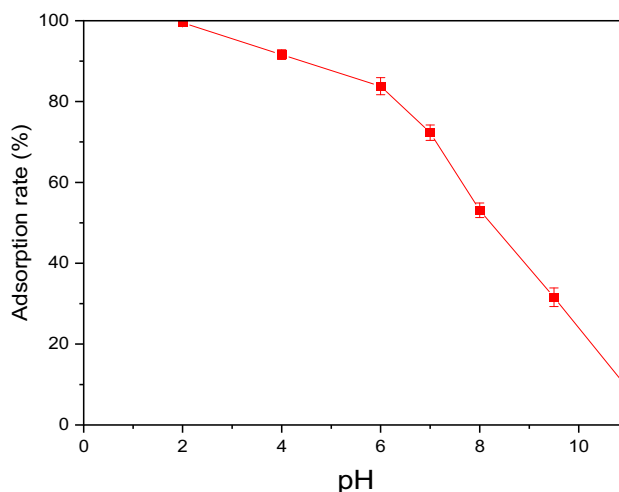


Figure 4. Effect of solution pH on the adsorption rate of $\text{Cr}(\text{VI})$.

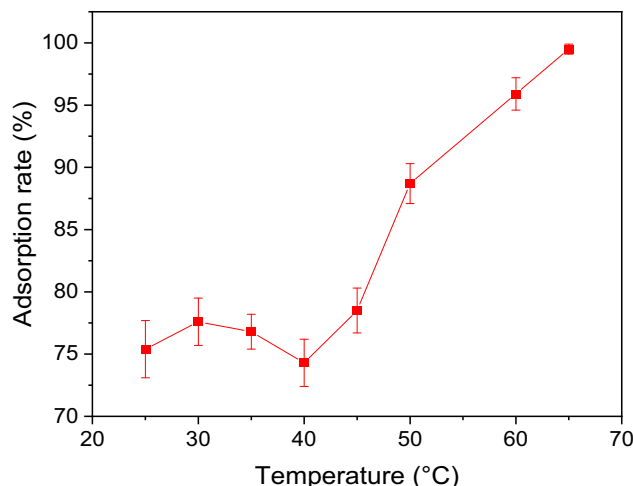


Figure 5. Effect of solution temperature on the adsorption rate of Cr(VI).

the IL and the anion. Elevated temperature is conducive to anion exchange reactions between Cr(VI) and the IL anion, promoting the adsorption of Cr(VI) onto the adsorbent surface. Therefore, the optimal adsorption temperature is determined to be 65°C.

3.2.3 Effect of Fe₃O₄@PEG@IL dosage on adsorption

Increasing the dosage of the adsorbent can provide more active sites for the adsorption of Cr(VI), thereby enhancing the adsorption efficiency of heavy metal ions. However, excessive addition of the adsorbent will increase operational costs. Therefore, it is necessary to comprehensively consider both the adsorption rate and operational costs to

determine the appropriate dosage of the adsorbent. The influence of the adsorbent dosage on the adsorption rate of Cr(VI) is shown in Figure 6. When the adsorbent dosage is 5 mg, the adsorption rate of Cr(VI) is approximately 53.4%. As the adsorbent dosage gradually increases to 25 mg, the adsorption rate of Cr(VI) also increases to 99.5%. A further increase of the adsorbent dosage does not significantly change the adsorption rate of Cr(VI). Therefore, the optimal adsorbent dosage is determined to be 25 mg.

3.2.4 Adsorption kinetics

To analyze the adsorption kinetics of Fe₃O₄@PEG@IL for Cr(VI), the variation of adsorption rate with adsorption

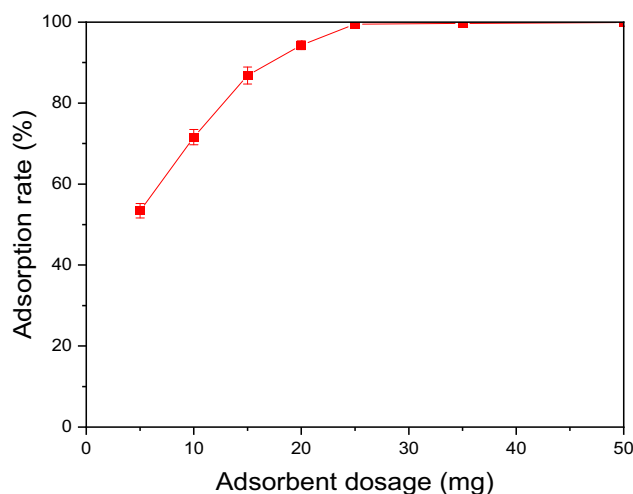


Figure 6. Effect of adsorbent dosage on the adsorption rate of Cr(VI).

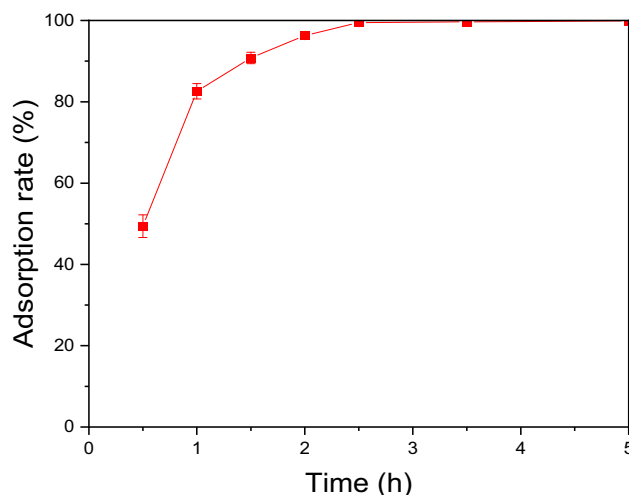


Figure 7. Effect of adsorption time on the adsorption rate of Cr(vi).

time was investigated, as shown in Figure 7. In the initial stage of the adsorption reaction, the adsorption rate of Cr(vi) rapidly increases with the extension of adsorption time, reaching 82.6% at 1 h. This is primarily because, in the initial stage, there are numerous active sites on the adsorbent surface, facilitating complexation with Cr(vi). The time required to reach equilibrium for the adsorption of Cr(vi) in the aqueous environment by Fe₃O₄@PEG@IL primarily depends on the synthesis conditions of the adsorbent [18], including the structure of the IL (which affects the number of active sites) and the specific surface area of the adsorbent. As the adsorption reaction proceeds, the increase in the adsorption rate of Cr(vi) slows down, reaching 99.5% adsorption rate at 2.5 h. Further extension of the adsorption reaction time does not significantly affect the adsorption rate of Cr(vi). Therefore, the optimal adsorption time was determined to be 2.5 h. These results indicate that equilibrium adsorption of Cr(vi) by Fe₃O₄@PEG@IL is achieved within 2.5 h.

The observed dependency leads to the hypothesis that for the adsorbent Fe₃O₄@PEG@IL, rapid adsorption equilibrium is not only due to the strong coordination and good affinity of the adsorbent for metal ions but also due to the availability of active sites. Furthermore, fitting of the adsorption kinetics data of Cr(vi) onto Fe₃O₄@PEG@IL reveals excellent agreement with the pseudo-second-order model ($R^2 = 0.993$). Additionally, the calculated equilibrium adsorption capacity (q_e) closely matches the experimental data. According to the pseudo-second-order model, the rate-limiting step involves the formation of coordination bonds between the metal ions and surface functional groups during chemical adsorption.

3.3 Influence of IL types on the adsorption performance of Fe₃O₄@PEG@IL for Cr(vi)

The length of the alkyl chain of the imidazole cation significantly affects the polarity and charge strength of the IL, thereby influencing the adsorption performance of Fe₃O₄@PEG@IL for Cr(vi). Therefore, this study investigated the variation of the adsorption rate of Cr(vi) with adsorption time when the alkyl chain length of the imidazole IL cation is 2, 4, 6, and 8, respectively. The experiments were conducted under the conditions of a solution pH of 3.0, a solution temperature of 65°C, and an adsorbent dosage of 25 mg. The results are presented in Figure 8. It can be observed from the graph that as the alkyl chain length of the imidazole IL cation increases, the adsorption performance of Fe₃O₄@PEG@IL for Cr(vi) gradually improves, although the enhancement is not significant. When the alkyl chain length is 2, the adsorption rate of Cr(vi) by Fe₃O₄@PEG@IL is 76.5% after 1 h of adsorption. As the alkyl chain length increases to 8, the adsorption rate of Cr(vi) by Fe₃O₄@PEG@IL increases to 87.6% after 1 h of adsorption.

3.4 Selective adsorption performance of Fe₃O₄@PEG@IL for Cr(vi)

As is known, multiple heavy metal ions may coexist in actual water environments. Therefore, the interference from other heavy metal ions (such as Pb²⁺, Hg²⁺, Cd²⁺, etc.) in the solution on the adsorption of Cr(vi) by

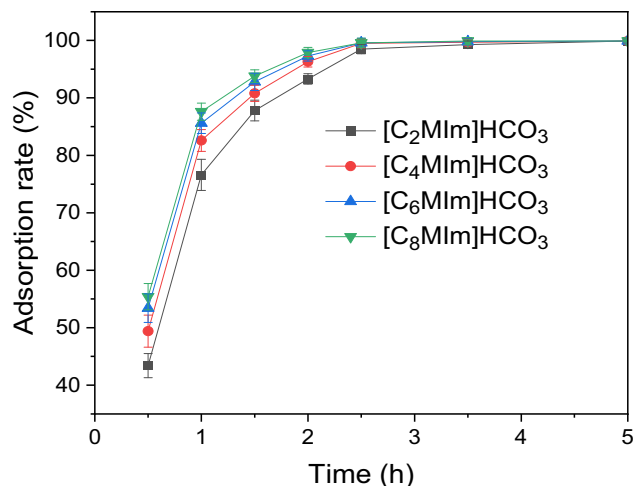


Figure 8. Influence of the alkyl chain length of the imidazole cation on the adsorption rate of Cr(VI).

$\text{Fe}_3\text{O}_4@\text{PEG}@\text{IL}$ is a practical consideration. In this study, common heavy metal ions such as Pb^{2+} , Hg^{2+} , Cd^{2+} , and Cu^{2+} were chosen as interfering ions, and the adsorption performance of $\text{Fe}_3\text{O}_4@\text{PEG}@\text{IL}$ for Cr(VI) in the presence of interfering ions was investigated. The results are presented in Figure 9. When the concentrations of interfering ions Pb^{2+} , Hg^{2+} , Cd^{2+} , and Cu^{2+} are 100 times the concentration of Cr(VI), the adsorption rate of Cr(VI) is still greater than 95%. This indicates that these interfering ions have a minimal impact on the adsorption of Cr(VI) by $\text{Fe}_3\text{O}_4@\text{PEG}@\text{IL}$. Under strong acidic conditions, Pb^{2+} , Hg^{2+} , Cd^{2+} , and Cu^{2+} all carry positive charges, and the adsorbent $\text{Fe}_3\text{O}_4@\text{PEG}@\text{IL}$ surface is also positively charged. Hence, there exists electrostatic repulsion between these positively charged heavy metal ions and $\text{Fe}_3\text{O}_4@\text{PEG}@\text{IL}$,

making it challenging for $\text{Fe}_3\text{O}_4@\text{PEG}@\text{IL}$ to adsorb these positively charged heavy metal ions. On the other hand, Cr(VI) exists in the form of $\text{Cr}_2\text{O}_7^{2-}$ in the solution. Therefore, these heavy metal ions do not interfere with the adsorption of Cr(VI) by $\text{Fe}_3\text{O}_4@\text{PEG}@\text{IL}$. Consequently, $\text{Fe}_3\text{O}_4@\text{PEG}@\text{IL}$ can selectively adsorb Cr(VI) in the presence of various heavy metal cations.

3.5 Regeneration and reusability of the adsorbent

The choice of magnetic nanoparticles as a carrier for preparing adsorbents in this study is crucial because their magnetic properties allow for the recovery and reuse of

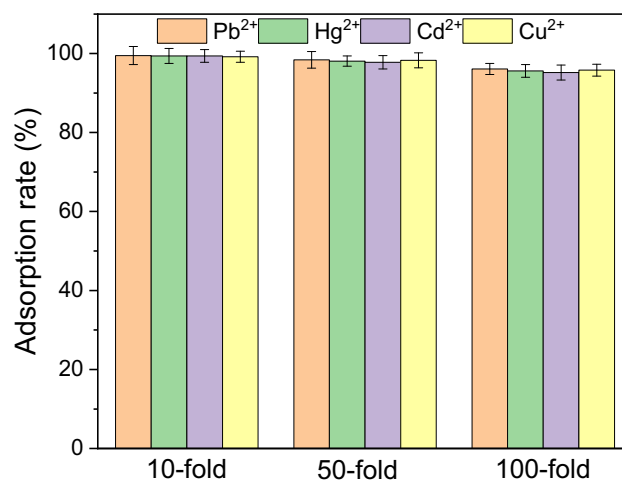


Figure 9. Adsorption rate of Cr(VI) in the presence of coexisting heavy metal cations.

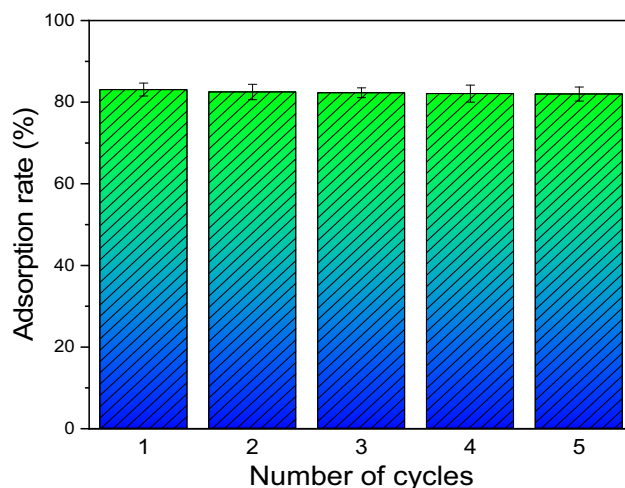


Figure 10. Adsorption/desorption experiments of $\text{Fe}_3\text{O}_4@\text{PEG}@\text{IL}$ for $\text{Cr}(\text{VI})$. Temperature: 25°C ; adsorption time: 2.5 h; desorption reagent: 8% hydrazine hydrate.

the adsorbent. After $\text{Fe}_3\text{O}_4@\text{PEG}@\text{IL}$ adsorbs $\text{Cr}(\text{VI})$, an external magnetic field can be applied to the water solution, and under the influence of magnetic force, the adsorbent can be recovered from the solution. Subsequently, the adsorption agent can be regenerated through hydrazine hydrate reduction, dissolving the adsorbed $\text{Cr}(\text{VI})$ on the surface and converting it into less toxic $\text{Cr}(\text{III})$. Using 8% hydrazine hydrate as the reducing agent for adsorbent regeneration, the desorption rate of $\text{Cr}(\text{VI})$ is around 83.0%. The adsorbent can be reused for up to five cycles, with no significant reduction in both adsorption and desorption performances, as shown in Figure 10. In summary, employing a reduction method for the desorption of adsorbed $\text{Cr}(\text{VI})$ offers two advantages. First, the toxic $\text{Cr}(\text{VI})$ is reduced to less toxic $\text{Cr}(\text{III})$, and due to the positive charge of $\text{Cr}(\text{III})$, there is electrostatic repulsion between $\text{Cr}(\text{III})$ and the adsorbent $\text{Fe}_3\text{O}_4@\text{PEG}@\text{IL}$, facilitating effective desorption. Second, the reduction reaction is mild, promoting the regeneration and repeated use of the adsorbent, unlike strong alkaline desorbing agents such as high-concentration NaOH , which can cause a vigorous reaction.

3.6 Discussion

In this study, the ion liquid-modified magnetic nanoparticle composite material $\text{Fe}_3\text{O}_4@\text{PEG}@\text{IL}$ was successfully synthesized and comprehensively characterized. TEM revealed that the surfaces of Fe_3O_4 microspheres, following PEG encapsulation and IL modification, exhibited increased smoothness, with the IL effectively loaded onto the surface, enhancing material dispersion. FTIR spectroscopy

analysis further confirmed successful IL loading and the composite material's functional group structure.

The adsorption performance was systematically optimized by adjusting the solution pH, temperature, $\text{Fe}_3\text{O}_4@\text{PEG}@\text{IL}$ dosage, and adsorption time. Under optimal conditions, $\text{Fe}_3\text{O}_4@\text{PEG}@\text{IL}$ demonstrated exceptional adsorption performance for $\text{Cr}(\text{VI})$, achieving a remarkable adsorption rate of 99.5%. Adsorption kinetics studies determined a suitable adsorption time of 2.5 h, signifying equilibrium within this timeframe. Temperature studies identified the optimal adsorption temperature as 65°C .

Furthermore, the impact of varying alkyl chain lengths of imidazolium cations on the adsorption performance of $\text{Fe}_3\text{O}_4@\text{PEG}@\text{IL}$ for $\text{Cr}(\text{VI})$ was thoroughly investigated. Results showed that increased chain length led to improved adsorption performance. In the presence of multiple metal ions, $\text{Fe}_3\text{O}_4@\text{PEG}@\text{IL}$ exhibited selective adsorption for $\text{Cr}(\text{VI})$, presenting favorable conditions for its application in real water environments. Successful regeneration and repeated use of the adsorbent were achieved through hydrazine hydrate reduction, indicating good regenerability.

In summary, the synthesized $\text{Fe}_3\text{O}_4@\text{PEG}@\text{IL}$ demonstrated excellent adsorption performance and regenerability, offering an effective method for treating harmful heavy metals, particularly $\text{Cr}(\text{VI})$, in water. Future research could further explore its performance under more complex real-world water conditions, such as the presence of coexisting ions and organic compounds, to provide a more comprehensive assessment of its practical application.

4. Conclusions

With the increasing severity of heavy metal pollution in water, it is imperative to take effective measures for the removal of heavy metals. Therefore, in this study, we designed and synthesized four imidazolium-based ILs $[C_nMI_m]HCO_3$ ($n = 2, 4, 6, 8$) for modifying magnetic nanoparticles Fe_3O_4 , resulting in the composite material $Fe_3O_4@PEG@IL$. The microstructure, structural characteristics, and thermal stability were characterized through TEM, FTIR, and TGA. Subsequently, $Fe_3O_4@PEG@IL$ was applied to the selective adsorption of $Cr(VI)$ in water. Optimization of adsorption conditions, including water solution pH, temperature, $Fe_3O_4@PEG@IL$ dosage, and adsorption time, was performed. The influence of the alkyl chain length of imidazolium on the adsorption rate of $Cr(VI)$ was investigated. The interference of heavy metal cations and inorganic anions on the adsorption of $Cr(VI)$ was analyzed. Finally, the regeneration and reusability of the adsorbent were explored. The main conclusions are as follows:

- (1) $Fe_3O_4@PEG@IL$ exhibits good dispersibility, and modification with ILs does not disrupt the functional group structure on the surface of Fe_3O_4 . Additionally, it possesses good thermal stability.
- (2) Optimal conditions for $Fe_3O_4@PEG@IL$ adsorption of $Cr(VI)$ were determined: a water solution pH of 3.0, a solution temperature of 65°C, a $Fe_3O_4@PEG@IL$ dosage of 25 mg, and an adsorption time of 2.5 h.
- (3) The alkyl chain length of the imidazolium cation in $Fe_3O_4@PEG@IL$ affects the adsorption rate of $Cr(VI)$; as the alkyl chain length increases, the adsorption rate of $Cr(VI)$ also increases.
- (4) $Fe_3O_4@PEG@IL$ exhibits high adsorption selectivity for $Cr(VI)$. Heavy metal cations, such as Pb^{2+} , Hg^{2+} , Cd^{2+} , and Cu^{2+} , do not interfere with the adsorption of $Cr(VI)$. The adsorbent is easily recoverable and demonstrates good reusability.

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Author contributions

Hong Jin: Conceptualization, Methodology, Writing – Original Draft, Supervision. Sufang Zhou: Data Curation, Investigation, Writing – Review & Editing. Xueqing Wu: Formal Analysis, Visualization, Project Administration.

Conflict of interest statement

There are no competing interests in this experiment.

Ethical compliance

This experiment did not involve humans or animals.

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