Kinetics Studies on Toxic Hexavalent Chromium Removal from Aqueous Solutions by Magnetic Nano-Magnetite

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INTRODUCTION

Heavy metal chromium is widely used in industrial production such as electroplating, tanning, metal polishing, dye production and printing (Aroua et al. 2007). A large amount of chromium-containing wastewater is discharged into rivers without strict treatment and it is listed as the most toxic pollution in wastewater (Gu et al. 2013), which places a heavy burden on the environment and ecology. Chromium exists mainly in the form of Cr(III) and Cr(VI) in water, and the toxicity of Cr(VI) is much higher than Cr(III), which is 100 times that of Cr(III). In addition, Cr(VI) is easily released in water, so it can easily enter the body of animals and plants to cause damage. Therefore, reducing or immobilizing Cr(VI) to Cr(III) in sewage is a very important strategy for the treatment of heavy metal chromium pollution. According to the toxicity of chromium to the human body, the World Health Organization stipulates that the maximum concentration of Cr(VI) in drinking water is 50 µg/L, and the United States Environmental Protection Agency has stipulated that the total chromium content in national drinking water must not exceed 100 µg/L (Zhu et al. 2012).

At present, the treatment technologies for Cr(VI) pollution in sewage mainly include ion exchange method (Gode & Pehlivan 2005, Pehlivan & Cetin 2009), adsorption method (Bhattacharya et al. 2008, Koby 2004), electrochemical precipitation method (Golder et al. 2011, Golder et al. 2007), biological method (Barrera-Díaz et al. 2012) and reverse osmosis method (Yoon et al. 2009). Among them, the adsorption method has been widely studied and applied to actual sewage treatment for its advantages such as low cost, high efficiency, simple treatment process and no secondary pollution. The key to the adsorption method is the choice of adsorbent, commonly used adsorbents include activated carbon (Gupta et al. 2013), biomass adsorbents (Bilal et al. 2013), clay minerals (da Fonseca et al. 2006), and zeolites. These materials can effectively remove heavy ions from wastewater. In recent years, with the development of nanotechnology and nanomaterials, there are more and more types of nanomaterials that can be used to adsorb heavy metal ions. And the nanometre material itself has the characteristics of small particle size and huge specific surface area, which is conducive to the adsorption of heavy metals and has greatly promoted the treatment of heavy metal ions in sewage. A large number of studies have shown that graphene, carbon nanotubes and other nano-materials have a good adsorption effect on Cr(VI) (Luo et al. 2013, Salam 2017, Sharma et al. 2015, Sherlala et al. 2018, Zhu et al. 2012). However, after...
the adsorption of nano-materials is completed, they still have good dispersibility in the water. It is difficult to enrich and recover nano-materials from the water bodies by traditional methods such as centrifugation and filtration, which will exacerbate environmental pollution (Lu et al. 2016).

Therefore, people have gradually favoured the application of magnetic nano-materials in water pollution control. The unique surface effect and magnetic response characteristics of magnetic nano-materials make it to have the advantages of efficient enrichment and simple desorption in the process of water pollution adsorption and removal, which can effectively avoid secondary pollution to the ecological environment. Ferric oxide is the main component of magnetite. It is rich in natural magnetite, widely distributed and inexpensive. The preparation of magnetic Fe₃O₄ with special properties has aroused great interest from scientific researchers. Research finds that Fe₃O₄ nanoparticles synthesized under different conditions have a regular structure (Fan & Yao 2007). Therefore, many researchers have prepared a series of Fe₃O₄-based composite magnetic nano-materials and successfully applied them to the adsorption of heavy metal ions, dyes and other pollutants (Du et al. 2017, Hu et al. 2011, Shen et al. 2012).

In this study, pure magnetic nano-Fe₃O₄ was prepared by chemical precipitation method, and the adsorption capacity of pure magnetic nano-Fe₃O₄ for Cr(VI) was explored from the three aspects of pH, amount of adsorbent and initial concentration of Cr(VI).

MATERIALS AND METHODS

Materials

The reagents used in this experiment include ferric trichloride (FeCl₃⋅6H₂O), ferrous dichloride (FeCl₂⋅4H₂O), concentrated ammonia, potassium dichromate (K₂Cr₂O₇), diphenylcarbazide (C₁₃H₁₄N₄O), acetone, concentrated sulfuric acid and nitrogen were all of the analytical grade and used without further processing.

Synthesis of the Adsorbent

In this experiment, magnetic nano-Fe₃O₄ was prepared by a chemical co-precipitation method. Firstly, dissolved 8.115 g of ferrous chloride (FeCl₂⋅4H₂O) and 3.98 g of ferric chloride (FeCl₃⋅6H₂O) in 160 mL of distilled water. Secondly, transferred it into a 250 mL three-necked flask and placed in a thermostatic water bath at 80°C and continuously passed nitrogen through for 30 minutes at a stirring speed of 350 rpm to remove dissolved oxygen in the water. Finally, 40 mL of concentrated ammonia was slowly added dropwise, and the reaction was continued for 30 minutes. After the reaction was finished, the precipitate was filtered, washed repeatedly with distilled water and dried in an oven at 80°C to obtain magnetic nano-Fe₃O₄ particles. After the materials were completed, to verify whether the magnetic nano-Fe₃O₄ can be easily separated from the solution, the prepared materials were dispersed in an aqueous solution, and then the magnet was used to separate them. The result is shown in Fig. 1. It could be seen that magnetic nano-Fe₃O₄ can be easily separated by the magnet.

Batch Adsorption Experiment

Accurately weighed 0.2829 g of dried K₂Cr₂O₇ was dissolved in distilled water, then transferred into a 1 L volumetric flask to prepare the stock solution of 20 mg/L. It was later diluted to the corresponding concentrations in subsequent experiments. During the experiment, it was diluted to a certain ratio and heated in a constant temperature water bath at 25°C. At a speed of 350 rpm, a certain amount of magnetic nano-Fe₃O₄ was added for reaction, and a small amount was sucked out with a syringe at a specified time point. The solution was filtered through 0.45 μm. After the filtrate was added with a developer, the wavelength was adjusted to 540 nm for absorbance measurement.

Experimental Data Analysis

Add 0, 0.10, 0.25, 0.50, 1.00, 2.00, 3.00, 4.00, and 5.00 mL chromium standard solutions to a series of 25 mL colorimetric tubes and dilute to the mark with water. The absorbance was then measured following the same pretreatment and measurement procedures as the water sample. Then, a standard curve of absorbance Cr(VI) concentration was plotted based on the measured absorbance of Cr(VI), and the equation was obtained as y = 38.219x - 0.02738, R² = 0.9998. Due to the high correlation coefficient (R²=0.9998), it had been seen that there was a good linear relationship between concentration and absorbance, which indicated that the accuracy of hexavalent chromium concentration is higher. Then the amount of adsorption could be calculated by equation 1.
\[ q_e = \frac{(C_0 - C_e)V}{W} \] ...

Where, \( q_e \) is the equilibrium concentration of Cr(VI) (mg/L), \( C_0 \) and \( C_e \) are the initial and equilibrium concentration of Cr(VI) (mg/L), respectively. \( V \) is the volume of Cr(VI) solution (L) and \( W \) is the weight of magnetic nano-Fe\(_3\)O\(_4\) (g).

**RESULTS AND DISCUSSION**

**Effect of Initial pH on Adsorption of Cr(VI) by Magnetic Nano-Fe\(_3\)O\(_4\)**

Under the condition of the initial concentration of Cr(VI) (10 mg/L) and the dosage of magnetic nano-Fe\(_3\)O\(_4\) (1 g/L), the effect of the initial pH on the efficiency of removing Cr(VI) is shown in Fig. 2. As shown in the figure, the adsorption efficiency of Cr(VI) depended on the solution pH and increased with the decreasing pH. The pH change of the water environment will affect the stability of various forms to a certain extent. Cr(VI) ions mainly exist as HCr\(_2\)O\(_7\)\(^-\) at pH < 1, Cr\(_2\)O\(_7\)\(^2-\) at pH 1-6, and CrO\(_4\)\(^2-\) at pH > 7 (Zang et al. 2007). As the pH value increases, the chromate anion will change from Cr\(_2\)O\(_7\)\(^2-\) to CrO\(_4\)\(^2-\), and the area occupied by the average single Cr(VI) adsorption increases, so the adsorption of Cr(VI) by the magnetic nano-Fe\(_3\)O\(_4\) decreases significantly. In addition, the change of pH affects the surface charge of Fe\(_3\)O\(_4\); as the pH decrease, H\(^+\) increases in the solution and soon interact with -OH on the surface of Fe\(_3\)O\(_4\) resulting in the increasing of -FeOH and -FeOH\(^2+\), and then Fe\(_3\)O\(_4\) with a positive charge on the surface in the solution is more likely to adsorb negatively charged Cr\(_2\)O\(_4\)\(^2-\) ion (Wang et al. 2011). As the pH increases, the OH\(^-\) concentration in the solution also increases. On the contrary, the concentration of OH\(^-\) in the solution increases with pH increasing, leading to the surface -FeO\(^-\) iron concentration of magnetic nano-Fe\(_3\)O\(_4\) increasing. At this time, the negatively charged CrO\(_4\)\(^2-\) and the negatively charged iron oxide in the solution will have electrostatic repulsion between the surfaces, which will reduce the adsorption capacity of Cr(VI) by magnetic nano-Fe\(_3\)O\(_4\).

**Effect of Dosage of Magnetic Nano-Fe\(_3\)O\(_4\) on Cr(VI) Removal Efficiency**

Under the same conditions Cr(VI) concentration of 10 mg/L and pH 6, the effect of the addition amount of magnetic nano-Fe\(_3\)O\(_4\) on the adsorption efficiency of Cr (VI) is shown in Fig. 3. It can be seen that with the increase of the dosage, the adsorption amount per unit amount of the adsorbent became smaller but the adsorption capacity of Cr(VI) does increase with the increase of the dosage. This may be due to the increase in the amount of adsorbent added to a certain extent, which will lead to a decrease in the specific surface area and efficiency of the adsorbent, resulting in a reduction in the number of active sites (Akçay et al. 2009).

**Effect of Initial Concentration on the Removal Efficiency of Cr(VI) by Magnetic Nano-Fe\(_3\)O\(_4\)**

The effect of the initial concentration on the removal efficiency and removal rate of Cr(VI) by magnetic nano-Fe\(_3\)O\(_4\) under the condition of pH 6 and the dosage of magnetic nano-Fe\(_3\)O\(_4\) (1 g/L) are shown in Fig. 4. It can be seen that the adsorption amount per unit amount of the adsorbent gradually increases with the increase of Cr(VI) concentration. When the concentration increased from 10 mg/L to 100 mg/L, the concentration of Cr(VI) adsorbed per unit amount of adsorbent increased from 9.19 mg/g to 28.5 mg/g. There are sufficient active sites in contact with Cr(VI) ions, which increases the adsorption efficiency.
Fig. 4: Effect of initial Cr(VI) concentration on the kinetics of Cr(VI) removal by magnetic nano-Fe₃O₄.

**Adsorption Isotherm**

The adsorption isotherm refers to the relationship curve between the concentrations of solute molecules in the two phases when the adsorption process on the two-phase interface reaches equilibrium at a certain temperature. At a certain temperature, the relationship between the concentration of separated substances in the liquid and solid phases can be expressed by the adsorption equation. The relationship between the adsorbent and the adsorbate can be deduced from the graph. To understand the adsorption effect and maximum adsorption capacity of this adsorbent, it is necessary to establish an equilibrium curve and select the most suitable curve.

The Langmuir equation is one of the commonly used adsorption isotherm equations. It was proposed by the physical chemist Langmuir Itying in 1916 based on molecular motion theory and some assumptions. Langmuir adsorption isotherm can be expressed by equation 2.

\[
\frac{q_e}{C_e} = \frac{1}{q_m} + \frac{1}{k_Lq_m} \quad \text{(2)}
\]

Where, \(q_e\) is the adsorption amount of hexavalent chromium at equilibrium (mg/L), \(C_e\) is Cr(VI) concentration at equilibrium (mg/L), \(q_m\) is saturated adsorption capacity (mg/L), and \(k_L\) is the equilibrium constant of Langmuir adsorption isotherm.

Freundlich isotherm describes actual adsorption, which is an empirical formula. It is derived from the modification of the Langmuir idealization equation. Therefore, it is considered that adsorption is reversible and is not strictly monolayer adsorption. It can be expressed by equation 3.

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \text{(3)}
\]

Where, \(q_e\) is the adsorption amount of Cr(VI) in equilibrium (mg/g), \(C_e\) is the concentration of Cr(VI) at equilibrium (mg/L), and \(K_F\) is Freundlich constant.

Tempkin considers the effects of some indirect adsorbate/sorbent interactions and indicates that due to these interactions, the heat of adsorption of all molecules in the layer decreases linearly with coverage. And Tempkin isotherms can be represented by equation 4.

\[
q_e = \frac{RT}{b_T} \ln C_e + \frac{RT}{b_T} \ln K_F \quad \text{(4)}
\]
The dependence of adsorption on the concentration of Cr(VI) in equilibrium was studied, and the experimental data were fitted to the Langmuir model, Freundlich model and Temkin model, respectively. The fitting results are shown in Fig. 5 and the linear correlation coefficient and the model constants are given in Table 1. As can be seen from Table 1, the linear correlation coefficients ($R^2$) of the Langmuir model and Freundlich model were 0.9888 and 0.9994, respectively. Both of them have extremely higher than $R^2$ of the Langmuir model. Therefore, the adsorption behaviour of Cr(VI) by magnetic nano-Fe$_3$O$_4$ was more suitable for the Freundlich model description. In the meanwhile, according to the Langmuir model, the maximum adsorption amount of Cr(VI) by magnetic nano-Fe$_3$O$_4$ was calculated to be 34.0136 mg/g, indicating that nano-Fe$_3$O$_4$ has higher adsorption performance.

**Adsorption Kinetics**

To investigate the adsorption process of Cr(VI) by magnetic nano-Fe$_3$O$_4$, the experimental data were fitted by pseudo-first-order kinetics, pseudo-second-order kinetic and the intraparticle diffusion model. The Kinetic formulas can be expressed by equations 5-7.

\[ Ln(q_e - q_t) = Lnq_e - kt \]  
\[ \frac{t}{q_t} = \frac{1}{k_1} + \frac{t}{k_2q_e} \]  
\[ q_t = k_{id}t^{1/2} + C \]

Where, $q_e$ and $q_t$ (mg/g) are the amounts of Cr(VI) at equilibrium and at any time $t$. While $k_1$ and $k_2$ are the rate constants of pseudo-first-order and pseudo-second-order adsorption. And $k_{id}$ is the rate constant of the intraparticle diffusion model and $C$ is truncation. The kinetic parameters were obtained by a linear regression method. The results are shown in Fig. 6 and Table 2, respectively. It could be found that the process was mainly controlled by chemisorption.
that the linear correlation coefficient of the pseudo-second-order kinetics was much higher than the linear correlation coefficient of the pseudo-first-order kinetics and the intra-particle diffusion model, indicating that pseudo-second-order kinetics was more suitable for describing the adsorption behaviour of hexavalent chromium by magnetic nano-Fe\(_2\)O\(_4\). This illustrated that the process was mainly controlled by chemisorption.

**CONCLUSION**

In this study, the adsorption properties of chromium ions by magnetic nano-Fe\(_2\)O\(_4\) were studied at different pH, different dosage of magnetic nano-Fe\(_2\)O\(_4\) and different Cr(VI) concentrations, respectively. In addition, the adsorption process of nano-Fe\(_2\)O\(_4\) to Cr(VI) was explored by fitting the experimental data with the adsorption isotherm model and adsorption kinetics. The experimental results showed that the adsorption rate and the amount of adsorption gradually increased when the solution pH increased, and increased with the increasing of the initial concentration of Cr(VI) and the dosage of magnetic nano-Fe\(_2\)O\(_4\). Besides, the data fitting results showed that the adsorption of Cr(VI) by magnetic nano-Fe\(_2\)O\(_4\) conformed to the Freundlich isotherm adsorption model and the maximum adsorption amount of Cr(VI) was 34.0136 mg/g, suggesting that magnetic nano-Fe\(_2\)O\(_4\) was excellent adsorbent. Moreover, the adsorption process corresponded to pseudo-second-order kinetic, which was mainly controlled by chemisorption.

**ACKNOWLEDGEMENTS**

The authors gratefully acknowledge the financial support of the National Natural Science Foundation of China (Grant No. 41807468), Zhejiang Provincial Natural Science Foundation of China (Grant No. LY18E080018), Shaoxing Public Welfare Project (Grant No. 2017B70042), State Key Laboratory of Pollution Control and Resource Reuse Foundation (Grant No. PCRRF18021).

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