Facile Preparation of Magnetic Graphene Oxide and Attapulgite Composite Adsorbent for the Adsorption of Ni (II)

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Abstract. Graphene oxide (GO) is an excellent absorbent for heavy ion from wastewater, but it is hard to separate from water. To improve the adsorption capacity and separation performance of GO to nickel-containing wastewater, a composite magnetic GO-ATP adsorbent (MGA) was prepared by magnetizing GO and attapulgite (ATP) using ferroferric oxide and then carrying out hydrothermal reaction. The adsorption capacity and mechanism of MGA were investigated based on Ni2+ as targeted pollutant. Experimental results showed that the pH value significantly affects the removal rate of Ni2+, which is mainly due to that OH− in wastewater reacts with Ni2+, resulting in sediment that leads to the increase of removal rate. MGA can achieve max adsorption capacity of Ni2+ to 190.8 mg/g at pH = 5, and the adsorption process was mainly determined by chemical adsorption, which was in line with pseudo-secondary dynamics model. The adsorption was basically homogeneous monolayer adsorption with heat release, which was more agree with Langmuir adsorption isotherm equation. The adsorption process of Ni2+ by MGA. The adsorption process was a spontaneous process and an exothermic reaction. It can be confirmed that the prepared MGA adsorbent can realize slurry separation using magnetic separation principle and has high adsorption capacity to Ni2+.

1. Introduction

Graphene oxide GO contains several oxygen-containing functional groups including hydroxy group (-OH), epoxy group (-C=O), carboxy group (-COOH), with high specific surface area [1]. Compared with other carbonaceous materials, GO has better environmental friendliness and biological compatibility [2]. Oxygen-containing functional groups can serve as adsorption sites for heavy metal ions in wastewater [3]. Due to the binding action between oxygen-containing functional groups and heavy metal ions, the heavy metal ions in wastewater can be removed[4], so that the purpose of wastewater purification can be realized. In addition, due to the existence of these oxygen-containing functional groups, GO can be steadily distributed in water or other polarity organic solvents[5]. However, according to current literature reported on pure GO or GO-based absorbent, harsh preparation conditions, complex preparation method, and hard separation and high cost are often involved. Therefore, inorganic clay minerals with excellent adsorption and separation capacities were adopted to be coupled with GO, so as to prepare heavy metal ions absorbent with excellent property and lower price.

At present, there are many domestic and foreign researches on GO composite material, while there has been no researches on composite of GO and inorganic clay attapulgite (ATP). GO is in two-dimensional plane form, while a single crystal of ATP is in fibriform [6].

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This study aims to prepare a novel composite in "plane-needle" structure by inserting needle-like ATP on GO surface, so as to improve GO property and reduce the cost in treatment of wastewater containing heavy metals.

To improve separation performance, nano-Fe₃O₄ was used to magnetize absorbent, so that the slurry can be separated by magnetic attraction. In addition[7, 8], the adsorption property and mechanism were investigated using common heavy metal pollutant Ni²⁺ as target pollutant.

2. Materials and methods

2.1. Materials
The 2mg/mL aqueous solution of graphene oxide was purchased from Nano technology Co., Ltd. ATP was purchased from Anhui Guangming Attapulgite Clay Plant. Other reagents were of analytical purity or excellent purity. Deionized water was prepared by in laboratory. Ni²⁺ stock solution was prepared by nickel chloride configuration. The pH was adjusted by 0.1mol/L HCl solution or 0.1mol/L NaOH solution.

2.2. Methods

2.2.1 Preparation of composite absorbent of magnetic graphene oxide and attapulgite. Pour 2mg/L GO aqueous solution into high temperature reaction kettle, and then add certain amount of ferroferric oxide, let them react at 200℃ for 8h. Then, remove supernatant liquor, dry and grind residue, resulting in magnetic GO powder. Add certain amount of magnetic GO into 10% acetic acid solution while keeping magnetic stirring for 10min, resulting in dispersion system of magnetic GO. Similarly, add certain amount of ATP into methanol solution while keeping magnetic stirring for 10min, resulting in ATP dispersion system. Subsequently, mix the two systems by certain ratio, keep magnetic stirring for 24h at room temperature, stand for 3h, remove supernatant liquor, then dry the residue at 150℃ for 5h to obtain solid product, and grind it into powders, which is the final product-composite absorbent of magnetic GO-ATP (MGA).

2.2.2 Adsorption experiment. Add certain amount of MGA into Ni²⁺ aqueous solution of different initial concentrations and different pH values, and then transfer the mixture solution into a conical flask for oscillatory reaction at 250r/min for certain period of time. After that, place the conical flask on a magnet, let it stand for 3min, remove supernatant. Then, atomic absorption spectrophotometer (Spectr AA110/220, Varian, United States) was used to measure the concentration of Ni²⁺. The average value of 3 parallel experiment results was adopted as the final result. The removal rate of Ni²⁺ can be obtained by the equation below:

$$\eta = \frac{C_0 - C_e}{C_0} \times 100\%$$

where $C_0$ is Ni²⁺ initial concentration, and $C_e$ is Ni²⁺ equilibrium concentration, respectively, mg/L; $\eta$ represents removal rate, %.

3. Result and discussion

3.1. Effect of pH
The $C_0$ of Ni²⁺ was 100mg/L, the concentration of MGA absorbent was 1.4g/L, and the removal rates of Ni²⁺ at different pH values are shown in Figure 1. From Figure 1 we can know that the removal rate of Ni²⁺ by MGA increases with pH value. Within the pH value range of 2-7, the removal rate increases slowly, which indicates that pH value under acid condition does not significantly affect removal rate; Within the pH value range of 7-10, the pH value significantly affects the removal rate of Ni²⁺, which is mainly due to that OH⁻ in wastewater reacts with Ni²⁺, resulting in sediment that leads to the increase
of removal rate. To remove the influence of OH\(^-\) to experiment results, pH value was determined to 5 in follow-up studies.

![Graph showing the effect of pH of Ni\(^{2+}\) adsorbed on MGA.](image)

**Figure 1.** Effect of pH of Ni\(^{2+}\) adsorbed on MGA.

### 3.2. Adsorption kinetics

Adsorption mechanism can be analyzed based on two kinetic models. The pseudo-first order kinetic model is shown as below [9]:

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t
\]

\[
q_t = \frac{(C_0 - C_e)V}{m}
\]

In both above equations, \(q_t\) is the adsorption capacity at time \(t\), mg/g; \(q_e\) is equilibrium adsorption capacity, mg/g; \(k_1\) is rate constant, min\(^{-1}\); \(m\) is the mass of absorbent, g; \(V\) is the volume of adsorption system solution, L.

The pseudo-second order kinetic model is shown as below [10]:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e^2} t
\]

where \(k_2\) is the rate constant of second-order kinetics, g/(mg·min).

To carry out nonlinear fitting, equation (3) and (4) was rewritten into non-linear form:

\[
q_t = q_e(1 - e^{-k_1 t})
\]

\[
q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}
\]

The nonlinear fitting results of pseudo-first order kinetic model and pseudo-second order kinetic model [11] are shown in Figure 2. The fitting parameters are summarized in Table 1.

|                       | Pseudo-first order model | Pseudo-second order model |
|-----------------------|--------------------------|----------------------------|
| \(K_1\) (min\(^{-1}\)) | \(q_e\) (mg/g) | \(R^2\) | \(K_2\) (g/(mg·min)) | \(q_e\) (mg/g) | \(R^2\) |
| 0.0692 | 46.58 | 0.9421 | 0.0020 | 50.68 | 0.9962 |

According to Table 1, it can be known that the adsorption of Ni\(^{2+}\) by MGA is more in line with pseudo-second order kinetics, with \(R^2=0.996\), which indicates that the adsorption rate is mainly determined by chemical adsorption process [12]. This result reveals that such adsorption reaction
involved electron transfer and exchange and the formation of chemical bonds. Within the first 5 min, the rate of chemical adsorption reaction is quick, leading to a significant acceleration of adsorption rate.

![Image of adsorption kinetics](image)

**Figure 2.** Adsorption kinetics of Ni\(^{2+}\) on MGA.

### 3.3. Adsorption isotherm

The Langmuir and Freundlich isotherm adsorption model was used to fit the experimental data. As a classic adsorption model proposed by I. Langmuir in 1918 [13], Langmuir model assumes that the absorbent surface is fully homogenous, i.e. all adsorption sites have identical adsorption energy, and only monolayer adsorption took place for adsorbate. Langmuir model has been extensively used to describe various adsorption phenomena in gas and solution, of which the equation is expressed as follow:

\[
q_e = \frac{q_{\text{max}} K_L C_e}{1 + K_L C_e}
\]  

where \(K_L\) is equilibrium adsorption constant, which reveals the relation between Ni\(^{2+}\) binding site and affinity; \(q_{\text{max}}\) is the max adsorption capacity of Ni\(^{2+}\) by composite absorbent, mg/g.

Being proposed by H. M. Freundlich in 1906 [14], Freundlich model is another classic frequently-used adsorption model. Freundlich model assumes that the absorbent surface is inhomogeneous, i.e. the energies of adsorption sites are not identical but distributed in exponential curve. Freundlich model equation is shown as below:

\[
q_e = K_F C_e^{\frac{1}{n}}
\]

where \(K_F\) represents Freundlich empirical constant, \(n\) is surface heterogeneity coefficient.

The nonlinear fitting results of adsorption isotherms for different initial concentrations of Ni\(^{2+}\) at 298K are shown in Figure 3. The fitting parameters are summarized in Table 2.

**Table 2.** Parameters of two adsorption isotherm models for Ni\(^{2+}\) on MGA.

| Langmuir | Freundlich |
|----------|------------|
| \(q_{\text{max}}\) (mg/g) | \(K_F\) (mg/g) | \(1/n\) | \(R^2\) |
| \(K_L\) (L/mg) | \(R^2\) | |
| 190.8 | 0.046 | 0.9932 | 18.38 | 0.500 | 0.9719 |
3.4. Adsorption thermodynamics

The adsorption thermodynamics parameters ($\Delta H^0$, $\Delta G^0$, and $\Delta S^0$) of Ni$^{2+}$ on absorbent surface can be calculated by temperature-dependent thermodynamic equilibrium constant $K_0$. The calculation equation of standard free energy $\Delta G^0$ is shown as below [15]:

$$\Delta G^0 = -RT \ln K_0 = \Delta H^0 - T\Delta S^0$$  \hspace{1cm} (9)

where $T$ is absolute temperature, K; $K_0$ is the thermodynamic equilibrium constant in mg/L, which can be calculated by $\frac{d e}{e}$; $R$ is universal gas constant, $8.314/(\text{mol} \cdot \text{K})$. According to equation (9), the standard entropy change ($\Delta S^0$) and standard enthalpy change ($\Delta H^0$) can be calculated according to the liner equation below:

$$\ln K_0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$ \hspace{1cm} (10)

The adsorption thermodynamics parameters of Ni$^{2+}$ on absorbent surface are shown in Table 3.

| $T$ (K) | $\Delta G^0$ (kJ/mol) | $\Delta S^0$ (J/(mol·K)) | $\Delta H^0$ (kJ/mol) |
|---------|-----------------------|--------------------------|-----------------------|
| 298     | -5.37                 |                          |                       |
| 308     | -5.88                 | -8.71                    | 0.05                  |
| 318     | -6.13                 |                          |                       |

The thermodynamic parameters of adsorption reaction is not only associated with adsorbate property, but also with absorbent property. According to Table 3, the $\Delta G^0$ less than 0 and $\Delta H^0$ greater than 0, which indicates the adsorption process of Ni$^{2+}$ by MGA was a spontaneous process [16, 17]. The $\Delta S^0$ is negative illustrates that adsorption process of Ni$^{2+}$ by MGA was an exothermic reaction [18].

4. Conclusion

MGA is a simple and low-cost heavy metal ions absorbent, which can be prepared by simple magnetization and hydrothermal reactions. A good slurry separation effect can be realized by magnetic force. The prepared MGA absorbent had large adsorption capacity of Ni$^{2+}$, and it was a spontaneous adsorption process. The prepared MGA absorbent can be used in treatment of heavy metal wastewater, which enjoys certain potential of application.

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