Preparation of Graphene Oxide-Molecular Sieve Composite Adsorbent and its Adsorption Performance for Heavy Metals in Water

Li Xiuling*
College of Chemistry and Bioengineering, Hechi University, Yizhou 546300, China

*Corresponding author: lixiuling@hcu.edu.cn

Abstract. Graphene has inherent physical and chemical properties, but there are few reactive sites on the surface of graphene, and its use is limited. In the field of water treatment, especially in the adsorption treatment of heavy metals, it has shown great advantages and good development prospects. Dye wastewater is one of the more difficult industrial wastewaters to treat. Among various processes for removing dye wastewater, adsorption technology is considered to be the most promising method of water purification due to its fast, efficient, and low energy consumption characteristics. Molecular sieves have the characteristics of good adsorption selectivity, stable structure, easy regeneration, low price, and environmental protection. They are widely used as adsorbents. However, the adsorption efficiency of a single molecular sieve on organics is also low. In recent years, molecular sieve composite adsorption materials have begun to enter our field of vision. Hydrothermal treatment technology simply and quickly prepared composite materials with different graphene oxide content through chemical action, and studied the synergistic effect between the two composites on the adsorption performance of pollutants.

Keywords: Graphene oxide, Molecular sieve, Composite adsorbent, Heavy metals

1. Introduction
Wastewater containing heavy metals has become a topic of common concern in the field of environmental protection in recent years due to its strong toxicity, bioaccumulation, and difficulty in body excretion [1]. Among the current treatment methods for this type of wastewater, the adsorption method is widely used as the core technology of wastewater treatment due to its remarkable effective effect and convenient operation. The general adsorbents in the engineering field mainly include adsorbents such as activated carbon, zeolite, resin and polymer [2]. However, the disadvantages of this existing adsorbent are low adsorption capacity and low adsorption efficiency. Therefore, in order to overcome the inherent shortcomings of existing adsorbents, there is an urgent need to develop new and effective adsorbents [3]. In recent years, carbon nanomaterials represented by carbon nanotubes and graphene oxide have become a hot spot for adsorbent research by global environmental experts due to their unique hollow structure, strong adsorption capacity, and extremely large surface. The unique properties of graphene oxide have designed and synthesized a series of environmentally friendly graphene oxide-based composite adsorption materials that are simple to prepare, fast in
adsorption rate, large in adsorption capacity, easy to separate, reusable, inexpensive and efficient [4]. At this stage, researchers have used scanning electron microscopy, energy scattering spectroscopy, Fourier infrared spectroscopy, and X-ray diffraction to characterize the physical and chemical properties of the new molecular sieve composite adsorbent. The static adsorption method was also used to study the effects of different influencing factors on the removal of pollutants from the water by the molecular sieve composite adsorption materials; the adsorption process and the adsorption rate limiting steps were discussed, and the results all showed a new molecular sieve composite adsorption material-graphite oxide The adsorption capacity of one to heavy metals in water is strong [5]. The effects of various factors and their interactions on the adsorption behavior were evaluated by establishing a response surface. At the same time, X-ray photoelectron spectroscopy was used to discuss the adsorption mechanism between adsorbents and pollutants at the microscopic molecular level [6]. The dynamic model is used to analyze the penetration curve, which provides a theoretical basis for the practical application of the new molecular sieve composite adsorbent [7].

In recent years, heavy metal pollution including lead has become one of the environmental issues that people are increasingly concerned about. Lead and its soluble salts are both toxic and difficult to degrade in the environment. As the food chain gradually accumulates, it is harmful to humans, animals and plants. The reason is serious harm to human health and the ecological environment [8]. China's "12th Five-Year Plan for Prevention and Control of Heavy Metal Pollution" designated lead as the main object of prevention and control, so the treatment of lead and other heavy metal wastewater must be addressed [9]. Therefore, in order to eliminate these pollution problems, academic researchers also treat industrial wastewater and provide practical scientific and technical methods [10]. Moreover, heavy metal ions have the characteristics of strong stability, difficulty in collecting, and strong toxicity, which not only change the composition, structure and function of soil, but also indirectly threaten human health through various channels.

2. Algorithm establishment

2.1 Adsorption kinetics

There are different adsorption kinetic algorithms for the description of adsorption mechanism, there are mainly quasi-first-order kinetic models and quasi-second-order kinetic models. The curve equation of the quasi-first order kinetic model is shown in (1), and the linear equation is shown in (2):

\[ q_t = q_0 \left(1 - e^{-k_1t}\right) \]  

\[ \lg (q_0 - q_t) = \lg q_e - \frac{k_1}{2.303} t \]  

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

In the formula, \( q_t \) is the amount of adsorbate adsorbed per unit mass of adsorbent at time \( t \), mg/g; \( k_1 \) is the rate constant, \( min^{-1} \); \( V \) is the volume of the adsorption system solution, L; \( m \) is the mass of the adsorbent, g; Other symbols have the same meaning as before.

The curve equation of the quasi-two-stage dynamics algorithm is shown in (4) and the linear equation (5) is shown:

\[ q'_t = \frac{q_e^2k_2t}{1+q_e k_2t} \]  

\[ \frac{t}{q_1} = \frac{1}{q_e^2k_2} + \frac{1}{q_e} \]  

2.2 Adsorption isotherm

The Langmuir and Freundlich isotherm equations are used to adjust the adsorption isotherm. The Langmuir adsorption isotherm model assumes that the adsorption sites on the adsorbent surface are uniform, and each adsorption site has the same adsorption capacity, that is, fault adsorption. The curve equation is shown in equation (6), and the linear equation is shown in equation (7):

\[ q_e = \frac{q_{max}KLC_e}{1+K_2C_e} \]
\[
\frac{C_e}{q_e} = \frac{C_e}{q_{\text{max}}} + \frac{1}{q_{\text{max}} K_L}
\]  

(7)

In the formula, \(K_L\) is the Langmuir model constant, L/mg; \(q_{\text{max}}\) is the theoretical maximum adsorption capacity, mg/g; other symbols have the same meaning as before.

The Freundlich adsorption isotherm model assumes that the adsorption on the adsorbent surface is multilayer adsorption. The curve equation is shown in (8), and the linear equation is shown in equation (9):

\[
q_e = K_f C_e^{1/n}
\]

(8)

\[
\lg q_e = \frac{1}{n} \lg C_e + \lg K_f
\]

(9)

In the formula, \(K_f\) and \(n\) are Freundlich model constants; \(n\) is related to the adsorption strength; other symbols have the same meaning as before. The size of \(K_f\) reflects the size of adsorption capacity.

2.3 Principle of adsorption kinetics

Adsorption mechanics is the main research topic of adsorption and many influencing factors. The adsorption effect and adsorption speed are mainly determined by the interaction between adsorbent, temperature, pressure and other factors.

2.4 Principle of adsorption isotherm

The adsorption isotherm refers to the relationship curve between the concentration of solute molecules at a specific temperature when the adsorption process of solute molecules at the two-phase interface reaches equilibrium. Only a certain amount of gas is adsorbed to the solid surface, at a certain temperature, corresponding to a certain pressure of the adsorbent. The adsorption isotherm can be obtained by measuring the adsorption capacity under a series of relative pressures. Adsorption isotherms are basic data for studying adsorption phenomena and solid surfaces and pores. It can study the properties of surfaces and pores, and calculate the specific surface and size distribution of pores.

3. Modeling Method

The study explored the adsorption performance of composite molecular sieve through sequencing batch experiments. The experiment first prepares a certain concentration of pollutant solution (concentration range 50~1000mg/L), respectively take 200mL pollutant solution into a batch of 250mL conical flasks with stopper, and add a certain quality of composite molecular sieve material. In the experiment, the pH value of the pollutant solution was adjusted by dropping 0.1mol/L HCl or 0.1mol/L NaOH solution. The concentration of residual pollutants in the solution was determined by atomic absorption method.

The thermodynamic parameters \(\Delta G\), \(\Delta H\), \(\Delta S\) are used to explore the adsorption characteristics of graphene oxide-molecular sieve composite adsorbent for heavy metals in water. The thermodynamic parameters can be calculated based on the thermodynamic equilibrium constant selenium that changes with temperature (10).

\[
K_0 = \frac{a_s}{a_e} = \frac{v_s C_s}{v_e C_e}
\]

(10)

In the formula, \(a_s\) is the activity of adsorbed heavy metal ions; \(a_e\) is the activity of heavy metal ions in the solution at equilibrium; \(C_s\) is the mass of metal ions adsorbed by a unit mass of adsorbent, mg/g; \(C_e\) heavy metal ion adsorption equilibrium Concentration, mg/L; \(v_s\) and \(v_e\) are the activity coefficients of heavy metal ions in the solution when they are adsorbed and equilibrium, which are considered to be zero in the adsorption experiment; they can be drawn to zero by drawing a straight line \(\ln(C_s/C_e)\sim C_s\) and extrapolating \(C_s\).

The standard free energy \(\Delta G\) can be calculated by formula (11).

\[
\Delta G = -RT\ln K_0
\]

(11)

In the formula, \(R\) is the universal gas constant, 8.314J/(mol \cdot K); \(T\) is the absolute temperature, K.

The standard enthalpy change \(\Delta H\) and the standard entropy change \(\Delta S\) can be obtained by
formula (12).

$$\ln K_0 = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$  \hspace{1cm} (12)

The removal efficiency and adsorption amount of heavy metals are calculated, and the calculation formula is as follows:

$$\text{Heavy metal removal rate (')} = \frac{C_0 - C_e}{C_0} \times 100 \hspace{1cm} (13)$$

$$q_t = \frac{(C_0 - C_t)V}{W} \hspace{1cm} (14)$$

$$q_e = \frac{(C_0 - C_e)V}{W} \hspace{1cm} (15)$$

$q_e$ and $q_t$ are the ammonia nitrogen exchange capacity (mg/g) at equilibrium and time $t$, respectively; $C_0$, $C_t$ and $C_e$(mg/L) are the initial reaction time, time $t$, and the ammonia nitrogen in the solution at equilibrium concentration. $W$(g) is the mass of chitosan-coated mesoporous microporous composite molecular sieve, and $V$(L) is the total volume of the solution.

4. Evaluation results and research

Adjust the pH of $Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}$ these 5 common heavy metal ion mixed solutions in water to 5 and place them in a 100mL conical flask. The final concentration of each ion is 50mg/L. Add a certain amount of graphene oxide-molecular sieve to the mixed ion solution system. Adsorbent, so that the concentration of the graphene oxide adsorbent in the system is 0.069/L, 0.129/L, 0.189/L, 0.249/L, 0.309/L, and the reaction system is 30mL, and then placed at 25. C shake in a constant temperature water bath shaker for 2h. After shaking, centrifuge, detect and calculate the removal rate.

![Figure 1](image-url)  \hspace{1cm} \textbf{Figure 1.} Comparison of the competitive adsorption rate of heavy metal ions under different adsorbent dosage conditions(unit:%)\

It can be seen from Figure 1 that the adsorption curve of $Pb^{2+}$ is located above the adsorption curve of the other 4 heavy metal ions. The $Pb^{2+}$ adsorption degree of graphene oxide is obviously stronger than that of other heavy metal ions. The adsorption order of graphene oxide to these 5 heavy metal ions is $Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+} > Ni^{2+}$. When the concentration of the composite adsorbent is less than 0.129/L, the adsorption capacity of graphene oxide to $Cd^{2+}$ and $++$ is zero. When the concentration of the composite adsorbent is greater than 0.129/L, the graphene oxide starts to absorb...
Cd^{2+} and Ni^{2+}. Perform adsorption.

Early scholars believed that the selection order of heavy metal competitive adsorption depends on the nature of heavy metal ions, including ion radius, electronegativity, hydrolysis constant, water and ion radius and charge-to-diameter ratio. Table 1 shows the basic physical and chemical property parameters of the five heavy metals lead, copper, zinc, cadmium and nickel.

| Ion species | Ion radius (pm) | Electronegativity | Hydrolysis constant | Water and ion radius (nm) | Charge-to-diameter ratio |
|-------------|----------------|-------------------|---------------------|--------------------------|-------------------------|
| Pb^{2+}     | 119            | 2.33              | 7.80                | 0.40                     | 1.68                    |
| Cu^{2+}     | 73             | 1.90              | 7.34                | 0.42                     | 2.74                    |
| Zn^{2+}     | 74             | 1.65              | 8.96                | 0.43                     | 2.10                    |
| Cd^{2+}     | 95             | 1.69              | 9.20                | 0.43                     | 2.70                    |
| Ni^{2+}     | 69             | 1.91              | 9.86                | 0.40                     | 2.90                    |

It can be seen from Table 1 that the order of adsorption selectivity of hematite to Pb, Cu, Zn, Cd and Ni is the same as the results of this paper, both are Pb^{2+}>Cu^{2+}>Zn^{2+}>Cd^{2+}>Ni^{2+}. In general, the adsorption selectivity order of Pb and Cu are both higher, and the adsorption selectivity order of Cd and Ni is relatively lower. Only the order of the adsorption selectivity of multi-walled carbon nanotubes for Pb is replaced by the position of Cu and Zn. According to the corresponding theory, the smaller the ion radius, the easier it is for metal ions to penetrate the boundary layer and be adsorbed by multi-walled carbon nanotubes.

![Figure 2. The adsorption rate of the cycle experiment](image)

It can be seen from Figure 2 that as the number of cycles increases, the adsorption and removal rate of graphene oxide on heavy metals in water decreases, and the adsorption rate of 0.5mol/L HCl solution on graphene oxide that adsorbs heavy metals also decreases. On the whole, the adsorption rate has not decreased much. After 6 adsorption-desorption cycles, the adsorption rate is still 74.8% of the initial adsorption, which indicates that graphene oxide has a high recycling efficiency and is expected to be applied to the actual treatment of heavy metal wastewater.

5. Conclusion

Graphene oxide, a new type of nanomaterial, can be mixed with metals, metal oxides or organics to form graphene composites with high porosity, high specific surface area and abundant active
oxygen-containing functional groups. The material not only has strong adsorption capacity for heavy metal ions in water, but also has strong adsorption capacity for some radioactive elements. Graphene oxide-molecular sieve composite adsorbent is a new material with excellent physical and chemical properties. It has great advantages in the adsorption treatment of heavy metal ions and has a wide range of application prospects in the field of water treatment. The new type of nano-adsorption material graphene oxide not only has the characteristics of water dispersibility and large specific surface area, but also contains a large number of oxygen-containing functional groups. The preparation of graphene oxide into a new nano-composite adsorption material and environmental engineering demonstration A strong outstanding advantage. However, the price of graphene oxide is relatively high. At present, there are relatively few researches on the regeneration of graphene oxide materials. Research on related green regeneration technologies can be actively carried out, and the development of graphene oxide and its composite materials can be effectively promoted.

References
[1] Repp S, Harputlu E, Gurgen S, et al. Synergetic effects of Fe 3+ doped spinel Li 4 Ti 5 O 12 nanoparticles on reduced graphene oxide for high surface electrode hybrid supercapacitors[J]. Nanoscale, 2018, 10(4):1877-1884.
[2] Zubir N A, Zhang X, Yacou C, et al. Fenton-Like Degradation of Acid Orange 7 Using Graphene Oxide-Iron Oxide Nanocomposite[J]. Journal of Advanced Materials, 2018, 6(7):1382-1388.
[3] Vinothkannan M, Kim A R, Gnana Kumar G, et al. Sulfonated graphene oxide/Nafion composite membranes for high temperature and low humidity proton exchange membrane fuel cells[J]. RSC Advances, 2018, 8(14):7494-7508.
[4] Guo D Y, Fan L N, An X, et al. The Effect of Metal Modified Mesoporous Molecular Sieve SBA-15 on Hydrogen Production by Steam Reforming of Ethanol[J]. Journal of Molecular Catalysis, 2019, 33(1):66-74.
[5] Garnett M H, Newton J A, Ascough P L. Advances in the Radiocarbon Analysis of Carbon dioxide at the NERC Radiocarbon Facility (East Kilbride) using Molecular sieve Cartridges[J]. Radiocarbon, 2019, 61(6):1-11.
[6] Agliullin M R, Khairullina Z R, Kutepov B I. Crystallization of the Granulated Molecular Sieve SAPO-11 Having High Crystallinity and a Hierarchical Pore Structure[J]. Kataliz v promyshlennosti, 2020, 20(3):167-173.
[7] Yuan Y, Han Y, Yang C, et al. Deep eutectic solvent functionalized graphene oxide composite adsorbent for miniaturized pipette-tip solid-phase extraction of toluene and xylene exposure biomarkers in urine prior to their determination with HPLC-UV[J]. Microchimica Acta, 2020, 187(7):1-9.
[8] AmonradaSaning, ServannHerou, DechaDechtrirat, et al. Green and sustainable zero-waste conversion of water hyacinth (Eichhornia crassipes) into superior magnetic carbon composite adsorbents and supercapacitor electrodes[J]. RSC Adv. 2019, 9(42):24248-24258.
[9] Benavides L C L, Pinilla L A C, Serrezuela R R, et al. Extraction in Laboratory of Heavy Metals Through Rhizofiltration using the Plant Zea Mays (maize)[J]. International Journal of Applied Environmental Sciences, 2018, 13(1):9-26.
[10] Abdulrasheed M, Roslee A F, Zakaria N N, et al. Effects of heavy metals on diesel metabolism of psychrotolerant strains of Arthrobacter sp. from Antarctica[J]. Journal of Environmental Biology, 2020, 41(5):966-972.