Research on Water Treatment Method Based on Graphene Composites

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Abstract. In this paper, the graphene material prepared by graphite and zeolite acted together to produce paper cup composite material to adsorb cadmium ion in water. The effects of adsorption time, pH value, the amount of stone composite, the concentration of cadmium ion and sodium ion on the adsorption of cadmium ion were discussed respectively. The results show that the content of cadmium ion in water is the least when the adsorption time is 2h and pH is 5.4. with the increase of the amount of graphene/zeolite composite, the existence of sodium ion will inhibit the adsorption of cadmium ion. The adsorption of cadmium ions commonly used in water treatment was studied in this paper.

Keywords: Graphene, zeolite composite, Water treatment, Sodium ion, Cadmium ion.

1. Introduction

With the continuous development of human society, the aggravation of heavy metal pollution affects the development of human society. Cadmium ions will pollute water sources and do great harm to human tissues and organs [1].

Fig. 1 Water circulation schematic diagram
As shown in Figure 1, heavy metal ions pollution in drinking water has attracted more and more attention. Pollution of water-rich in water mainly comes from drainage of chemical industry electroplating electronic industry and waste discharged from aquaculture etc. It has carcinogenic teratogenic mutagenic and persistent and biological accumulation.

Cadmium can accumulate in the human body for a long time, and the half-life in the body will be more than 10 years \[2\]. In exchange, membrane separation, adsorption, electrolysis, and chemical precipitation are commonly used to remove cadmium from water \[3\]. Among these methods, the adsorption method with simple operation has its unique advantages, so using adsorbents to remove cadmium ions has become an important research direction of water pollution treatment. Graphene is a new type of monolayer carbon atomic material. Graphene has many good properties, which has attracted great attention of scholars in the fields of electronics, adsorption, energy, materials and so on \[4\]. Zeolite is a tetrahedral ore with a framework structure, which contains molecular-sized porous crystals and has many ion exchanges points \[5\]. Because of their ability to screen molecules, they are called molecular sieves. In this paper, graphene is used to modify zeolite, and its water solubility is significantly increased. The modified zeolite was used to remove cadmium ion from water, and the factors such as pH, dosage, adsorption time and concentration of cadmium ion were analyzed.

2. Experimental part

2.1. Main drugs and instruments
Graphite (AR, purity>99% 4000mesh), hydrazine hydrate, artificial zeolite (97%), CVD Tubular Furnace, other reagents are analytically pure and the water is deionized water.

2.2. Experimental method

2.2.1. Preparation of graphene. 2g graphite, 1gNaNO3 and 46 mL concentrated sulfuric acid were placed in a 200mL-dried round bottom flask and stirred in an ice water bath for 1 hour. After that, add 6gKMnO4 to the flask and stir for 1 hour, then move the stirred solution to a constant temperature water bath at 38℃ for another 2 hours. Then carefully add 92mL deionized water to the flask, control the temperature at about 94℃, continue stirring, add 280mL deionized water after 40 minutes, take 10 mL of H2O2 and H2O2 concentration of 5%, change the solution color from brown-black to golden yellow, after filtration, rinse the filter with dilute hydrochloric acid and deionized water with the concentration of 5%HCl, wash to neutral, adjust the drying oven to 50 ℃, and dry to get graphite oxide. The graphite oxide 300mg is put into the aqueous solution of 300mL, and then ultrasonic for 55 minutes. After ultrasonic, 7 mL hydrazine hydrate is added. Under the condition of stirring, the temperature is raised to 90 ℃ and the reaction time is 3 hours, the graphene solution is obtained. Filter and wash and vacuum dry at 55 ℃.

2.2.2. The activation of graphene. The amount of graphene was dispersed into aqueous solution by ultrasonic dispersion adding sodium hydroxide (graphene): NaOH as 10:3 drying box drying then heating furnace tube heating helium as protective gas heating up to 790 ℃lasting 90 minutes washing to neutral drying with deionized water.

2.2.3. The treatment of zeolite. Zeolite treated zeolite was treated with acid and alkali in order of stirring when stirring. Then washed into neutral water distilled water and dried aside.

2.2.4. Preparation of graphene/zeolite composites. Graphite powder was added into ethanol solution ultrasonic 10 hours to obtain graphene dispersion solution called appropriate amount of treated zeolite added into graphene dispersion liquid mixing evenly filtering drying. After completing one smear, 6 layers of graphene composite materials were obtained after repeated operation over 5 times.
2.2.5. Removal of cadmium ions in water. 150mg graphene/zeolite composites were added to 150ml 15mg /L cadmium ion solution, with the pH value adjusted to 5.4, stirred for 60min, centrifuged at 12000r/min for half an hour, and the liquid in the centrifuged tube was added to the automatic sampler of atomic absorption spectrometer to determine the content of cadmium ions.

3. Experimental results
Selection of cadmium ion removal conditions for graphene/zeolite composites in water:

3.1. Influence of adsorption time on Cd$^{2+}$ removal rate of graphene/zeolite composites in water

![Graph showing influence of adsorption time on Cd$^{2+}$ removal rate](image)

**Fig. 2** Influence of experimental time on adsorption of cadmium ions on graphene/zeolite composites : (pH=5.4)

It was found from Figure 2 that graphene/zeolite composites had excellent adsorption efficiency at 2.0 h and high removal rate of Cd$^{2+}$ was found. When time increases, removal rate decreases when 2.0 h, removal rate basically unchanged, and unit mass graphene/zeolite composites adsorb cadmium ions basically constant. Therefore graphene/zeolite composites can reach good adsorption effect in a very short time.

3.2. Influence of pH value on removal of Cd$^{2+}$ from graphene/zeolite composites

![Graph showing influence of pH on removal of Cd$^{2+}$](image)

**Fig. 3** Influence of pH on adsorption of Cadmium ions on graphene/zeolite composites (2h)
It can be seen from Figure 3 that when pH is between 0.5-3, the removal rate increases with the increase of pH; when pH is between 3-5.4, the removal rate increases rapidly; when pH exceeds 5.4, the removal rate changes little; when pH reaches 6.5, the removal rate increases rapidly. Because graphene/zeolite composites have different states at different pH:

Under acidic conditions:
\[ \text{MOH} + \text{H}^+ = \text{M}^+ + \text{H}_2\text{O} \]

Under basic conditions:
\[ \text{MOH} + \text{OH}^- = \text{MO}^- + \text{H}_2\text{O} \]

When the pH value of the solution is less than 5.4, the surface of graphene/zeolite composite is positively charged and has electrostatic repulsion with Cd\(^{2+}\) ions. When the pH value increases, OH\(^-\) increases, electrostatic repulsion decreases, adsorbability increases, and removal rate increases. When pH was between 5.4-6.5, the removal rate changed little, indicating that the surface charge of the composite material changed little. When pH value is greater than 6.5, OH\(^-\) combines with Cd\(^{2+}\) to form Cd(OH)\(_2\) precipitation. OH\(^-\) in solution plays a decisive role in the removal of Cd\(^{2+}\).

3.3. Influence of the amount of graphene/zeolite composite on the removal of Cd\(^{2+}\)

Fig. 4 Influence of composite material amount on Cd\(^{2+}\) adsorption Effect (2h)

Fig. 4 shows that with the increase of the amount of graphene/zeolite composites, the removal rate of Cd\(^{2+}\) also increases. With the increase of graphene/zeolite composites, the removal rate of negative ions in the solution increases. Ion exchange may be responsible for the increased removal rate.

3.4. Influence of ionic strength on removal of Cd\(^{2+}\) from graphene/zeolite composites

Fig. 5 Influence of Na\(^+\) on adsorption of Cadmium ions on graphene/zeolite composites (2h)
When the increased concentration of Na\(^+\) and Cd\(^{2+}\) removal rate is less, the cadmium ions adsorption amount is reduced, the main reasons:

1. The cadmium ions and graphene/zeolite composite formation of electric double layer, with the addition of sodium ions ruined the original electric double layer structure, sodium ion and cadmium ion competition combined with graphene/zeolite composites, thus reduce cadmium ion removal rate. This further indicates that the cadmium ion adsorption mechanism of graphene/zeolite composites is exchange adsorption, which is consistent with the result of the amount of graphene/zeolite composites.

2. The increase in ionic strength also prevents cadmium ions from moving towards the surface of graphene/zeolite composites.

3.5. Influence of Cd\(^{2+}\) concentration on the adsorption effect of graphene/zeolite composites

![Graph](image)

**Fig. 6** Influence of Cadmium ion concentration on adsorption of Cd\(^{2+}\) by Graphene/Zeolite composites (2h)

When the Cd\(^{2+}\) ion concentration is less than 22 mg/L, with the increase of concentration of Cd\(^{2+}\), graphene/zeolite composite materials for the adsorption of Cd\(^{2+}\) also increased, but when the concentration of Cd\(^{2+}\) above 22 mg/L, graphene/zeolite composites of Cd\(^{2+}\) adsorption ability become weak, because Cd\(^{2+}\) ion concentration in 22 mg/L, composite material to achieve adsorption limit, Cd\(^{2+}\) ion the repulsion between the much larger than when low concentration, cause The adsorption capacity of the composite decreased.

3.6. Mechanism of Cd\(^{2+}\) adsorption by graphene/zeolite composites

The surface charge of the graphene/zeolite composites affects the adsorption of Cd\(^{2+}\). According to the experiment, when pH<5.4, the surface of the composite has a positive charge, which repelled the adsorption of Cd\(^{2+}\). At pH>5.4, the surface of the material is negatively charged, which is conducive to the removal of Cd\(^{2+}\). In addition, graphene/zeolite composites have large specific surface area and many adsorption points, which is conducive to Cd\(^{2+}\) adsorption. Therefore, the adsorption of Cd\(^{2+}\) by graphene/zeolite composites is the result of the interaction of physical and chemical factors.

4. Conclusions

Graphene/zeolite composites can be used to remove Cd\(^{2+}\) from water. The optimal conditions for adsorbing Cd\(^{2+}\) from the composites are as follows: the adsorption time is 2h, PH=5.4, and the removal rate will increase with the increase of the amount of the composites. Other cations in the water will
affect the adsorption rate of Cd$^{2+}$. The results show that the graphene/zeolite composite can be a good material for removing Cd$^{2+}$ from water.

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