

Synthesis of magnetic g-C₃N₄ by one-step method and its adsorption performance for Cd(II)

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Abstract. A novel magnetic g-C₃N₄ (Fe₃O₄-g-C₃N₄) was prepared in one step and used to removal Cd (II) from aqueous solution. VSM, FT-IR, SEM, laser particle analyses and XRD were used to character Fe₃O₄-g-C₃N₄. The kinetic data was more described by Pseudo-second-order model. Langmuir model to describe isotherms data is more convincing and the predicated maximum adsorption capacity for Cd (II) is 204.5 mg/g.

1. Introduction

Heavy metal pollution is a major problem and a wide concern to the research group due to highly toxic, biology accumulation and carcinogenic. Hence, removal of heavy metal ions from wastewater is gaining increasing scrutiny by researchers. So far, there are a variety of ways to treat heavy metals in wastewater, including liquid membrane, ion exchange, reverse osmosis, precipitation and adsorption [1]. Among those methods, adsorption method was considered to a favourable and promising method due to its easy operation, high-efficiency and low-cost. Up to now, various of adsorbent materials have been applied to removal heavy metal ions from aqueous solution such as nano tubes, graphene, biomaterials and clays. Part of those adsorbent have had a good adsorption performance, but complex preparation procedures, lower recovery efficiency and low separation efficiency have restricted their commercial application. Hence, the preparation of adsorbent materials with simple synthesis, highly efficient separation has become a new challenge for researchers.

Recently, carbon nitrogen materials have made great progress due to their mechanical properties electronic properties and low friction coefficient. There are five crystalline structures of carbon nitride according to theoretical calculation, in which g-C₃N₄ have aroused special attention because of the higher stability than others. Moreover, g-C₃N₄, one of tris-triazine units connected with planar π -conjugated materials, has been widely used into various fields including catalysts, CO₂ capture, hydrogen evolution and fuel cells. So far, various of methods have been used to prepare g-C₃N₄. Among those methods, the pyrolysis method was considered to be the most classic and simple method [2]. However, g-C₃N₄ which was prepared by pyrolysis, A has a layered structure closely packed and is difficult to quickly separate from aqueous solution. It is difficulty to apply in adsorption field.



Magnetic separation is considered to be a fast and efficient separation method for the separation of adsorbents from aqueous solutions, which compare to the traditional separation method (filtration, sedimentation and centrifugation) [3]. Over the past few years, the development of magnetic adsorbent has achieved good performance, some of which have good adsorption capacity and fast magnetic response capability [4]. Nevertheless, the synthesis of magnetic adsorbent need two or even more steps in the fabrication, which restricted their commercial application [5]. To the best of our knowledge, the application of the magnetic g-C₃N₄ by the one-step synthesis in the field of adsorption has not been reported.

In this study, we take one-step method to prepare magnetic g-C₃N₄ used adsorbent for removal Cd (II) from aqueous solution. The characteristics of adsorption for Cd (II) on Fe₃O₄-g-C₃N₄ were assessed by batch experiment. The effect of pH, kinetics, isotherms on the removal of Cd (II) were investigated.

2. Experimental

2.1. Materials

Melamine, hydrochloric acid, Fe₃O₄ were purchased from Guoyao Chemical Reagents Corp, (Shanghai, China).

2.2. Synthesis of Fe₃O₄-g-C₃N₄

g-C₃N₄ is prepared by Ma [3] method.

Fe₃O₄ (1.6g, 20nm) was added in water (deionized water, 100 mL) and then g-C₃N₄(0.4 g) was added in mixed solution. Finally, the mixed solution was sonicated for 24 h. The product was separated by use of magnet and be dried at 60 ° C for 18 h.

3. Results and Discussion

The SEM (Carl Zeiss, Germany) image of Fe₃O₄-g-C₃N₄ are shown in Fig.1 As shown in Fig. 1, it can be found that the morphology of Fe₃O₄-g-C₃N₄ is lamellar structure and the lamellar spacing is about 20 nm. The results of laser particle analysis show that the size of the Fe₃O₄-g-C₃N₄ is in the range of 500 to 2000 nm, which is consistent with the size of g-C₃N₄. In addition, the particle size of Fe₃O₄ is 80-120 nm [6,7]. It indicates that Fe₃O₄ has been fully embedded in g-C₃N₄.

Fig.2. shows that the XRD(RigakuIV, Japan) patterns of magnetic Fe₃O₄ and Fe₃O₄-g-C₃N₄. The diffraction peaks of Fe₃O₄ at 2θ of 30.1°, 35.5°, 43.1°, 53.4°, 57.0° and 62.6° corresponded to the (220), (311), (400), (422), (511) and (440) planes, which could be indexed to Fe₃O₄ (JCPDS: 85-1436). In addition, 2θ of 27.8° is ascribed to g-C₃N₄, indicating that g-C₃N₄ have successfully inserted on Fe₃O₄.

The FT-IR (Perkin Elmer, USA) results of Fe₃O₄ and Fe₃O₄-g-C₃N₄ are shown in Fig.3. As for Fe₃O₄, peak at 568 cm⁻¹ is contributed to Fe-O bond. Broad peaks at 3000-3500 cm⁻¹ are assigned to O-H bond. For g-C₃N₄, the signal at 806 cm⁻¹ belongs to heptazine ring. Series of peaks in the region between 1100 and 1800 cm⁻¹ signify the characteristic peak of s-triazine derivatives. Peaks at 3100-3500 cm⁻¹ are assigned to N-H bond. For Fe₃O₄-g-C₃N₄, it contains all peaks of Fe₃O₄ and g-C₃N₄, except broad peaks at 3200-3500 cm⁻¹ and two peaks at 2200-2000cm⁻¹. This may be due to the reaction of Fe₃O₄ and g-C₃N₄, thus changing the structure of the C₃N₄ ring.

The corresponding magnetization saturation values for Fe₃O₄ and Fe₃O₄-g-C₃N₄ were 57.59 and 8.39 emu/g, respectively. The magnetization saturation values of Fe₃O₄-g-C₃N₄ have a significant decline, which can be explained that g-C₃N₄ has no magnetic properties, it shields the magnetization of the Fe₃O₄ [8].

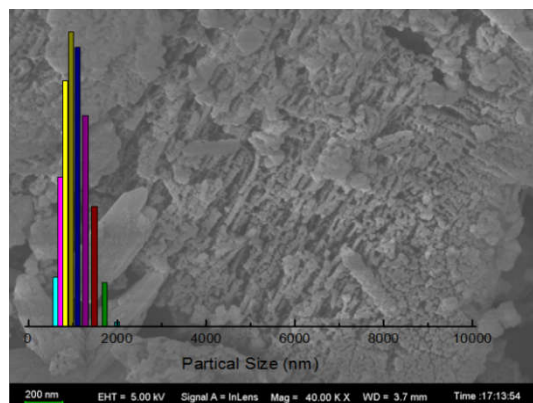


Fig. 1 SEM image and laser particle analysis of $\text{Fe}_3\text{O}_4\text{-g-C}_3\text{N}_4$.

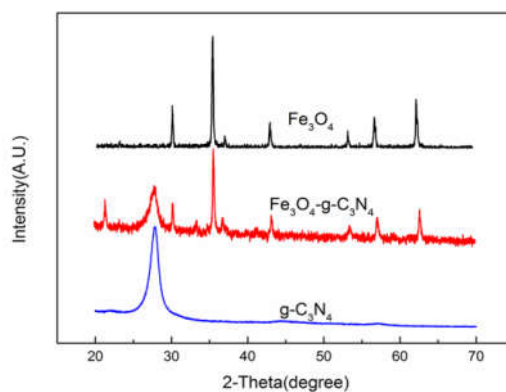


Fig. 2 XRD results of $\text{Fe}_3\text{O}_4\text{-g-C}_3\text{N}_4$

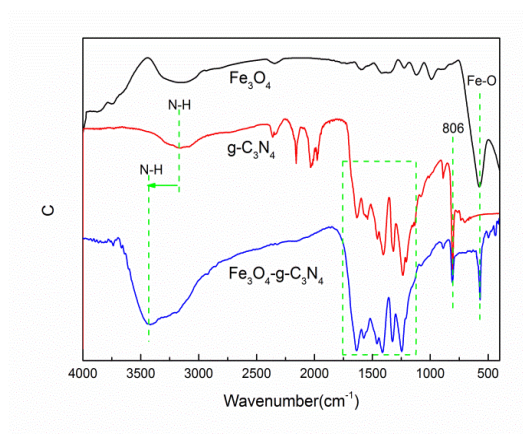


Fig. 3 FT-IR results of $\text{Fe}_3\text{O}_4\text{-g-C}_3\text{N}_4$

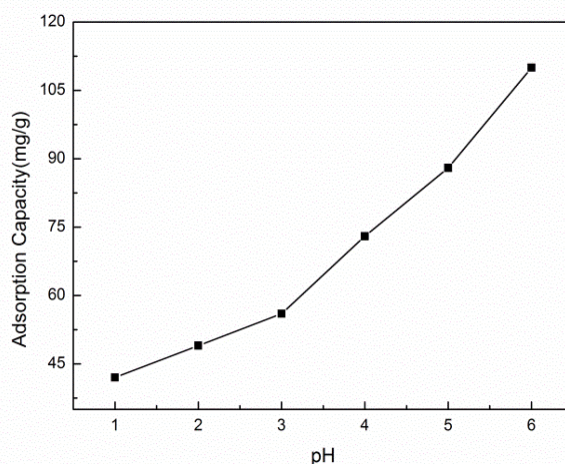


Fig. 4 Effect of pH on adsorption capacity

3.1. Effect of pH

pH is considered to be an important factor which influence the adsorption progress. It is well known that metal ions would precipitate, if the pH value of solution is greater than 6. As shown in Fig.4, the adsorption capacity of Cd(II) both experienced a slow increase at pH 1.0-3.0, followed by a fast rise over the pH range of 3.0-6.0. The maximum adsorption capacity for Cd(II) were occurred at pH 6.0. The influence mechanism can be explained by point of zero charge (PZC) of the adsorbents. When the pH of solution is lower than PZC, the surface charge of the adsorbent is positive, resulting in the approach of metal ions become difficult due to repulsive forces. The PZC of $\text{Fe}_3\text{O}_4\text{-g-C}_3\text{N}_4$ is around 3.0. There is electrostatic repulsion between metal ions and $\text{Fe}_3\text{O}_4\text{-g-C}_3\text{N}_4$ when the values of pH is lower than 3. While the values of pH is higher than 3, the electrostatic repulsion become electrostatic attraction. This is consistent with the rate of increase in adsorption capacity.

3.2. Adsorption Kinetics

The relationship between contact time and adsorption capacity are shown in Fig.4. As shown in Fig.4, it can be found that the adsorption of Cd(II) have reached equilibrium condition at 30 min. Pseudo-first-order model and pseudo-second-order model are used to analyze the rule of adsorption kinetics in experiment data. The fitting parameters are also shown in Fig.4. The pseudo-second-order model shows good fitting to the adsorption behavior of Cd(II) with excellent correlation coefficients, indicating that the adsorption rate of Cd(II) are controlled by chemical progress.

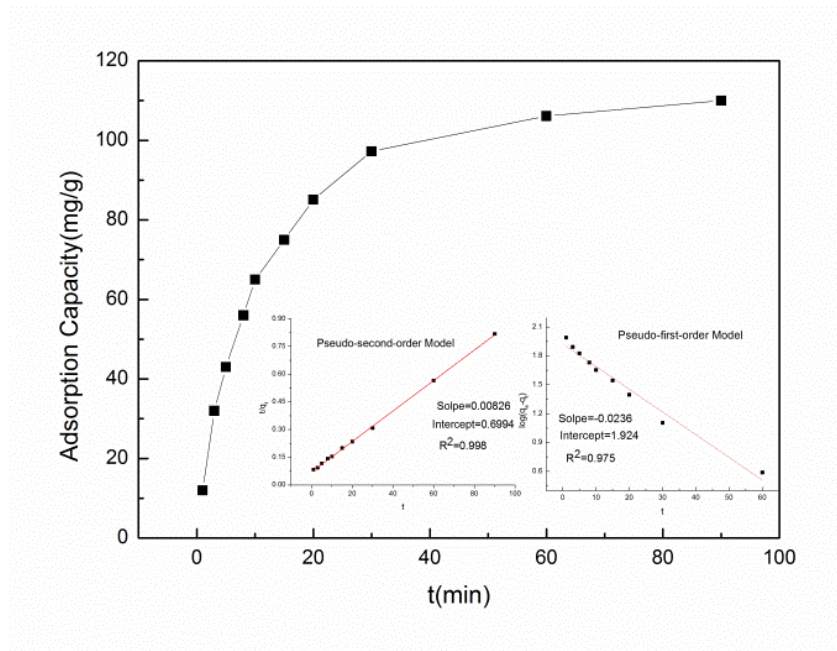


Fig. 5 Effect of contact time on adsorption

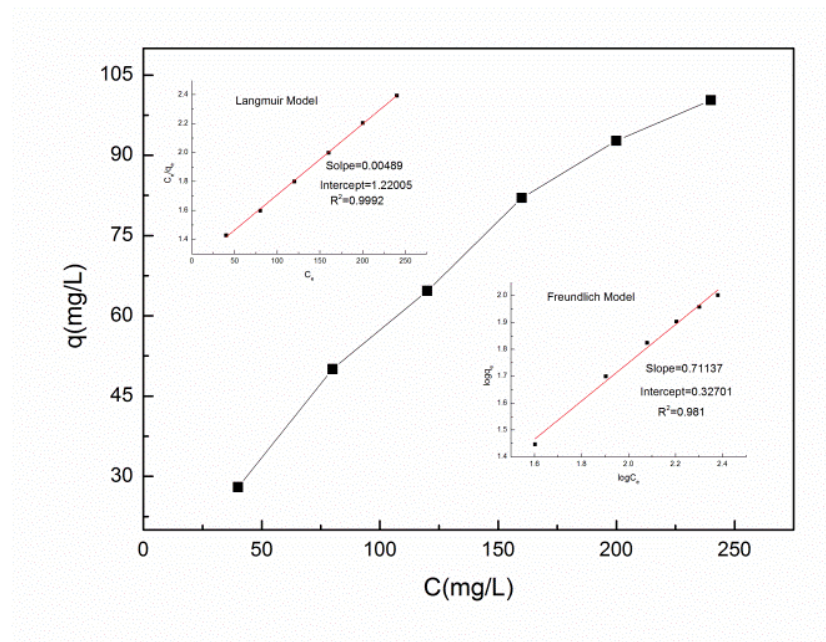


Fig. 6 Effect of the initial concentration on adsorption

3.3. Adsorption isotherms

The adsorption isotherms of Cd (II) by $\text{Fe}_3\text{O}_4\text{-g-C}_3\text{N}_4$ with corresponding Langmuir and Freundlich plots are shown in Fig. 5. As shown in Fig. 5, the correlation coefficients of Langmuir and Freundlich model were higher than 0.9, but the isotherm data of Cd (II) was better described by the Langmuir model compared to the Freundlich model. It suggested that the adsorption progress is monolayer and homogeneous. The predicted maximum adsorption capacity by Langmuir model for Cd (II) is 204.5 mg/g.

Conclusion

A new magnetic adsorbent ($\text{Fe}_3\text{O}_4\text{-g-C}_3\text{N}_4$) was first prepared by ultrasonic method. Many characterizations have confirmed that $\text{Fe}_3\text{O}_4\text{-g-C}_3\text{N}_4$ have successfully prepared. pH results show that the optimal pH of adsorption experiment was 6. Langmuir model suggested that the maximum adsorption capacity of $\text{Fe}_3\text{O}_4\text{-g-C}_3\text{N}_4$ is 204.5 mg/g.

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