Synthesis of Two Kinds of Mesoporous Diatomite by Microwave Assisted Sol-Gel Method and Its Adsorption of Ammonia Nitrogen in Wastewater

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Abstract. The microwave-assisted sol-gel method was used to synthesize mesoporous diatoms (DM) and magnetic mesoporous diatoms (MDM), and used as adsorbent to remove ammonia nitrogen from water. The effect of reaction time, solution pH, and initial concentration of ammonia nitrogen on adsorption was studied, and the adsorption Kinetics and thermodynamic characteristics of DM and MDM were analyzed. The results showed that at 25 °C, when the dosage of DM and MDM was 4 g/L, the initial concentration of ammonia nitrogen in the solution was 50 mg/L, the value of pH was 7, and the adsorption time was 30 min, the adsorption of ammonia nitrogen in solution by DM and MDM was 6.95 and 7.79 mg/g, respectively. DM and MDM had good adsorption effect on ammonia nitrogen, and the adsorption process complied with the Pseudo-second-order kinetics equation and Freundlich isothermal adsorption model.

1. Introduction

In recent years, with the rapid development of economy and the gradual expansion of production scale, Ammonia nitrogen (NH₃-N) in water is increasing year by year due to the discharge of domestic sewage and industrial wastewater [1]. When untreated ammonia nitrogen wastewater is discharged into water, it will lead to eutrophication of water body due to excessive ammonia nitrogen content, which will seriously affect the survival of aquatic organisms and further affect human health [2]. Therefore, the treatment of wastewater before discharge is particularly important. Since 2017, Zhejiang Province has vigorously carried out special rectification activities to “eliminate the inferior V water” and put water environment management to a new height.

At present, the removal methods of ammonia nitrogen mainly include chemical precipitation method [3], break-point chlorination [4], and adsorption method, among which adsorption method is favored due to its wide source of materials, various types, cheap and easy access. However, the preparation of adsorbents mostly using expensive and toxic chemical reagents to synthesize. Therefore, the use of natural mineral materials becomes a new method to reduce the synthesis cost. Due to its rich species, high porosity (generally 25-65%), small pore size, low density, large specific surface area,
and good adsorption performance, diatomaceous earth is widely used in filtration adsorption and catalyst carrier [5]. Diatomite (D) was used as the source of Silicon in the experiment. Diatomite Mesoporous (DM) and Magnetic Mesoporous (MDM) were prepared by microwave assisted sol-gel method. This method can greatly reduce the synthesis time. In order to achieve rapid solid-liquid separation after adsorption of ammonia nitrogen, magnetic modification of DM was carried out. On this basis, the adsorption effect of the two adsorbents on ammonia nitrogen was measured separately, and the influence of reaction temperature, initial concentration of solution, pH, reaction time and dosage on the adsorption of ammonia nitrogen were discussed, so as to provide a basis for the search for a new and efficient ammonia adsorption material.

2. Experiment

2.1. Materials
Diatomite (SiO₂: 68%), purchased at Diatomite Earth Co., Ltd., Changbai County, Jilin Province; Sodium hydroxide (NaOH), hexadecyltrimethylammonium bromide (CTAB), sulfuric acid (H₂SO₄), potassium tartrate sodium, etc. are all pure analysis and purchased by China National Pharmaceutical Group Chemical Testing Co., Ltd.; Simulated ammonia nitrogen wastewater is prepared using anhydrous ammonium chloride dissolved in deionized water; Fe₃O₄ is prepared by chemical precipitation method with reference to the literature [6].

2.2. Method

2.2.1. Synthesis of Mesoporous Diatoms (DM). According to the molar ratio between SiO₂, CTAB, Na₂O, and H₂O at a dose of 1.0:0.2:0.3:100, firstly, take an appropriate amount of diatomaceous soil, add distilled water, NaOH, and 3 hours of water bath and alkaline leaching time at 95 °C to fully dissolve the diatomaceous soil. Secondly, dissolve the right amount of CTAB into a small amount of distilled water, slowly add the CTAB solution to the above system under strong stirring, and continue the reaction for 0.5h. Then dilute H₂SO₄ solution is used to adjust the pH to about 10 and the gel material is transferred to two neck flasks and placed in a microwave chemical reactor for further reaction for 70 min. Finally, turn to 200 mL of PTFE lining thermal water kettle, crystallization 4 h under 105 °C, cooled to room temperature will be obtained after the material 2 ~ 3 times with ethanol, the suction filter, after drying to constant weight under 75 °C, it turns into a crucible into the muffle furnace to 1 °C/min to 550 °C temperature programmed after calcination was DM, See Figure 1.

![Figure 1. Schematic diagram of DM preparation process](image)

2.2.2. Synthesis of Magnetic Mesoporous Diatoms. A pretreated DM was weighed and added to 15mL deionized water and was continuously stirred to spread evenly. Then, 2.5 g Fe₃O₄ solids were added to the above solution to fully disperse; 10 min after ultrasonic oscillator was put into 100 mL high pressure reaction kettle, reaction 4 hours under 80 °C, under 60 °C dry to constant weight, after grinding and 60 mesh screen, MDM was prepared and standby.
2.2.3. Ammonia nitrogen removal experiment. Take a certain amount of D, DM, and MDM adsorbents and put them in a 250 mL cone-shaped bottle. Add 100 mL of ammonia nitrogen wastewater at an appropriate concentration, oscillate at a set temperature and set oscillation intensity for a certain period of time, then remove the supernatant quickly after finishing. After filtration and separation by a 0.45 μm needle filter, the ammonia nitrogen concentration in the filter is determined, and the adsorption of the adsorbent to the adsorbent is calculated according to formula (1):

\[
q_e = \frac{(C_0 - C_t)V}{m}
\]

In the formula, \(q_e\): sorption of the adsorbent (mg/g); \(C_0\): Initial concentration of ammonia nitrogen in solution (mg/L); \(C_t\): concentration of ammonia nitrogen (mg/L) at T time in solution; \(V\): solution volume; \(m\): quality of adsorbent (g).

3. Results and discussion

3.1. Effect of pH on solution

When the temperature is 25 °C, the dosage of D, DM and MDM adsorbents is 4g/L, and the initial concentration of ammonia nitrogen wastewater is 50 mg/L, and the reaction time is 30 min, the effect of pH on the removal of ammonia nitrogen wastewater from the three adsorbents is shown in Figure 2 (a).

From Figure 2 (a), the effect of pH on the adsorption of ammonia nitrogen is significant, and the adsorption effect of diatomaceous soil to ammonia nitrogen is poor. At pH 7, compared with the modified DM of CTAB, the magnetically modified MDM has the best effect on the adsorption of ammonia nitrogen. When the pH is low, the concentration of H⁺ in the system is high and the activity is strong, which leads to competitive adsorption with NH₄⁺. However, MDM occupies the adsorption site of the adsorbent part due to the presence of Fe³⁺ in the structure, resulting in lower adsorption under acidic conditions; With the increase of pH, the concentration of H⁺ in the solution decreases and the negative charge on the surface of the DM adsorbent increase, which is conducive to the reaction with NH₄⁺; The Fe³⁺ exchange ability in MDM is strong and the adsorption capacity is large. At pH 7, the adsorption of ammonia nitrogen by DM and MDM was 6.95 and 7.79 mg/g, respectively. However, when the pH is higher than 7, the NH₄⁺ gradually changes to the non-ionic NH₃. The NH₃ itself is not charged, which is not conducive to the exchange of cations in the adsorbent. Fe³⁺ in the MDM reacts with the OH-solution to form a precipitate. Therefore, the amount of ammonia nitrogen adsorbed by the two adsorbents is decreasing.

3.2. Effect of reaction time on adsorption of ammonia nitrogen

When the temperature is 25 °C, D, DM, and M-DM adsorbents are all 4 g/L, the initial concentration of ammonia nitrogen wastewater is 50 mg/L, and the pH is 7. The effect of reaction time on ammonia nitrogen removal is shown in Figure 2 (b).

It can be seen from Figure 2 (b) that D has a low adsorption of ammonia nitrogen at different reaction times. The adsorption of ammonia nitrogen by DM and MDM adsorbents in the first 20 min showed a rapidly increasing trend, but the adsorption amount of MDM is relatively slow because the adsorbent surface after magnetic modification has more binding sites and strong exchange capacity of Fe³⁺, which increases the adsorption of ammonia nitrogen in the system. However, with the extension of reaction time, the adsorption site gradually covers up, and the adsorption tends to be stable. The change rate of DM at the initial stage of the reaction is faster because there are no ammonium ions attached to the adsorbent in the early stage of adsorption, and the adsorption rate is faster due to the difference in concentration. Both adsorbents gradually reached adsorption equilibrium after 30 min. At this time, the adsorption of ammonia nitrogen by DM and MDM adsorbents is 6.95 and 7.79 mg/g.
3.3. Effect of initial concentration on adsorption of ammonia nitrogen

When the temperature is 25 °C, D, DM, and MDM adsorbents are all 4 g/L, ammonia-nitrogen wastewater pH of 7, and the reaction time is 30 min. The effect of the initial concentration of wastewater on ammonia nitrogen removal is shown in Figure 2 (c).

It can be seen from Figure 2 (c) that when the initial concentration of ammonia nitrogen in the wastewater increased from 2 mg/L to 100 mg/L, after adsorption of 30 min, the adsorption of ammonia nitrogen by DM and MDM adsorbents increased from 3.22, 5.19 mg/g to 6.95 and 7.79 mg/g, respectively. When the ammonia nitrogen concentration is low, due to the lack of diffusion driving force provided by the concentration gradient, the adsorption of ammonia nitrogen by DM and MDM is low, and the difference of adsorption amount is small when concentration is low. With the increase in the concentration of ammonia nitrogen in the solution, the concentration difference between the solution and the adsorbent surface also increases. The active groups containing iron trioxide particles in MDM are more than those in DM, thus increasing the adsorption of ammonia nitrogen. The maximum value is reached when the initial concentration is 50 mg/L. When the concentration continues to increase, the adsorption amount will gradually become balanced due to the limited adsorption site on the adsorbent.

3.4. Effect of adsorbent dose

The temperature is 25 °C, the pH of ammonia nitrogen wastewater is 7, the initial concentration is 50 mg/L, and the reaction time is 30 min. The effect of the addition of D, DM and MDM adsorbents on the removal of ammonia nitrogen is shown in Figure 2 (d).

![Figure 2. Effect of four different factors on ammonia nitrogen adsorption](image)
(a) pH; (b) reaction time; (c) initial concentrations; (d) adsorbent dose

As can be seen from Figure 2 (d), with the increase in the amount of adsorbent, the amount of ammonia nitrogen adsorbed by DM and MDM increased significantly. When the amount of addition increased from 0.05 g to 0.20 g, the amount of ammonia nitrogen adsorbed by DM and MDM increased by 77.7 % and 23.5 % respectively. This is because compared with DM, the surface of MDM containing Fe³⁺ is relatively loose, and there are relatively many active groups exposed, making the adsorption of less input much higher than DM's adsorption of ammonia nitrogen. When the dosage of adsorbent is increased to 0.25g, the adsorption of ammonia nitrogen tends to be flat and the change range is small. The reason is that the continued increase in the amount of adsorbent will increase the adsorption per unit density in the wastewater, but the surface area of contact is not increased, so for the treatment of 50mL waste water, 0.20g of adsorbent can be selected.

3.5. Study of adsorption kinetics

At 25 °C, the ammonia nitrogen wastewater with different concentrations of 100 mL was oscillated with a certain mass of DM and MDM adsorbents in a constant temperature oscillator box to react, and different time periods were selected for sampling according to experimental requirements. The filtration membrane of 0.45 μm was used for measurement. The experimental results are fitted according to the pseudo-second-order kinetic equation, such as formula (2).

\[
\frac{t}{q_t} = \frac{1}{kq_e} + \frac{t}{q_e}
\]

(2)

In formula, \( q_e \) (adsorbed capacity of ammonia nitrogen at T time (mg/g)); \( q_t \) (adsorbed capacity of ammonia nitrogen at equilibrium time (mg/g)); \( t \) (time (min)); \( k \) (the pseudo-second-order constant rate (min⁻¹)).

![Graphs showing pseudo-second order adsorption kinetic curves for DM and MDM](image)

**Figure 3.** Pseudo-second order adsorption kinetic curves

The kinetic results, relative fitting parameters and equations of DM and MDM adsorbents for ammonia nitrogen adsorption are shown in Figure 3, from which it can be seen that the experimental results are well fitted by the pseudo-second-order kinetic equation. The \( q_e \) of DM and MDM calculated from the fitting equation is 5.08 and 7.41 mg/g, respectively, which is similar to the measured values of 6.95 and 7.79 mg/g, indicating that Lagrange adsorption Kinetics can describe the adsorption behavior of ammonia nitrogen well. The adsorption of ammonia nitrogen by the two adsorbents is chemical adsorption.
3.6. Adsorption isotherm curve

The adsorption isotherm was fitted by the Langmuir equation and the Freundlich equation (see Figure 4). The results of the ammonia nitrogen adsorption isotherm are showed in Table 1.

The Langmuir model assumes that adsorption occurs on the homogeneous surface of single-layer adsorption, rather than the reaction between adsorption ions [7]. The Langmuir model is expressed as follows:

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

(3)

In the formula, \(Q_e\): equilibrium adsorption per unit mass (mg/g); \(Q_{max}\): maximum adsorption capacity (mg/g); \(C_e\): Balanced concentration (mg/L); \(K\): Adsorption energy coefficient (L/mg).

The Freundlich model assumed that the adsorption is monolayer adsorption and occurs on uneven surfaces [8]. The Freundlich model is as follows:

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

(4)

In the formula, \(K_f\) is the Freundlich constant (mg/g); \(C_e\) is a measure of the adsorption capacity of the adsorbent (mg/L); \(1/n\) is a heterogeneity factor, a constant related to adsorption strength and surface heterogeneity.

![Figure 4. Fitting curves of Langmuir (a), Freundlich (b) equation adsorption isotherm model](image)

Table 1. Parameters in Langmuir and Freundlich adsorption isotherm models of NH3-N onto DM and MDM

|       | Langmuir          | Freundlich         |
|-------|-------------------|--------------------|
|       | Fitting equation  | \(q_{max}\)       | b       | \(R^2\)  | Fitting equation  | \(K_f\)  | \(1/n\) | \(R^2\)  |
| DM    | \(y=0.163x-0.06\) | 6.13               | 2.72    | 0.985    | \(y=0.136X-0.05\) | 0.891   | 0.136   | 0.986    |
| MDM   | \(y=0.0025x+0.7823\) | 40                 | 0.003   | 0.9463   | \(y=0.1116X+0.6783\) | 4.767   | 0.1116  | 0.9418   |

From table 1, it can be seen that the correlation coefficients \(R^2\) of Langmuir and Freundlich equations are all greater than 0.9, proving that the two equations could better describe the adsorption behavior. Among them, the \(b\) of both equations in the Langmuir equation is greater than 0, indicating that the adsorption process is relatively easy to complete, which is a benign adsorption. The \(q_{max}\) of DM and MDM is larger than the experimental data, which proves that it has a good application prospect. For DM and MDM, the Freundlich equation can better describe the adsorption of ammonia.
nitrogen, and two of $1/n$ in the Freundlich equations are less than 1, indicating that the adsorption is benign adsorption. Through data fitting, it can be seen that the adsorption of ammonia nitrogen by DM and MDM conforms to the Langmuir equation and the Freundlich equation, indicating that it may be either monolayer adsorption, multi-molecule adsorption, or both cases exist at the same time.

4. Conclusions
(1) Mesoporous diatoms (DM) and magnetic mesoporous diatoms (MDM) can be used as adsorbents to remove ammonia nitrogen in water at 25 ℃, when DM and MDM dosing quantity of 4 g/L, initial concentration of 50 mg/L solution of ammonia nitrogen, pH of 7, and the adsorption time is 30 min, the adsorption amount of ammonia nitrogen in the solution by DM and MDM is 6.95 and 7.79 mg/g, respectively.

(2) Lagrange adsorption Kinetics can describe the adsorption behavior of ammonia nitrogen well, and the adsorption of DM and MDM adsorbents is a chemical adsorption of ammonia nitrogen.

(3) Both the Langmuir and Freundlich equations can describe the adsorption behavior of ammonia nitrogen on DM and MDM adsorbents well.

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