Study on synergistic effect of removal of nitrogen and phosphorus by mixed modified zeolite

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Abstract. Sodium chloride-modified zeolite Z-Na for the removal of ammonia nitrogen and lanthanum-modified zeolite Z-La for the removal of phosphorus were prepared by sodium chloride modification and lanthanum chloride modification. Through adsorption kinetics and isotherm model fitting, the synergistic effect of pollutants in the removal of ammonia nitrogen and phosphorus by these two zeolites was explored. The results show that in the case of composite pollutants, the presence of phosphorus can inhibit the adsorption of ammonia nitrogen by Z-Na, (the adsorption rate is reduced from 2.3840 ℎ⁻¹ to 1.3442 ℎ⁻¹, and the maximum adsorption capacity is 13.6612 mg / g reduced to 11.8906 mg / g); the presence of ammonia nitrogen will promote the adsorption of phosphorus by Z-La (adsorption rate increased from 1.0623 ℎ⁻¹ to 4.8595 ℎ⁻¹, while the maximum adsorption capacity is almost unchanged).

1. Introduction

According to China Ecological Environment Status Bulletin in 2018, among the 1,935 water quality sections (points) monitored by surface water across the country, the proportion of IV to inferior V is 29.0%, and total phosphorus and ammonia nitrogen are the primary pollutant indicators [1]. Controlling the content of ammonia nitrogen and phosphorus in water bodies has become an essential problem in water pollution control in China.

In recent years, zeolites and their synthetic materials have been widely applied in water treatment processes [2-3]. The current researches focus on the simultaneous removal of ammonia nitrogen and phosphorus, ignoring the synergistic effects of ammonia nitrogen and phosphorus during the reaction. At the same time, studies have shown that natural zeolite can improve its removal of phosphate radicals after being modified effectively, but it also will significantly reduce the adsorption effect of ammonia [2,4,5]. If only one zeolite material is used, the zeolite ratio cannot be adjusted based on the concentration ratio of nitrogen and phosphorus.

To solve the problems mentioned above, this study used two modified zeolites to remove ammonia nitrogen and phosphorus, respectively. The synergistic effects of ammonia nitrogen and phosphorus in the adsorption process of mixed modified zeolite were studied by the model fitting of kinetics and isotherm. This research provides theoretical and technical support for more flexible and economical ammonia nitrogen and phosphorus removal methods.

2. Materials and methods

2.1. Materials and equipment
The natural zeolite used in the test was from Jinyun County, Zhejiang Province. After screening, washing and drying, 100 mesh-40 mesh natural zeolite is selected as the experimental raw material. The chemical composition of the initial experimental sample is shown in Table 1.

| SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | K$_2$O | CaO | MgO | Na$_2$O |
|---------|-------------|-------------|--------|-----|-----|--------|
| 69.58   | 12.2        | 0.87        | 1.13   | 2.59| 0.13| 2.59   |

Main reagents: sodium chloride, ammonium chloride, lanthanum chloride, ethanol, phosphoric acid, sodium hydroxide, Nessler's reagent, potassium sodium tartrate, molybdate, ascorbic acid. All are analytically pure.

Main instruments: constant temperature oscillator, pH meter, analytical balance, drying box, spectrophotometer, filter

2.2. Experimental method

2.2.1. Preparation of NaCl modified zeolite

Weigh 5.00g of natural zeolite into a 250mL Erlenmeyer flask, add 50mL of 80g / L sodium chloride solution, place in a shaker with a frequency of 160r / min and a temperature of 60 ° C, and shake for 4h. After taking out, it was washed and dried to obtain a sodium-modified zeolite which is named Z-Na.

2.2.2. Preparation of LaCl$_3$ modified zeolite

Alkali solution pretreatment: Weigh 10.00g of natural zeolite into a 250mL Erlenmeyer flask, add 100mL of a sodium hydroxide solution with a concentration of 1mol / L, put it into a shaker with a frequency of 160r / min and a temperature of 30 ° C, and shake for 2h. After taking out, wash until the supernatant is neutral. Lye pretreated zeolite after drying. LaCl$_3$ modified: Weigh 0.40g of lanthanum chloride and 50mL of 20% ethanol in a 250mL Erlenmeyer flask, put it in a shaker with a frequency of 160r / min and a temperature of 80 degrees Celsius, and shake for 2 h. After taking out, it was washed with deionized water and dried to obtain a lanthanum-modified zeolite which is named Z-La.

2.2.3. Adsorption kinetics test

The initial concentration of ammonia nitrogen was 50 mg / L, the initial concentrations of phosphoric acid were set to 0, 3, 30, and 60 mg / L, the Z-Na dosage was 7.5 g / L, the temperature was 25 degrees Celsius, and the oscillation rate was 160 r / min. Sampling is performed at intervals to test the remaining concentration of ammonia nitrogen in the sample. The initial concentration of phosphoric acid was 60 mg / L, the initial concentrations of ammonia nitrogen were set to 0, 50, 100, and 300 mg / L, respectively, and the Z-La dosage was 10 g / L. Sampling is performed at intervals to test the remaining concentration of phosphorus in the sample. The other experimental conditions are the same as above.

2.2.4. Adsorption isotherm test

The initial concentration of ammonia nitrogen in each group is 30, 40, 50, 60, 80, 120, and 150 mg / L, and 150 mg / L, the initial concentration of phosphoric acid is set to 0, 3, 30, and 60 mg / L, and the Z-Na dosage is 7.5 g / L, Shake for 12h. The other experimental conditions are the same as above. The initial concentration of phosphoric acid in each group is 6, 12, 18, 24, 30, 48, 60, 90 mg / L, the initial concentration of ammonia nitrogen is set to 0, 50, 100, and 300 mg / L, and the Z-La dosage is 2 g / L, shake for 12h. The other experimental conditions are the same as above.

3. results and discussion

3.1. Adsorption kinetics test
The solid-liquid adsorption process is usually described using pseudo-first-order and pseudo-second-order equations [2,4,6]. (1) and (2):

\[
\ln \left( \frac{q_t}{q_e} \right) = \ln \frac{q_e}{k_1 t} \tag{1}
\]

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

Where \( q_t (mg \cdot g^{-1}) \), \( q_e (mg \cdot g^{-1}) \) are the adsorption amount at any moment of adsorption and adsorption equilibrium; \( k_1 (h^{-1}) \) and \( k_2 (h^{-1}) \) are the kinetics constants.

The adsorption process of porous adsorbents usually includes 3 steps: film diffusion, intra-particle diffusion, and adsorption reactions on the surface of the adsorbent [6]. Quasi-first-order and quasi-second-order kinetic models cannot identify the diffusion mechanism, so we decided to describe the adsorption process by intra-particle diffusion model (3):

\[
q_t = k_i t^{1/2} + A \tag{3}
\]

where \( k_i (mg \cdot (g \cdot h^{1/2})^{-1}) \) is the intraparticle diffusion rate constant and A (mg/g) is a constant providing an indication of the thickness of the boundary layer.

3.1.1. Kinetics for ammonia removal by Z-Na

![Fig.1. Effect of the initial concentration of phosphate root on ammonia removal by Z-Na](image)

![Fig.2. Intra-particle diffusion plots for ammonium removal by Z-Na](image)

![Fig. 3. Kinetic model fitting curve for ammonia removal by Z-Na](image)
Table 2. Kinetics parameters of NH4+ removal by Z-Na

| Model          | Initial concentration of PO₄ (mg/L) | Kinetic parameters | R²   |
|----------------|-------------------------------------|--------------------|------|
| Pseudo-second  | 0                                  | 2.3840             | 6.716| 1.0000 |
| order          | 3                                  | 2.4025             | 6.452| 0.9999 |
|                | 30                                 | 1.5343             | 6.423| 0.9998 |
|                | 60                                 | 1.3442             | 6.177| 0.9999 |

As can be seen from Figure 1, most ammonia nitrogen adsorption reaction can be balanced within 3h. The whole adsorption process shows the characteristics of early rapid adsorption and late slow balance. The removal rate of Z-Na to ammonia nitrogen (initial concentration is 50 mg/L) is 91% when the solution does not contain PO₄, and the removal rate of ammonia nitrogen decreases gradually with the increase of phosphoric acid concentration in the solution. The pseudo-second-order kinetic model, which is based on chemical adsorption, fitted well the experimental data as can be seen in Figure 2. It can draw that the adsorption process of ammonia nitrogen by Z-Na is mainly ion exchange [9] [10]. The data in Table 2 shows that as the concentration of phosphate ions increases, the apparent reaction rate of adsorption decreases. It means that the presence of phosphorus appears to inhibit the adsorption of ammonia by Z-Na.

Table 3. Intra-particle diffusion parameters for ammonium removal by Z-Na

| Initial concentration of PO₄ (mg/L) | A    | kp1  | R²      | A   | kp2  | R²   |
|-------------------------------------|------|------|---------|-----|------|------|
| 0                                  | 4.5066| 1.8865| 0.9877  | 6.2386| 0.1921| 1.0000|
| 3                                  | 3.7415| 2.355 | 0.9994  | 6.0204| 0.2136| 0.9935|
| 30                                 | 3.6161| 2.2843| 0.9987  | 5.4998| 0.4176| 0.9772|
| 60                                 | 3.0958| 2.5057| 0.9847  | 5.0349| 0.5332| 0.9962|

The intra-particle diffusion model fitted well the experimental data as can be seen in Figure 3. The entire adsorption process is divided into two linear regions, and the fitted straight line does not pass through the origin. It shows that the adsorption of ammonia nitrogen by Z-Na is controlled by film diffusion and internal diffusion [2]. It can be seen from Table 3 that with the increase of the phosphoric acid concentration, the intra-particle diffusion adsorption rate constant gradually increases. This is contrary to the law of quasi-second-order kinetic adsorption rate decrease, which may be due to the increase of the phosphoric acid concentration increases the internal diffusion rate and the film diffusion process rate decreases. The decrease is greater than the increase. So, the overall speed has slowed down.

3.1.2. Kinetics for phosphate removal by Z-La

![Fig.4. Effect of the initial concentration of ammonia root on phosphate removal by Z-La](image-url)
Fig. 5. Intra-particle diffusion plots for phosphate removal by Z-La

Fig. 6. Kinetic model fitting curve phosphate removal by Z-La

Table 4. Kinetics parameters of phosphate removal by Z-La

| Model                  | Initial concentration of NH₄⁺ (mg/L) | Kinetic parameters | R²   |
|------------------------|-------------------------------------|--------------------|------|
|                        |                                     | k₂/h⁻¹             | qₑ/(mg · g⁻¹) |      |
| Pseudo-second order    | 0                                   | 1.0623             | 6.329 | 0.9999 |
|                        | 50                                  | 1.4265             | 6.293 | 0.9998 |
|                        | 100                                 | 3.6455             | 6.305 | 1.0000 |
|                        | 300                                 | 4.8495             | 6.297 | 0.9999 |

The most reactions can reach equilibrium in about 2 hours as can be seen in Figure 4. It is similar to the adsorption process of ammonia nitrogen. The removal rate of phosphorus by Z-La (the initial concentration is 60mg / L) can reach more than 99% when the adsorption equilibrium, but as the concentration of phosphoric acid in the solution increases, the time to reach equilibrium increases.

The pseudo-second-order kinetic model fitted well the experimental data as can be seen in Figure 5. In the absence of ammonia, the apparent reaction rate of phosphorus removal is 1.0623  h⁻¹, and the equilibrium adsorption capacity is 6.329 mg / g. As the concentration of phosphorus increases, the apparent reaction rate gradually increases. At 60 mg / L, the rate increased to 4.8495  h⁻¹. This may be due to Z-La still has a good ability to adsorb ammonia nitrogen, and the surface charge increases after the adsorption of ammonia cations, which enhances the electrostatic attraction of Z-La to phosphates in negative charges [16]. The change in the equilibrium adsorption capacity is negligible, it may be due to the number of active sites on the zeolite surface has not changed.

Table 5. Intra-particle diffusion parameters for phosphate removal by Z-La

| Initial concentration of NH₄⁺ (mg/L) | A    | k_p1  | R²   | A    | k_p2  | R²   |
|-------------------------------------|------|-------|------|------|-------|------|
| 0                                   | 2.6308 | 2.9158 | 0.9998 | 5.5700 | 0.2534 | 0.9896 |
| 50                                  | 2.4400 | 3.3055 | 0.9981 | 5.8906 | 0.1119 | 0.9735 |
| 100                                 | 4.4395 | 1.8546 | 0.9129 | 5.8111 | 0.2414 | 0.9937 |
| 300                                 | 4.2177 | 2.2288 | 0.8938 | 5.9765 | 0.1598 | 0.9504 |
The fitting parameters of the intra-particle diffusion model are shown in Table 5. Similar to the ammonia nitrogen adsorption process, the adsorption of Z-La on phosphorus is controlled by film diffusion and internal diffusion [2]. However, it can be seen that when the concentration of phosphoric acid reaches 100 mg / L and more, the linear fitting effect of the first stage is worse than that of the low-concentration time, while the second stage doesn’t have this phenomenon. It may be that when the concentration of phosphoric acid increases, the larger the adsorption rate, the faster the reaction proceeds to the second stage. That is, the breakpoints of the two curves are advanced. This also led to irregularities in the fitting parameters of the intra-particle diffusion model between 50 and 100 mg / L of ammonia. But the law remains the same within a certain range. As the ammonia concentration increases, the rate of the internal diffusion process in the first stage increases, and the rate in the second stage decreases.

3.2. Phosphate and ammonium isotherms

The phosphate and ammonium equilibrium sorption were evaluated according to Langmuir and Freundlich isotherms Equations [2,11].

\[
\frac{C_e}{q_e} = \frac{C_e}{q_{\text{max}}} + 1/(K_L q_{\text{max}}) \quad (4)
\]

\[
\log q_e = \log K_F + \frac{\log C_e}{n} \quad (5)
\]

where \(C_e\) (mg/L) represents equilibrium adsorption concentration; \(q_{\text{max}}\) (mg/g) represents the maximum adsorption.

3.2.1. Isotherms for ammonia removal by Z-Na

![Fig.7. Isotherms for ammonia removal by Z-Na](image)

| Initial concentration of PO4-(mg/L) | Langmuir | Freundlich |
|-----------------------------------|----------|------------|
|                                   | \(q_m\) (mg/g) | \(K_L\) (L/mg) | \(R^2\) | \(K_F\) (L/mg) | \(n\) | \(R^2\) |
| 0                                 | 13.6612  | 0.1230     | 0.9949 | 2.8366  | 2.583  | 0.9300 |
| 5                                 | 12.9870  | 0.1415     | 0.9979 | 3.0395  | 2.839  | 0.9584 |
| 30                                | 11.9761  | 0.1723     | 0.9963 | 3.3986  | 3.317  | 0.9838 |
| 60                                | 11.8906  | 0.1352     | 0.9984 | 2.8675  | 2.968  | 0.9455 |

The fitting parameters are shown in Table 6. It was found that the fitting correlation coefficients \(R^2\) of the two were higher than 0.9000, indicating that chemical and physical adsorption coexisted during the adsorption of ammonia by Z-Na at 25 °C. In the Freundlich adsorption isotherm model, as the concentration of phosphoric acid increases, the value of \(n\) also increases, and \(2<n<10\), which indicates that the adsorption of ammonia nitrogen by Z-Na is easy to carry out, but the difficulty is getting more and more [9]. This is the same conclusion reached by kinetics.

According to the comparison fitting correlation coefficient \(R^2\) and the closeness of the theoretical maximum adsorption capacity to the experimentally obtained adsorption capacity, it can be drawn that the Langmuir model fitted well the adsorption process of ammonia nitrogen by Z-Na [11]. With the increase of phosphorus, the maximum adsorption capacity of Z-Na for ammonia decreased from
13.6612 mg/L to 11.8906 mg/L. It shows that Z-Na can inhibit the adsorption of ammonia in the presence of P. It may be due to when the solution Ph is in the range of 3.0 to 7.0, the phosphate mainly exists in the form of $H_2PO_4^-$, and the ionized $H^+$ is smaller than $NH_4^+$. Therefore, it will lead to competition between $H^+$ and $NH_4^+$ adsorption site [10], thereby reducing the adsorption capacity of Z-Na to ammonia.

3.2.2. *Isotherms for phosphorus removal by Z-La*

![Isotherms for phosphorus removal by Z-La](image)

Table 7. Isotherm parameters of P adsorption onto Z-La

| Initial concentration of NH$_4^+$ (mg/L) | Langmuir | Freundlich |
|-----------------------------------------|----------|------------|
|                                         | $q_m$(mg/g) | $K_L$(L/mg) | $R^2$ | $K_F$(L/mg) | $n$ | $R^2$ |
| 0                                      | 7.5019    | 9.1301     | 0.9998 | 5.7319      | 11.42 | 0.9029 |
| 50                                     | 7.1736    | 9.5479     | 0.9996 | 5.4601      | 11.20 | 0.9450 |
| 100                                    | 7.3529    | 5.3543     | 0.9993 | 5.5386      | 11.24 | 0.9196 |
| 300                                    | 7.4963    | 2.1242     | 0.9988 | 5.5642      | 11.29 | 0.9314 |

The fitting parameters are shown in Table 7. The fitting effect is similar to the process of Z-Na adsorption of ammonia nitrogen. The adsorption of Z-La to phosphorus is a process in which both chemical and physical adsorption coexist, and the adsorption process is Preference adsorption [5].

The maximum adsorption capacity calculated by fitting the Langmuir isotherm model is similar to the experimentally obtained maximum adsorption capacity, indicating that the adsorption process of Z-La to phosphorus can be well fitted by Langmuir isotherm model, so the adsorption of Z-La to phosphorus is also Single-layer adsorption [11-12]. As can be seen from Table 7, the presence of ammonia nitrogen has little effect on the adsorption of phosphorus by Z-La. Z-La is capable of adsorbing and removing phosphorus by three functions: complexation, electrostatic adsorption and chemical action, among which the contribution rate of electrostatic attraction is far less than that of complexation [9]. Therefore, Z-La can adsorb part of ammonia ions and accelerate the adsorption rate of phosphate, but it cannot significantly affect the maximum adsorption capacity of zeolite for phosphorus removal.

4. Conclusions

Under the conditions of single pollutants and composite pollutants, the adsorption processes of Z-Na to ammonia and Z-La to phosphorus all conform to the pseudo-second-order kinetic model. The adsorption of both is controlled by both film diffusion and particle diffusion processes. Both phosphate and ammonium sorption were well described by the Langmuir isotherm. The effects of phosphorus (0~60mg/L) on the adsorption of ammonia by Z-Na include: slowing the adsorption rate (6.716mg/g ~6.177mg/g), reducing the equilibrium adsorption capacity and the maximum adsorption capacity (13.6612mg/g ~ 11.8906mg/g). The effects of ammonia nitrogen (0 ~ 300mg/L) on the adsorption of phosphorus by Z-La include: increasing the adsorption rate (1.0623h$^{-1}$ ~ 4.8459h$^{-1}$),...
almost not affecting the equilibrium adsorption capacity (6.329mg/g ~ 6.297mg/g) and maximum adsorption capacity (7.5019mg/g ~ 7.4963mg/g).

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