Study on simultaneous degradation of nitrogen and phosphorus in wastewater from sludge dewatering removal by mixing sodium and lanthanum modified zeolite

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Abstract. This paper studied the adsorption of nitrogen and phosphorus in wastewater from sludge dewatering by sodium and lanthanum modified zeolite. Under the condition of initial concentration of 50mg/L, the dosage of 7.5g/L and reaction time of 3h, the removal rate of ammonium reached 92% by sodium zeolite; while the removal rate of phosphate reached 99% by lanthanum zeolite under the condition of initial concentration of phosphorus 60mg/L, the dosage of 10g/L and reaction time of 12h. Two kinds of modified zeolite were mixed to synchronously remove nitrogen and phosphorus from wastewater from sludge dewatering. The results showed that the removal of phosphate by lanthanum zeolite was motion influenced by the concentration of ammonium in the solution, and the existence of lanthanum zeolite was useful to promote the removal of ammonium. Otherwise, sodium zeolite did not have the ability to adsorb phosphate, and the capacity of ammonium adsorption decreased with the increase of phosphate concentration in the solution. When the mass mixing ratio of sodium zeolite and lanthanum zeolite was 4:6, the removal rates of ammonia nitrogen and phosphorus reached 89.6% and 97.5% respectively.

1. Introduction
Wastewater from sludge dewatering, as a by-product of sludge dehydration, contains a large amount of organic matter and high concentration of ammonia nitrogen and phosphorus [1-3], which is generally mixed directly with the incoming water from sewage treatment plants and entered into the subsequent biochemical treatment system. It is easy to cause the impact load on the treatment of small scale towns and rural sewage treatment facilities, affect the process operation effect, and even cause the system operation collapse. With the emphasis of society on sludge disposal, independent sludge disposal sites will also appear. For these two cases, the proper treatment of sludge removal water becomes an imminent production problem.

Natural zeolite is the most commonly used adsorbent in China due to its adsorption capacity and ion exchange performance, high adsorption rate of ammonia nitrogen, strong selectivity, no secondary pollution, and large reserves, low price [4-6]. However, due to the influence of external environmental conditions on the formation of natural zeolites, the pores are not uniform and the degree of interconnection is poor, and the pores are blocked due to impurities [7, 8]. In addition, phosphorus in the sludge removal water mainly exists in the form of phosphate, and the structure of natural zeolite Si-Al is negatively charged, which has poor adsorption of phosphate [9].

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At present, zeolite and its modified materials have been widely used in sewage treatment, but they are mostly used in the treatment of low concentration sewage. The zeolite modification methods and adsorption conditions for the simultaneous removal of high concentration ammonia nitrogen and phosphorus are relatively few. In this paper, the optimized modified zeolite was mixed into the wastewater from sludge dewatering by using the high removal rate of ammonia nitrogen by sodium zeolite and the high removal rate of phosphate by lanthanum zeolite. The aim is to realize the simultaneous removal of nitrogen and phosphorus, and to provide a new idea and a certain research basis for solving the problem of wastewater from sludge dewatering treatment.

2. Materials and methods

2.1. Experimental materials and reagents
The natural zeolite used in the experiment was the oblique zeolite from Jinyun, Zhejiang province, which was used after sieving, washing and drying.
Reagents: KI, HgI₂, NaOH, NaCl, LaCl₃, C₃H₆O₇KNa·4H₂O, C₂H₅OH, C₆H₈O₆, KH₂PO₄, NH₄Cl, are all Guaranteed Reagent (GR).

2.2. Experimental instruments
Water Bath Temperature Oscillator (HWS24), Uv-visible Spectrophotometer (UV-765), pH meter (PHS-3C), Electronic Analytical Balance (ESJ), Ultrasonic Cleaning machine (JH-20), Electric drum wind Drying oven (DHG-9145).

2.3. Preparation of modified zeolite

2.3.1. Preparation of sodium zeolite. 5g natural zeolite was weighed in a 250mL conical flask, 50mL sodium chloride solution with a concentration of 80g/L was added, and 160r/min was put into a 60°C oscillator, which was oscillated for 4h. After taking out, clean and dry to get sodium zeolite.

2.3.2. Preparation of lanthanum zeolite. Lye pretreatment: Weigh 10g natural zeolite in 250mL conical flask, add 100mL NaOH solution with concentration of 1mol/L, put it into 160r/min, oscillate it for 2h with a 30°C oscillator. After taking out, clean the top clear liquid to be neutral, dry to get the lye pretreatment zeolite.
Weigh 0.4g lanthanum chloride and 50mL 20% ethanol in a 250mL conical bottle, put it into a 160r/min oscillator at 30°C, and oscillate for 1h. Take out and add 5g lye treated zeolite, adjust the pH of the solution to 11, and then put it into a 160r/min oscillator at 80°C, and oscillate for 2h. Lanthanum zeolite was obtained by cleaning and drying with deionized water.

2.4. Experimental methods
A simulated water sample of 100mL was placed in a 250mL conical flask, a certain amount of sodium and lanthanum zeolite were added, and the adsorption test was conducted at 160 r/min at 30°C. Then the supernatant was taken and filtered through a 0.45 µm membrane to determine the concentration of ammonia nitrogen and phosphorus.

2.5. Analysis methods
Ammonia concentration was determined by sodium reagent spectrophotometry at 420nm and phosphorus concentration was determined by molybdenum-antimony anti-spectrophotometry at 700nm. When the adsorption equilibrium is reached, the removal rate and adsorption capacity of modified zeolite to ammonia nitrogen and phosphorus are calculated by the following equation [10]:
$$\eta = \left(\frac{c_0 - c_e}{c_0}\right) \times 100$$
Where, \( q \) is the equilibrium adsorption capacity, mg/g; \( \eta \) is the removal rate, %; \( C_0 \) is the initial concentration of ammonia nitrogen and phosphorus in the solution, mg/L; \( C_e \) is the concentration of ammonia nitrogen and phosphorus in the solution at equilibrium, mg/L; \( V \) is solution volume, L; \( M \) is the quality of adsorbent, g.

3. Results and discussions

3.1. Influence of zeolite dosage on the adsorption effect of ammonia nitrogen and phosphorus

As shown in Figure 1, 2, for ammonia nitrogen solution of 50mg/L and phosphorus solution of 60mg/L, the removal rate of ammonia nitrogen and phosphorus increases in the solution with the increase of zeolite dosage after adsorption for 12h. And the adsorption capacity decreases with the increase of zeolite dosage, which is consistent with the research results of Liu C.L. et al [11,12]. When the dosage of sodium zeolite is 0.75g, the removal rate of ammonia nitrogen is 91.2% and the adsorption capacity is 6.46mg/g. Then, with the increase of the dosage of sodium zeolite, the removal rate of ammonia nitrogen increases slowly. When the dosage of lanthanum zeolite was 1g, the phosphorus removal rate was 96.7% and the adsorption capacity was 6.33mg/g. After that, with the increase of the dosage of lanthanum zeolite, the phosphorus removal rate hardly increased. This is because as the mass concentration of residual ammonia nitrogen and phosphorus decreases, the mass concentration gradient of ammonia nitrogen and phosphorus decreases in the solution, resulting in the reduction of removal rate [13].

![Figure 1. Effects of sodium zeolite dosage on the adsorption of ammonia nitrogen](image-url)
3.2. Influence of time on the adsorption effect of ammonia nitrogen and phosphorus

In order to explore the change of the adsorption process of sodium and lanthanum zeolite on ammonia nitrogen and phosphorus with time, the removal rate of 0.75g sodium zeolite on ammonia nitrogen and the removal rate of 1g lanthanum zeolite on phosphorus were determined at different times. The results are shown in Figure 3, 4.

**Figure 2.** Effects of lanthanum zeolite dosage on the adsorption of phosphorus

**Figure 3.** Effects of time on the adsorption of ammonia nitrogen by sodium zeolite
According to Figure 3, the process of ammonia nitrogen removal rate changing with adsorption time is divided into two stages: rapid adsorption stage and adsorption equilibrium stage. Within 1 hour of adsorption, ammonia nitrogen in the solution was quickly absorbed, and the removal rate quickly reached 88.67%. After 3 hours, the adsorption equilibrium was reached, and the removal rate reached 91.67%. At this time, the adsorption capacity was 6.49mg/g. At the beginning of adsorption, the ammonia nitrogen concentration in the solution was large and the driving force was strong, so the adsorption rate was fast. With the progress of the reaction, the concentration of ammonia nitrogen in the solution decreases, the mass transfer impetus decreases gradually, and the adsorption rate slows down, reaching a slow equilibrium process [14].

Generally, with the increase of reaction time, the more complete the adsorption reaction, the easier the process to reach adsorption equilibrium[15]. As shown in Figure 4, the adsorption process of lanthanum modified zeolite on phosphorus is different from that of sodium zeolite on ammonia nitrogen, which shows a slow increasing trend. The removal rate and adsorption capacity of phosphorus increased with time. At 12h, the removal rate of phosphorus can reach 99.14% and the adsorption capacity is 6.23mg/g. The zeolite modified by LaCl$_3$ can easily form surface coordination complex with cation and anion, so lanthanum zeolite can absorb ions and ions in water to achieve the purpose of phosphorus removal [16-18].

**Figure 4.** Effects of time on the adsorption of phosphorus by lanthanum zeolite

3.3. Degradation of nitrogen and phosphorus by sodium and lanthanum zeolite respectively

Wastewater from sludge dewatering solutions with ammonia concentration of 50mg/L and phosphorus concentration of 60mg/L were selected. 0.75g of sodium zeolite and 1g of lanthanum zeolite were respectively put into them for adsorption for 12h. The results were compared with the adsorption results in ammonia solution and phosphorus solution as shown in Figure 5.
Figure 5. Effects of sodium and lanthanum zeolite on the removal of ammonia nitrogen and phosphorus

As shown in Figure 5, sodium zeolite has almost no removal capacity for phosphorus in solution, and 0.75g of sodium zeolite can only remove 1.3% phosphorus. The presence of phosphorus in the solution reduced the removal rate of ammonia nitrogen by sodium zeolite from 93.1% to 83.7%, but the presence of ammonia nitrogen did not affect the removal effect of lanthanum zeolite on phosphorus. Zeolite adsorption of ammonia nitrogen is mainly with physical adsorption, ion exchange with inorganic salt to modification of zeolite, the cation can be of natural zeolite in the original cation exchange, changed the internal aperture and cationic type zeolite, thus giving zeolite new ion exchange performance, so sodium zeolite has good adsorption ability to ammonia nitrogen [19]. Zeolite modified by LaCl₃ can greatly improve its phosphorus removal performance, and the phosphorus removal rate of zeolite can reach 99%. It is speculated that after the zeolite is treated with LaCl₃, La³⁺ is adsorbed on the zeolite surface in the form of oxide. In the solution, metal ions on the surface will coordinate with water molecules to form hydrated oxide [20-22]. The zeolite loaded with LaCl₃ has a positive electric group La-OH₂⁺ on its surface, which generates electrostatic attraction with the negatively charged phosphate in the sludge removal water, and generates a complex containing phosphorus to remove phosphorus. The properties of sodium hydroxide were improved to remove the silicon from zeolite structure, thus reducing the Si-Al ratio, but not substantially changing the skeleton structure. The alkali metal cation can also exchange with the cation in zeolite to enhance the ion exchange capacity [23]. Lye pretreatment enables lanthanum zeolite to have a certain adsorption capacity of ammonia nitrogen (67.8%), but its adsorption capacity of ammonia nitrogen in solution is not as good as that of sodium zeolite (93.1%), which may be because lanthanum chloride does exist on the surface and pores of zeolite, blocking the pores of zeolite and reducing its adsorption capacity of ammonia nitrogen.

3.4. Effects of initial mass concentration of phosphorus on adsorption of ammonia nitrogen by sodium zeolite

In order to study the effects of phosphorus initial mass concentration on ammonia nitrogen in sludge removal water adsorbed by sodium zeolite, adsorption experiments were carried out on sludge removal water with different phosphorus concentration. Since the sodium zeolite has almost no removal capacity for phosphorus, and the ammonia nitrogen in the solution does not affect the adsorption of
lanthanum zeolite on phosphorus, the corresponding proportion of lanthanum zeolite is added according to the concentration of phosphorus in the solution to achieve the purpose of phosphorus removal. The curve of removal rate of ammonia nitrogen in solution with the addition amount of sodium zeolite is shown in Figure 6.

![Figure 6. Effects of initial mass concentration of phosphorus on the adsorption of ammonia nitrogen by sodium zeolite](image)

As shown in Figure 6, the removal rate of ammonia nitrogen increases with the increase of sodium zeolite dosage on the whole. Moreover, the lower the initial mass concentration of phosphorus, the greater the change of adsorption degree of sodium zeolite to ammonia nitrogen in the solution. When the dosage of sodium zeolite was less than 0.5g, the results showed that the higher the initial mass concentration of phosphorus, the higher the removal rate of ammonia nitrogen in the solution. This may be because when less sodium zeolite is added, the ammonia nitrogen in the solution cannot be fully absorbed. As more lanthanum zeolite is added to the solution with higher phosphorus content, these lanthanum zeolites will also absorb the ammonia nitrogen in the solution, which increases the removal rate of ammonia nitrogen [24]. When the dosage of sodium zeolite reached 0.75g, ammonia nitrogen in different solutions reached adsorption equilibrium. Afterward, the ammonia nitrogen in the solution was mainly absorbed by sodium zeolite with the increase of sodium zeolite dosage. Due to the ions exchange between phosphate and potassium ions in the solution and sodium zeolite, the nitrogen removal performance of the sodium zeolite is reduced. Therefore, when the adsorption reaches an equilibrium, the adsorption capacity of the sodium zeolite to ammonia nitrogen will decrease with the increase of the phosphorus concentration in the solution [25].

3.5. Effects of mixture ratio of sodium and lanthanum zeolite on simultaneous degradation of nitrogen and phosphorus

In order to achieve the synchronous removal of ammonia nitrogen and phosphorus in sludge removal water, sodium zeolite and lanthanum zeolite were mixed for adsorption, and their mixing ratio was changed. The adsorption results of ammonia nitrogen and phosphorus in solution were shown in Figure 7. As shown in Figure 7, the mixed adsorbents with different ratios of ammonia nitrogen and phosphorus at 50mg/L and phosphorus at 60mg/L have different removal effects on nitrogen and phosphorus by adding 2g mixed modified zeolite to the wastewater from sludge dewatering. When the proportion of sodium zeolite was the largest, the removal effect of phosphorus in the solution was the worst, the removal rate was only 51.2%. With the increase of the proportion of lanthanum zeolite in the adsorbent, the removal rate of phosphorus increased significantly. When the ratio was 4:6, the
removal rate of phosphorus in the solution was 97.5%, and the adsorption of phosphate reached an equilibrium. Afterward, the removal rate of phosphorus no longer changed significantly with the increase of lanthanum zeolite dosage.

It can also be seen from Figure 7 that with the change of the mixture ratio of sodium zeolite and lanthanum zeolite, the removal rate of ammonia nitrogen in the solution does not change much, which is in the range of 80-90%. When the ratio of sodium zeolite was 4:6, the removal rate of ammonia nitrogen reached 89.6%. This may be because lanthanum zeolite has a certain ability to absorb ammonia nitrogen after sodium hydroxide pretreatment. But the adsorption effect is not as good as that of sodium zeolite. Therefore, when the ratio of sodium zeolite added decreases, the removal rate of ammonia nitrogen in solution decreases slightly due to the increase of the ratio of lanthanum zeolite [26]. When the ratio of sodium zeolite to lanthanum zeolite is 4:6, the effect of simultaneous degradation of nitrogen and phosphorus is better.

Figure 7. Effects of mass mixing ratio of sodium and lanthanum zeolite on the removal of ammonia nitrogen and phosphorus

4. Conclusions

(1) The optimal conditions for adsorption of ammonia nitrogen by sodium zeolite: the dosage of sodium zeolite is 7.5g/L, 3h, 30°C, 160r/min, and the removal rate of ammonia nitrogen could reach 92%. The optimal conditions for phosphorus adsorption by lanthanum zeolite: the dosage of lanthanum zeolite is 10g/L, 12h, 30°C, 160r/min, and the phosphorus removal rate could reach 99%.

(2) Sodium zeolite adsorbs ammonia nitrogen quickly, but does not have the ability to absorb phosphorus, and the adsorption capacity of ammonia nitrogen decreases with the increase of phosphorus concentration in the solution. The process of phosphorus adsorption by lanthanum zeolite is slow, and it has certain adsorption effect on ammonia nitrogen.

(3) 2g mixed zeolite was added to the wastewater from sludge dewatering with ammonia concentration of 50mg/L and phosphorus concentration of 60mg/L. When the mass ratio between sodium zeolite and lanthanum zeolite is 4:6, the removal rate of ammonia nitrogen is 89.6% and that of phosphorus is 97.5%, and a better synchronous degradation of nitrogen and phosphorus effect is obtained.
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