

Study of simultaneous adsorption of ammonium and phosphate in waters by La-F4A zeolites prepared from spent FCC catalyst

Chang Liu^a, Zhaofu Qiu^{b*}, Zhaoyang Shan^c, Zhen Yan^d

State Key Laboratory of Environmental Risk Assessment and Control for Chemical Process of Environmental Protection, East China University of Science and Technology, Shanghai 200237, China

Abstract—The problem of resource disposal of massive spent fluid catalytic catalyst needs to be solved urgently. Thus an environmentally friendly, highly efficient and economical cost adsorbent used for nitrogen and phosphorus removal was prepared from spent fluid catalytic catalyst. A novel 4A zeolite adsorbent loaded with lanthanum hydroxide (La-F4A) was prepared by acid leaching pretreatment, alkali fusion roasting hydrothermal and co-precipitation method. And use La-F4A in the study of simultaneous adsorption of ammonia-nitrogen and phosphorus in water. Adsorption experiments were carried out under the condition that the primordial concentrations of PO₄ and NH₄⁺-N were respectively 1 & 10mg/L. La-F4A has an adaptive adsorption ability on NH₄⁺-N and PO₄ in the pH range of 4-9. When the temperature is 298K, the dosage is 1.0 g/L, the contact time is 240 min, and test water pH=7, the maximum adsorption capacities for NH₄⁺-N and PO₄ are 7.64 mg/g and 0.93 mg/g respectively. The behaviours accord with the pseudo-second-order adsorption kinetic model. The adsorption of PO₄ conforms to the Langmuir isotherm model while NH₄⁺-N conforms to the Freundlich isotherm model. Coexisting anions have almost no effect on the adsorption of PO₄, coexisting cations have different inhibitory effects on the adsorption of NH₄⁺-N. After four desorption cycles, the removal efficiency of La-F4A for NH₄⁺-N and PO₄ was 77% and 93% of the initial capacity. There are both chemical adsorption and physical adsorption in the process. The ammonium removal mechanism is the ion exchange between NH₄⁺ and Na⁺ in the framework, and the phosphate removal mechanism is the ligand exchange between PO₄ and hydroxyl to form LaPO₄. La-F4A is regarded to be an excellent adsorbent for ammonium and phosphate removal.

1. Introduction

Fluid catalytic cracking (FCC) is a secondary crude oil processing method for modern refineries to transform heavy oil to light oil. The catalyst used in the FCC process is called FCC catalyst.

With the increasing demand for light oil such as gasoline and diesel, the annual growth rate of FCC catalyst usage is about 3.76%, China's demand is growing even faster¹. This means that more and more deactivated FCC catalysts are being produced. Spent FCC catalysts contain a rich amount of rare earth elements such as cerium and lanthanum (La), as well as heavy metals including iron, vanadium, nickel. Direct discharge not only pollutes the environment but also spends resources². Therefore, it is essential to study the resource utilization of spent FCC catalyst.

In recent years, various methods have been developed to treat and dispose of spent FCC catalyst, including landfilling³, chemical regeneration to remove heavy metals⁴, the recovery of rare earth elements and valuable metals^{5,6}. Another promising method is using them as raw materials for the production of new synthetic materials. Scholars have utilized spent FCC catalyst for the preparation of adsorbents used in the removal of CO₂ and

other gases, and heavy metals such as Ni, Zn, and Cu^{7,8}. It has become a research hotspot, because it not only reduces the cost of new materials, but also reduces the environmental pollution caused by the disposal.

Eutrophication of water bodies refers to the overproduction of organic matter caused by inputs of nitrogen and phosphorus. Water treatment nitrogen and phosphorus removal technologies include chemical precipitation, biological methods, adsorption, membrane separation, electrochemical methods, etc. Adsorption method is often used for low-concentration nitrogen and phosphorus in wastewater due to the simple operation and high removal efficiency. Among various adsorbents, zeolites are widely used in the adsorption of ammonium due to their low price and excellent cation exchange capacity^{9,10}. Lanthanum-based materials have excellent affinity for phosphate. Lanthanum is relatively cheap and environmentally friendly among the rare earth elements^{11,12}. At the same time, the harmless waste FCC catalyst can be used as raw material to prepare adsorbent, but there is no research on efficient simultaneous adsorption of nitrogen and phosphorus, which provides a new idea for its resource utilization.

This study will explore the preparation of high-efficiency ammonium and phosphate removal adsorbent

^ahljmdjlc@163.com, ^b*zfqiu@ecust.edu.cn, ^c834545738@qq.com, ^d3313355241@qq.com

from spent FCC catalyst. Firstly, the spent FCC catalyst was treated harmlessly by acid leaching, and then various conditions for hydrothermal processes of zeolite 4A were optimized respectively. Finally, the particle adsorbent La-F4A was prepared by loading lanthanum hydroxide on the surface. La-F4A was applied to the batch adsorption experiments of ammonium and phosphate to explore its adsorption performance and mechanism, which provided useful reference for the resource utilization of spent FCC catalyst and advanced treatment of nitrogen and phosphorus in tail water.

2. Materials & methods

2.1 Reagents and instruments

The sample of the spent FCC catalyst was supplied by a chemical plant in East China. All the chemical reagents used in the experiment are analytically pure. The experimental water is deionized water.

Instruments: Water bath constant temperature shaker (SHA-C, Benjifei, China), UV-visible spectrophotometer (UV-5500, Benjifei, China), Brunauer-Emmett-Teller surface area and pore analyzer (ASAP 2460, Micromeritics, America), scanning electron microscopy (Regulus 8100, Hitachi, Japan), X-ray diffraction (Mini Flex 600, Rigaku, Japan), X-ray photoelectron spectrometer (K-Alpha, Thermo Scientific, America), Fourier Transform Infrared Spectrometer (Nicolet iS20, Thermo Scientific, America).

2.2 Preparation of adsorbents

For the preparation method of F4A, see the reference13: Screen the spent FCC catalyst sample with a 100-mesh sieve for later use. Weigh 8.0000 g of spent FCC catalyst sample into a 250 mL conical flask, add 100 mL HCl solution with a concentration of 1 mol/L. Shake it in water bath at 75°C and 120 rpm for 8 h, and then regulate pH value to 7.0±0.1. Filter and wash with deionized water for several times, and dry at 105°C for 2 h. Put the dried sample with solid NaOH into agate mortar according to the mass ratio of 1:1.4, ground them evenly and then transfer to crucibles. Roast in muffle furnace at 700°C for 2 h and cool. Transfer to a 150 mL PTFE lined bottle after grinding, and add deionized water at solid-liquid ratio of 1:6. Stir by magnetic force for 1 h to make it mix evenly, and then let it stand at room temperature for 20 h. Transfer to reaction kettles and keep hydrothermal reaction for 10 h at 90°C. Adjust the pH value to 6.5±0.1 after cooling, filter and wash the sample. Finally, dry at 105°C overnight to obtain zeolite 4A, which is named as F4A.

Preparation of La-F4A: Prepare lanthanum chloride (LaCl₃) solutions with mass fractions of 0.04%, 0.08%, 0.12%, 0.16%, 0.20%, 0.40%, 0.60% and 0.80% respectively, adjust the pH value to 10.0±0.2. Add F4A into solutions in the solid-liquid ratio of 1:50, oscillate at 25°C at 200 rpm for 8 h. Filter and wash samples with deionized water for several times, dry at 80°C overnight.

Grind through a 100-mesh sieve to obtain new adsorbents with different mass fractions of La, which are named as x wt.% La-F4A.

2.3 Batch adsorption experiments

According to *GB 18918-2002*, aqueous solution was prepared with ammonium initial concentration of 10 mg/L and phosphate of 1 mg/L as test water, using ammonium chloride (NH₄Cl) and dipotassium phosphate (KH₂PO₄) respectively.

Add 100 mL of test water into a 250 mL erlenmeyer flask, weighing 0.1000 g x wt. % La-F4A and add into test water. Adjust the pH value to 7.0±0.1, oscillate and absorb at 25°C and 200 rpm for 4 h. Filter with 0.45µm after standing, examine contents of NH₄⁺-N and PO₄ in the supernatant respectively. Determine the optimal loading fraction of LaCl₃ according to the test results. Using the same adsorption test method, control test conditions to explore influence of dosage, pH value, coexisting ions on the removal of NH₄⁺-N and PO₄. And fit the adsorption isotherm and kinetic models of La-F4A. After adsorption of NH₄⁺-N and PO₄ in the test water for 4 h, La-F4A was desorbed with 1 mol/L NaOH solution for 10 h. After desorption, La-F4A is subjected to a new adsorption experiment, which is a cycle of regeneration.

The concentration of NH₄⁺-N in the solution was determined according to *HJ 535-2009*. The concentration of PO₄ was determined according to *GB 11893-89*.

3. Results & discussions

3.1 Effect of LaCl₃ mass fraction on adsorption of ammonium and phosphate

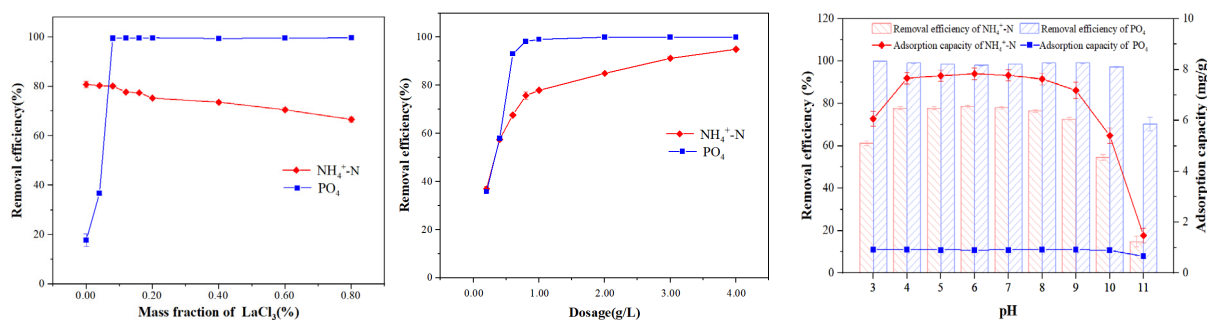
LaCl₃ was used to modify the prepared F4A. In alkaline environment, La(OH)₃ was loaded on the surface of F4A by coprecipitation.

Materials with different LaCl₃ fractions (x wt.% La-F4A) are used to adsorb test waters, where x=0.04%, 0.08%, 0.12%, 0.16%, 0.20%, 0.40%, 0.60%, 0.80%. Their adsorption effect on NH₄⁺-N and PO₄ is shown in Fig.1 (a). When the mass fraction of LaCl₃ is 0.00-0.08%, the removal efficiency of PO₄ rises sharply to over 99.5%, and the removal efficiency of NH₄⁺-N decreases slightly to 80.2%. With the continuing increase of LaCl₃ mass fraction, the removal of PO₄ remained basically stable, while the that of NH₄⁺-N decreased obviously. To sum up, the optimal loading fraction of LaCl₃ should be 0.08%, and it should be used as the adsorbent for the following batch adsorption experiments. For convenience, 0.08 wt.% La-F4A would be simplified as La-F4A.

3.2 Effect of dosage on adsorption of ammonium and phosphate

The curve of removal efficiency with dosage of La-F4A is shown in Fig.1 (b). When the dosage range of La-F4A is 0.20-1.00g/L, the removal rate of PO₄ rapidly rise to above 99.0%, and that of NH₄⁺-N significantly rise to about 77.9%. The removal efficiency of PO₄ and NH₄⁺-N can reach 100.0% and 95.0% by increasing the dosage of La-F4A, but the adsorption capacity will be greatly reduced, which weakens the practical performance of the adsorbent. According to the actual emission standards and the economic costs, the dosage of La-F4A is 1.00 g/L.

3.3 Effect of pH value on adsorption of ammonium and phosphate



(a) Effect of LaCl₃ mass fraction (b) Effect of dosage of La-F4A (c) Effect of pH value of solution
 Fig.1 Effect of different factors on adsorption of NH₄⁺-N and PO₄

3.4 Adsorption kinetics

The time curve and adsorption kinetics of La-F4A adsorbing NH₄⁺-N and PO₄ are shown in Fig.2.

The adsorption of NH₄⁺-N reached 96.8% of the maximum after 10 min. For PO₄, it reached 79.9% of the maximum after 60 min. Their initial adsorption speeds are both fast, and the whole process reaches equilibrium

Table 1 Kinetics parameters for NH₄⁺-N and PO₄ adsorption on La-F4A

Substance	T (K)	Q _e (mg/g)	Pseudo-first order			Pseudo-second order		
			k ₁ (min ⁻¹)	Q _e (mg/g)	R ₁ ² (%)	k ₂ (g/(mg·min) ⁻¹)	Q _e (mg/g)	R ₂ ² (%)
NH ₄ ⁺ -N	298	7.5629	1.4538	7.3995	91.99	0.2536	7.6353	99.99
PO ₄	298	0.9097	0.0869	0.8015	72.60	0.1000	0.9345	99.74

3.5 Adsorption isotherms

The adsorption isotherm results of La-F4A on NH₄⁺-N and PO₄ were shown in Fig.3. Langmuir and Freundlich isotherm models were used to simulate the data, and model constants and correlation coefficients are listing in Table2.

Temperature has little effect on the removal of NH₄⁺-N. The adsorption of PO₄ has a high correlation with

The removal efficiency and adsorption capacity of La-F4A for NH₄⁺-N and PO₄ are affected by pH value as shown in Fig.1 (c).

When the solution pH=3, La-F4A has a maximum adsorption capacity of 0.93 mg/g for PO₄. The adsorption capacity of La-F4A for PO₄ remains above 0.90 mg/g at the pH of 4-9. When pH > 10, the removal efficiency began to decline faster and faster. The removal effect of La-F4A on NH₄⁺-N has a relatively obvious relationship with pH value. Under neutral and weakly acidic conditions, the adsorption capacity is higher, and maximum adsorption capacity of 7.83 mg/g occurs when pH=6. The adsorption capacities of NH₄⁺-N in the pH value range of 4-8 are all higher than 7.60 mg/g. When pH>8, the adsorption capacity of NH₄⁺-N decreased and very quickly. And the adsorption effect of La-F4A on NH₄⁺-N is poor when pH=3.

after about 240 min. The equilibrium adsorption capacity of La-F4A for N and P can reach 7.56mg/g and 0.91mg/g.

The fitting parameters of experimental data are shown in Table 1. The data show pseudo-second-order model has the highest R², and the theoretical number is close to the experimental number, which is more congenial to describe the adsorption behavior.

temperature. The adsorption of PO₄ on La-F4A conformed to the Langmuir isotherm, indicating its single-layer chemical adsorption process. The Freundlich model fitted the adsorption of NH₄⁺-N. The inflection points of the isothermal line indicated that the adsorption of NH₄⁺-N was a multi-layer process, and it was deduced that chemical adsorption and physical adsorption existed simultaneously in the adsorption process.

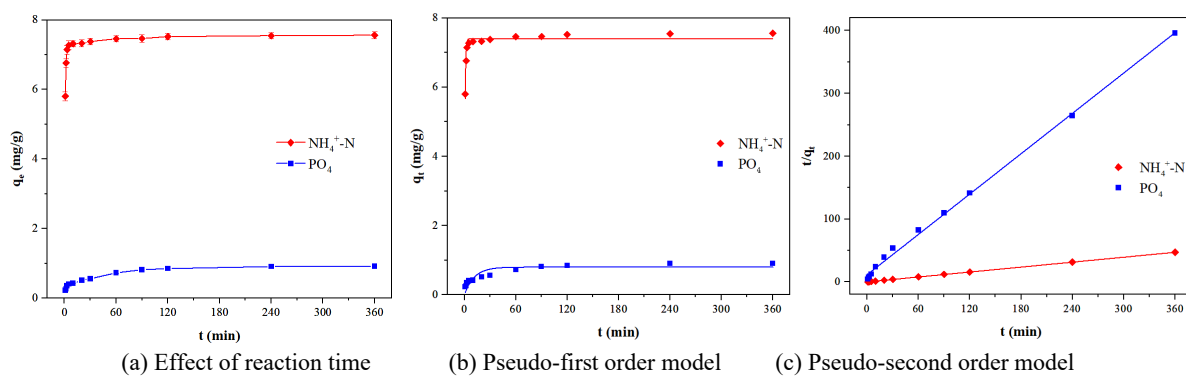


Fig.2 The time curve and adsorption kinetics fitting of $\text{NH}_4^+\text{-N}$ and PO_4

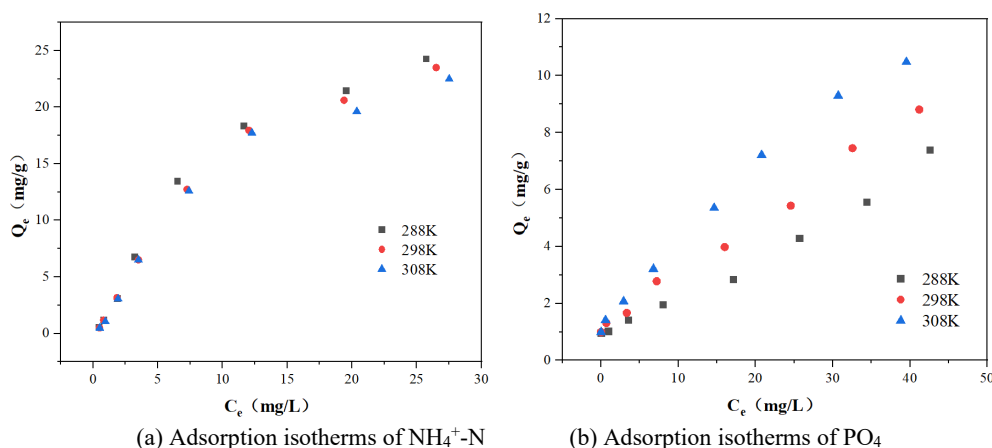


Fig.3 Adsorption isotherms of $\text{NH}_4^+\text{-N}$ and PO_4 on La-F4A

Table 2 Estimated isotherm parameters for $\text{NH}_4^+\text{-N}$ and PO_4 adsorption on La-F4A

substance	T(K)	Freundlich			Langmuir		
		n	$K_F(\text{mg/g})$	$R^2(\%)$	$q_m(\text{mg/g})$	$K_L(\text{L/mg})$	$R^2(\%)$
$\text{NH}_4^+\text{-N}$	298	1.1502	0.0870	99.79	12.3988	0.0053	99.61
	308	1.1753	0.0905	99.64	10.1098	0.0066	99.57
	318	1.1839	0.0907	99.75	9.4509	0.0070	99.69
substance	T(K)	Freundlich			Langmuir		
		n	$K_F(\text{mg/g})$	$R^2(\%)$	$q_m(\text{mg/g})$	$K_L(\text{L/mg})$	$R^2(\%)$
PO_4	298	1.2678	0.1327	99.73	8.2088	0.0107	99.66
	308	1.2880	0.1492	99.67	8.0197	0.0122	99.95
	318	1.2561	0.1550	99.45	9.5773	0.0111	99.92

3.6 Effect of coexisting ions on adsorption of ammonium and phosphate

The effects of common cations on $\text{NH}_4^+\text{-N}$ adsorption and common anions on PO_4 adsorption were studied. The concentration of ions was set at 1 mmol/L and 10 mmol/L. The effect of coexisting ions is shown in Fig.4 (a)&(b).

The existence of anions has almost no interference on the adsorption of PO_4 , while SO_4^{2-} promotes the removal

of PO_4 to some extent, which indicates the high selectivity of lanthanum-loaded adsorbent for PO_4 . The existence of cations inhibited the adsorption of $\text{NH}_4^+\text{-N}$, with the effect of $\text{Ca}^{2+} > \text{K}^+ > \text{Na}^+ > \text{Mg}^{2+}$. These cations exchanged with some sites of La-F4A and formed the competition with $\text{NH}_4^+\text{-N}$. The ion concentration in the practical secondary effluent can't meet the test concentration, so La-F4A can be applied to the advanced treatment of ammonia nitrogen.

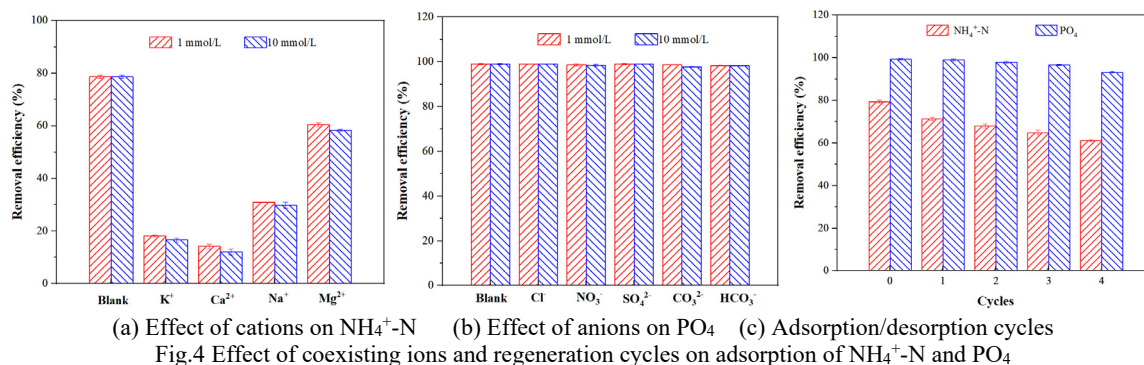


Fig.4 Effect of coexisting ions and regeneration cycles on adsorption of $\text{NH}_4^+\text{-N}$ and PO_4

3.7 Desorption and regeneration of La-F4A

In theory, phosphate can be dissolved from the LaPO_4 solid phase under strongly basic conditions ($\text{pH}>13$)¹⁴. Four cycles of adsorption/desorption experiments were carried out on La-F4A and its reusability is shown in Fig.4 (c).

After four cycles of regeneration, the removal efficiency of PO_4 and $\text{NH}_4^+\text{-N}$ are 93.8% and 77.0% of the initial adsorption capacity. It shows that most adsorption sites can be regenerated, and adsorption and desorption are mutually reversible processes. La-F4A is a promising adsorbent.

3.8 Mechanism of ammonium and phosphate adsorption

Various characterization methods were used to analyse the adsorbents.

The N_2 adsorption-desorption experiments were carried out on commercial zeolite 4A (Myriel, China), F4A and La-F4A synthesized in the experiment. The BET surface areas (S_{BET}) the total pore volume (V_{tot}) of commercial zeolite 4A were $51.64 \text{ m}^2/\text{g}$ and 0.0264

cm^3/g . The S_{BET} of F4A and La-F4A were $528.12 \text{ m}^2/\text{g}$ and $751.80 \text{ m}^2/\text{g}$ respectively, while the V_{tot} were $0.5074 \text{ cm}^3/\text{g}$ and $0.7028 \text{ cm}^3/\text{g}$ respectively. The S_{BET} and V_{tot} of F4A and La-F4A are increased by dozens of times compared with commercial zeolite 4A, which is beneficial for the target pollutants to adhere or enter, indicating the excellent adsorption performance. The S_{BET} and V_{tot} of La-F4A are higher than F4A, proving that the introduction of La can effectively improve the physical and chemical properties of the adsorbents.

The XRD patterns of spent FCC catalyst, F4A and La-F4A were shown in Fig.5 to study their crystal structures. The metals in catalyst mainly exist in form of metal oxides, and most of them exist in the amorphous phase. The main mineral components are SiO_2 and Al_2O_3 , with a small amount of La_2O_3 and Ce_2O_3 . F4A and La-F4A both showed obvious characteristic peaks of zeolite 4A, which indicated that the loading modification process of LaCl_3 basically did not affect the structure. F4A did not show the characteristic peaks of lanthanum-related compounds, which proves that La had been leached. La-F4A did not show either, which may be due to uneven distribution on the surface, or may exist in the amorphous state.

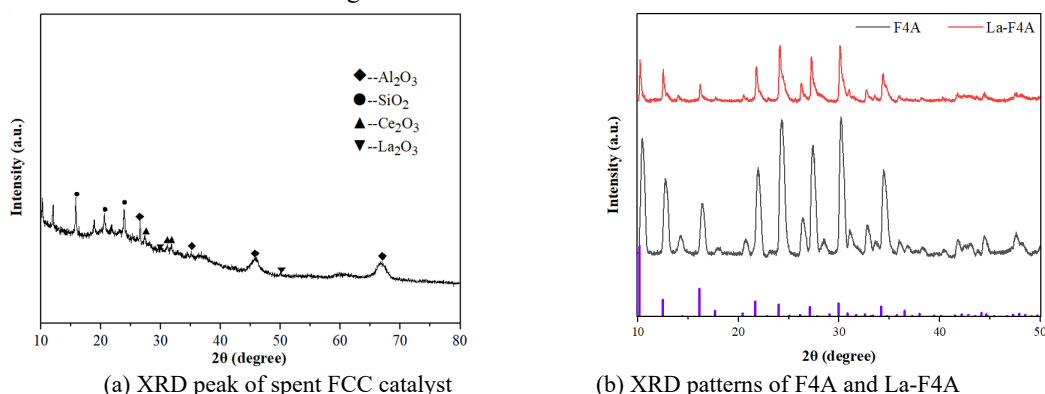
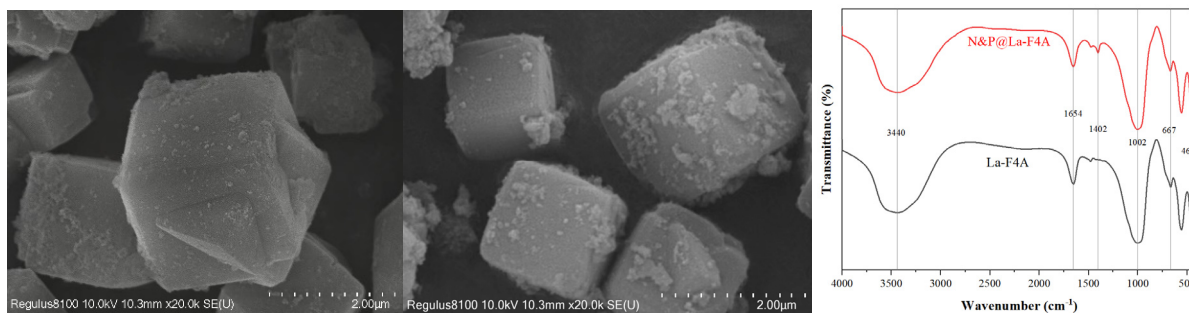


Fig.5 The XRD patterns of different materials

Fig.6 (a)&(b) shows the surface morphology of F4A and La-F4A, respectively. Particle surface of F4A is relatively flat and smooth, while the surface of La-F4A is covered with a misty layer and after loading $\text{La}(\text{OH})_3$. It is judged that lanthanum is loaded on the surface of F4A

in amorphous state, verifying the XRD results. There are a lot of debris attached to the surface of La-F4A, which may be caused by the crushing of particles during oscillation and grinding.

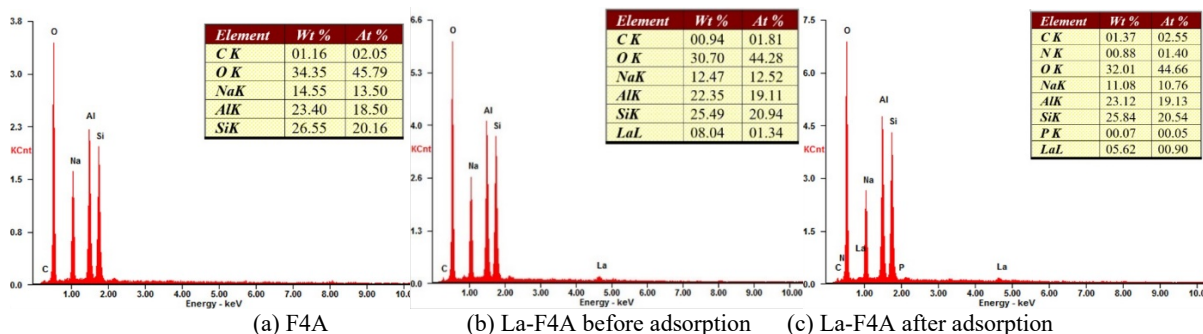


(a) The SEM image of F4A (b) The SEM image of spent La-F4A (c) The FT-IR spectrum
 Fig.6 Surface morphology photographs and FT-IR spectrum of F4A and La-F4A

The FT-IR spectra of La-F4A with and without adsorbing $\text{NH}_4^+\text{-N}$ and PO_4 was shown in Fig.6 (c). The peaks at 3440cm^{-1} and 1654cm^{-1} respectively represent the stretching vibration and bending vibration of O-H bond, showing that there are a lot of hydroxyl groups on the surface of La-F4A. 1002cm^{-1} is the antisymmetric stretching vibration of Si-O-Al. 667cm^{-1} is the symmetric stretching vibration of T-O (Si or Al). 465cm^{-1} stands for the bending vibration of Si-O. 560cm^{-1} corresponds to the double-ring vibration of molecular sieve. All above shows that the material has the structure of A-type zeolite. After adsorption, peak of N-H bending vibration emerged at 1402cm^{-1} . It shows that $\text{NH}_4^+\text{-N}$ is mainly transferred to La-F4A by chemical adsorption. There was no new peak of phosphorus-bond after adsorption, which

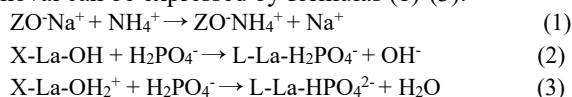
indicated that PO_4 only adheres to the surface of La-F4A, and did not enter the pores.

Energy-dispersive X-ray spectroscopy (EDS) showed the elements of the adsorbents in Fig.7. There was no La in F4A, while the peak of La was obviously observed in La-F4A, which proved that La was successfully loaded on the surface of F4A. After adsorption, a small amount of N and P elements exist in La-F4A. The content of Na in La-F4A before adsorption is equivalent to the total content of Na and N after adsorption, indicating that the mechanism of ammonium adsorption may be the exchange between Na^+ and NH_4^+ . The content of La decreased obviously after adsorption, which might be due to the reaction with PO_4 to generate LaPO_4 precipitate, which fell off the surface of La-F4A.



(a) F4A (b) La-F4A before adsorption (c) La-F4A after adsorption
 Fig.7 The EDS spectra and element distribution of the adsorbents

Possible mechanisms of ammonium and phosphate removal can be expressed by formulas (1)-(3).



4. Conclusions

To sum up, the conclusions of this study are as follows:

(1) In this study, F4A was prepared from spent FCC catalyst by alkali melting-hydrothermal method. La-F4A was prepared by coprecipitation with $\text{La}(\text{OH})_3$, which showed a high adsorption capacity for ammonium and phosphate.

(2) Adsorption was rapid within 1h and met equilibrium in 4h. The maximum adsorption capacity of La-F4A were 7.64 mg/g for $\text{NH}_4^+\text{-N}$ and 0.93 mg/g for PO_4 at 25°C . La-F4A had a wide application range

(pH=4-9) in the field of nitrogen and phosphorus removal.

(3) The adsorption behavior of $\text{NH}_4^+\text{-N}$ and PO_4 conformed to the pseudo-second order kinetic model. The adsorption of PO_4 was fitted with Langmuir isotherm model while $\text{NH}_4^+\text{-N}$ matched Freundlich isotherm model.

(4) Coexisting anions had little effect on the adsorption of PO_4 . Coexisting cations had competitive effects on the adsorption of $\text{NH}_4^+\text{-N}$. After four cycles of adsorption/desorption, La-F4A still retained high adsorption capacity for $\text{NH}_4^+\text{-N}$ and PO_4 .

(5) There are both chemical adsorption and physical adsorption in the process. The removal mechanism of PO_4 is the ligands exchange with $\text{La}(\text{OH})_3$ to generate LaPO_4 . The removal mechanism of NH_4^+ is ion exchange with Na^+ in La-F4A skeleton.

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