Performance of Nitrogen and Phosphorus Removal in Petrochemical Wastewater by Zeolited Fly Ash

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Abstract. The zeolitized fly ash was synthesized by alkali melt hydrothermal method. The cation exchange capacity of zeolitized fly ash was far greater than the raw material fly ash. The main component was NaP1 zeolite (Na$_6$Al$_6$Si$_{10}$O$_{32}$·12H$_2$O), followed by mullite, and a small amount of heterozygous crystals. The effect of synthetic zeolite dosage, pH value, adsorption time and reaction temperature on the effect of nitrogen and phosphorus removal in petrochemical wastewater were investigated. The results showed that when the zeolitized fly ash dosage was 9 g/L, the petrochemical wastewater pH value was 6~8, adsorption time was 30 min and the reaction temperature was 30℃, the synthetic zeolite had the best effect on the removal of TN and TP in petrochemical wastewater, and the removal was 65.5%, 91.4% respectively. Besides, the concentrations of TN and TP in the effluent were 11.04 mg/L, 0.31 mg/L respectively. The concentrations met the sewage discharge standard in petrochemical industry of "Liaoning sewage comprehensive discharge standard" (DB21 1627-2008). This study was to realize the comprehensive utilization of solid waste and achieve the purpose of waste and waste.

1. Introduction
As a byproduct of coal combustion, coal fly ash was a major solid waste of coal-fired power plants$^{[1-2]}$. Generally, combustion of 4 t coal could produce 1 t fly ash$^{[3]}$. According to statistics, in 2015, production of fly ash in China was about 540 million t, but the utilization rate was less than 40%.$^{[4]}$ In the northern heating season of China, the production of fly ash produced by the thermal power plant was large, and the construction project was in a stop state at this time$^{[5]}$. A large number of fly ash could not be utilized rationally, and secondary pollution such as dust would be generated.

Due to the similar composition of fly ash and zeolite, Holler$^{[6]}$, first used fly ash to synthesize zeolite molecular sieve by hydrothermal activation method Otala found that the adsorption capacity of fly ash zeolite was better than natural zeolite$^{[7]}$. Synthetic zeolite was widely used in environmental protection field, such as remove the heavy metal ions$^{[8]}$ and radioactive substances$^{[9]}$ in the sewage or sludge, separating the SO$_x$, CO$_x$ and volatile Hg$^{[10-11]}$, capture CO$_2$ from the atmosphere$^{[12]}$. The research of zeolitized fly ash in the simultaneous removal of nitrogen and phosphorus from wastewater was mainly focused on simulated wastewater and removal og ammonia and phosphorus. Therefore, it is necessary to expand the research on simultaneous removal of nitrogen and phosphorus by zeolitized fly ash in actual wastewater.

In this paper, the zeolitized fly ash was synthesized by alkali melt hydrothermal method. The effect of synthetic zeolite dosage, pH value, adsorption time and reaction temperature on the effect of
nitrogen and phosphorus removal in petrochemical wastewater were investigated. It provided technical support for the comprehensive utilization of fly ash.

2. Materials and methods

2.1. Experimental materials
The fly ash was taken from a thermal power plant in Shenyang. The petrochemical wastewater was taken from the effluent of aeration tank in PetroChina Fushun Petrochemical Company. The total nitrogen (TN) content was 32 mg/L, the total phosphorus (TP) content was 3.6 mg/L, and the pH value was 7.6.

2.2. Synthesis of zeolite from fly ash
Alkali melt-hydrothermal synthesis [15]: Put the fly ash in the oven at 105 °C for 6 h, cooled to room temperature, sifted 80 mesh screen, and put in the dryer. Got fly ash and NaOH with mass ratio of 1:1.2, pulverized after mixing, put them in the resistance furnace at 600 °C for 1.5 h, and cooled to room temperature. The melt and distilled water were mixed with 17.25% solid liquid and stirred evenly. Put the mixture in a 80 °C water bath with a magnetic stirrer for 2 h and 200 r/min, and then took them out and put them in a reaction kettle, which was put on the oven at 105 °C. 6 h later, the reaction kettle was taken out, and the crystallization products were centrifuged after cooling. Washed the crystallization products until the supernatant pH reached about 7~9. The obtained solid was dried for 24 h in the 105 °C oven, sifted 100 mesh screen and placed in the dryer.

2.3. Influence factors of nitrogen and phosphorus removal
The effect of synthetic zeolite dosage (3, 5, 7, 9, 11, 13, 15, 17 g/L), pH value (3~11), adsorption time (5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60 min) and reaction temperature (10, 15, 20, 25, 30, 35, 40, 45, 50 °C) on the effect of nitrogen and phosphorus removal in petrochemical wastewater were investigated. Repeated three times for each group, then average values were obtained.

2.4. Index determination
Analysis of crystalline components: D/max-RB X ray diffractometer of Japan Rigaku Corporation was used, and the detection conditions were Cu target, Kα1 ray, 40 kV, 40 mA, graphite monochromator, Si solid detector, the scanning rate of 2 °/min, the scanning angle range of 10°~70°.
Cation exchange capacity (CEC, cmol/kg): Mixed 5 g zeolitized fly ash with 100 mL ammonium acetate solution which concentration was 1 mol/L. Put them in rocking bed at 30 °C and 150 r/min for 24 h, and then centrifuged 10 min at 5000 r/min. The supernatant was extracted with ammonia nitrogen distillation titration method [16] to determine the concentration of NH₄⁺, and the cation exchange capacity was calculated.
The total nitrogen content was determined by the People's Republic of China environmental protection standard "water quality - total nitrogen determination, alkaline potassium persulfate digestion and ultraviolet spectrophotometry" (HJ 636-2012). The total phosphorus content was determined by the People's Republic of China environmental protection standard "water quality - determination of phosphate and total phosphorus, continuous flow ammonium molybdate spectrophotometry" (HJ 670-2013).

3. Results and discussion

3.1. Characterization of fly Ash and its synthetic products
The main component of fly ash used in this study: SiO₂ was 47.41%, Al₂O₃ was 23.19%, Fe₂O₃ was 8.51%, CaO was 3.63%, TiO₂ was 2.01%, MgO was 1.06%, Na₂O was 0.85% and the loss of ignition was 2.33%. According to the stipulation of "fly Ash used in cement and concrete" (GB/ T 1596-2005).
Total content of SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$ in fly ash was ≥70%, belonged to Class F. It was low calcium fly ash and had pozzolanic activity.

The XRD pattern of fly ash is shown in Fig. 1(a). The main crystal of fly ash used in this study was quartz and mullite containing silicon and aluminum, and the rest was amorphous phase. The XRD pattern of zeolited fly ash is shown in Fig. 1(b). The main composition of zeolite synthesized from fly ash was NaP1 zeolite (Na$_6$Al$_6$Si$_{10}$O$_{32}$·12H$_2$O), followed by mullite, and a small amount of heterocrystals.

The CEC results showed that the CEC values of fly ash and zeolited fly ash were 7.89 cmol/kg and 232 mol/kg, respectively. The cationic exchange capacity of NaP1 zeolited fly ash was much larger than that of raw material fly ash, and its material structure had changed, which could be used as adsorption material in water treatment [13].

![XRD pattern of fly ash(a) and zeolited fly ash(b)](image-url)

**Fig. 1 XRD pattern of fly ash(a) and zeolited fly ash(b)**

### 3.2. Zeolite dosage
Effect of zeolitized fly ash dosage on the removal of TN and TP was shown in Fig. 2. The removal rates of TN and TP increased significantly when the dosage of zeolited fly ash was less than 7 g/L. When the dosage reached 9 g/L, the removal rates of TN and TP were basically stable, which were 64.9% and 90.8%, respectively. At this time, the concentrations of TN and TP in effluent water were 11.23 mg/L and 0.33 mg/L, respectively.

![Effect of zeolitized fly ash dosage on the removal of TN and TP](image-url)

**Fig. 2 Effect of zeolitized fly ash dosage on the removal of TN and TP**

### 3.3. Wastewater pH value
Effect of pH value on the removal of TN and TP in petrochemical wastewater was shown in Fig. 3. When the pH value of petrochemical wastewater was 6 ~ 8, the nitrogen and phosphorus removal rate was better, and reached the maximum when pH was about 8, which was 66.4% and 90.9%, respectively. The concentrations of TN and TP in effluent were 10.75 mg/L and 0.33 mg/L, respectively. When pH < 5 and pH > 9, the removal rate of nitrogen and phosphorus decreased.
significantly. It can be seen that the zeolited fly ash was suitable for the treatment of neutral alkaline petrochemical wastewater. Since the initial pH value of petrochemical wastewater used in this study was 7.6, it could not be adjusted in subsequent experiments and practical applications.

Fig. 3 Effect of pH value on the removal of TN and TP in petrochemical wastewater

3.4. Adsorption time
Effect of adsorption time on the removal of TN and TP in petrochemical wastewater was shown in Fig. 4. When the adsorption time was within 20 min, the removal rate of TN and TP in petrochemical wastewater increased significantly with the increase of adsorption time. As the adsorption time continued to increase, the removal rate of TN and TP did not increase significantly. When the adsorption time reached 30 min, the removal rate of TN and TP was basically stable, which were 63.4% and 89.5%, respectively. At this time, the concentrations of TN and TP in the effluent were 11.71 mg/L and 0.38 mg/L, respectively.

Fig. 4 Effect of adsorption time on the removal of TN and TP in petrochemical wastewater

3.5. Reaction temperature
Effect of reaction temperature on the removal of TN and TP in petrochemical wastewater was shown in Fig. 5. When the reaction temperature was below 25°C, the removal rate of TN and TP in the petrochemical wastewater increased with the increase of the reaction temperature. As the reaction temperature continues to increase, the removal rate of TP tended to be stable, while the removal rate of TN decreased gradually at the reaction temperature of 40°C. When the reaction temperature was 30°C, the removal rate of TN and TP in petrochemical waste water was better, which removal rate was 65.5% and 91.4%, respectively. At this time, the concentrations of TN and TP in the effluent were 11.04 mg/L and 0.31 mg/L, respectively, which met the industry of "Liaoning sewage comprehensive discharge standard" (DB21 1627-2008) Discharge Standards for Sewage in Petrochemical Industry (TN≤15 mg/L, TP≤0.5 mg/L) [17]. Under the same conditions, the removal rate of TN and TP in
petrochemical waste water was 43.1% and 67.3%, respectively. The concentrations of TN and TP in the corresponding effluent were 18.21 mg/L and 1.18 mg/L, respectively.

![Graph](image)

**Fig. 5** Effect of reaction temperature on the removal of TN and TP in petrochemical wastewater

### 4. Conclusions

The main composition of zeolite synthesized from fly ash by alkali melting hydrothermal method was NaP1 zeolite ($Na_6Al_6Si_{10}O_{32}·12H_2O$), followed by mullite, and a small amount of heterocrystalline. The cation exchange capacity of synthetic zeolite was much larger than that of raw material fly ash, and its material structure had changed, so it could be used as adsorption material in water treatment.

The effect of zeolited fly ash dosage, pH value, adsorption time and reaction temperature on the effect of nitrogen and phosphorus removal in petrochemical wastewater were investigated. The results showed that when the zeolitized fly ash dosage was 9 g/L, the petrochemical wastewater pH value was 6–8, adsorption time was 30 min and the reaction temperature was 30℃, the synthetic zeolite had the best effect on the removal of TN and TP in petrochemical wastewater, and the removal was 65.5%, 91.4% respectively. Besides, the concentrations of TN and TP in the effluent were 11.04 mg/L, 0.31 mg/L respectively.

Zeolited fly ash was used for synchronous nitrogen and phosphorus removal in petrochemical wastewater. The concentrations met the sewage discharge standard in petrochemical industry of "Liaoning sewage comprehensive discharge standard" (DB21 1627-2008). This study was to realize the comprehensive utilization of solid waste and achieve the purpose of waste control by waste.

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