Research Article

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Study on the removal of high contents of ammonium from piggery wastewater by clinoptilolite and the corresponding mechanisms

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Abstract: In this study, a clinoptilolite was applied to remove ammonium from piggery wastewater. The performance of ammonium removal and the correspondingly mechanisms were discussed. Under the optimal conditions of clinoptilolite dosage of 12 g/L, solution pH value of 8.3, shaking speed of 280 rpm and contact time of 55 min obtained by using response surface methodology (RSM), 19.7 mg of ammonium can be adsorbed onto 1 g of clinoptilolite, which was declined when metal cations were presented in the piggery wastewater. The ammonium adsorption process by the clinoptilolite can be well fitted by Langmuir isotherm with a spontaneous nature and pseudo-second-order kinetics model. Furthermore, column study showed that to some extent, the increased flow rate was beneficial to the removal of ammonium, and the ammonium adsorption capacity of clinoptilolite in column study was much higher than those in batch study.

Keywords: Clinoptilolite; Piggery wastewater; Ammonium; Response surface methodology (RSM).

1 Introduction

High contents of ammonium have been caused seriously water pollution and threatened human health, and hence, prevention of nitrogen pollution is now required [1,2]. Among the widely used processes for ammonium removal, the biological method has provided an effective solution [3,4]. However, biological systems were only effective in treating wastewater with low concentration of ammonium, especially lower than 100 mg/L [5,6]. Therefore, development of effective processes toward to the removal or recycling of high contents of ammonium is necessarily. In last decades, ion exchange processes were gaining on interests in the treatment of wastewaters that contained high contents of ammonium. In the application of ion exchange in actual projects, zeolites that abundantly presents in nature, were the preferred inorganic cation exchangers, which has been considered as an efficient and cost competitive in commercial plants for the removal of ammonium [7,8]. There were more than 50 known naturally occurring zeolites all over the world, in which clinoptilolite has been reported as the most abundant one which can be used to remove ammonium [9].

Many factors affected ammonium from the piggery wastewater by using clinoptilolite, including clinoptilolite dosage, solution pH, shaking speed and contact time. In general, an appropriate combination of these factors was needed to increase ammonium removal rate, and optimization was usually done in most studies by changing the single factor while all other factors remain the same. Since the interaction between the factors was neglected, it cannot achieve an accurate exactly optimal value. To solve this problem, Response Surface Method (RSM), a statistical technique that used to build multivariate equations and evaluate their optimal values, can provide a better alternative to traditional methods because it included the effects of multiple factors and the interaction between their roles [10].

Objective of this study is to evaluate the performance of clinoptilolite for ammonium removal from the piggery wastewater by batch and column systems. Response surface methodology (RSM) was used to search the optimum conditions of ammonium removal. Kinetic models and adsorption isotherms mechanisms were
discussed. Furthermore, a column study was conducted to discuss the effect of flow rate and initial ammonium concentration on clinoptilolite exchange, and the regeneration of clinoptilolite.

2 Materials and Methods

2.1 Materials

The clinoptilolite for ammonium removal was purchased from Jingyun Mining Plant, Zhejiang province, China. The ores are high silica zeolites while the contents of harmful elements (Mn and Ti) are low. Chemical composition (in %) of the clinoptilolite were: SiO$_2$=65.10, Al$_2$O$_3$=12.00, Na$_2$O=1.79, CaO=2.03, K$_2$O=6.55, MgO=0.13, Loss of ignition=10.20. Particle size of the clinoptilolite was in the range of 0.3-0.6 mm, and the specific external area was 157.17–191.50 m$^2$/g.

2.2 Wastewater quality

The aqueous solution used here was digested swine wastewater supplied by a pig farm at Zhengzhou, Henan province, China. Concentrations of chemical oxygen demand (COD), ammonium, total phosphorus (TP) and suspended solid (SS) of this solution were 1425, 844, 26 and 200 mg/L, respectively.

2.3 Batch study for ammonium removal

Effects of clinoptilolite dosage, solution pH, contact time and initial ammonium concentration on ammonium removal from piggery wastewater were investigated according to the following experiments methods: a glass beaker (1 L) was placed on a six-breaker jar tester in which 1 L of piggery wastewater was poured and then a given dosage of clinoptilolite was added. The mixture was mixed with an agitation speed of 300 rpm for 10 min and allowed to rest 30 min. The supernatant was collected and analyzed to determine remaining ammonium concentration.

The amount of adsorbed ammonium by clinoptilolite ($q_e$) and the removal rate of ammonium ($\eta$) were calculated according to the following equations:

$$q_e = \frac{V(C_0 - C_e)}{m}$$  \hspace{1cm} (1)

$$\eta = \frac{C_0 - C_e}{C_0} \times 100\%$$  \hspace{1cm} (2)

where $C_0$ and $C_e$ are the initial and final ammonium concentrations (mg/L), respectively. $V$ is the piggery wastewater volume (L) and $m$ is clinoptilolite weight (g).

2.4 RSM experimental design

In the RSM, central composite design (CCD) was selected to design the experiments, in which clinoptilolite dosage ($x_1$), solution pH ($x_2$), initial ammonium concentration ($x_3$), contact time ($x_4$) and shaking speed ($x_5$) were selected as the influence parameters, and the ammonium adsorbed ($q_e$) was selected as the response variable ($y$). Their relationship was fitted by a second–order model as Eq.(3) and the actual design ran by the statistic software, Design–expert 8.0.5 is given in Table S1.

$$y = \beta_0 + \sum_{i=1}^{m} \beta_i x_i + \sum_{i<j}^{m} \beta_{ij} x_i x_j + \sum_{i=1}^{m} \beta_{ii} x_i^2$$  \hspace{1cm} (3)

2.5 Adsorption kinetic, isotherm and thermodynamic data analysis

Pseudo-first-order, pseudo-second-order and intraparticle diffusion models were used to discuss the kinetic characteristics of ammonium adsorption by clinoptilolite, which were described in [11]. Freundlich, Langmuir and Tempkin isotherm models were used to discuss the isotherm characteristics of ammonium adsorption by clinoptilolite, which were described in [12]. Thermodynamic data such as $\Delta$Ho, $\Delta$Go and $\Delta$So can be obtained from Langmuir constants and determined according to [13].

2.6 Column study

Column tests were carried out using a Polymethylmethacrylate (PMMA) column whose inner diameter was appeared as 20 mm. The bed with 20 cm and 60 cm$^3$ in height and volume was filled with the clinoptilolite. Column tests were designed to discuss the removal of ammonium under different flow rate and initial ammonium concentration. The piggery wastewater was pumped to the clinoptilolite column by up–flow at rates 3, 6, and 9 BV/h by using a peristaltic pump. Solution samples from the column exit were collected to determine
the remained ammonium level. HCl was chosen as the regeneration solution to regenerate the clinoptilolite column by down–flow mode after ammonium adsorption. After the regeneration finished, another loading cycle was then carried out.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

3.1 Ammonium removal using natural clinoptilolite

As seen from Figure S1, ammonium adsorbed onto unit of clinoptilolite ($q_e$) was increased rapidly with the increasing clinoptilolite dosage and reached to a peak of 18.6 mg/g when clinoptilolite dosage was 15 g/L, and correspondingly, ammonium removal rate was reached 33.1%. Increasing clinoptilolite dosage continuously had negative effects on the increase of $q_e$, which may be attributed to the great concentration pressure at equilibrium [16].

The existing form of ammonium, $NH_4^+$ and $NH_3$, affected the performance of clinoptilolite in ammonium removal, which was depend on the pH values of the wastewater [15,16]. In this study, Figure S2 showed that $q_e$ increased gradually with the increasing pH value of the piggery wastewater, and reached a maximum value of 18.2 mg/g at pH point of 8. When pH value was above 9, $q_e$ declined and ammonium removal rate dropped dramatically, which can be explained by the fact that ammonium was converted into “free” ammonia ($NH_3$), which can not be exchanged. At the pH value below 6, hydrogen ions (H$^+$) concentration raises with the decreasing pH, which increased the competition for exchange sites with $NH_4^+$, which caused a decline of $q_e$ [17].

Figure S3 depicted $q_e$ by clinoptilolite as functions of contact time. A rapid increase was observed within the first 30 min, followed which a slow increase trend was observed in contact time range of 30-60 min, and a plateau was seen at in contact time range of 60-120 min. That is to say, the adsorption equilibrium is reached after just a short time. This may be caused by fast diffusion of ammonium from the wastewater phase to the external surface of the clinoptilolite, followed which, the pore diffusion into the intraparticle structure and active sorption sites to attain equilibrium were occurred [18].

As seen from Figure S4, $q_e$ increased gradually and reached its balance of 18.3 mg/g eventually with the increasing initial ammonium concentration, which is a result of the increasing driving force to the surface sorption. For lower initial ammonium concentrations, equilibrium time was lower. This may be because of the increased competition for exchange sites with the increasing initial ammonium concentration [18].

Figure S5 revealed that there was a significant reduction in $q_e$ from 19.4 to 6.7, 9.1, 11.4 and 12.8 mg/g, respectively, when 160 mg/L of Ca$^{2+}$, Mg$^{2+}$, K$^+$ and Na$^+$ were presented in the piggery wastewater, which may be due to the competition of these cations with $NH_4^+$ for exchange sites in clinoptilolite. There was another phenomenon that after completion of ammonium adsorption, the compositions of Mg$^{2+}$ and Ca$^{2+}$ in clinoptilolite were declined, which may be due to the ion exchange between $NH_4^+$ and Mg$^{2+}$/Ca$^{2+}$ [19]. Thus, ammonium removal by clinoptilolite was mainly carried out by the ion exchange reaction:

$$NH_4^+ + Zeolite \rightarrow (Ca^{2+}, Mg^{2+}) + Zeolite + NH_3$$

(4)

Due to the strong affinity of the clinoptilolite to Na$^+$ and K$^+$, the above reaction would be taken place from right to the left, when the concentration of Na$^+$ and K$^+$ in wastewater increased, thereby lead to the decline of ammonium uptake. Researchers have reported that the order of the effect of cations on ammonium removal is Ca$^{2+}>Mg^{2+}>Na^+>K^+$ [20].

3.2 Optimization of ammonium removal conditions by RSM

Following equation represents empirical relationship between $q_e$ ($y$) and the influence parameters ($x_1-x_5$).

$$y = 24.6 - 3.34x_1 + 1.12x_2 - 0.04x_3 + 0.21x_4 + 3.67x_5$$
$$+ 0.62x_1x_2 + 10.24x_1x_5 + 2.49x_2x_3 - 11.45x_3x_5$$
$$- 1.19x_4x_5 + 5.43x_1x_4 + 3.96x_2x_5$$
$$- 2.97x_3x_4 - 6.79x_1x_3 + 1.75x_5x_3$$
$$- 8.45x_1^2 + 1.21x_2^2 - 0.46x_3^2 + 5.98x_4^2 - 5.69x_5^2$$

(5)

Statistical testing of this model was performed with the Fisher’s statistical method for analysis of variance (ANOVA). Results showed that the above model was significant at 95% confidence level because ‘Prob>F<0.05 and $F_{\text{statistic}}>2.57$. In addition, the value of $R^2$ of 0.8933 displayed that only 11.67% of the total variation was not explained by the above model.

Results of the significance testing for the coefficient of the above model were summarized in Table 1. In linear
terms, shaking speed and clinoptilolite dosage were significant. Clinoptilolite dosage was significant due to the pore adsorption and ion exchange for ammonium. Shaking speed was significant due to its contribution to the mixing of clinoptilolite in piggery wastewater [21]. The quadratic of pH was the significant higher order terms, because the pH value determines the state of ammonia nitrogen, $\text{NH}_4^+$ in acidic environment and $\text{NH}_3$ in strong alkaline environment (pH>10). Three interaction terms were pH value and clinoptilolite dosage, initial ammonium concentration and clinoptilolite dosage, shaking speed and clinoptilolite dosage.

Figure 1a showed that when the contact time, shaking speed and the initial ammonium concentration are kept at central level, the clinoptilolite was positive effective on ammonium removal in alkaline environment. Figure 1b showed that when the pH, contact time and shaking speed are at central level, the ammonium adsorption can get to an anticipant value at a low clinoptilolite dosage when initial ammonium concentration was lower than 500 mg/L approximately. Higher ammonium concentration provided stronger driving force for ammonium which occupies the cations sites on the effective pores of clinoptilolite [22]. Figure 1c showed that shaking was beneficial to the removal of ammonium by clinoptilolite, while ammonium removal became difficult when the shaking speed was kept at a high level.

According to the target that 100% of ammonium can be removed by the clinoptilolite, the optimal condition was calculated as: clinoptilolite of 12 g/L, pH value of 8.3, initial ammonium concentration of 420 mg/L, contact time of 55 min and shaking speed of 280 rpm. Under this condition, $q_e$ was appeared as 19.7 mg/g, and the corresponding ammonium removal rate can be calculated as 56.3%.

**Table 1:** Coded levels for five variables framed by the Central Composite Design.

| Independent variables | Regression coefficients | Degrees of freedom | Standard error | Prob > F |
|-----------------------|-------------------------|--------------------|----------------|---------|
| $x_1$                 | 0.04008                 | 1                  | 0.70           | <0.0001 |
| $x_5$                 | 10.8234                 | 1                  | 0.70           | 0.0047  |
| $x_1x_2$              | 1.5330×10^{-3}          | 1                  | 1.41           | 0.0291  |
| $x_1x_3$              | 4.3000×10^{-3}          | 1                  | 1.41           | 0.0131  |
| $x_1x_5$              | -2.2857×10^{-3}         | 1                  | 1.41           | 0.0245  |
| $x_5^2$               | -0.8649                 | 1                  | 0.95           | <0.0001 |

**Figure 1:** Significant interaction terms for ammonium removal by clinoptilolite: (a) pH-Clinoptilolite, (b) Clinoptilolite-Initial ammonium concentration, (c) Shaking speed-Clinoptilolite.
Table 2: Significance of quadratic model coefficient of ammonium adsorbed ($q_e$).

| Kinetic models          | Parameters | $q_e$ (mg/g) | $R^2$  |
|-------------------------|------------|--------------|--------|
| **Pseudo-first-order**  |            |              |        |
| Initial concentration (mg/L) | 200 0.0041 | 11.76        | 0.7887 |
|                         | 400 0.0072 | 14.38        | 0.7621 |
|                         | 600 0.0084 | 16.62        | 0.6869 |
|                         | 800 0.0161 | 19.94        | 0.8101 |
|                         | 1000 0.0198| 19.93        | 0.7244 |
| Temperature (°C)        |            |              |        |
|                         | 25 0.0046  | 18.98        | 0.8845 |
|                         | 35 0.0033  | 18.11        | 0.8758 |
|                         | 45 0.0031  | 16.93        | 0.8523 |
| pH                      |            |              |        |
|                         | 5 0.0037   | 18.66        | 0.8311 |
|                         | 8 0.0083   | 18.94        | 0.8993 |
|                         | 11 0.0074  | 15.59        | 0.8746 |
| agitation speed (rpm)   |            |              |        |
|                         | 100 0.0044 | 18.57        | 0.9214 |
|                         | 200 0.0049 | 18.28        | 0.8876 |
|                         | 300 0.0071 | 18.96        | 0.8343 |
| **Pseudo-second-order** |            |              |        |
| Initial concentration (mg/L) | 200 0.0028 | 14.95        | 0.9962 |
|                         | 400 0.0047 | 17.34        | 0.9974 |
|                         | 600 0.0059 | 20.17        | 0.9978 |
|                         | 800 0.0133 | 25.05        | 0.9993 |
|                         | 1000 0.0137| 22.93        | 0.9992 |
| Temperature (°C)        |            |              |        |
|                         | 25 0.0047  | 22.55        | 0.9964 |
|                         | 35 0.0045  | 22.32        | 0.9877 |
|                         | 45 0.0037  | 20.97        | 0.9699 |
| pH                      |            |              |        |
|                         | 5 0.0046   | 19.83        | 0.9989 |
|                         | 8 0.0108   | 22.51        | 0.9963 |
|                         | 11 0.0057  | 21.95        | 0.9977 |
| agitation speed (rpm)   |            |              |        |
|                         | 100 0.0034 | 22.21        | 0.9924 |
|                         | 200 0.0046 | 22.53        | 0.9932 |
|                         | 300 0.0062 | 22.98        | 0.9966 |
3.3 Adsorption kinetics

Table 2 summarized the fitting results of pseudo-first and second-order models toward to the ammonium adsorption process by clinoptilolite. The higher initial ammonium concentration, the higher $k_1$ and $k_2$ values, the higher adsorption capacity. In addition, $k_1$ and $k_2$ decreased with the increasing temperature, the decreasing pH and the decreasing agitation speed. The correlation coefficient values ($R^2$) of the pseudo–first–order model lower than 0.90 indicating a poor description of the ammonium adsorption process. On the contrary, $R^2$ of the pseudo–second–order model higher than 0.95 and the very closely data between the calculated and the experimental $q_e$, confirmed that the process of ammonium adsorption by clinoptilolite could be well described by the pseudo–second–order kinetic model [23]. From Table 3, the higher initial ammonium concentration, the higher diffusion rate of ammonium into clinoptilolite, due to the driving force brought by initial ammonium in piggery wastewater [24], while shaking speed has the opposite effect.

Researches on intraparticle diffusion models showed that the process of ammonium adsorbed onto clinoptilolite mainly occurred both onto external surface of the clinoptilolite and inside its particles [24]. Figure 2 showed that the first step line with high slopes ($t^{1/2}$ ranged in 0-9.49 min$^{1/2}$) was the external surface adsorption, the second step line with lower slopes ($t^{1/2}$ ranged in 9.49-14.49 min$^{1/2}$) represented the intraparticle diffusion, and the third step line with null slope ($t^{1/2}$ ranged in 14.49-18.97 min$^{1/2}$) may be attributed to the process of ammonium adsorbed onto exchangeable sites in clinoptilolite. All in all, Figure 2 depicted that the intraparticle diffusion model fitted the ammonium adsorption well and there was a fast external surface adsorption followed by slow intraparticle diffusion [25,26].

3.4 Adsorption isotherms

From Table 4, $q_m$ calculated using Langmuir isotherm model was found to be 29.1 mg/g at 25°C, higher than the 12.3 mg/g by Chilean natural zeolite and 25.8 mg/g by Turkish zeolite [27,28]. The $R_L$ values were found between 0 and 1 confirmed that the adsorption of ammonium by the clinoptilolite is propitious, thus, the clinoptilolite was a potential ion-exchanger for ammonium removal. The Freundlich and Tempkin parameters were also presented in Table 4.

In summary, the ammonium removal process by clinoptilolite can be best fitted by the Langmuir isotherm ($R^2$ values at different temperature were all higher than 0.9). For the Freundlich isotherm, on the one hand, the clinoptilolite has a homogeneous surface with a uniform distribution of heat of adsorption over the surface, on the other hand, $R^2$ values at different temperature were all lower than 0.90, so it was not well fitted [23]. For Tempkin isotherm, $R^2$ values at different temperature were the lowest (below 0.90), so it was also not well fitted.
3.5 Thermodynamics

Thermodynamic parameters were calculated from Langmuir constant under different temperature conditions (25, 35, and 45°C), and summarized in Table 5. The negative $\Delta G^o$ showed the spontaneous in nature of the ammonium adsorption. The negative $\Delta H^o$ showed the exothermic in nature. The negative $\Delta S^o$ showed the decreased randomness at the solid–liquid interface during ammonium adsorption by clinoptilolite. The higher temperature, the more negative the $\Delta G^o$, $\Delta H^o$ and $\Delta S^o$, the more energetically favorable adsorption.

3.6 Ion exchange mechanisms

After completion of ammonium adsorption, the cations contents of clinoptilolite were detected. From Figure 3, compared to the raw clinoptilolite, the compositions of Mg$^{2+}$ and Ca$^{2+}$ were decreased, indicated that Ca$^{2+}$ and Mg$^{2+}$ were the main exchangeable ions. At low ammonium concentrations, the compositions of Mg$^{2+}$ in solid phase decreased rapidly in the adsorption process, meaning that Mg$^{2+}$ played an important part in ion exchange. When initial ammonium increased, the compositions of Ca$^{2+}$ in the solid phase decreased rapidly and replaced Mg$^{2+}$ gradually as a major role in ion exchange.

According to the ion exchange fundamentals [19], ammonium ions transferred from wastewater phase onto clinoptilolite through ion exchange process can be expressed by Eq.(6):

$$Zolite - M^{m+} + nNH_4^+ \leftrightarrow Zolite - nNH_4^+ + M^{m+}$$

where $M$ represented exchangeable ions and $n$ was electric charge number.

Assuming that Ca$^{2+}$, Mg$^{2+}$, Na$^+$ and K$^+$ were the mainly exchangeable cation in clinoptilolite, the ion exchange capacity (IEC) can be defined as their sum as Eq.(7):

$$IEC = [N^+] + [K^+] + 2[Ca^{2+}] + 2[Mg^{2+}] = [NH_4^+]$$

Figure 4 showed the variation of equivalent concentrations of Mg$^{2+}$, Ca$^{2+}$, Na$^+$ and K$^+$ in piggery wastewater with different initial ammonium. The equilibrium ion exchange capacity (IEC) of 1.67 meq/g was almost equal to the ammonium adsorption capacity, indicated that ion exchange played leading role in ammonium removal. The theoretical ion exchange capacity (TIEC) can achieved 2.86 meq/g if all of the alkaline–earth cation in clinoptilolite were replaced, higher than the actual value of 1.67 meq/g, indicated that there were about 58% of the exchangeable sites were available for ammonium removal. Figure 4 also

| T (°C) | $k_L$ (L/mg) | $q_m$ (mg/g) | $R^2$ | $R_t$ | $k_f$ (mg/g) | $1/n$ | $R^2$ | $K_t$ (L/mg) | RT/b | $R^2$ |
|--------|---------------|---------------|--------|--------|---------------|--------|--------|--------------|------|--------|
| 25     | 0.018         | 29.09         | 0.9109 | 0.287  | 0.071         | 0.921  | 0.7937 | 4.21         | 0.8173 | 0.7852 |
| 35     | 0.023         | 28.14         | 0.9831 | 0.271  | 0.079         | 0.973  | 0.8438 | 3.48         | 0.8521 | 0.8419 |
| 45     | 0.035         | 27.36         | 0.8783 | 0.264  | 0.082         | 0.944  | 0.8572 | 2.77         | 0.8734 | 0.8326 |

Table 5: Kinetic constants of Film and Particle diffusion models.

| T (K) | $\Delta G^o$ (kJ/mol) | $\Delta H^o$ (kJ/mol) | $\Delta S^o$ (kJ/mol) |
|-------|------------------------|------------------------|------------------------|
| 298   | -20.47                 | -121.62                | -0.339                 |
| 308   | -21.66                 | -124.84                | -0.335                 |
| 318   | -23.39                 | -127.38                | -0.327                 |
showed that the exchange order of alkaline-earth cations in the clinoptilolite for ammonium is \( \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+ \), slightly different from that reported in [29], may be due to the difference in chemical compositions of tested zeolites. Exchange equivalent capacity of \( \text{Mg}^{2+} \) was 38%–54% at different initial ammonium, which was 37%–49% of \( \text{Ca}^{2+} \) and 3%–8% of \( \text{Na}^+ \) and \( \text{K}^+ \), indicated that \( \text{Mg}^{2+} \) and \( \text{Ca}^{2+} \) were the dominant cation which can effectively exchanged with \( \text{NH}_4^+ \), while the strong affinity of clinoptilolite to \( \text{Na}^+ \) and \( \text{K}^+ \) by the clinoptilolite made their exchange performances poor [2].

Table 6 listed the comparison of the equivalences of adsorbed ammonium and released exchangeable cations. In ammonium removal, if ion exchange is the only way, the equivalence of the cations released into piggery wastewater should be equal to that of the ammonium adsorbed by clinoptilolite. However, there was about 14–26% excess equivalence of ammonium was appeared, indicated that both ion exchange and adsorption were involved in ammonium removal by clinoptilolite.

### 3.7 Column study

#### 3.7.1 Effect of flow rate and initial ammonium on clinoptilolite exchange

Figure S6 proved a general reverse connection between \( q_e \) and initial flow rate. It can be observed that the higher the flow rate, the lower ammonium concentration of the samples collected from the column exit. The increasing flow rate caused a decreasing retention time, which further resulted in less ammonium removal [2]. Furthermore, the capacity of clinoptilolite in column study was much higher than that in batch study. Take the flow rate of 9 BV/h as example, the amount of ammonium absorbed by the clinoptilolite reached to 24.8 mg/g. As seen from Figure S7, it was found that the \( q_e \) was enhanced with the increasing initial ammonium, which reached its peak at initial ammonium of 700 mg/L. The reason was listed in section 3.1 (Figure S4).

#### 3.7.2 Regeneration

Various representative eluents such as distilled water, 0.2 mol/L HCl and NaCl were selected for desorption of the saturated clinoptilolite, after desorption for 2 h, there were 5.2%, 88.4% and 99.4% of adsorbed ammonium can be desorbed by distilled water, NaCl (0.2 mol/L) and HCl (0.2 mol/L), respectively. As seen from Table S2, the adsorption efficiency decreased slightly with the increasing cycle times. Furthermore, to the best of our knowledge, desorption time was the most important factor for ammonium desorption from the saturated clinoptilolite, and it can be concluded from desorption kinetics of amount of ammonium desorbed against contact time. The desorption process was completed very rapidly and more than 90% of adsorbed ammonium could be desorbed within 30 min, indicated that the clinoptilolite in this study can be regenerated easily and used circulating.

### 4 Conclusion

This study provided an ammonium removal method from piggery wastewater adsorption/ion exchange by clinoptilolite. The adsorption of ammonium by clinoptilolite was a fast process, who establishes
its equilibrium within 60 min. When the dosage of clinoptilolite was adjusted to 15 g/L, the ammonium adsorbed onto unit mass of clinoptilolite \( q_e \) achieved to the peak value of 18.6 mg/g, which was declined when metal cations were presented in the piggery wastewater. Under the optimal conditions obtained by RSM that clinoptilolite dosage of 12 g/L, solution pH value of 8.3, shaking speed of 280 rpm and contact time of 55 min, theoretical value of \( q_e \) can reach 19.7 mg/g. Column study demonstrated that the clinoptilolite in this study can be regenerated easily and used circulating.

**Conflict of Interest:** All of the authors declare that they have no conflict of interest.

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