

Original Research

# Nitrogen and Phosphate Recovery from Source-Separated Urine by Dosing with Magnesite and Zeolite

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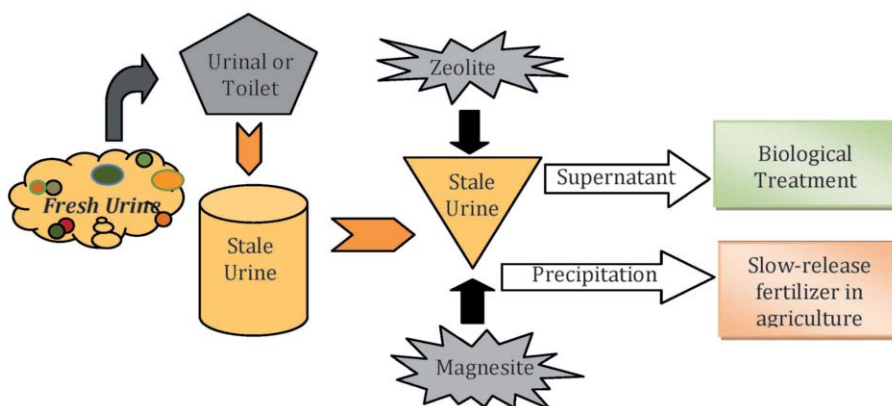
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## Abstract

There is increasing interest in source separation and treatment of urine so as to recover nitrogen and phosphate more efficiently than treating combined wastewater. Although previous studies primarily focused on struvite precipitation for the recovery of phosphorus, the composition of urine changes during storage. The present study compared the precipitation conditions for fresh urine and hydrolyzed urine. The optimal conditions for struvite crystallization were obtained from orthogonal experiment and single-factor optimization. The pH of fresh urine should be adjusted to around 9.5-10.0 to make the reaction thorough, while this was unnecessary for hydrolyzed urine. To reduce cost, magnesite was selected as an alternative for pure MgO, which presented similar efficiency for phosphate recovery. About 92.4% of phosphorus and 87.2% of ammonia-nitrogen were recovered from urine when adding 2.5 g/L of magnesite and 375 g/L of zeolite to get struvite crystals and nitrogen-rich zeolite as a slow-release fertilizer.

## Graphical Abstract



**Keywords:** urine, struvite, orthogonal experiment, zeolite, adsorption

## Introduction

Recent studies have shown that urine separation systems have many advantages over conventional combined wastewater collection system regarding nutrient recovery and pollutant emissions [1]. For example, nitrogen and phosphorous can be recovered to reduce the nutrient load and alleviate the eutrophication situation of accepting waters. It reports that about 80% of the nitrogen, 50% of the phosphate, and 60% of the potassium from domestic wastewater emanates from urine [2]. Ammonium or urea is the indispensable component of fertilizer, which can be acquired from urine [3, 4].

Phosphate and ammonia-nitrogen in wastewater can be simultaneously recovered by struvite formation, and the precipitate can be used directly as slow release fertilizers in agricultural production to ease the problem of the shortage for phosphate rock resources [5, 6]. Hanhoun et al. [7] suggested that the method of struvite crystallization precipitation can replace other biochemical technology for phosphate removal and have an application prospect.

However, phosphate recovery was highly associated with pH, the molar ratio of Mg:N:P, and reaction time in the solution [8], which may also be affected by the characteristics of wastewater. Actually, urea hydrolysis occurred due to the presence of urease-positive bacteria in toilets and wastewater collection systems, thus the composition of urine changes accordingly [9]. During transportation and storage, urea is hydrolyzed to ammonium and bicarbonate ions, leading to a significant increase of ammonium concentration. To investigate the joint effects of these parameters on struvite formation, an orthogonal test and further comparison between the fresh urine and hydrolyzed urine was carried out in the present study.

Furthermore, the removal rate of ammonia-nitrogen in the struvite precipitation process is limited, and such a high concentration of ammonia-nitrogen in the remaining solution is difficult to be handled via traditional biological processes. Zeolite showed high adsorption capacity for ammonia-nitrogen [10]. Thus it can be used as an adsorbent to further decrease the N content in the effluent. Meanwhile, adding nitrogen-rich zeolite will have a significant effect of improving fertilizer utilization. However, the applications of zeolite for ammonia removal were mostly adopted in wastewater with relatively low levels of ammonia. The adsorption properties of hydrolyzed urine with a high level of ammonia-nitrogen needs to be investigated.

Therefore, the objectives of this study are as follows:

- 1) to optimize the dosing ratio of magnesium and operating conditions,
- 2) to investigate the properties of zeolite adsorption for a high level of ammonia-nitrogen,
- 3) to testify the synchronous recovery efficiency for phosphate and ammonium.

Table 1. Composition of synthetic human fresh urine.

Salt	Concentration/ (g·L <sup>-1</sup> )	Concentration/ (mmol·L <sup>-1</sup> )
CaCl <sub>2</sub>	0.44	(Ca <sup>2+</sup> ) 4
MgCl <sub>2</sub> ·2H <sub>2</sub> O	0.52	(Mg <sup>2+</sup> ) 4
NaCl	4.8	-
Na <sub>2</sub> SO <sub>4</sub>	2.34	(SO <sub>4</sub> <sup>2-</sup> ) 16
Na <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> ·2H <sub>2</sub> O	0.65	(C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> <sup>3-</sup> ) 2.3
Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	0.02	(C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> ) 0.15
Creatinine	1.1	-
KH <sub>2</sub> PO <sub>4</sub>	2.72	(PO <sub>4</sub> <sup>3-</sup> ) 20
KCl	1.5	-
NH <sub>4</sub> Cl	1	(NH <sub>4</sub> <sup>+</sup> ) 19
Urea	25	-

## Material and Methods

### Synthetic Fresh Urine and Hydrolyzed Urine

Synthetic human fresh urine was prepared according to conventional urological methods [11], whose compositions are presented in Table 1. To get the hydrolyzed urine, the fresh urine was diluted five-fold with deionized water and added 5 g/L urease. Fresh urine represented urine composition before urea hydrolysis and precipitation having occurred naturally, while hydrolyzed urine represented urine composition following complete urea hydrolysis and spontaneous precipitation due to associated pH. When completely hydrolyzed, the pH of hydrolyzed urine was approximately 8.37, and the concentration of ammonia-nitrogen and phosphate were 90 mmol/L and 3.54 mmol/L, respectively.

### Experiment Design

#### Phosphate Recovery Experiment

As presented in Table 2, factors selected for the orthogonal experiment (L<sub>9</sub>) were pH, n<sub>Mg</sub>:n<sub>p</sub>, and reaction time. Then, each factor was optimized separately based on the results of the orthogonal experiment. All the tests were carried out using hydrolyzed urine in beakers containing 400 mL solution with varying conditions and shaken by a rotational speed of 200 rpm. 5 mol/L NaOH and 1 mol/L HCl solutions were used to adjust pH. MgO was selected as the precipitate agent. The mixture of solid and liquid were separated by centrifuge, following struvite precipitation tests conducted using the orthogonal experiment. After precipitation, the supernatants were analyzed for pH, total phosphorus (TP), and ammonia-nitrogen (NH<sub>4</sub><sup>+</sup>-N) concentrations.

Table 2. Results of orthogonal test for phosphate recovery.

No.	Factor level			PO <sub>4</sub> <sup>3-</sup> -P
	pH	n <sub>Mg</sub> :n <sub>P</sub>	Reaction time/(min)	Recovery/%
1	9	1.0	20	89.6
2	8	1.8	20	84.3
3	7	1.8	30	52.3
4	7	1.4	20	43.2
5	9	1.8	10	80.6
6	7	1.0	10	20.1
7	9	1.4	30	96.7
8	8	1.0	30	81.5
9	8	1.4	10	62.8

### Ammonia-Nitrogen Removal Experiment

Firstly, different amounts of zeolite (20-40 mesh), i.e., 125 g/L, 250 g/L, 375 g/L, 500 g/L, and 750 g/L were dispersed into 400 mL NH<sub>4</sub>Cl solution (0.1 mol/L ammonia-nitrogen) with magnetic stirring for ammonia-nitrogen adsorption experiment to investigate the characteristics of sorption. The adsorption capacity for ammonia (Eq. 1) was calculated as follows:

$$q_t = V(C_0 - C_t)/m \quad (1)$$

...where  $q_t$ : adsorption capacity, mg/g;  $C_0$ : the initial concentration of ammonium, mg/L;  $C_t$ : the solution of ammonium in  $t$  reaction time, mg/L;  $V$ : the volume of solution, L; and  $m$ : the dosage of zeolite in reaction, g.

Secondly, batch mode adsorption isotherm and kinetic studies were carried out at 35°C. Water samples containing 10, 100, 250, 500, 1000, and 1500 mg/L of ammonia-nitrogen were prepared for adsorption isotherm experiment. An amount of 25 g/L zeolite was introduced into conical flasks. The flasks were placed in a constant temperature oscillator at a rotational speed of 200 rpm for 48 h to achieve sorption equilibrium. And then approximately 375 g/L of zeolite was weighed for adsorption kinetic experiment. Three kinetic models (Eq. 2-4) were used to evaluate the sorption process, i.e. pseudo-first order, pseudo-second order, and intra-particle diffusion. The sample was placed in a 400 mL solution with 0.1 M ammonia-nitrogen. The solution was stirred at 200 rpm. Then the solution was filtered using a 0.45 μm filter membrane and the concentrations of ammonia-nitrogen in the filtered solution were measured.

The pseudo-first order model [12, 13]:

$$\ln(q_e - q_t) = \ln q_e - k_1 \cdot t \quad (2)$$

The pseudo-second order model:

$$t/q_t = 1/k_2 \cdot q_e^2 + t/q_e \quad (3)$$

The intra-particle diffusion model:

$$q_t = k_i \cdot t^{1/2} \quad (4)$$

### Synchronous Recovery of P and N

According to the optimum conditions of phosphate recovery gained in the above study, the hydrolyzed urine was diluted and dosed with untreated magnesite, which was carried out in beakers containing 400 mL solution at a rotational speed of 200 rpm. After 30 min the determined amount of zeolite was applied in the same beaker to adsorb the remaining ammonia-nitrogen. The mixture of solid and liquid was separated and analyzed as described above.

### Analytic Methods

The suspension pH was measured with pH meter (Five Easy Plus FE20, METTLER TOLEDO, Switzerland). The phosphate content of the liquid was determined by the molybdenum blue/stannous chloride method. The ammonia-nitrogen was analyzed by the Nessler reagent spectrophotometric method. The precipitation containing struvite was filtered through 0.45 μm filter film. To check the formation of struvite crystals, the obtained precipitates were dried at 35°C for 48 h and then analyzed by X-ray diffraction (XRD, Bruker D8 Advance diffractometer with Cu Kα1 radiation, λ = 1.5406 Å), operated at 40 kV and 40 mA (scanning step: 0.02°/s).

## Results and Discussion

### Experimental Condition Optimization for Phosphate Recovery

#### Orthogonal Experiment

The phosphate recovery in this study was based on the formation of struvite, the orthogonal table L<sub>9</sub> was designed, and nine groups of experiments were conducted with the results shown in Table 2. Previous research has also investigated the influencing factors for struvite precipitation. Ryu et al. [14] demonstrated that struvite precipitation was highly pH dependent and the optimum reaction for phosphate recovery was observed at pH 10.0. Uysal et al. [6] obtained a high purity of struvite precipitation with n<sub>Mg</sub>:n<sub>P</sub> in the range of 0.78-1.78. In the present tests, the highest phosphate recovery of 96.7% was achieved under conditions of pH, n<sub>Mg</sub>:n<sub>P</sub> and reaction times were 9, 1.4, and 30 min, respectively. In addition, to get the most significant factor in the struvite precipitate tests, an analysis of variance was applied, as shown in Table 3 [15, 16]. F value is used to represent the impact of corresponding factor and a higher value shows a statistically significant effect. Herein, pH was the most significant factor affecting the phosphate recovery rate, which corresponded to the previous studies [15, 16]. While the influence of n<sub>Mg</sub>:n<sub>P</sub> was less than reac-

Table 3. Variance analysis for orthogonal test.

Factor level	Sum of squares (type III)	df	Variance	F	Sig.
pH	4,125.3	2	2,062.6	1,199.2	0.001
$n_{Mg}:n_P$	113.2	2	56.6	32.9	0.030
Reaction time	837.9	2	419.0	243.6	0.004
Deviation	3.4	2	1.7	-	-

$$R^2 = 0.997$$

tion time, it is different from the previous study, which presented that phosphate recovery was highly associated with  $n_{Mg}:n_P$  rather than reaction time [17]. This might be related to the difference in phosphate concentrations.

#### Single Factor Optimization

To validate the results of orthogonal experiments, three further tests with respective factors were conducted with all other conduction factors fixed at those determined at optimum. Fig. 1a shows the phosphate recovery first increased but slowly decreased with the pH increasing. When the initial pH was set at 8.0 and 9.0, the phosphate recovery rates were 93.8% and 96.2%, respectively. pH was associated with the ionic form of  $PO_4^{3-}$ ,  $NH_4^+$ , and  $Mg^{2+}$  in the reaction.  $PO_4^{3-}$  mainly existed in the form of  $H_2PO_4^-$  at a lower pH, while  $NH_4^+$  can be easily converted into free ammonia under alkaline pH. Moreover, the experiment results agreed with the theoretical calculation proven by Wu et al. [18], in which the solubility of struvite crystals is higher in acidic solution and lower at pH between 8.0 and 11.0, while the solubility of struvite will increase again when  $pH > 11.0$ . When the hydrolyzed urine was diluted for 5-fold, a steady pH range of 8.3-8.5 could be reached, which was close to the optimum pH required for struvite precipitation. Therefore, taking the economic aspect into consideration as well, further pH adjustment would be unnecessary in the subsequent struvite precipitation process. It was beneficial

to reduce additional costs and achieve the goal for phosphate recovery.

Fig. 1b shows the effect of different reaction times on  $PO_4^{3-}$ -P recovery. It demonstrated that the phosphate recovery increased slightly as time increased, and finally was greater than 98.3% after 25 min reaction time. In addition, Fig. 2a shows that the corresponding characteristic peak of struvite crystals in the sediment was acuter and peak width was narrower when the reaction time extended from 10 min to 30 min. According to the Scherrer equation:

$$D = R\lambda / \beta \cos\theta \quad (5)$$

...where  $D$  is the crystallite size in the direction perpendicular to the lattice planes, which increases gradually and the crystalline gets better with the decrease of  $\beta$ , where  $\beta$  is the half width at half-maximum of the X-ray diffraction peak in radians. Previous studies illustrated that nucleation and nuclei growth were the two processes in the formation of struvite crystals [19]. Fig. 2 displays the characteristic peaks of struvite occurring after 10 min and was getting higher as time extended. It indicated the struvite precipitation crystalline was better as time passed [20, 21]. To promote the growth of struvite crystals, the optimal reaction time was extended to appropriately 30 min.

Fig. 1c shows the phosphate recovery rate could reach close to 90% when  $n_{Mg}:n_P$  was 1:1. It was further confirmed that the ratio of  $n_{Mg}:n_P$  had little effect on phosphate recovery.

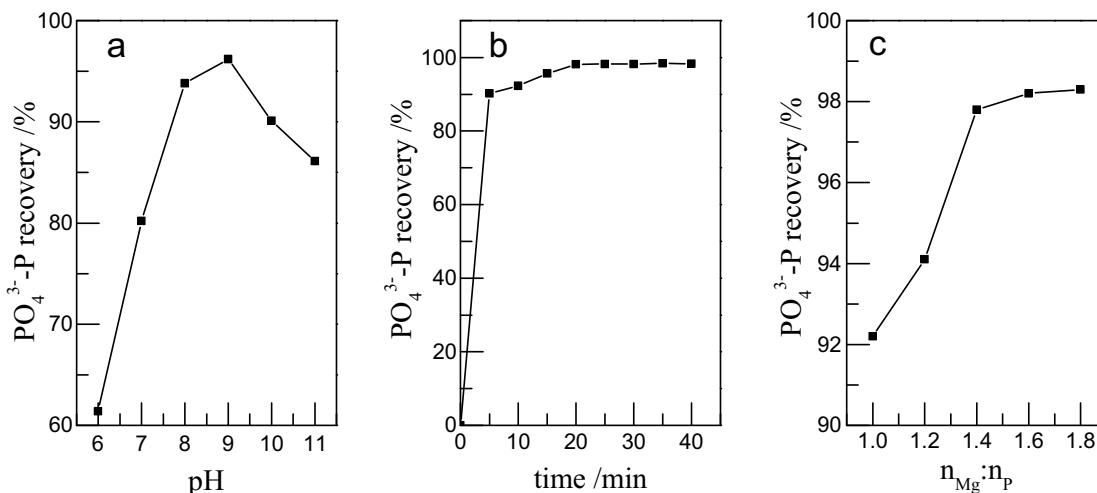


Fig. 1. Influence of the single factor for  $PO_4^{3-}$ -P recovery rate: a) pH, b) reaction time, and c)  $n_{Mg}:n_P$ .

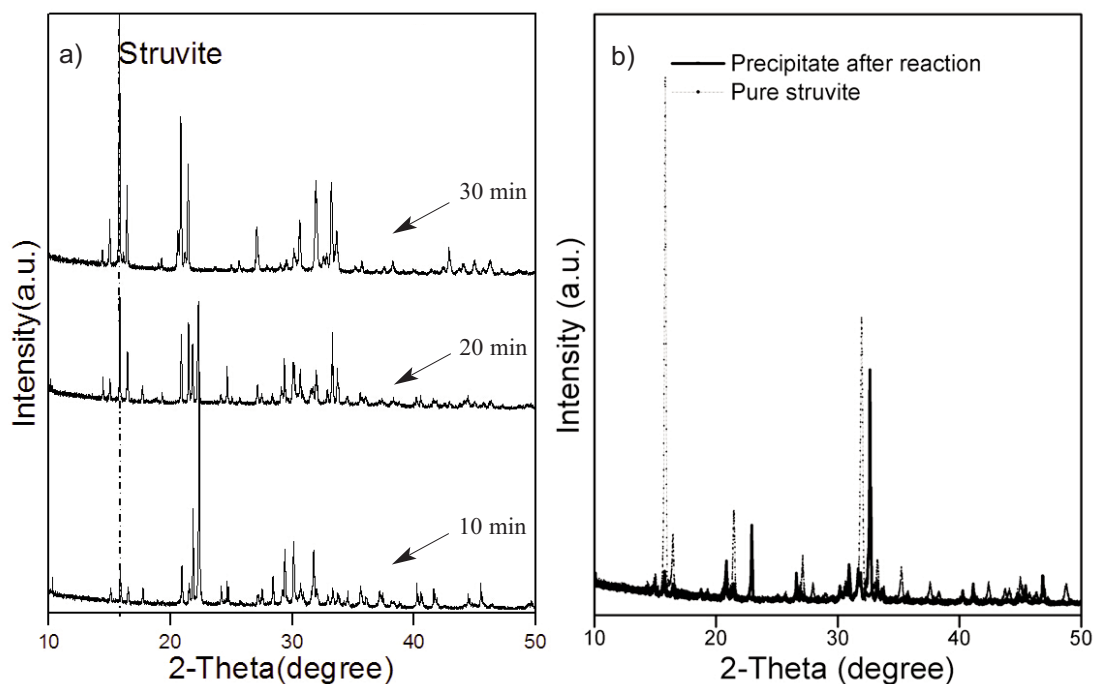


Fig. 2. a) X-ray Diffractograms (XRD) of sediment in different reaction times, and b) XRD of precipitate and pure struvite.

Considering the utilization of Mg-source, the ratio of  $n_{Mg}:n_p=1.4:1$  was chosen for optimum operating conditions.

#### Ammonia Sorption by Zeolite

Fig. 3 shows ammonia-nitrogen adsorption by adding different amounts of zeolite. It indicates that the equilibrium absorption capacity of zeolite reduced from 11.0 mg/g to 4.9 mg/g when increasing zeolite from 125 g/L to 750 g/L. The maximum adsorption rate was found to be 0.26 mg  $NH_3-N/(g\text{-zeolite}\cdot h)$  when 375 g/L zeolite was added. The experimental results of the Langmuir and Freundlich adsorption isotherms of zeolite-absorbing ammonia-nitro-

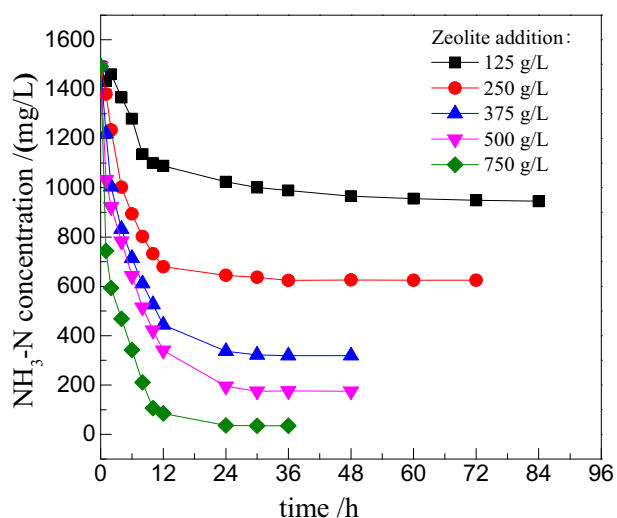


Fig. 3. The adsorption of ammonia-nitrogen with different amounts of zeolite addition.

gen show that the correlation coefficient of the Langmuir adsorption was 0.98, which was higher than that of the Freundlich adsorption. The ammonia-nitrogen adsorption isotherm was well-reproduced to the Langmuir adsorption isotherm model, which meant that the ammonia-nitrogen adsorption type of zeolite involved monolayer coating. The  $q_m$  and  $k$  values in Langmuir's equation were calculated as 13.2 and 0.0065, respectively. The fitting equation (Eq. 6) of Langmuir adsorption isotherms was:

$$q_e = 0.086C_e / (1 + 0.0065C_e) \quad (6)$$

...where  $q_e$  is equilibrium solid phase concentration (mg/g), and  $C_e$  is equilibrium liquid phase concentration (mg/L). Maximum monolayer adsorption capacity of zeolite was found to be 13.2 mg/g, which is comparable to other research, ranging from 11.5 to 17.45 mg/g [22, 23]. This above analysis means that the zeolite has a great adsorption potential of ammonia-nitrogen. Considering that the demand of adsorbent dosage for source separated urine with a high concentration of ammonia-nitrogen increase significantly, the modification of zeolite could be considered in our future study to improve its adsorption capacity.

Meanwhile, the residual ammonia-nitrogen content presented in Fig. 3 shows that the characteristics of ammonia-nitrogen adsorption of this zeolite was fast adsorption and slow balance, as time passed [24]. In the first stage of adsorption reaction, the ammonia adsorption rate increased. At the 10 h adsorption time, the adsorption rate slowed down and the concentration of ammonia-nitrogen in the effluent would remain constant.

The kinetics fitting curves and parameters of ammonia-nitrogen adsorption were compared in Fig. 4. The results obtained from adsorption kinetic experiments were used to

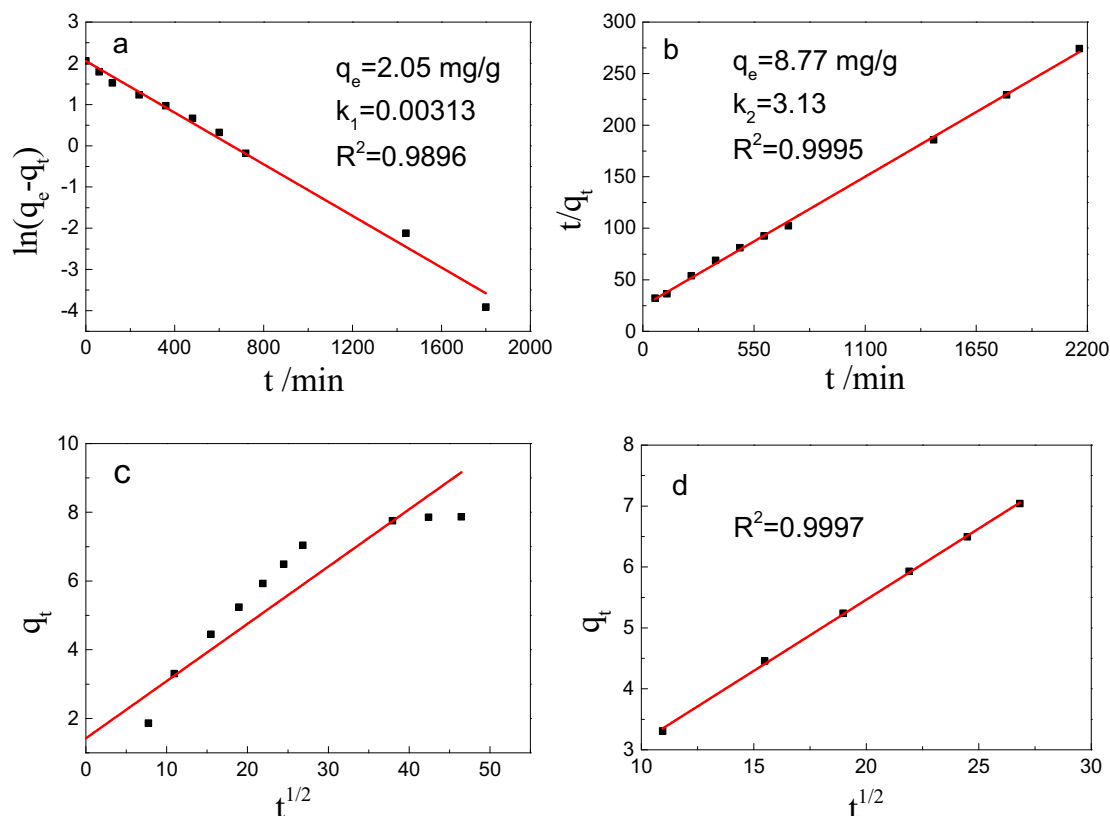


Fig. 4. Kinetics fitting curve of adsorption: a) pseudo-first order models, b) pseudo-second order models, c) intra-particle diffusion models (the whole time), and d) intra-particle diffusion models (2~10h).

study the rate-limiting step in the adsorption process, such as mass transport and chemical reaction processes. Based on the correlation coefficient ( $R^2$ ) of three adsorption kinetic models, Fig. 4 shown  $R^2$  of the pseudo-second order models was 0.9995, which is greater than 0.9896 in the pseudo-first order models. So the pseudo-second order kinetic equation had been better used to represent the whole adsorption of ammonia-nitrogen using zeolite. However, the best fitting model for 2 h to 10 h adsorption time might possibly be the intra-particle diffusion equation. Fig. 4d shows plots of the linearized form of the intra-particle diffusion equation in Eq. 4 for 2 h to 10 h during the sorption process. The  $R^2$  for the linear plot of  $q_t$  against  $t^{1/2}$  from the intra-particle diffusion equation was greater, to 0.9997.

#### *Synchronous Recovery of Nitrogen and Phosphate from Urine*

An important disadvantage of treating urine by struvite precipitation is the requirement of an Mg-source for the precipitation process, which is associated with additional costs. To restrain cost, the untreated magnesite (which contained 44% of MgO) was used in the present study for phosphate recovery. The determined dosage of untreated magnesite was added into the hydrolyzed urine (diluted for 5-fold) to get the optimum ratio of  $n_{\text{Mg}}:n_{\text{p}}=1.4:1$  as discussed previously. After reacting for 30 min, the phosphate recovery rate was 92.4%. The remaining concentration of ammonia-nitrogen was 890 mg/L, which was lower than

theoretical value calculated from struvite precipitation. This indicates that ammonia-nitrogen could not only participate in the reaction for struvite formation, but also be absorbed by natural ore. The comparison of XRD between the precipitate formed in experiment and the pure struvite purchased shows that struvite crystals really generated in the precipitate as shown in Fig. 2b. However, the XRD results generated from the precipitation showed a more noisy pattern with reduction in peak size and definition. This indicated the composition of precipitate was complex and the production of struvite crystal was little.

Adsorption ammonia-nitrogen experiment continued by adding zeolite of 375 g/L in the liquid after phosphate recovery test. The ammonia-nitrogen removal rate was 83.6% after reacting for 26 h. In the aggregate, the phosphorus recovery rate and the ammonia-nitrogen removal rate was 92.4% and 88.4%, respectively. Therefore, the utilization of natural ore has a considerable application prospect and economic value in phosphorus and ammonia-nitrogen recovery of urine.

#### **Conclusion**

Considering the influence of pH value on the ion forms of  $\text{PO}_4^{3-}$ ,  $\text{NH}_4^+$ , and  $\text{Mg}^{2+}$ , and the solubility of the reaction product, the optimal pH value was 8.0~10.0. The optimum conditions for struvite crystallization were:  $n_{\text{Mg}}:n_{\text{p}}=1.4:1$ , reaction time as 30 min, and no further pH adjustment

because the pH of hydrolyzed urine was suitable for struvite crystallization. Maximum monolayer adsorption capacity was found to be 13.16 mg/g for zeolite. By dosing 2.5 g/L of natural magnesite and 375 g/L of zeolite, 92.4% of phosphorus and 87.2% of ammonia were recovered from urine. The precipitate containing struvite crystals and nitrogen-rich zeolite could be used as a slow-release fertilizer, thus this study has considerable practical reference value.

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