

# Simultaneous immobilization of ammonium and phosphate from aqueous solution using zeolites synthesized from fly ashes

X. D. Ji, M. L. Zhang, Y. Y. Ke and Y. C. Song

## ABSTRACT

Zeolites were synthesized from silica-rich (SF-Z) and calcium-rich (CF-Z) fly ashes, respectively, and their performance in immobilizing ammonium and phosphate was investigated through batch experiments. The cation exchange capacity and phosphate immobilization capacity of SF-Z were identified as 2.79 meq/g and 12.97 mg/g while those of CF-Z were 0.69 meq/g and 87.41 mg/g, respectively. The mixture of SF-Z and CF-Z (MSC-Z) immobilized simultaneously ammonium and phosphate, and the ratio of SF-Z to CF-Z depended on the ammonium and phosphate concentrations in wastewater and the discharge standard. The adsorption processes of ammonium and phosphate on MSC-Z followed Ho's pseudo-second-order model and the intra-particle diffusion was a rate-controlling step. The Langmuir model produced better suitability to the equilibrium data. The thermodynamic study revealed that the adsorption of both ammonium and phosphate on MSC-Z was an endothermic reaction. After treatment by MSC-Z, the ammonium and phosphate concentrations in wastewater from a sewage treatment plant decreased from 7.45 and 1.42 mg/L to 2.06 and 0.51 mg/L, respectively, and met Surface Water Environment Quality Standard in China. These results show that the immobilization of ammonium and phosphate in wastewater can be achieved by the combination of zeolites synthesized from silica-rich and calcium-rich fly ashes.

**Key words** | ammonium and phosphate, calcium-rich fly ash, immobilization, silica-rich fly ash, synthesized zeolite

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## INTRODUCTION

Fly ash is a waste material generated from electric power plants. The generation rate of fly ash is approximately 500 million tons per year worldwide and it is predicted to increase (Kankyo Gijyutsu Kyokai and Nippon Fly Ash Kyokai 2000; Basu *et al.* 2009). It is abundant in aluminum oxide, calcium oxide and ferric oxide, and is classified into two groups, silicate-rich fly ash ( $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 > 70\%$ ) and calcium-rich fly ash ( $50\% < \text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 < 70\%$ ) (Vassilev & Vassileva 2007). Except for a small proportion of fly ash used as a building material, most of it is disposed of in piles and landfills, causing severe environmental problems due to its fine structure and toxic elements. As one of the environmentally-friendly and economically-viable solutions, the fly ash was converted into zeolite, which has been widely attempted for pollutants removal in gas, wastewater and polluted soil (Querol *et al.*

2002; Molina & Poole 2004). The results showed that the fly-ash derived zeolite exhibited potential as adsorbents for the removal of metals, organics,  $\text{SO}_2$  and so on.

Excessive discharge of nitrogen and phosphorus from both point and nonpoint sources contributes to the eutrophication of receiving water bodies (Schindler *et al.* 2008). The development of efficient techniques for removal of these nutrients has attracted great interest, especially for simultaneous removal of ammonium and phosphate (Yan & Cui 2006). Great efforts have been conducted to remove ammonium and phosphate using the synthesized zeolite from fly ash (Ruiz *et al.* 1997; Murayama *et al.* 2003; Tanada *et al.* 2003; Chen *et al.* 2006; Karadag *et al.* 2006; Zhao *et al.* 2009; Zhang *et al.* 2011a; Hamdi & Srasra 2012; Lu *et al.* 2012). The results showed that the zeolites synthesized from silica-rich fly ashes exhibit high ammonium

exchange capacity (Moutsatsou *et al.* 2006; Zhang *et al.* 2011b). The zeolite synthesized from calcium-rich fly ash however exhibits high phosphate immobilization capacity (PIC) (Chen *et al.* 2006; Zhang *et al.* 2011c). To immobilize simultaneously ammonium and phosphate, previous studies synthesized zeolite from silicate-rich fly ash, and then treated the synthesized zeolites with the chemical reagent (such as  $\text{CaCl}_2$ ) to improve their PIC (Murayama *et al.* 2003; Wu *et al.* 2006; Zhang *et al.* 2007). The obtained products exhibited a good performance in simultaneously immobilizing ammonium and phosphate. However, this not only increases the treatment cost but also produces the difficult-handling salt solutions. The different performance of zeolites synthesized from silica-rich and calcium-rich fly ashes in the ammonium and PIC reminds us that the simultaneous immobilization of ammonium and phosphate may be achieved by the combination of the two synthesized zeolites, whereas that has received little attention.

In the present study, zeolites are synthesized from silica-rich fly ash (SF-Z) and calcium-rich fly ash (CF-Z), respectively. The effectiveness of the mixture of SF-Z and CF-Z (MSC-Z) in immobilizing simultaneously ammonium and phosphate from aqueous solution is investigated. The adsorption kinetics, equilibria and thermodynamics of ammonium and phosphate on MSC-Z are analyzed. The performance of MSC-Z in the simultaneous immobilization of ammonium and phosphate in wastewater from a sewage treatment plant is also studied.

## MATERIALS AND METHODS

### Zeolite synthesis and characteristics

The silica-rich fly ash (SF) and calcium-rich fly ash (CF) were obtained from a power plant in China. The main chemical composition of SF was  $\text{SiO}_2$ : 75.69%,  $\text{Al}_2\text{O}_3$ : 6.43%,  $\text{Fe}_2\text{O}_3$ : 5.45%, and  $\text{CaO}$ : 3.31%. That of CF was 30.76, 14.31, 10.27 and 37.55%, respectively. An alkaline fusion followed by the hydrothermal method was used to synthesize zeolite (Wang *et al.* 2009). The structural identification of the fly ashes and synthesized zeolites, such as chemical compositions, X-ray diffraction (XRD), PIC, cation exchange capacity (CEC) and special surface area (SSA), was conducted using the measures described previously (Chen *et al.* 2006; Zhang *et al.* 2011a). The zeolite content in synthesized zeolites was analyzed using a software named X'Pert Highscore Plus. The point of zero charge ( $\text{pH}_{\text{PZC}}$ ) was estimated by the mass titration method.

### Batch experiments

Aqueous solutions containing both ammonium and phosphate were prepared from anhydrous  $(\text{NH}_4)_2\text{HPO}_4$  and  $\text{NH}_4\text{Cl}$  (analytical grade), respectively. A special amount of MSC-Z was added in 25 mL of the aqueous solution in a 100 mL stoppered conical flask, and then stirred for 28 h (sufficient time to reach equilibrium based on the previous studies) in a temperature-controlled shaker at 180 rpm. During the period, the pH of the solution was adjusted by adding 1 mol/L of HCl or NaOH (the optimal pH for the simultaneous immobilization of ammonium and phosphate based on the previous experiments).

The effect of pH on the ammonium and phosphate removal using MSC-Z was conducted in the pH range of 3.0 and 11.0 at MSC-Z dosage of 8 g/L with the SF-Z/CF-Z ratio of 4. The performance of MSC-Z in immobilizing simultaneously ammonium and phosphate was investigated at MSC-Z dosage of 8 g/L and the SF-Z/(CF-Z + SF-Z) ratio range of 0 to 1. The effect of contact time was determined by analyzing the adsorptive uptake of ammonium and phosphate from aqueous solutions on MSC-Z at different time intervals (0–28 h), and different kinetics models were used to fit the experimental data. Adsorption isotherm experiments were carried out at 25, 35 and 45 °C with different initial ammonium and phosphate concentrations (10–40 mg  $\text{PO}_4^{3-}\text{-P/L}$  and 50–200 mg  $\text{NH}_4^+\text{-N/L}$ ). The ammonium and phosphate adsorption from the real wastewater collected from a sewage treatment plant in Beijing, China, was also conducted with MSC-Z dosage of 2–20 g/L and the SF-Z/CF-Z ratio of 4:1.

When the adsorption equilibrium was achieved, the resultant solutions are filtered using 0.45  $\mu\text{m}$  cellulose acetate membrane. The concentrations of ammonium and phosphate remaining in the resulting supernatant were determined respectively using Nesslerization and molybdenum-blue ascorbic acid method with spectrophotometer (SEPAC 2002). As for the Nesslerization method, the seignette salt and Natrium reagent were the color development reagents. The solution was measured at 420 nm wavelength, which corresponds to maximum absorbance. For the molybdenum-blue ascorbic acid spectrophotometric methods, the color development reagents were molybdate and ascorbic acid. The measurement was made at 700 nm wavelength. Adsorption quantity and removal efficiency were calculated by the difference of the initial and final concentrations of ammonium and phosphate. All the experiments were conducted in duplicate. The concentrations of metals ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) in the real wastewater were measured

using an inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 2000, PerkinElmer Co., USA).

## RESULTS AND DISCUSSION

### Comparison of fly ashes and synthesized zeolites in composition and nutrient immobilization

As shown in Figure 1, the major crystalline phase was quartz and mullite for SF while it was anhydrite and quartz for CF. The SSA of SF was determined as 3.147 m<sup>2</sup>/g, while that of CF was 0.894 m<sup>2</sup>/g. The main crystalline phase was identified as faujasite for SF-Z, while it was gismondine for CF-Z. The main chemical composition of SF-Z was determined as SiO<sub>2</sub>: 33.79%, Al<sub>2</sub>O<sub>3</sub>: 27.41%, Fe<sub>2</sub>O<sub>3</sub>: 3.08%, and CaO: 2.60%, and those of CF-Z were 23.75, 9.06, 9.37 and 32.51%, respectively. The results showed that the synthesized zeolites had similar chemical compositions to their corresponding raw fly ashes. The SSA of SF-Z was obtained as 27.015 m<sup>2</sup>/g, while that of CF-Z was 45.511 m<sup>2</sup>/g. The zeolite content of SF-Z was calculated as 80%, while that of CF-Z was 21%. This was because, for CF-Z, Ca-compound in fly ash could act as a zeolite synthesis inhibitor through the formation of calcium silicate, which caused lower content of zeolite in CF-Z than SF-Z and thus its poor performance in ammonium adsorption (Juan et al. 2007).

The PIC of CF-Z was determined as 87.41 mg/g, while that of SF-Z was 12.97 mg/g. The CEC of SF-Z and CF-Z

was 2.79 and 0.69 meq/g, respectively. As the PIC and CEC represent to a certain extent the phosphate and ammonium removal capacity of adsorbent, this indicates that CF-Z has a higher phosphate uptake capacity, whereas SF-Z exhibits a stronger ammonium uptake capacity. This may be because the calcium phosphate precipitation and adsorption are the major mechanisms for phosphate removal by fly ash and its derived zeolite (Pengthamkeerati et al. 2008; Lu et al. 2009). Thus, the higher Ca content and the larger SSA favor the phosphate removal of CF-Z. On the other hand, the ammonium immobilization is achieved by ion exchange with the exchangeable Na<sup>+</sup>-ions in zeolite (Sarioglu 2005; Zhang et al. 2011b). The higher zeolite content of SF-Z therefore accounts for its higher ammonium adsorption capacity.

### Effect of pH on ammonium and phosphate immobilization using MSC-Z

Based on the above analyses, we mixed SF-Z and CF-Z together. The ammonium and phosphate removal by MSC-Z was investigated at pH values ranging from 3.0 to 11.0. The results in Figure 2 show that as the pH of the solution increased from 3.0 to 9.0, the ammonium removal efficiency increased from 24.3 to 54.5%, and then decreased to 24.9% until pH 11.0. This may be because the conversion from NH<sub>4</sub><sup>+</sup> to NH<sub>3</sub> at pH values above 9.0 and the hydrogen ion competition below pH 9.0 result in the decrease of removal efficiency (Murayama et al. 2005; Wu et al. 2006). For

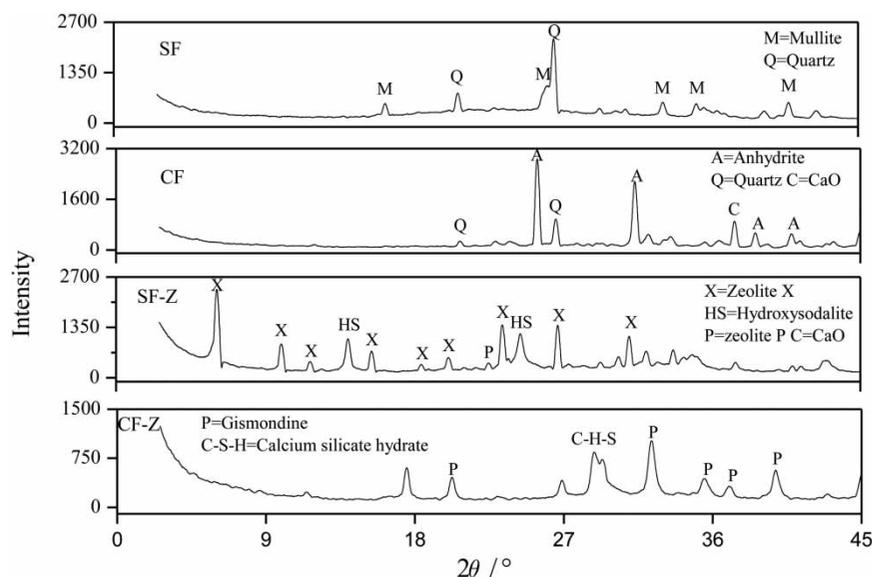
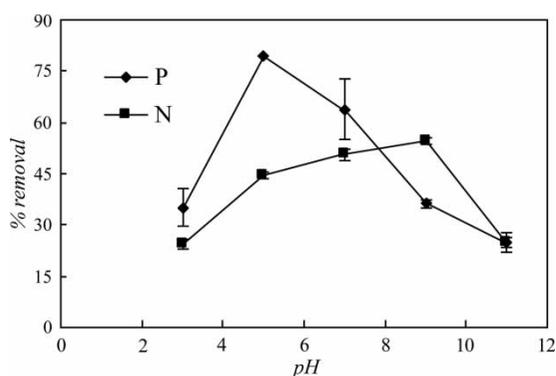


Figure 1 | XRD patterns of fly ashes and their derived zeolites.

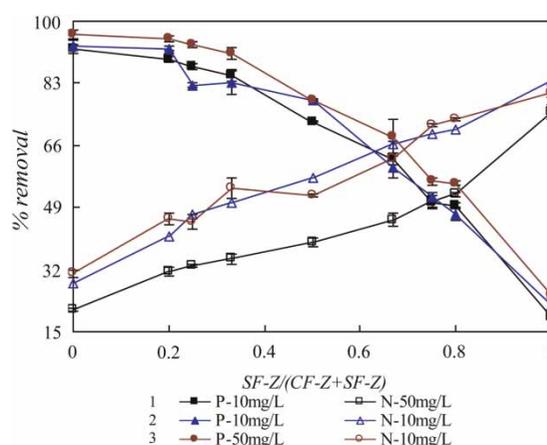


**Figure 2** | Effect of pH on ammonium and phosphate removal by MSC-Z ( $C_{NO} = 50$  mg/L;  $C_{PO} = 10$  mg/L; adsorbent dosage = 8 g/L;  $T = 25$  °C).

phosphate, the removal efficiency increased from 35.1 to 79.7% with pH increasing from 3.0 to 5.0, and afterwards decreased following the increase of pH and reached the minimum of 24.7% at pH 11.0. This is because the acidic conditions below pH 5.0 and the decrease of released  $Ca^{2+}$  amount above pH 5.0 was unfavorable to the calcium phosphate precipitation and led to the decrease of phosphate removal efficiency (Zhang *et al.* 2011c). Considering simultaneously ammonium and phosphate, the pH of aqueous solution in the following experiments was adjusted to 7.5. The pHzpc of SF-Z and CF-Z was determined as 7.8 and 7.1, respectively (Figure 1 in the Supplementary Material, available online at <http://www.iwaponline.com/wst/067/690.pdf>). At pH 7.5, the zeta of SF-Z and CF-Z was close to 0, which decreased the effect of the electrical double layer on the ammonium and phosphate adsorption.

### Effect of SF-Z/CF-Z ratio on ammonium and phosphate removal using MSC-Z

The simultaneous immobilization of ammonium and phosphate by MSC-Z with different SF-Z/CF-Z ratios was investigated, and the results are showed in Figure 3. The results show that, following the increase of SF-Z/(CF-Z + SF-Z) ratio from 0 to 1, the phosphate removal efficiency of MSC-Z decreased from 92.36–96.23% to 18.96–24.96% in three solutions while the ammonium removal efficiency increased from 21.03–31% to 75.06–83.45%. In the solutions of 1 and 2 containing different ammonium concentration, the phosphate removal efficiencies were almost equal to each other when the SF-Z/(CF-Z + SF-Z) ratio was the same. In the solutions of 2 and 3 with different phosphate concentration, the ammonium removal efficiencies were almost equal. This indicates that the ammonium



**Figure 3** | Simultaneous removal efficiency of phosphate and ammonium by MSC-Z at different SF-Z/CF-Z ratios ( $T = 25$  °C, pH = 7.5, adsorbent dosage = 8 g/L).

concentration had little effect on the phosphate removal of MSC-Z and the phosphate concentration also did not influence the ammonium removal.

The results in Figure 3 also show that the ammonium and phosphate removal efficiencies varied with the SF-Z/CF-Z ratio. As for the different wastewaters, to obtain the simultaneous removal of ammonium and phosphate, the optimal SF-Z/CF-Z ratio in MSC-Z thus should depend on the ammonium and phosphate concentrations in the wastewater and the corresponding discharge standard. For example, for the solution of 1, its N/P ratio was 5. In the Surface Water Environment Quality Standard in China (GB3838–2002), the N/P ratio is also 5 in the surface water at class I-δ. To make the solution meet the discharge standard, the optimal SF-Z/(CF-Z + SF-Z) ratio should be 0.8 since the removal efficiencies of ammonium and phosphate of MSC-Z were the same at this ratio and the N/P ratio of the effluent thus was also 5.

### Adsorption kinetics

In order to investigate the adsorption mechanisms of ammonium and phosphate on MSC-Z, the adsorption kinetics data were tested by the Lagergren first-order, Ho's pseudo-second-order and intra-particle diffusion kinetic models, respectively (Weber & Morris 1962; Motoyuki 1990; Ho & McKay 1999). The equations of these models are presented in the following forms:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

$$q_t = k_{\text{ipd}} t^{0.5} + C \quad (3)$$

where  $q_e$  and  $q_t$  are the amounts of adsorbate adsorbed on the adsorbent ( $\text{mg g}^{-1}$ ) at equilibrium and at time  $t$ , respectively. The values  $k_1(\text{min}^{-1})$  and  $k_2(\text{g mg}^{-1} \text{min}^{-1})$  are the rate constants of the first- and second-order models, respectively. Value  $k_{\text{ipd}}$  is the intra-particle diffusion rate constant ( $\text{mg g}^{-1} \text{min}^{-1/2}$ ).  $C$  is the intercept.

The results in Table 1 show that the adsorption kinetic data fit both Lagergren's first-order and Ho's pseudo-second-order models very well ( $R^2 > 0.9$ ). Judging by the higher  $R^2$  values, the Ho pseudo-second-order model explains the kinetic processes of the ammonium and phosphate uptake on MSC-Z better. This is consistent with the kinetics process of ammonium and phosphate on other adsorbents in the literature, such as bentonite, natural zeolite, trimetal oxide and so on (Table 1 in the Supplementary Material, available online at <http://www.iwaponline.com/wst/067/690.pdf>). For the phosphate, the plot of  $q_e$  versus  $t^{1/2}$  was a straight line, and the regression coefficient was 0.9372 (Table 2). This indicates that the intra-particle diffusion is the rate-controlling step for the phosphate uptake on MSC-Z. On the other hand, for the ammonium, the plot of  $q_e$  versus  $t^{1/2}$  was not a straight line over the whole time range and exhibited bilinearity, suggesting that there were two successive adsorption steps in the ammonium uptake process. The first linear portion is attributed to the boundary layer diffusion and the final linear portion is due to the intra-particle diffusion (Abramian & El-Rassy 2009). The first stage was faster than the

second, indicating that the second stage, i.e. intra-particle diffusion, is highly involved in the rate control of the ammonium uptake on MSC-Z.

## Adsorption isotherms

The adsorption isotherm characterizes the equilibrium of adsorbate in the solid phase with the adsorbate in solution. To investigate the adsorption mechanism of ammonium and phosphate on MSC-Z, the adsorption isotherm experiments were conducted at 25, 35, 45 °C, respectively. The adsorption data of ammonium and phosphate on MSC-Z were analyzed using Langmuir and Freundlich models (Freundlich 1906; Langmuir 1918). The linear forms of the two isotherm models are written as:

$$\text{Langmuir equation } \frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b} \quad (4)$$

$$\text{Freundlich equation } \log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

where  $C_e$  is the equilibrium concentration of ammonium and phosphate in solution ( $\text{mg}\cdot\text{L}^{-1}$ );  $q_e$  is the amount of ammonium and phosphate adsorbed on MSC-Z ( $\text{mg g}^{-1}$ );  $q_m$  and  $b$  are the maximum monolayer adsorption capacity ( $\text{mg g}^{-1}$ ) and the binding constant, respectively;  $K_F$  and  $n$  are indicative of the extent of the adsorption and the adsorption intensity, respectively.

The coefficients of determination in Table 2 reflect that the Langmuir model ( $R^2 = 0.9092\text{--}0.9689$ ) yielded a better

**Table 1** | Rate constants and correlation coefficients for the studied kinetic models

Adsorbate	Lagergren first-order	Ho's pseudo-second-order		$R^2$	Intra-particle diffusion	
	$R^2$	$K_2$ (g/mg min)	$q_e$ (mg/L)		$k_{\text{ipd}}$	$R^2$
Phosphate	0.9762	0.0073	0.79	0.9873	0.018	0.9372
Ammonium	0.9006	0.0026	4.14	0.9823	0.5095, 0.0728	0.978, 0.9494

**Table 2** | Langmuir and Freundlich isotherm parameters and correlation coefficients for phosphate and ammonium adsorption on MSC-Z (adsorbent dosage = 8 g/L, pH = 7.5)

Adsorbate	Temp (°C)	Langmuir parameters		$R^2$	Freundlich parameters		$R^2$
		$q_m$ ( $\text{mg g}^{-1}$ )	$b$ ( $\text{L mg}^{-1}$ )		$K_F$ ( $\text{mg g}^{-1}$ )	$1/n$	
Phosphate	25	3.06	0.0908	0.9092	0.414	0.527	0.8688
	35	3.19	0.107	0.9678	0.479	0.514	0.9175
	45	3.44	0.111	0.9756	0.526	0.514	0.9567
Ammonium	25	9.57	0.0283	0.926	2.358	0.373	0.914
	35	10.57	0.0393	0.9689	1.916	0.318	0.8974
	45	13.66	0.0416	0.9661	1.973	0.379	0.9167

fit than the Freundlich model ( $R^2 = 0.8688\text{--}0.9567$ ). This suggests that the homogeneous uptake happens for both ammonium and phosphate uptake on MSC-Z, i.e. the adsorption of ammonium and phosphate onto MSC-Z was one monolayer. For the phosphate, the obtained Langmuir constant,  $q_m$ , was 3.06, 3.19 and 3.44 mg/g at 25, 35, 45 °C, respectively. For the ammonium, that was 9.57, 10.57 and 13.66 mg/g at 25, 35, 45 °C, respectively. For both ammonium and phosphate, the obtained constant  $b$  was very low, and the Freundlich constant  $1/n$  obtained was also smaller than 1. All of these confirm an uptake process favorable for the ammonium and phosphate removal using MSC-Z.

A comparison of ammonium and phosphate removal capacity of various adsorbents is shown in Table 1 and 2 in the Supplementary Material (available online at <http://www.iwaponline.com/wst/067/690.pdf>). Despite the different methods and experimental conditions in different studies, it is still obvious that SF-Z and CF-Z had higher adsorption capacity for ammonium and phosphate, respectively. MSC-Z had high potential for removing simultaneously ammonium and phosphate from aqueous solutions.

### Adsorption thermodynamics

The thermodynamic parameters of ammonium and phosphate uptake on MSC-Z, i.e. enthalpy ( $\Delta H$ ), entropy ( $\Delta S$ ) and, free energy ( $\Delta G$ ) changes, are calculated from the Langmuir constant  $b$  obtained above. The computing formulae are expressed as:

$$\ln b = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (6)$$

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

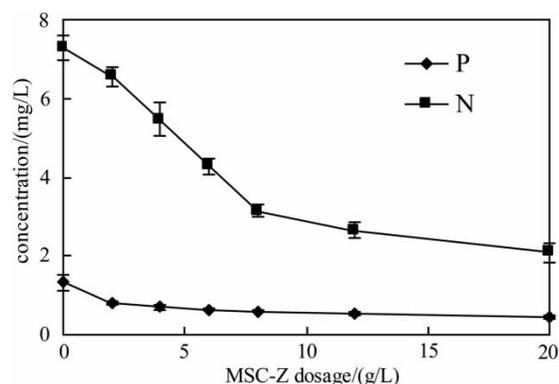
The obtained free energy changes ( $\Delta G$ ) for both ammonium and phosphate were negative values. For ammonium,  $\Delta G$  was determined as  $-15.55$ ,  $-16.58$ ,  $-17.62$   $\text{KJ}\cdot\text{mol}^{-1}$  at 25, 35, 45 °C, respectively. For phosphate, it was  $-22.50$ ,  $-23.53$ ,  $-24.55$   $\text{KJ}\cdot\text{mol}^{-1}$  at three different temperatures, respectively. This showed that their uptake on MSC-Z is spontaneous. The  $\Delta H$  was obtained as 15.29 and 7.96  $\text{KJ}\cdot\text{mol}^{-1}$  for ammonium and phosphate, respectively. The positive  $\Delta H$  values indicated that the adsorption was an endothermic reaction for both ammonium and phosphate on MSC-Z. This suggested that the adsorption capacity of ammonium and phosphate on MSC-Z increased with

temperature, which was consistent with the results obtained in the adsorption isotherm section.  $\Delta S$  was calculated respectively as 103.47 and 102.24  $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  for ammonium and phosphate. The positive values of entropy ( $\Delta S$ ) show that randomness increases the removal of ammonium and phosphate by MSC-Z. These results were consistent with those of most adsorbents used in the previous studies (Table 1 in the Supplementary Material).

### Simultaneous immobilization of ammonium and phosphate in real wastewater using MSC-Z

The concentrations of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  in the wastewater from the sewage treatment plant were measured as 80.25, 23.34, 62.55 and 35.13 mg/L, respectively. The ammonium and phosphate concentrations in the wastewater were determined as 7.45 and 1.42 mg/L, respectively. According to the discharge standards of pollutants for the municipal wastewater treatment plant (GB 18918–2002) in China, the wastewater belongs to class  $\bar{B}$  level (ammonium concentration  $\leq 8.0$  mg/L and phosphate concentration  $\leq 1.5$  mg/L). The ammonium and phosphate concentrations in the wastewater, after treatment by MSC-Z, are presented in Figure 4. The results show that the ammonium and phosphate concentrations increased with the increase of MSC-Z dosage. When MSC-Z dosage was 20 g/L, the ammonium and phosphate concentrations in the wastewater after treatment were 2.06 and 0.51 mg/L, respectively, which met basically the Surface Water Environment Quality Standard in China (GB3838–2002)  $\delta$  (phosphate concentration  $\leq 0.5$  mg/L, ammonium concentration  $\leq 2.0$  mg/L).

The other ions in the wastewater can compete with ammonium and phosphate for the adsorption sites,



**Figure 4** | Performance of MSC-Z in ammonium and phosphate removal in real wastewater from the sewage treatment plant ( $T = 25$  °C,  $\text{pH} = 7.5$ ,  $C_{\text{P}0} = 1.42$  mg/L,  $C_{\text{N}0} = 7.45$  mg/L).

especially for cations competing with ammonium (Zhang *et al.* 2011a). The initial ammonium concentration in real wastewater was 7.45 mg/L. The ammonium removal efficiency was obtained as 57.7%. For the synthesized solution in the section 'Effect of SF-Z/CF-Z ratio', the solution contained 50 mg  $\text{NH}_4^+\text{-N/L}$ . Other experimental conditions were the same as the real wastewater. The obtained ammonium removal efficiency was 52.54%. Under the significant difference of ammonium initial concentration in the synthesized solution and in the real wastewater, the ammonium removal efficiencies were almost equal to each other. This indicates that the existing cations in real wastewater compete the exchange sites with ammonium-ions. To reach the same removal efficiency, the dosage of MSC-Z should be higher for the real wastewater than for the synthesized solution.

The results obtained above show that MSC-Z can immobilize simultaneously phosphate and ammonium from aqueous solution, and can be used as a promising material for the ammonium and phosphate removal in municipal and industrial wastewater. The previous study showed that the small amount of harmful elements (such as As, Mn, Pb, etc.) in fly ash dissolve into alkaline solution after hydrothermal treatment, and the synthesized zeolite is safe (Inada *et al.* 2005). Thus, the final phosphate and ammonium bearing zeolite product can be used as fertilizer or soil amendment because the zeolite has not only water-keeping ability but also slow-releasing ability for P and N components.

## CONCLUSIONS

MSC-Z could immobilize simultaneously ammonium and phosphate from wastewater, and the ratio of SF-Z to CF-Z depended on the ammonium and phosphate concentrations in wastewater and the corresponding discharge standard. The uptake of ammonium and phosphate on MSC-Z followed Ho's pseudo-second-order model, and the intra-particle diffusion was the rate-controlling step. The homogeneous uptake happened for both ammonium and phosphate uptake on MSC-Z, and their adsorption was a spontaneous and endothermic reaction. These results showed that MSC-Z could be used as a promising material for ammonium and phosphate immobilization in municipal and industrial wastewater. The final ammonium and phosphate bearing zeolite product could be utilized as fertilizer or soil amendment.

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## REFERENCES

- Abramian, L. & El-Rassy, H. 2009 Adsorption kinetics and thermodynamics of azo-dye Orange II onto highly porous titania aerogel. *Chemical Engineering Journal* **150**, 403–410.
- Basu, M., Pande, M., Bhadoria, P. B. S. & Mahapatra, S. C. 2009 Potential fly-ash utilization in agriculture: a global review. *Progress in Natural Science* **19** (10), 1173–1186.
- Chen, J. G., Kong, H. N., Wu, D. Y., Hu, Z. B., Wang, Z. S. & Wang, Y. H. 2006 Removal of phosphate from aqueous solution by zeolite synthesized from fly ash. *Journal of Colloid and Interface Science* **300**, 491–497.
- Kankyo Gijyutsu Kyokai and Nippon Fly Ash Kyokai 2000 *Coal Ash Handbook*. Tokyo.
- Freundlich, H. M. F. 1906 Uber die adsorption in losungen. *Zeitschrift fur Physikalische Chemie (Leipzig)* **57A**, 385–470.
- Hamdi, N. & Srasra, E. 2012 Removal of phosphate ions from aqueous solution using Tunisian clays minerals and synthetic zeolite. *Journal of Environmental Sciences* **24** (4), 617–623.
- Ho, Y. S. & McKay, G. 1999 Pseudo-second order model for sorption processes. *Process Biochemistry* **34**, 451–465.
- Inada, M., Eguchi, Y., Enomoto, N. & Hojo, J. 2005 Synthesis of zeolite from coal fly ashes with different silica-alumina composition. *Fuel* **84**, 299–304.
- Juan, R., Hernández, S., Andrés, J. M. & Ruiz, C. 2007 Synthesis granular zeolitic materials with high cation exchange capacity from agglomerated coal fly ash. *Fuel* **86**, 1811–1821.
- Karadag, D., Koc, Y., Turan, M. & Armagan, B. 2006 Removal of ammonium ion from aqueous solution using natural Turkish clinoptilolite. *Journal of Hazardous Material* **136**, 604–609.
- Langmuir, I. 1918 The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of America Chemistry Society* **40**, 1361–1367.
- Lu, S. G., Bai, S. Q., Zhu, L. & Shan, H. D. 2009 Removal mechanism of phosphate from aqueous solution by fly ash. *Journal of Hazardous Materials* **161**, 95–101.
- Lu, J. B., Liu, H. J., Liu, R. P., Zhao, X., Sun, L. P. & Qu, J. H. 2012 Adsorptive removal of phosphate by a nanostructured Fe–Al–Mn trimetal oxide adsorbent. *Powder Technology* **233**, 146–154.
- Molina, A. & Poole, C. 2004 A comparative study using two methods to produce zeolites from fly ash. *Minerals Engineering* **17**, 167–173.
- Motoyuki, S. 1990 *Adsorption Engineering*. Elsevier, Amsterdam, 25, pp. 1–39.
- Moutsatsou, A., Stamatakis, E., Hatzitzotzia, K. & Protonotarios, V. 2006 The utilization of Ca-rich and Ca-Si-rich fly ashes in zeolites production. *Fuel* **85**, 657–663.

- Murayama, N., Yoshida, S., Takami, Y., Yamamoto, H. & Shibata, J. 2003 Simultaneous removal of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  in aqueous solution and its mechanism by using zeolite synthesized from coal fly ash. *Separation Science and Technology* **38**, 113–129.
- Pengthamkeerati, P., Satapanajaru, T. & Chularuengsookorn, P. 2008 Chemical modification of coal fly ash for the removal of phosphate from aqueous solution. *Fuel* **87** (12), 2469–2476.
- Querol, X., Moreno, N., Umaña, J. C., Alastuey, A., Hernández, E., López-Soler, A. & Plana, F. 2002 Synthesis of zeolites from coal fly ash: an overview. *International Journal of Coal Geology* **50**, 413–423.
- Ruiz, R., Blanc, C., Pesquera, C., Gonzílez, F., Benito, I. & López, J. L. 1997 Zeolitization of a bentonite and its application to the removal of ammonium ion from waste water. *Applied Clay Science* **12**, 73–83.
- Sarioglu, M. 2005 Removal of ammonium from municipal wastewater using natural Turkish (Dogantepe) zeolite. *Separation and Purification Technology* **41** (1), 1–11.
- Schindler, D. W., Hecky, R. E., Findlay, D. L., Stainton, M. P., Parker, B. R., Paterson, M. J., Beaty, K., Lyng, G. M. & Kasian, S. E. M. 2008 Eutrophication of lakes cannot be controlled by reducing nitrogen input: results of a 37-year whole-ecosystem experiment. *PNAS* **105**, 11254–11258.
- SEPA (State Environmental Protection Administration of China) 2002 *Monitoring and Analysis Methods of Water and Wastewater*, 4th edn. China Environmental Science Press, Beijing.
- Tanada, S., Kabayama, M., Kawasaki, N., Sakiyama, T., Nakamura, T., Araki, M. & Tamura, T. 2003 Removal of phosphate by aluminum oxide hydroxide. *Journal of Colloid and Interface Science* **257**, 135–140.
- Vassilev, S. V. & Vassileva, C. G. 2007 A new approach for the classification of coal fly ashes based on their origin, composition, properties, and behaviour. *Fuel* **86**, 1490–1512.
- Wang, C. F., Li, J. S., Wang, L. J., Sun, X. Y. & Huang, J. J. 2009 Adsorption of dye from wastewater by zeolites synthesized from fly ash: kinetic and equilibrium Studies. *Chinese Journal of Chemical Engineering* **17** (3), 513–521.
- Weber, W. J. & Morris, J. C. 1962 Advances in water pollution research: removal of biologically resistant pollutants from waste waters by adsorption. *Proceedings of the International Conference on Water Pollution Symposium* **2**, 231–266.
- Wu, D. Y., Zhang, B. H., Li, C. J., Zhang, Z. J. & Kong, H. N. 2006 Simultaneous removal of ammonium and phosphate by zeolite synthesized from fly ash as influenced by salt treatment. *Journal of Colloid and Interface Science* **304**, 300–306.
- Yan, J. & Cui, Y. B. 2006 *Sewage Treatment Technology of Constructed Wetland* (in Chinese). Chemical Industry Press, Beijing.
- Zhao, Y., Wang, J., Luan, Z. K., Peng, X. J., Liang, Z. & Shi, L. 2009 Removal of phosphate from aqueous solution by red mud using a factorial design. *Journal of Hazardous Materials* **165**, 1193–1199.
- Zhang, B. H., Wu, D. Y., Wang, C., He, S. B., Zhang, Z. J. & Kong, H. N. 2007 Simultaneous removal of ammonium and phosphate by zeolite synthesized from coal fly ash as influenced by acid treatment. *Journal of Environmental Science* **19**, 540–54.
- Zhang, M. L., Zhang, H. Y., Xu, D., Han, L., Niu, D. X., Zhang, L. Y., Wu, W. S. & Tian, B. H. 2011a Removal of ammonium from aqueous solutions using zeolite synthesized from fly ash by a fusion method. *Desalination* **271**, 111–121.
- Zhang, M. L., Zhang, H. Y., Xu, D., Han, L., Niu, D. X., Zhang, L. Y., Wu, W. S. & Tian, B. H. 2011b Ammonium removal from aqueous solution by zeolites synthesized from low-calcium and high-calcium fly ashes. *Desalination* **277** (1–3), 46–53.
- Zhang, M. L., Zhang, H. Y., Xu, D., Han, L., Zhang, J., Zhang, L. Y., Wu, W. S. & Tian, B. H. 2011c Removal of phosphate from aqueous solution using zeolite synthesized from fly ash by alkaline fusion prior to hydrothermal treatment. *Separation Science and Technology* **46** (14), 2260–2274.

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