

Effects of Calcination Conditions and Fe/Al Molar Ratio on Structure and Properties of Mixed Fe/Al-PILCs

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ABSTRACT

Fe/Al-PILCs were prepared by using Na-smectite and hydroxyl-FeAl oligocations. The effects of preparation conditions, such as calcination way, calcination temperature and Fe/Al molar ratio were examined, respectively. The results show that basal spacing, thermal stability, BET surface areas and porosity of Fe/Al-PILCs decrease with increasing Fe/Al molar ratio. The structure of Fe/Al-PILCs is easier to be destroyed by calcinating directly the intercalated products than calcinating up to specific temperature with heat rate of 1 °C/min. Cation exchange capacities of Fe/Al-PILCs decrease with increasing of calcination temperature. Fe/Al-PILCs obtained under selected conditions are mesoporous materials and are found to be excellent adsorbent for Zn(II) and As(V). Equilibrium adsorption capacities of Zn(II) and As(V) on Fe-Al-PILCs decrease with increasing calcination temperature. The maximum sorption capacities of Zn(II) and As(V) are higher when Fe/Al molar ratio is 1.0 than 0.5.

Keywords: Fe/Al-PILCs, calcination way, calcination temperature, Fe/Al molar ratio, structure and property

1 INTRODUCTION

Metal oxide pillared interlayer clays (PILCs) is a new group of porous materials with larger pore size and high permanent porosity obtained by separating the clay sheets with a molecular prop or pillaring agent, which have been most extensively studied and employed as adsorbents in recent years [1-4]. The advantages of pillared clays include increased surface area and pore volumes, which results in greater adsorption capacity and better flow properties when compared to the un-pillared parent clays. Smectite is a potential and important adsorption material because of its large surface area, large number of interlayer exchangeable inorganic cations and abundance in nature. Metal oxide pillared smectite was found to be excellent adsorbent for copper, cobalt, nickel and zinc cations [5, 6]. Fe/Al pillared smectite has been studied because iron oxide pillars have potential interesting magnetic properties [1, 7] and iron-pillared smectite has potential anion exchangeability [8]. Moreover, because of poor thermal stability of iron-pillared smectite, Fe/Al pillared smectite was paid more attention.

However, little research on effects of preparation conditions on structure and properties of Fe/Al-PILCs has been conducted [9,10]. Arsenic and metal contamination are a common co-occurrence in many contaminated environments [11-13]. In this paper, effects of calcination conditions and Fe/Al molar ratio on basal spacing, thermal stability, cation exchange capacities (CEC), BET surface areas and porosity of Fe/Al-PILCs and co-sorption properties of Zn(II) and As(V) on Fe/Al-PILCs were studied.

2 MATERIALS AND METHODS

Na-bentonite used in this investigation was Na-volclay provided by Südchemie AG, and is composed of 79.8% of smectite, 4.4% of quartz, 2.8% of muscovite, 4.0% of K-feldspar, 4.1% of plagioclase, 1.2% of calcite and 3.6% of gypsum. Na-smectite was obtained by purifying and classifying Na-bentonite by sedimentation, and the < 2 µm fraction was collected. Na-smectite was further treated by 5% Na₂CO₃ solution before being used to prepare Fe/Al-pillared smectite. Analytical grade ZnCl₂ [Zn(II)] and Na₂HAsO₄ [As(V)] and deionised water were used in the preparation of the stock Zn(II) and As(V) solutions. The stock solutions were diluted to prepare for working solutions.

Fe/Al-pillared smectite was prepared by the method of Zhao *et al.* [9]: 0.1 mol/L AlCl₃·6H₂O was gradually added to an aqueous 0.1 mol/L FeCl₃·6H₂O solution with Fe/Al molar ratio of 0.5 and 1.0. 0.1 mol/L Na₂CO₃ solution was then added to these solutions at a rate of about 4 mL/min with constant stirring until a final OH/(Al+Fe) ratio of 2.0 was reached. The resulting solutions were aged for two weeks and then aged at 120 °C for 4 h before use. 3.0g of Na-smectite was dispersed in 1000 mL of deionised water with magnetic stirring. The pillaring solution was added dropwise into the vigorously stirred smectite suspension to obtain ratio of 10 mmol Al+Fe/g of smectite (about 1-2 h). The reaction mixture was stirred for an additional 2 h, and aged for 16 h at room temperature. The precipitated product was then separated from the solution by centrifugation, washed with deionized water until chloride-free, then air-dried at 120 °C. The pillared clay samples were obtained by calcinating up to specific temperature with heat rate of 1 °C/min for 2h or calcinating directly the dried

intercalated products for 2 h at specific temperature (150 °C, 175 °C, 200 °C, 250 °C, 300 °C, 350 °C, 400 °C and 500 °C).

All the samples were characterized by using X-ray diffraction (XRD, Siemens model D5000). The diffraction patterns were recorded over an angular range of 2–25° 2θ and counting time was 4 s per 0.02° 2θ step. Cation exchange capacities were determined with Cu-Triethylenetetramine (Cu-trien) method. BET specific surface area and pore volume were determined by measuring the N₂ isotherm at 77 K with a Quantachrome Autosorb1-MP device (Quantachrome Instruments, USA), and calculated with the BET method [14].

The co-sorption experiments of Zn(II) and As(V) were conducted in 50 mL polypropylene centrifuge tubes where 0.06 g (Fe/Al molar ratio is 0.5) or 0.04 g (Fe/Al molar ratio is 1.0) of Fe/Al-pillared smectite was mixed with 0.05–2.00 mmol/L of Zn(II) and 0.25 mmol/L of As(V) or 0.05–2.00 mmol/L of As(V) and 0.25 mmol/L of Zn(II) in 0.01 mol/L NaNO₃ background electrolyte solution (20 mL). The pH value of the suspension was adjusted to 6.5 by addition of either 0.1 mol/L HNO₃ or 0.1 mol/L NaOH to avoid the effect of pH value. The pH value was measured at 6 h intervals and readjusted to 6.5 as necessary. The suspension was shaken continuously for 24 h at a speed of 180 round per min and room temperature to ensure complete Zn(II) and As(V) adsorption. After centrifuging at 4500 rpm for 15 min the suspension was filtrated through a 0.45 μm cellulose acetate membrane and the concentrations of Zn(II) and As(V) in the filtrates were determined using inductively coupled plasma-atomic emission spectrometry (ICP-AES). The adsorbed Zn(II) and As(V) was calculated from the differences between the initial and final equilibrium concentrations.

3 RESULTS AND DISCUSSION

3.1 The Effects of Preparation Conditions on Basal Spacing of Fe/Al-PILCs

The results of X-ray diffraction of Fe/Al-PILCs prepared under different conditions were listed in Table 1.

Table 1: Basal spacing (d001) of Fe/Al-PILCs prepared under different conditions (way 1: calcinated with heat rate of 1 °C/min; way 2: calcinated under specific temperature)

temperature (°C)	Fe/Al=0.5		Fe/Al=1.0	
	way 1	way 2	way 1	way 2
intercalated	1.8453		1.5078	
150	1.6647	1.7835	1.4296	1.3261
175	1.6208	1.7408	1.4636	1.3500
200	1.6612	1.7523	1.4195	1.2240
250	1.5638	1.7915	1.4296	1.2996
300	1.5855	1.7370	1.4451	1.1790
350	1.6929	1.6578	1.3017	—
400	1.6787	—	—	—
500	—	—	—	—

From Table 1 we can see that basal spacing (d001) of intercalated smectite by hydroxyl-FeAl oligocations is evidently enlarged no matter Fe/Al molar ratio is 0.5 (1.8453 nm) or 1.0 (1.5078 nm), compared with the original Na-smectite (1.1082 nm), but the larger d001 value of Fe/Al-PILCs can be obtained when Fe/Al molar ratio is 0.5 than 1.0. These results are accordant with those reported by Zhao *et al.* [9]. The peak intensity of (001) line of Fe/Al-PILCs is greatly decreased with increasing calcination temperature at the temperature range 150–500 °C, although the d001 values change slightly. The structure of Fe/Al-PILCs is destroyed when calcination temperature is up to 500 °C with heat rate of 1 °C/min but only 400 °C was found by calcinating directly the intercalated products when Fe/Al molar ratio is 0.5. The same results and lower temperature were found when Fe/Al molar ratio is 1.0. These results show the thermal stability of Fe/Al-PILCs is affected by calcination conditions and Fe/Al molar ratio.

3.2 The Effects of Preparation Conditions on CEC of Fe/Al-PILCs

The CEC values of Fe/Al-PILCs prepared under different conditions were found to be much smaller than that of original Na-smectite (88 cmol/kg) (as shown in Table 2). Moreover, the CEC values of Fe/Al-PILCs slightly decrease with increasing calcination temperature no matter Fe/Al molar ratio is 0.5 or 1.0. These are probably due to formation of Al₂O₃ and iron oxide prop in the interlayer of smectite. More Al₂O₃ and iron oxide prop can be formed with increasing calcination temperature. Less effects of Fe/Al molar ratio on CEC values were found.

Table 2: CEC values of Fe/Al-PILCs prepared under different conditions (calcinated with heat rate of 1 °C/min)

clay	CEC (cmol/kg)
<2μm Na-smectite	88
Fe/Al=0.5, 150 °C	35
Fe/Al=0.5, 250 °C	32
Fe/Al=0.5, 300 °C	30
Fe/Al=0.5, 350 °C	26
Fe/Al=0.5, 400 °C	21
Fe/Al=1.0, 150 °C	38
Fe/Al=1.0, 250 °C	33
Fe/Al=1.0, 300 °C	29
Fe/Al=1.0, 350 °C	22
Fe/Al=1.0, 400 °C	18

3.3 The Effects of Preparation Conditions on BET Surface Areas and Porosity of Fe/Al-PILCs

From Table 3 we can see both BET surface areas and porosity of Fe/Al-PILCs prepared under different conditions are greatly increased after pillaring. The larger BET surface area (270.7 m²/g for Fe/Al=0.5 and 186.0 m²/g for Fe/Al=1.0) and porosity ((0.2071 cm³/g for Fe/Al=0.5

and $0.2026 \text{ cm}^3/\text{g}$ for Fe/Al=1.0) were found when Fe/Al molar ratio is 0.5 than 1.0 at the same calcination temperature ($300 \text{ }^\circ\text{C}$) with heat rate of $1 \text{ }^\circ\text{C}/\text{min}$. Fe/Al-PILC with the largest BET surface areas ($525.1 \text{ m}^2/\text{g}$) and porosity ($0.4278 \text{ cm}^3/\text{g}$) was obtained when Fe/Al molar ratio is 0.5, calcinated up to $400 \text{ }^\circ\text{C}$ with heat rate of $1 \text{ }^\circ\text{C}/\text{min}$ for 2h.

Table 3: BET surface areas and porosity of Fe/Al-PILCs prepared under selected conditions (calcinated with heat rate of $1 \text{ }^\circ\text{C}/\text{min}$).

clay	BET surface area (m^2/g)	Pore volume (cm^3/g)
<2 μm Na-volclay	45.9	0.0635
Fe/Al=0.5, $300 \text{ }^\circ\text{C}$	270.7	0.2071
Fe/Al=0.5, $350 \text{ }^\circ\text{C}$	250.6	0.2018
Fe/Al=0.5, $400 \text{ }^\circ\text{C}$	525.1	0.4278
Fe/Al=1.0, $300 \text{ }^\circ\text{C}$	186.0	0.2026

Pore size distribution of different samples was shown in Figure 1. As shown in Figure 1, all the Fe/Al-PILCs obtained under selected conditions are mesoporous materials.

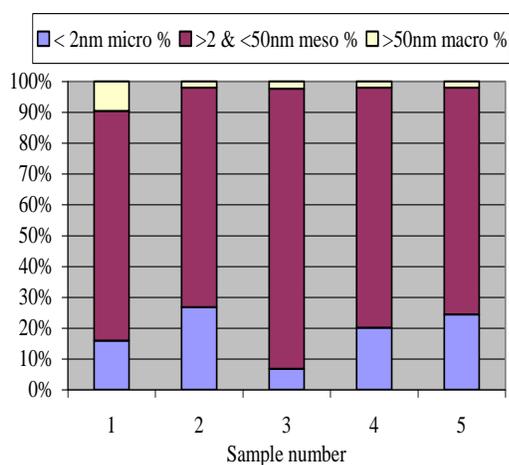


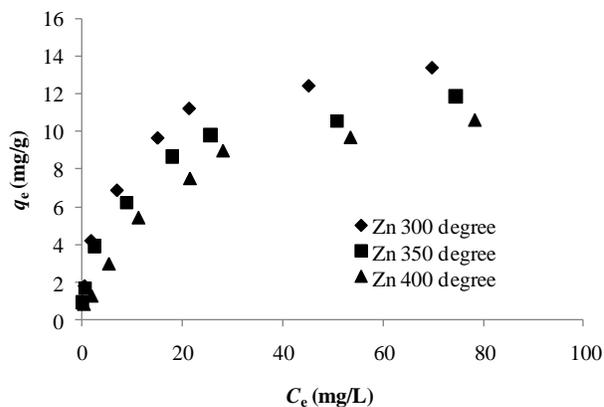
Figure 1: Pore size distribution of different samples
1, <2 μm Na-volclay;

- 2, Fe/Al=0.5, $300 \text{ }^\circ\text{C}$ calcination with heat rate of $1 \text{ }^\circ\text{C}/\text{min}$;
- 3, Fe/Al=1.0, $300 \text{ }^\circ\text{C}$ calcination with heat rate of $1 \text{ }^\circ\text{C}/\text{min}$;
- 4, Fe/Al=0.5, $350 \text{ }^\circ\text{C}$ calcination with heat rate of $1 \text{ }^\circ\text{C}/\text{min}$;
- 5, Fe/Al=0.5, $400 \text{ }^\circ\text{C}$ calcination with heat rate of $1 \text{ }^\circ\text{C}/\text{min}$.

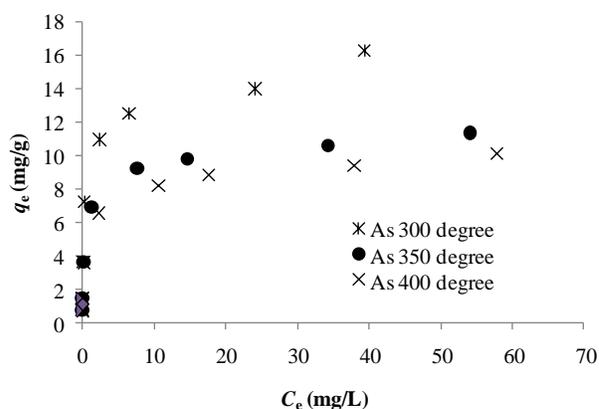
3.4 The Effects of Preparation Conditions on Co-sorption of Zn(II) and As(V) by Fe/Al-PILCs

The sorption isotherms of Zn(II) and As(V) co-sorption on mixed Fe-Al-PILCs calcinated at different temperatures when Fe/Al molar ratio is 0.5 were shown in Figure 2. As seen in Figure 2, Fe/Al-PILCs obtained under selected conditions are excellent adsorbent for Zn(II) and As(V). Equilibrium adsorption capacities of Zn(II) and As(V) decrease with increasing calcination temperature at

different initial concentrations of Zn(II) and As(V). On the one hand, this is probably due to lower CEC values of Fe/Al-PILCs calcinated at higher temperature, on the other hand, more important, this is probably due to formation of $\alpha\text{-Fe}_2\text{O}_3$ at higher calcination temperature [9].



(a)



(b)

Figure 2: Sorption isotherm of Zn(II) (a) and As(V) (b) co-sorption on mixed Fe-Al-PILCs calcinated at different temperatures

(Fe/Al molar ratio 0.5, room temperature, adsorbent dosage $0.06 \text{ g}/20\text{mL}$, pH 6.5 ± 0.1 , shaking time 24 h, $C_0(\text{As})=18.56\text{mg/L}$, $C_0(\text{Zn})=14.27\text{mg/L}$)

The isotherm results of Zn(II) and As(V) co-sorption on mixed Fe-Al-PILCs calcinated at $300 \text{ }^\circ\text{C}$ when Fe/Al molar ratio is 0.5 and 1.0 at a room temperature of $25 \text{ }^\circ\text{C}$ were analyzed using Langmuir isotherms. The results were listed in Table 4. As seen in Table 4, the Langmuir isotherm fits quite well with the experimental data (correlation coefficient $R^2 > 0.99$). This indicates that the Langmuir model is very suitable for describing the sorption equilibrium of Zn(II) and As(V) on Fe-Al-PILCs prepared under selected conditions. The fact that the Langmuir isotherm fits the experimental data very well may be due to

the homogeneous distribution of active sites on Fe-Al-PILCs surface since the Langmuir equation assumes that the surface is homogeneous. The maximum sorption capacities of Zn(II) and As(V) on Fe-Al-PILCs (Q_0) are 16.98 mg/g and 16.29 mg/g when Fe/Al molar ratio is 1.0, respectively, which are higher than 13.95 mg/g and 15.87 mg/g when Fe/Al molar ratio is 0.5, respectively.

Table 4: Langmuir constants and correlation coefficients for co-sorption of Zn(II) and As(V) on mixed Fe-Al-PILCs with different Fe/Al molar ratio (calcinated at 300 °C with heat rate of 1 °C/min)

parameters	Fe/Al molar ratio 0.5		Fe/Al molar ratio 1.0	
	Zn	As	Zn	As
Q_0 (mg/g)	13.95	15.87	16.98	16.29
b (L/mg)	0.23	1.45	0.22	1.31
R^2	0.9929	0.9924	0.9913	0.9977

4 CONCLUSIONS

(1) Fe/Al-PILCs were prepared under different conditions and found to be strongly dependent on calcination temperature, calcination way and Fe/Al molar ratio. Basal spacing of Fe/Al-PILCs decreases when Fe/Al molar ratio is improved from 0.5 to 1.0. The thermal stability of Fe/Al-PILCs decreases with increasing Fe/Al molar ratio. The structure of Fe/Al-PILCs is easier to be destroyed by calcinating directly the intercalated products at specific temperature than calcinating up to specific temperature with heat rate of 1°C/min. The CEC values of Fe/Al-PILCs were found to be much smaller than that of original Na-smectite and decrease with increasing of calcination temperature. Both BET surface areas and porosity of Fe/Al-PILCs are greatly increase after pillaring. Fe/Al-PILC with the largest BET surface areas and porosity was obtained when Fe/Al molar ratio is 0.5, calcinated up to 400°C with heat rate of 1°C/min for 2h. All the Fe/Al-PILCs obtained under selected conditions are mesoporous materials.

(2) Equilibrium adsorption capacities of Zn(II) and As(V) decrease with increasing calcination temperature at different initial concentrations of Zn(II) and As(V). Langmuir model is very suitable for describing the sorption equilibrium of Zn(II) and As(V) on Fe-Al-PILCs prepared under selected conditions. The maximum sorption capacities of Zn(II) and As(V) on Fe-Al-PILCs are 16.98 mg/g and 16.29 mg/g when Fe/Al molar ratio is 1.0, respectively. The values decrease when Fe/Al molar ratio is 0.5. Fe/Al-PILCs obtained under selected conditions are excellent adsorbent for Zn(II) and As(V).

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