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Zeolite A synthesized from alkaline assisted pre-activated halloysite for efficient heavy metal removal in polluted river water and industrial wastewater

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ABSTRACT

High quality zeolite A was synthesized through a hydrothermal process using alkaline-assisted pre-activated halloysite mineral as the alumina and silica source. The synthesis conditions employed in this study were finely tuned by varying the activating temperature, sodium hydroxide content, water content and Si/Al ratio. The obtained zeolite A showed excellent adsorption properties for both single metal cation solutions and mixed cation solutions when the concentrations of the mixed cations were comparable with those in polluted natural river water and industrial wastewater. High adsorptive capacities for Ag^+ (123.05 mg/g) and Pb^{2+} (227.70 mg/g) were achieved using the synthesized zeolite A. This observation indicates that the zeolite A synthesized from alkaline-assisted pre-activated halloysite can be used as a low-cost and relatively effective adsorbent to purify heavy metal cation polluted natural river water and industrial wastewater.

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Introduction

The widespread contamination of drinking water sources by heavy metal ions, such as lead, chromium, zinc, nickel, and copper, is of major concern because of their toxicity, persistence and bioaccumulative nature (Hafiza et al., 2015; Fu and Wang, 2011; Ciszewski and Grygar, 2016; Turhanen et al., 2015; Simeonidis et al., 2016). These kinds of heavy metal pollution can lead to serious human health hazards through the food chain, and especially from drinking water, which can harm the whole biological environment (Hafiza et al., 2015). The pollution of rivers by heavy metals has been taking place in many countries in recent years. The concentrations of heavy metals in the water of several famous rivers are higher than the guidelines issued by the World Health Organization (WHO) (Temnerud et al., 2013; Li et al., 2011; Shiller, 1997; Liu and Li, 2011; Kurniawan et al., 2006). Moreover, the pollution in many small rivers is even more serious.

In past decades, a lot of effort has been made toward the purification of natural river water for drinking purposes.

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Various methods, such as adsorption, flotation, phytoremediation, electrochemical treatment, membrane filtration, and chemical precipitation, have been used for heavy metal removal in drinking water (Shannon et al., 2008; Chong et al., 2010; Thompson, 2015). Of the methods, adsorption is an environmentally friendly and low-cost method which has been widely used in the treatment of polluted water. There are many adsorbents that can be used in industry to remove heavy metal cations in processing natural water or industrial wastewater, including ion exchange resins (Eldin et al., 2016), activated carbon (Jurado-sánchez et al., 2014), clay minerals (Zhu et al., 2016), and zeolites (Ghasemi et al., 2016). Zeolites are often chosen not only because of the porous structures of these materials, but also because they can provide excellent heavy metal adsorption capacity without the high price of more complex adsorption media. Among the different types of zeolites, zeolite A is of particular interest as an adsorbent. It is expected to have the best adsorption capacity and selectivity among the most common low-cost zeolites (Dyer and Emms, 2005; Higgins et al., 2002). During the past years, zeolite A has been employed in a few different systems as an absorbent to remove hazardous materials, including heavy metals at different concentration levels, however, studies on the use of Zeolite A to remove heavy metals cations in complex cation solutions at levels similar to those in river water have been scarce.

Herein, we employed an alkaline pre-activated hydrothermal synthesis method (Li et al., 2012; Liu et al., 2015; Yue et al., 2014), by using halloysite mineral, which has a crystal structure similar to kaolinite but with much higher purity and quality, as a source material to prepare pure and highly crystalline zeolite A. Parameters affecting the synthesis such as temperature, amount of alkali for activation, and amount of water in the mixtures used for crystal growth, were carefully investigated. Subsequently, the prepared zeolite A was used as an adsorbent to remove heavy metal cations from aqueous solutions, both for single metal cation solutions and mixed solutions, where the selectivity for different heavy metal cations was determined. Parameters affecting adsorption, such as the effect of competitive innocuous cations and initial metal cation concentration, were studied as well. The low (0.1 mmol/L for each cation) and high (1 mmol/L for each cation) concentrations in this study were comparable to those in contaminated water in typical rivers over the world and industrial wastewater, respectively (Fig. 1). The results indicated that the synthesized zeolite A exhibited high adsorption selectivity and capacity for removing heavy metal cations in both contaminated natural river water and industrial wastewater.

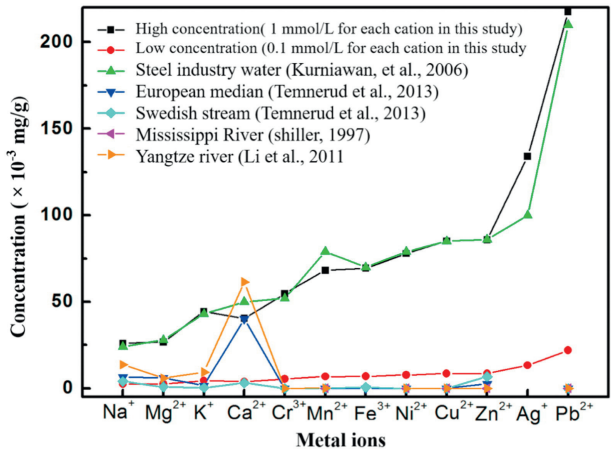

Fig. 1 – Comparison of metal concentrations in natural river water, industrial wastewater and the simulated solutions used in this study.

1. Experimental section

1.1. Characterization

Both the raw minerals and the synthesized zeolite A were characterized by powder X-ray diffraction (PXRD), Fourier Transform Infrared spectroscopy (FT-IR), and scanning electron microscopy (SEM). PXRD patterns were obtained by using a PANalytical X'Pert X-ray diffractometer with Cu Kα (λ = 1.5406 Å) radiation operating at 45 kV and 40 mA over the 2θ range of 5°–50°. Fourier transform infrared spectra (FT-IR) were recorded on a Varian 670-IR spectrometer in the range 400–4000 cm^{-1}. Scanning electron microscopy (SEM) was performed using a SU-7000F SEM, operating at an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) images and energy dispersive X-ray (EDX) spectrum were obtained with a JEOL FEG 2100 microscope. N_2 adsorption and desorption isotherms were measured using a Micromeritics ASAP2020 device at 77 K. A ThermoFisher ICAP 6500 inductively coupled plasma mass spectrometer (ICP) was used to measure the concentrations of cations after absorption.

1.2. Raw materials

Halloysite is an aluminosilicate clay mineral, consisting of alumina octahedral sheets and silica tetrahedral sheets in 1:1 stoichiometric ratio. In our experiments, natural halloysite mineral was purchased from Sigma and used as the silica and alumina source. Both SEM and TEM images (Fig. 2a–b) showed that the halloysite mineral particles had a cylindrical shape, and the nanotubular particles were hollow and open-ended. The typical powder X-ray diffraction (PXRD) pattern in Fig. 2c indicates the seriously disordered features of the halloysite contributed by the layer stacking. The energy-dispersive X-ray spectrum (EDX) in Fig. 2d shows that the raw mineral had a Si/Al ratio of 1:1 without any other metal cations.

1.3. Synthesis of zeolite A

The activation process of the raw minerals, which is used to destroy the layered edge-shared AlO_6 octahedra, is crucial for synthesis of pure zeolite A. Both the temperature and alkaline content can influence the activation process. Normally, high temperature up to 1000°C is needed in order to break the Al–O bonds in an AlO_6 configuration (Lee et al., 1999). In order to decrease the energy requirement, alternatively, alkali can be introduced in the combustion step to activate the mineral, as

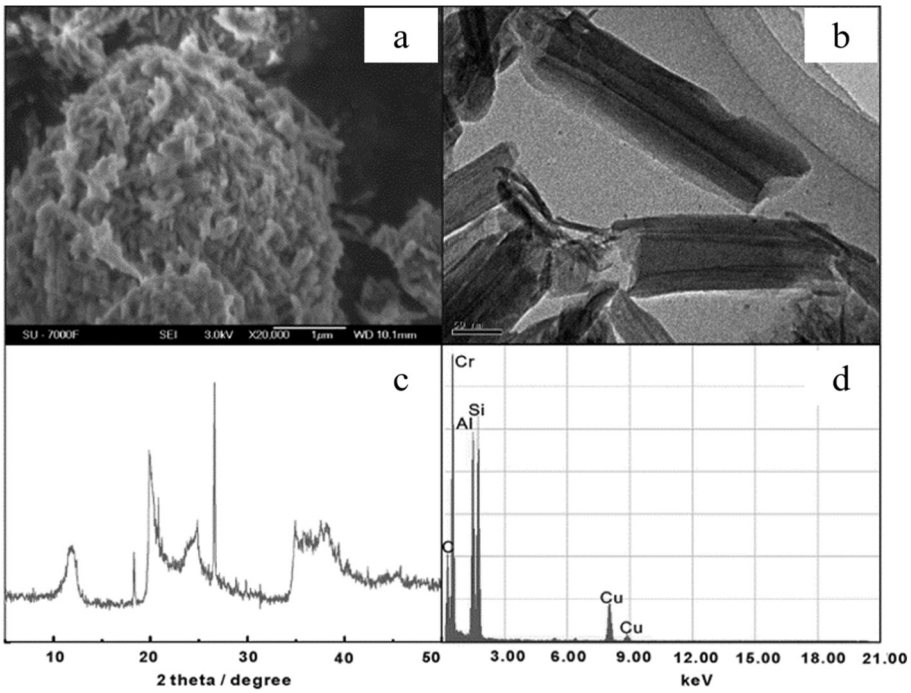

Fig. 2 – Characterization of the raw halloysite mineral. (a) SEM image. (b) TEM image. (c) PXRD pattern. (d) TEM EDX spectrum, Cr and Cu signals are contributed by the TEM grids.

reported by Li et al. (2012) for kaolinite. However, the alkali solid may be mixed with the raw mineral to form a heterogeneous slurry, and the stability and purity of the product can be assured (Guth et al., 1986). In addition, extra crystal seeds may also be needed to obtain an oriented product. In this study, in order to activate the natural aluminosilicate effectively to achieve a homogenous product free of crystal seeds, a combined strategy using a thermal and alkali activation method was used to depolymerize the inactive halloysite into highly active alumina and silica species, which is superior to the traditional thermal decomposition method, as discussed by Feng et al. (2009), and Zhao et al. (2010). Through this strategy, alkaline-assisted calcination activation or alkaline calcination combined with hydrothermal processes can be utilized to achieve pure zeolites.

In our study, we employed a short activation time and did not use any seeds in the synthesis. Only the cheap halloysite, H_2O and sodium hydroxide were utilized as raw materials. For a typical recipe, 2.94 g of the raw halloysite and 2.4 g of NaOH powder were mixed in a beaker, then 20 mL of water was added to obtain a clear solution. Afterwards, the resulting mixture of NaOH-H_2O-halloysite was treated at 800°C in a muffle furnace with air recirculation for 4 hr. Then the thermally and alkali-activated halloysite was gently added into deionized water (40 mL) with magnetic stirring for 30 min until the solid was completely dissolved. A homogenous gel was achieved from the mixed solution and sealed in a Teflon tube. The Teflon tube was kept at 100°C for 4 h to allow the gel to crystallize. The obtained zeolite product was cooled down to room temperature, washed with distilled water three times, and then dried overnight at room atmosphere.

1.4. *Heavy metal cation adsorption experiments*

For adsorption experiments, simulated river water and industrial wastewater were prepared with both single metal cations and mixed cationic solutions at concentrations close to levels in natural river water and industrial wastewater, as shown in Fig. 1. For single metal cations, two important parameters, the maximum removal percentage and adsorptive capacity for each metal cation, including heavy metals and innocuous metals, were obtained. The selectivity of the synthesized zeolite A for the mixed metals was obtained by comparison of the distribution coefficients. Low, moderate and high heavy metal concentrations (0.1, 0.5, and 1 mmol/L for each cation), with/without innocuous cations, were investigated, respectively. The low (0.1 mmol/L) metal concentration was close to levels in contaminated river water, and the high (1 mmol/L) concentration was close to that in industrial wastewater.

The batch experiments were carried out in centrifuge tubes containing 10 mL 1 mmol/L solutions of XNO_3 (X = Ag^+, Na^+, K^+), $X(NO_3)_2$ (X = Ca^{2+}, Mg^{2+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}), $X(NO_3)_3$ (X = Cr^{3+}, Fe^{3+}) solutions. 4.1 mg and 20 mg as-synthesized zeolite A were added to each solution, respectively. Two series of single metal solutions and adsorbents were obtained. After 8 hr, the adsorbent was removed by centrifugation at 12,000 r/min. The concentrations of metal cations in the supernatant solution were determined by inductively coupled plasma mass spectrometry (ICP-MS). The removal rate and adsorptive capacity were evaluated using the following Eqs. (1)–(2):

$$q_e = (C_0 - C_f)V/mM \quad (2)$$

$$R = (C_0 - C_f)/C_0 \quad (1)$$

where R (%) is the removal percentage after adsorption, q_e (mg/g) is the amount adsorbed per gram of adsorbent, C_0 (mmol/L) is the initial concentration of metal cation solution, C_f (mmol/L) is the residual concentration of solution after adsorption, V (L) is the volume of the metal cation solution, m (mg) is the mass of the adsorbent used and M (g/mol) is the molar mass of the metal.

Using simulated contaminated river water and industrial wastewater, the selectivity of the prepared zeolite A for mixtures of metal cations was measured. In order to validate the comparative adsorption between metal cations, 200 mg zeolite A was mixed with the corresponding concentrations of mixed heavy metal solutions (Ag^+, Pb^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, Cr^{3+}, Fe^{3+}) with and without innocuous cations (Na^+, Ca^{2+}, Mg^{2+}, K^+), respectively. After 8 hr, the metal ion concentrations in the supernatant solutions were determined by ICP-MS analysis. The distribution coefficients (K_d), which indicate the ratio of the metal cations adsorbed in the adsorbent and the residual in the solution in a specific adsorbate and adsorbent system, were calculated as follows:

$$K_d = (V\,((C_0 - C_f)/C_f))/mM \quad (3)$$

where C_0 and C_f are the initial and final concentration of each metal cation (mmol/L) after the adsorption, V is the volume (mL) of the testing solution, m is the amount of the solid sorbent (g) used in the adsorption experiment, and M (g/mol) is the molar mass of the metal.

2. Results and discussion

2.1. Effects of different parameters on synthesis

The synthesis conditions are crucial for obtaining well-crystallized zeolite A. In order to achieve the optimum synthesis conditions, a series of synthetic parameters such as temperature, amount of alkali for activation, and amount of water in the final mixed solution for crystal growth, were investigated. The PXRD patterns of all the products were studied for comparison (Fig. 3). Among all the examined parameters, the amount of alkali employed in the synthesis has an obvious impact on the final products, since different amounts can lead to different extents of Al–O bond destruction in the AlO_6 octahedra. To study the effect of sodium hydroxide on the activation of halloysite mineral, four different quantities of NaOH including 0, 2.4, 4.8 and 7.2 g were used with 2.94 g raw halloysite in 20 mL water at 800°C. The mole ratios of Na/(Si + Al) of 0:1, 1.5:1, 3:1 and 4.5:1 were obtained. The PXRD patterns for different products (Fig. 3a) indicated that the best ratio of Na/(Si + Al) to activate halloysite is 1.5:1. Temperature is another important factor in depolymerizing the halloysite mineral in order to destroy the high-energy Si–O and Al–O bonds. The effect of temperature on activation was investigated from 200 to 800°C in 200°C increments and 4 hr heating time using 2.4 g of raw halloysite and 2.94 g NaOH in 20 mL water. Four different thermally activated halloysite samples were obtained to synthesize zeolite A. The PXRD patterns of the different products are given in Fig. 3b. The result implied that the best activation temperature for halloysite is 800°C, and lower temperature (600°C) generates zeolite Y phase, together with other unknown impurities. The amount of water in the synthesis is also crucial for the final products. In order to determine the optimum water content, three samples with 40, 20 and 10 mL deionized water added to 2.94 g halloysite and 2.4 g NaOH were activated at 800°C, and then crystallized at 100°C. The PXRD patterns of the different products are given in Fig. 3c. Well-crystallized zeolite A was achieved with 40 mL water. In addition to the aforementioned parameters, the Si/Al ratio of the raw minerals can also influence the products. Montmorillinite mineral, which has a Si/Al ratio of 2:1, was used to synthesize zeolite A using the same process and parameters as for halloysite. The PXRD patterns (Fig. 3d) show that no zeolite A was obtained with montmorillinite as the raw material, indicating that the Si/Al ratio of raw minerals is a significant factor in high quality zeolite A synthesis.

2.2. Characterization of synthesized zeolite A

Through optimization of the hydrothermal synthesis process, cube-like zeolite A particles were obtained as shown in Fig. 4a. The PXRD pattern shown in Fig. 4b confirmed that the obtained sample is high purity zeolite A. The typical diffraction peaks corresponding to halloysite raw material totally disappeared under the optimized experimental conditions. All PXRD peaks agreed well with the characteristic peaks of zeolite A. The PXRD of the crystals had a low background and strong, sharp reflections, indicating that the synthesized zeolite A was well crystallized. The FT-IR spectrum in Fig. 4c shows the typical bands of zeolite A representing the asymmetric and symmetric stretch (970 cm^{-1}), double rings (548 cm^{-1}) and bending (667 and 462 cm^{-1}) of (Al, Si) – O (Alkan et al., 2005). The N_2 adsorption and desorption isotherms are shown in Fig. 4d, exhibiting a type IV step-like isotherm, which indicates that the synthesized material is featured with a hydrophilic porous wall structure and has high adsorption capacity at low P/P_0. The adsorption capacity of the synthesized zeolite for N_2 is 14.05 cm^3/g at 77 K under 1 bar pressure, which is typical for a Linde Type A (LTA) zeolite with Na:Al:Si = 1:1:1.

2.3. Adsorption of heavy metal cations

2.3.1. Adsorption of single cations

In order to find the maximum removal rate and adsorptive capacity of the synthesized zeolite A toward metal cations, two series of experiments were carried out: One in solutions with excess adsorbent, and the other one in solutions with inadequate adsorbent. The maximum removal percentages indicate the amounts of metal cations that can be adsorbed if sufficient adsorbent is added, and the maximum adsorptive capacities indicate the maximum total amounts of cations taken up per gram of adsorbent. The adsorption experiment data are listed in Table 1. The maximum removal percentage for heavy metals reached nearly 100%, if sufficient adsorbent was added into the solutions. However, only about half of the initial amount of innocuous cations could be removed, except for Ca^{2+}, even if a very large amount of adsorbent was added.

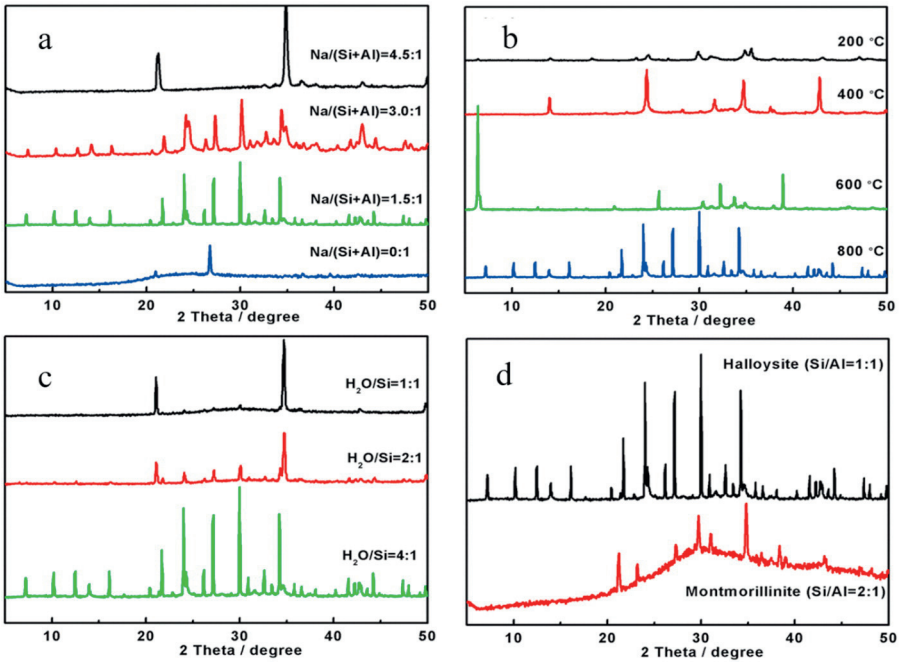

Fig. 3 – PXRD patterns of products obtained with (a) different alkali amounts, (b) different activation temperatures, (c) different water amounts for the final crystallization, and (d) different Si/Al ratios.

The maximum cation uptake was more than 45 mg/g for heavy metals and less than 40 mg/g for innocuous metals. For heavy metal cations, the adsorbent exhibited quite high adsorptive capacities, especially for Ag^{+} (123.05 mg/g) and Pb^{2+} (227.70 mg/g), following the order $Pb^{2+} \gg Ag^{+} \gg Cu^{2+} \approx Zn^{2+} > Cr^{3+} \approx Fe^{3+} \approx Mn^{2+} \approx Ni^{2+}$. For innocuous cations, the adsorbent showed relatively low adsorptive capacity, especially for Mg^{2+}. This tendency appears to depend on the

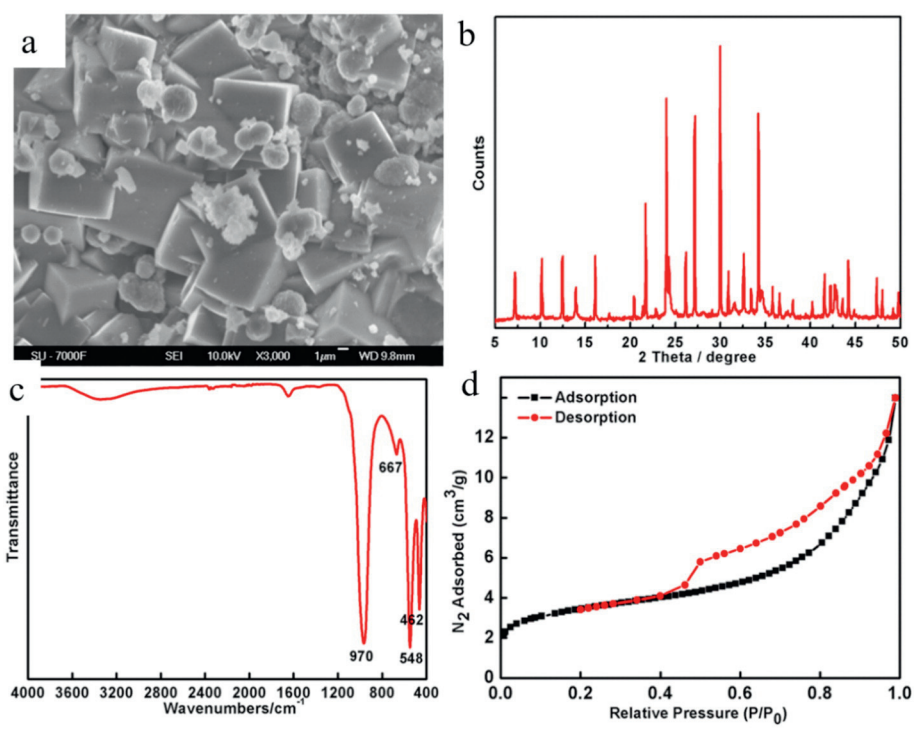

Fig. 4 – Characterization of synthesized zeolite A obtained from halloysite. (a) SEM image, (b) PXRD pattern, (c) FT-IR spectrum, (d) N_2 adsorption and desorption isotherms.

Table 1 – Removal percentage (R) and adsorptive capacity of zeolite A for metal cations.

Single cations	0.2 g adsorbent		0.0041 g adsorbent	
	q_e (mg/g)	Maximum R (%)	Maximum q_e (mg/g)	R (%)
Mg^{2+}	8.4	62.6	8.4	12.5
K^+	11.4	50.6	39.9	43.2
Ca^{2+}	17.0	100	38.0	37.6
Cr^{3+}	27.0	100	46.8	31.6
Mn^{2+}	34.7	100	45.4	27.7
Fe^{3+}	34.5	98.4	46.2	28.7
Ni^{2+}	38.9	100	45.4	31.1
Cu^{2+}	44.2	100	62.4	37.5
Zn^{2+}	43.6	100	56.9	32.7
Ag^+	66.3	100	123.1	44.2
Pb^{2+}	115.9	100	227.7	39.3

10 mL of $X(NO_3)n$ solution with 1 mmol/L of each cation.

atomic weight of the different cations, but it indicates that our material is superior to other low-cost absorbents as reported in the literature. For example, Abollino et al. (2003) reported that the total adsorption capacities of Pb^{2+}, Cr^{3+}, Mn^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} by Na-montmorillonite were 9.58, 5.13, 3.22, 3.04, 3.63 and 3.61 mg/g, respectively. Asrari et al. (2010) reported that the maximum adsorption capacities achieved by using rice husks to remove Zn^{2+} and Pb^{2+} were 19.617 and 0.6216 mg/g respectively. The maximum adsorption capacities for activated carbon were found to be 38, 9.9, and 6.84 mg/g for Cu^{2+}, Zn^{2+} and Cr^{3+}, respectively (Monser and Adhoum, 2002). Liang et al. (2013) reported that the maximum sorption capacity for an ion-exchange resin was determined to be 194.553, 59.998, 42.450 and 41.847 mg/g for Pb^{2+}, Cu^{2+}, Ni^{2+} and Cr^{3+}, which is similar to our synthesized zeolite A, but with much higher cost. The overall adsorption capacities for natural zeolite studied by Alvarez-Ayuso et al. (2013) were around 4.11, 2.01, 3.45, and 5.95 mg/g for Cr^{3+}, Ni^{2+}, Zn^{2+}, and Cu^{2+}, respectively. Biosorption of heavy metal cations was investigated as well, (Putra et al., 2014) and the maximum adsorption capacities for Zn^{2+} and Cu^{2+} were 3.89, 23.81 mg/g for coconut tree sawdust, 34.48, 35.71 mg/g for eggshell and 3.65, 40.00 mg/g for sugarcane bagasse. Hui et al. (2005) compared the adsorption capacity of coal fly ash-prepared zeolite 4A with that of commercial zeolite 4A, and the maximum adsorption capacities for Ni^{2+}, Cu^{2+}, Zn^{2+}, Cr^{3+} were found to be 8.96, 50.45, 30.80, and 41.61 mg/g for coal fly ash-prepared zeolite 4A and 7.90, 53.45, 31.58, and 45.29 mg/g for commercial zeolite 4A. Compared with the results above for the removal of these heavy metals, it is clear that the zeolite A synthesized from halloysite has a higher adsorption capacity, which might be attributed to the greater amounts of Na^+ ions in the zeolite A framework and on the surface.

2.3.2. Adsorption of mixed cations

Since not only heavy metals but also innocuous cations are present in natural river water, it is important to study the selectivity of our synthesized zeolite A toward different cations. The selectivity toward metal ions in the simulated contaminated river water and industrial wastewater was measured by a batch method over a range of initial concentrations. The adsorption data are listed in Table 2. The distribution coefficient (K_d), which means the ratio of the adsorbed metal cations and the residual ions in the solution, can indicate the selectivity of an adsorbent. In a specific adsorbate and adsorbent system, a higher K_d value for a metal cation means it has a higher selectivity for adsorption. In our experiment, three different solution concentrations were used. The general tendency of the distribution coefficient is heavily dependent on the concentration of the metal cations. The lower the concentration, the higher the distribution coefficients achieved, as shown in Fig. 5. A possible explanation is that, in order to achieve the same equilibrium chemical potential for metal cations in the solution and in zeolite A, a higher percentage of metal cations would be adsorbed by zeolite A in the lower concentration system.

Furthermore, the distribution coefficients for different metals are different. For heavy metals, regardless of whether

Table 2 – Adsorptive selectivity of Zeolite A for metal cations.

	Distribution coefficient K_d value			
	Without innocuous cations		With innocuous cations	
High concentration (1 mmol/L)	pH 3.49 → 6.20		pH 3.37 → 6.13	
	Fe^{3+}	11.1	Mg^{2+}	2.1
	Mn^{2+}	20.4	Ca^{2+}	8.2
	Ni^{2+}	24.6	Fe^{3+}	12.4
	Zn^{2+}	34.5	Ni^{2+}	22.2
	Cr^{3+}	49.8	Mn^{2+}	28.2
	Cu^{2+}	55.3	Zn^{2+}	28.2
	Pb^{2+}	113.6	Cr^{3+}	34.7
	Ag^+	2500	Cu^{2+}	64.3
			K^+	84.7
			Pb^{2+}	128.0
			Ag^+	3950
Moderate concentration (0.5 mmol/L)	pH 4.36 → 6.51		pH 4.32 → 6.45	
	Fe^{3+}	66.7	Mg^{2+}	9.8
	Ni^{2+}	88.5	Ca^{2+}	57.6
	Mn^{2+}	141.2	Fe^{3+}	58.2
	Cr^{3+}	197.5	Mn^{2+}	59.5
	Zn^{2+}	197.7	Ni^{2+}	65.0
	Cu^{2+}	354.8	Zn^{2+}	114.6
	Pb^{2+}	2783	K^+	133.8
	Ag^+	32,450	Cr^{3+}	135.7
			Cu^{2+}	188.9
			Pb^{2+}	1102
			Ag^+	25,950
Low concentration (0.1 mmol/L)	pH 5.16 → 6.83		pH 5.06 → 6.76	
	Fe^{3+}	5500	K^+	365.3
	Mn^{2+}	7735	Mg^{2+}	5887
	Ni^{2+}	8950	Ca^{2+}	9850
	Cu^{2+}	9033	Fe^{3+}	10,350
	Cr^{3+}	13,700	Ni^{2+}	10,850
	Zn^{2+}	17,783	Mn^{2+}	11,150
	Pb^{2+}	26,200	Cu^{2+}	17,616
	Ag^+	51,950	Zn^{2+}	26,700
			Cr^{3+}	27,700
			Pb^{2+}	88,283
			Ag^+	103,950

0.2 g adsorbent, 10 mL solution of $X(NO_3)_n$ with high (1 mmol/L), moderate (0.5 mmol/L) and low (0.1 mmol/L) concentrations of each cation.

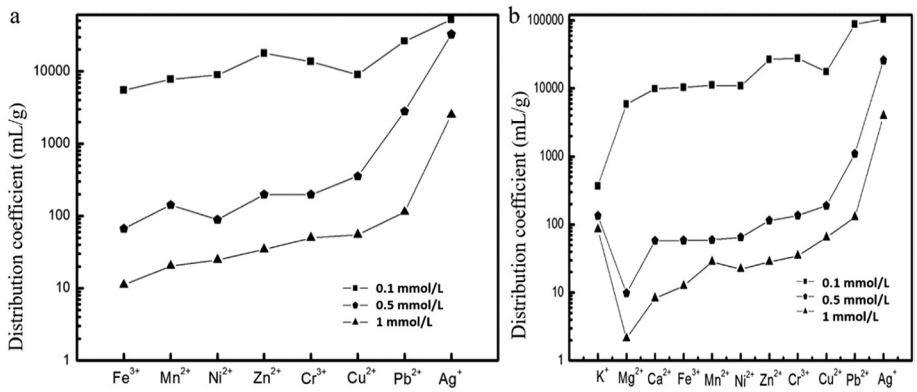

Fig. 5 – Distribution coefficient values at low (0.1 mmol/L), moderate (0.5 mmol/L) and high concentration (1 mmol/L) in the absence (a) and presence (b) of innocuous cations.

they are mixed with innocuous metals, the selectivity can be divided into three groups (Fig. 5a and b). The first group included Ag^+ and Pb^{2+}, which revealed relatively high adsorptive selectivity with respect to others, with Ag^+ showing higher selectivity than Pb^{2+}. The second group consisted of Cr^{3+}, Cu^{2+} and Zn^{2+}, which exhibited lower adsorptive selectivity than Ag^+ and Pb^{2+} but higher than the third group, which is made up of Fe^{3+}, Mn^{2+} and Ni^{2+}. The selectivity order of the three groups was consistent in the different concentration solutions with and without innocuous cations, with the order of Ag^+ ~ Pb^{2+} > Cr^{3+} ~ Cu^{2+} ~ Zn^{2+} > Mn^{2+} ~ Ni^{2+} ~ Fe^{3+}, although the orders in each group showed slight changes.

For innocuous cations, Ca^{2+} and Mg^{2+} displayed lower adsorptive selectivity than other heavy metal cations in all cases, for example, Ag^+(103,950) > Pb^{2+}(88,283.3) > Cr^{3+}(27,700) > Zn^{2+}(26,700) > Cu^{2+}(17,616.7) > Mn^{2+}(11,150) > Ni^{2+}(10,850) > Fe^{3+}(10,350) > Ca^{2+}(9850) > Mg^{2+}(5887.5) at low initial concentrations (0.1 mmol/L), and the K_d value of Ca^{2+} was higher than that of Mg^{2+}. The adsorptive selectivity of K^+ changed significantly with concentration, being the lowest in 0.1 mmol/L solutions but third only to Pb^{2+} and Ag^+ in 1 mmol/L solutions due to unknown reasons. Moreover, the increase in the removal rate for each cation with decreasing initial concentration was due to higher number of adsorption sites available for ion exchange on the adsorbent materials at low concentrations. This implies that the synthesized zeolite A is a good adsorbent, which showed a high selectivity toward heavy metals in mixed solutions even in the presence of innocuous cations.

In addition, the pH values of the solutions increased generally after adsorption. The low pH values of initial solutions were the result of hydrolysis of the acid salts. During the ion exchange, the metal cations were removed so as to reduce the hydrolysis, thus increasing the pH. Also it could be seen that the adsorption of different cations impacted each other. The cation uptakes changed much more in mixed solutions than in single ones. For instance, the adsorptive capacities were very similar for the heavy metal ions Cr^{3+} and Mn^{2+}, but after mixing these ions, the K_d values showed an obvious difference. It should be noted that the adsorption of multiple metal cations by an adsorbent is complicated. The higher concentration of Na^+ in the solution after adsorption implied that the adsorption mechanism is ion exchange, and also could be seen from Table 3. Basically, the metals adsorbed by zeolite A and Na^+ desorbed from

Table 3 – Charge balance after adsorption of metal cations.

Single cations	Metals C_0–C_f (mmol/L)	Na^+C_f (mmol/L)	Mixed cations		Metals C_0–C_f (mmol/L)	Na^+C_f (mmol/L)
Mg^{2+}	0.14	0.56	High concentration (1 mmol/L)	Without innocuous cations	7.90	8.01
K^+	0.41	0.56				
Ca^{2+}	0.38	0.77		With innocuous cations	8.82	9.02
Cr^{3+}	0.36	1.22				
Mn^{2+}	0.33	0.71	Moderate concetration (0.5 mmol/L)	Without innocuous cations	6.83	6.97
Fe^{3+}	0.33	1.04				
Ni^{2+}	0.33	0.69		With innocuous cations	7.77	7.82
Cu^{2+}	0.39	0.82				
Zn^{2+}	0.35	0.75	Low concentration (0.1 mmol/L)	Without innocuous cations	1.83	2.02
Ag^+	0.46	0.54				
Pb^{2+}	0.44	0.96		With innocuous cations	2.30	2.45

0.0041 g adsorbent with 1 mmol/L metal concentration.

zeolite A into the residual solutions maintain the charge balance, not only for the single cations but also mixed cations, because the adsorbents are required to maintain electrical neutrality.

The selectivity of zeolites could be the result of a combination of interactions, where the dominant interactions should be the electrostatic forces and hydrogen bonding forces involved between the hydrated metal ions and the zeolite framework (Akkermans et al., 2013; Jiang et al., 2013; Majdan et al., 2003; Ikhsan et al., 1999; Inglezakis et al., 2004). The order of selectivity is likely to be related to different forces within the framework and the characteristics of the metal cations in the solution, not just the charge and radius of the cations, because neither of these factors can explain the order of selectivity. According to previous studies (Eisenman, 1962; Ouki and Kavannagh, 1997), if cation absorption materials such as zeolites are placed in a solution containing several different metal salts, the preference of the exchanger for one metal over another depends on whether the difference between the hydration free energy and electrostatic interactions with exchange sites predominates. However, it is not easy to determine the hydration free energy, because the changes in water content of hydrated metals after adsorption by zeolites, which could also be a factor in determining selectivity, are uncertain (Eisenman, 1962).

3. Conclusions

In conclusion, high quality zeolite A has been successfully synthesized from natural halloysite mineral by a hydrothermal method under moderate conditions. Zeolite A exhibited a high adsorption capacity toward heavy metal cations, especially for Ag^+ (123.05 mg/g) and Pb^{2+} (227.70 mg/g), in both typical polluted river water and industrial wastewater. The order of selectivity toward heavy metals can be divided into three groups, which is consistent in the different concentration solutions with and without innocuous cations, with the order of $Ag^+ \sim Pb^{2+} > Cr^{3+} \sim Cu^{2+} \sim Zn^{2+} > Mn^{2+} \sim Ni^{2+} \sim Fe^{3+}$. More importantly, the heavy metals exhibited higher adsorptive selectivity than innocuous cations at various concentrations when they co-existed in the solution. The adsorption capacity for heavy metal removal is higher than other reported adsorbents. Based on these results, it is concluded that the zeolite A prepared from halloysite mineral can be used as a low-cost and relatively effective adsorbent for the removal of heavy metals from contaminated river waters and wastewaters. This study indicates that the zeolite A synthesized by our strategy could be a good candidate for purification of river water for drinking purposes.

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