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Research paper

An insight into the comprehensive application of opal-palygorskite clay: Synthesis of 4A zeolite and uptake of Hg^{2+}

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ABSTRACT

To availably utilize opal-palygorskite clay, dry beneficiation technique was applied to separate opal and palygorskite clay. Based on separated opal from opal-palygorskite clay, 4A zeolite was successfully synthesized by using a hydrothermal method. Box-Behnken was used to optimize Na_2O/SiO_2, H_2O/Na_2O and SiO_2/Al_2O_3 with cation exchange capacity (CEC) as the response value. The optimum parameters was determined to be Na_2O/SiO_2 = 1.0, H_2O/Na_2O = 40, and SiO_2/Al_2O_3 = 2.0, and CEC got the maximum of 2.99 mmol/(g·dry zeolite) under the conditions. The as-obtained 4A zeolite was characterized by using X-ray diffraction (XRD), thermo gravimetric analysis (TG), acid-base titration, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and then was applied to remove Hg^{2+} from aqueous solution. The maximum removal capacity of Hg^{2+} was 41.99 mg/g and adsorption equilibrium was obtained with contact time of 2 h. Effects of pH, ionic strength, temperatures, metal cations, strippant kinds and cycle times on removal behaviors of Hg^{2+} onto 4A zeolite were investigated by batch experiments. The kinetics and isotherms of Hg^{2+} adsorption fitted well by pseudo-second kinetic and Langmuir models. When Hg^{2+}-adsorbed 4A zeolite was desorbed using 1 mol/L $NaNO_3$ solution, the adsorption efficiency was maintained about 70% after four cycles.

1. Introduction

Mercury pollution became increasing critical environmental challenge in recent years due to its widespread distribution, intense toxicity and difficulty of control (Arshadi et al., 2017). Hg^{2+} pollution commonly rooted in coal-fired power factories, color alkali plants and so on (Liu et al., 2016). Mercury ramifications were widespread in water, air and soil which connected negatively with the health and ecosystem. Thus it was emergent to explore efficient removal ways for dealing with mercury pollution. Series of techniques had been researched to capture mercury such as adsorption, chemical precipitation, and membrane filtration (Huang et al., 2017; Shirzadi and Nezamzadeh-Ejhieh, 2017). Among them, adsorption was one of the most outstanding techniques due to its simplicity of working, high efficiency with respect to other techniques (Ram and Chauhan, 2018). In recent years, different natural and synthetic adsorbents such as chitosan, clay minerals, fly ash, activated carbons, and zeolite were investigated (Cui et al., 2013; Zhuo et al., 2017). Among those adsorbents, zeolite drew more attentions because of their special porous structure, high specific area and low cost (Su et al., 2016; Sun et al., 2017).

4A zeolite was a type of crystalline aluminium-containing silicate with homogeneous micro-channels and it had a pore diameter of 4 Å (Tang et al., 2017). Its three-dimensional pore structure was composed of sodalite cages and Na^+ was used to compensate the negative charge arising from the replacement of Si by Al in the framework (Meng et al., 2017). Therefore, 4A zeolite had been widely used in both laboratory and industry due to high exchange capability and environmental friendliness (Shen et al., 2017). Generally, zeolites were synthesized by using various low-cost materials like grain husk, kaolin, fly ash, diatomite and so on (Gougazeh and Buhl, 2018; Koshy and Singh, 2016; Volli and Purkait, 2015). In Huangni mountain of Xuyi city, Jiangsu province, approximately 100 thousand tons opal-palygorskite clay had not been effectively utilized every year (Chen et al., 2004). Thus low cost beneficiation was urgent needed to obtain higher grade palygorskite clay and opal. Previous study showed that the main component of opal from opal-palygorskite clay is opal-CT, which could react with alkaline easily (Wilson, 2014). So that kind of opal could be the excellent and cheap material for the synthesis of 4A zeolite.

In order to obtain 4A zeolite products with excellent adsorption performance, the optimization of synthetic parameters were necessary. In addition, response surface methodology (RSM) was the combination of mathematical and statistical methods that could analyse complex processes with more than two factors for the optimum parameters (Mante et al., 2013; Nandiwale et al., 2015). It also analysed the

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comprehensive influence of independent variables by establishing a functional relationship between multifactor and response value based on the rational utilization of factor experimental design (Chen et al., 2018).

Therefore, in this study, 4A zeolite was synthesized based on hydrothermal method using opal from the separation of opal-palygorskite clay. The preparation process was optimized based on Box-Behnken of RSM and the influence of independent variables was also analysed. Characterization means such as XRD, TG-DTG, acid-base titration, XPS and SEM were applied to illustrate the property of optimized product. In addition, we also explored how pH, ionic strength, time, temperature, common metal cations to influence Hg^{2+} sorption. The aim of this study was to separate opal and palygorskite from opal-palygorskite clay, to prepare 4A zeolite using the separated opal and to investigate the performance, mechanism, regeneration and the effect of water chemistry (pH, time, co-existing ions, etc) of the prepared 4A zeolite on Hg^{2+} adsorption. It was believed that this study would provide novel way for the comprehensive utilization of opal-palygorskite clay.

2. Experimental

2.1. Synthesis of 4A zeolite

4A zeolite was synthesized by a hydrothermal treatment based on opal. Natural opal from Xuyi County, Jiangsu Province, China underwent extrusion, crushing, and screening after dry beneficiation process to obtain opal particles < 0.075 mm. Opal powder was added to 20% HCl solution followed by shaking for 4 h under 70 °C. The ratio of opal powder to HCl solution was 1 g to 3 mL. The mixture was centrifuged and then washed by deionized water followed by drying at 110 °C overnight. The dried acid-treated opal (3 g), $NaAlO_2$, NaOH and H_2O were mixed at certain molar ratio of SiO_2/Al_2O_3, Na_2O/SiO_2 and H_2O/Na_2O. The mixture was transferred into the reactive kettle and then heated in an oven at certain temperature. After definite time, the product was centrifuged, washed, and dried at 105 °C overnight.

2.2. Experimental design

Based on our previous research, the crystallization time was set to 3 h and crystallization temperature was kept at 85 °C to obtain pure product. Therefore, Na_2O/SiO_2 (X_1), H_2O/Na_2O (X_2), and SiO_2/Al_2O_3 (X_3) were selected as variables, CEC (Y) of product was considered as the response parameter. A three-level-three-factor Box–Behnken design was created by Design expert software (8.0.6 trial version). Three factors in experiment were coded of −1, 0 and + 1 representing low levels, medium levels and high levels and concrete design data were listed in Table 1.

2.3. Characterization and analysis

2.3.1. Characterization

The chemical composition of opal-palygorskite clay was analysed on X-ray Fluorescence Spectrometer (Shimadzu 1800, Japan) with Rh radiation. The mineral composition of the material and products was examined via XRD patterns by a Dandong haoyuan 2700 diffractometer using Cu Kα radiation, with the tube voltage of 40 kV, the current of 30 mA, scan range of 3–70° and scan speed of 4°/min. TG and DTG were measured with SEIKO 7300 Thermo Gravimetry/Differential Thermal Analyzer under nitrogen atmosphere. The zeta potential of 4A zeolite at 1 mmol/L $NaNO_3$ was determined by a Nano-ZS90 Zetasizer. SEM imaging was performed on a JSM-6490LV instrument with the energy dispersive X-ray facility. And XPS data for products were obtianed by Thermo Scientific K-Alpha instrument.

Table 1
Factors and levels of Box-Behnken design.

Level	Factors		
	Na_2O/SiO_2	H_2O/Na_2O	SiO_2/Al_2O_3
−1	0.8	20	1.3
0	1.0	40	2.0
1	1.2	60	2.7

2.3.2. Analysis

CEC was measured according to the procedure in the National Light Industry Standard of QB 1768–2003 of China. $CaCl_2$ solutions with initial concentration of 5 mmol/L were adjusted pH to 10 by HCl or NaOH solutions. The aforementioned solution with 1.0 g/L synthetic product was shaken under vigorous stirring conditions for 20 min at 35 ± 1 °C. After the adsorption process and centrifugation, the supernatant was detected with atomic absorption spectrometer (Wayee WYS 2200, China). Next, the CEC was calculated from the wasting Ca^{2+} concentration and labelled as mmol/(g·dry zeolite).

2.4. Adsorption experiments

The stock solutions of Hg^{2+} was received by dissolving $Hg(NO_3)_2$ with concentrated HNO_3 solution and then was deliquated by deionized water to acquire work solutions. NaOH and HNO_3 solution were used to adjust the pH of Hg^{2+} working solution. Batch adsorption experiments were carried out by 1.0 g/L 4A zeolite with Hg^{2+} solutions in the presence of $NaNO_3$. $NaNO_3$ solution was used to provide electrolyte for the adsorption process. The foregoing test showed the solid-to-liquid ratio of 1.0 g/L was suitable towards the Hg^{2+} adsorption experiment. The mixed solution reacted under vigorous stirring conditions at constant temperature. The selectivity of the prepared 4A zeolite to Hg^{2+} solution containing five cations including NH_4^+, Cu^{2+}, Pb^{2+}, Zn^{2+}, and Ca^{2+} was evaluated. After sorption process, liquid phase was obtained by centrifugation at 3500 rpm for 5 min. The remained concentration of Hg^{2+} in suspension was determined by using Milestone DMA-80. The adsorption capacity (Qe, mg/g) of Hg^{2+} was calculated from the decrement of Hg^{2+} concentrations during the adsorption process and the formulation was listed as follows:

$$Qe = V \times (C0 - Ce)/m \quad (1)$$

C_0 and Ce (mg/L) were initial and equilibrium concentration of Hg^{2+}, m (g) was weight of 4A zeolite, and V (mL) was suspension volume. The regeneration performance of 4A zeolite were tested 4 successive cycles of Hg^{2+} sorption, desorption, and washing. The desorption agents were chosen as deionized water, 1 mol/L HNO_3, 1 mol/L $NaNO_3$ and 1 mol/L $Ca(NO_3)_2$ solutions.

3. Results and discussion

3.1. Separation and characterization of opal-palygorskite clay

Opal-palygorskite clay was piled up in an open environment for weathering by the alternation of drying and wetting followed by screening using sieves with different particle diameters. The chemical composition and the phase composition of different particle size opal-palygorskite clay after screening were measured by XRD and XRF, respectively. Based on the results of XRD and XRF, the content of opal and palygorskite were calculated according to the crystal chemical formula of palygorskite. According to previous research (Wang et al., 2018), opal and palygorskite could be availably separated by griddle with particle diameter of 4 mm. And the result indicated in oversize product, the content of opal was about 73.8% and about 16.8% was palygorskite. The oversize product was selected for the synthesis of 4A zeolite after certain purifying process. The chemical composition of opal-palygorskite clay measured by XRF showed that this sample mainly contained SiO_2 83.15 wt%, MgO 5.41 wt%, Fe_2O_3 2.17 wt%, Al_2O_3 1.91 wt