

Sorption of Cu^{2+} , Cd^{2+} , and Pb^{2+} using modified zeolite from coal fly ash

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Abstract

The coal fly ash (CFA) was modified to zeolite X using fusion method with cationic exchange capacity (CEC) of about 140 meq/100 g. The zeolite was used as an effective sorbent for Cu^{2+} , Cd^{2+} , and Pb^{2+} . The pseudo-second order kinetic model was appropriate for the description of the kinetic performance of the sorption. It required a longer time to reach equilibrium for higher initial metal concentration and lower sorbent dose but all reached equilibrium within 120 min. External mass transfer step seemed to take part as a rate limiting step for the sorption of Pb^{2+} at low initial concentration and high sorbent dose, on the contrary, the process was controlled more significantly by intraparticle diffusion step at high initial concentration and low sorbent dose. However, Cu^{2+} was found to be generally controlled by intraparticle diffusion step at all concentration range examined in this work. The sorption of Cd^{2+} , on the other hand was controlled both by external mass transfer and intraparticle diffusion steps at all range of initial concentration. Langmuir and Dubinin–Radushkevich isotherms were applied to describe equilibrium data. The order of maximum sorption capacity in a unit of mol kg^{-1} was: Pb^{2+} (2.03) > Cu^{2+} (1.43) > Cd^{2+} (0.870). The sorption energy fell in the range of physisorption. Equilibrium sorption capacity and removal percentage were governed by both initial concentration and sorbent dose. A general mathematical model was developed for describing the sorption under the variations in initial metal concentration and zeolite doses. This model was proven to be reasonably accurate with additional sets of experiments.

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1. Introduction

The combustion of coal in the power plant generally creates a large quantity of fly ash (or coal fly ash, CFA) as a by-product. Several alternatives are proposed and implemented for the treatment of CFA, such as the use as cement supplement. This is because CFA possesses pozzolanic property [1]. In cases where there are no feasible economical options, they are mostly land-filled. CFA could also be used in the neutralization of acid mine drainage as reported by Somerset et al. [2]. Conversion of CFA to zeolite is one of the potential alternatives for handling of the CFA as it is often constituted of high contents of silica and alumina which are the basic foundation in the formation of zeolite. Previous reports demonstrated the success in the conversion of CFA to zeolite. For instance, Faujasite and zeolite P were reported to

be synthesized from the reaction between CFA and NaOH [3], whereas phillipsite and hibschite were found to occur from the reaction between lignite CFA and calcium hydroxide [4]. Zeolites are widely used in several applications such as catalysts for hydrogenation, alkylation, and isomerization, and sorbents for the removal of contaminants, e.g. heavy metals, toxic gas, dyes, and organic pollutants such as benzene and alcohol. Generally, there are two major methods in the synthesis of zeolite from CFA: hydrothermal and fusion methods, where the fusion method was reported to provide higher cation exchange capacity (CEC) than the hydrothermal at the same conditions, and therefore was considered more suitable for the adsorption of the cationic metal species [5].

For sorption applications, zeolites were often reported to exhibit high sorption capacity, sorption affinity, and cation exchange capacity for divalent sorbates. Lee et al. [6] reported that the synthesized zeolites from CFA had greater adsorption capabilities for Pb^{2+} than the original fly ash (6–7 times) and natural zeolites (3–5 times). Erdem et al. [7] reported that

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natural zeolites hold great potential for the sorption of several heavy metal cations, e.g. Co^{2+} , Cu^{2+} , Zn^{2+} and Mn^{2+} , and this could be used as alternative for activated carbon.

This work focused on the investigation of the conversion of CFA to zeolite, and the examination of the sorption characteristics and mechanism of the zeolite product in the removal of Cu^{2+} , Cd^{2+} and Pb^{2+} from aqueous solution was achieved through kinetic and equilibrium studies. A general mathematical model was proposed to describe the relationship between the initial concentration, sorbent dose and equilibrium sorption capacity/removal percentage of the metal.

2. Materials and methods

2.1. Preparation and characterization of sorbent

Coal fly ash was collected from the National Power Supply Co. Ltd., Prachinburi province, Thailand. The CFA was dried at 120°C for 3 h before being stored in desiccators. This CFA was converted to zeolite using the fusion method as described in the work of Molina and Poole [5]. The method started with mixing CFA with ground NaOH anhydrous pellet at a weight ratio of about 1:1.75. The homogeneous mixture was then calcined in a nickel crucible at high temperature (550°C) for 1 h. The fusion product was ground and transferred to a 250 mL Erlenmeyer flask with screw cap which contained 85 mL of deionized water, and then immersed in a shaker water bath at 30°C for 24 h. The mixture was subsequently crystallized in an oven at 90°C for 2 h. The solid product was separated from the solution using centrifugation and then washed with DI water until the pH of solution was down to 10–11 and then dried overnight (about 12 h) at 110°C .

Cation exchange capacity of the zeolite product was determined using Sodium acetate method according to the US-EPA method 9081 [8]. The product was then analyzed with X-Ray Diffractometer, SIEMENS (D5000), to investigate the zeolitic phase using Cu $K\alpha$ radiation ($\lambda = 0.154056\text{ nm}$), with Ni filter. The X-Ray Fluorescence spectrophotometer, ARL, 9400 was used to determine the overall mineral composition of the product. The dry solid samples were analyzed for density in gas (helium) and water pycnometers. The particle size distribution (PSD) of product was determined by Laser Particle Size Analyzer, Malvern, Mastersizer-S long bed Version 2.19 using water as a medium. The Surface area analyzer, Thermo Finnigan, Sorptomatic 1990 was used for determining the specific surface area (SAA), whereas the total pore volume (TPV) of the product was determined using BET technique based on adsorption characteristics of N_2 gas on the sample at 77 K. The point of zero charge (PZC) was determined by measuring the surface charge of product in the DI water solution at various pH using Zeta Meter electrophoresis, Zeiss/3.0+. The pH of DI water was adjusted by nitric acid and sodium hydroxide to the desired pH.

2.2. Experimental procedure of sorption study

To determine the effect of initial concentration on sorption kinetics, the experiment was performed by mixing 0.03 g

dried zeolite in 30 mL of the synthetic metal ion solution (sorbent dose = 1.0 g L^{-1}) with an initial metal concentration in the range of $0\text{--}5\text{ mol m}^{-3}$. The pH was chemically controlled at five using $\text{CH}_3\text{COONH}_4/\text{CH}_3\text{COOH}$ buffer system. The mixtures were mixed in a rotary shaker at a rate of 150 rpm for 0–2 h and the temperature of the solution was controlled at $21 \pm 2^\circ\text{C}$. Suspended solids were separated out with GF/C filter. Metal ions concentrations were then measured in the filtrate by atomic absorption spectrophotometer (AAS). Experiments were repeated at least three times to ensure the accuracy of the results. More repetitions were carried out in cases where %relative standard deviation exceeded 15%.

To investigate the sorbent dose on sorption kinetics, the experiment was conducted in a similar fashion with that described in the previous paragraph. However, in this experiment, the initial concentration was fixed at 5 mol m^{-3} whereas the sorbent dose was varied in the range of $0.5\text{--}3\text{ g L}^{-1}$.

The equilibrium sorption experiments were conducted using the sorbent dose in the range of $0.5\text{--}3\text{ g L}^{-1}$ and the initial concentration in the range of $0\text{--}8\text{ mol m}^{-3}$ at the contact time of 120 min, the same conditions as those stated in the first paragraph of this section.

2.3. Calculations

2.3.1. Removal efficiency and sorption capacity of metal ions

The removal efficiency of metal ion is calculated from:

$$\% \text{Removal} = \frac{(C_o - C_f)}{C_o} \times 100 \quad (1)$$

The sorption capacity of metal ion is the amount of metal ion sorbed on the zeolite which can be calculated based on the mass balance principle where:

$$q = \frac{V(C_o - C_f)}{m} \quad (2)$$

In these two equations, q represents the amount of metal uptaken per unit mass of the zeolite (mol kg^{-1}), V the volume of the solution (m^3), m the dry mass of the zeolite (kg), C_o and C_f initial and final concentrations (mol m^{-3}), respectively.

2.3.2. Sorption kinetic model based on reaction order

Two sorption kinetic models were used in this work to describe the sorption characteristics. The first model was the pseudo-first order rate equation developed by Lagergren [9]. The model can be expressed in Eq. (3)

$$\frac{dq}{dt} = k_1(q_e - q) \quad (3)$$

Integrating Eq. (3) from $t = 0$ to $t = t$ and $q = 0$ to $q = q$ results in:

$$q = q_e(1 - e^{-k_1 t}) \quad (4)$$

The second model was pseudo-second order rate equation as expressed in Eq. (5) [10–14].

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (5)$$

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