Chemical Engineering Journal 145 (2009) 483–488

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Removal of lead, copper, nickel, cobalt, and zinc from water by a cancrinite-type zeolite synthesized from fly ash

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ARTICLE INFO

Article history:
Received 27 November 2006
Received in revised form 27 April 2008
Accepted 6 May 2008

Keywords:
Fly ash
Zeolite
Ion exchange
Heavy metals
Water treatment

ABSTRACT

As a low Si/Al ratio zeolite, cancrinite received very scant study in previous studies on the adsorption removal of heavy metals from water. In this study, a cancrinite-type zeolite (ZFA) was synthesized from Class C fly ash via the molten-salt method. Adsorption equilibriums of Pb^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+} on ZFA were studied in aqueous solutions and were well represented by Langmuir isotherms. The increase of pH levels during the adsorption process suggests that the uptake of heavy metals on ZFA was subjected to an ion exchange mechanism. It is found that the maximum exchange level (MEL) follows the order: Pb^{2+} (2.530 mmol g^{-1}) > Cu^{2+} (2.081 mmol g^{-1}) > Zn^{2+} (1.532 mmol g^{-1}) > Co^{2+} (1.242 mmol g^{-1}) > Zn^{2+} (1.154 mmol g^{-1}). Comparison with previous studies shows that the MEL of ZFA is higher than the commonly used natural zeolites; and it is also comparable to (or higher than) several synthetic zeolites and ion exchange resins. The high MEL of heavy metals on ZFA is attributed to the high cation exchange capacity (CEC) and proper pore size of cancrinite. The pseudo-first-order kinetics suggests that the ion exchange processes were diffusion-controlled.

1. Introduction

Heavy metals such as lead, copper, nickel, cobalt, and zinc are naturally occurring elements. Small amounts of these elements are common in our environment and they are actually necessary for our health. But large amounts of any of them may cause acute or chronic toxicity [1–3]. Heavy metals in human bodies tend to bioaccumulate, which may result in damaged or reduced mental and central nervous function, and damage to blood composition, lungs, kidneys and liver. The regulatory levels of health metals in drinking level are presented in Table 1 [4–6].

As many heavy metal salts have high solubility in water, many different treatment techniques such as chemical precipitation, coagulation–precipitation, adsorption and ion exchange have been developed to remove heavy metals from contaminated water [7–9]. Coagulation–flocculation and chemical precipitation are perhaps the most widely used, however they both have the drawbacks of difficult sludge disposal and more importantly the diminished effectiveness when treating water with low heavy metal levels [10]. Membrane filtration and reverse osmosis were also reported [11]. However, these methods usually involve expensive materials and high operation costs. Other methods such as electrodialysis, membrane electrolysis and electrochemical precipitation have also been investigated however their applications have been limited due to the high energy consumption [12]. On the other hand, as a cost-effective method ion exchange process normally involve low-cost materials and convenient operations, and they have been proved to be very effective for removing contaminants from water such as ammonia and heavy metals [12–14]. Moreover, ion exchange is particular effective for treating water with low concentration of heavy metals which is very common in practice [9].

The development of potential low-cost adsorbents with high exchanged levels is essential to facilitate the application of ion exchange processes for heavy metal removal. Various materials, including natural and synthetic zeolites, polymeric resins, have been studied for this purpose [15]. Zeolites are known excellent adsorbents that can readily adsorb and exchange metal cations with positive charges in their framework. Studies on heavy metal removal using natural and synthetic zeolites as ion exchangers have been reported [2,11,16]. Cancrinite-type zeolites received scant study for heavy metal removal in reported studies. In this study, we synthesized a cancrinite-type zeolite (ZFA) from Class C fly ash via a molten-salt method. The synthesized product, designated as ZFA, was used as an ion exchanger to remove Pb^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+} from water. The synthesized ZFA was expected to have high exchange levels for heavy metal cations due to its low Si/Al ratio [17]. The uptake of heavy metal cations on ZFA was studied for its mechanism, equilibrium and kinetics. The maximum exchange

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Abbreviations: ZFA, zeolite synthesized from fly ash; MEL, maximum exchange level (mmol g^{-1}); CEC, cation exchange capacity (meq g^{-1}).

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doi:10.1016/j.cej.2008.05.001

Nomenclature

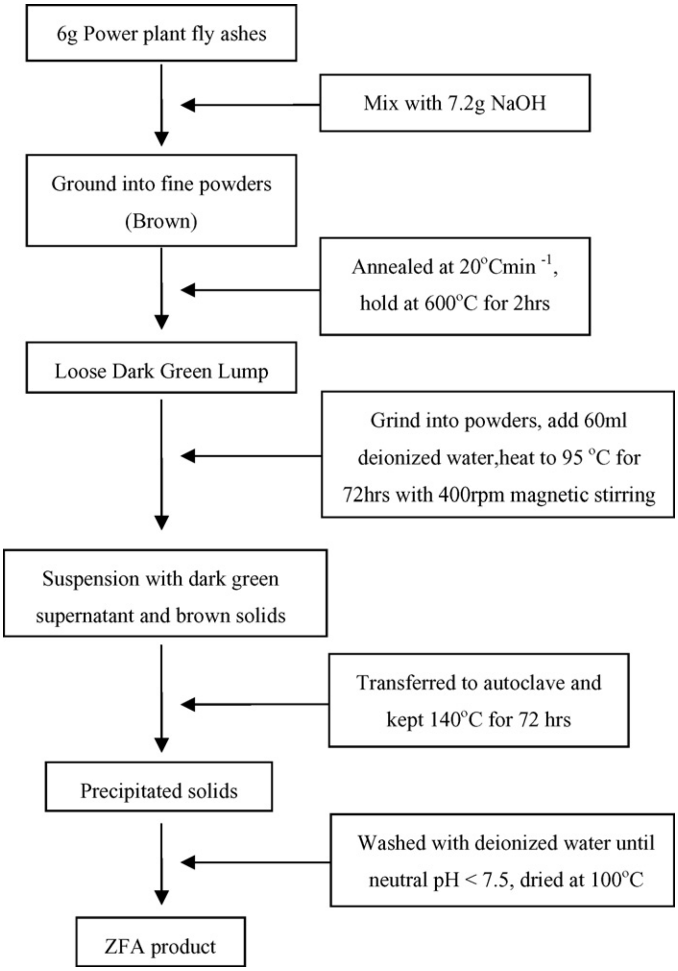
C	concentration of heavy metals (mmol l^{-1})
C_0	initial concentration of heavy metals (mmol l^{-1})
C_{eq}	concentration of heavy metals at equilibrium (mmol l^{-1})
d_c	charge density of cation (m^{-3})
k	kinetic constant of ion exchange process (s^{-1})
q_{eq}	exchanged cations at equilibrium on per mass of ZFA (mmol g^{-1})
Q	valence of cations
Q_0	maximum exchange level of cations on per mass of ZFA (mmol g^{-1})
r	diameter of cation (m)

level (MEL) for different heavy metal species was compared with reported results of other ion exchangers.

2. Experimental

2.1. Preparation and characterization of ZFA

Fly ashes were sampled from the Grand Lake Power Generation Plant (owned by N.B. Power Co.) in New Brunswick, Canada. The preparation of ZFA has been described in our previous work [18,19] and it is presented in the diagram below.



The crystal structure of ZFA was determined by powder X-ray diffraction (XRD) on a Bruker AXS D8 advance X-ray diffractometer. The specific surface area of ZFA was determined by nitrogen adsorption–desorption isotherms at 77 K on a Quantachrome Autosorb-1 Surface Area and Pore Size Analyzer. The BET specific surface area was determined by fitting the linear portion of the plot to the BET equation. Pore size distribution was calculated from the desorption plot of the adsorption–desorption isotherms using the Barrett–Joyner–Halenda (BJH) method.

2.2. Adsorption isotherms

The adsorption isotherms of heavy metals on ZFA were studied in a batch mode in an air-conditioned room with the temperature of 25.0 ± 2.1 °C as monitored by a digital wall-mounted thermometer (Cole-Parmer). Heavy metal nitrates were supplied from Aldrich (Reagent Grade) and used as received. Stock solutions of 4 mmol l^{-1} of $Pb(NO_3)_2$, $Zn(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, and $Cu(NO_3)_2 \cdot 2.5\ H_2O$ were prepared, respectively. Each solution was diluted to obtain a series of solutions containing 0.5–4 mmol l^{-1} heavy metals. Calculated amounts of $NaNO_3$ (99.0%, Aldrich) were added to keep a constant total exchange charge of 8 meq l^{-1} in the solutions, where 1 eq equals 1 mol positive charge. ZFA was added in each solution to give an adsorbent loading of 0.5 g l^{-1}. After adding ZFA, and drops of nitric acid (ACS grade, Fisher) were added to adjust the initial pH to 6.0 ± 0.2 for each solution. Polyethylene bottles containing 100 ml solution of each sample were sealed and shaken at 400 rpm for 72 h on an orbital shaker (KS-130, IKA). The pH was monitored by pH meter (Acumet 3000, Fisher) and re-adjusted to 6.0 ± 0.2 at set time intervals (t = 2, 24, 48, 72 h) to avoid the precipitation of heavy metal cations. The solution was filtered through a 0.45-μm nylon syringe filter (Cole-Parmer). The concentration of heavy metals in the filtration was determined by ICP-AES (inductively coupled plasma-atomic emission spectrometry, Spectro Ciros).

2.3. Adsorption kinetics

The amount of heavy metals exchanged with ZFA was studied as a function of time in batch experiments. A total amount of 500 ml solution with an initial concentration of 4 mmol l^{-1} heavy metal were mixed with 0.5 g ZFA and stirred at 400 rpm on a magnetic stirrer. The solution was acidified before adding the ZFA to avoid the cation precipitation caused by the pH increase. The pH of solution was examined and re-adjusted at the time intervals when samples were collected. Aliquots of samples (10 ml) were collected at set time intervals and immediately filtered by pushing through the 0.45-μm syringe filters. The concentration of heavy metal cations in the filtrate was determined by ICP-AES.

3. Result and discussion

3.1. Characterization of fly ash and ZFA

Fly ashes were sampled from the Grand Lake power generation plant, owned by N.B. Power Co. in New Brunswick, Canada. Fly ashes were used as received. The composition of fly ash has been determined in our previous study as: SiO_2: 31.6 wt.%; Al_2O_3: 27.8 wt.%; Na_2O: 27.7 wt.%; CaO: 6.4 wt.%; Fe_2O_3: 2.1 wt.%; P_2O_5: 1.5 wt.%; MgO: 1.4 wt.%; SO_3: 0.9 wt.%; other: 0.7 wt.% [18]. It can be categorized as Class C fly ash in terms of ASTM C618-99 specification.

The crystallographic structures of ZFA have been determined in our previous work [18]. The XRD pattern in Fig. 1 shows that the dominant phase in ZFA is carbonate cancrinite