Journal of Hazardous Materials 289 (2015) 1–8

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

The removal of caesium ions using supported clinoptilolite

D.A. De Haro-Del Rio, S. Al-Joubori, O. Kontogiannis, D. Papadatos-Gigantes, O. Ajayi, C. Li, S.M. Holmes*

School of Chemical Engineering and Analytical Science, The University of Manchester, Oxford Road, Manchester M13 9PL, UK

HIGHLIGHTS

- Natural clinoptilolite was supported over carbon structures produced from wastes.
- Carbon–clinoptilolite showed an improved Cs^+ ions sorption capacity.
- Overall kinetic rate was improved using carbon–clinoptilolite composite.
- Diffusive resistances were modified using the composite and pure zeolite.
- Final disposition volume can be reduced up to 60% by encapsulation.

ARTICLE INFO

Article history:
Received 14 October 2014
Received in revised form 2 February 2015
Accepted 11 February 2015
Available online 12 February 2015

Keywords:
Cs^+ ion removal
Supported clinoptilolite
Kinetics
Intraparticle diffusion

ABSTRACT

In this paper, the sorptive kinetic and diffusional characteristics of caesium ion removal from aqueous solution by carbon-supported clinoptilolite composites are presented. Natural clinoptilolite was supported on carbonaceous scaffolds prepared from date stones. Thermal treatment was applied to produce voids in the carbon which was conditioned using polydiallyldimethylammonium chloride to facilitate the clinoptilolite attachment. This method allowed the formation of a consistent zeolite layer on the carbon surface. The composite was applied in the removal of non-radioactive caesium ions showing an enhanced uptake from 55 mg g^{-1} to 120.9 mg g^{-1} when compared to clinoptilolite. Kinetic studies using Pseudo First Order model revealed an enhanced rate constant for carbon–clinoptilolite (0.0252 min^{-1}) in comparison with clinoptilolite (0.0189 min^{-1}). The Pseudo-First Order model described the process for carbon–clinoptilolite, meanwhile Pseudo Second Order model adjusted better for pure clinoptilolite. Diffusivity results suggested that mass transfer resistances involved in the Cs^+ sorption are film and intraparticle diffusion for natural clinoptilolite and intraparticle diffusion as the mechanism that controls the process for carbon–clinoptilolite composite. The most significant aspect being that the vitrified volume waste can be reduced by over 60% for encapsulation of the same quantity of caesium due to the enhanced uptake of zeolite.

1. Introduction

Radioactive caesium ions are a by-product of the fission of the fuel used to produce energy in nuclear power plants [1]. These fission products can be harmful to environment and human health. Unfortunately, catastrophic accidents have occurred in Chernobyl, Ukraine in 1986, where radioactive caesium ^{134}Cs and ^{137}Cs and iodine ^{131}I isotopes were released to the environment causing one of the worst environmental disasters in history [2]. Also, in 2011 in Fukushima, Japan an earthquake and a consequent tsunami destroyed the structure of the nuclear reactor leading to the emission of radioactive iodine, caesium and radioactive gases to the atmosphere [3].

Chemical precipitation, electrodialysis, adsorption and ion exchange are some of the different methods that have been investigated for the removal of highly soluble caesium species [4,5], for both clean up after incidents and waste water treatment under normal operation. However, these methods have their drawbacks, the use of chemical compounds as precipitating agents leads to the generation of high volume of toxic sludge making this technique undesirable. Electrochemical methods are very costly, since high-energy consumption is involved. Adsorption and ion exchange methods play an important role in the trapping of radionuclides

---

* Corresponding author. Tel: +44 161 306 4376; fax: +44 161 306 9321.
E-mail address: stuart.holmes@manchester.ac.uk (S.M. Holmes).

http://dx.doi.org/10.1016/j.jhazmat.2015.02.032

because materials are generally cheap, systems are easy to implement and sometimes can be regenerated where appropriate.

Zeolites are crystalline aluminosilicates with interconnected microporosity (defined as pores in the range or 2 nm or smaller [6]), zeolitic materials have a negatively-charged framework caused by the substitution of Si atoms by Al atoms within the structure which are usually balanced with extra-framework cations or protons [7]. The most abundant natural zeolite on earth is clinoptilolite which belongs to the zeolite family heulandite and is characterised as having Si/Al > 4 ratio [8]. Generally, the electroneutrality in clinoptilolite is maintained by Na^+, K^+ and Ca^+ ions. Due to its low cost and high availability, clinoptilolite has been heavily utilized in the removal of Cs^+ ions [9,10]. However, due to the microporous characteristics of zeolites, sorption performance is limited because of low diffusion rates [11]. The production of hierarchical materials has been demonstrated to over-come these problems and also to enhance sorption rates [12,13]. Some methods of the production of hierarchical materials include chemical treatment and the use of environmentally harmful chemical reagents. Also has been reported the use of costly, macroporous, sacrificial templates which have to be removed by thermal treatment [14,15].

In this study, a cheap and efficient method of supporting natural clinoptilolite using agro-industrial residues, which are converted into carbonaceous supports is described and the materials characterized. The preparation of materials is based upon the chemical modification of the scaffolds' surface by the use of polyelectrocations, providing positive electrical potential suitable for zeolite attachment. These supports will provide micro-architecture and auxiliary porosity in the composite. The evaluation of the prepared materials in the sorption of non-radioactive Cs^+ ions from aqueous solutions was carried out; the effect of parameters such as pH and dosage was investigated. Finally, kinetic soprtion data was analyzed using kinetic models and the intraparticle diffusion mechanism was investigated by using the Weber–Morris and Boyd models.

2. Experimental

2.1. Preparation of hierarchical zeolite composites

Natural clinoptilolite (HEU) was obtained from Turkey and it was used without any further conditioning. The chemical composition[1] was found to be SiO_2 71.0%, Al_2O_3 11.8%, TiO_2 0.10%, Fe_2O_3 1.7%, Na_2O 0.4%, K_2O 2.4%, CaO 3.4% and MgO 0.10%. Carbonaceous supports were produced using date stones (DS); they were cut, washed with deionised water and dried at 70 °C for 12 h. Then, the stones were heated inside of a tubular furnace under a nitrogen atmosphere and subject to a thermal treatment (200 °C, 600 °C and 900 °C) for 2 h, each step at a ramp rate of 5 °C min^{-1} in order to produce the scaffolds for the zeolite particles. After the thermal treatment, the carbon was crushed and sieved. Polydiallyldimethylammonium chloride (PDDA, 20,000 MW, Sigma) solution (c in 0.1 M NaCl, pH 9.5) was used to provide a positive zeta potential on carbon surface under ultrasonic mixing for 1 h (1 g of carbon in 20 ml solution), the PDDA excess was removed with deionised water and the carbon was dried overnight at 70 °C. Clinoptilolite (HEU) particles were dispersed in 0.1 M NaCl solution to promote particle mobility and solid retention. PDDA-treated carbons were then submerged in a zeolite suspension (1% wt in 0.1 M NaCl) and ultrasonicated for 1 h (1 g of carbon in 20 ml of suspension). A range of pH values (2–10) was studied for deposition of zeolite onto the carbon at constant ionic strength (0.1 M NaCl). Finally, the material (DS-HEU) was recovered by filtration washed with deionised water, to remove zeolite that was not attached to the carbon, and dried at 70 °C overnight.

2.2. Materials characterisation

Particle size distribution and ζ potential were assessed by Malvern Zetasizer 1000HS, X-ray diffraction was carried out to perform structural analysis and quality control of materials using a Rigaku powder diffractometer; to study materials' microtopography, and see how zeolite was distributed on the supports of scanning electron microscopy (SEM), was conducted using an FEI Quanta 200 and to determine the zeolite/carbon ratio thermogravimetric analyzes using QA5000 were conducted under an O_2 atmosphere.

2.3. Batch sorption studies

Caesium removal experiments were carried out using CsCl (Sigma–Aldrich) solutions. The initial pH was adjusted using 0.1 M HCl or 0.1 M NaOH accordingly. The experiments were carried out at 25 °C (±1 °C) in a controlled-temperature room. In a typical run, 100 ml of Cs^+ solution (400 mg l^{-1}, pH 5) was contacted with 0.5 g of material and stirred in an orbital rocker for 5, 10, 20, 30, 60, 120 and 180 min, after which the suspension was separated by filtration. The quantitative analysis of the samples was made by ICP-OES (Varian). The effect of initial pH (2–10) and dosage (0.1, 0.2, 0.3, 0.4 and 0.5 g) was conducted in order to find the best conditions. All samples were measured by duplication and the averages are presented. The associated error and reproducibility were given by the standard deviation of repeated sample measurements, and no more than 5% of error was allowed, the error bars are presented in corresponding results.

The Cs^+ uptake was quantified using:

$$q = (C_0 - C)\frac{V}{m}$$

where C_0 (mg l^{-1}) is the initial caesium concentration, C (mg l^{-1}) is the concentration after time t, V (l) is the solution volume and m (g) the mass of sorbent.

In order to quantify the sorption performance of the zeolite present in the composite, the equation:

$$q_{\text{composite}} = q_z x_z + q_c x_c$$

was used. Where q_z and q_c are the experimental uptake values for zeolite and carbon, respectively; and x_c and x_z are weight fractions for carbon and zeolite, respectively, in the composite; they were obtained by TGA analysis. The theoretical uptake of the ions into the zeolite present in the composite, q_{z*} can be calculated from

$$q_{z*} = \frac{q_{\text{composite}} - q_c x_c}{x_z}$$

3. Results and discussion

3.1. Materials characterization

Zeta potential plots for clinoptilolite, date stones (DS) and date stones after treatment (DS-PDDA) are shown in Fig. 1. For DS, it is clear that the influence of the solution pH on the surface chemistry, having at pH 2 a positive zeta potential value close to 40 mV and at pH 10 a value close to −40 mV showing the isoelectric point at pH ~4.8. Clinoptilolite only presents net negative potential over the range of pH analyzed, the increase of pH drives the zeolite zeta potential to more negative values. This is believed due to the

---

[1] Holistic valley. (December 2014). Clinoptilolite [technical data]. Retrieved from http://www.holisticvalley.co.uk/wp-content/uploads/2012/11/Tech-Clinoptilolite-0-300um.pdf.