



Efficiencies of chitosan nanoparticles and crab shell particles in europium uptake from aqueous solutions through biosorption: Synthesis and characterization



Elon I. Cadogan^{a,*}, Ching-Hwa Lee^a, Srinivasa R. Popuri^b, Hang-Yi Lin^a

^a Department of Environmental Engineering, Da-Yeh University, Changhua 51591, Taiwan, ROC

^b Department of Biological and Chemical Sciences, The University of the West Indies, Cave Hill Campus, Barbados 11000, West Indies

ARTICLE INFO

Article history:

Received 10 January 2014

Received in revised form

11 June 2014

Accepted 11 June 2014

Available online 30 July 2014

Keywords:

Europium

Chitosan nanoparticles

Biosorption

Langmuir

Kinetics

Characterization

ABSTRACT

The US Department of Energy declared Europium as one of the most critical rare earth elements. Industrial and radioactive wastewater containing Europium(III) may pose a problem to the environment when discharged into the groundwater or aquatic streams. This work reports the uptake of Europium from aqueous solution by biosorption onto crab shells powder and chitosan nanoparticles as novel biosorbents for Europium(III) ion. Chitosan Nanoparticles were synthesized by the ionic gelation method. Equilibrium and kinetic studies were conducted by batch adsorption studies in order to find the optimum metal uptake conditions with the present biosorbents. The extent of adsorption was found to be a function of solution pH, contact time, metal ion concentration and adsorbent dose. The experimental data were fitted to Langmuir, Freundlich and Temkin isotherms and the data were analyzed on the basis of Lagergren pseudo-first order, pseudo-second order and Weber–Morris models. The maximum monolayer adsorption capacity of the Chitosan nanoparticles and crab shell powder was found to be 114 and 3.2 mg g⁻¹ respectively. The results indicated the Chitosan nanoparticles could remove Europium(III) more effectively than the crab shell powder under optimum conditions. Characterization and ligand complexation behavior of the chitosan nanoparticles and crab shell powder were extensively investigated by Dynamic Light Scattering (DLS), Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA), X-ray diffraction (XRD) and scanning electron microscopy analysis (SEM).

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Europium (Eu) is a rare earth element that has been identified in various wastes including nuclear waste and due to its environmental toxicity Eu removal from wastewaters is becoming critical (Geleel et al., 2008; Chen et al., 2009). Eu is a lanthanide element with the oxidation state of +3 in aqueous solutions and can be considered as an analog for trivalent transuranic nuclides. Europium oxide is used in fluorescent powders due to its advantages such as high light-emitting efficiency, coating stability and cost recovery (Tang et al., 2011). In addition, Europium is also used in magnetic bubble storage devices and in the manufacture of tinted lenses, optical filters, atomic reactor control materials, shielding and structural materials (Franville et al., 2001; Wang et al., 2004; Agarwal et al., 2013). The mobility of radionuclides into the

environment is highly dependent upon their adsorption and hence determines their physiochemical behavior and stability. In order to avoid environmental toxicity, to recover the valuable rare earth Eu and to treat Eu containing wastewater effluents, the recovery of Eu is highly essential in both economical and environmental aspects.

Generally, trace concentrations of metal ions are removed by precipitation, reduction-oxidation, ion exchange, filtration, reverse osmosis and electro-chemical methods (Chong and Volesky, 1995; Leusch et al., 1995). Europium can be separated from various matrices by two common methods, namely solvent extraction and ion exchange (Sivaiah et al., 2004; Xie et al., 2014). However, these methods are inefficient due to consumption of large amounts of chemicals that may cause health problems. Biosorption is considered a potential instrument for the removal of metal ions from waste solutions and for precious metals recovery and is considered as an alternative to the conventional methods (Nghah et al., 2011). Previous studies have been conducted to determine the adsorption behavior of Eu on phyllosilicate minerals such as attapulgite, kaolinite, montmorillonite (Zhao et al., 2011), without a major

* Corresponding author. Tel.: +886 975 917377; fax: +886 4 8511336.
E-mail address: elon.cadogan@gmail.com (E.I. Cadogan).

emphasis on the adsorption of Eu on chitosan nanoparticles (CsNp). Metwally et al., 2009 conducted a study using chitosan benzoyl thiourea to investigate the sorption behavior of ^{60}Co and $^{152+154}\text{Eu}$ radionuclides from aqueous solution.

In this study crab shell particles (CbP) of *Ranina ranina* and extracted chitin deacetylated to chitosan, to synthesize CsNp were used as Eu(III) biosorbents. Pristine chitin, poly- β -2-acetamide-(2-deoxy-D-glucopyranose), is the most important nitrogen containing bioorganic polymer found in the ocean (McCarthyPratum et al., 1997). Chitosan, poly- β -2-amino-(2-deoxy-D-glucopyranose), has available amino groups on its polymeric chain, which has a high potential for metal chelation and provides a pathway for chemical modifications (Muzzarelli, 1973; Tikhonov et al., 1996; Jayakumar et al., 2007; Suman et al., 2013). Due to the nature of chitosan and its high metal binding capability, chitosan has been used for the adsorption of heavy metals including Cadmium, Chromium, Copper, Mercury, Nickel, Lead and Zinc (Vijaya et al., 2008; Popuri et al., 2009; Sun et al., 2009; Laus and Tadeu de Fávère, 2011; Ngah et al., 2011).

The main objective of this study was to evaluate the sorption behavior and capacities of the novel biosorbents CbP and CsNp for the biosorption of Eu(III). The adsorption data was subjected to the most popular kinetic models to determine the kinetic order of biosorption and the most widely used isothermal models to determine the possible mechanism responsible for Eu(III) biosorption. In addition, these biosorbents were thoroughly characterized before and after adsorption by various analytical techniques to confirm the accumulation of Eu(III) onto the biosorbent's surface.

2. Materials and methods

2.1. Materials

Eu(III) stock solutions of concentrations 10, 20, 30, 40, 50, 75 and 100 mg L⁻¹ were prepared by diluting the original solution of 1000 mg L⁻¹ obtained from Merck Co. Ltd. Germany. The Eu(III) was present in the form of Eu₂O₃ in 2–3% HNO₃ solution. Each stock solution was used within 24 h of dilution to reduce the possibility of micro-precipitation of the metal ion due to long standing. Analytical grade hydrochloric acid, nitric acid, sodium hydroxide and tripolyphosphate (TPP) were obtained from Katayama Chemical Co. Ltd. Taiwan. Deionized water was used throughout for metal ion dilutions.

2.2. Preparation of biosorbents

Waste shells of *Ranina ranina*, the spanner crab, were collected locally in Taiwan from local restaurant suppliers. The shells were washed with deionized water and sun dried for 24 h. The dried shells were crushed to particle size of 50-mesh. For biosorption experiments, 50-mesh crab shells were used directly. Chitosan was extracted from crab shells through several chemical methods such as: demineralization, deproteinization, deacetylation, and decoloration. The ground shells were demineralized via reflux with 1 N HCl for 3 h at 60 °C with a solid/solvent ratio of 1:15 (w/v). The obtained solid was dried and washed with deionized water until the pH reached neutral followed by vacuum filtration. Deproteinization of the obtained solid was carried out with 3% NaOH solution and the contents were stirred for 6 h at 80 °C with a solid/solvent ratio of 1:10 (w/v). The residue was again washed, filtered and dried at room temperature for 48 h. Deacetylation was conducted in 45% NaOH for 4 h with a solid/solvent ratio of 1:10 (w/v). Decoloration of the resulting chitosan was done by sun drying for 6 h. The obtained chitosan was used to prepare the chitosan nanoparticles.

2% chitosan solution was prepared by dissolving 2 g of chitosan in 98 ml of 1% acetic acid solution. Nanoparticles of chitosan were prepared via the ionotropic gelation process by the gradual addition of 100 ml of 1000 mg L⁻¹ TPP solution to the 100 ml of 2% chitosan solution. The solution was stirred at room temperature for 24 h. The resulting reaction mixture was centrifuged for 20 min at 6000 rpm. After centrifugation the CsNp were settled at the bottom of the tube and the supernatant liquid was discarded. These CsNp were further washed with deionized water, dried and used for Eu(III) adsorption studies.

2.3. Biosorption studies

Biosorption experiments were carried out in 50 ml Erlenmeyer flask containing 25 ml of the required concentration (10–100 mg/L) of Eu(III). A known mass of biosorbent (crab shells 100 mg, chitosan nanoparticles 10 mg) was added to each flask and agitated at 25 °C at 60 rpm in a temperature controlled rotary shaker. The effect of agitation time on the biosorption of Eu(III) was conducted at a concentration of 10 mg L⁻¹. Biosorption of Eu(III) onto CbP and CsNp was investigated by measuring the equilibrium concentration adsorption capacity, at different time intervals (5, 10, 15, 20, 30, 60 and 120 min) with an agitation speed of 60 rpm using an ultrasonic shaker in a temperature control unit. The Erlenmeyer flasks were maintained at a constant temperature of 25 ± 0.5 °C.

The initial unchanged pH was 2.1. The pH of the solution was adjusted accordingly with 0.1 N HCl or 0.1 N NaOH and the temperature were maintained at 25 °C. The effect of pH of the medium on metal removal was studied by performing equilibrium sorption experiments at different pH values while keeping the metal ion concentration, the amount of biosorbent, contact time, and the temperature constant. After attaining equilibrium, adsorbent was separated by filtration using with a Polyvinylidene fluoride syringe filter and the aqueous-phase concentration of Eu(III) was determined with Inductively coupled Plasma-Atomic Emission spectrophotometer (ICP-AES). The equilibrium uptake capacity of the CbP and CsNp for Eu(III) ion was calculated according to mass balance,

$$q_e = v(C_i - C_e)/m \quad (1)$$

where q_e was the amount adsorbed per unit mass of adsorbent (mg g⁻¹), C_i and C_e were, respectively, initial and equilibrium concentrations of metal ion (mg L⁻¹), m was the mass of adsorbent (g) and v was volume of solution in liters. Control experiments were conducted with metal ion solutions in absence of biosorbent and found no metal adsorption by the walls of the container. Each experiment was repeated three times independently and the means were taken. Standard deviation and analytical errors were calculated and maximum error was found to be ±5%.

Analysis of equilibrium data was important for the industrial application of biosorption since it gives information for comparison among different biomaterials under various operating procedures. Adsorption isotherm models were widely employed phenomena to examine the relationship between sorbed (Q_e) and aqueous concentrations (C_e). Although a range of isotherm models were available to study the equilibrium data, of which the most popular Langmuir and Freundlich adsorption isotherms were employed for this study. The data on adsorption of Eu(III) on CbP and CsNp were also correlated with the Temkin isotherm.

The Langmuir isotherm model was used to estimate the maximum uptake values of Eu(III) onto the biosorbents and the Freundlich isotherm was used to define the relationship between the uptake capacity of Eu(III) and the residual concentration of Eu(III) at equilibrium. The Langmuir and Freundlich isotherms were

Download English Version:

<https://daneshyari.com/en/article/4364628>

Download Persian Version:

<https://daneshyari.com/article/4364628>

[Daneshyari.com](https://daneshyari.com)