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Potentiality of uranium biosorption from nitric acid solutions using shrimp shells

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ABSTRACT

Biosorption has gained important credibility during recent years because of its good performance and low cost. This work is concerned with studying the potentiality of the chitin component of the shrimp shells for uranium biosorption from nitric acid liquid solutions. The structural characteristics of the working chitin have been determined via Fourier Transform Infrared Spectroscopy (FTIR). The surface morphology was examined using Scanning Electron Microscopy (SEM). The adsorption capacity of biomass was investigated experimentally. The influence of contact time, pH, metal ion concentration, solution volume to mass ratio and temperature were evaluated and the results were fitted using adsorption isotherm models. The kinetic of uranium biosorption was also investigated as well as biosorption thermodynamic.

1. Introduction

The chemical and radiological toxicity of natural uranium is actually well documented (Brugge et al., 2005). The environmental protection agency (EPA) has classified uranium as a confirmed human carcinogen and suggested that zero tolerance is the only safe acceptable limit (USEPA, 1996). In addition, the EPA finalized a realistic regulation level of 30 $\mu g\,l^{-1}$ is the maximum uranium contaminant level. According to the stringent environmental regulations that exist against the release of uranium contaminants into the environment, it is therefore greatly desirable to develop efficient, economical and viable methods for the treatment of uranium wastes.

Various kinds of adsorbents have been widely produced and applied for the removal of radionuclides and heavy metals (Kuribayashi et al., 1987). Although many adsorbents have excellent performance, the cost is relatively high in comparison with the greatly available natural waste products (Kuribayashi et al., 1988). Biosorption is a physicochemical process that occurs naturally in certain biomass which allows it to passively concentrate and bind contaminants onto its cellular structure (Volesky and Bohumil, 1990). In practice scientists and engineers are hoping that biomass can provide an economical alternative for removing toxic heavy metals and radionuclides from industrial wastewater and aid in environmental remediation (Kratochvil and Volesky, 1998). Abundant natural polymers or agriculture waste products can be economically used as potential biosorbents for different metals (Demirbas, 2008; Faroog et al., 2010; Ray et al., 2010; Sud et al., 2008). Thus, extensive research has evaluated variety of biosorbents such as fungi (Kapoor and Viraraghavan, 1998), yeast (Ashkenazy et al., 1997), bacteria (Diels et al., 1995), algae (Zhang et al., 1999), chitin (Hoshi et al., 1997) and chitosan (Kang et al., 1999).

Chitin, an environmental friendly material, is considered as biodegradable and biocompatible. It is a natural long chain polysaccharide polymer of N-acetyl-D-glucosamine, a derivative of glucose. It is the second most abundant resource (next to cellulose) in nature. Chitin is the main component of the exoskeletons of anthropods such as crustaceans (e.g.; crabs, lobsters and shrimps). Besides its resistance to the action of acids, it is worth noting that chitin is recognized as an excellent metal ligand, forming stable complexes with many metal ions (Chui et al., 1996). The formation of coordination complex between the metal and the chitin nitrogen or oxygen has been reported (Sağ and Aktay, 2000). Gyliene et al. (2002) have pointed that some of metal ions, such as Fe^{3+} and Pb^{2+}, are sorbed much better on chitin.

The use of chitin as powder is very difficult for its separation after adsorption as well as application in chromatograph column (Yan and Viraraghavan, 2001). It is also well known that chitin is insoluble in many solvents however; it is very brittle leading to a limitation in its reactivity and process ability for utilization.

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The aim of this research was to study the ability of chitin for grafting uranium from nitric acid solutions. Therefore, the chitin component of the working shrimp shell was separated using a proper extraction procedure and its structural characteristics were determined. The relevant optimum conditions for uranium adsorption were then studied under varying experimental conditions using batch operation mode. Adsorption isotherm modeling, sorption kinetics and thermodynamics were investigated to determine the probable physical characteristics of the applied process.

2. Material and method

2.1. Material

2.1.1. Material preparation

Fresh shrimp shells provided for the experiments were supplied from local market Cairo, Egypt. The shells were first separated from the head and legs then washed for several times with deionized water before drying at 40 °C. The dried shells were cut to almost uniform flakes. The shrimp shell flakes characterized by the presence of chitin, the material which is responsible for uranium grafting in our study, so it was recommended to quantify its percent before use.

2.2. Chitin extraction

Chitin extraction parameters were occurred by mild acidic and alkaline treatments (Manni et al., 2010). Initial step of extraction was carried out by acidic treatment using 1 N HCl solution at room temperature for 2 h followed by filtration, neutralization and washing with deionized water. Next step, deproteination, was performed using alkaline treatment with 2 N sodium hydroxide solution at 60–65 °C then followed by neutralization by washing. Final step, demineralization, has done by 1 N HCl solution at room temperature for 3–5 h. Chitin extraction yield was 24–28%.

2.3. Material characterization

Chitin in the shrimp shell was characterized by the following technique:

a) Fourier Transform Infrared Spectrometer (FTIR): (FTIR) model Thermo Scientific Nicolet IS10, Germany was used for the determination of the structural characteristics of the working chitin.
b) Scanning Electron Microscope (SEM): SEM model Philips XL 30 ESEM is considered as the most reliable and convenient tool for the study of physical structure of biosorbents (Warshawsky et al., 1981) as well as mineralogical investigations. The analytical conditions involved 25–30 kV accelerating voltage, 1–2 mm beam diameter and 60–120 s counting times. Minimum detectable weight concentration is ranging from 0.1 to 1 wt% while the realized precision is well below 1%.

2.4. Decalcification of shrimp shells before uranium adsorption

The shrimp shells consist of several layers where calcium carbonate is concentrated mainly in the outer tough layer. The principle behind decalcification of shrimp shell is that calcium carbonate in the shells will react with dilute nitric acid medium to form soluble calcium nitrate, water and carbon dioxide (Eq. (1)).

$$CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + H_2O + CO_2 \quad (1)$$

The given out CO_2 bubbles from the reaction of calcium carbonate in the shell with the nitrate medium may delay the process of uranium adsorption. Therefore when all calcium carbonate in the shells react with HCl, most of the pore spaces are already opened which accommodate the adsorbed uranium (Eq. (2))

$$CaCO_3 + 2\,HCl \rightarrow CaCl_2\,(aq) + CO_2 + H_2O \quad (2)$$

2.5. Adsorption studies

Several batch biosorption experiments were carried out using 100 ml conical flasks by stirring 50 ml uranium solutions with different concentrations after adding 1 g dry weight of the working biosorbent for 1 h and then all the conical flasks were sealed with a silicon cap to minimize evaporation. The amount of uranium metal ion adsorbed was calculated from the following equation:

$$Q_e = (C_0 - C_e) \times V/M \quad (3)$$

where Q_e is the amount of uranium metal ions adsorbed onto the unit mass of the sorbent ($mg\,g^{-1}$), C_0 and C_e are the initial and equilibrium metal concentrations ($mg\,l^{-1}$) in the solution, respectively, while V is the solution volume (L) and M is the dry weight of biosorbent (g).

Uranium concentration in the different aqueous stream solutions was measured via its arsenazo (III) complex using SP-8001 UV–VIS Spectrophotometer at wavelength 655 nm (Marczenko, 1976). The arsenazo (III) reagent (Avocado) solution was prepared by dissolving 0.25 g together with 0.5 g sodium acetate in 100 ml deionized water. The uranium solutions were prepared by diluting the standard uranium stock solution assaying 1000 $mg\,l^{-1}$ in nitric acid solution (TEDIA, USA) to the desired concentrations using deionized water. On the other hand, a digital pH meter (Jenway, UK) was used for pH adjustment.

3. Results and discussion

3.1. Environment friendly preparation

The particles' size, shape and surface morphology as well as specific surface area of bio-adsorbent fully depend on the preparation method. In addition, easy to prepare, easy to use, hazard free and environment friendly treatments are the requirement for sustainable preparation of bio-adsorbents. In these circumstances, this research adopted a simple preparation method rather than the expensive and high-tech pyrolysis and non-environment friendly acid/base treated methods. In this research the shrimp shells were treated with 0.5 N HCl solution in order to remove calcium carbonate present in the shells before the adsorption experiments then dried and ground to uniform flakes.

3.2. Characteristics of biosorbent

3.2.1. Fourier transform infrared spectrometer characterization

FTIR spectra are a useful tool to identify molecular to functional groups (Dong and Ozaki, 1997). The yield of chitin from the separated shell is 1.245 g obtained from 5 g shrimp shell sample. The IR spectrum of the chitin (Fig. 1) isolated from the shrimp shell contains six major peaks; 3433 cm^{-1}, 2929 cm^{-1}, 1647 cm^{-1}, 1548 cm^{-1}, 1213 cm^{-1} and 1024 cm^{-1}. The band observed at 3433 cm^{-1} in shell spectra indicates the presence of N–H (primary amine) and O–H (alcoholic) stretching groups, this result agrees with (Gow et al., 1987) which found that the IR spectrum of a chitin exhibited major peaks at 3446 cm^{-1} for –OH stretching and –NH