Egyptian Journal of Petroleum (2014) **23**, 221–228

Egyptian Petroleum Research Institute

Egyptian Journal of Petroleum

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FULL LENGTH ARTICLE

Preparation of chitosan from the shrimp shells and its application for pre-concentration of uranium after cross-linking with epichlorohydrin

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Received 24 June 2013; accepted 26 August 2013
Available online 4 July 2014

KEYWORDS

Uranium;
Chitosan;
Thermodynamic;
Adsorption

Abstract Chitosan (CTS) was first prepared by proper treatment of shrimp shells and the cross-linked chitosan (CCTS) was then synthesized by its reaction with epichlorohydrin (*ECH*) under alkaline conditions. Adsorption of uranium from aqueous nitrate solution onto CCTS was investigated batch wise. The adsorption isotherm and the adsorption kinetic as well as thermodynamic studies of this adsorption are carried out. The influence factors on uranium (VI) adsorption were optimized and were found to include an initial pH of 3 and a contact time of 120 min. The Langmuir adsorption model was then applied for the mathematical description of the obtained adsorption equilibrium and where its data greatly agree with that model and where the maximum adsorption capacity was estimated to be 903 mg/g. Adsorption kinetics data were also tested using pseudo-first-order and pseudo-second-order models and where the studied adsorption followed the latter. In addition, determination of the thermodynamic parameters ($\Delta G°$, $\Delta H°$ and $\Delta S°$) using van't Hoff equation has indicated that the prepared CCTS can conveniently be used for uranium adsorption from its aqueous solution.

1. Introduction

Uranium element is one of the most important resources to secure energy. The main sources of uranium are soils, tailings of some mineral processing activities, black sand and sea water. It is usually found in the environment in the hexavalent form as the mobile, aqueous uranyl ion (UO_2^{+2}). On the other hand, uranium is in demand for nuclear power production, and has different applications including nuclear power plants,

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Peer review under responsibility of Egyptian Petroleum Research Institute.

Production and hosting by Elsevier

 http://dx.doi.org/10.1016/j.ejpe.2014.05.009

manufacture of nuclear weapons, electron microscope and glass and pottery glaze [1].

Extensive efforts have recently been made toward the development of new technologies for separation of U (VI) from aqueous solutions [2].

The most used methods for the separation and preconcentration of uranium include precipitation, co-precipitation, solvent extraction, membrane dialysis, chromatographic extraction, ion exchange and floatation [3,4]. Among these various methods, adsorption is an economically feasible method and it has been emerged as the promising technique for adsorption of U from aqueous solutions especially for effluents with moderate and low concentrations. In acidic solutions, uranium exists as U (VI), whereas in neutral or basic pH conditions, it normally exists as neutral or anionic species by complex formation with anionic ligands such as OH^- or CO_3^{2-} [5]. Chitosan is found to have excellent adsorption capacity for various heavy metals. Chitosan is derived from polysaccharide chitin which is well known as a low cost, abundant, renewable marine polymer coming from the structural components of the shells of crustaceans, such as shrimps, lobsters, and crabs; it is the most plentiful natural polymer next to cellulose. Chitosan is produced at an estimated amount of one billion tons per year [6]. The molecular structure of chitosan is represented by a β (1 → 4) linked linear biopolymer consisting of 80% poly (D-glucosamine) and 20% poly (*N*-acetyl-D-glucosamine). The element uptake by chitosan is primarily attributed to the amine and hydroxyl groups present in the polymer chain, which can interact with various metallic species through ion exchange and/or chelation mechanism.

Crosslinking has become the focus for the preparation of CTS polymers in order to prevent dissolution of the hydrophilic polymer chains in an aqueous environment and improve engineering properties [7,8].

In general, the resins made of chitosan as a base material are more hydrophilic than synthetic resins such as polystyrene, poly (styrene-divinylbenzene), polyethylene, and polyurethane; therefore the sorption kinetic is very fast [9]. Different kinds of cross-linking agents such as glutaraldehyde [10], epichlorohydrin and ethylene glycol diglycidyl ether have been used in the cross-linking reaction of chitosan. Aldehyde cross-linking may result in the loss of adsorption capacity because some amine groups are involved in the crosslinking reaction [11]. However, an advantage of epichlorohydrin is that it does not eliminate the cationic amine function of chitosan [12].

In the present work, cross-linked chitosan was synthesized by the reaction of chitosan with epichlorohydrin under alkaline conditions. The uranium adsorption behavior on CCTS was investigated.

2. Methods

2.1. Preparation of chitosan and ECH–CCTS

Chitin of the Egyptian shrimp shells was first purified via its successive treatment with NaOH and HCl solutions in a manner for its deproteinization and demineralization, respectively. This was followed by de-colorization with acetone. The removal of acetyl groups from the purified chitin was achieved by mixing with NaOH in a solid to solvent ratio of 1:10 (w/v). The resulting CTS flake was rinsed with distilled water, filtered, and then dried for 24 h [13,14]. In order to prepare CCTS, the latter with 82% degree of de-acetylation and 110 KDa of molecular weight was dissolved in acetic acid followed by gradual addition of ECH and drop wise addition of 5% (w/v) NaOH solution where the ECH–CCTS was obtained as a white solid precipitate. The reaction of CTS with ECH might be cross-linked at hydroxyl groups to form the ECH–CCTS [15], as shown in Scheme 1.

2.2. Preparation of the uranium solution

The uranium solution assaying 300 ppm was prepared by dissolving a fraction of the uranium wet crude concentrate (23% U) prepared at the Gattar pilot plant in HNO_3 acid. The former is obtained by sulfuric acid heap leaching of Gattar mineralization followed by its concentration by Chinese anion exchanger resin D263 B. From the obtained eluate, Gattar uranium concentrate (sodium diuranate) was prepared by adding NaOH solution at pH 7.

2.3. Experimental procedure

2.3.1. Adsorption experiments

Several series of batch adsorption experiments have first been performed using a synthetic CCTS (10 mg) and 50 ml of the Gattar uranium solution (300 ppm) in order to optimize the relevant adsorption factors. Adsorption studies were conducted for optimizing U adsorption conditions such as contact time, initial pH and temperature.

2.3.2. Adsorption isotherm

For the isotherm experiments, the initial solution pH was kept at 3 with solution of (300 ppm U) at four different temperatures 30, 40, 50 and 60 °C. The effect of initial concentration (300 mg L^{-1}) and different temperatures (30–60 °C) on adsorption rate was studied by keeping the mass of the CCTS as 10 mg and, optimized volume of solution and pH conditions. Flasks were shaken in a thermostatic shaker at different times (30, 45, 60, 120 and 180 min.) with mixing rate of 300 rpm and the working slurry was filtered and the remaining uranium in the supernatant solution was determined by using the titration method. The amount of adsorption at equilibrium time t, q_e (mg/g), was calculated by:

$$q_e = \frac{(C_o - C_e \times V)}{W} \tag{1}$$

Where C_o and C_e are the liquid-phase concentrations of uranium at initial and equilibrium time, respectively; V the volume of the solution (L); W is the mass of dry adsorbent used (g). The adsorption efficiency of the uranium from aqueous solution was calculated as follows:

$$\text{Adsorption efficiency}(\%) = \frac{C_o - C_e}{C_0} \times 100 \tag{2}$$

2.3.3. Desorption process

The regeneration of the loaded CCTS is among the important factors in economical technology. Desorption batch experiments were carried out using different desorption agents such as HNO_3, Na_2CO_3, HCL and pure distilled water. After having adsorbed the U ions, the CCTS (10 mg) was washed with