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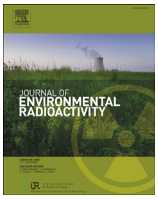

Sorption of uranium from aqueous solutions using palm-shell-based adsorbents: a kinetic and equilibrium study

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In this study adsorbents based on palm shell powder as well as modified and activated palm shell powder were studied to analyze their behavior in sorbing U^{6+} by both batch and fixed column modes. Seven different two-parameter isotherm models were applied to the experimental data to predict the sorption isotherms. The ΔG^0 values from Langmuir and thermodynamic calculations indicate physisorption as the major mechanism for adsorption of uranium. Usefulness of various kinetic models like pseudo first order, pseudo second order, intraparticle diffusion, Bangham, Elovich and Liquid film diffusion were tested. The adsorption capacities were found to be greater than 200 mg/g for all the adsorbents under study. The column data were fitted by Thomas, Yoon and Nelson as well as Wolborska models. The Thomas and Yoon and Nelson models were best to fit the breakthrough curves under the experimental conditions studied.

1. Introduction

Metal contamination of the aquatic environment has become an issue of importance with respect to environmental and human health. Recently studies sought to quantify the adsorption of metals from industrial wastes and subsurface environment through sorption (Veglio et al., 2003). Processing steps in the nuclear fuel cycle generate wastewater streams containing a variety of dissolved metals, including lanthanide and actinide elements. The problem lies in the continuous production of high-volume, often low activity, waste requiring continuous treatment. Remediation of radionuclides from aqueous solutions has been studied extensively, because of their toxicity even at low concentration (Zhang et al., 2002; Bezrodny et al., 2002; Griffin, 1999). Special interests are raised when dealing with uranium contamination of the environment. Major concerns with uranium are its mobility as it is highly soluble in the pH ranges of acid rain and occurs in hexavalent form as a mobile hydrated uranyl ion. Uranium can cause transient chemical damage to the kidneys if present at a level above 0.1 mg/kg of body weight (Mehra et al., 2007). Several physical, chemical, and biological methods are available for the removal of uranium(VI) from contaminated water. However, these methods include toxic byproducts, some do not work in acidic pH, and some are proven to be relatively costly (Torresdey et al., 2002). Biosorption is a term that describes the removal of metals ions by the binding to living/non-living biomass from an aqueous solution. Unlike physical and chemical treatments, biosorption can reduce the operational costs and many potential sources of biological material are cheaply and readily available (Wood, 1992; Hobson and Poole, 1988). Many biosorbents have been used for removal of uranium from aqueous solutions, acid mine drainage and process solutions (Bayramoglu et al., 2006; Kalin et al., 2005; Khani et al., 2008; Li et al., 2004; Parab et al., 2005).

As a local agro-waste we have used palm shell, which is available throughout coastal Asia (Kushwaha et al., 2008, 2009, Sreelatha and Padmaja, 2008, 2010). The *Borassus flabellifer* species of palm is available in coastal India. In this study, emphasis was on the use of palm shell powder as well as modified and activated palm shell powder as cost effective adsorbents for the removal of uranium. The efficiency of uranium adsorption was assessed using the best fit with the adsorption data of the two-parameter models, namely Freundlich, Langmuir, Temkin, Dubinin-Radushkevich (DR), Flory-Huggins, Elovich and Halsey isotherms. Usefulness of various kinetic models like Pseudo First order, Pseudo Second order, Intraparticle diffusion, Bangham, Elovich and Liquid film diffusion were tested. The applicability of various isotherms and kinetic models were determined by their r^2 value and error analysis. The objectives of the study were: 1) to explore the potential use of palm shell and palm shell based adsorbents for adsorption of

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uranium, and 2) to study the influence of various parameters on adsorption.

2. Materials and methods

2.1. Preparation of adsorbent material

The palm shell powder (PSP) was treated with sulphuric acid (APSP) for oxidation of surface functional groups and then further treated with: i) steam (SAPSP) at 14psi pressure in presence of air ii) persulfate (PAPSP) for further oxidation and iii) thermal treatment at 900 °C (9AAC) for increasing porosity and surface area. The palm shell powder was modified with formaldehyde (MPSP) to protonate the functional groups present and to polymerize the color imparting components of PSP. As prepared and characterized PSP, APSP, SAPSP, PAPSP, 9AAC and MPSP (Kushwaha et al., 2012a, b) were tested for uptake studies of U^{6+}.

2.2. Batch uptake

A stock solution of U^{6+} was prepared by dissolving 2.11 g of uranyl nitrate (Sulab) in slightly acidified double distilled water and making up to 1 L to give 1000 mg/L of uranyl solution. Working standards were prepared by diluting different volumes of the stock solution to obtain the desired concentration.

Batch adsorption experiments were conducted at 30 °C by agitating 0.1 g of adsorbent with 25 mL of uranyl ion solution of desired concentration maintained at pH 1.0 (using 0.1N HNO_3) in 100 mL stoppered conical flasks in a thermostated rotary mechanical shaker at 180 rpm for 4 h (except for the contact time experiments). The effect of the initial concentration (100–1000 mg/L) was also studied in order to determine the effect of the parameter on the adsorption of metal from the solution. The optimum equilibrium time was determined as the contact time required for the concentration of metal in the solution to reach equilibrium and was obtained by varying the contact time in the range 30–240 min.

At the end of the predetermined time intervals, the suspensions were filtered and the uranium content in the filtrate was analysed using arsenazo III (Lopez-de-Alba et al., 1997) by spectrophotometer. The uptake of uranyl ion by the adsorbents under study (q_e) was calculated from the difference between the initial and final concentration as follows:

$$q_e = (C_i - C_e)/m; \tag{1}$$

where, C_i – initial concentration of metal ion mg/L; C_e – Equilibrium concentration of metal ion mg/L; m – Mass of adsorbent g/L; q_e – Amount of metal ion adsorbed per gram of adsorbent. Each experimental result was obtained by averaging the data from three parallel experiments.

Adsorption isotherm experiments were also performed by agitating 0.1 g of the adsorbent under study with a series of 25 mL solutions at pH 1.0, containing different initial concentrations of (100–1000 mg/L) at 30 °C. After the established contact time (4 h) was attained, the suspension was filtered, and supernatant was analyzed for the metal concentration. The adherence of the equilibrium isotherm and data obtained to different adsorption isotherms models as given in Table 1 was tested.

Similarly the uranium adsorption data obtained after agitating solution containing 100 mg/L of uranium for various contact times with the adsorbents under study at pH 1 were calculated to determine the order of reaction rate and the adherence to different kinetic models as given in Table 1 was tested.

Thermodynamic parameters of the adsorption process (ΔG^0, ΔH^0 and ΔS^0) could be determined from the experimental data obtained at various temperatures using following equations:

$$\frac{\ln\Box q_e}{C_e} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{2}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{3}$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (K). Values of correlation coefficients and standard deviation were used to compare the models. SD was calculated using the equation.

$$SD = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(x_i - \overline{x})^2} \tag{4}$$

2.3. Desorption studies

0.1 g of uranium loaded adsorbents under study was treated with 10 mL of different desorbing solutions like 0.1M EDTA, 0.1M NH_3 and 0.1M HCl for a period of 30 min in a thermostated rotary mechanical shaker. After 30 min the amount of metal desorbed from the adsorbents under study was determined by spectrophotometer. The adsorption-desorption experiments were repeated for three cycles.

2.4. Column studies

Column experiments were conducted in a glass column with an internal diameter of 1 cm and a length of 30 cm packed with the adsorbent under study. U^{6+} solution of known concentration (1000 mg/L) at pH 1 was passed through the column of adsorbent at a flow rate of 1 mL/min. Samples from the column effluent were collected at regular intervals and analyzed by atomic absorption spectrometry. The break-through time has been chosen when the concentration of the effluent is 1 mg/L. Adherence of the column data to three different models (Thomas, Yoon and Nelson and Wolborska models) was studied using equations as described in Table 1.

3. Results and discussion

3.1. Uptake studies

3.1.1. Contact time variation

Contact time variation shows that equilibrium is achieved faster (30 and 80 min) when 9AAC and APSP were used as the adsorbents as compared to other adsorbents under study (PSP, SAPSP, PAPSP and MPSP) where equilibrium was achieved in 180 min (Fig. 1). The rate of adsorption is very fast initially with about 96% of total uranium being removed within few minutes followed by a decreased rate with the approach of equilibrium. The removal rate is high initially due to the presence of free binding sites which gradually become saturated with time resulting in decreased rate of adsorption as equilibrium approaches. This indicates that the adsorption is mainly through surface binding. Similar observations were made by Das et al. (2007).

3.1.2. Amount of adsorbent variation

The effect of dose of adsorbents under study on the removal of uranium is shown in Fig. 2, which illustrates the adsorption of