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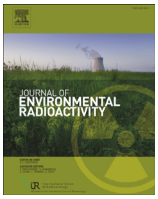

Biosorption of U(VI) by modified Hottentot Fern: Kinetics and equilibrium studies

Ke Zhou [a], Yaochi Liu [a, *], Zhaoguang Yang [a, b], Houzhi Liu [a]

[a] School of Chemistry and Chemical Engineering, Central South University, Lushan South Road 932, Changsha, Hunan, 410083, China
[b] ShenZhen Research Institute of Central South University, Yuanna Road 607, Shenzhen, Guangdong, 518057, China

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ABSTRACT

Batch experiments were conducted to investigate the biosorption of U(VI) onto Hottentot Fern (Cyclosorus interruptus). The selective adsorption, the adsorption of different sections of Cyclosorus interruptus (CI), and the adsorption of polluted CI compared with that of unpolluted one were studied in detail. The raw CI and the CI modified by $CaCl_2$, $MgCl_2$, $MgCl_2/H_2O_2$ were investigated for adsorption of U(VI) from aqueous solution. The results indicate that raw CI showed good adsorption selectivity for U(VI), compared with the adsorption of Cu(II), Co(II) and Ni(II). The stem of CI possesses a prominent adsorption capacity compared to the leaf and root of CI, and the unpolluted CI showed its superiority in adsorption capacity than the polluted CI. Adsorption rate was very fast during the first 30 min in the whole adsorption process. The pseudo-second-order kinetics model was proposed for the adsorption of U(VI) and the equilibrium data fitted well to Langmuir adsorption isotherms. The maximum adsorption capacity of R-CI, Ca-CI, Mg-CI and Mg/H_2O_2-CI is 41.67, 52.63, 62.50 and 71.43 mg g^{-1} at 20 °C, respectively.

1. Introduction

With the development of technology, uranium has become a great concern to our civilization (Khalili and Al-Banna, 2015; Yu et al., 2015). The uranium mining and hydrometallurgy process leads to the pollution of groundwater, soil and sediments, which causes a serious threat to the ecological environment and human beings (Li et al., 2015; Tan et al., 2015). Hence, the removal of U from wastewater makes considerable significance. A number of chemical, physical and biological technologies have been developed to control the pollution (Delhomenie and Heitz, 2005; Gadd, 2009). In recent years, there has been considerable interest in the use of adsorbents such as algae, bacteria, fungi, agricultural by-products and residues (Yi et al., 2016; Venkata Subbaiah et al., 2011; Saini and Melo, 2015; Garg et al., 2004; Jeon et al., 2007; Kadirvelu et al., 2003).

Fern is a plant with vascular tissue, which is mainly composed of xylem and phloem. It has been previously reported to be a hyperaccumulator of several metals and metalloids, including As and Pb (Ma et al., 2001; Gonzaga et al., 2006; Kertulis-Tartar et al., 2009). The xylem of the fern contains a vessel or duct molecule that can transport water and salts (Edwardl and Sherwin, 1998). In terms of molecular structure, a fern is largely composed of cellulose, pectin (galacturonic acid), hemicellulose, lignin, chlorophyll pigments and other low molecular weight compounds, including limonene (Zhou et al., 2016a; b). This kind of material is expected to be a very good biological adsorbent.

In this paper, Cyclosorus interruptus (CI, a kind of fern in the Marsh Fern family with broad distribution all over the world) was used as a precursor material for the adsorption of U(VI) from aqueous solution. Experiment about the selective adsorption, the adsorption of different sections of CI, and the adsorption between the polluted and unpolluted CI were studied. The CI modified by different chemical agent was also conducted. Kinetics and adsorption equilibrium data were analyzed in detail.

2. Materials and methods

2.1. Materials

All chemicals used were of analytical reagent grade or better. Deionized water (18.2 MΩ) was used in all experiments. The U_3O_8 powder was analytical grade and purchased from China Medicine

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* Corresponding author.
E-mail address: liuyaochi72@163.com (Y. Liu).

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Co. Ltd. Stock uranium solutions (1.0 g l^{-1}) were prepared by dissolving an accurately weighed amount of the above U_3O_8 powder in nitric acid solution, and further diluted prior to use. The stock solution of Cu(II), Ni(II), Co(II) was prepared in 4.0 g l^{-1} concentration using $Cu(NO_3)_2 \cdot 5H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ and $Co(NO_3)_2$, and diluted to the appropriate concentrations when used. The pH of solution was adjusted to the required value by 0.01 mol l^{-1} HNO_3 or 0.01 mol l^{-1} NaOH solutions. Prior to use, all the laboratory glassware were kept for 12 h in 5% (v/v) HNO_3 solution and then rinsed with deionized water.

2.2. Preparation of adsorbent

The unpolluted CI was collected from Yuelu Mountain (112.9342° E, 28.1757° N) in Changsha, China. The polluted CI was attained from Ganxi River (112.5617° E, 25.5281° N) which badly polluted by heavy metals. These plants were washed twice with running tap water and five times with deionized water, and separated into leaf, stem and root section. The washed biomasses were oven-dried at 60 °C for 2 days, ground to pass a 60-mesh (0.254 mm) sieve, and then stored in polyethylene bags, respectively. The adsorbents thus obtained were designated as raw CI (R-CI).

The stem of unpolluted cyclosorus interruptus was modified as follows: 20.0 g of raw CI was soaked in 400 ml 2.0 mol l^{-1} $CaCl_2$ solution for 6 h at 50 °C. Excess of $CaCl_2$ was removed by rinsing with deionized water. The biomass was then dried overnight in an oven at 60 °C. The resultant material was designated as Ca-CI. The same protocol was followed when treating CI with $MgCl_2$, and the treated sample was designated as Mg-CI.

The stem of unpolluted cyclosorus interruptus (20.0 g) was soaked in 400 ml 2 mol l^{-1} $MgCl_2$ solution for 6 h at 50 °C in presence of 30 ml 8 mmol l^{-1} H_2O_2. Excess of $MgCl_2$ and H_2O_2 was removed by rinsing with deionized water. The biomass was then dried overnight in an oven at 60 °C. The resultant material was designated as Mg/H_2O_2-CI.

2.3. Adsorption equilibrium experiments

For kinetics studies, 0.3 g of raw CI (the stem of plant) and modified CI (including Ca-CI, Mg-CI and Mg/H_2O_2-CI) were added into 1000 ml 20 mg l^{-1} U(VI) solution at pH 5.5 and 20 °C, respectively. While 20 mg l^{-1} U (VI), Co(II), Ni(II), and Cu(II), are extremely high concentrations rarely encountered in contaminated or uncontaminated environmental systems, these concentrations were selected for this study to reduce experimental error. Additional adsorption testing would be required to confirm the affinity of these adsorbents under lower metals concentrations. Based on the adsorption kinetics experiments, the isotherms adsorption experiments were conducted at pH 5.5. These mixtures were shaken on a constant temperature oscillator at 20 °C at the agitation speed of 120 rpm for 12 h, and the adsorption experiments were allowed to reach equilibrium.

An alternative adsorption experiment was performed by contacting 0.3 g of CI with a solution of U(VI), Cu (II), Ni (II) and Co (II) (1000 ml, 20 mol l^{-1}) at 20 °C, respectively. The adsorption experiments of different sections of CI were conducted by mixing 0.3 g of leaf, stem and root with 1000 ml 20 mg l^{-1} U(VI) solution at 20 °C, respectively. The adsorption experiments of polluted and unpolluted CI were conducted by mixing 0.3 g of polluted and unpolluted CI (the stem section of CI) with 1000 ml 20 mg l^{-1} U(VI) solution at 20 °C, respectively. The solution pH was adjusted daily to 5.5 ± 0.01 by using 0.01 mol l^{-1} HNO_3 or 0.01 mol l^{-1} NaOH. All experiments were monitored until adsorption equilibrium was achieved.

The biomass was removed by filtration through a 0.45 μm membrane filter (WondaDisc) and the filtrate was diluted, and then measured for ions concentration by an ICP-OES (Inductively Coupled Plasma-optical Emission Spectrometer, PerkinElmer-Optima 8000 DV, USA). The amount of U(VI) adsorbed Q ($mg \cdot g^{-1}$) was calculated using the following equation:

$$Q = \frac{V(C_0 - C_e)}{m} \quad (1)$$

where C_o and C_e ($mg \cdot l^{-1}$) are the initial and equilibrium metal ions concentration in the solution, respectively. V (l) is the solution volume and m (g) is the mass of the adsorbent.

3. Results and discussion

3.1. Adsorbent characterization

3.1.1. FT-IR spectrum of the stem of unpolluted CI

Fourier Transform Infrared (FT-IR) spectrums were measured by a Nicolet 510P Fourier transformed infrared instrument in 500–4000 cm^{-1} with a resolution of 1.0 cm^{-1}. They were used to detect different functional groups and whether the materials were modified successfully. From Fig. 1, it can be seen that, the broad band around 3420 cm^{-1} was attributed to the surface hydroxyl groups, adsorbed water and amine groups. The peak at 2926 cm^{-1} was assigned to C-H asymmetrical stretching of methyl groups on the surface (Han et al., 2010). These groups were present on the lignin structure.

The peaks located at 1732 and 1627 cm^{-1} were characteristics of the carbonyl group stretching from carboxylic acids and ketones (Hanif et al., 2009). They could be conjugated or non-conjugated to aromatic rings (1732 and 1627 cm^{-1}, respectively). The peaks associated with the stretching in aromatic rings (from lignin) were verified at 1508 cm^{-1}. The FT-IR spectrum of CI illustrates that ionizable groups such as carboxyl and hydroxyl existing in CI were able to interact with protons, metals or positive dye ions.

The modification process can be studied by FT-IR spectroscopy. The new peak near 1428 cm^{-1} of Fig. 1 (1–3) was attributed to the stretch vibration of C-O from the carboxyl group. Other new peaks appeared between 1152 and 1057 cm^{-1} suggested the vibration of C-O. These results indicated that Ca^{2+} or Mg^{2+} was introduced into CI successfully and H_2O_2 had a pre-activated function for CI.

The absorption peak at 1257 cm^{-1} is the indication of sulfate

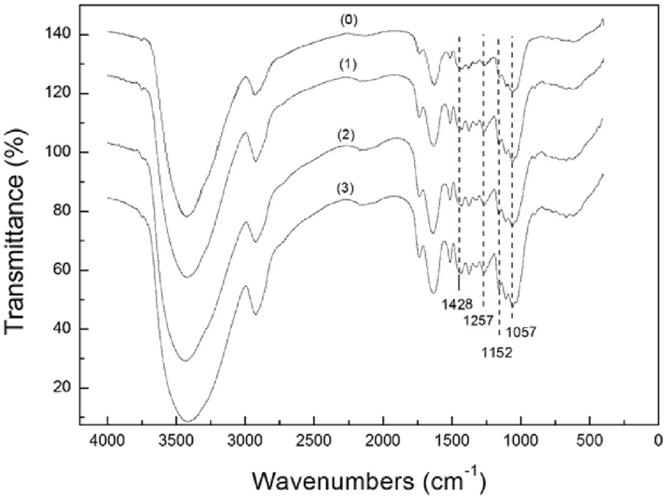

Fig. 1. FT-IR spectra of CI: (0) R-CI; (1) Ca-CI; (2) Mg-CI; (3) Mg/H_2O_2-CI.

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