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Biosorption of uranium by human black hair

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ABSTRACT

Naturally available low cost materials have gained importance as effective alternative to conventional sorbents for the removal of metal ions from water. The present study describes the use of black hair waste as a sorbent for the removal of uranium ions from an aqueous medium. Alkali treatment of the biomass resulted in a significant increase in its uptake capacity. The optimum pH and contact time for uranium removal were 4.5 and 2 h respectively. It was observed that the experimental data fits well in Ho's pseudo-second order kinetic model. Binding of uranium to the biomass was confirmed using FT-IR spectroscopy. Thus, the present study could demonstrate the utility of human black hair to remove uranium from aqueous medium.

1. Introduction

A surge in industrialization has led to an increase in metal contamination of aquatic bodies, causing a worldwide problem. Also, metal toxicity and non-biodegradability pose a challenge related to health hazards. Hence, there is a need for economical methods to treat such waste. Uranium is one such metal that is known to pollute the environment through activities associated with nuclear industry. It has both radiochemical and toxicological effects. Excessive amounts of uranium can cause nephritis in human beings and due to carcinogenicity, lead to bone cancer (Katsoyiannis, 2007). Maximum contaminant level (MCL) of uranium in potable drinking water has been established as 15 $\mu g\ L^{-1}$ by WHO (2004). A large amount of uranium gets added every year to the sea by the global fresh water streams (Sodaye et al., 2009). Thus, the removal of uranium from waste water is a subject of continual research. Conventional systems of treatment are best suited for solutions having high metal concentrations. With increasing stringency in regulations and the possibility of discharge limits decreasing even further, there arises a need to devise alternative or complementing systems for waste treatment.

Biosorption is becoming one of the most attractive and efficient processes to remove metals and radionuclides. Biosorbents have shown potential for accumulating metal ions present in low concentrations in the medium. In view of this, natural materials have been attracting much interest as sorbents. To date, various natural materials such as *Cladophora hutchinsiae* (Tuzen and Sari, 2010), *Aspergillus fumigatus* (Wang et al., 2010), *Catenella repens* (Bhat et al., 2008) and rice straw (Ding et al., 2012) have been reported for metal removal. Melo and D'Souza (2004) reported on the use of a natural bioresource, *Ocimum basilicum* seeds, for chromium uptake. Chakraborty et al. (2007) further investigated this resource for cesium and strontium removal, whereas Gupte et al. (2012) applied it for biosorption of copper. Non-living biomasses of filamentous fungi and bacteria have been reported in our laboratory for the removal of uranium from aqueous medium (Bhainsa and D'Souza, 1999; Sar and D'Souza, 2001).

Recently, Saini and Melo (2013) showed the use of biosynthesized melanin pigment for the removal of uranium from an aqueous system in a batch process. Also, Kar and Misra (2004) showed the use of keratin fiber extracted from bird feathers for the separation of metals from water. Suyama et al. (1996) used chicken feathers directly for the biosorption of precious metals such as gold and platinum. Black hair is a bioresource that contains keratin as well as melanin in a naturally immobilized form. The black hair fiber mainly consists of keratin proteins that comprise about 65–95% of the total hair fiber by weight. The remaining constituents are water, lipids, melanin and trace elements (Robbins and Crawford, 1991). The majority of the hair shaft mass comprises the cortex, which is responsible for mechanical properties of the hair fiber. Inside the cortex are the melanin granules that constitute about 3% by weight of hair (Carolina et al., 2007). In India, and other

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countries in the sub-continent, there is large availability of black hair which was the primary reason for choosing black hair for the present study. To the best of our knowledge, black hair has not been investigated for uranium bioremediation.

The advantage of human black hair waste over other similar biosorbents is because hair is an abundant and cheap bioresource. Moreover the properties like high tensile strength, non-toxicity and water insolubility make it more attractive for biosorption. It is highly resistant to the action of acids, other harsh chemicals and also to environmental degradation, all of which might have adverse effects on other types of biomass. Many biomass materials require further processing in terms of pelletization or immobilization unlike hair which can be used directly. Therefore the application of this material for treating waste water is economical and involves the utilization of one waste to treat another waste. Thus, in the present study, removal of uranium was studied using human black hair waste which is widely available as a natural resource. The factors affecting the sorption process such as pH, equilibration time and initial uranium concentration were investigated. Kinetics of the adsorption process was studied and equilibrium sorption data was fitted into well known adsorption isotherms. The presence of uranium on the biomass was confirmed with the help of FT-IR spectroscopy.

2. Materials and methods

2.1. Biomass

The black hair samples collected from a nearby salon were thoroughly washed with detergent and water to wash out any impurities and then with acetone, to remove oil/lipids. The biomass was then dried at 303 °K for 24 h and stored at room temperature for further use.

2.2. Preparation of biomass

Alkali treatment of hair was carried out by using varying concentrations of NaOH. For this, 100 mg of dried hair sample was added to 25 mL of different concentrations of NaOH (0.01, 0.1, 0.2 N, 0.3 N) respectively and left for treatment overnight at 298 °K on an orbital shaker (MAXQ 4000, Thermo Scientific) at 150 rpm. After 24 h the alkali was decanted and hair samples were washed thoroughly with distilled water to get rid of traces of NaOH. After washing, the hair samples were further dried completely at 303 °K for 24 h and stored at room temperature. The resulting biomass is referred to as treated biomass.

2.3. Solutions

Uranium stock solution of 2000 mg L^{-1} was prepared by dissolving the required amount of uranyl nitrate hexahydrate (Merck, Germany) in distilled water at room temperature and later diluted to the desired concentration as required. All the other chemicals used were of analytical grade.

2.4. Batch sorption studies

Biomass (0.2 N NaOH treated hair) at 2 g L^{-1} was kept in contact with 200 mg L^{-1} of uranium solution unless otherwise indicated. The pH of the solution was adjusted to the required value by adding 0.1 N NaOH or HNO_3 before contact with the biomass. The samples were agitated at 150 rpm on orbital shaker maintained at 298 °K. Aliquots were collected at regular time intervals and centrifuged (Spinwin, Tarsons, 5585 × g) for 5 min, to quantify the residual uranium concentration in the supernatant. A solution without the biomass was kept as control in all the experiments. All studies were performed in triplicates and the data represented are mean of triplicates with standard deviation as the error bar.

2.5. Kinetic and equilibrium studies

For kinetic studies, uranium solution (pH 4.5) at 200 mg L^{-1} was kept in contact with treated hair and samples of liquid were taken at regular intervals for measurement of uranium. Kinetic modeling of uranium sorption onto treated hair was done by using Lagergren's pseudo-first and Ho's pseudo-second-order equations. Equilibrium studies were carried out by varying the initial uranium concentration from 100 to 500 mg L^{-1} at a fixed sorbent concentration of 2 g L^{-1}. Samples were taken after 24 h of contact, as it was sufficient for the reaction to reach equilibrium. The relation between sorbed and aqueous concentration of uranium at equilibrium was examined using Langmuir and Freundlich adsorption isotherms.

2.6. Uranium estimation and metal uptake capacity

Uranium concentration was estimated in the supernatant obtained after centrifuging, by using Arsenazo III reagent (Shumate et al., 1978). Uranium uptake per gram of hair was calculated using the following equation:

$$q_e = (C_0 - C_e)V/W \quad (1)$$

where q_e represents the metal uptake capacity, 'C_0' and 'C_e' represent the concentration of uranium (mg L^{-1}) before and after sorption respectively. 'V' stands for the volume of uranium solution in L and 'W' is the amount of hair used in grams.

2.7. Desorption study

For desorption studies, different eluents such as hydrochloric acid, nitric acid, sulfuric acid, sodium carbonate and sodium bicarbonate were added at a constant molar concentration of 1 M. The solutions were agitated at 150 rpm on an orbital shaker and the % desorption was calculated using the following equation:

$$\%\text{desorption} = (U_{\text{desorbed}}/U_{\text{adsorbed}}) \times 100 \quad (2)$$

where U_{desorbed} represents the concentration of uranium in the supernatant after desorption and U_{adsorbed} is the concentration of uranium bound to hair after the adsorption cycle. Before carrying out the desorption study, adsorption of uranium on treated hair was performed. For this, treated hair (2 g L^{-1}) was contacted with 50 mL of 100 mg L^{-1} uranium solution at pH 4.5. After 24 h of contact, the solution was centrifuged in order to quantify uranium present in the supernatant and the hair pellet was dried at 310 °K for 3 h. After drying, 5 mL of respective 1 M eluent was added to the uranium bound hair pellet for desorption.

2.8. FT-IR analysis of treated hair bound with uranium

Treated hair (1 g L^{-1}) was kept in contact with uranium solution of 200 mg L^{-1} (pH 4.5) at 298 °K and agitated at 150 rpm. After 24 h of contact the solution was centrifuged and the pellet obtained was dried completely and used for FT-IR analysis. Treated hair (1 g L^{-1}) incubated in distilled water under the above mentioned conditions served as a control. For FT-IR, hair samples with and without uranium were cut into fine pieces with the help of a scissor and mixed with IR grade KBr powder (4% w/w). The mixture was then ground using a mortar and pestle and the FT-IR spectrum of this ground mixture was recorded using Jasco FT-IR 660 plus spectrometer. The