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Selective sorption of uranium (IV) from hydrochloric acid media by agro-industrial byproducts

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ABSTRACT

An investigation was conducted on different agro-industrial byproducts to evaluate their potentiality for selective sorption of U^{4+} ion from hydrochloric acid media (4 M). All experiments were performed in batch mode at ambient temperature. Among the tested biomasses, rice bran was selected because of high sorption of U^{4+}. The sorption capacity obtained from distribution isotherm indicated value of 42.9 mg g^{-1} for rice bran. Additionally, the sorption equilibrium was achieved in less than 5 min. With the increase in the amount of granular zinc, uranium uptake efficiency was improved from 14% to 98%. The sorption efficiencies of uranium by rice bran in the concentration range of 133–3333 mg L^{-1} were relatively constant (>91.5%) with RSD less than 1.5%. The selectivity coefficient value of rice bran for U^{4+} ion was >621-fold and >5460-fold greater than Ln^{+3} ions and Zn^{2+} ion respectively. The maximum desorption of uranium was observed in the first stage (>89.7%) with $(NH_4)_2CO_3$ and $(NH_4)_2C_2O_4$. The selected biosorbent has the potential to be applied on an industrial scale due to economic and operational benefits.

1. Introduction

To process and reprocess uranium at industry, various acids with high concentration are frequently used for dissolution of uranium-bearing precipitation obtained from leaching process. Recovery of this metal ion is a challenging task because of its associated high acidic environment (Siva Kesava Raju et al., 2007).

The technologies such as ion exchange, lime softening, greensand filtration, precipitation and co-precipitation, and so forth were used for their ability to separate actinides from aqueous solutions (Munter, 2013). But over the years, solvent extraction (SX) has been proved to be promising in this area because of having simple operation and using several extractants. Even though SX technique is a widely used process, it has a number of limitations like the third phase formation, disposal of large volumes of extractants and organic solvents, large space requirements, and slow kinetics (Preetha et al., 2002). Over the last few decades, owing to the economic and operational reasons such as low operating expenses, the minimum ratio of chemical waste and/or biological sludge volume and high efficiency in detoxifying a very dilute effluent, biosorption of elements has become the center of wide interest in the processing and reprocessing plants and waste management (Kratchovil and Volesky, 1998).

Several studies have been carried out so far on the topic of uranium separation using various biomasses. Table 1 summarizes some of the important results obtained from a literature survey on uranium biosorption. As seen from the table, all biosorption studies were conducted in the pH ranging from 3.0 to 5.8, and no studies have been specifically performed in highly acidic solution. Considering that uranium ion exists mostly in acidic or highly acidic leach liquors obtained from processing and reprocessing plants, thus finding biosorbent/biosorbents that effectively separate this radionuclide from real aquatic environments, is inevitably required.

A review on radionuclides sorption reveals that agro-industrial byproducts were less focused on in the separation of uranium ion in contrast to other biomasses. Therefore, seven types of biomaterials including pine tree sawdust (PTSD), tea factory waste (TFW), rice bran (RB), wheat bran (WB), rice hull (RH), orange peel (OP) and lemon peel (LP) were assessed for the study. This research aims to find an effective low-cost biosorbent with the potentiality

Abbreviations: ICP-OES, inductively coupled plasma optical emission spectrometer; *R%*, the sorption efficiency of uranium; C_o, the initial concentrations (mg L^{-1}) of analyte ions in solution; C_e, the equilibrium concentrations (mg L^{-1}) of analyte ions in solution; q_{sorp}, the amount of uranium adsorbed onto biomass (mg/g); *m*, the sorbent weight in g; *V*, the volume of the sample solution in L; SD, the standard deviation; RB, rice bran; K_{Zn}^{U}, selectivity coefficient.

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Table 1
Biosorption of uranium using various biomaterials.

Biomass	Q_{max}(mg/g), Optimum pH, Temp.(°C), t_{eq}[a]	References
Algea		
Padina sp.	400, 4, 30, 2 h	Hai-bin et al. (2011)
Sargassum fluitans	330, 3.2, NA[b], 3 h	Omar et al. (2008)
Systoseira indica	371, 4, 25, 3 h	Nakajima and Tsuruta (2004)
Systoseira indica	224, 4, 30, 3 h	Bhainsa and D'Souza (2001)
Fungi		
Aspergillus niger AHU7 120	28, 5.8, 25, 1 h	Psareva et al. (2005)
A. niger AHU7296	81, 5.8, 25, 1 h	Psareva et al. (2005)
A. oryzae AHU7216	86, 5.8, 25, 1 h	Psareva et al. (2005)
Fusarium oxysporum IAM 5009	85, 5.8, 25, 1 h	Psareva et al. (2005)
Mangrove end. fungus sp.	15.5, 4, 25, 60 min	Saleem and Bhatti (2011)
Mucor hiemalis IAM 6088	227, 5.8, 25, 1 h	Psareva et al. (2005)
Yeasts		
Brewery yeast	574, 4.5, 25, NA	Xia et al. (2013)
Candida krusei AHU3993	3, 5.8, 25, 1 h	Psareva et al. (2005)
Cryptococcus albidus AHU38 12	64, 5.8, 25, 1 h	Psareva et al. (2005)
Debaryomyces hansenii AHU3759	137, 5.8, 25, 1 h	Psareva et al. (2005)
Endomycopsisfibligera AHU4 113	25, 5.8, 25, 1 h	Psareva et al. (2005)
Bacteria		
Pseudomonas aeruginosa	31.6, 3.5, 30, 30 min	Winter (1999)
Arthrobacter cireus	13.6, 3.5, 30, 30 min	Winter (1999)
Bacillus subtilis	52.4, 3.5, 30, 30 min	Winter (1999)
Micrococcus luteus	38.8, 3.5, 30, 30 min	Winter (1999)
Zooglea ramigera	49.7, 3.5, 30, 30 min	Winter (1999)
Plant Biomass/Agriculture Waste		
Eichhornia crassipes	371, 5, NA, 30 min	Loveland et al. (2006)
Cork	59.4, 5.2, 22, 2 h	Baumann (1980)
Citrus grandis	45.6, 4, 30, 60 min	Das (2012)
Banyan leaves	NA, 3, 20, 50 min	Cotton (2006)

[a] t_{eq}: Equilibrium time.
[b] NA: Not available.

to separate uranium selectively from hydrochloric acid solutions via a rapid and simple operational process in ambient temperature (25 °C).

2. Materials and methods

2.1. Reagents

All reagents were of pro-analysis grade quality and purchased from Merck Company. A stock solution of 1000 mg L^{-1} metal ions was prepared by dissolving appropriate amounts of $UO_2(NO_3)_2{\cdot}6H_2O$, $Th(NO_3)_4{\cdot}5H_2O$, $ZrOCl_2{\cdot}8H_2O$, $HfOCl_2{\cdot}8H_2O$, $Ce(NO_3)_3{\cdot}6H_2O$, $La(NO_3)_3{\cdot}6H_2O$, $Nd(NO_3)_3{\cdot}6H_2O$, $YCl_3{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$ $Cu(NO_3)_2{\cdot}3H_2O$, $ZnCl_2$, $Pb(NO_3)_2$, $Cd(NO_3)_2{\cdot}4H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$, $Ca(NO_3)_2{\cdot}4H_2O$, $Sr(NO_3)_2$ and $BaCl_2{\cdot}2H_2O$ in 1000 mL double distilled water that was slightly acidified. Working solutions were prepared daily by dilution of the stock solution with the distilled water.

2.2. Preparation of biosorbents

PTSD (from local sawmills in Tehran, Iran), OP and LP (from the fruit juice factories in Tehran, Iran), RB, RH and WB (from micro industry of rice and wheat processing in Mazandaran, Iran) and TFW (from the highland tea factories located in Lahijan, Iran) were collected as the biomaterials of this study. The samples were rinsed three times with water (except TFW washed 10 times with boiling water) and finally with distilled water once more and dried in 60 °C oven for 24 h. The dried biosorbents were ground (except RB and WB) and sieved into the particle sizes of 250–350 μm.

2.3. Apparatus

The determination of all metal ions was performed by a Perkin-Elmer Optima 7300 DV inductively coupled plasma optical emission spectrometer (ICP-OES). A Gilson model minipuls 3 peristaltic pump was used to adjust the flow rate in the column method. A Gallenkamp orbital shaker incubator was applied for shaking.

2.4. Procedure

2.4.1. Batch method

2.4.1.1. Sorption process. All batch experiments were performed at room temperature (25 ± 1 °C), using 50 mL capped tubes. A 10 mL solution containing exactly the known concentration of uranium (100 mg L^{-1}) with 1 g granular zinc and 10 mg ascorbic acid was prepared in 4 M HCl. After 30 min of reaction (the reaction time required for converting UO_2^{2+} into U^{4+}), the solution was contacted with 75 mg RB for 10 min. Next, the biomass was filtered and washed with distilled water until filtrate reached 10 mL. The concentrations of the metal ions (the equilibrium concentration) in the filtrate were determined directly by ICP-OES. The sorption efficiency of uranium (R%) was calculated by using the Eq. (1):

$$R(\%) = (C_o - C_e/C_o) \times 100 \quad (1)$$

where C_o and C_e are the initial and equilibrium concentrations (mg L^{-1}) of analyte ions in solution.

For investigation of sorption capacity of sorbent, aliquots of 10 mL of sample solution with different concentrations of uranium were contacted with 75.0 mg of sorbent. The amount of uranium adsorbed onto biomass, (q_{sorp}, mg g^{-1}) was calculated by using the Eq. (2):

$$q_{sorp} = (C_o - C_e)V/m \quad (2)$$

where C_o and C_e are the initial and equilibrium concentrations (mg L^{-1}) of analyte ions in solution, respectively. m is sorbent weight in g and V is the volume of the sample solution in L.

2.4.1.2. Desorption process. The desorption studies on uranium-loaded biomass were conducted employing various eluting agents such as NH_4NO_3, $(NH_4)_2SO_4$, EDTA, $(NH_4)_2CO_3$ and $(NH_4)_2C_2O_4$. After optimizing the eluting agents concentration, the amounts of 0.5 M NH_4NO_3, 0.1 M $(NH_4)_2SO_4$, 0.1 M EDTA, 0.2 M $(NH_4)_2CO_3$ and 0.2 M $(NH_4)_2C_2O_4$ were used for trial. To desorb uranium, the filtered biomass was eluted with 10 mL of the mentioned eluting agents. The desorption process was carried out in three stages. Then, the concentrations of uranium ions in eluent solution (The equilibrium concentration) were determined directly by ICP-OES.

The amount and the percentage of desorbed uranium in the eluent solution were calculated by using the Eqs. (3) and (4), respectively:

$$q_{des} = C_{des}V/m \quad (3)$$

$$\%desorption = [q_{des}/q_{sorp}] \times 100 \quad (4)$$

where q_{des} is eluted metal content (mg/g), m is sorbent weight in g, V is the volume of the sample solution in L and C_{des} is metal concentration in eluent solution (mg L^{-1}).

2.4.2. Continuous mode

In the continuous mode, 1.0 g biomass was filled into a glass tube (10 cm long and 1 cm i.d.) consisted of filter and stop cock. After cleaning through passing the double distilled water, the