Characterization of U(VI) sorption and leaching on clay supported biomass sorbents

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Abstract.
In previous studies we demonstrated that matrixes generated from fungal biomass and a montmorillonite (BMMTs) are efficient as biosorbents in batch uranium removal systems. The objective of this article is to evaluate the U(VI) sorption capacity of BMMT in continuous systems for its removal from effluents and to determine the reusability of the sorbent and the recovery of the uranium testing different leaching solutions. Upflow BMMT columns were performed in order to optimize the system for continuous sorption techniques. BMMTs loaded with U(VI) treatment with leaching solutions allowed calculating U(VI) extraction percentages. These results indicated the possibility of the use of clay supported biomass sorbents in upflow columns, the recycling of the sorbent and U(VI) recovery after processes of U(VI) sorption.

Introduction

Uranium is a threatening metal that has been brought into the environment in excessive amounts due toactivities associated with the nuclear industry. However, due to fossil fuel depletion and climate change, uranium arises as a strategic and valuable metal with potential global nuclear energy expansion. Biosorption has been proposed as a potential alternative not only for removing toxic heavy metals but also as a technique to concentrate and recover valuable metals diluted in the environment. Several biosorbents based on non-living biomass have demonstrated an excellent uranium adsorption performance. For example, fungi, yeast, bacteria, and algae, have been reported to bind uranium in excess [1]. The high sorption capacity, easy regeneration and low-costs make biomass based separation processes of special interest for purification of large volumes of wastewater with low metal concentration levels to be removed. But one of the technological drawbacks of biosorption is that the separation process is difficult and/or expensive to accomplish.

In previous studies we demonstrated that matrixes generated from fungal biomass and a montmorillonite (BMMTs) are efficient as biosorbents in batch uranium removal systems. BMMTs showed higher adsorption efficiency than montmorillonite or biomass even at low concentrations of U(VI) [2]. The objective of this article is to evaluate the U(VI) sorption capacity of BMMT systems in fixed-bed upflow-through columns for its removal from effluents and to determine the reusability of the sorbent and the recovery of the uranium testing different leaching solutions.

Materials and methods

Clay biopolymers (BMMTs) were generated from a bentonite (montmorillonite) and two fungi genus: *Acremonium* sp. and *Aphanocladium* sp. [2]. Pellets from BMMT (*Acre* sp.) and BMMT (*Apha* sp.) were generated by extrusion with a polyethylene bag and dried at 70ºC. The best relation between clay and biomass was selected according to the matrix stability (pellets from BMMTs containing 5% MMT (w/v) disintegrated progressively as the aqueous solution passed through the column).

For *batch* leaching experiments BMMTs were loaded with aqueous solutions (as a preliminary step before testing real wastewater solutions) with initial concentrations of 100 and 300 ppm U(VI) until equilibrium was reached. U(VI) adsorbed on BMMTs were extracted with commercial H_2SO_4 0,2 N and HCO_3^- 0,5 M in a suspension 1% (w/v).

Fixed-bed columns (volume of 0,8 ml) were filled with BMMTs 1% pellets and loaded with solutions of 35, 55 and 69 ppm U(VI). A peristaltic pump was used at a flow rate of 0.65 ml/min.

The quantity of U(VI) adsorbed on solid matrixes was quantified by gamma spectrometry using an ultra low germanium detector, as previously described [3] (detection limit: 0.2 mg uranium). U(VI) concentration in solution was determined spectroscopically by Arsenaze (III).

Results and discussion

Uranium adsorption capacity of MMTs and BMMTs was determined and discussed in a recent paper [2]. Uranium adsorption on BMMTs was studied up to concentrations of 300 ppm uranium and showed an average adsorption capacity of 100 mg/g and good coagulation properties. Despite the many papers on biosorption processes, few of them showed the recovery of the metal from the loaded matrix and the regeneration of the sorbent. One difficulty is the determination of the amount of metal remaining in the matrix. In the case of uranium, we use the radioactive characteristic of the element to determine its concentration by a high sensibility, non destructive method.

U(VI) adsorbed on BMMTs was determined by Arsenaze III as the difference between initial and final concentration of the supernatant; and by gamma-ray spectroscopy of sorbent samples in order to validate the Arsenaze III technique. After adsorption, both techniques indicated similar results (data not shown). But after the lixiviation process some molecules from the biomass of BMMTs could be released to the supernatant (also some labile ions from clay interlayer) and possibly interfered with the U(VI) determination by Arsenaze III. So the only feasible technique to determine U(VI) lixiviation from BMMTs is gamma-ray spectroscopy.

Treatment of U(VI) loaded MMT and BMMTs with leaching solutions allowed calculating U(VI) extraction percentages (Table 1).

These results indicated the possibility of recycling the sorbent after processes of U(VI) sorption, because U(VI) extraction from the loaded BMMTs was at least 80% the total amount of the retained metal in the solid. The concentration of the resulting solution is high enough to recover the metal, indeed its concentration is much larger than that present in brine rejected by integrated nuclear desalination plants [4]. Uranium recovery (from HCO_3^- lecheate) could be achieved by lowering pH to eliminate all carbonates, and the rise of pH to precipitate uranium [5].

From the results of uranium retention and recovery in the matrixes in batch experiments, separation columns for continuous processes were designed. Figure 1 shows upflow-through fixed-bed columns profiles for BBMT (*Aphanocladium*sp.) (1%) as examples. Inlet concentration at the exit of the column was achieved for all columns. Efficiencies for continuous sorption processes depended on the inlet concentration of the solution employed. Uranium removal efficiencies were calculated for each inlet concentration (Table 2 and 3).

Table 1. U(VI) content in samples before and after leaching, leachate concentration and U(VI) recovery percentages

Sample	C_o U [mg/g]	C_f U [mg/g]	U concentration in leachate [mg/l]	% U recovery
MMT 100[(1)]	95,4			
MMT 300[(2)]	106,3			
MMT 100 H_2SO_4 C[(3)]		16,7	787,6	82,5
MMT 100 HCO_3^-[(4)]		8,3	871,0	91,3
MMT 300 H_2SO_4 C		15,0	913,5	85,9
MMT 300 HCO_3^-		6,3	1000,5	94,1
BMMT (*Acremonium* sp.) (1%) 100	38,8			
BMMT (*Acremonium* sp.) (1%) 300	63,0			
BMMT (*Acremonium* sp.) (1%) 100 H_2SO_4 C		15,7	230,4	59,4
BMMT (*Acremonium* sp.) (1%) 100 HCO_3^-		5,3	334,5	86,3
BMMT (*Acremonium* sp.) (1%) 300 H_2SO_4 C		8,7	543,3	86,2
BMMT (*Acremonium* sp.) (1%) 300 HCO_3^-		5,9	571,1	90,6
BMMT (*Aphanocladium* sp.) (1%) 100	95,1			
BMMT (*Aphanocladium* sp.) (1%) 300	124,0			
BMMT (*Aphanocladium* sp.) (1%) 100 HCO_3^-		4,6	904,7	95,2
BMMT (*Aphanocladium* sp.) (1%) 300 H_2SO_4 C		16,8	1072,8	86,5
BMMT (*Aphanocladium* sp.) (1%) 300 HCO_3^-		4,9	1191,9	96,1

C_o, U(VI) quantity on the BMMT before lixiviation. C_f, U(VI) quantity on the BMMT after lixiviation.
[(1) (2)] U(VI) content in samples equilibrated with a U solution with an initial concentration of 100 or 300 ppm U(VI) (0.1% w/v) before treatment with leaching solutions.
[(3) (4)]U(VI) content in samples equilibrated with a U solutionwith an initial concentration of 100 or 300 ppm U(VI) (0.1% w/v) after treatment with leaching solutions: HCO_3^- or H_2SO_4 C.
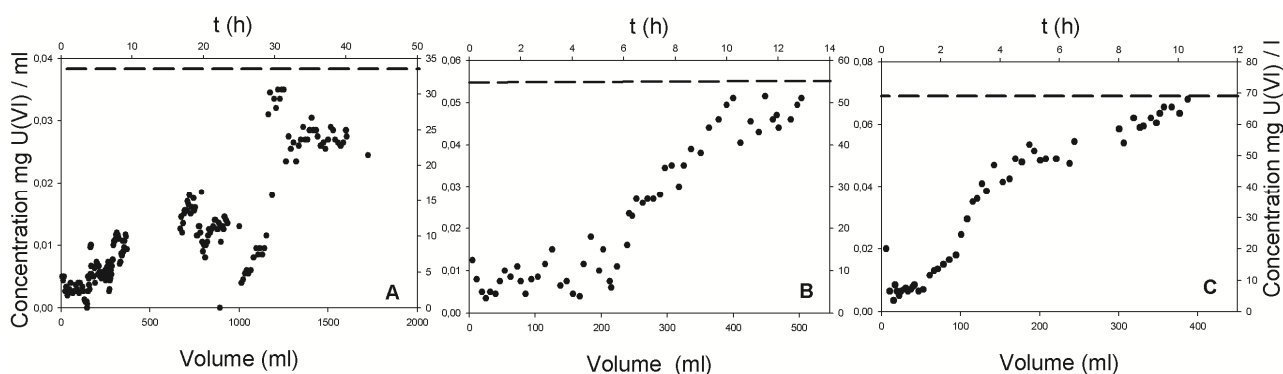

Figure 1. U(VI) concentration at the exit of the column as a function of the total volume or time in BBMT (*Aphanocladium*sp.) (1%) upflow-through columns.(A), inlet concentration of 35 ppm of U(VI); (B), inlet concentration of 55 ppm of U(VI) and (C), inlet concentration of 69 ppm of U(VI). The dashed line indicates the inlet concentration (C_o).

Tables 2 and 3 indicate efficiencies and parameters from columns. Q_{max} is given as the maximum amount of U(VI) adsorbed for each BMMT in *batch* experiences. Q^{din} is the maximum total amount of U(VI) retained in the column. Total efficiency is calculated as Q^{din} / total mass of U(VI) through the column. For an initial concentration of 35 ppm, columns from BMMT (*Aphanocladium* sp.) presented a higher efficiency than columns made from BMMT (*Acremonium* sp.) pellets (Table 2). On the other hand, BMMT (*Acremonium* sp.) presented a higher efficiency than BMMT (*Aphanocladium* sp.) for the inlet solution containing 55 ppm U(VI) (Table 3).

Table 2. U(VI) sorption columns from BMMT (*Aphanocladium* sp.) (1%) at three different inlet solutions.

Q_{max}= 156 mg U(VI) / g BMMT	35 ppm U(VI)	55 ppm U(VI)	69 ppm U(VI)
Breakthrough point efficiency	70%	75%	55%
Total efficiency	55%	54%	39%
Time	44 hs	13 hs	10 hs
Adsorbed U(VI) (Q^{din})	75 mg/g	35 mg/g	23 mg/g
Efficiency (Q^{din}/ Q_{max})*100	48%	22%	15%

Table 3. U(VI) sorption columns from BMMT (*Acremonium* sp.) (1%) at three different inlet solutions.

Q_{max}= 142 mg U(VI) / g BMMT	35 ppm U(VI)	55 ppm U(VI)	69 ppm U(VI)
Breakthrough point efficiency	54%	70%	82%
Total Efficiency	43%	45%	34%
Time	39 hs	17 hs	10 hs
Adsorbed U(VI) (Q^{din})	56 mg/g	45 mg/g	23 mg/g
Efficiency (Q^{din}/ Q_{max})*100	39%	32%	16%

The more concentrated the inlet solution, the faster the fixed-bed column saturation was, thus presenting a lower efficiency (Table 2 and 3). Besides the fact that values for Q^{din} are lower than Q_{max}, BMMTs presented an efficient sorption performance for continuous sorption processes not only for their maximum metal uptake but also for the stability of the material. Efficiencies were considerable for these types of processes. The difficulty of analyzing the dynamic sorption behaviour and the decrease in Q_{max} values stems from the fact that such systems involve the sorption equilibrium behaviour, mass transfer, and fluid flow properties all at the same time [6].

Conclusions

BMMTs presented an efficient alternative for U(VI) retention that indicated the possibility of uranium extraction and recovery, as was achieved by other authors through the years with different materials [1, 6, 7]. The use of gamma-ray spectroscopy allowed the study of loaded BMMTs for its regeneration without the use of a destructive method. Adsorption columns indicated the potential efficiency of the sorbent for developing a greater scale process aimed to develop economic and efficient biofilters, as components of BMMTs are very economic. This is one more method for recovering U(VI) with the advantage of being easy to separate from solution (BMMTs have very good coagulation properties) and to manipulate in order to develop greater scale adsorption methods.

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