

## Adsorption of hexavalent uranium on biomass by-product

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The effectiveness of the uranium removal by olive cake from aqueous solutions has been demonstrated in batch type experiments under normal atmospheric conditions. The adsorption capacity has been evaluated by using both Langmuir and Freundlich isotherms. The optimum pH regarding for uranium adsorption on olive cake is 7.5. The amount of adsorbed uranium is governed by the amount of active sites on the biomass surface indicating an inner sphere complexation. The adsorption of uranium on olive cake is an endothermic and entropy-driven process and does not depend on the ionic strength of the solution.

### Introduction

Pollution of the environment with uranium and associated health effects to human have recently become of major concern, particularly due to the use of depleted uranium in armour-breaking bullets.<sup>1</sup> Indeed, uranium in environmentally significant concentrations is found near uranium mining and processing facilities and usually involves large volumes of wastewater.<sup>2</sup> Removal of uranium from such large volumes of wastewaters will require a cost effective remediation technology. Conventional technologies relying on mineral adsorbents or chemical flocculating agents are relatively expensive. Biosorption technologies in which living or dead biomass is used to accumulate heavy metals are methods that often replace conventional processes for remediating metal pollution in wastewaters.<sup>3</sup> The major drawback of these microbial systems is the cost of growing a sufficient quantity of bacterial or algae biomass.<sup>4</sup> Alternatively, the removal of dissolved metals by plant tissues has been studied using a variety of biomasses that represent byproducts from other commercial processes with little commercial value and thus representing good candidates for the development of inexpensive biosorption processes. Olive cake (olive pomace), which is a very abundant agricultural waste in the Mediterranean area, is studied as a possible biosorbent for heavy metal removal from aqueous solutions.<sup>5,6</sup> The present paper reports the adsorption of hexavalent uranium on olive cake at various experimental conditions (e.g. uranium concentration, amount of adsorbent, ionic strength, pH, temperature, and contact time) and discusses the effect of these parameters on uranium adsorption.

### Experimental

A periodically mixed batch technique was selected for the batch adsorption experiments. All experiments were carried out under normal atmospheric conditions at

25±1 °C. Test solutions were prepared by dissolution of uranyl nitrate (UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 99.99%, Merck Co) in aqueous solution. The ionic strength (0.1M and 1.0M) in the test solutions was adjusted by addition of sodium perchlorate (NaClO<sub>4</sub>, Aldrich Co). Solutions without background electrolyte (electrolyte-free solutions) are denoted by *I*=0.0M. The adsorbent, e.g., olive cake (granulated material) used in this study was pre-treated by means of hexane extraction. Hexane extraction is an industrial process applied in order to extract oil residues from the “pressed” olive cake. The by-product of the hexane extraction was sieved and the particle fraction between 200 and 500 µm, was selected for the adsorption experiments and was used without any further purification or other pre-treatment. The BET surface area of the adsorbent was measured by N<sub>2</sub>-adsorption (Micromeritics Co, ASAP 2000) and has shown that olive cake has no internal surface. The concentration of the adsorbent active sites was determined by NH<sub>3</sub>-TPD (thermal programmed desorption of pre-adsorbed NH<sub>3</sub>)<sup>7</sup> and was found to be 0.59 mmol·g<sup>-1</sup>. This value is close to the corresponding value given in literature determined by acid/base titration.<sup>6</sup>

Immediately after the addition of 100 ml of the test solutions to the adsorbent, the bottles were shaken and left to reach equilibrium. During the equilibration period the bottles with the test solutions were shaken regularly. Following three-day equilibration time, the solutions were first centrifuged at 5000 rpm (Lab centrifuge, Memmert Co.), then passed through a 0.45-µm Millex filter (Type GV) and the concentration of uranium in solution was determined by spectrophotometry using Arsenazo III.<sup>8</sup>

To investigate the effect of various parameters (e.g., pH, initial uranium concentration, amount of adsorbent, etc.) on uranium adsorption, five different classes of experiments were conducted. In these experiments the parameter under investigation was varied while other experimental parameters were kept constant.

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The effect of pH was studied in an adsorption system (0.2 g adsorbent and 200 ml of the test solution:  $[U(VI)] = 1 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$ ) in which pH was varied between 4 and 10 by addition of  $\text{HClO}_4$  or  $\text{NaOH}$ . For studying the effect of initial uranium concentration, the latter was varied between  $5 \cdot 10^{-4}$  and  $5 \cdot 10^{-6} \text{ mol} \cdot \text{l}^{-1}$ , at a prefixed amount of adsorbent (adsorbent dosage = 0.1 g per 100 ml). The effect of the amount of olive cake was investigated by adding different amounts of adsorbent (between 0.0125 and 0.2 g) into a 125-ml polyethylene screw capped bottle, containing 100 ml test solutions of constant uranium concentration ( $1 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$ ). The effect of temperature was studied between 25 and 70 °C and measurements were carried out after an equilibration time of three days. The amount of adsorbent ( $1 \text{ g} \cdot \text{l}^{-1}$ ), initial uranium concentration ( $1 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$ ) and pH in the test solutions (100 ml) were kept constant. For kinetic studies certain amount of olive cake ( $1 \text{ g} \cdot \text{l}^{-1}$ ) was mixed with uranium solution ( $1 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$ ). Samples withdrawn at time intervals were centrifuged and the uranium concentration was determined by photometry.

## Results and discussion

Figure 1 shows the effect of pH on the  $K_d$  value and, hence, on the uranium removal by adsorption on olive cake. The optimum pH for the removal of uranium by olive cake was found to range from 7 to 8 with a maximum at about pH 7.5. This value is higher than corresponding values given in the literature for uranium adsorption on microorganisms and algae, indicating that, in the case of olive cake, surface groups of weaker acidity (e.g., phenolic groups) play an important role in uranium adsorption on the surface.<sup>9</sup>

Increased proton concentration leads to gradual protonation of the surface groups and destabilization of the surface adsorbed uranium species ( $\text{pH} < 7$ ). According to Fig. 1, this effect seems to be less favoured at increased ionic strengths. On the other hand, uranium adsorption decreases in alkaline test solutions because of the higher carbonate concentrations in these solutions. Increased carbonate concentrations lead to desorption of uranium from the solid surface by stabilizing soluble uranium carbonate species.<sup>10</sup> Since for  $\text{pH} > 7$  both adsorbent surface and adsorbate are negatively charged, uranium adsorption on olive cake can be ascribed to inner sphere complex formation and not to electrostatic interaction between opposite charged particles.

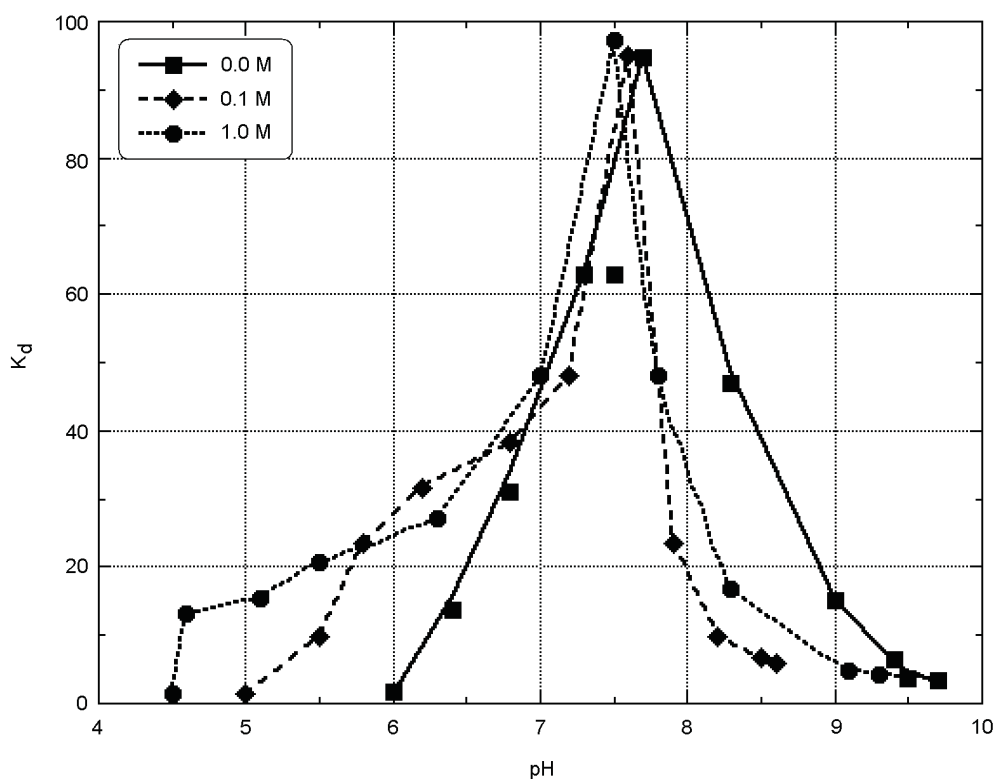


Fig. 1.  $K_d$  values as a function of pH for the uranium adsorption onto olive cake at various ionic strengths (background electrolyte aquatic  $\text{NaClO}_4$ ), under normal atmosphere and 25 °C;  $[U(VI)] = 1 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$ , mass of adsorbent =  $1 \text{ g} \cdot \text{l}^{-1}$

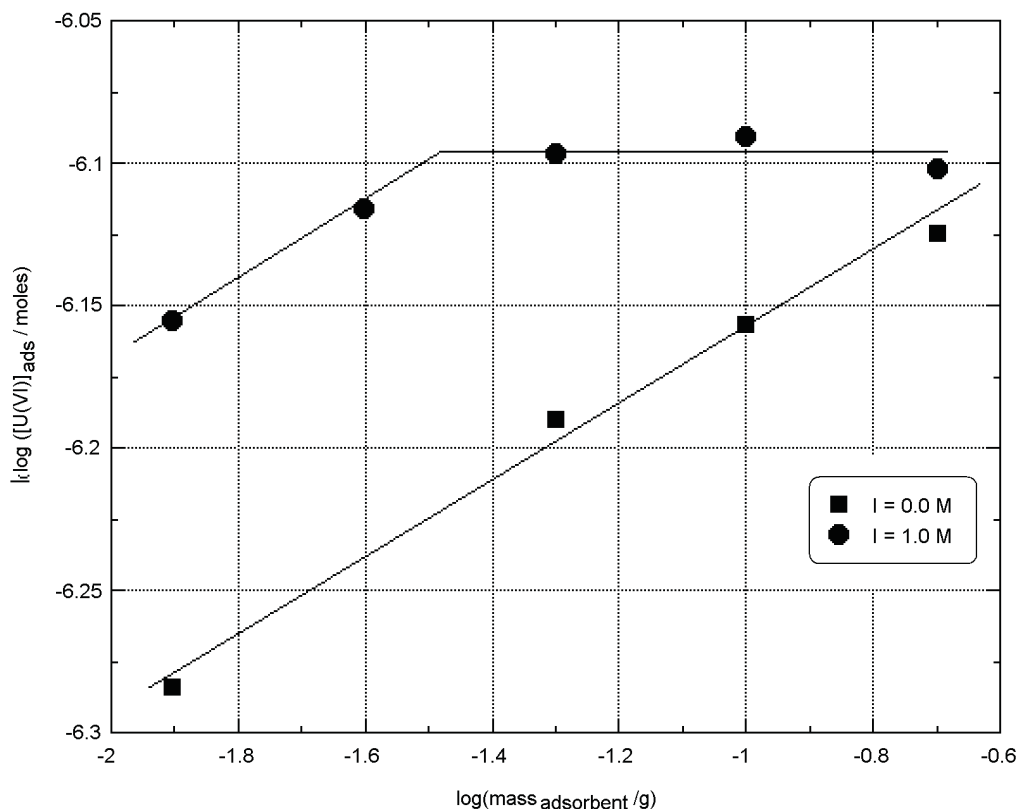


Fig. 2.  $\log ([U(VI)])$  as a function of  $\log (\text{mass}_{\text{adsorbent}})$  for the uranium adsorption onto olive cake at various ionic strengths (background electrolyte aquatic  $\text{NaClO}_4$ ), at pH 7.5, normal atmosphere and 25 °C;  $[U(VI)] = 1 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$ , mass of adsorbent = 1  $\text{g} \cdot \text{l}^{-1}$

Irrespective of the ionic strength the experimental adsorption data follow both the Langmuir and Freundlich isotherm models, indicating that the maximum adsorption capacity is governed by the amount of active sites (basically carboxylic and phenolic groups) on the biomass surface. The evaluated data are summarized in Table 1. Surprisingly, the maximum amount of uranium adsorbed on olive cake at  $I = 1.0 \text{ M}$  is almost three times higher than the corresponding amount adsorbed at  $I = 0.1 \text{ M}$  and  $I = 0.0 \text{ M}$ . This effect can be attributed to the “salting out”, which results in lower  $\text{CO}_2$  solubility in solutions of increased salinity and, hence, to lower carbonate concentration and destabilization of soluble uranium-carbonate species<sup>9</sup> or to the formation of a new uranium solid phase ( $\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}$ ) which is predominantly formed in solutions of higher ionic strengths at  $\text{pH} > 7$  and is less soluble than  $\text{UO}_2(\text{OH})_2$ .<sup>11</sup>

In Fig. 2 the adsorbate amount is expressed in mol uranium (logarithmic scale) per mass of the adsorbent (logarithmic scale). Figure 2 shows clearly that the maximum removal efficiency of uranium is about ten times higher in solutions of  $I = 1.0 \text{ M}$  compared to electrolyte-free solutions. Quantitative adsorption of uranium in solutions of  $I = 1.0 \text{ M}$  is reached at adsorbent

mass of 0.03 g, whereas the amount of adsorbent needed to remove quantitatively similar amounts of uranium from electrolyte-free solutions is 0.25 g. Moreover, there is a linear correlation between adsorbent mass and adsorbed uranium indicating on the formation of inner-sphere complexes. The curves corresponding to the solutions of different salinity are parallel indicating on similar adsorption mechanism. Comparison of active surface sites available on the olive cake surface expressed, in mol per gram as determined by thermal programmed desorption of  $\text{NH}_3$  (0.59  $\text{mmol NH}_3 \cdot \text{g}^{-1}$  adsorbent), with the amount (in mol) of uranium adsorbed per gram adsorbent (0.1 and 0.3  $\text{mmol U(VI)} \cdot \text{g}^{-1}$  adsorbent) reveals that at optimum removal conditions (in solutions with  $I = 1.0 \text{ M}$ ) each uranium(VI) moiety is associated with two active sites of the adsorbent surface.

The effect of temperature on uranium adsorption on olive cake was investigated to estimate the corresponding thermodynamical data based on the Van't Hoff equation. Evaluation of the data revealed that the adsorption of uranium on olive cake is an endothermic ( $\Delta H^\circ = (50 \pm 10) \text{ kJ} \cdot \text{mol}^{-1}$ ) and entropy-driven ( $\Delta S^\circ = (170 \pm 30) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ) spontaneous process.

Table 1. Values of  $q_{max}$  and  $K_L$  and  $1/n$  and  $K_F$  constants for uranium adsorption on olive cake calculated by linear regression of the experimental data according to the Langmuir model and Freundlich model, respectively

Ionic strength	$q_{max}$ , mol/kg	$\log K_L$	$R$
0.0	$0.09 \pm 0.04$	4.6	0.995
0.1	$0.1 \pm 0.1$	4.3	0.991
1.0	$0.3 \pm 0.5$	4.2	0.991
	$1/n$	$\log K_f$	
0.0	0.73	1.9	0.998
0.1	0.78	2.1	0.983
1.0	0.99	3.6	0.996

Conditions:  $5 \cdot 10^{-4} \text{ mol} \cdot \text{l}^{-1} < [\text{U(VI)}] < 5 \cdot 10^{-6} \text{ mol} \cdot \text{l}^{-1}$ , amount of solid phase =  $1 \text{ g} \cdot \text{l}^{-1}$ , pH 7.5.

Furthermore, there was no significant difference between thermodynamical data obtained from measurements carried out in solutions of different salinity, indicating that chemical reactions leading to uranium adsorption on olive cake surface are identical.

The kinetics of uranium adsorption onto olive cake follows the first order rate expression given by Lagergren.<sup>12</sup> The apparent  $k_{ad}$  value evaluated for the U(VI) adsorption in electrolyte-free solutions at 25 °C and pH 7 is found to be  $2.3 \cdot 10^{-3} \text{ min}^{-1}$ .

### Conclusions

The results obtained from this study lead to the following conclusions: (a) the optimum pH for uranium removal by olive cake is pH 7.5, (b) the experimental data can be fitted satisfying both the Langmuir and the Freundlich model, (c) the adsorption capacity is found to

be  $0.1 \text{ mmol} \cdot \text{l}^{-1}$  for solutions with  $I \leq 0.1 \text{ M}$  and  $0.3 \text{ mmol} \cdot \text{l}^{-1}$  for solutions with  $I = 1.0 \text{ M}$ , (d) the adsorption is based on inner-sphere complexation, most probably leading to the formation of 1:2 uranium chelation, where both carboxylic and phenolic groups are active and (e) the adsorption of U(VI) on olive cake is an endothermic, entropy-driven process and follows a first order rate expression.

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