Adsorption isotherm of uranyl ions by scales of Corvina fish

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Abstract: Fish scale is a by-product of fishery. The scales are mainly formed by hydroxyapatite and collagen, forming a kind of natural composite with a large specific surface area that intensifies the adsorption process. In this paper, the potential of adsorption of scales of Corvina fish for uranyl ions from nitric solutions was studied. Equilibrium and kinetic studies in adsorption of uranyl ions in batch systems were carried out at room temperature. Equilibrium time was reached at 5 min for 0.1 g L⁻¹ uranyl solution with a removal efficiency over 82%, and at 1 min of contact, about 60% removal was observed. These preliminary results are very promising, showing great prospects of application of fish scales as a biosorbent for uranyl ions in radioactive wastewater treatment processes with sustainable technology.

Keywords: biosorbents; fish scales; Corvina fish; uranium adsorption; sustainable technology.


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1 Introduction

Biosorption is one of the promising technologies for the removal of toxic metals from industrial waste and natural waters. This technology has distinct advantages over conventional methods: it is non-polluting, easy to operate and offers high efficiency of treatment of wastewaters containing low metal concentrations and the possibility of metal recovery (Febrianto et al., 2009). Furthermore, the biosorption process offers a potential advantage, i.e., is the low-cost biomass available in abundance as sorbent (Bailey et al., 1999; Yu et al., 2007; Nadeem et al., 2008; Gupta and Suhas, 2009). Certain types of living or dead biomass have the ability to bind and concentrate metals having good sorption properties. Many kinds of biomass have been investigated as sorbents for the removal of metals from wastewater. There are many reports of algae (Khani et al., 2006; Hussain et al., 2009), bacteria (Sahmoune et al., 2008) and agricultural wastes (Khan et al., 2004; Yamamura and Yamaura, 2007) that remove large amounts of toxic metals. Also, fish scales in fishery waste management have been reported as adsorbents in biosorption processes due to their high binding capacities (Stepnowski et al., 2004; Liu et al., 2008; Santos et al., 2009). The scales are mainly formed by hydroxyapatite and collagen, forming a kind of natural composite with a large specific surface area that intensifies the adsorption process.

In this paper, the potential of adsorption of scales of Corvina fish for uranyl ions from nitric solutions was studied. Influence of contact time and the isotherm on biosorption of uranium (U) were investigated. Both the Langmuir and the Freundlich isotherm models were evaluated to examine the biosorption capacity of fish scales for UO$_2^{2+}$ ions.

2 Experimental

2.1 Materials and preparation of scales of Corvina fish as biosorbent

A standard solution of uranyl nitrate was prepared by dissolution of U$_3$O$_8$ nuclear pure obtained from the Environment and Chemistry Centre at the Nuclear and Energy Research Institute (IPEN), São Paulo, Brazil. The U(VI) nitric solutions, of pH 4, were prepared by diluting from standard solution in distilled water. All chemicals used (NaOH, HNO$_3$ and Arsenazo III) were of analytical grade.
Scales of Corvina fish were washed several times with tap water, sun-dried, triturated and sieved (30–42 mesh). The scale powder obtained was stored and investigated as a biosorbent of uranyl ions from nitric solutions.

2.2 Batch method

The adsorption experiments were carried out by the batch method. Fifty milligrams of scale biosorbent were contacted with 2.0 mL of U solution under shaking at 360 rpm for a specific time interval at room temperature (27 ± 1ºC). The supernatant was separated by centrifugation for 10 min. The U concentration of the supernatant was measured at 650 nm using a spectrophotometer UV-Vis, model B582 Micronal, by the Arsenazo III method (Yamaura et al., 2002).

An investigation of the effect of agitation time on U adsorption, from a nitric solution of pH 4, was performed to determine the equilibrium time. The removal percentage was determined by equation (1). All experiments were performed in duplicate and the averaged values were presented.

\[
\text{Removal\%} = \left( \frac{C_0 - C}{C_0} \right) \times 100
\]

where \( C_0 \) is the initial concentration of U ions (mg L\(^{-1}\)) in the solution, and \( C \) is the final concentration of U ions (mg L\(^{-1}\)) after contact by shaking.

2.3 Equilibrium adsorption isotherm

Studies of the adsorption equilibrium isotherm were conducted by the batch method and centrifugation of solutions with U concentrations from 50 to 500 mg L\(^{-1}\) at pH 4 for 25 min of shaking at room temperature. The supernatant was subjected to U concentration measurements (\( C_{eq} \), mg L\(^{-1}\)). The amount of sorbed U onto the biosorbent (\( q_{eq}, \) mg g\(^{-1}\)) was calculated using equation (2). These data were evaluated by the Langmuir and Freundlich adsorption isotherm equations, two equilibrium isotherm models used to interpret the efficiency of metal sorption (Faust and Aly, 1987).

\[
q_{eq} (\text{mg g}^{-1}) = \left( \frac{C_0 - C_{eq}}{V/M} \right)
\]

where \( V \) is the volume of the solution (in litres) in contact with the biosorbent, and \( M \) is the mass (in grams) of the biosorbent.

The Langmuir isotherm model assumes monolayer adsorption and is presented by equations (3) and (4).

\[
\text{Langmuir model} : q_{eq} = \frac{Q_{max} \times K_L \times C_{eq}}{1 + K_L \times C_{eq}}
\]

\[
\text{Langmuir model in linear form} : \frac{C_{eq}}{q_{eq}} = \frac{1}{Q_{max} \times K_L} + \frac{C_{eq}}{Q_{max}}
\]

where \( q_{eq} \) is the adsorbed metal amount per unit mass of the adsorbent (mg g\(^{-1}\)), \( C_{eq} \) is the equilibrium concentration of the metal in the solution (mg L\(^{-1}\)), \( Q_{max} \) is the maximum adsorption capacity (mg g\(^{-1}\)) and \( K_L \) (L mg\(^{-1}\)) is the constant related to the free energy of adsorption.

A straight line is obtained by plotting \( C_{eq}/q_{eq} \) against \( C_{eq} \), and the slope and intercept are used to calculate the \( Q_{max} \) and \( K_L \), respectively.
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The Freundlich model is presented by equations (5) and (6), which indicates that the surface of adsorbent is heterogeneous.

Freundlich model: \( q_{eq} = K_F C_{eq}^{1/n} \)  

Freundlich model in linear form: \( \log q_{eq} = \log K_F + 1/n \times \log C_{eq} \)  

where \( K_F ((\text{mg g}^{-1})(\text{L mg}^{-1})^{1/n}) \) is a parameter of relative adsorption capacity of the adsorbent related to the temperature, and \( n \) is a characteristic constant for the adsorption system. A plot of \( \log q_{eq} \) against \( \log C_{eq} \) gives a straight line, and the slope and intercept correspond to \( 1/n \) and \( \log K_F \), respectively.

3 Results and discussion

3.1 Equilibrium time

The study of the contact time on U adsorption from nitric solutions (100 mg L\(^{-1}\)) of pH 4 was carried out to determine the equilibrium time. The result is shown in Figure 1. The removal percentage increases with the increase in contact time and reveals a rapid removal during the first few minutes of contact until reaching a state of equilibrium in 5 min at room temperature. At 1 min of contact, about 60% removal was observed. The attained removal percentage in equilibrium was over 82% of U from the nitric solution of pH 4. Based on these results, a contact time of 25 min was assumed to be suitable for subsequent experiments of sorption isotherm of solutions of pH 4.

Figure 1  Influence of contact time on UO\(_2\)^{2+} removal from nitric solutions (100 mg L\(^{-1}\)) of pH 4 by the scale biosorbent (see online version for colours)

3.2 Equilibrium adsorption isotherm

The equilibrium adsorption isotherm was obtained by plotting the amount of sorbed U on the scale biosorbent \( (q_{eq}) \) against equilibrium concentration \( (C_{eq}) \) in the solution and is presented in Figure 2. This shows that the amount of sorbed U increases with the increase in equilibrium concentration up to a maximum value, which is related to the maximum adsorption capacity of the scale biosorbent.
Figure 2  Equilibrium adsorption isotherm for $\text{UO}_2^{2+}$ adsorption onto the scale biosorbent at 27 ± 1°C (see online version for colours)

![Equilibrium adsorption isotherm](image)

The linearised Langmuir and Freundlich isotherms were applied for the system and are, respectively, shown in Figures 3 and 4. Their parameter values were calculated and are presented in Table 1.

Figure 3  Linearised Freundlich isotherm for $\text{UO}_2^{2+}$ adsorption onto the scale biosorbent at 27 ± 1°C (see online version for colours)

![Linearised Freundlich isotherm](image)

Figure 4  Linearised Langmuir isotherm for $\text{UO}_2^{2+}$ adsorption onto the scale biosorbent at 27 ± 1°C (see online version for colours)

![Linearised Langmuir isotherm](image)
Table 1 shows that the value of the correlation coefficient equal to 0.995 of the Langmuir model is higher than of the Freundlich model. This indicates that the adsorption of U ions onto the biosorbent is best described by the Langmuir model, and therefore, a monolayer of adsorbed U was formed, with a maximum adsorption capacity of 16.3 mg g⁻¹.

The correlation coefficient for the Freundlich plot is 0.933, which suggests a validity of the model over the range of studied concentration. Freundlich plot showed a slope of 1/n less than 1, indicating a non-linear sorption of U with increase in the concentration. The observed value of $K_F$, 1.1652 [(mg g⁻¹)(L mg⁻¹)⁺¹/n], indicated a significant affinity between the scale biosorbent and uranyl ions.

4 Conclusions

A biosorbent was prepared from scales of Corvina fish and investigated for U removal from nitric solutions by adsorption. The adsorption kinetics showed to be quick. The equilibrium time was found to be 5 min for 100 mg L⁻¹ U, representing 82% removal. The Langmuir isotherm model fitted the isotherm data better than the Freundlich model, and the maximum adsorption capacity of the biosorbent was of 16.3 mg U per gram of the scale biosorbent. These preliminary results are very promising, showing great perspectives of application of scales of Corvina fish as biosorbent for uranyl ions in radioactive wastewater treatment processes with sustainable technology.

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References


