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ADSORPTION ISOTHERM OF URANYL IONS BY FISH SCALES OF CORVINA

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ABSTRACT

Fish scale is 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. The scales were washed several times with faucet water, sun-dried, triturated and sieved. 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 removal efficiency over 82%, and at 1 min of contact was observed about 60% of removal. The equilibrium isotherm was obtained and the Langmuir model fitted best. These preliminary results are very promising, showing great perspectives of application of the fish scales as biosorbent for uranyl ions in radioactive wastewater treatment processes with a sustainable technology.

1. INTRODUCTION

Biosorption is one of the promising technologies for the removal of toxic metal from industrial waste and natural waters. This technology has distinct advantages over conventional methods, it is nonpolluting, easy to operate, offers high efficiency of treatment of wastewaters containing low metal concentrations and possibility of metal recovery [1]. Futhermore, the biosorption process offers a potential advantage that is the low cost biomass available in abundance as sorbent [2, 3, 4, 5]. Certain living or dead biomass has 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 waters. There are many reports of algae [6, 7], bacteria [8] and agricultural wastes [9,10] that remove large amounts of toxic metals. Also, fish scales in fishery waste management have been reported as adsorbents in biosorption processes due to the high binding capacities [11, 12, 13]. 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 were investigated. Both the Langmuir and Freundlich isotherm models were evaluated to examine biosorption capacity of fish scales for UO_2^{2+} ions.

2. EXPERIMENTAL

2.1. Materials and Preparation of Scales of Corvina Fish as Biosorbent

Standard solution of uranyl nitrate was prepared by dissolution of U_3O_8 nuclear pure obtained from Environment and Chemistry Centre at Nuclear and Energy Research Institute (IPEN), BR. The U(VI) nitric solutions, pH 4, were prepared by diluting from standard solution in distilled water. All chemicals used (NaOH, HNO_3, ArsenazoIII) were analytical grade.

Scales of *Corvina* Fish were washed several times with faucet water, sun-dried, triturated and sieved (30-42 mesh). The scale powder obtained was stored and investigated as biosorbent of uranyl ions from nitric solutions.

2.2. Batch Method

The adsorption experiments were carried out by batch method. Fifty milligrams of scale biosorbent were contacted with 2.0 mL of U solution under shaking of 360 rpm for a time interval at room temperature of 27±1ºC. The supernatant was separated by centrifugation for 10 min. The uranium concentration of supernatant was measured at 650 nm using a spectrophotometer UV-Vis, mod. B582 Micronal, by Arsenazo III method [14].

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

$$\text{Removal } \% = (C_0 - C) \times 100/C_0 \qquad (1)$$

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 adsorption equilibrium isotherm were conducted by batch method and centrifugation for solutions of U concentrations from 50 to 500 mg L^{-1} at pH 4, for 25 min of shaking at room temperature. The supernadant was subjected for U concentration measurements. The amount of U adsorbed onto biosorbent (q_e, mg g^{-1}) was calculated using the Eq. 2. These data were evaluated by Langmuir and Freundlich adsorption isotherm equations, two equilibrium isotherm models usually used to interpret the efficiency of metal sorption [15].

$$q_e \text{ (mg g}^{-1}) = (C_0 - C) \times V/M \qquad . \qquad (2)$$

Where V is the volume of solution (L) in contact with the biosorbent and M is the mass (g) of the biosorbent.

Langmuir isotherm model assumes monolayer adsorption, and is presented by the Eq. 3 and 4.

$$\text{Langmuir model: } q_{eq} = Q_{max} * K_L * C_{eq}/(1+K_L*C_{eq}) \quad (3)$$

$$\text{Langmuir model in linear form: } C_{eq}/q_{eq} = 1/(Q_{max}*K_L) + 1/\,Q_{max} *C_{eq} \quad (4)$$

Where q_{eq} is the metal amount adsorbed per unit mass of adsorbent (mg g^{-1}), C_{eq} is the equilibrium concentration of metal in the solution (mg L^{-1}), Q_{max} is the maximum adsorption capacity (mg g^{-1}), and K_L ((mg g^{-1})(L mg^{-1})$^{1/n}$) 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.

The Freundlich model is presented by the Eq. 5 and 6, which indicates that the surface of adsorbent is heterogeneous.

$$\text{Freundlich model: } q_{eq} = K_F *C_{eq}^{\ 1/n} \quad (5)$$

$$\text{Freundlich model in linear form: } \log q_{eq} = \log K_F + 1/n *\log C_{eq} \quad (6)$$

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

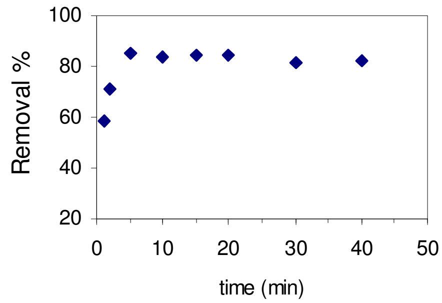

Figure 1. Influence of the contact time on UO_2^{2+} removal from nitric solutions (100 mg L^{-1}) at pH 4 by scale biosorbent.

3.2. Equilibrium Adsorption Isotherm

The equilibrium adsorption isotherm was obtained by plotting the amount of U sorbed on scale biosorbent (q_{eq}) against equilibrium concentration (C_{eq}) in the solution, and is presented in Fig. 2. The Figure shows that the amount of U sorbed increases with the increase in equilibrium concentration until a maximum value which is related to the maximum adsorption capacity of the scale biosorbent.

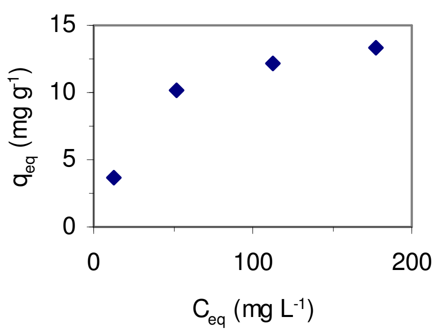

Figure 2. Equilibrium adsorption isotherm for UO_2^{2+} adsorption onto scale biosorbent at 27±1ºC.

The linearized Langmuir and Freundlich isotherms were applicated for the system and are, respectively, shown in Fig. 3 and 4, and their parameter values were calculated and presented in Table 1.

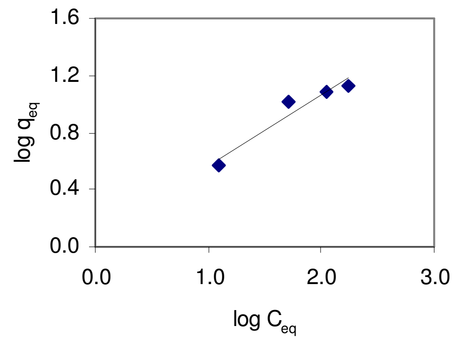

Figure 3. Linearized Freundlich isotherm for UO_2^{2+} adsorption onto scale biosorbent at 27±1ºC.

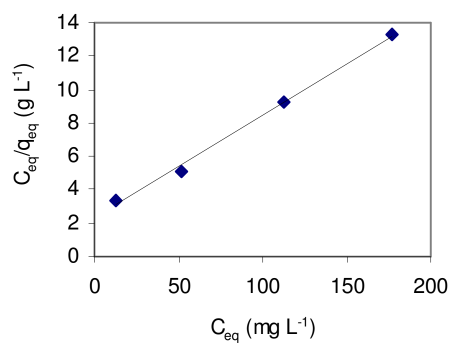

Figure 4. Linearized Langmuir isotherm for UO_2^{2+} adsorption onto scale biosorbent at 27±1ºC.

In 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 biosorbent was 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 nonlinear sorption of U with 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.

Table 1. Parameter values of the Langmuir and Freundlich isotherms for adsorption of the UO_2^{2+} ions by scale biosorbent, from nitric solutions in pH 4.

Isotherm model	Q_{max} (mg g^{-1})	K_L (L mg^{-1})	1/n	K_F (mg g^{-1})(L mg^{-1})$^{1/n}$	correlation coefficient, r^2
Langmuir	16.3	0.0264	-----	-----	0.995
Freundlich	-----	------	0.4947	1.1652	0.933

4. CONCLUSIONS

A biosorbent was prepared from scales of *Corvina* fish and investigated for U removal from nitric solution 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 Freundlich model, and the maximum adsorption capacity of the biosorbent was of 16.3 mg U per g of scale biosorbent. These preliminary results are very promising, showing great perspectives of application of the fish scales of *Corvina* as biosorbent for uranyl ions in radioactive wastewater treatment processes with a sustainable technology.

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