Biosorption of Silver by Macrophyte *Salvinia Cucullata*

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Silver removal from aqueous solutions by macrophyte *Salvinia cucullata* was investigated in static and dynamic system. The macrophyte *Salvinia cucullata* showed high potential for removing silver in previous tests using three different macrophytes. Batch experiments were performed at a constant temperature, adjusting solution pH in contact with *Salvinia cucullata*. Pseudo-first order, pseudo-second order and intra-particle diffusion models were used to analyze the kinetic curves. Equilibrium data were analyzed using Langmuir and Freundlich models. Adsorption essays at fixed bed were also carried out according to a study of outflow based on results from mass transfer zone (*MTZ*). The single-component essays showed that silver ions have affinity to macrophyte adsorptive sites. The maximum adsorption capacity increased significantly in the dynamic system of fixed bed compared to static batch.

1. Introduction

The recovery of heavy metals and other pollutants has been the focus of much research considering both environmental and economic aspects related to it. The main problem of heavy metal's pollution is the possibility of significant and abrupt alterations in the ecosystem mainly due the easy incorporation of those components in living beings (Volesky and Holan, 1995). Different methods have been used in wastewater's treatment as solvent extraction, ion exchange mechanism and membrane technologies. In this context, adsorption is also an important method, whose main goal is to remove those metals and release an effluent with concentration established by legislation. Moreover, the adsorption might be used to recover valuable materials in order to reduce process costs (Kentish and Stevens, 2001).

Choosing adsorption as a decontaminating method, other recent challenge is the investigation of materials used as adsorbent since it is necessary good removal efficiency and environmental and economic performance. In this context, the use of macrophytes (dead and dried aquatic plants) has been recently investigated due its low cost and availability (Lima et al., 2011). The use of macrophytes is based on different mechanisms varying from metabolic actions (like transport, internal compartmentation and extracellular precipitation) to chemical and physical affinity between the metal and the biological material (Fourest and Roux, 1992).

Silver is an extremely important heavy metal because of its industrial use and elevated economic value. This material is used in several industrial activities as the production of battery, mirrors and photographic film and also as a disinfectant agent in pharmaceutical and food industries (Çoruh et al., 2010). Thus, the treatment of wastewater contaminated with silver is very relevant because this metal, in elevated concentrations, may cause several negative health effects (Song et al., 2011).

In this study, the silver adsorption using the macrophyte *Salvinia cucullata* as bioadsorbent was evaluated. To verify the removal potential of the macrophyte, the process was carried out in static and dynamic systems.

2. Material and Methods

2.1 Affinity tests using five different macrophites

Affinity tests between silver and five macrophytes (*Lemna minor, Spongia, Pistia stratiotes, Salvinia natans and Salvinia cucullata*) were performed. The bioadsorbents were initially dried at 60 ºC for 24 hours and then crushed, sieved and prepared by size classification. 1 gram of macrophyte was added to 100 mL of

Ag$^+$ solutions (100 mg/L) and silver concentration was verified after 1 hour. The removal percentage (*%R*) of silver was obtained by Eq(1):

$$\%R = \left(\frac{C_0 - C_e}{C_0}\right) \cdot 100 \qquad (1)$$

where C_0 is the initial concentration of metal ions and C_e is the concentration of metal ions in the solution of the equilibrium time.

2.2 Batch sorption procedure

Adsorption experiments were performed in batch, at room temperature under constant stirring (225 rpm). 1 gram of *Salvinia cucullata* was added to 100 mL of Ag$^+$ single solutions (100 mg/L). By a metallic speciation study, it was verified that silver's precipitation occurs in pH values over 9.2, approximately. Therefore, the pH of the solutions was measured at the beginning and the end of each experiment and it was not necessary to adjust it. At specific time intervals (from 0.5 to 360 minutes), solution aliquots were removed and centrifuged. The supernatant liquid was diluted and its concentration was determined by atomic absorption spectrometry. The concentrations of metal ion in the solid phase (*q*) at each time were obtained by Eq(2):

$$q(t) = \frac{V}{m}\left(C_0 - C(t)\right) \qquad (2)$$

where, C_0 is the initial concentration of metal ions, $C(t)$ is the concentration of metal ions at time t, V is the volume of solution and m is the mass of dry macrophyte.
The removal percentage (*%R*) was calculated using the Eq(1).
The kinetic models of pseudo-first-order and pseudo-second-order, given by Eq(3) and Eq(4) respectively, were used. Adjustments pseudo-first-order and pseudo-second-order were obtained by nonlinear regression.

$$q = q_e(1 - e^{-k_1 t}) \qquad (3)$$

$$\frac{q}{q_e} = \frac{k_2 q_e t}{1 + k_2 t} \qquad (4)$$

Where, k_1 and k_2 are the rate constants in min^{-1} and g/mmol.min respectively, q_e is the concentration of metal ion in the solid phase at equilibrium in mmol/g.
When there is possibility for diffusing the adsorbate species into the adsorbent pores, the intraparticle diffusion rate constant (k_i) can be obtained from Eq(5):

$$q = k_i t^{0.5} + c \qquad (5)$$

In this case, the intraparticle diffusion has a significant effect on the control of the adsorption process kinetics. The q versus $t^{0.5}$ graph provides a straight line passing by the y axis with an inclination equal to the value of k_i. The c values provide an approximation of the boundary layer thickness, the greater the c value, the greater the boundary layer effect is. The deviation of the straight line from the origin may be attributed to a difference in mass transfer between the initial and final adsorption stages.
Kinetic data have been analyzed using the model given by Boyd et al. (1947):

$$Bt = -0.4977 - \ln(1 - q/q_e) \qquad (6)$$

Eq(6) is used to calculate Bt values at different time, t. The calculated Bt values were plotted against time. The relation between Bt and t is linear. The slope value, B, was used to calculate the effective diffusion coefficient, D_i (cm^2/s) using the Eq(7):

$$B = \pi^2 D_i / r^2 \qquad (7)$$

2.3 Adsorption isotherm

Adsorption isotherm was obtained at temperature of 273 K. 0.5 grams of macrophyte were put into Erlenmeyer flasks, each of them filled with 50 mL of heavy metal solution at different concentrations (2 to 500 ppm). The time of the experiments was determined from the kinetic experiment and the pH of the Ag$^+$ solutions was adjusted at approximately 5.2 using nitric acid 0.1 mol/L.

With the purpose to establish the relationship between the amount of adsorbed metal by macrophyte and its equilibrium concentration in aqueous system, Langmuir and Freundlich isotherm models were used to fit the experimental data.

The model of Langmuir (1918) was originally developed assuming monolayer adsorption on a surface of the adsorbent with a finite number of adsorption sites. The Langmuir equation is expressed by Eq(8):

$$q* = \frac{q_m b C_e}{1 + b C_e}$$

(8)

Where C_e is the concentration of the adsorbate at equilibrium in the liquid phase (mmol/L) and $q*$ is the concentration of the adsorbate in the solid phase (mmol/g), b (L/g) and q_m (mmol/g) are Langmuir constant related of the adsorbate–adsorbent equilibrium and the maximum adsorbed amount on the monolayer, respectively.

The Freundlich model assumes that adsorption takes place on heterogeneous surfaces of an adsorbent. Eq(9) represents this model.

$$q* = K C_e^n$$

(9)

Where, K and n are Freundlich coefficients.

2.4 Column sorption procedure

Essays in dynamic system were performed in a glass column with 1.5 cm internal diameter. The height of the bed used in experiments was 15.0 cm. The macrophyte *Salvinia cucullata* were deposited inside the column and put in contact with deionized water for 2 hours.

The solutions containing the metal species were fed at the base of the column through a peristaltic pump (Masterflex) at a constant flow 4 mL/min. Column effluent samples were collected at time intervals preset by FC203 fraction collector (Gilson).

The capacity of silver removal was verified by the amount of total removal until the saturation point (q_t) and the amount of useful removal until de breakthrough point (q_u). Those parameters were calculated by Eq(10) and Eq(11) respectively, obtained by the mass balance in the column.

$$q_u = \frac{C_0 V}{1000 m} \int_0^{t_b} \left(1 - \frac{C|_{Z=L}}{C_0}\right) dt$$

(10)

$$q_t = \frac{C_0 V}{1000 m} \int_0^{\infty} \left(1 - \frac{C|_{Z=L}}{C_0}\right) dt$$

(11)

Where C_0 is the initial concentration of silver (mmol/L),), C is the concentration of silver at time t, t_r is the time until the rupture point (min), Q is the flow used in the system (L/min) and m is the mass of the adsorbent put in the column (g). The integrate part was calculated by the area below the curve $1-C/C_0$ versus time until the bed exhaustion (q_t) and until the breakthrough point (q_u). The software Origin 6.0 was used to calculate the area.

The Mass Transfer Zone (MTZ) is calculated based on the q_u/q_t ratio according to Eq(12), given by Geankoplis (1993):

$$MTZ = \left(1 - \frac{q_u}{q_t}\right) \cdot Ht$$

(12)

MTZ has a maximum value which corresponds to the bed height (Ht) and, as the efficacy of mass transference increases, this value decreases until reaching the ideal condition where MTZ is zero and the breakthrough curve is a step function.

The percentage of total removal (%RT) during adsorption was obtained considering the metal fraction in solution retained in the adsorbent solid, from total effluent used in the adsorption process until bed saturation. The amount of adsorbed metal is calculated considering the curve area ($1-C/C_0$) versus t. The integral of metal adsorption curves was determined through the *Origin* version 6.0 software.

3. Results and Discussion

3.1 Affinity tests using five different macrophytes

Previous tests were performed towards to verify the affinity between silver and five macrophytes *(Lemna minor, Spongia, Pistia stratiotes, Salvinia natans and Salvinia cucullata)*. The results obtained are shown in Figure 1.

From Figure 1A, it is possible to notice that the macrophyte *Salvinia cucullata* presented a removal percentage higher than the other macrophytes. Using Eq(2) it was also possible to obtain Figure 1B, and verify that *Salvinia cucullata* is the macrophyte with major capacity of removal, approximately 0.035 mmol/g. Thus, this bioadsorbent was chosen to be used in static and dynamic systems in the following experiments.
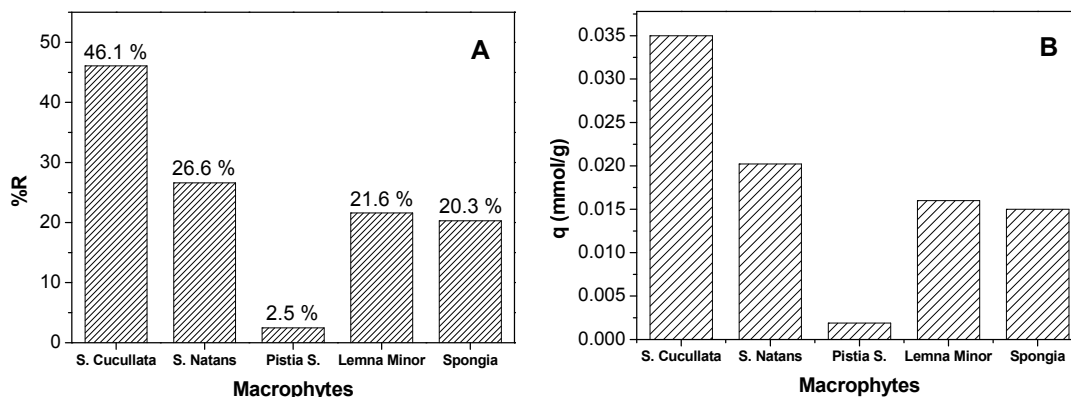

Figure 1: Affinity of Silver obtained for five macrophytes used as bioadsorbents.

3.2 Batch adsorption

Kinetic adsorption of Ag by *Salvinia cucullata* essays were performed in a batch system at a concentration of 100 mg/L. Figure 2 presents the kinetics removal of silver from single aqueous solutions.
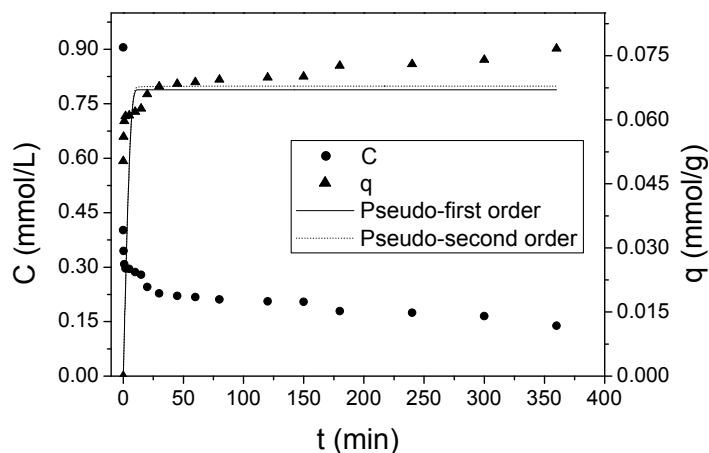

Figure 2: Kinetic curves for Ag on Salvinia cucullata.

From Figure 2, the equilibrium time in the removal of silver was 200 min. The maximum amount of silver adsorbed was 0.075 mmol of metal/g of macrophyte. The percentage of total removal of silver in this system was approximately 85 %.

The models proposed to evaluate the removal rate adjusted well to the experimental data. The effectiveness of adjustment can be verified by the behaviour of similarity between the experimental curve and the adjusted curve (Figure 2). The removal rate constants k_1 and k_2, obtained from the pseudo-first-order and pseudo-second-order modelling, were 16.15 min^{-1} and 25.98 g/mmol.min, respectively.

According to Figure 3, silver removal by macrophyte shows two phases. In the first stage, the instantaneous diffusion has been completed in about 1 min. In the second stage, the gradual diffusion showed a linear relationship, indicating that diffusion is a significant step for the process. The k_i value was calculated in the range 1-360 min being found 8.35x10^{-4} mmol/g.min$^{-0.5}$. In this analysis, the linear

regression coefficient, R^2, is 0.92, indicating that gradual intraparticle diffusion is a rate limiting step. The D_i value was estimated to be 5.15×10^{-5} cm^2/s.
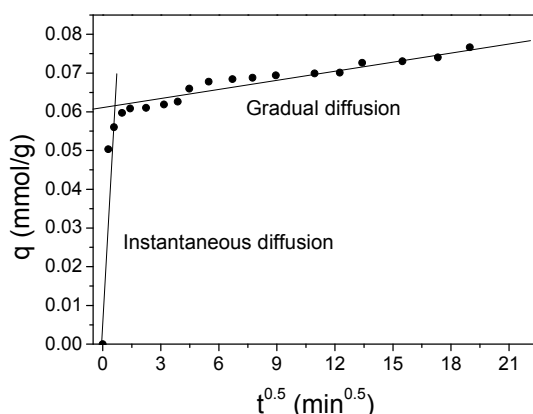

Figure 3: Intraparticle diffusion for Ag on Salvinia cucullata.

3.3 Equilibrium adsorption

The amount of metal ions adsorbed per mass unit of macrophyte ($q*$) gradually increases as the initial concentration of the adsorbate solution increases. When the initial solution has a low concentration, the ratio between the number of ions and the number of adsorptive sites available is small; consequently, adsorption depends on the initial concentration. Therefore, as the concentration of ions increases, adsorption also increases. In high concentrations of ion, each unit mass of adsorbent is subjected to a larger number of ions, as shown in Figure 4.

The Langmuir and Freundlich models were adjusted to experimental data through the Gauss–Newton nonlinear estimation method in Statistic 7.0 for Windows® software. Both models presented good results for isotherm´s adjustments, verified by the correlation coefficient values (R^2). R^2 was 0.983 for Langmuir and 0.926 for Freundlich model. The maximum adsorbed capacity given for Langmuir was 0.196 mmol/g. The Langmuir isotherm is specific for monolayer adsorption, which was the case in this study, while the Freundlich model is better applied to adsorption at heterogeneous sites on the surface of a solid, with a mechanism that has not yet been established. The Langmuir equilibrium coefficient b determines the direction of the equilibrium adsorbate–adsorbent macrophyte (solid phase) + Ag$^+$ (aqueous phase) = macrophyte−Ag$^+$. The b parameter obtained for silver adsorption was 2.5 L/g, indicating that the equilibrium moves to the right side, with the resulting formation of the adsorbate–adsorbent complex.

The value obtained for the Freundlich constant n is approximately 0.53 for adsorption in batch. According to Treybal (1980) this range indicates that the adsorptive characteristics of the macrophyte are suitable for silver adsorption.
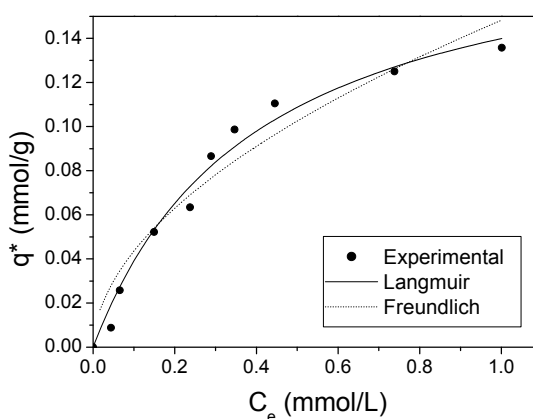

Figure 4: Adsorption isotherm for silver removal on macrophyte Salvinia cucullata, adjusted to the models Langmuir and Freundlich.

3.4 Silver dynamic removal

A preliminary study was conducted with outflow of 4 mL/min in order to analyze silver removal in *Salvinia cucullata*. Figure 5 shows breakthrough curve in the outflow studied.
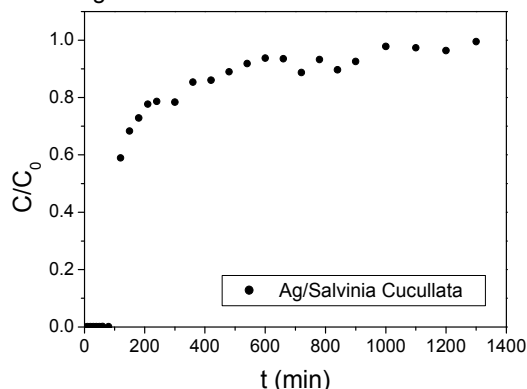

Figure 5: Breakthrough curve of systems Ag/Salvinia Cucullata, $C_0 = 2.55$ mmol/L with flow of 4 mL/min.

It can be noticed that this curve presents strong resistance to bed saturation. Using the flow of 4 mL/min outflow, it was obtained a short MTZ length of 9.75 cm and a high resistance to saturation of the bed for silver removal by *Salvinia cucullata*. The amount of metal retained in the bed to the point of rupture (q_u) until saturation (q_t) were 0.701 and 0.245 mmol/g, respectively, and the %RT was 18 %. Comparing the two removal systems used in this study (batch and fixes bed), it was verified that q_t is ten times greater than q, the amount adsorbed in equilibrium time, and q_u is major that q_m given by Langmuir model. This suggests that silver removal efficiency using *Salvinia cucullata* depends on the system.

4. Conclusions

From adsorption experiments carried out in the static and the dynamic systems used for removal of silver ions on *Salvinia cucullata*, it was found that the removal of silver from single component solution depends on the system. The results indicated that the batch kinetics of silver ions adsorption by macrophyte is rapid, requiring a minimum time 200 min to reach equilibrium. The maximum adsorbed capacity given for Langmuir was 0.196 mmol/g. Comparing the results of fixed bed and batch, it was noticed that fixed bed presents a major amount of adsorbed silver.

Acknowledgements

References

Boyd G.E., Adamson A.E., Meyers L.S., 1947, The exchange of adsorption ions from aqueous solutions by organic zeolites II. Kinetics, Journal of American Chemical Society, 69, 2836-2848.
Çoruh S., Senel G., Ergun O.N., 2010, A comparison of the properties of natural clinoptilolites and their ion-exchange capacities for silver removal, Journal of Hazardous Materials, 180, 486-492.
Fourest E., Roux J.C., 1992, Heavy metal biosorption by fungal mycelial by-products: mechanisms and influence of pH, Applied Microbiology and Biotechnology, 37, 399-403.
Kentish, S. E., Stevens, G. W., 2001, Innovations in separations technology for the recycling and re-use of liquid waste streams, Chemical Engineering Journal, 84, 149-159.
Lima L.K.S., Kleinubing S.J., Silva E.A., Silva M.G.C., 2011, Removal of Chromium from wastewater using macrophyte Lemna Minor as biosorbent, Chemical Engineering Transactions, 24, 303-308, DOI:10.3303/CET1125051.
Song X., Gunawan P., Jiang R., Leong S.S.J., Wang K., Xu R., 2011, Surface activated carbon nanospheres for fast adsorption of silver ions from aqueous solutions, Journal of Hazardous Materials, 194, 162-168.
Treybal R.E., 1980, Mass Transfer Operations. McGraw Hill, New York, USA.
Volesky B., Holan Z. R., 1995, Biosorption of heavy metals, American Chemical Society and American Institute of Chemical Engineers, 235-251.