Kinetic Modeling Biosorption of Cr(VI) using *Mucor* sp. and *Aspergillus* sp. Inactive Biomass

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***Abstract*— Biosorption kinetics of Cr (VI) from aqueous solutions by *Mucor* sp. and *Aspergillus* sp. inactive biomass were studied. Kinetic experiments were done with 50 mg/L as initial concentration using 0.5 g of inactive biomass in 50 mL of aqueos solutions at pH 2.0 and T= 25° C. The Cr (VI) uptake was found to be rapid for *Aspergillus* sp. inactive biomass reached 85% of equilibrium capacity of biosorption in 120 min while *Mucor* sp. inactive biomass reached after 24 h of contact. The experimental data were analyzed using three sorption kinetic models; the pseudo-first order, pseudo-second order and intraparticle diffusion. The pseudo-second order equation described the biosorption kinetics of Cr (VI) with high correlation coefficient (R^2>0.99) and better than the other equations. The q_e value obtained was 6.093 mg/g and 6.235 mg/g to *Mucor* sp. and *Aspergillus* sp. inactive biomass, respectively.**

Keywords—Biosorption, Biomass, Chromium, Kinetics, Models.

I. INTRODUCTION

Industrialization has resulted in the introduction of pollutants into the environment, such as heavy metals. Chromium is one of the heavy metals that due to its toxicity make it an important and urgent research topic. The presence of this metal affects the environment and human health. This can cause dermatitis, nausea, skin allergies, damage to the lungs and nervous system, and also has mutagenic and carcinogenic properties in humans [1]. Therefore, it is necessary to remove Cr (VI) ions from drinking water and wastewater. Among the main industries producing chrome as waste are mining and refining, aluminum production, steel plants, leather tanning, chrome plating, fly ash from incinerators, paints, alloys and in the production of inorganic chemicals [2]. The conventional methods of elimination of heavy metals is carried out by physical-chemical methods such as reverse osmosis, solvent extraction, coagulation, ion exchange, chemical precipitation, membrane separation processes, redox processes, filtration, incineration, recovery by evaporation, neutralization, electro Dialysis and electrochemical treatment [3]. These methods involve high capital investments, incomplete removal of metals, high energy requirements and generation of toxic waste that require treatment [4]. Microorganisms have been reported to act as sorbent materials to remove heavy metals from wastewater [5]. The strategy consists of a chromium (VI) sorption, taking advantage of the characteristics of the microbial biomass. This biosorption technology has advantages of low operating cost, is effective in dilute solutions and generates minimum effluent [6]. Extensive investigations have been carried out for the elimination of metallic ions using strains of several microorganisms[7][8][9]. Studies have shown that the treatment of Cr (VI) on the surfaces of biomaterials achieves high and effective removal percentages[10][2][11].

The objective of this research was to study the biosorption kinetics of Cr (VI) by *Mucor* sp. and *Aspergillus* sp. inactive biomass. In order to analyzed the experimental data of biosorption kinetics, the pseudo-first order, pseudo-second order and intraparticle diffusion rate equations were used.

II. METHODOLOGY

A. *Preparation of inactive fungal biomass*

The fungi used in the present work were isolated from contaminated soils and were identified by the gender *Mucor* and *Aspergillus*, and belong to the strain collection of Institute of Biotechnology (UANL). Fungal strains was activated and, grown in 500ml Erlenmeyer flasks containing 300ml of medium (saccharose 40g/L, KH_2PO_4 4g/L, $MgSO_4$ 0.75 g/L, NH_4Cl 1 g/L, citric acid 3 g/L, cysteine 0.5 g/L, NaCl 1 g/L, $CaCl_2$ 0.1 g/L, Na_2HPO_4 6 g/L) [12] on shaking incubator at 200 rpm, temperature room (26 ± 2° C). After 7 days of incubation in a rotatory shaker, the biomass obtained was separated through the filter paper and was dried at 50° C for 72h, before powdered in a mortar and pestle. The dried biomass was stored in a desiccator and used for the following experiments.

B. *Preparation of Cr (IV) solution*

Stock solution of Potassium dichromate ($K_2Cr_2O_7$) was prepared from chemical reactants of analytical grade, using 1000mg/L $K_2Cr_2O_7$ in double distilled water and was diluted to various desired concentrations as required. Concentrations varied in each case. Initial pH was adjusted at 4.5 with 0.1N HCl and 0.1N NaOH.

C. *Biosorption Experiment*

The Cr (VI) biosorption studies were performed using dried fungal biomass. For uptake capacity, 50 ml of $K_2Cr_2O_7$ [50 mg/L] were taken in 125 ml Erlenmeyer flasks and 0.5 g of biomass were added. Control was without biomass. Biosorption experiments were performed in a rotatory shaker (200 rpm, 25°C). A 1 ml sample from each experiment flask(s) was taken and centrifuged at 6,000 rpm for 10 min, each 15 min during 2 h, then each 12 h until 48 h.

D. *Chromium analysis*

Cr(VI) was analyzed spectrophotometrically after complexation of the metal ion with 1,5-diphenylcarbazide. Absorbance was recorded at 540 nm, using Shimadzu (UV-1201, UV–VIS) spectrophotometer using standard method (Clesceri et al. 1998). Cr(VI) was analyzed spectrophotometrically after forming a colour compound of Cr(VI) with 1,5-diphenylcarbazide. Absorbance was recorded at 540 nm, using Perkin Elmer (Lamda 35, UV–VIS) spectrophotometer using standard method [7].

E. *Mathematical Modeling of the process*

Evaluation of biosorption capacity was performed by subjecting the data obtained from biosorption studies to the following kinetics and isotherm models and linear plots were drawn by using Microsoft Excel 2007.

The uptake capacity of Cr(VI) ions per unit of sorbent (mg metal ions/g dry biosorbent) is calculated from the mass balance as follows[13]:

$$q = \frac{(C_o - C)/V}{M} \qquad (1)$$

where: q is the quantity of the ions adsorbed by a given quantity of biosorbent, [mg/g]; C_o is the initial concentration of Cr(VI), [mg/L]; C is the concentration of Cr(VI) after the process of biosorption, [mg/L]; V is the volume of the liquid phase, [L]; M is the quantity of the biosorbent, [g].

The data obtained in the removal test were analyzed with three kinetic models, which explain different biosorption processes:

a) Pseudo-first-order: Lagergren model explains a process of biosorption that is carried out in an active way, in which the contaminant is introduced to the biosorbent[14]. Equation 2 shows the linearized form of this model.

$$log(q_e - q_s) = log\, q_e - \frac{k_1}{2.303} t \qquad (2)$$

where: q_e is the amount of adsorbed Cr (VI) on the biosorbent at the equilibrium, [mg/g]; q_s *is* the amount of adsorbed Cr (VI) on the biosorbent at any time t, [mg/g]; k_1 is the Lagergren rate constant of the first-order biosorption, [g/mg/min]. A plot of log (q_e - q_t) vs. t should give a straight line confirming the applicability of the kinetic model. In a true first-order process log q_e should be equal to the intercept of a plot of log (q_e - q_t) against t.

b) Psuedo-second-order: In this model, it is explained that the biosorption process occurs on the surface of the biosorbent by means of a mass transfer. Equation 3 shows the linearized form of this model[15].

$$\frac{t}{q_s} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (3)$$

where: k_2, is the rate constant of second order biosorption, [g/mg/min]. The q_e and k_2 can be calculated from the slope and intercept of the plot of t/q vs. t.

c) Intraparticular diffusion: When the data conform to this model, it means that the biosorption process is carried out by two stages, first an adsorption on the surface and subsequently the contaminant is introduced into the biosorbent [16]. Equation 4 shows the linearized form of this model.

$$q_s = k_i t^{1/2} + C \qquad (4)$$

where: C (mg/g) is the intercept and k_i is the intraparticle diffusion rate constant (mg/g/min^{½}). In the three models the adjustment of the data with the model is evaluated by obtaining the coefficient R^2 ≈1.

III. RESULTS

A. *Effect of contact time*

The relation between removal Cr (VI) and process time were studied to see the rate of Cr (VI) removal. The data obtained from the biosorption of Cr (VI) on the inactive biomass of *Aspergillus* sp. showed that a contact time of 60 min was sufficient to achieve equilibrium and the adsorption did not change significantly with further increase in contact time. This behavior was not the same for *Mucor* sp. inactive biomass, which presents two possible stages of equilibrium. The q_e value obtained was 6.093 mg/g and 6.235 mg/g to *Mucor* sp. and *Aspergillus* sp. inactive biomass, respectively. The percentage removal of Cr (VI) with increase of contact time using *Mucor* sp. and *Aspergillus* sp. are presented in Figure 1. It was found that more than 70% removal of Cr (VI) concentration occurred in the first 15 min using *Aspergillus* sp. biomass while *Mucor* sp. does it until after 12 h of contact. The rapid sorption achieved at the beginning of the contact time using *Aspergillus* biomass is due to the charge that has the surface of the biomass, which favors the sorption of Cr (VI) to pH 2. The slow rate of Cr (VI) sorption is probably due to the electrostatic impediment between the Cr adsorbed into the biomass surface and the Cr available in the solution as well as the slow pore diffusion of the Cr (VI) into the bulk of the adsorbent [17].

B. *Kinetic models applied to the sorption of Cr (VI)*

There are different strategies to find out what is the mechanism that describes the process of sorption of Cr (VI) by inactive biomass of *Aspergillus* sp. and *Mucor* sp. This process may be due to a chemical reaction, mass transfer and/or intrapartícular diffusion; to find the true mechanism, kinetics models were used in which the experimental data obtained were adjusted.

Figure 2 shows the Lagergren pseudo-first order kinetic plot for the adsorption of Cr (VI) onto inactive biomass of both fungi. The pseudo first order rate constant k_1 values were calculated from the slope of Figure 2. The calculated k_1 values and their corresponding linear regression correlation coefficient values are shown in Table 1. The linear regression correlation coefficient value R^2 found 0.847 and 0.615 to *Mucor* sp. and *Aspergillus* sp. inactive biomass respectively, which shows that this model cannot be applied to predict the adsorption kinetic model.

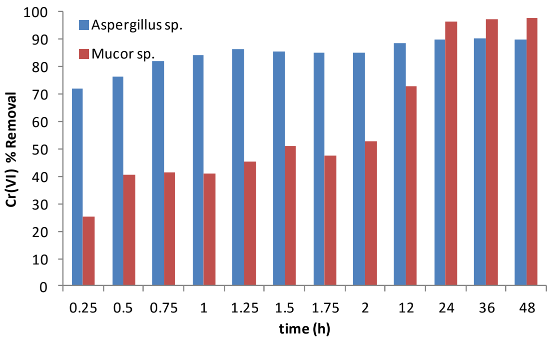

Fig. 1. *Effect of contact time on the removal of Cr(VI) using Mucor sp. and Aspergillus sp. inactive biomass (0.5 g / 50 mL) at pH 2.0, T = 25°C.*

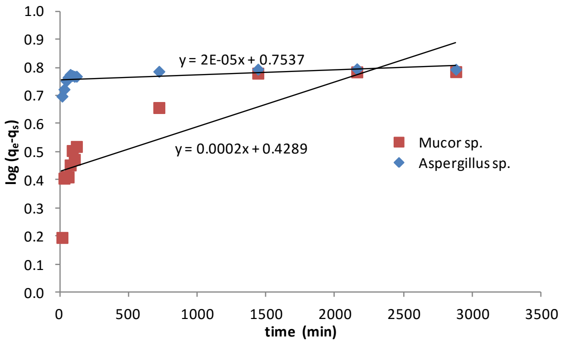

Fig. 2. *Pseudo-first order kinetics for Cr (VI) (50 mg/L) sorption onto inactive biomass of Mucor sp. and Aspergillus sp. Conditions: adsorbent dosage 0.5 g / 50 mL, pH 2.0, T = 25°C.*

The sorption kinetic may be described by pseudo-second order model [18]. The pseudo-second order rate constant k_2, the calculated q_e value and the corresponding linear regression correlation coefficient value R^2 are given in Table 1. The sorption reaction can be most satisfactorily by the pseudo-second-order kinetic model for Cr(VI) sorption onto both inactive biomass found on the theory that the rate limiting step may be chemisorption relating valency forces through sharing or exchange of electrons between adsorbent and adsorbate [19].

The second order rate constants were used to calculated the initial sorption rate, given by the Equation 5 [20]:

$$v = k_2 q_e^2 \tag{5}$$

The higher R^2 values confirm that the sorption data are well represented by pseudo-second order kinetics and supports the assumption behind the model that the sorption is due to mass transfer (Figure 3). The values of the initial sorption rate were 0.066 mg/g/min and 1.117 mg/g/min to *Mucor* sp. and *Aspergillus* sp. inactive biomass respectively.

TABLE I. KINETIC MODELS PARAMETERS

Biomass		***Mucor* sp.**	***Aspergillus* sp.**
First-order kinetic model	q_e	2.685	5.672
	k_1	3.66 x10^{-4}	4.33 x10^{-5}
	R^2	0.847	0.615
Second-order kinetic model	q_e	6.274	6.232
	k_2	0.002	0.029
	v	0.066	1.117
	R^2	0.998	0.999
Intraparticle diffusion	K_{id}	0.087	0.016
	C	2.036	5.542
	R^2	0.968	0.727

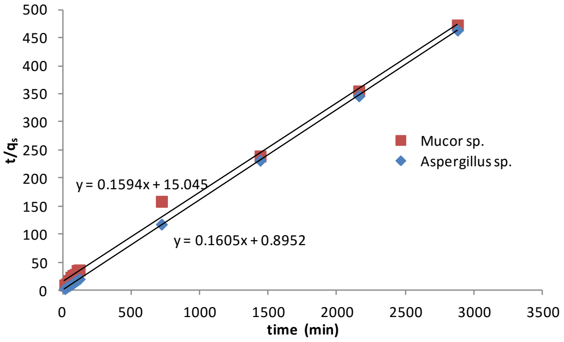

Fig. 3. *Pseudo-second order kinetics for Cr (VI) (50 mg/L) sorption onto inactive biomass of Mucor sp. and Aspergillus sp. Conditions: adsorbent dosage 0.5 g / 50 mL, pH 2.0, T = 25°C.*

The possibility of intraparticle diffusion was analyzed using the experimental data (Figure 4). This model explains that the adsorbate species are most probably transported from the bulk of the solution into the solid phase through transport process, which is the rate limiting step in sorption process. If the plot of q_s vs. $t^{½}$ gives a straight line, then the sorption process is controlled by intraparticle diffusion only. However, if the data exhibit multi-linear plots, then two or more steps influence the sorption process. The values of K_{id} and C can be determined from the slope and intercept of the plots q_s versus $t^{½}$. The K_{id} values were calculated and shown in Table 1. Values of intercept C (Table 1) give an idea about the thickness of the boundary layer, the larger intercept the greater is the boundary layer effect [21]. *Mucor* sp. inactive biomass showed greater tendency to present this type mechanism of sorption, with a C value of 2.036 mg/g while *Aspergillus* sp. was 5.542 mg/g. The R^2 values given in the table 1, *Aspergillus* sp. inactive biomass value is not close to unity indicating that this model is not applicable to describe this biosorption process, but *Mucor* sp. inactive biomass value is 0.968 so it can be suggested that this mechanism also occurs as time increases.

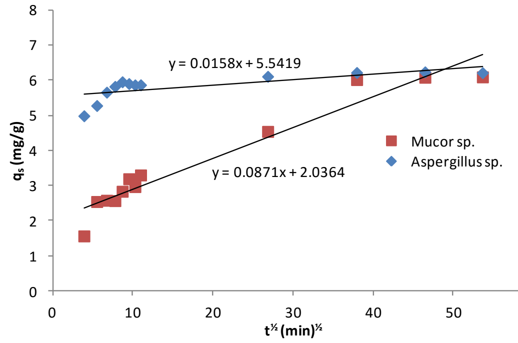

Fig. 4. *Intraparticle diffusion plot for Cr(VI) (50 mg/L) sorption onto inactive biomass of Mucor sp. and Aspergillus sp. Conditions: adsorbent dosage 0.5 g / 50 mL, pH 2.0, T = 25°C.*

IV. CONCLUSIONS

The data obtained from the removal of Cr(VI) with the inactive biomass of *Mucor* sp. and *Aspergillus* sp showed an adjustment for the pseudo second order model, with linear regressions of R^2 = 0.99 and R^2 = 1 respectively, while in the intraparticle diffusion model the regressions were 0.97 (*Mucor* sp) and 0.73 (*Aspergillus* sp), and from the pseudo first order model, R^2 = 0.85 (*Mucor* sp.) and R^2 = 0.61 (*Aspergillus* sp) were obtained. The high correlation values confirm that the adsorption data are well represented by the pseudo-second order kinetics and supports the assumption of the adsorption model is due to a mass transfer. Regarding the constant of the speed of removal, k_2, *Mucor* sp. obtained 0.002 g/mg/min while *Aspergillus* showed values of 0.029 g/mg /min. Regarding the values of q_e *Mucor* sp. obtained 6.274 mg/g and *Aspergillus* sp. 6.232 mg/g. The results presented here have fundamental relevance in understanding about of the Cr(VI) biosorption process occur in this type of inactive biomass.

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