Journal of
Applied Sciences

Effect of Calcium Competition on Chromium Adsorption by Fungi Biomass

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Abstract: The kinetics and thermodynamic of adsorption of a mono-solute of chromium ions and of a bi-solute of chromium and calcium ions by fungi biomass (*Streptomycine rimosus*) was investigated in a batch system. The experimental data were analyzed based by Langmuir isotherm and a Pseudo second order mechanism, in the both the mono-and bi-solute adsorption systems, in order to predict the rate constant of adsorption, the equilibrium capacity. The results indicate that the adsorption mechanism is described by Langmuir isotherm and a Pseudo-second-order. The equilibrium adsorption capacity and the equilibrium rate constant increased with an increase in the initial chromium concentration in both mono-and bi-solute adsorption systems. The adsorption capacity of chromium decreased with an increase in calcium concentration.

Key words: Adsorption, chromium, fungi biomass, kinetics, calcium

INTRODUCTION

The removal of the chromium ions from industrial wastewater is an important problem to be solved. Chromium is considered as priority pollutants because of their high toxicity at low concentrations (Aksu *et al.*, 1990; Dean *et al.*, 1972; Tobin *et al.*, 1998).

The used biological materials for heavy metal removal and recovery technologies have gained important credibility during recent years, because of the good performance and low cost of this complexing material (Mullen *et al.*, 1992; Tobin *et al.*, 1994; Volesky and Holan, 1995). The natural affinity of biological compounds for metallic elements could contribute to economically purifying heavily metal-loaded wastewater. Among the various resources in biological wastes, dead biomass of micro-organisms (bacteria, yeasts, fungi, algae) exhibits particularly interesting metal-binding capacities (Fourest *et al.*, 1994; Tobin *et al.*, 1994; Volesky *et al.*, 1995; Namasivayam and Yamuna, 1995; Periasamy *et al.*, 1995; Sag *et al.*, 2000; Salim *et al.*, 1994; Yasemin *et al.*, 2005). *Streptomyces remosus*, a filamentous fungus can accumulate chromium (Fourest *et al.*, 1992; Aksu *et al.*, 1990). These properties are attributed to the high content of complexing functional groups in their cellular wall (e.g., amino, amide, hydroxyl, carboxyl, sulfhydryl, phosphate radicals) (Brady *et al.*, 1995).

Many of the studies on chromium biosorption have focused on simple metal sorption systems (Aksu *et al.*, 1990; Nourbash *et al.*, 1994; Bai *et al.*, 2001; Sag *et al.*, 1996). Competitive sorption systems have also been reported, for example, lead and nickel by Microspora (a micro-alga) and Lemna monor (duckweed, an aquatic plant) (Axiell *et al.*, 2003), as well as chromium/calcium and chromium/NaCl by waste crab-shells (Yeoung *et al.*, 2002) and by mucor biomass (Tobin *et al.*, 1998).

Chromium adsorption kinetics have been extensively studied and it has been commonly observed that the adsorption rate is very rapid at the beginning of the process, then the rate shows as equilibrium is approached. Several groups of researchers have described the reaction order of sorption in metal-biosorbent systems using various kinetic models. Traditionally, kinetics have been described by the Lagergren first-order equation (Periasamy *et al.*, 1995). However, it was reported that a Pseudo-second-order model provides a more appropriate description of the mono-and bi-solute binding of copper and nickel to peat and *Chlorella vulgaris* (Mehta and Gaur, 2001) than does a first-order equation.

The adsorption of chromium ions by fungi biomass (*Streptomycine rimosus*) was studied in this study and the effects of the initial chromium ion concentration and the addition of calcium ions were investigated. A Langmiur model sorption and Pseudo-second-order model was developed and was used to analyse the data for the sorption of chromium ions by fungi biomass (*Streptomycine rimosus*).

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MATERIALS AND METHODS

Materials: The biomass used is the *Streptomycine rimosus,* coming from the SAIDAL-complex manufacturing unit of antibiotics Medea-Algeria. This antibiotic by-product is a mud of Mycelium resulting from the extraction of the fermented gelatine meat-broth for the manufacture of the oxytetracycline.

This biomass underwent a pre-treatment which consists of repeated washing with distilled water until the elimination of the impurities, drying in a drying oven during 48 h, then crushing and sifting to obtain an easily storable powder of granulometry ranging from 100 to 700 μm. Then a chemical treatment is underwent which consists in introducing the dried biomass into a solution of hydroxide sodium of 0.01 N concentration. The biomass is maintained in suspension by agitation during 30 min at ambient temperature, repeatedly filtered and washed with distilled water then dried in the drying oven at 50°C during 2 h and an air-tight container.

Stock solutions of chromium (III) (3 g L^{-1}) and calcium (II) (1000 mg L^{-1}) were prepared in distilled water using $Cr_2(SO_4)_3$ and calcium hydroxide ($Ca(OH)_2$; all working solutions were prepared by diluting the stock solution with distilled water.

Methods
Effect of the initial concentration: A volume of 100 mL of $Cr_2(SO_4)_3$ solution with a concentration ranging from 455 to 2600 mg L^{-1} was placed in a 250 mL conical flask and set at pH 4.8. 0.3 g of the biomass fungi (*Streptomycine rimosus*) was accurately weighed and added to the solution. The conical flask was then shaken at a constant speed of 300 rpm in a shaking water bath with temperature 20°C. Samples (2.5 mL) were withdrawn at suitable time intervals and the filtrates was analysed by atomic absorption spectrophotomertry (Perkin Elmer, 2380).

Effect of the addition of calcium ions: Appropriate amounts of chromium (III) and calcium (II)were added to produce solutions containing 455 mg L^{-1} chromium (III) and 50 mg L^{-1} calcium (II), 455 mg L^{-1} chromium (III) and 100 mg L^{-1} calcium (II) and 455 mg L^{-1} chromium (III) and 150 mg L^{-1} calcium (II). A 0.3 g of the biomass fungi (*Streptomycine rimosus*) was added to each 100 mL volume of the various chromium (III) and calcium (II) solutions and agitated at 300 rpm, with the temperature set at 20°C for all experiments. Samples (2.5 mL) were withdrawn at suitable time intervals and the filtrates was analysed by atomic absorption spectrophotomertry (Perkin Elmer, 2380). The experiments were repeated using 1076, 1630 and 2600 mg L^{-1} of chromium (III).

RESULTS AND DISCUSSION

In order to investigate the mechanism of adsorption, the adsorption reaction order and equilibrium sorption isotherms of chromium were determined using a Pseudo-second-order mechanism expression (Weber *et al.,* 1963; Ho and McKay, 2000; Wu *et al.,* 2001) and the Langmuir isotherm equation (Langmuir, 1918).

Pseudo-second order model: The reaction rate of a reaction is defined as the change in concentration of q reactant or product per unit time. The concentrations of products do not appear in the rate law because the reaction rate is being studied under conditions where the reverse reactions do not contribute to the overall rate. The reaction order and rate constant must be determined by experiments. A Pseudo-second-order rate law expression demonstrates how the rate depends on the sorption capacity but not the concentration of the sorbate (Ho and Augustine, 2005). The sorption kinetics may be described as being Pseudo-second-order. The differential equation is

$$dq_t/dt = k(q_e-q_t)^2 \qquad (1),$$

Where k is the rate constant of sorption (g mg^{-1} min^{-1}), qe the amount (mg g^{-1}) of chromium ions sorbed onto the surface of the fungi biomass at any time.

Separating the variables in the equation above gives

$$dq_t/(q_e-q_t)^2 = kdt \qquad (2)$$

Integrating this for the boundary conditions t = 0 to t and q_t = 0 to q_t, gives

$$1/(q_e-q_t) = 1/q_e + kt \qquad (3)$$

Thus, a plot of $1/(q_e-q_t)$ against t of Eq. 3 should give a linear relationship with a slop of k and an intercept of $1/q_e$

Sorption models: The partitioning of a solute (metal ions) between the liquid (aqueous solution) and solid (biomass) phases is commonly described by the Langmuir isotherm model.

The Langmuir model corresponds to the following equation:

$$q_e = q_m \frac{bC_e}{1+bC_e} \qquad (4)$$

where C_e is the metal concentration in solution at equilibrium (mg L^{-1}), q_e is the amount of chromium adsorbed per unit weight of dry biomass at equilibrium
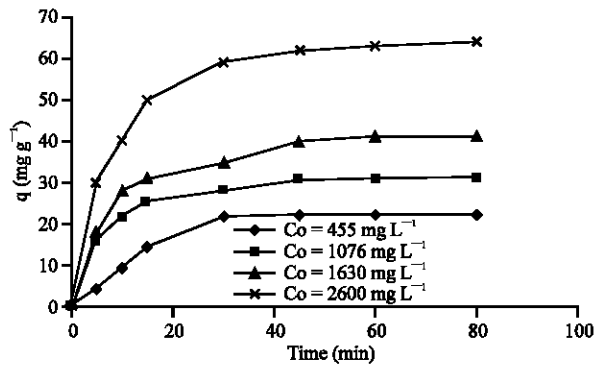
Fig. 1: Effect of initial concentration of chromium on its sorption onto fungi biomass (*Rhizopus arrhizus* (Biomass concentration = 3 g L^{-1}; p Hi = 4.8; T = 20°C)
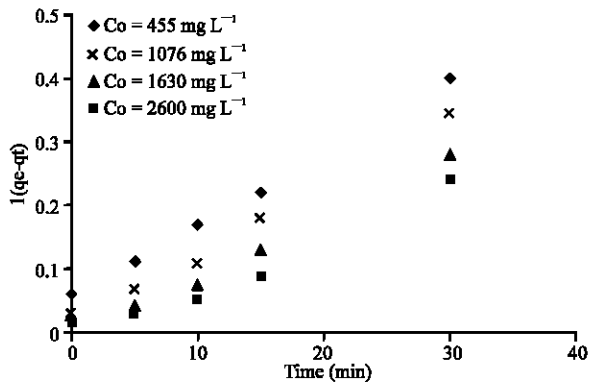

Fig. 2: plot of $1/(q_e-q_t)$ against t for chromium sorption at various initial chromium concentrations (Biomass concentration = 3 g L^{-1}; p Hi = 4.8; T = 20°C)
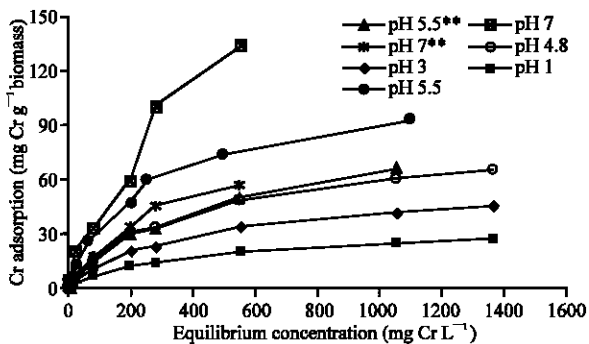

Fig. 3: Effect of pH and influence of precipitation on uptake (** indicates where precipitations effects have been subtracted)

(mg g^{-1}), q_m is the maximum amount of metal adsorbed per unit weight of dry biomass, corresponding to saturation of the sorbent binding sites by metal ions to form a complete monolayer on the surface at high Ce (mg g^{-1}) and b is a binding stability constant related to the affinity of the solute for the binding sites (L mg^{-1}).

Effect of initial chromium concentration: The rate of chromium sorption on the biomass fungi was determined as a function of the initial chromium concentration using initial concentrations of 455, 1076, 1630 and 2600 mg L^{-1}. The results in Table 1, show the applicability of the Pseudo-second-order equation for the system of chromium with biomass fungi for initial chromium (III) concentrations ranging from 455 to 1630 mg L^{-1}. Table 1 lists the rate constant, k, the equilibrium sorption, (q_e) at various concentrations of chromium (III). The equilibrium sorption (Table 1 and Fig. 1) increased from 22.1 to 64.2 mg g^{-1} and the value of rate constant (Table 1 and Fig. 2) increased from 0.010 to 0.097 mg g^{-1} min^{-1} with an increase in the initial concentration of chromium (III) from 455, 1076, 1630 and 2600 mg L^{-1}. This could have been due to the driving force of higher concentrations (Ho *et al.*, 2005). Figure 1 shows plot of the experimental data points for the sorption of chromium (III) by fungi biomass as function of time. These plots show that, for all initial chromium concentrations, the amount of chromium (III) sorbed increased rapidly with time at the beginning and became very slow towards the end of the process. The plots also demonstrate that the sorption increased for lower initial chromium concentration at any specific time. Furthermore, a large fraction of the total amount of chromium (III) was removed within a short period of time. There was also an effect on the contact time required to reach saturation due to the variation in the initial chromium concentration.

Effect of initial pH on chromium adsorption: The effect of pH on the adsorption capacity of chromium with biomass of *Streptomycine rimosus* was identified, when the pH value was raised from 1 to 4.8, the adsorption capacity was enhanced significantly from 27 to 64 mg g^{-1} biomass. Absorption studies at pH 5.5 and 7.0 marked precipitation effects augmented the biosorption removal of chromium from solution resulting in apparent sequestration levels of in excess of 93 and 133 mg g^{-1}, respectively as shown in Fig. 2. As can be seen in the figure, when the precipitation component is subtracted the net biosorption values are in good agreement with each other and those observed at pH 4.8 (Tobin *et al.*, 1998).

The adsorption potential is not affected by precipitation or basification of the medium, in this case the basification caused by the addition of Ca(OH)$_2$ from where the appearance of the precipitation of metal does not affect the potential of adsorption (Stein and Schwedt, 1994).
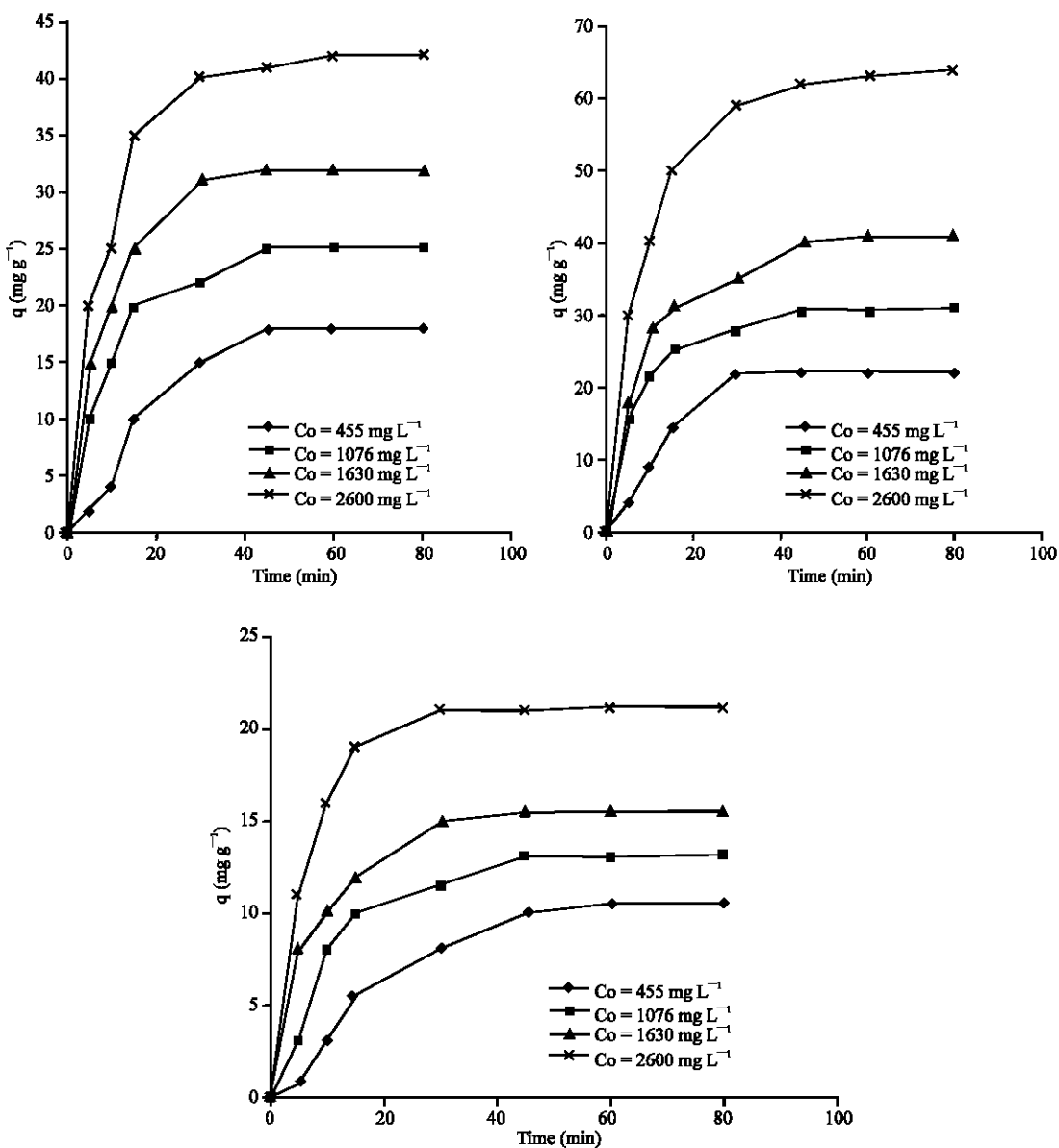
Fig. 4: Effect of various calcium concentrations of calcium ions added at various initial chromium concentration (Biomass concentration = 3 g L^{-1}; p Hi = 4.8; T = 20°C). (a) Ca^{+2} = 50 mg L^{-1} ; (b) Ca^{+2} = 100 mg L^{-1} ; (c) Ca^{+2} = 150 mg L^{-1}

The optimal pH for adsorption of chromium by mycelia by-products of *Streptomycine rimosus* was around 4.8 (Fig. 3).

Effect of added calcium: The effect of added calcium was evaluated for various initial chromium concentrations (455, 1076, 1630 and 2600 mg L^{-1}). In each initial chromium concentration, various calcium concentration (50, 100 and 150 mg L^{-1}) were mixed with the chromium solutions. Figure 4 shows a plot of experimental data points for the adsorption of chromium (III) at various calcium

concentration (50, 100, 150 mg L^{-1}) added at various initial chromium concentrations (455, 1076, 1630 and 2600 mg L^{-1}). The Pseudo-second-order constants from a series of kinetics experiments are shown in Table 1. The results in Table 1 show that increasing concentrations of calcium had a significant effect on the uptake of chromium in the bi-solute system. The equilibrium sorption capacity and the equilibrium rate constant all increased with an increase in the initial chromium concentrations in all cases at a particular calcium concentration such as 50, 100 and 150 mg L^{-1}. At particular initial chromium concentration,
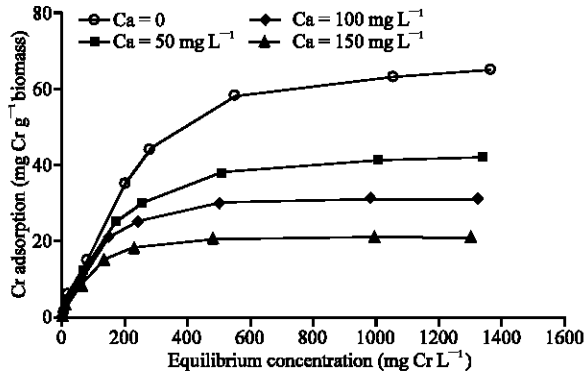
Fig. 5: Effect of various calcium concentrations of calcium ions added at equilibrium sorption isotherms of Cr by *Rhizopus arrhizus* during 5 h. (Biomass concentration = 3 g L^{-1}; p Hi = 4.8; T = 20°C)
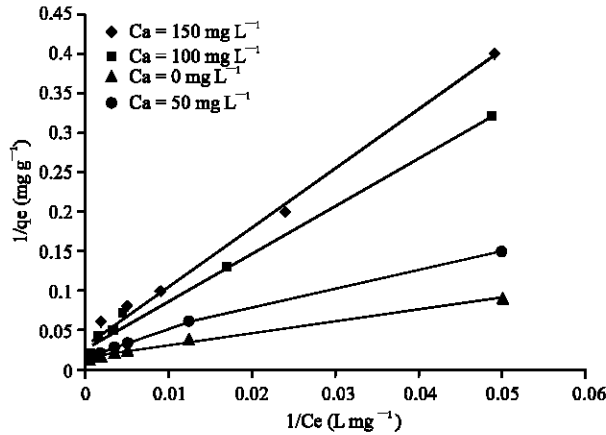

Fig. 6: Langmuir transformations of equilibrium sorption isotherms at various calcium concentration ions (Biomass concentration = 3 g L^{-1}; p Hi = 4.8; T = 20°C)
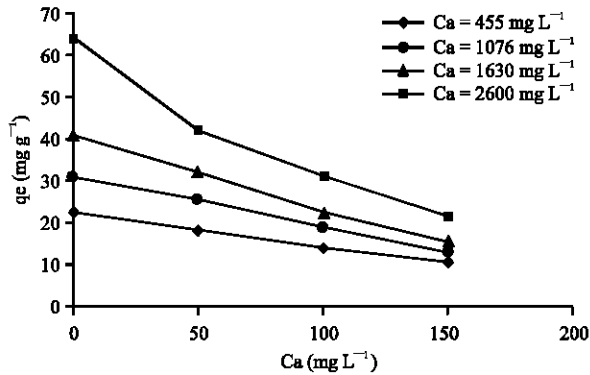

Fig. 7: Effect of calcium concentrations on the sorption of chromium by biomass fungi at various chromium concentration ions. (Biomass concentration = 3 g L^{-1}; p Hi = 4.8; T = 20°C)

Table 1: Parameters for the effect of added calcium on the sorption of chromium at various initial chromium concentrations

C$_a$(mg L^{-1})	C$_0$ (mg L^{-1})	q$_a$ (mg g^{-1})	k (mg g^{-1} min^{-1})	R^2
0	455	22.1	0.1250	0.999
	1076	30.9	0.0999	1.000
	1630	41.0	0.0667	0.998
	2600	64.2	0.0415	0.997
50	455	18.1	0.147	1.000
	1076	25.4	0.119	0999
	1630	32.1	0.0497	0.998
	2600	42.0	0.0693	0.994
100	455	14.1	0.151	1.000
	1076	19.0	0.143	0.997
	1630	22.3	0.134	0.992
	2600	31.2	0.0991	0.994
150	455	10.5	0.167	1.000
	1076	13.1	0.171	0.991
	1630	15.5	0.138	0.995
	2600	21.2	0.150	0.989

Table 2: Sorption isotherm coefficients of Langmuir model

Ca (mg L^{-1}) Calcium concentration	Langmuir model		
	q$_m$ (mg g^{-1})	b (L mg^{-1})	R^2
0	64	0.19	0.989
50	42	0.15	0.990
100	31	0.10	0.991
150	21	0.08	0.990

the equilibrium sorption capacity decreased with an increase in calcium concentration. This may have been due to competition occurring in the bi-solute sorption systems of chromium and calcium on the fungi biomass

Equilibrium adsorption isotherms of chromium by dead biomass at various calcium concentrations shown in Fig. 5. The data were transformed to the reciprocal Langmuir format as sees in Fig. 6. The obtained coefficients correlation R^2 from linear regression of Langmuir model, the values of the sorption equilibrium constant (b) and the maximum sorption capacity of biomass for the chromium ion are presented in Table 2. The maximum sorption capacities of fungi biomass for the chromium ion were lower than in their respective mono-solute systems.

Figure 7 demonstrates this effect and shows that, as the calcium concentration increased from 0 to 150 mg L^{-1}, the chromium sorption capacity decreased. These results similar those are obtained by Ho and Augustine in the study of the effects of calcium competition on lead sorption by pal kernel fibre (Ho *et al.*, 2005).

CONCLUSIONS

The kinetics of a sorption of mono-solute of chromium ions and a bi solute of chromium and calcium ions by fungi biomass (*Streptomycine rimosus*) were well correlated by a Pseudo-second order expression and a Langmiur model adsorption. The equilibrium adsorption capacity and the equilibrium rate constant increased with

an increase in the initial chromium concentration in both mono-and bi-solute adsorption systems. The adsorption capacity of chromium decreased with an increase in calcium concentration.

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