

Thermodynamic of Chromium Sorption on Biomass Fungi from Aqueous Solution

¹K. Louhab, ¹J. Addad, ¹S. Barr and ²B. Goma

¹Department of Environment, Faculty of Engineer Sciences,
University of Boumerdes, 35000-Boumerdes-Algeria

²Ecole des mines d'Albi-Carmaux-Albi, France

Abstract: The thermodynamics of chromium ions sorption from aqueous solution on biomass fungi have been investigated. The experimental data was analysed by Langmuir and Scatchard isotherms. The equilibrium sorption capacity of chromium ions was determined from Langmuir and Scatchard equation at different temperature. Bad correlation coefficients were obtained for the Langmuir adsorption equilibrium constant. Various thermodynamics parameters, ΔH°_{ads} , ΔS°_{ads} and equilibrium constant values were computed at different temperature. The results show that the sorption of the chromium ions on biomass fungi is spontaneous and exothermic nature process, the thermodynamics parameters are dependent of the temperature and the equilibrium sorption capacity.

Key words: Adsorption, biomass fungi, chromium, thermodynamic

INTRODUCTION

Mining activities, agriculture run off, industrial and domestic effluents are mainly responsible for the increase of the metals released into the environment. Metals that are released into the environment tend to persist indefinitely, accumulating in living tissues throughout the food chain and are posing a serious threat to the environment and public health (Aksu and Kusta, 1991; Tobin and Roux, 1998; Fourest and Roux, 1992; Gadd and Rome, 1988; Brady and Tobin, 1995).

There are numerous methods currently employed to remove and recover the metals from our environment. These include chemical oxidation and reduction, membrane separation, liquid extraction, carbon adsorption, ion exchange, electrolytic treatment, electro precipitation, coagulation, flotation, evaporation, hydroxide and sulfide precipitation (Dean *et al.*, 1972; Brauckmann, 1998). These methods differ in their effectiveness and cost. They also often tend to treat the metal totally as waste without the possibility of recycling. Experiments showed that most of conventional methods produce some complexes with other compounds and interfere other treatment processes or environment.

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 (Volesky and Holan, 1995; Volesky, 1987). The natural affinity of biological compounds for metallic elements

could contribute to economically purifying heavily metal-loaded waste water (Tobin *et al.*, 1984; Hu and Ofamja, 2005; Aksu *et al.*, 1990). Among the various resources in biological wastes, dead biomass of microorganisms (bacteria, yeasts, fungi, algae) exhibits particularly interesting metal-binding capacities (Volesky and Holan, 1995; Tobin *et al.*, 1984). Streptomycin rimosus, a filamentous fungus can accumulate chromium (Fourest and Roux, 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 and Tibin, 1995).

Microbial biomasses are produced in fermentation plants to synthesize valuable biomolecules (e.g., antibiotics, enzymes, flavouring agents, organic acids), and generate important amounts of biological by-products that can be easily harvested and valorised in biosorption technologies.

In this study, the adsorption capacity of biomass fungi for chromium ions has been investigated by determined the equilibrium isotherm at various temperatures. In each system two isotherms, the Langmuir and Scatchard have been analysed.

MATERIALS AND METHODS

Biomass preparation: The biomass used is the *streptomycin 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 μ m. Then a chemical treatment is underwent which consists in introducing the dried biomass into a solution of hydroxide sodium of 0.01N 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.

Chromium uptake: A volume of 100 mL of Cr₂(SO₄)₃ solution with a concentration ranging from 126 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 (*streptomycin 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 temperatures 10, 20, 30, 35 and 40°C, respectively. After shaking the flasks for 2 h, the biomass fungi was separated by filtration by atomic was analysed for remaining chromium using a Perkin Elmer 2380 atomic absorption spectrophotometer. The experiments are carried out with the laboratory environment and pollution of the university of Boumerdes Algeria

RESULTS AND DISCUSSION

Equilibrium studies: The analysis of the isotherm data is important to develop an equation an equation, which accurately represents the results and could be used fir design purposes. In order to investigate the sorption isotherm, two models were analysed: the langmuir (Langmuir, 1918) and the Scatchard isotherm (Scatchard, 1949). The Langmuir sorption isotherm (Langmuir, 1918) is perhaps the best know of all isotherms describing sorption. The theoretical Langmuir isotherm is often used describe sorption of a solute from a liquid solution as:

$$q_e = KC_e q_m / 1 + KC_e \tag{1}$$

The constants q_m and K are the characteristics of the Langmuir equation and can be determined from q linearised from of Eq.(1), represented by :

$$1/q_e = 1/C_e q_m K + 1/q_m \tag{2}$$

where C_e is the metal concentration in solution at equilibrium (mg L⁻¹), q_e is the amount of chromium sorbed per unit weight of dry biomass at equilibrium (mg g⁻¹), q_m is q_e for a complete monolayer (mg g) K is sorption equilibrium constant (L mg⁻¹).

The development of the Eq. (1) leads to a representation according to Scatchard (1949).

$$q_e/C_e = Kq_m - Kq_e \tag{3}$$

Linear Scatchard plots (q_e/C_e vs q_e) reflect binding to sites of a single type while non-linear plots have been interpreted as indicating multiple types of binding.

Equilibrium absorption isotherms of Cr (III) by dead biomass of *Streptomyces remosus* with pH 4.8 at different temperature shown in Fig. 1. Both curves are concave to the x-axis which is characteristic of microbial metal binding although saturation uptake levels were not attained at the equilibrium solution concentration involved. In contrast, in the present study uptake is seen to increase with solution concentration of up to 1400 mg L⁻¹ and saturation is not evident in Fig. 1. When the data were transformed to the reciprocal Langmuir format a clearly non-linear plot resulted as sees in Fig. 2. The obtained coefficients correlation R² from linear regression of Langmuir model are presented in Table 1. This non-conformity to idealised Langmuir behaviour may be interpreted as indicating complex adsorption processes involving multiplayer, interactive or multiple site type binding or some combination of these phenomena (Scatchard, 1949; Bases and Mesner, 1976; Stein and Schwedt, 1994).

The values of q_m and K, given by supposing a single type of site and an absorption of the Langmuir type, decrease with the temperature, as we see in the following Table 1 and Fig. 2.

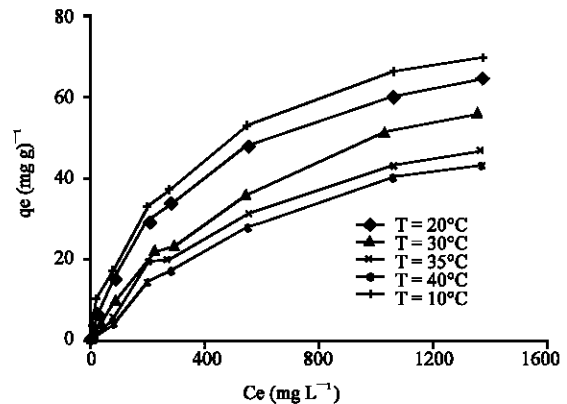


Fig. 1: Equilibrium sorption isotherms of Cr by *Rhizopus arrhizus* during 5 h at different temperature (Biomass concentration = 3g L⁻¹; p Hi = 4.8)

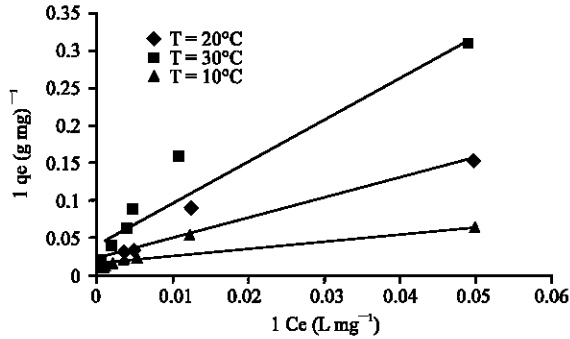


Fig. 2: Langmuir transformations of equilibrium sorption isotherms

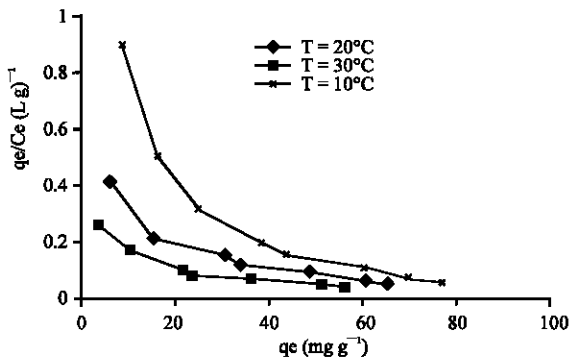


Fig.3: Scatchard plot of pH 4.8 uptake data at different temperature

Table.1: Sorption isotherm coefficients of Langmuir model at different temperature

Temperature (°C)	qm (mg g ⁻¹)	K (sorption equilibrium constant) L mg ⁻¹	R ²
10	70.0	1.005 10 ⁵	0.9012
20	65.0	4.148 10 ⁶	0.9089
30	56.1	2.395 10 ⁶	0.9072

The data were further transformed to the Scatchard format as shown in Fig. 3, which also resulted in a clearly non-linear plot. As has been discussed elsewhere, linear Scatchard plots reflect binding to sites of a single type while non-linear plots have been interpreted as indicating multiple types of binding (Tobin and Roux, 1998). In this study the highly curved nature of the Scatchard plot indicates the existence of multiple types binding sites in the biomass and/or multiple forms of chromium in solution. Moreover, the authors (Bases and Mesner, 1976; Stein and Schwedt, 1994) show that chromium may exist in the form of: Cr(III), Cr(OH)⁺, CrSO₄⁺, Cr₂((OH)₂(SO₄)₂)²⁺, CrOHSO₄, Cr₂(OH)₂(SO₄)₂.

In order to study the influence of the temperature, a series of experiments was led to different temperatures ranging between 10 and 40°C (Fig.1), for one duration of setting in liquid solid contact of approximately 5 h. It is noted that the quantity of adsorbed chromium decreases

when the temperature of the solution increases. This observation shows that the absorption of the ion chromium by biomass fungi is exothermic (Addad, 2002).

Determination of the isosteric heat of adsorption: The isosteric heat of adsorption ΔH°_{ads} (enthalpy of adsorption) is the quantity of heat developed during the adsorption of a mole of Cr(III) per fungi gram of biomass. It is given by the relation of Clausius Clapeyron (Ball and Fuerstenau, 1971; Zarouki and Thames, 1990)

$$\left(\frac{d \ln C_e}{dT}\right)_{q_e} = -\frac{\Delta H_{ads}}{RT^2} \quad (4)$$

$$(\ln C_e)_{q_e} = \frac{\Delta H_{ads}}{RT} + \text{Constante} \quad (5)$$

With a constant q_e (or degree of constant covering), the values of C_e according to T are obtained from the isotherms of adsorption of Fig. 1. While carrying $\ln C_e$ according to $1/T$, we obtain a series of right-hand side whose slope enables us to determine ΔH_{ads} and the ordinate in the beginning enables us to calculate the entropy of adsorption ΔS_{ads} . In the same way one can deduce the constant from balance according to the temperature and the adsorbed quantity with balance (degree of covering).

K is given by the following equation (Ball and Fuerstenau, 1971).

$$K = e^{-\Delta G^{\circ}_{ads}/RT} = e^{-\Delta S^{\circ}_{ads}/R} e^{-\Delta H^{\circ}_{ads}/RT} \quad (6)$$

On the Fig. 4 and 5 are respectively presented the evolution of the enthalpy of adsorption and the entropy of adsorption. It is noted that the heat of absorption decreases when the quantity of absorbed chromium increases.

For small absorbed quantities (q_e), the energy of absorption is about 14 kcal mole⁻¹; then becomes equal to

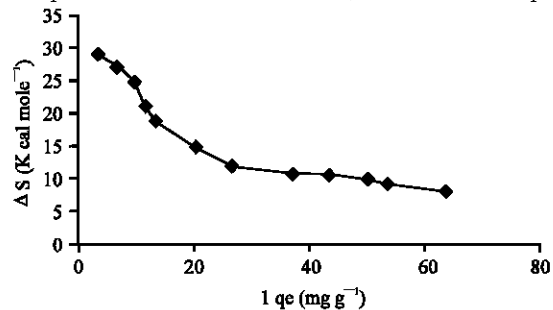


Fig. 4: Evolution of the adsorption heat according to the quantity of the chromium adsorbed (Biomass concentration = 3g L⁻¹; p Hi = 4.8)

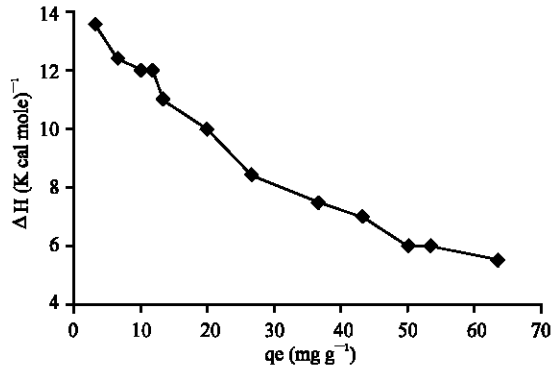


Fig. 5: Evolution of the adsorption entropy according to the quantity of the chromium adsorbed (Biomass concentration = 3g L⁻¹; p Hi = 4.8)

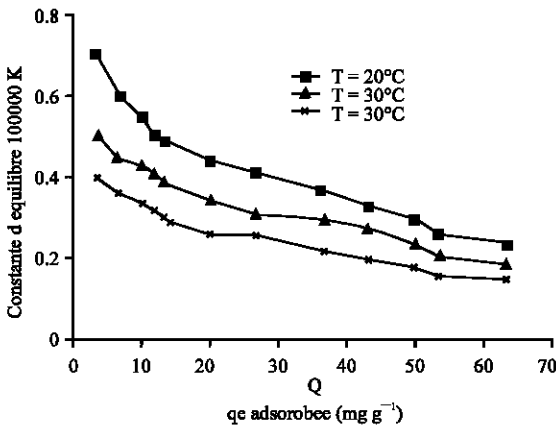


Fig.6: Evolution of the equilibrium constant according to the qe at different temperatures

5.1 kcal mole⁻¹ for great absorbed quantities. We can conclude that absorption is slightly chemical for small absorbed quantities and becomes a physical absorption with great absorbed quantities. The same tendency was noted for the entropy of adsorption.

The results of Fig. 6 give the variation of the pseudo constant of balance K according to the temperature and the quantity of chromium adsorbed (q_e). The constant of balance decreases with the increase in the quantity of chromium adsorbed. For homogeneous surfaces and in the absence of interactions between the sites of adsorption, the constant of balance would be independent of the adsorbed quantity. However for solids having a heterogeneous reactive surface and/or multiform of the adsorbate, the constant of balance varies with the adsorptive quantity. The interactions between ions in adsorbed phase and/or various affinities of adsorption tend to decrease the energy of adsorption, which is translated by a reduction in the constant of balance K (Ball and Fuerstenau, 1971; Zerouki and Thomas, 1990).

According to the results relating to the study of the determination of the constant of balance K, we can conclude the existence from multiform from interactions between the sites from the fungi biomass and/or from multiform of chromium in the solution.

CONCLUSIONS

Biomass fungi are able to sorbs chromium ions from aqueous solutions. The equilibrium sorption capacity of chromium ions was determined from Langmiur and Scatchard equation at different temperature. Bad correlation coefficients were obtained for the Langmiur adsorption equilibrium constant. This is supported by the non-conformity the Langmuir model and non-linear Scatchard transformations described above, this non-conformity to idealised Langmuir behaviour may be interpreted as indicating complex adsorption processes involving multiplayer, interactive or multiple site type binding or some combination of these phenomena. The sorption of chromium ions on biomass fungi is of a spontaneous and exothermic nature. It was noted that an increase in the temperature resulted in a higher chromium loading per unit weight of the biomass fungi.

REFERENCES

- Addad, D., 2002. Removal of chromium by biomass fungi. Thesis, University of Boumerdes.
- Aksu, Z., Y. Sag and T. Kutsal, 1990. A comparative study of the adsorption of chromium(VI) ionsto *C. vulgaris* and *Z. ramigera*. Environ. Technol., 11: 33-40.
- Aksu, Z. and T. Kusta, 1991. Biosorption process for removing lead(II) ions from waste water by using vulgaris. J. Chem. Technol. Biotechnol., 52: 109-118.
- Ball, B. and D.W. Fuerstenau, 1971. Disc. Faraday. Soc., 52: 361.
- Bases, C.F., Jr. and R.E. Mesner, 1976. The Hydrolysis of Cations. John Wiley and Sons, New York.
- Brady, J.M. and J.M. Tobin, 1995. Binding of hard and soft metal ions to *Rhizopus arrhizus* biomass. Enzyme. Micob. Technol., 17: 791-796.
- Brauckmann, B.M., 1998. Industrial Solution Amenable to Biosorption. In Biosorption. Volesky, B. (Ed.). CRC Press, Boca Raton, FL.
- Dean, J.G., F.L. Bosqui and K.H. Lanouette, 1972. Removing heavy metals from waste water. Environ. Sci. Technol., 6: 518-524.
- Fourest, E. and L.C. Roux, 1992. Heavy metal biosorption by fungal mycelial by products: Mechanisms and influence of pH. Applied Microbiol. Biotechnol., 37: 399-403.

- Gadd, G.M. and C.De Rome, 1988. Eds., Heavy Metal and Radionulide Uptake by Fungi and Yeasts. In Kelly Eds. Biohydrometallurgy, UK.
- Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.*, 40 : 1361-1403.
- Scatchard, G., 1994. The attraction of proteins for small molecules and ions. *Ann. N.Y. Acad. Sci.*, 51: 145-149.
- Stein, K. and G. Schwedt, 1994. Speciation of chromium in the waste water from a tannery. *Frenius J. Anal. Chem.*, 350: 38-43.
- Tobin, J.M., D.G. Cooper and R.J. Neufeld, 1984. Uptake of metal ions by *Rhizopus arrhizus* biomass. *Applied Environ. Microbiol.*, 47: 821-824.
- Tobin, J.M. and J.C. Roux, 1998. Mucor biosorbent for chromium removal from tanning effluent. *Wat. Res.*, 32: 1407-1416.
- Volesky, B., 1987. Biosorbents for metal recovery. *Trends Biotechnol.*, 5: 96-101.
- Volesky, B. and Z.R. Holan, 1995. Biosorption of heavy metals. *Biotechnol. Prog.*, 11: 235-250.
- Yuh-Shan, H. and E.A. Ofomaja, 2005. Effects of calcium competition on lead sorption by palm kernel fibre. *J. Hazardous Mat.*, B120: 157-162.
- Zarouki, M. and G. Thomas, 1990. Etude del'adsorption de complexes cyanurés sur charbon actif. *J. Chim. Phys.*, 87: 1715-1762.