Thermodynamic of Chromium Sorption on Biomass Fungi from Aqueous Solution

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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, $\Delta H^\circ_{a,s}, \Delta S^\circ_{a,s}$ 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 (Voletsky and Holan, 1995; Voletsky, 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 (Voletsky and Holan, 1995; Tobin et al., 1984). Streptomycin remosus, 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 Tobin, 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 streptomycyn remosus, coming from the SAIDAL-complex manufacturing unit of antibiotics Medea-Algeria. This

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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 undergone 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.

**Chromium uptake:** A volume of 100 mL of Cr₃( 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 (*streptomyces 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 absorption spectrophotometer. The experiments are carried out with the laboratory environment and pollution of the university of Bramerdes 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 for 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:

\[
q_e = Kq_a C_e \frac{1}{1 + Kq_a} \tag{1}
\]

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

\[
1/q_e = 1/C_e q_a K + 1/q_a \tag{2}
\]

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), \(q_a\) is \(q_e\) for a complete monolayer (mg g⁻¹) \(K\) is sorption equilibrium constant (L mg⁻¹).

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

\[
\frac{q_e}{C_e} = Kq_m - Kq_a \tag{3}
\]

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 rimosus* 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 seen 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 multiphase, 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; pH = 4.8)](image_url)
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

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>qm (mg g⁻¹)</th>
<th>K (sorption equilibrium constant) L mg⁻¹</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>70.0</td>
<td>1.065 10²</td>
<td>0.9012</td>
</tr>
<tr>
<td>20</td>
<td>65.0</td>
<td>4.148 10⁶</td>
<td>0.9089</td>
</tr>
<tr>
<td>30</td>
<td>56.1</td>
<td>2.395 10⁶</td>
<td>0.9072</td>
</tr>
</tbody>
</table>

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 (Basu and Mesner, 1976; Stein and Schwedt, 1994) show that chromium may exist in the form of: Cr(III), Cr(OH)²⁺, CrSO₄⁻, Cr₃(OH)₄(SO₄)²⁻, CrOHSO₄⁻, Cr(OH)₃(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 Δ Hₘᵦᵢᵦ (enthalpy of adsorption) is the quantity of heat developed during the adsorption of a mole of Cr(III) per fungicide gram of biomass. It is given by the relation of Clausius Clapeyron (Ball and Fuerstenau, 1971; Zarouki and Thanes, 1990)

\[
\frac{(d \ln C_e)}{d T} = -\frac{\Delta H_{ads}}{RT^2}
\]

\[
\ln C_e = \frac{\Delta H_{ads}}{RT} + \text{Cons tan te}
\]

With a constant qₐ (or degree of constant covering), the values of Ce according to T are obtained from the isotherms of adsorption of Fig. 1. While carrying Ln Ce according to 1/T, we obtain a series of right-hand side whose slope enables us to determine Δ Hₘᵦᵦ, and the ordinate in the beginning enables us to calculate the entropy of adsorption Δ Sₘᵦᵦ. 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).

\[
K = e^{-\frac{\Delta H_{ads}}{RT}} = e^{-\frac{\Delta H_{ads}}{R}} \cdot e^{-\frac{\Delta S_{ads}}{RT}}
\]

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 (qₑ), 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, pH = 4.8)
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 Langmuir and Scatchard equation at different temperature. Bad correlation coefficients were obtained for the Langmuir 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 multiplety, 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