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Batch and Continuous Packed Column Studies Biosorption by Yeast Supported onto Granular Pozzolana

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Abstract**—**The removal of chromium by living yeast biomass immobilized onto pozzolana was studied. The results obtained in batch experiments indicate that the immobilized yeast on to pozzolana is a excellent biosorbent of Cr(V) with a good removal rates of 85–90%. The initial concentration solution and agitation speed affected Cr(V) removal. The batch studies data were described using the Freundlich and Langmuir models, but the best fit was obtained with Langmuir model. The breakthrough curve from the continuous flow studies shows that immobilized yeast in the fixed-bed column is capable of decreasing Cr(VI) concentration from 15mg/l to a adequate level.

Keywords**—**Biosorption, yeast, chromium, kinetic biosorption, fixed biomass.

I. Introduction

NOWADAYS, the presence of toxic pollutants in liquid effluents has become an issue of growing concern for humanity and its ecosystem. Wastewater generated as a result of domestic, industrial and agricultural activities often contains various regulated compounds, both organic and inorganic in nature. The effluents emanating from industries such tanning, metallurgy, surface treatment, etc., produce important quantities of liquid waste containing chromium in the Cr(VI) form. Various techniques can be utilized to the treatment of effluent wastewater rich in chromium (VI) such as, chemical precipitation [1], electro-chemical precipitation , ion exchange, ultrafiltration, reverse osmosis [2], solvent extraction and activated carbon adsorption [3].But, several of these methods been found to be limited, since they often involve high capital and operational costs and may also be associated with the generation of secondary wastes which present treatment problems [4], especially when the metal ion concentration is lower than 100mg [5]. Therefore, there is currently a need for new, innovative and low cost effective methods for the removal of Chromium (VI) or other element toxic from wastewaters at safe adequate level, assumes greater the important credibility during recent years because of its eco-friendly nature and excellent performance.

Biosorption is an effective and versatile method and can be easily adopted in low cost to remove chromium from large amount of industrial wastewaters. A variety of naturally abundant biomaterials and microorganisms have been explored by researchers for the bioremoval of heavy metal form wastewater including algae, mosses, fungi, yeast, or biosorption using living and dead cells [6]. The biological treatment processes have many advantages, compared to conventional methods, low operation cost and steady performance.

Biological system employing processes such as, bioremoval in packed bed biofilm bioreactor appear to be an effective technology for the removal of heavy metals from wastewater, as they allow to maintain a high biomass concentration and activity during the treatment, at the same times, the start up of the bioreactor is minimized. However, very little is known about the performance of Cr (VI) reduction by yeast.

The purpose of the present work was to evaluate the biosorption capacity of living yeast in packed bed reactor to reduce chromium concentration content in aqueous solution to an acceptable level in batch system. The biosorption kinetics is studied to explore the effect of initial chromium concentration, sped agitation and temperature. Moreover, the adsorption of metal ions onto immobilized yeast packed in a column was also examined.

II. Materials and Methods

A. Microorganism and Inoculum Preparation

The biosorbent (yeast) used in this study, was isolated from the plant of domestic wastewater treatment of Chlef city/Algeria. The yeasts were grown in 250ml Erlenmeyer flask in agitated enrichment media containing following composition at 18°C: glucose 10g/l ; peptone of casyne 0.2g/l ; NH_4NO_3, 0.571g/l and to the final KH_2PO_4, 0.35g/l. An inoculum of 10% (v/v) of a 48h old culture was used for the Cr(VI) removal studies.

B. Adsorbate

The stock solution was prepared by dissolving a known quantity of potassium dichromate ($K_2Cr_2O_7$) (AR grade) in de-

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ionized water. The stock solution was finally diluted to obtain standard solutions.

C. Batch Studies

Batch study was conducted in an Erlenmeyer flask (500ml) using media (300ml) containing chromium, to which a 10% (v/v) inoculums was added. The support was pozzolana with an average particle size of 30mm and $4m^2/g$ area.

The process was monitored with time till the substrate limiting condition was reached. The samples were periodically withdrawn and centrifuged at 3000rpm for 20min and the supernatant liquid was separated and analyzed for residual Cr(VI) concentration.

D. Packed Bed Column Continuous Flow Studies

Packed bed experiment was conducted at room temperature (25±2°C) in a Plastic column of length 40cm and internal diameter 2.5cm, the column was packed with yeast immobilized onto 160 and 200g of the grain of pozzolana, to obtain a 35 and 45cm bed height. Solution of 15mg/l was pumped from bottom to top through the column at a desired flow rate by a peristaltic pump (Prominent, modèle E 2100). The Samples were periodically collected and analyzed for metal concentrations.

E. Cr (VI) Analysis

The change in Cr (VI) concentration due to adsorption was determined colorimetrically according to Standard Methods. A purple-violet colored complex was developed in the reaction between Cr(VI) and 1,5-diphenylcarbazide in acidic condition. The intensity of this complex was read at 540nm wave length using a UV visible spectrophotometer OPTIZEN 2010 type, pH measures are done on a pH-meter (HANNA 120). The removal efficiency (E) of each tested system and the metal uptake q(mg.g-1) was determined by the following equations:

$$E(\%) = \frac{(C_0 - C_t)}{C_0}.100 \quad (1)$$

$$q_t = \frac{(C_0 - C_t).V}{m} \quad (2)$$

where q_t ($mg.g^{-1}$) is the amount of metal sorbed by adsorbent, C_0 and C_t are the initial and final concentrations (mg/l) of the metal, respectively; V is the volume of solution (ml), and m is the mass (g) of the adsorbents used. Each experiment was performed twice at least under identical conditions.

III. Results and Discussion

A. Potential of the Immobilized Cells Yeast to Remove Chromium (VI)

This experiment was performed to show that the yeast isolated from wastewater was capable of removing Cr(VI). Fig. 1 shows that Cr(VI) concentration decreased from 40 to 8.4mg.L-1 after 150h. Beyond no subsequent change in Cr(VI) concentration was observed suggesting that available sites on the biosorbent are saturated. This removal of chromium by yeast is due to the cell walls composition which is compound from a large number of complex organic and their polymers, such as glucan (28%), mannan (31%), proteins (13%), lipids (8%), chitin and chitosan (2%). Such compounds possess numerous functional groups, including carboxylate, hydroxide, amine, imidazole, sulfate and sulfhydryl, with various charge distributions and geometries, so they can selectively bind certain metal ions. Binding is attributed to ion exchange, adsorption, complexation, microprecipitation and crystallization processes occurring on the cell wall [7].

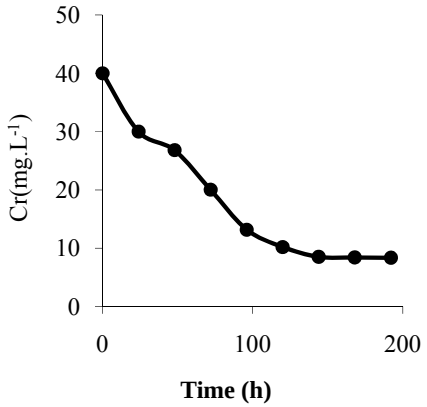

Fig. 1 Removal of Cr(VI) by yeast versus time

B. Effect of Agitation Speed

The effect of agitation speed on Cr (VI) removal by yeast was studied by varying the speed from 40 to 200rpm in rotary shaker. Results are presented in Fig. 2. Fig. 2 demonstrates that equilibrium concentration (C) decreased from 11.8 to 4mg/1 when the speed was increased from 40 to 120rpm. This can be explained that, the increasing of agitation speed decreased the boundary layer resistance to mass transfer in the bulk and resulted in an increase in the driving forces of diffusion of Cr(V) ions in the biofilm. Also, it can be seen, that the equilibrium concentration (C) decrease when the agitation speed increase more than 120rpm, and optimum speed was 120rpm.

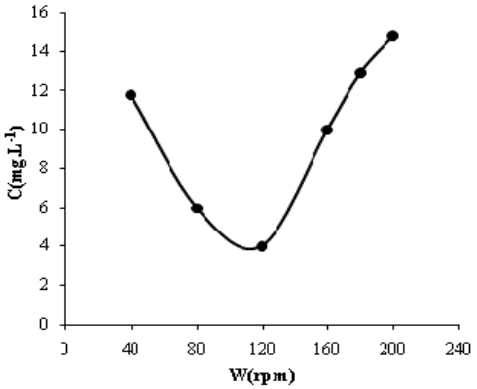

Fig. 2 Effect of agitation speed on chromium removal (Initial Cr (VI) concentration 40 mg/l)

C. Effects of Temperature

Temperature is an important factor that has an effect on microbial Cr(VI)-reduction. The effect of temperature on chromium removal by the yeast immobilized onto pozzolana was investigated at five different temperatures: 18, 22, 25, 30 and 35°C. As can be seen from Fig. 3, the removal of chromium by biosorption onto immobilized yeast increases faintly (from 80 to 96%) with increasing in temperature from 18 to 25°C, indicate that the biosorption process is controlled by diffusion. Further, the removal efficiency of chromium by immobilized yeast decreased with increasing in temperature up to 25°C, indicating that the process is in exothermic nature. The exothermic nature of chromium biosorption has also been reported for the biosorption of chromium onto Pine sawdust [8]. The optimum temperature for Cr(VI) removal by immobilized yeast was 25°C.

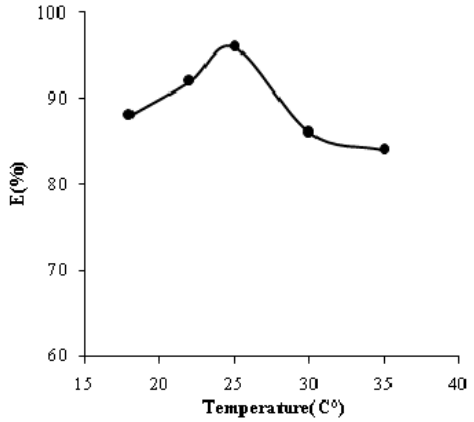

Fig. 3 Effect of Temperature on chromium removal (initial concentration 40 mg/l, biomass dosage 0.4 g/l)

D. Effect of Initial Metal Ion Concentration

The effect of initial Cr (VI) concentration were evaluated in the range of 30 to 120mg/l, these values of concentration correspond to the concentration of the metal ion which the physic-chemical methods have been found to be limited.

The variation of the removal efficiency with initial chromium concentrations were depicted in Fig. 4, the results indicate that the complete removal of chromium was achieved when the Chromium concentration increase from 30 to 60 mg/l. The higher percentage in removal efficiency at the initial stage could be due to the availability of larger number of surface sites of the adsorbent [9]. Also it can be seen from Fig. 4, that the removal efficiency decreases when the initial Cr (VI) was increased further 60mg.L-1. But the equilibrium uptake value was increased with increasing in Cr (VI) concentration.

Mohamed et al. [10] reported that at lower concentrations the ratio of surface active sites to the total metal ions in the solution is high and hence all metal ions interact with the adsorbent. However active sites gradually declined, the reaction rate becomes slower and reaches to equilibrium when the surface area becomes almost saturated.

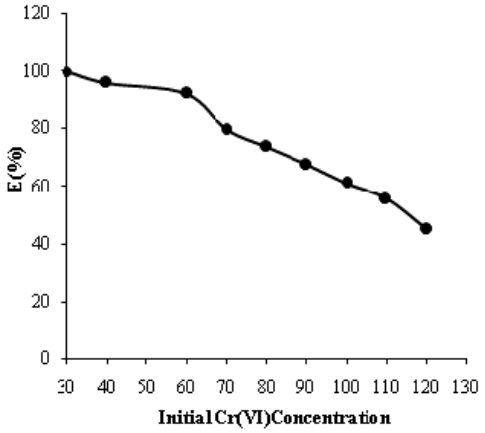

Fig. 4 Effects of initial concentration of metals ions on the biosorption capacity (At biosorbant concentration 0.4g/l, temperature 25°C and speed agitation 120rpm)

IV. Biosorption Kinetics

In order to investigate the mechanism of Cr (VI) biosorption process onto immobilized yeast, both of Lagergren pseudo first-order and pseudo second-order kinetic models Ho and McKay, [12] have been used to fit the experimental data.

The pseudo-first-order rate expression of Lagergren is given by the following equation [11]:

$$\mathrm{Log}_{10}(q_e - q_t) = Log(q_e) - \frac{k_1}{2.3} t \quad (3)$$

where qe and qt are the amounts of are the amount of the solute adsorbed at equilibrium and at any time t, in mg.g-1 and K1is the first -ordre rate constant (h^{-1}) for biosorption. Values of K_1 calculated from the slope of the plots of log ((qe- qt) versus t are shown in Fig. 5.

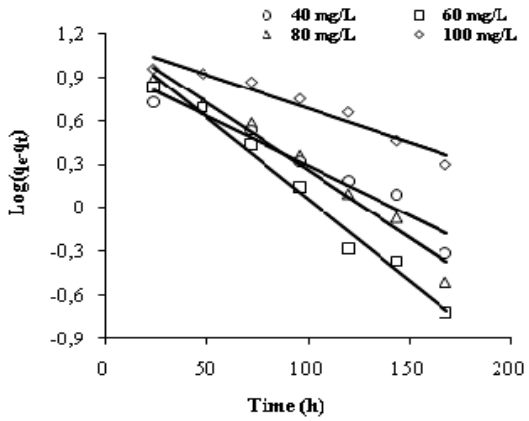

Fig. 5 Linearized form of the Pseudo-first-order of chromium removal by immobilized yeast onto granular pozzolana

The pseudo-second-order rate expression is expressed as [11], [12]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where $q^2$is the maximum biosorption capacity (mg/g) for the pseudo-second-order biosorption, q_t(mg/g) the amount of the solute adsorbed at equilibrium at time t and k_2 is the equilibrium rate constant of pseudo-second-order biosorption ($g.mg^{-1}$/ h). Values of k_2 and q^2 were calculated from the plot of t/qt against t (Fig. 6).

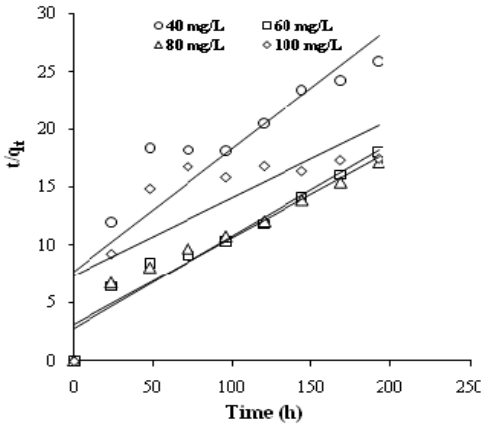

Fig. 6 Linearized form of the Pseudo-second-order of chromium removal by immobilized yeast onto granular pozzolana

Figs. 5, 6 show a plot of linearized form of the pseudo first-order model and the pseudo second-order model. A comparison of the pseudo-first-order and pseudo second-order biosorption rate constant is presented in Table I. From the result shown in Table I, it is important to note the correlation coefficients R^2 obtained for pseudo- first order kinetic model are highest than 0.95 for all concentrations. Furthermore The calculated equilibrium values qe, cal of the pseudo-first-order kinetic model show good agreement with the experimental values of qe, exp than those calculated of the pseudo-second-order kinetic model. Then, we can deduce that the biosorption of chromium (VI) by the immobilized yeast is fitted by pseudo-first-order kinetic model. Similar kinetic results have been reported in the literature [13].

TABLE I
THE FIRST-ORDER AND SECOND-ORDER ADSORPTION RATE CONSTANTS, CALCULATED QE, CAL AND EXPERIMENTAL QE VALUES FOR DIFFERENT INITIAL CHROMIUM CONCENTRATIONS

Initial Cr(VI) Concentration	q_e,exp (mg/g)	First-order kinetic model			Second-order kinetic model		
		K_1 (h^{-1})	q_e,cal (mg/g)	R^2	K_2 qeq,cal	R^2 (h−1)	($g.mg^{-1}$/h)
40	28.8	0,0138	34,77	0,95	0.00146	36.77	0.76
60	41,62	0,023	43.4	0,98	0.00227	56.81	0.92
80	44,15	0,0184	56.23	0,97	0.00177	60.09	0.91
100	46.14	0,0105	54,94	0,94	0.00067	58.48	0.58

V. ADSORPTION ISOTHERMS

There are several mathematical models in the literature, can been used to describe biosorption isotherm. The Langmuir and Freundlich isotherm models are widely used for modeling equilibrium data. The Langmuir model is valid for monolayer adsorption onto a surface containing a finite number of identical sites and it is can describe by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{bQ_0} + \frac{1}{Q_0} C_e \quad (5)$$

where Ce is the equilibrium concentration (mg./l), qe is the amount adsorbed at equilibriumtime (mg/g), and Q_0 and b are Langmuir constants related to the adsorption capacity and energy, respectively. The plot of Ce/qe vs. Ce is linear.

The Freundlich adsorption isotherm is represented by the following equation:

$$\ln q_e = \ln K + \frac{1}{n} \ln C_e \quad (6)$$

where Ce is the equilibrium concentration (mg/l), qe is the amount of metal adsorbed at equilibrium time (mg/g), and k and n are Freundlich constants. n gives an indication of the favourability and k the capacity of adsorbent. The linear plot of log qe vs. log Ce shows that the adsorption follows the Freundlich isotherm model.

The equilibrium parameters with the correlation coefficients for applying the Freundlich and Langmuir equations to the biosorption of chromium (VI) on to immobilized yeast onto granular pozzolana are presented in Table II, the isothermal adsorption data are shown in Fig. 7. The maximum uptake capacity Q_0 and the equilibrium constant b in the Langmuir model are 47.61 mg/g and 0.98 respectively. The result also show the Langmuir isotherm (R^2 = 0.998) has à better fitting than the Freundlich model (R^2 = 0.78). This can be due to the small surface area of the immobilized yeast than the

adsorbent. Therefore, only monolayer adsorption occurred on its surface.

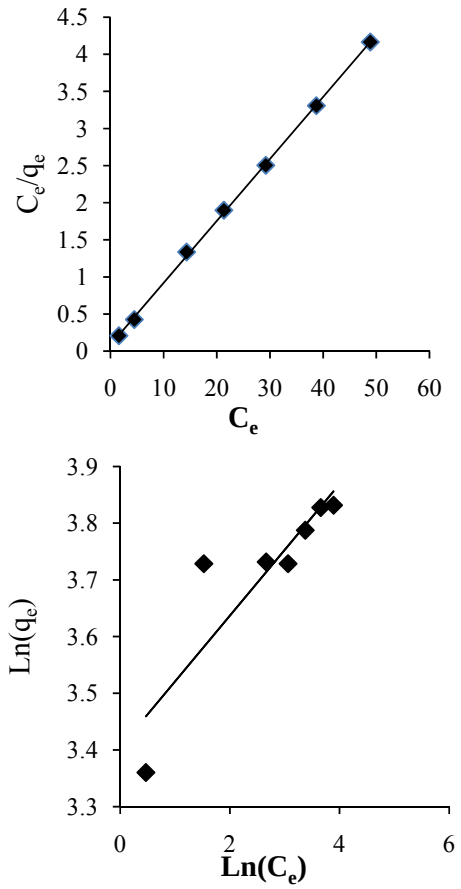

Fig. 7 Langmuir and Freundlich isotherms for biosorption of chromium (VI)

TABLE II
LANGMUIR AND FREUNDLICH MODEL REGRESSION CONSTANTS

Langmuir constants			Freundlich constants		
Qmax(mg/g)	b(l.mg^{-1})	R^2	K(l.g^{-1})	n	R^2
47.61	1.1	0.998	8.004	8.69	0.78

VI. FIXED-BED COLUMN WITH CONTINUOUS FLOW

The column packed with immobilized yeast onto pozzolana was designed to operate a continuous liquid flow system for Cr (VI) biosorption. Fixed-bed breakthrough curves at two different weights of support (160 and 200g) were obtained to illustrate the capability of column operation Fig. 8.

It is easily seen from Fig. 8, the typical S-shaped curves obtained for the two heights of the column, which indicates that the chromium biosorption by immobilized biomass in continuous mode is favorable. Before the breakthrough point, chromium concentration in the effluent was too low and the breakthrough point emerged around 4000 and 5800ml respectively for H= 60 and 75cm. Biosorption column was saturated rapidly after breakthrough point for the both heights. A sharply increase in breakthrough curve suggests the good biosorption performance of immobilized yeast on to pozzolona [14] . Consequently, chromium ions were effectively removed in column operations by immobilized biomass developed in this study. Other fixed-bed column studies have also demonstrated similar sorption efficiencies of algal, microbial and plant biomasses [15]-[17].

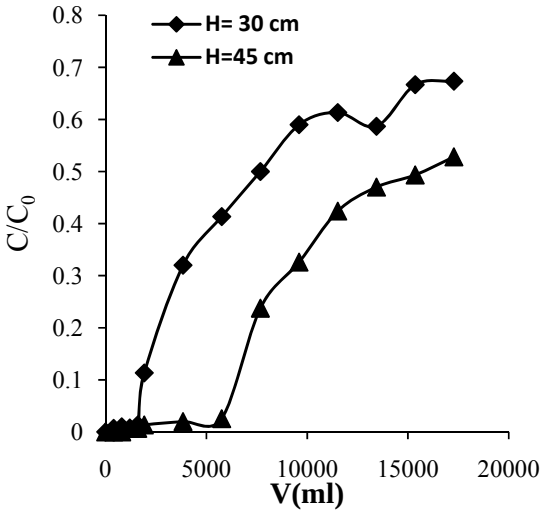

Fig. 8 Breakthrougth curve of chromium biosorption column (inlet concontration 15mg/l; feed rate 2ml/min)

VII. CONCLUSION

The present study showed that the biosorption by immobilized yeast onto granular pozzolana can be considered as an alternative technology for sequestering chromium from industrial effluent such as tannery and metallurgies in batch process. The advantages of using this biosorption then adsorbent towards chromium (VI) treatment are the simplicity of the required system and without secondary wastes. Maximum biosorption of chromium (VI) (E = 100%) were obtained when initial concentration is under 30mg/l. The sorption data obtained from batch studies at optimized conditions have been shown that: the biosorption kinetic is fitted widely by pseudo- first-order than second order.

The removal efficiency increased with the decrease capacity when the temperature increase indicated that the nature of biosorption process is exothermic. However, before this technology can be fully optimized for environmental applications, further study is needed such as establishment of the exact mechanisms of biosorption by the immobilized yeast, understand the metal ion transformations in the cells and the development of ways to stabilize the catalytic activity immobilized yeast. For the development of a continuous fixed-bed column bioreactor system for onsite operations, it is also necessary to determine its removal efficiency for other pollutant.

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