Removal of chromium ions from liquid waste solutions using immobilized *Cunninghamella elegans*

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Abstract: The removal of chromium ions from aqueous waste solution using Ca-alginate (CA) beads, immobilized alive and dead *Cunninghamella elegans* beads was investigated in batch and fixed bed column. In batch studies the behavior of the adsorption was investigated through studding the influences of contact time, pH, initial Cr(VI) concentration, immobilized fungal biomass (IFB) load and temperature. The Cr(VI) removal rate increased with a decrease in pH and increase in initial Cr(VI) concentration. The maximum removal of Cr(IV) achieved at pH 2.0. The immobilized fungal biomass increased the Ca-alginate sorption capacity by at least two fold. Equilibrium and kinetic analyses were done to estimate sorption capacities, rates and the possible reaction mechanisms. Langmuir and Freundlich isotherms were used to fit the equilibrium isotherm. The desorption of Cr(IV) using dist. H_2O was found to be efficient than other alkaline solutions, because it maintain the viability and mechanical strength of the different beads throughout five repeated cycles with little decrease in its removal capacities. Column experiments were also done to evaluate the continuous removal of chromium ions by the different beads. The effect of; bed heights (4.5, 9.0, 13.5 cm), feed flow rates (1, 2, 3ml/min) and inlet chromium ions concentrations (25, 50, 100 ppm) on the breakthrough curve were studied using immobilized dead *Cunninghamella elegans* (*Cun. el.*) beads. According to the sorption capacity, the immobilized dead *Cun. el.* beads can be considered as a suitable biosorbent for applications.
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1 Introduction

The increase of environmental contamination as a consequence of industrial development is a challenge that society must face. Growing attention is being paid to the health hazards presented by the existence of heavy metals in the environment; their accumulation in living tissues throughout the food chain poses a serious health problem (**Loukidou, 2004**).

Wastewaters, produced during dye and pigment production, film and photographic processing, galvanometry, metal cleaning, plating and electroplating, leatherworking, and mining can contain undesirable amounts of chromium(VI) anions in relation to established water standards (**Volesky, 2001**)**.** Because of these differences, the discharge of Cr(VI) to surface water is regulated to below 0.05 mg/l by the US EPA, while total Cr, including Cr(III), Cr(VI) and its other forms, is regulated to below 2mg/l (**Baral, 2002**). Chromium Cr(VI) is known to be toxic to both plants and animals, as strong oxidizing agent and a potential carcinogen (**Costa, 2003**). Cr(III) is generally only toxic to plants at very high concentrations and is less toxic or nontoxic to animals (**Anderson, 1997**). Strong exposure to Cr(VI) causes cancer in the digestive tract and lungs, epigastric pain, nausea, vomiting, severe diarrhea and hemorrhage. It is therefore essential to remove Cr(VI) from wastewater before disposal (**Gupta, 2001**).

Thus, the development of new, cost-effective, more environmentally friendly methods is needed. Biosorption of heavy metals by biomaterials has been suggested as a potential alternative to the existing physicochemical technologies for detoxification and recovery of toxic and valuable metals from wastewaters. Many biomaterials such as seaweed (**Yun *et al.*, 2001**), micro-algae (**Gupta, 2001**), fungi (**Kapoor, 1995**) and various other plant materials (**Gardea-Torresdey, 2000**) have been studied for their chromium binding abilities. Most reports related with the Cr(VI) biosorption with dead fungal biomass have claimed that Cr(VI) was removed from aqueous systems by ‘ ‘ anionic adsorption ’ ’ (**Prakasham, 1999; Bai, 2002, 2003**). The cell walls of the microbial biomass are mainly composed of polysaccharides, proteins, and lipids, which contain functional groups such as carboxylate, hydroxyl, sulphate, phosphate, and amino groups that bind to heavy metals (**Parka, 2005**).

The objective of the present work is to evaluate the effects of various parameters such as contact time, pH, initial Cr(VI) concentration, immobilized fungal biomass (IFB) load and temperature on chromium biosorption by control Ca-alginate (CA) beads, immobilized alive and dead *Cunninghamella elegans* beads. Also, the sorption equilibrium and kinetic analyses were done to estimate the sorption capacity, rates and the possible reaction mechanisms. The desorption of Cr(IV) was studied together with the reuse of the different beads for repeated cycles. Column experiments were also done to investigate the behavior of the different beads in removing

chromium ions in continuous system. The effect of bed height, feed flow rate and inlet chromium ions concentrations on the breakthrough curve were studied using immobilized dead *Cun. el.* beads.

2 Material and Methods

2.1. Chemicals

All chemicals used were of analytical purity grades. Cr(IV) solution was prepared as stock solution from $K_2Cr_2O_7$ salt and other concentrations were obtained by dilution. Concentrated hydrochloric acid and sodium hydroxide were used for pH adjustment.

2.2. Biomass production

The *Cunninghamella elegans* species was isolated from soil of the repository site at Waste Management Facility, Hot Laboratory Center, Atomic Energy Authority of Egypt. The isolation and biomass production was done as; (**Abdel-Razek, 2009**). The obtained fungal biomass was saved in refrigerator for use as alive biomass. The dead biomass was obtained by autoclaving for 15 min at 121ºC and 1.5 Kgf/cm^2, washed with bi-distilled water and then kept in refrigerator.

2.3. Immobilization of fungal biomass (IFB)

The fungal biomass (alive or dead) was oven-dried at 60°C for 24 hrs. The dried biomasses were ground, sieved to particle size ranged from 0.25µm to 0.3µm and then stored in a dessicator at lab temperature for use. The control Ca-alginate (CA) beads were prepared by injecting 10 ml of 4% sod. alginate gel into 2% $CaCl_2$ solution. The immobilized fungal biomass (IFB) beads were prepared by mixing the desired weight of dried fungal biomass with 10 ml of 4% sod. alginate gel thoroughly, then injected into 2% $CaCl_2$ solution. The formed beads of (CA) and (IFB) were left in $CaCl_2$ solution for one hour, and then washed twice with bi-distilled water. The obtained beads have a diameter 2.5-3.0 mm (**Omar, 2010**). The obtained beads were kept in refrigerator at 4°C for use.

2.4. Removal of Cr(IV)

2.4.1. Batch studies

In batch experiment, 50 ml of Cr(IV) ions solution was added to 50 beads of CA or IFB (alive or dead) in 250 ml Erlenmeyer flask. The experiment conditions were adjusted where; pH was 2 ± 0.2, temperature was 25 ± 3°C and stirring rate was 150 rpm using environmental orbital shaker. Samples were taken at different contact times and the amount of the ions accumulated on the different beads was estimated. The quantitative determination of chromium was carried out using atomic absorption spectrophotometer (Buck) model 210 VGP.

2.4.2. Column studies

A fixed bed column made of glass with 1 cm inner diameter and 20 cm height was used. The metal solution of known concentration was pumped at fixed flow rate by a peristaltic pump. The temperature and pH of the solution maintained constant. The difference in removal efficiency of (CA) and (IFB) alive and dead beads in fixed bed column was investigated. The effect of bed height, feed flow rate and inlet chromium ions concentration on the breakthrough curve was studied using immobilized dead *Cun. el.* beads.

2.5. Biosorption/desorption cycles

The accumulated beads of (CA) and (IFB) were eluted using different solutions; H_2O, HCO_3, NaOH and KOH, then the beads were washed with bi-distilled water. The best eluting solution was used for desorption of Cr(IV) for five consecutive cycles. The concentration of metal ions in the eluted solution was determined to calculate the desorption ratio.

2.6. Calculations

The uptake amount of metal ion (mg) at time (t) by 50 beads of (CA) and (IFB) (Q_t) = C_0-C_t; where: C_0 is the initial concentration, (C_t) is the concentration of metal ion solution at different contact times (t). The percent uptake of metal ion = Q_t/C_0 X100. The adsorbed amount (mg/g) = (C_0 − C_t)V/m. Where; V is the volume of test solution and m is the adsorbent dry weight in gram.

Desorption ratio = amount of Cr(IV) ions desorbed/amount of Cr(IV) ions adsorbed X 100.

3. Results and Discussion

3.1. Effect of pH

The effect of pH on Cr(IV) removal was studied at pH range 1.5 - 5.5, at 25°C and initial Cr(IV) concentration 100 ppm. The biosorption of Cr(IV) increased with the decrease in the pH of the solution, and the maximum uptake occurred at pH 2.0 ± 0.2 (Fig.1). Most reports indicated that; Cr(VI) biosorption by fungal biomass from aqueous systems is anionic adsorption (**Bai, 2003**) and the optimum pH for Cr(IV) biosorption ranged from (1.5-2.0) (**Gokhale, 2009**).

3.2. Effect of temperature

The effect of temperature was studied using initial Cr(IV) concentration 500 ppm at pH 2.0 ± 0.2. The results showed that, the rate of Cr(IV) sorption increased with an increased in temperature from 15°C to 25°C. At the temperature range (25 – 35°C) the absorption capacity is nearly constant, then further increase in temperature result in slight decrease in Cr(IV) biosorption (Fig. 2). Similar trend toward temperature effect was reported (**Okeke, 2008**).

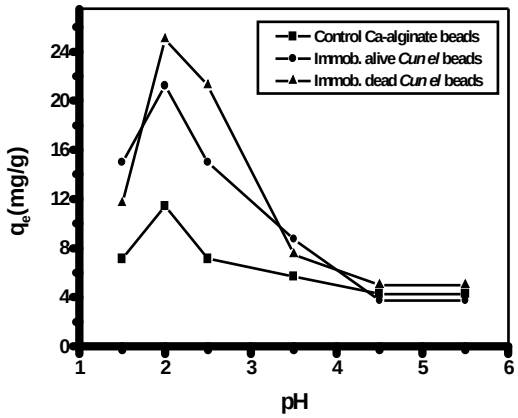

Fig. (1): The effect of pH on the adsorption of Cr(IV) ions from 100 ppm Cr(IV) solution by the different beads.

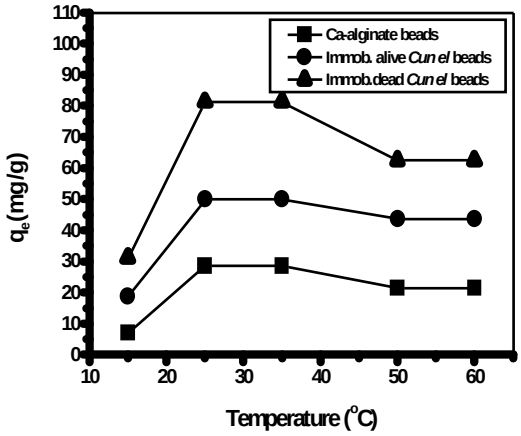

Fig. (2): The effect of temperature on the adsorption of Cr(IV) ions from 500 ppm Cr(IV) solution by the different beads.

3.3. Effect of immobilized biomass

The weight of biomass to be immobilized is an important parameter in the immobilization process (**Abdel-Hameed, 2006**). For constant volume of Ca-alginate gel (10 ml), different dry weights 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 of fungal biomass (alive or dead) were mixed. The effect of immobilized fungal biomass on the biosorption was studied at 25°C and pH 2.0, with initial Cr(IV) concentration of 100 ppm. Results showed that, the removal Cr(IV) increased as the immobilized weight increased up to 0.3g/10 ml Ca-alginate gel Fig. (3)**,** then further increase lead to decrease in the equivalent capacity (q_e) of the IFB beads. This could be explained by the interaction between the active groups of the excess fungal biomass and that of the gel, resulting in decreasing the free and available active sites on both the immobilized fungal biomass and the gel (**Abdel-Razek, 2009**).

3.4. Effect of metal ion concentration

The effect of initial Cr(IV) ion concentration on the removal of Cr(IV) by the different kind of beads was studied using different initial concentrations from 25 to 1000 ppm, at pH 2.0 and temperature 25°C. The amount of Cr(IV) ion removed increased with increase the initial ion concentration up to 500 ppm, then further increase in concentration has no effect Fig. (4). The immobilized dead *Cun. el.* beads showed high metal removal than the immobilized alive beads which in turn better than control Ca-alginate beads (**Tunali, 2005**). Unlike the other metal ions, at low Cr(IV) concentrations the removal percentage didn't reach 100%, this explained by the anion adsorption mechanism and the low pH at which adsorption occurred (**Bai, 2003**).

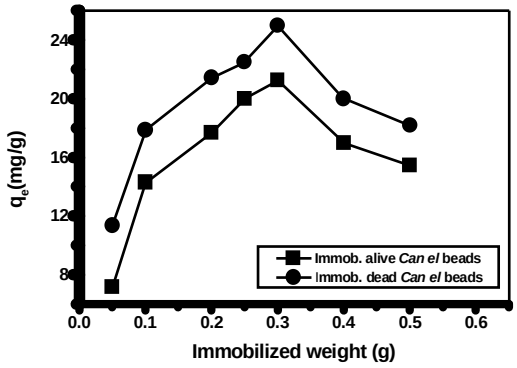

Fig. (3): The effect of immobilized weight load on the adsorption of Cr(IV) ions from 100 ppm Cr(IV) solution.

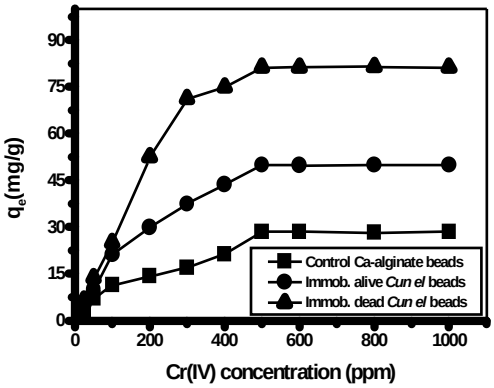

Fig.(4): The effect of initial ion concentration on the adsorption of Cr (IV) ions by the different beads.

3.5. Biosorption time of Cr(VI)

The effect of contact time on biosorption of chromium ions by control CA beads, and IFB alive or dead beads was studied using initial Cr(IV) ion concentration 500 ppm at pH 2.0 and temperature 25°C. Fig. (5) Shows the effect of time course on the removal of Cr(VI) by different beads. It showed that Cr(VI) gets sorbed onto the beads after 60 min. This

suggested that, biosorption process is slow and reaches saturation within 60 min similar data was obtained by **Loukidou (2004).**

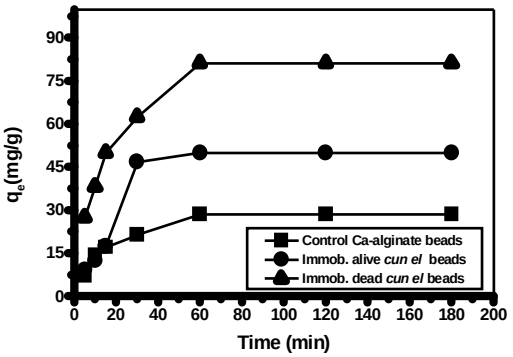

Fig. (5): The effect of time on the adsorption of Cr(IV) ions from 500 ppm Cr(IV) solution by the different beads.

3.6. Desorption and reusability studies

The regeneration of the biosorbent is one of the key factors in assessing their potential for commercial application (**Iqbal, 2004**). The desorption of adsorbed Cr(VI) was studied using different desorption agents; H_2O and 0.01N (HCO_3, NaOH and KOH). All desorption agents achieve 85-100% desorption for Cr(IV) Fig.(6). It was found that all alkaline solutions have a degeneration effect on the alginate beads either control or immobilized, while H_2O maintain the beads efficiency and mechanical strength. Therefore, only H_2O was used as desorption agent for the accumulated beads in five consecutive adsorption/desorption cycles using the same Cr(IV) concentration (500 ppm). The adsorption efficiency of different beads for Cr(VI) did not change significantly and a slight decrease was observed after the second and third cycle Fig.(7). These results indicated that, the immobilized alive and dead fungal beads could be used repeatedly in chromium(VI) adsorption studies with relatively low decrease in the total adsorption capacity.

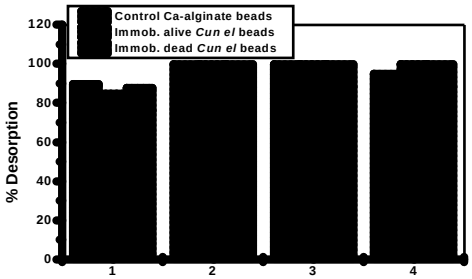

Fig. (6): The percent desorption of the different eluting solutions for the different beads.

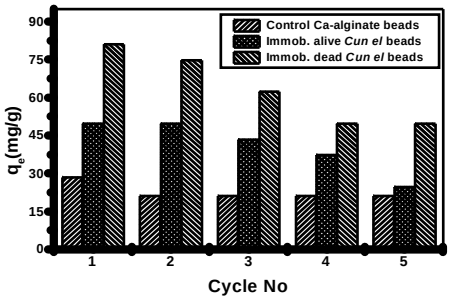

Fig. (7): The adsorption capacity of the different beads through five consecutive repeated cycles.

3.7. Sorption kinetics

The study of adsorption kinetics describes the solute uptake rate and evidently this rate controls the residence time of adsorbent at the solid-solution interface. The kinetics of Cr(IV) adsorption on CA and IFB beads were analyzed using pseudo first order (**Lagergren, 1898**) and pseudo second order (**Ho, 2004**). The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2). A relatively high R^2 value close or equal to (1) indicates that the model successfully describes the kinetics of the adsorption.

3.7.1. Pseudo-first-order model

The behavior of the batch sorption process of Cr(IV) was analyzed using Lagergren first order kinetics model (**Lagergren, 1898; Ghorai, 2005**) which is given by the equation:

$$\log (q_e-q_t) = \log q_e - K_1/2.303\ t$$

where; q_e and q_t are concentration (mg/g) of Cr(IV) onto the biosorbent at equilibrium and at time t, respectively. The slope and intercept of the plots of log (q_e-q_t) versus t, as shown in Fig.(8) were used in calculating the pseudo first order rate constant (min^{-1}) and the theoretical equilibrium sorption capacities (q_e), respectively. The values of K_1, q_e and the linear correlation coefficients (R^2) were presented in Table (1).

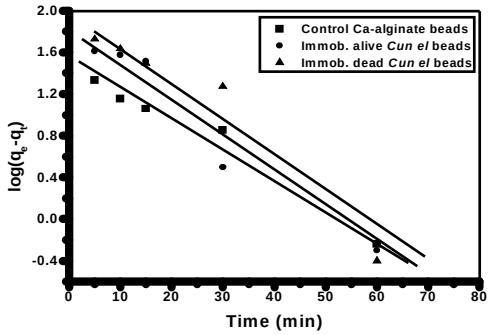

Fig. (8): Lagergren Kinetic model for adsorption of Cr(IV) ions from 500 ppm Cr(IV) solution by the different beads.

The values of R^2 indicated that the Cr(IV) biosorption didn't fit well the first order equation.

3.7.2. Pseudo second-order model

A pseudo second-order model was also used to describe the kinetics of Cr(IV) sorption onto the biosorbents. This model is expressed as:

$$t/q_t = 1/K_2q_e^2 + 1/q_e\ t$$

where; K_2 is the rate constant of pseudo second-order equation (mg/g. min). The kinetic plots of t/q_t versus t for Cr(IV) sorption onto the different beads are represented in Fig.(9). The product $K_2q_e^2$ is the initial sorption rate represented as $h = k_2q_e^2$. The kinetics parameters of this model were calculated from the slope and intercept of the linear plots and are given in Table (1). The relations are linear and the values of the correlation coefficient (R^2) suggest a strong relationship between the parameters. The correlation coefficients were higher compared to the results obtained from the first –order kinetic model. So, it is possible to suggest that the sorption of Cr(IV) followed the pseudo second-order kinetics model.

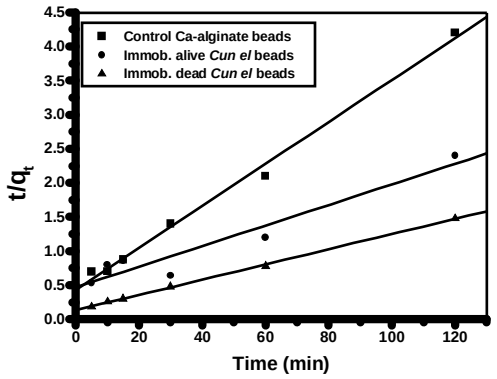

Fig. (9): Pseudo – second order kinetic plots for the adsorption of Cr(IV) ions from 500 ppm Cr(IV) solution by the different beads

3.8. Adsorption isotherms

The biosorptive metal ions uptake can be quantitatively evaluated from experimental biosorption equilibrium isotherm. There are two widely accepted and easily linearized adsorption isotherm models, Freundlich and Langmuir models, commonly used in the literature.

3.8.1. Langmuir isotherm

The Langmuir sorption isotherm was tested in the following linearized form:

$$C_e/q_e = 1/Q_0b + 1/Q_0\ .\ C_e$$

where; C_e and q_e are concentration of sorbate in solution and at the sorbent surface at equilibrium, and Q_0 and b are characteristic constants related to adsorption capacity and energy of adsorption, respectively. In Fig. (10), C_e/q_e is plotted against C_e for Cr(IV). The slope of this linear plot gives the value of Q_0 whereas from the intercept the value of b was computed (Table 2). The Langmuir isotherm assumes that ions are sorbed on definite sites that are monoenergetic on the sorbent surface and each site can accommodate only one molecule or ion. The sorbed ions cannot migrate across the surface or interact with neighboring molecules (**Langmuir, 1918**).

Table (1): Calculated parameters of the pseudo-first order and pseudo-second order kinetic models for Cr(IV) sorption onto control CA and IFB beads.

Type of beads	Pseudo First Order Parameters			Pseudo Second Order Parameters				
	K_1 min^{-1}	$q_{e\ calc.}$ (mg/g)	R^2	K_2 mg $g^{-1}min^{-1}$	h	$q_{e\ calc.}$ (mg/g)	R^2	$q_{e\ exp.}$ (mg/g)
Control Ca-alginate	0.0637	31.27	0.9849	0.02180	2.311	32.53	0.97704	28.57
Immob. alive *Cun.el.*.	0.0866	76.00	0.9788	0.00484	2.131	66.36	0.96052	50.00
Immob. dead *Cun.el.*	0.0888	117.89	0.9789	0.00920	7.416	89.77	0.99957	81.25

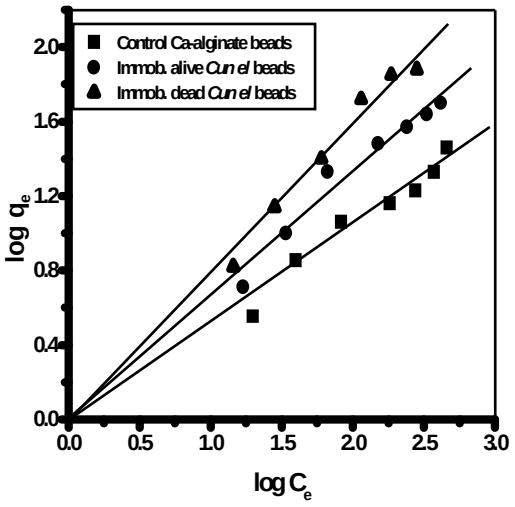

Fig. (10): Langmuir adsorption isotherm for adsorption of Cr(IV) ions from 500 ppm Cr(IV) solution by the different beads.

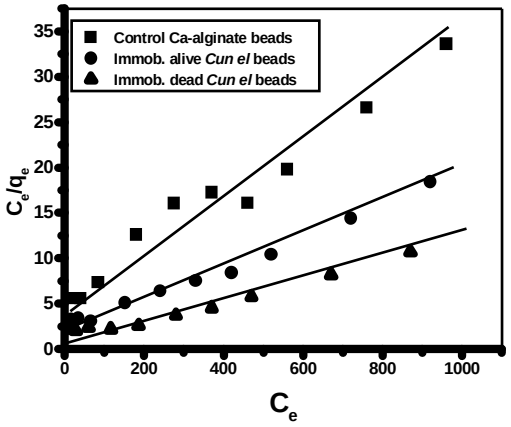

Fig. (11): Freundlich adsorption isotherm for the adsorption of Cr (IV) ions from 500 ppm Cr(IV) solution by the different beads.

3.8.2. Freundlich isotherm

The Freundlich sorption isotherm can be expressed by:

$$\log q_e = \log K_F + 1/n \log C_e$$

where; K_F and n are Freundlich constant characteristic of adsorption capacity and adsorption intensity, respectively. The plot of log q_e vs. log C_e will give a straight line, if it is followed Freundlich sorption isotherm Fig.(11). The slope and intercept of the linear Freundlich equation are equivalent to 1/n and log K_F, respectively. The Freundlich sorption isotherm encompasses the heterogeneity of the surface and exponential distribution of sites and their energies (**Freundlich, 1939**). The characteristic Freundlich constant 1/n should be less than unity.

The steep slope of 1/n close to unity indicates high sorptive capacity at higher equilibrium concentrations. The Freundlich parameters are given also in Table (2).

3.9. Column studies

Column operations do not have sufficient contact time for attainment of equilibrium. Hence, in addition to equilibrium studies, there was a need to perform biosorption studies using a column. The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and the dynamic response of adsorption column. The breakthrough curves show the loading behavior of metal to be removed from solution in a fixed bed and is usually expressed in terms of adsorbed metal concentration (C_{ad} = inlet metal concentration (C_0) − outlet metal concentration (C_t)) or normalized concentration defined as the ratio of effluent metal concentration to inlet metal concentration (C_t /C_0) as a function of time or volume of effluent for a given bed height (**Aksu, 2004**). Effluent volume (V_{eff}) can be calculated from the following equation:

$$V_{eff} = Q\,t$$

where t and Q are the total flow time (min) and volumetric flow rate (ml min^{-1}), respectively. The area under the breakthrough curve (A) obtained by integrating the adsorbed concentration (C_{ad}; mg l^{-1}) versus t (min). Plot can be used to find the total adsorbed metal quantity (maximum column capacity).

Table (2): Langmuir and Freundlich isotherms parameters for different biosorbent beads

Type of beads	Langmuir isotherm parameters			Freundlish isotherm parameters			$q_{e\ exp.}$ (mg/g)
	Q_0 (mg/g)	b	R^2	1/n	K_F mg/g	R^2	
Control Ca-alginate	35.49	0.0503	0.9836	0.5831	0.8726	0.9815	28.57
Immob. alive *Cun. el.*	60.20	0.0702	0.9943	0.6819	0.9570	0.9817	50.00
Immob. dead *Cun. el.*	99.00	0.0750	0.9951	0.8549	0.8840	0.9895	81.25

Total adsorbed metal quantity (q_{total}; mg) in the column for a given feed concentration and flow rate is calculated from the following equation:

$$q_{total} = QA/1000$$

Total amount of metal ions sent to column (m_{total}) is calculated from the following equation:

$$m_{total} = C_0 Q\, t_{total} / 1000$$

Total removal percent calculated from the following equation:

Total removal(%) = q_{total}/ m_{total} X 100

Equilibrium metal uptake (q_{eq}) (or maximum capacity of the column) in the column is defined by the total amount of metal sorbed (q_{total}) per gram of sorbent (X) at the end of total flow time;

$$q_{eq} = q_{total} /x$$

The breakthrough is usually defined as the phenomenon when the effluent concentration from the column is about 3–5% of the influent concentration (**Chen, 2000; 2003**).

The breakthrough curves of Cr(VI) adsorption by the control CA and IFB (alive or dead) beads were studied using bed depth 9 cm, inlet Cr(IV) concentration 100 ppm with flow rate 1 ml/min. The control Ca-alginate beads showed earlier breakthrough and exhaustion time followed by immobilized alive *Cun. el.* beads, while immobilized dead beads showed the best breakthrough curve and longer exhaustion time Fig.(12)**.** The treated volumes were 82, 200 and 275 ml for control, immobilized alive, and dead *Cun. el.* beads, respectively, Table (3). The column equilibrium capacities were 10.6, 21.2 and 26.0 mg/g dry weight for CA, alive and dead IFB beads, respectively. This indicates that, the IFB increased the removal efficiency of the CA beads.

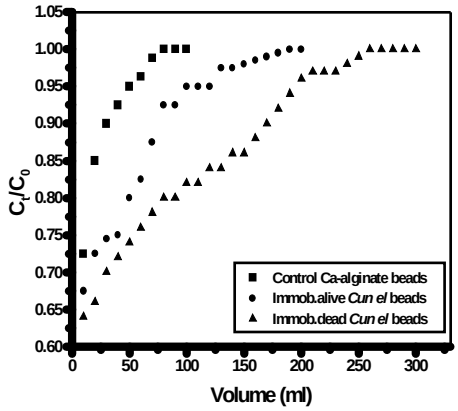

Fig. (12): Breakthrough curves for the different beads (C_0 = 100 mg l^{-1}, pH = 2.0, bed height = 9 cm).

3.9.1. Effect of bed depth

The breakthrough curves of Cr(VI) removal by immobilized dead *Cun. el.* beads at different bed depths (4.5, 9 & 13.5 cm) and fixed inlet Cr(VI) ions concentration 100 ppm are shown in Fig. (13). An earlier breakthrough and exhaustion time were observed for low bed depth. Table (3) shows that the increase in the bed height result in increase of q_{total} and the total removal percent of Cr(IV) ions, where 24.8, 26.0 and 30.7 mg/g dry weight were removed at bed height; 4.5, 9 and 13.5 cm, respectively.

3.9.2. Effect of flow rate

The breakthrough curves of Cr(VI) adsorption by immobilized dead *Cun. el.* beads at different flow rates (1, 2 & 3 ml min^{-1}) and at fixed bed height of 9 cm are shown in Fig. (14). An earlier breakthrough and exhaustion time were observed in the profile, when the flow rate was increased to 3 ml min^{-1}. The flow rate also influenced the Cr(VI) uptake capacity as 26.0, 23.4 and 20.8 mg g^{-1} dry weight, were recorded at flow rates 1, 2 and 3 ml min^{-1}, respectively. The breakthrough curve becomes steeper when the flow rate is increased with which the break point time and adsorbed Cr(VI) ion concentration decreases. The probable reason behind this is that, when the residence time of the solute in the column is not long enough for adsorption equilibrium to be reached at that flow rate, the Cr(VI) solution leaves the column before equilibrium occurs (**Ghorai, 2005**). Thus, the contact time of metal ions with immobilized dead *Cun. el*. beads is very short at higher flow rate, causing a reduction in removal efficiency.

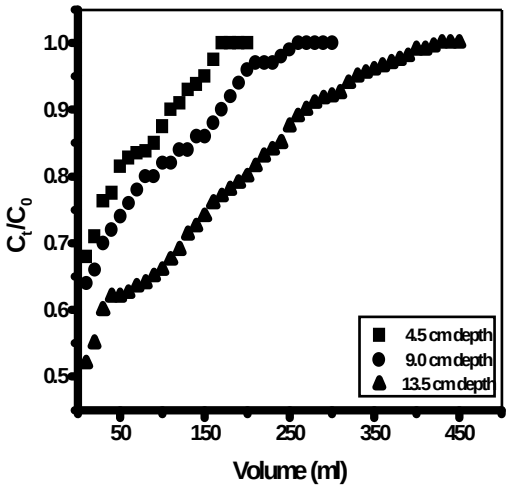

Fig. (13): Breakthrough curves of immobilized dead *Cun. el.* beads at different bed heights (C_0 = 100 mg l^{-1},Q=1 ml min^{-1}, pH =2.0).

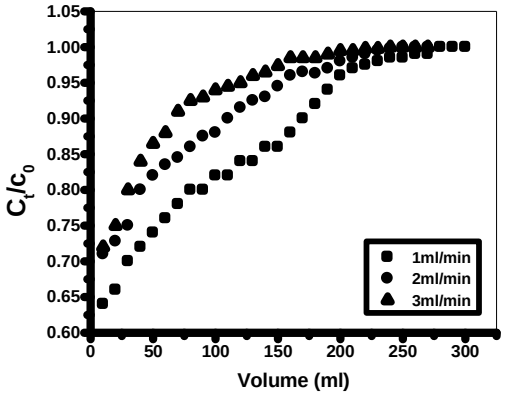

Fig. (14): Breakthrough curves obtained at different flow rates (C_0 = 100 mg l^{-1}, pH = 2.0, bed height = 9 cm).

3.9.3. Effect of feed Cr(VI) concentration

In the sorption of chromium(VI) to immobilized dead *Cun. el.* beads, a change in inlet chromium(VI) concentration affected the operating characteristics of the fixed bed column. The sorption breakthrough curves obtained by changing inlet chromium(VI) concentration from 25 to 100 mg l^{-1} at 1 ml min^{-1} flow rate and 9 cm bed height are given in Fig.(15)**.** A decreased inlet Cr(VI) concentrations gave delayed breakthrough curves and the treated volume was also higher, since the lower concentration gradient caused slower transport due to decreased diffusion coefficient (**Padmesh, 2005**). At the highest metal concentration (100 mg l^{-1}), the immobilized dead *Cun. el.* beads bed saturated quickly leading to earlier breakthrough and exhaustion time. The maximum bed capacities at different initial Cr(VI) concentration, 25, 50 and 100 mg l^{-1} were 11.2, 18.8 and 26.0 mg g^{-1} dry weight, respectively. Table (3) shows that highest removal is obtained at the highest metal concentration, this explained by the driving force for adsorption depend on the concentration difference between the Cr(VI) ion on the adsorbent and the Cr(VI) ion in the solution (**Aksu, 2004**).

Table (3): The breakthrough curve parameters for the different beads and the effect of beads depth, flow rate and initial Cr(VI) concentration on; the total adsorbed quantity of Cr(VI) (q_{total}), equilibrium Cr(VI) uptake (q_{eq}) and total removal percentage by immobilized dead *Cun. el.* beads.

Type of Beads	Beads depth cm	C_0 mg/l	Q ml/ min	Total (min)	m_{total} mg	q_{total} mg	q_{eq} mg/g		Total Removal %
							wet	dry	
Control Ca-alginate	9	100	1	82.5	8.3	1.8	0.43	10.6	21.7
Immob. alive *Cun. el.*	9	100	1	200	20	5.3	1.7	21.2	26.5
Immob. dead *Cun. el.*	9	100	1	275	27.5	6.5	2.03	26.0	23.6
	4.5	100	1	175	17.5	3.1	1.94	24.8	17.7
	13.5	100	1	400	40	11.5	2.4	30.7	30
	9	100	2	137.5	27.5	5.8	1.83	23.4	21.3
	9	100	3	91.7	27.5	5.2	1.63	20.8	18.9
	9	50	1	375	18.8	4.7	1.47	18.8	25
	9	25	1	475	11.88	2.8	0.875	11.2	23.5

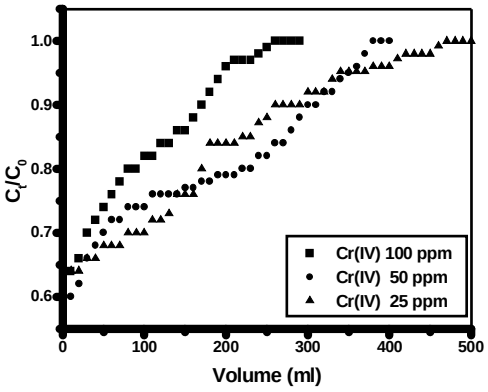

Fig. (15): Breakthrough curves obtained at different inlet Cr(VI) concentrations (Q=1ml min^{-1}, pH =2.0, bed height = 9 cm).

4. Conclusion

The objective of this work was to study the dependence of adsorption on adsorbent and adsorbate (chromium) by means of both batch and column studies. The present study indicated that the removal of Cr(VI) from aqueous waste solutions strongly depends on the pH of the solution, adsorbent mass, initial Cr(VI) concentration. The maximum adsorption capacity was obtained at pH 2.0. The capacity of adsorption of Cr(VI) increased with increasing temperatures up to 35ºC. Increase in the immobilized fungal biomass (IFB) of the adsorbent leads to increase adsorption capacity of the Ca-alginate (CA) beads owing to corresponding increase in the number of adsorption sites. The increase in IFB above certain limit (0.3 g/10 ml CA gel) result in increase in the amount removed and decrease in the equilibrium uptake capacity (q_e) of the IFB beads. The different kinetic models used in analyzing the

experimental data indicated that pseudo-second order sorption mechanism is predominant and the adsorption process is a chemical process. The experimental data fitted to both Langmuir and Freundlich isotherm models. Comparing the regression coefficient (R^2) for the two isotherms, it was found that Langmuir is the best with average R^2 value of 0.991 followed by Freundlich with average R^2 value of 0.984. The monolayer adsorption capacities (Q_0) were 35.49, 60.2 and 99.0 mg g^{-1} dry weight for CA, alive and dead IFB beads, respectively at optimum pH 2.0, temperature 25 ºC and time 120 min. Freundlich isotherm data showed that the affinity of dead IFB beads is higher than alive IFB and CA beads.

Column studies showed that IFB beads have higher adsorption capacity than CA beads and the removal efficiency of the dead IFB beads is slightly more than that of alive IFB beads. Studying the factor affecting the column performance on dead IFB beads showed that increasing the bed height and inlet Cr(IV) concentration lead to increase in Cr(IV) biosorption, while the increase in the flow rate lead to earlier breakthrough curve and a decrease in the Cr(VI) biosorption. The dead IFB beads could be used effectively for continuous removal of Cr(IV) from aqueous waste solutions.

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