

## Equilibrium Sorption Isotherms of Cr(III) on *Sphingomonas sp.* XJ2

GUO-XIANG XU<sup>1,\*</sup>, XU-QIANG LI<sup>2</sup> and WEN-BIN CHEN<sup>2</sup>

<sup>1</sup>Jiangsu Key Laboratory of Marine Biotechnology, Huaihai Institute of Technology, Lianyungang 222005, Jiangsu Province, P.R. China

<sup>2</sup>Department of Chemical Engineering, Huaihai Institute of Technology, Lianyungang 222005, Jiangsu Province, P.R. China

\*Corresponding author: Tel: +86 151 05131299; E-mail: lygcwb11@163.com

(Received: 12 March 2012;

Accepted: 9 January 2013)

AJC-12675

The present study was undertaken to develop a low cost effective adsorbent and adsorption process involved in the adsorption of heavy metal-contaminated industrial wastewater using the developed adsorbent. *Sphingomonas sp.* XJ2 is an excellent adsorbent for the adsorption efficiency of the chromium(III). Operational parameters such as pH, agitation time and adsorbent dosage, initial ion concentration and temperature were also studied. The optimal pH value for Cr(III) adsorption was 6. The maximum adsorption capacity of *Sphingomonas sp.* XJ2 for Cr(III) was 3.12 mmol/g. Adsorption data fitted well with the Langmuir and Freundlich models. However, Langmuir isotherm displayed a better fitting model than Freundlich isotherm because of the higher correlation coefficient than the former exhibited. Desorption studies were carried out with HCl, HNO<sub>3</sub>, EDTA, sodium carbonate and deionization water and quantitative recovery of the metal was evident. The result shows *Sphingomonas sp.* XJ2 is the excellent adsorbent for Cr(III).

**Key Words:** *Sphingomonas sp.* XJ2, Heavy metals, Adsorption isotherms.

### INTRODUCTION

Once heavy metals and toxic organic compounds discharged into the sea they will be absorbed and accumulate and amplify with the marine food chain, then leading to seriously damage to the quality of seafood, threatening ecosystems and human health. Therefore, it is significantly important to develop effective purification technique of main heavy metals pollution and organic compounds in indoor breeding water in order to improve the quality of farmed marine environment and ensure sustainable healthy development of the aquaculture industry.

In general, in areas contaminated by heavy metals the microbe resistance to heavy metal can be screened, these resistant organisms have a potential adsorption of heavy metals and they are also a great source of the heavy metal adsorbent and precipitant. Research of treating heavy metal wastewater through biosorbents has presented the trend of increasing year by year<sup>1</sup> and the growth rate has also increased year by year. It is suggested that biosorbents have been the focus and emphasis of research and application of heavy metal pollution and have a broad prospects, which will play a more far-reaching influence and role on governing aquatic environment problems and improving the quality of the aquatic environment. At present, trend of bio-adsorption research is looking for an adsorbent with a highly selective adsorption to a kind of metal. As micro-organism has advantages of rich source, low cost and special

structure of its cells, making it has great affinity and selectivity to heavy metal ions and has high efficiency of removing heavy metals. Microorganisms in marine sediment are in a highly oligotrophic and harsh environment in the long-term, which making them have a special metabolic regulation mechanisms to adapt to changing environments (especially the environment lacking nutrients) and efficiently adjust its growth to resist adverse environmental changes. They have a unique ability to degrade<sup>2,3</sup> on many substrates, ranging from the polycyclic aromatic hydrocarbon compounds, poly(vinyl alcohol) and polycyclic aromatic polymers to simple inorganic N and have a strong enrichment to a variety of heavy metals and the fact provides possibility of comprehensive utilization of the ocean microorganisms<sup>4</sup>. The marine microbial resources was used to study heavy metal adsorption by Kogej & Pavko<sup>5</sup> and Aksu & Acikel<sup>6</sup> who used *Chlorella vulgaris* (*Chlorella*) to adsorb Ni(II), Cu(II) in the range of pH 4.5-9.2, at room temperature, the adsorption capacity can achieve 150-250 mg/g, respectively. Hossain and Anantharaman<sup>7</sup> used *Bacillus subtilis* screened from seawater and Suhasini *et al.*<sup>8</sup> used biosorbent PFB1 (seaweed) to study the adsorption conditions, mechanism and application of As(III) and Co(II), the adsorption capacity could achieve 97.30 and 85 mg/g, respectively. From above reports it can be found that kinds of microorganisms could be used to control heavy metals selected through marine microbial resources, research on heavy metals in marine environmental management is few

and its application is mainly to deal with industrial wastewater. Therefore, the study trend of selecting and cultivating Strains have resistance to heavy metals from marine microbial and repairing heavy metal pollution in marine aquaculture has important significance on improving seafood quality and increasing economic efficiency. *Sphingosine aeromonas* has been applied to degrade aromatic compounds<sup>9</sup>, bromine acid and other organic pollutants, but research of heavy metals adsorption has not been reported. In this study, we used sphingosine *Aeromonas sphingomonas* strain RB2256 filtered out from sediment in the ocean water to adsorb nickel in seawater after fixed by *Sphingomonas sp.* XJ2. The objectives of this work is to study the removal capacity of alginate gel-beads for Cr(III) with a view to investigate the adsorptive capacity of the adsorbents by varying pH of solution, agitation time, initial ion concentration during the treatment of Cr(III) in aqueous solution.

## EXPERIMENTAL

An experimental solution containing Cr(III) was prepared by diluting 1 mL of stock solution of the metal to the desired concentrations. A stock solution of chromium(III) was obtained by dissolving the exact quantity of chromium sulphate in deionized water. The stock solution concentration of Cr(III) ion is 200 mg/L. The pH of experimental solution was adjusted by using 0.1 M NaOH and 0.1 M H<sub>2</sub>SO<sub>4</sub> and it varied between 4 and 7.

**Preliminary screen:** Through the above purification operations, we got eight kinds of bacteria. Inoculated the eight bacteria obtained from preliminary screen to the flat that contained Cr(III), each bacteria inoculated seven concentrations, respectively were 5, 10, 20, 40, 60, 80 and 100 mg/L. Poured in the biochemical incubator and cultured for 24 h. The result showed that, in the concentration gradient plate of the Cr(III), all the bacteria grew best in the plate of 20 mg/L concentration, there was few bacteria in the plate of above 60 mg/L concentration, almost imperceptible. The bacteria A, B, C grew better than the others, so chose bacteria A, B, C to culture.

The experiment showed that, Cr(III) had a certain inhibition to the bacteria's growth, bacteria also had a certain absorption of Cr(III) and it had a little influence on bacteria A. so it showed that, it had a good adaptability to Cr(III) and had a strong adsorption effect.

**Confirmatory test of induced adsorption capacity:** Respectively inoculated the active bacteria A solution to the culture medium without heavy metal and the media that contained 60 mg/L Cr(III), cultured them for 24 h in table concentrator in 200 r/min at 37 °C, respectively took 1 mL of them into the 50 mL culture medium whose Cr(III) concentration was 0.5 mmol/L, determined the OD value and Cr(III) concentration every 0, 4, 6, 8, 10, 15 and 25 h to investigate whether induction domestication strengthened the adsorption capacity of bacteria to lead. The result showed that, the biggest removal rate to Cr(III) of not tamed bacteria was 77 %, after several domestications (seven times), the highest removal rate of bacteria could reach 95 % gradually, so the induction domestication for bacteria could significantly improved the ionic adsorption of Cr(III), at the same time, we found that

bacteria also had a strong absorption capacity to the heavy metals in the testing process.

**Identification of bacteria:** Screened bacteria A that had the advantaged adsorption to Cr(III) in the marine sediment, the growth of it did not influence by heavy metal lead in basic. The growth properties of Bacteria A were: strains liked oxygen, the growth temperature range was 0-45 °C, the adapt pH range was 3.0-9.5, when NaCl concentration was 0-5 %, the growth cycle was about 36-42 h, after 10 h it went to the logarithmic growth phase, the maximum growth of bacteria achieved in 27 h, after 33 h, it entered the decay period.

The surface of the bacteria A was smooth and wet, edge indented, profile swelled, it was Gram-negative bacteria, presented rhabditiform, without spores and had flagellum. Preliminary evaluated that bacteria A was *Brevibacterium*. After sequenced, got the 16s rDNA sequence of strain XJ2 whose length was 1382 bp. Put the sequencing result of the strain into GenBank to conduct homology comparison with the BLAST software. The result of the sequence comparison showed that, it had high homology (95 %) with the *Sphingomonas* bacteria, the similarity level of isolated strains to *Sphingomonas sp.* KW07 and *Sphingomonas sp.* RB2256 in GenBank were 99.3 and 98.5 % respectively. Referred to "Bergey's Manual of Determinative Bacteriology", eventually identified the bacteria was *Sphingomonas sp.* XJ2.

**Gel bead synthesis:** The alginate bead was prepared by using dropping technique from a *Sphingomonas sp.* XJ2 aqueous solution. The polymer solution was prepared dissolving the alginate under magnetic stirring at 200 rpm for 3 h at 30 °C. The alginate solution was dropped with a microsyringe with 0.5 mm in diameter needle into a 2 % CaCl<sub>2</sub> solution. The beads were allowed to stand in the CaCl<sub>2</sub> solution for 5 h. Ca-Alg beads were then washed with bidistilled water before use.

*Sphingomonas sp.* XJ2 from brown algae of low viscosity grade (solution 2 %, w/v), was used without further purification. Anhydrous calcium chloride 99.2 % was additive reagent. The aqueous solutions of CaCl<sub>2</sub> concentration is 2 % (w/v).

**Adsorption experiments:** A series of sorption studies were carried out using calcium alginate gel under varying pH of medium, the initial concentration of Cr(III). Batch experiments were conducted at different temperature using the optimum conditions of all factors that influence adsorption such as agitation time, pH, initial ion concentration and other coexist ion.

Wastewater (50 mL) containing Cr(III) was placed in a 250 mL Erlenmeyer flask and 2 % (w/v) *Sphingomonas sp.* XJ2 was added. The mixture was mechanically agitated at 120 rpm on a reciprocate shaker. The Cr(III) concentration of the treated solution was analyzed at time interval between 0 and 3 h using standard methods recommended for examination of water and wastewater. The removal efficiency (E) of adsorbent on Cr(III) was measured as follows:

$$E (\%) = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

where C<sub>i</sub> and C<sub>f</sub> are the initial and final equilibrium concentration of chromium(III) in solution, respectively.

## RESULTS AND DISCUSSION

**Effect of agitation time:** Equilibrium time is another important operational parameter for an economical wastewater treatment process. Fig. 1 showed the removal efficiency of chromium as function of agitation time. Fig. 1 showed that increase in agitation time increased removal efficiency until equilibrium adsorption was established; other parameters such as pH, adsorbent dosage, initial ion concentration were kept at the optimum and temperature and agitation speed kept at 25 °C and 120 rpm, respectively. Equilibrium adsorptions were established within 1 h for *Sphingomonas sp. XJ2* in which Cr(III) adsorption efficiencies was 57 %.

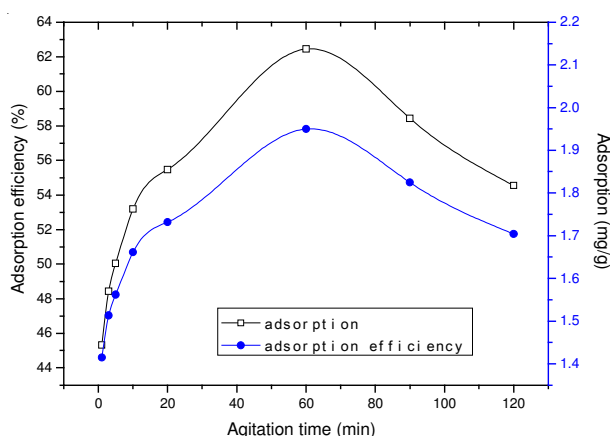


Fig. 1. Effect of agitation time on adsorption efficiency of on the adsorbent

**Effect of pH:** The pH of aqueous solution is an important operational parameter In the adsorption process because it affects the solubility of the metal ions, concentration of the degree of ionization of the adsorbate during reaction. Thus, the role of H<sup>+</sup> concentration was examined on the removal efficiency of chromium(III). The pH was varied from 4.0-6.5, other operational parameters (agitation time, adsorption dose, initial ion concentration ) were kept in optimum and temperature and agitation speed were kept at 25 °C and 120 rpm, respectively. Fig. 2 showed that increasing pH of the solution from 4.0-6.5 caused adsorption efficiency of Cr(III) and the adsorption efficiency decreased above pH 6 of solution. This may be due to the formation of nonsoluble hydroxyl complexes.

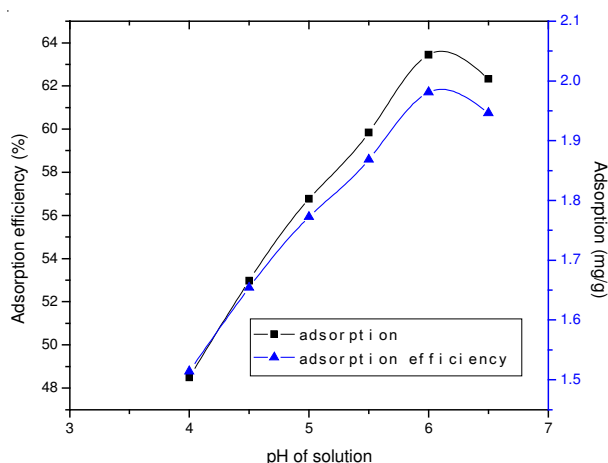


Fig. 2. Effect of pH on the adsorption of on the adsorbent

The onset of metal hydrolysis and precipitation begin at pH > 6. The hydrolysis of metal ions occurs by the replacement of metal ligands in the inner co-ordination sphere with the hydroxyl group. This replacement occurs after the removal of the outer hydration sphere of metal ions. Adsorption may not be related directly to hydrolysis of the metal ion, but instead, outer hydration sphere that precede hydrolysis. The H<sup>+</sup> concentration increase if pH is low, thus, competitive adsorptions between H<sup>+</sup> and Cr(III) result in low adsorption efficiency of Cr(III). Adsorption efficiency of Cr(III) ranged between 44 and 56 %.

**Effect of initial ion concentration:** The percentage removal of Cr(III) by the adsorbent initially increased rapidly with increasing Cr(III) and slowed down when Cr(III) concentration reached 60 mg/L (Fig. 3). At lower concentrations, Cr(III) in the solution would interact with the binding sites and thus facilitated 100 % adsorption. At higher concentration, more Cr(III) are left unadsorbed in solution due to the saturation of the sites. This indicates that energetically less favorable sites become involved with increasing ion concentration in the aqueous solution. The Cr(III) adsorption is attributed to different mechanisms of ion-exchange process, Cr(III) had to move through the pores of the adsorbent mass, but also through channels of the lattice and they had to replace exchangeable cations. Diffusion was faster through the pores and was retarded when the ions moved through the smaller diameter channel. In this case, the Cr(III) sorption could mainly be attributed to ion-exchange reaction in the micropores of the adsorbents.

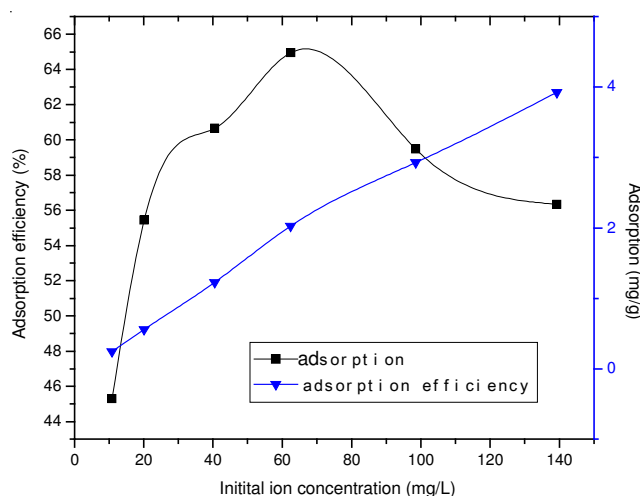


Fig. 3. Effect of initial ion concentration of by the adsorbents

**Effect of adsorption dosage:** Fig. 4 presents sorption of Cr(III) as function of adsorbents dosage. The dose of adsorbents was varied between 0.1-0.6 g, other operational parameters (agitation time, pH, initial ion concentration) were kept at the optimum and temperature and agitation speed were kept at 30 °C and 120 rpm, respectively.

From the results in Fig. 4, increasing dose of the adsorbents increased adsorption of Cr(III). This is expected because more binding sites for ions are available at higher of adsorbents. However, increasing the dose of the adsorbents above 0.5 g yielded no increase in the adsorption efficiency of Cr(III). The observation suggest the adsorption of Cr(III) ion

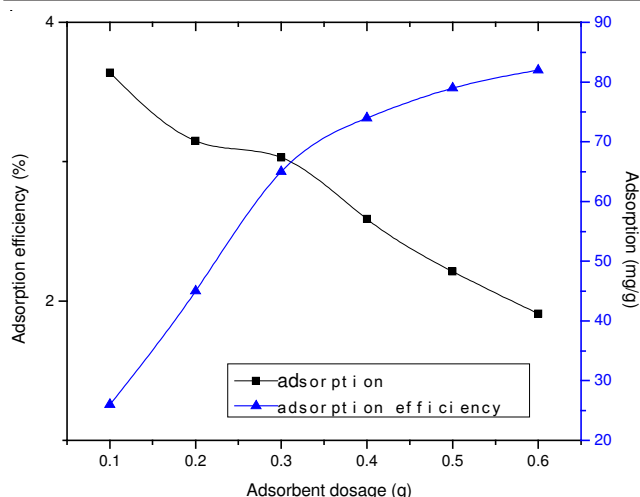


Fig. 4. Effect of adsorbent dose of alginate bead

is related to the repulsive electrostatic interaction between the alginate and Cr(III). Integrating all the factors including economy of adsorbents dosage and adsorption efficiency, the dose of adsorbent is selected 0.4 g.

**Adsorption isotherms:** Adsorption isotherms can be generated based on numerous theoretical models where Langmuir and Freundlich models are the most commonly used. The Langmuir model assumes that uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The model takes the following form:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (2)$$

where  $C_e$  is the equilibrium concentration (mg/L),  $q_e$  is the amount of metal ion adsorbed at specified equilibrium (mg/g),  $Q_0$  and  $b$  are the Langmuir constants related to adsorption capacity and energy of adsorption. The essential characteristics of Langmuir isotherm model can be explained in terms of a dimensionless constant separation factor or equilibrium parameter  $R_L$ , which is defined by

$$R_L = \frac{1}{1 + bC_0} \quad (3)$$

where  $b$  is Langmuir constant (L/mg) and  $C_0$  is initial concentration (mg/L). It has been shown using mathematical calculations that parameter  $R_L$  indicates the shape of isotherms as follows:

Values	Types of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$R_L < 1$	Favorable
$R_L < 0$	Irreversible

On the other hand, the Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface. The equation is commonly represented by

$$q_e = K_f C_e^{1/n} \quad (4)$$

where  $K_f$  and  $1/n$  are the Freundlich constants characteristics of the system, indicating the adsorption capacity and the adsorption intensity, respectively.

Therefore, a plot of  $\ln q_e$  versus  $\ln C_e$  enable the constant  $K_f$  and  $1/n$  to be determined. The Langmuir and Freundlich isotherms for the adsorbents prepared from *Sphingomonas sp. XJ2* in Figs. 5 and 7, respectively. The plots of  $C_e/q_e$  against  $C_e$  are linear (Fig. 5), showing the applicability of Langmuir isotherm to all types of adsorbent tested. Also the value of  $R_L$  between 0-1 shows the well adsorption of Cr(III) by *Sphingomonas sp. XJ2* (Fig. 6).

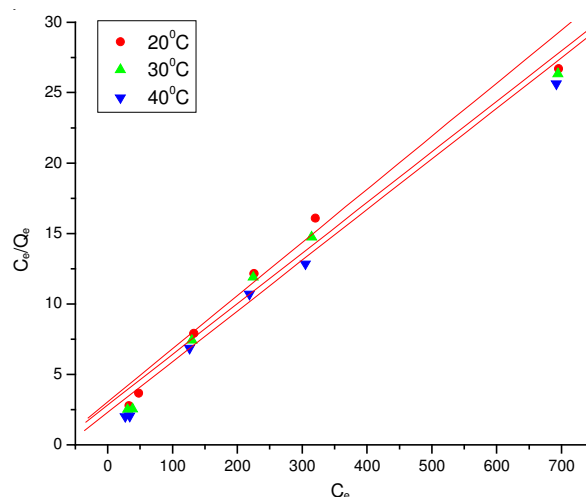
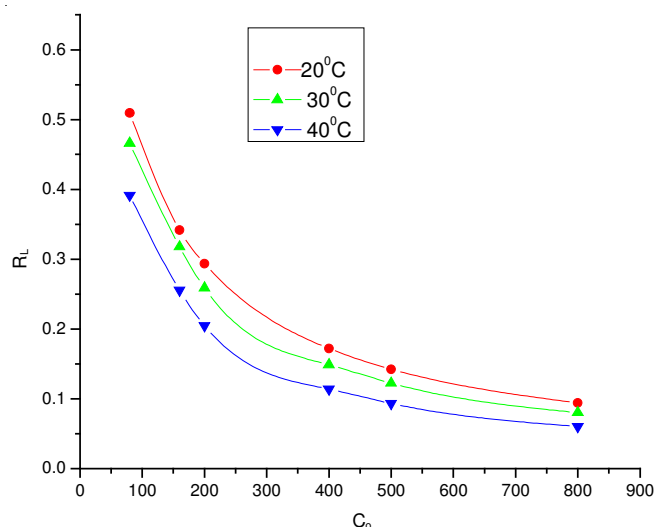


Fig. 5. Langmuir adsorption isotherm for the adsorption of Cr(III) by the adsorbents

Fig. 6. Correlation for  $R_L$  and  $C_0$ 

Freundlich isotherm was also a representative for the Cr(III) adsorption by adsorbent tested. The two models fitted well for the adsorption studies. However, Langmuir isotherm had a better fitting model than Freundlich isotherm. This is as a result of higher correlation coefficient exhibited by Langmuir isotherm (Table-1). Thus indicating to the applicability of monolayer coverage of the Cr(III) on the surface of the adsorbent. This can be explained by the fact the sorption of the Cr(III) is the monolayer adsorption.

**Kinetic experiments:** The kinetics of the sorption processes is an important parameter in order to evaluate the qualities of a good adsorbent and the efficiency of the removal. The uptake of the Cr(III) as a function of time was determined



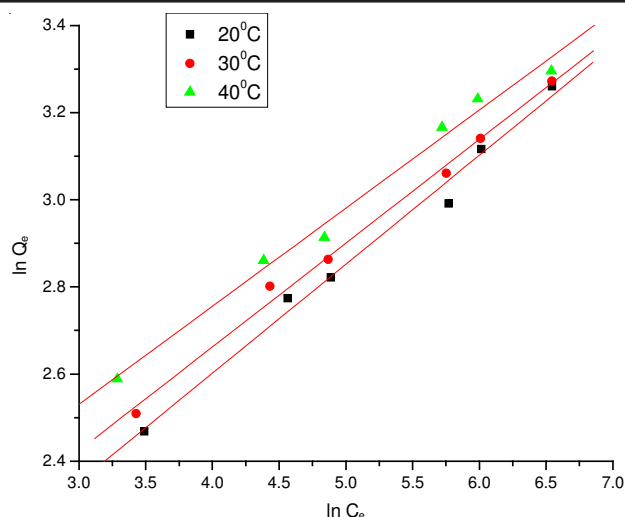


Fig. 7. Freundlich adsorption isotherm for the adsorption of Cr(III) by the adsorbents

Temperature (°C)	Langmuir constants			Freundlich constants		
	b (L/mg)	$q_e$ (mg/g)	$R^2$	$K_f$	1/n	$R^2$
20	0.01203	28.12	0.9952	5.21	0.2472	0.9915
30	0.01432	28.34	0.9958	6.45	0.2143	0.9841
40	0.01941	28.48	0.9981	7.60	0.1954	0.9775

$R^2$  = Correlation coefficient.

at various pH solution and for the evaluation of kinetics the experiments were conducted at pH 6, temperature 20, 30 and 40 °C and fixed amount of alginate beads.

The kinetic experiments were conducted in order to compare the behaviour of contaminates and adsorbent and the removal of Cr(III) is shown in Fig. 8 at various temperatures. For Cr(III) is removed from the solution within the first 10 min, after 1 h no significant sorption of Cr(III) was noticed.

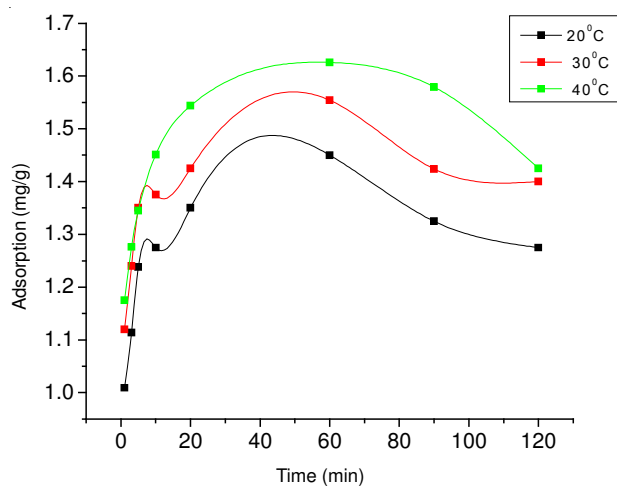


Fig. 8. Adsorption kinetics of Cr(III) on adsorbent

As shown in Fig. 8, the kinetics of the Cr(III) adsorption shows three different stages. In the first one, which occurs in the first *ca.* 10 min, a sharp increase of the adsorption is seen, indicating that the adsorption takes place at the exterior of the polymeric beads, on the surface of the particles. In the second stage, a gradual increase of the adsorption process can be observed, probably due to intrapore diffusion of the contaminant solution. In the last stage beyond 1 h, the uptake of Cr(III) ion increase very slow or remain constant, as the result of the saturation of the solid adsorbent with the solute.

**Desorption studies:** Desorption of the adsorbed Cr(III) ion from the adsorbents was studied in a batch system. The Cr(III) ions adsorbed onto adsorbents was eluted with HCl (0.01 M), HNO<sub>3</sub> (0.01 M), EDTA (0.01 M), sodium carbonate and deionization water. It was regenerated with different concentration of desorbents. The quantitative recovery of metal ions is possible. The desorption of HCl and EDTA are the best. This confirms that ions exchange is the phenomenon of the adsorption process.

In order to show the reusability of the beads, the adsorption-desorption cycle of Cr(III) ion was repeated three times using HCl (0.01 M). The adsorption capacities did not noticeably change during the repeated adsorption-desorption operations (only a maximum 3 % change was observed with the tested adsorbent). These results showed that the produced alginate beads can be repeatedly used in heavy metal adsorption studies without detectable losses in the adsorption capacities.

## Conclusion

The adsorption of Cr(III) ion on *Sphingomonas sp.* XJ2 was controlled by solution agitation time, pH and initial ion concentration. The equilibrium was well described by the Langmuir and Freundlich adsorption isotherms. However, Langmuir isotherm displayed a better fitting model than Freundlich isotherm because of the higher correlation coefficient that the former exhibited, thus, indicating to the applicability of monolayer coverage of Cr(III) ion on the surface of adsorbent.

## REFERENCES

1. N. Das, R. Vimala and P. Karthika, *Indian J. Biotechnol.*, **7**, 159 (2008).
2. O. Cho, K.Y. Choi, G.J. Zylstra, Y.-S. Kim, S.-K. Kim, J.H. Lee, H.-Y. Sohn, G.-S. Kwon, Y.M. Kim and E. Kim, *Biochem. Biophys. Res. Commun.*, **327**, 656 (2005).
3. P.M. Sarma, D. Bhattacharya, S. Krishnan and B. Lal, *Appl. Environ. Microbiol.*, **70**, 3163 (2004).
4. Q.F. Li and Y.X. Yuan, *J. Fishery Sci.*, **7**, 90 (2000).
5. A. Kogej and A. Pavko, *Chem. Biochem. Eng. Q.*, **15**, 75 (2001).
6. Z. Aksu and U. Acikel, *Process Biochem.*, **34**, 589 (1999).
7. Sk. Masud Hossain and N. Anantharaman, *Biochem. Eng. Q.*, **20**, 209 (2006).
8. I.P. Suhasini, G. Sriram, S.R. Asolekar and G.K. Sureshkumar, *Process Biochem.*, **34**, 239 (1999).
9. M. Gou, Y.Y. Qu, H. Yang Hua, J.T. Zhou, A. Li, X.-Y. Guan and F.-F. Ai, *Appl. Environ. Biol.*, **14**, 278 (2008).