

## Removal of chromium ions from aqueous solution by biosorption on to ternary biopolymeric microspheres

A K Bajpai\* & Leena Rai

Bose Memorial Research Laboratory, Department of Chemistry,  
Government Autonomous Science College, Jabalpur 482 001, India  
Email: akbmrl@yahoo.co.in; akbajpailab@yahoo.co.in

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Ternary biopolymeric microspheres of chitosan, yeast and gelatin were prepared and characterized by FTIR spectral analysis, particle size measurements and scanning electron micrograph techniques. Static and dynamic adsorption studies of chromium ions were performed onto the surface of the prepared microspheres at fixed pH and ionic strength of the aqueous solution. The adsorption data were supplied to Langmuir and Freundlich isotherm equations and various static parameters were calculated. The dynamic nature of the adsorption was quantified in terms of several kinetic constants such as rate constants for adsorption, Lagergren rate constant, and interparticle diffusion rate constant and pore diffusion coefficient. The influence of various parameters such as solid to liquid ratio, pH, temperature, and chemical composition of biopolymeric microspheres were investigated on the adsorption of dichromate ion. Various thermodynamic parameters were also calculated.

**Keywords:** Chromium removal, Biosorption, Ternary biopolymer microspheres, Chitosan, Yeast, Gelatin

Several industrial and agricultural processes and mining activities have increased the concentration of toxic contamination in water and wastewater around world<sup>1</sup>. The presence of toxic heavy metal contaminants in aqueous streams arising from the discharge of untreated metal containing effluents into water bodies gives rise to one of the most important environmental issues<sup>2</sup>. The anthropogenic sources of heavy metals include waste from the electroplating and metal finishing industries, metallurgical industries, tannery operations, chemical manufacturing, mine drainage, battery manufacturing leachates from land fills and ground water contamination from hazardous waste sites<sup>3</sup>.

Heavy metals are classified into the following three categories: toxic metals (Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn etc), precious metals (Pd, Pt, Ag, Au, Ru etc) and radionuclides (Ra, Am, etc)<sup>4</sup>. The presence of heavy metals in the environment is of major concern because of their transformation from relatively low toxic species into more toxic ones. Some metal ions such as Hg and Cd are highly toxic even in lower concentration 0.001-0.1 mg/L<sup>5,6</sup>.

The conventional methods for treatment of effluents contaminated with heavy metals involve physicochemical processes such as flocculation,

electrolysis, precipitation, ion exchange membrane technologies, reverse osmosis and crystallization. These processes may be ineffective or expensive especially when the heavy metal ions are present in solution in very low concentration (1-100 mg)<sup>7</sup>. On the contrary biological methods such as biosorption, bioaccumulation provide an attractive alternative to physicochemical methods for the removal of the heavy metal ions<sup>8</sup>. There are many reports on algae<sup>9</sup>, bacteria<sup>10</sup>, fungi<sup>11</sup>, yeast<sup>12</sup> or higher plants<sup>13</sup> that remove and accumulate large amount of heavy metal ions from their external environment.

The most commonly used naturally occurring biosorbents are totally renewable, their cost is low and their use and handling involve no additional risks. They may also be specifically selective for different pollutants and are generally disposed of by incineration<sup>14</sup>. Among commonly used adsorbents chitosan and yeast have shown potential to remove toxic metal ions from aqueous solution. The ability of chitosan to form complexes with metal ions, particularly transition metal and post transition metal ions is well documented and it is, therefore, considered as a promising adsorbent for removing heavy metals from polluted water<sup>15</sup>. Yeast cells of *S.*

*cerevisiae* have also been found capable of accumulating a wide range of heavy metal cations ( $\text{Fe}^{+3}$ ,  $\text{Cu}^{+3}$ ,  $\text{Hg}^+$ ,  $\text{Pb}^{+2}$ ,  $\text{Cd}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Ag}^+$ ,  $\text{Ni}^{+2}$ ,  $\text{Fe}^{+2}$ )<sup>16</sup>. In natural water chromium exists in its two environmentally important oxidation states, chromium (III) and chromium (VI), which have contrasting toxicities, mobility and bioavailability. In trace amounts chromium (III) is considered as an essential nutrient for numerous organisms but in higher amounts it is toxic and mutagenic<sup>17</sup>. Hexavalent chromium (VI) is the more toxic form of chromium released during many industrial processes including electroplating, leather tanning and pigment manufacture<sup>18</sup>. Due to the severe toxicity of Cr (VI) the EU Directorate, WHO and US-EPA have set the maximum contaminant concentration levels<sup>19</sup> for Cr (VI) in domestic water supplies as  $0.050 \text{ mg L}^{-1}$ .

Thus, realizing the seriousness of Cr (VI) induced toxicity the present work has been designed to develop an efficient biosorbent for removal of Cr (VI) ions from aqueous solution. The biosorbent chosen for achieving the laid objectives is ternary microspheres composed of chitosan, yeast and gelatin which either alone or in combination have been well recognized as potential sorbents for removal of toxic metal ions.

## Experimental Procedure

### Materials

Chitosan, yeast and gelatin (Loba Chemie, Mumbai India) of high purity grade were purchased from local chemical suppliers. Glutaraldehyde (Loba Chemie, Mumbai, India) was used as crosslinking agent. Silicon oil (Aldrich, USA) having viscosity 10,000 poise at  $25^\circ\text{C}$  was used as an oil phase for preparing the suspension. Potassium dichromate and other chemicals were of high purity grade and throughout the work double distilled water was used for making solutions.

### Preparation of microspheres

Solutions of gelatin (3 g) and yeast (2 g) were mixed with a solution of chitosan (1 g) on magnetic stirrer for about 20 min. A 3 mL aliquot of a homogeneous mixture of glutaraldehyde and silicon oil was added dropwise into the prepared suspension of yeast, gelatin and chitosan with the help of a syringe under constant stirring. The particles obtained were washed with acetone, then benzene and dried at  $80^\circ\text{C}$  for 4 h.

### Adsorption experiments

The adsorption experiments were carried out by the batch contact method as described elsewhere<sup>20</sup>. Firstly, the stock solution was prepared by dissolving potassium dichromate in 1 litre distilled water and than into 10 mL of diluted stock solution (1:1), 20 mg of water swollen microspheres were added as adsorbent. The suspension was shaken in a rotary shaker (Tempstar, India) for 4 h, which was found to be sufficient time to attain equilibrium adsorption. After shaking, 3 mL supernatant was mixed with reagent (diphenylcarzide solution) and the amount of chromium was assayed spectrophotometrically. The adsorbed Cr (VI) was calculated by the following equation,

$$\text{Adsorbed amount (mg/g)} = \frac{(C_i - C_f)V}{m} \quad \dots (1)$$

where  $C_i$  and  $C_f$  being the initial and final concentrations of  $\text{Cr}^{+6}$  solution (mg/mL), respectively,  $V$  being the volume of adsorbate solution and  $m$  is the weight of swollen microspheres, i.e. adsorbent.

### Characterization of microspheres

The FTIR spectra of native (unadsorbed) and Cr (VI) adsorbed microspheres were recorded on a FTIR spectrophotometer (FTIR-8400S, Shimadzu). To study the morphology of the prepared microspheres, the SEM analysis of the microspheres surface was carried out (STEREO SCAN, 430, Leica SEM, USA). The size of the prepared microspheres was determined by a particle size analyzer (Fritsch Particle Sizer, Germany).

### Surface charge determination

As the microspheres are composed of polyelectrolyte biomacromolecules, their surface bears a charge, which may be determined by EMF measurements. For determination of magnitude of surface charge, 1 g microspheres were allowed to swell in 25 mL of distilled water and the charge developed over the surface was measured by pH/EMF meter (Systronics  $\mu$  pH system 362, Ahmedabad, India). In a similar way, the  $\text{Cr}^{6+}$  adsorbed microspheres were also immersed into the same volume of water under identical condition and surface charge was determined.

## Results and Discussion

### FTIR

The FTIR spectra of native (before adsorption) and  $\text{Cr}^{+6}$  adsorbed biopolymeric microspheres are shown in Fig. 1a and 1b, respectively.

The IR spectrum of native microspheres (Fig. 1a) shows minor peak around  $1171\text{ cm}^{-1}$  corresponding to saccharide structure<sup>21</sup>. A sharp peak appearing at  $1615\text{ cm}^{-1}$  may be attributed to amide I bond ( $\text{nC=O}$ ), characteristic of chitosan with acetylated unit. A peak around  $3422\text{ cm}^{-1}$  may be assigned to overlapped absorption bands due to  $-\text{NH}$  and  $-\text{OH}$  symmetrical vibrational peaks, while a peak around  $2910\text{ cm}^{-1}$  may be due to the typical C-H stretch vibrations.

The spectrum (a) also indicates the presence of yeast as evident from the peaks observed at  $859\text{ cm}^{-1}$  (sugar region) and  $1513\text{ cm}^{-1}$  (protein region). Several peaks corresponding to vibration of  $-\text{OH}$ ,  $-\text{NH}$  and  $-\text{COOH}$  groups are also visible in the spectrum (a) thus confirming the presence of gelatin molecules in the blend microspheres.

A close examination of spectrum (b) reveals that bands at  $3422$ ,  $3186$  and  $2910\text{ cm}^{-1}$  are respectively shifted to longer wave numbers  $3529$ ,  $3215$ ,  $3083\text{ cm}^{-1}$ . Moreover, bands at  $1615$  and  $1171\text{ cm}^{-1}$  are also shifted towards longer wave numbers  $1675$  and  $1253\text{ cm}^{-1}$  respectively due to interaction of metal ions ( $\text{Cr}^{6+}$ ) with functional groups of biopolymer components. More importantly O-Cr-O bridging frequency<sup>22</sup> of  $\text{Cr}_2\text{O}_7^{2-}$  ions appear at  $770\text{ cm}^{-1}$ .

Thus FTIR spectral analyses of both the spectra confirm: (i) the presence of the biopolymer components chitosan, yeast and gelatin in the micrpsphere and (ii) the change in band position of some functional groups of microspheres after the sorption of  $\text{Cr}^{6+}$  ions indicating the prominent role of these groups in the biosorption of chromium.

#### Scanning electron microscopy (SEM)

The SEM image of metal ions adsorbed microspheres is depicted in Fig. 2 which indicates that the constituent biopolymer components of micrpspheres are not much compatible and, therefore, have resulted in a blend of heterogeneous nature. It is also visible from the image that the blend surface has porous type morphology with voids ranging in width as large as  $20\text{ }\mu\text{m}$ . This obviously accounts for good adsorbing property of the prepared biosorbent.

#### Particle size analysis

The particle size analysis of the prepared microspheres (Fig. 3) clearly indicates that the microsphere particles are quite heterogeneous, their

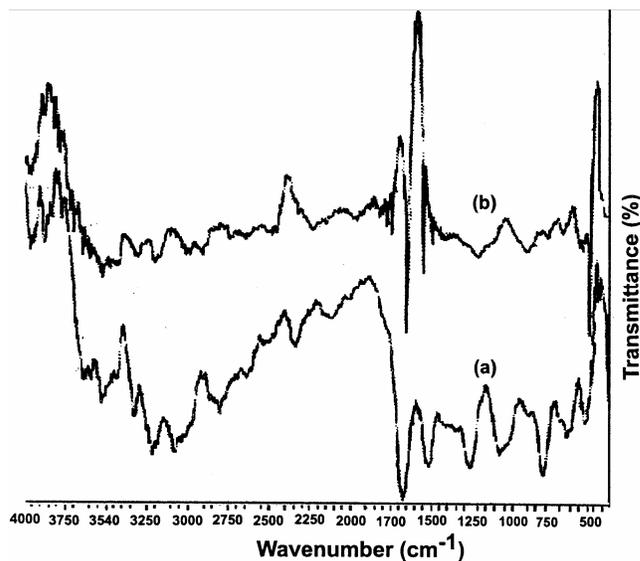


Fig. 1—FTIR spectra of (a) native and (b)  $\text{Cr}^{6+}$  adsorbed microspheres.

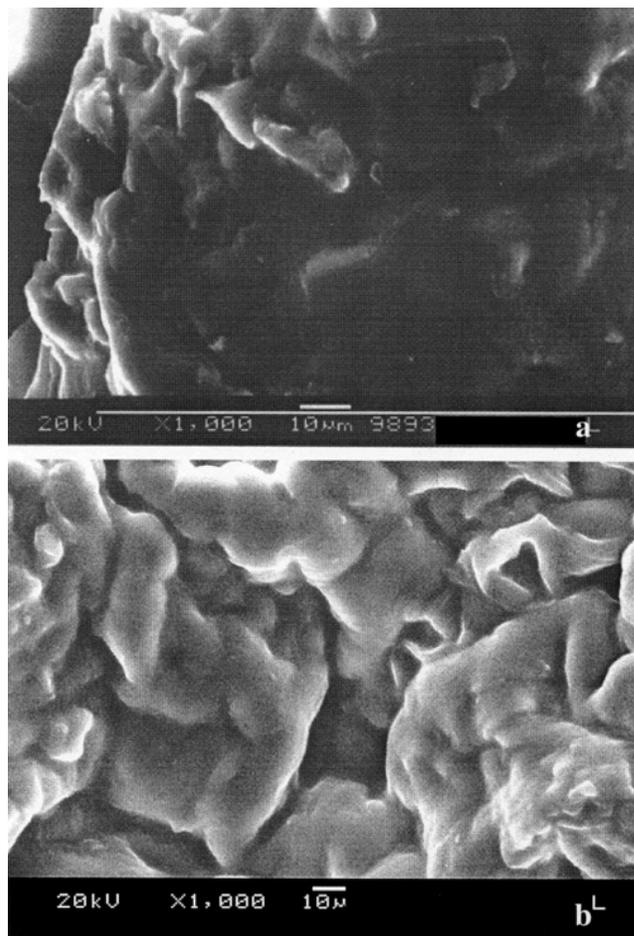


Fig. 2—SEM images of (a) native microspheres surface and (b)  $\text{Cr}^{6+}$  adsorbed microspheres surface.

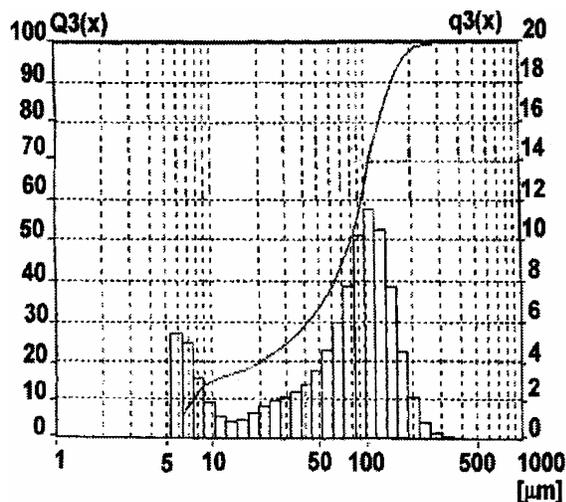


Fig. 3—Particle size distribution curve of microspheres.

average size varying between 6 to 732  $\mu\text{m}$ . However, 90 percent microspheres have an average dimension of 152  $\mu\text{m}$ .

#### Surface charge analysis

The surface charge data are shown in Table 1, which clearly indicate that the native microspheres (without adsorption) bear an EMF of -54.0 and 67.0 mV as absolute and relative EMF values, respectively. The same microspheres after adsorption of  $\text{Cr}^{6+}$  ions show much higher positive potential of + 92.8 and 115.0 mV for absolute and relative EMF, respectively. This clearly shows an increasing positive charge on microspheres surface which may be attributed to the adsorption of  $\text{Cr}^{6+}$  ions onto the microsphere surfaces.

#### Effect of initial metal ion concentration

The percent removal of metal ion was calculated using the equation

$$\%R = \frac{C_o - C_e}{C_e} \times 100 \quad \dots (2)$$

where  $\%R$  is percent removal and  $C_o$  and  $C_e$  are the initial and equilibrium metal ions concentration in solution, respectively.

The apparent adsorption capacity of the prepared biomass for metal ion was further determined at different metal ion concentrations (0.0050 to 0.040 mg/mL). The capacity in mM/g was calculated by the following relationship<sup>24</sup>.

$$\text{Capacity (mM/g)} = \frac{\%R}{100} \times \frac{C_o V}{m} \quad \dots (3)$$

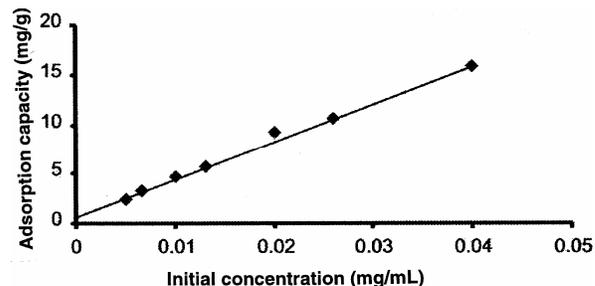


Fig. 4—Effect of concentration on adsorption capacity of  $\text{Cr}^{6+}$  for adsorption onto microspheres

Table 1—Data showing the surface charge on microsphere.

Microsphere	Absolute EMF (mV)	Relative EMF (mV)
Before adsorption (Native)	- 54.0	67.0
After adsorption	92.8	115.0

where  $C_o$  = initial concentration of metal ion solution,  $V$  = volume of metal ion solution,  $m$  = weight of microspheres (g), and  $\%R$  = percent removal of metal ions.

Figure 4 reveals the relation between adsorption capacity of microspheres and metal ion concentration which shows that as the metal ions concentration increases from 0.0050 to 0.040 mg/mL the adsorption capacity also increases with time at the beginning and becomes very slow towards the end of the process.

The reason for the observed increase in metal sorption could be the fact that with increase in metal ion concentration, greater number of metal ions approach at the binding sites and get adsorbed. There was no further increase in metal uptake when the active sites are fully exhausted by the metal ions<sup>25</sup>.

#### Adsorption isotherms

##### Langmuir isotherm

The application of biosorption process on the commercial scale requires proper quantification of the sorption equilibrium for process simulation. The Langmuir equation has been frequently used to give the sorption equilibrium<sup>26</sup>. The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. This isotherm equation is based on the following assumptions<sup>27</sup>: (i) metal ions are chemically adsorbed at a fixed number of well-defined sites, (ii) each site can hold only one ion, (iii) all sites are energetically equivalent, and (iv) there is no interaction between the ions.

The adsorption increases with the increase in initial metal concentration till the binding sites are not

saturated. The linearized Langmuir isotherm allows the calculation of adsorption capacities and Langmuir constant by the following equation.

$$\frac{C_e}{a} = \frac{1}{a_s K} + \frac{C_e}{a_s} \quad \dots (4)$$

where  $a$  is the amount of  $\text{Cr}^{6+}$  (mg/g) adsorbed at any equilibrium concentration,  $a_s$  is the amount of metal ion adsorbed at saturation (adsorption capacity),  $K$  is the adsorption coefficient.

The linear plot of  $C_e/a$  versus  $C_e$  (Fig. 5) indicates that the adsorption process follows Langmuir adsorption model<sup>28</sup>. The values of  $a_s$  and  $K$  determined from the slope and intercept of the linear plot have been found to be  $13.34 \text{ mg g}^{-1}$  and  $K$  is  $1500 \text{ mg}^{-1} \text{ dm}^3$ , respectively.

**$R_L$  Factor**

The essential characteristics of the Langmuir isotherm can be expressed in the form of dimensionless constant separation factor or equilibrium parameter ( $R_L$ ) as given below.

$$R_L = \left[ \frac{1}{1 + KC_o} \right] \quad \dots (5)$$

where  $K$  is the Langmuir constant and  $C_o$  is the initial concentration of Cr (VI)<sup>29</sup>. The  $R_L$  value indicates the shape of isotherm as given in Table 2<sup>30</sup>. The  $R_L$  values for different initial metal ions concentration (0.040 to 0.0050 mg/mL) are given in Table 2.

**Freundlich isotherm**

The Freundlich isotherm is a widely used model of adsorption of heavy metals from aqueous medium and may be represented as.

$$a = k_F C_e^{1/n} \quad \dots (6)$$

where  $C_e$  is the equilibrium concentration (mg/mL) is amount of adsorbed metal ions (mg/g)<sup>31</sup>,  $k_F$  is the Freundlich constant,  $a$  is the adsorbed amount of  $\text{Cr}^{6+}$  (mg/g),  $1/n$  a constant which determines the curvature and steepness of isotherm<sup>32</sup>. Also the value of  $n$  indicates the affinity of the adsorbate towards the biomass. The above equation is conveniently used in linear form as.

$$\ln a = \ln k_F + 1/n \ln C_e \quad \dots (7)$$

A plot of  $\ln a$  against  $\ln C_e$  gives a straight line which indicates that the adsorption process follows the Freundlich adsorption isotherm equation. The constants  $1/n$  and  $\ln k_F$  can be calculated from the

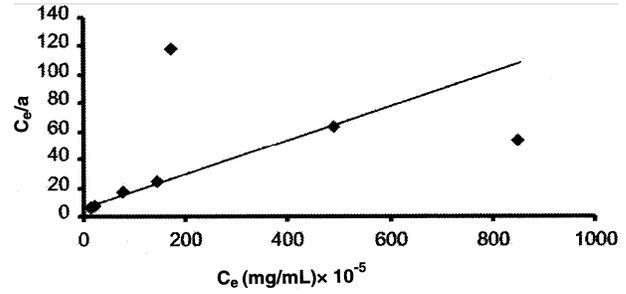


Fig. 5—Langmuir adsorption isotherms plot between adsorbed amount of  $\text{Cr}^{6+}$  ion and ratio of equilibrium concentration to adsorbed amount.

Table 2—Data showing  $R_L$  value for different metal ions concentration.

$R_L > 1$ , Unfavourable;  $R_L = 1$ , Linear;  $0 > R_L < 1$ , Favourable and  $R_L = 0$ , Irreversible

Sl. No.	Initial chromium ion concentration ( $C_o$ ) (mg/mL)	$R_L$
1	0.040	0.992
2	0.026	0.994
3	0.020	0.996
4	0.013	0.997
5	0.010	0.998
6	0.0067	0.998
7	0.0050	0.999

slope and intercept, respectively. A value of  $1/n$  between 1 and 10 represents beneficial adsorption. The calculated value of  $1/n$  is 2.33 and  $k_F$  value is  $1.949 \text{ mg/g}$ .

In the present case, therefore, the absorption equation may be written as

$$a = 1.949 C_e^{2.33} \quad \dots (8)$$

**Modified Freundlich isotherm**

Freundlich isotherm may be reduced to the modified Freundlich isotherm as given below:

$$\log \frac{a}{a_s - a} = \beta \log C_e + \log(A/a_s) \quad \dots (9)$$

where  $\beta$  and  $A$  are empirical constants which can be determined through linear regression analysis.

From the plot between  $\log a/(a_s - a)$  versus  $\log C_e$ , the values of  $\beta$  and  $A$  were calculated to be 2.6 and 14.62, respectively. It is clear from the numerical value of  $\beta$  that the distribution of  $\text{Cr}^{+6}$  ions is even over the active sites of the microspheres surfaces rather it is widely spread, thus indicating the hydrogenating of the microspheres surfaces<sup>33</sup>.

**Distribution coefficient**

The adsorption can also be quantified in terms of distribution coefficient,  $k_d$ , defined as the ratio of the

equilibrium concentration of the sorbed species to the equilibrium concentration of the species in solution. It is calculated from the following equation,

$$A = a_s k_d^\beta \quad \dots (10)$$

where,  $A$  is the measure of weighed average distribution coefficient and the parameter  $\beta$  describes the spread of the distribution coefficient about the average distribution coefficient ( $k_d$ ). The high value of  $k_d$  ( $1.034 \text{ mg g}^{-1}$ ) suggests a favourable distribution of  $\text{Cr}^{6+}$  ions. Similarly, the value of  $\beta$ , being greater than 1 indicates a higher spread of distribution coefficient<sup>34</sup> (Table 3).

#### Surface coverage

Another sorption isotherm<sup>35</sup> may also be given as

$$\log \theta/C = \log K + n \log (1-\theta) \quad \dots (11)$$

where  $\theta$  is the degree of surface coverage,  $n$  is the number of metal ion occupying sorption,  $K$  is equilibrium constant of adsorption and  $C$  is equilibrium metal ions concentration. A plot of  $\log \theta/C$  against  $\log (1-\theta)$  yields straight line as shown in Fig. 6. The values of  $K$  and  $n$  are also determined from the intercept and slope, respectively. Surface coverage is calculated by following equation.

$$KC = \frac{\theta}{\theta - C} \quad \dots (12)$$

On increasing the initial metal ion concentration the surface coverage on the biomass also increases until the surface is nearly fully covered with a monomolecular layer. The surface coverage ceases to vary significantly with concentration of the metal ion at high concentration and the reaction rate becomes independent of the metal ion concentration<sup>36</sup>.

#### Kinetics of adsorption

A common practice for studying the kinetics of the adsorption process is to monitor the change in concentration of the adsorbate solution at predetermined time periods.

The adsorbed amount of metal ions at different time intervals is determined and plotted against times as shown in Fig. 7. It is clear that the adsorbed amount of  $\text{Cr}^{6+}$  constantly increases with increasing time and then acquires a constant value because the rate of metal ion binding with microspheres is more at initial stage which gradually decreases and remains constant after an optimum adsorption.

#### Evaluation of $K_1$ and $K_2$

The kinetic model proposed by Bajpai *et al.*<sup>37</sup> may also be applied to a Langmuir type of adsorption process provided the adsorption increases linearly up to a definite time period.

$$\frac{1}{C} = \frac{k_1 t}{C_0} + \frac{1}{C_0} \quad \dots (13)$$

where  $C$  and  $C_0$  being the concentrations at time  $t$  and initial concentration of adsorbate solution respectively.

Table 3—Static and kinetic parameters for adsorption of  $\text{Cr}^{6+}$  ion onto biopolymeric microspheres.

Adsorption coefficient ( $K$ )	1500 ( $\text{mg}^{-1} \text{ dm}^3$ )
Adsorption capacity ( $a_s$ )	13.34 $\text{mg/g}^{-1}$
Separation factor ( $R_L$ )	0.03
Predicted sorption ( $k_F$ )	1.949 ( $\text{mg/g}$ )
Freundlich constant ( $1/n$ )	2.33
B	2.6
A	14.62
Rate constant for adsorption ( $k_1$ )	$0.98 \times 10^{-2}$ ( $\text{mg dm}^{-3} \text{ s}^{-1}$ )
Rate constant for adsorption ( $k_2$ )	$6.5 \times 10^{-6}$ ( $\text{mg dm}^{-3} \text{ s}^{-1}$ )
Lagergreen rate constant ( $k_{ad}$ )	$2.6 \times 10^{-4}$ ( $\text{mg g}^{-1} \text{ s}^{-1}$ )
Interparticle diffusion rate constant ( $k_p$ )	$2.6 \times 10^{-2}$ ( $\text{mg g}^{-1} \text{ s}^{-1/2}$ )
Pore diffusion constant ( $D$ )	$56.18 \times 10^{-10}$ ( $\text{cm}^2 \text{ s}^{-1}$ )
$k_d$	1.034 ( $\text{mg g}^{-1}$ )

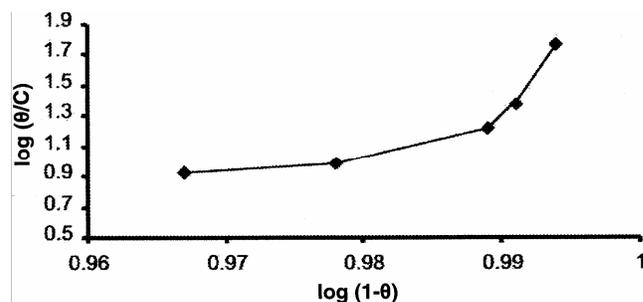


Fig. 6—Effect of concentration on the surface coverage for adsorption of  $\text{Cr}^{6+}$  onto microspheres.

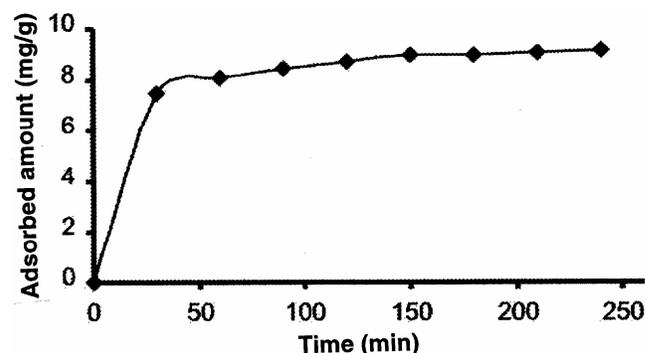


Fig. 7—Effect of contact time on the adsorbed amount for adsorption of  $\text{Cr}^{6+}$  ions onto microspheres.

Thus, a plot between  $1/C$  and  $t$  yields a straight line. From the slope of the plot the value of  $k_1$  has been calculated as  $0.98 \times 10^{-2} \text{ mgdm}^{-3} \text{ s}^{-1}$  (Table 3). Also as the adsorption constant ( $K=k_1/k_2$ ) is known the value of  $k_2$  may also be calculated<sup>38</sup>. The calculated value of  $k_2$  has been found to be  $6.5 \times 10^{-6} \text{ mg dm}^{-3} \text{ s}^{-1}$ .

#### Pseudo first order

The kinetics of sorption of heavy metal ions from wastewater have been studied using mostly pseudo first order given by Lagergreen<sup>39</sup>.

$$\frac{da}{dt} = K_{ad}(a_s - a) \quad \dots(14)$$

where  $a_s$  and  $a$  are adsorption capacities of adsorbent (mg/g) at equilibrium and at time  $t$ , respectively,  $k_{ad}$  is Lagergreen rate constant for pseudo first order adsorption. After integration and applying boundary conditions  $t = 0$  to  $t = t$  and  $a_s = 0$  to  $a_s = a_s$ , the integrated form of equation becomes<sup>40</sup>.

$$\log(a_s - a) = \log a_s - \frac{k_{ad}t}{2.303} \quad \dots(15)$$

A plot of  $\log(a_s - a)$  against  $t$  gives a straight line. The value of  $k_{ad}$  has been calculated to be  $2.6 \times 10^{-4} \text{ mg g}^{-1} \text{ s}^{-1}$ .

#### Intra particle diffusion

In the present study the biopolymeric beads are constantly agitated during the adsorption process, therefore, it is reasonable to assume that the rate is not limited by mass transfer from the bulk liquid to the beads external surface. One might then postulate that the rate-limiting step may be either film or interparticle diffusion. As they act one after the other, the slower of the two will be the rate determining step<sup>41</sup>.

The rate constant for intraparticle diffusion is obtained using the following equation

$$a = k_p t^{1/2} \quad \dots(16)$$

where  $k_p$  is the intra particle rate constant ( $\text{mg}^{-1} \text{ min}^{-1/2}$ ). Higher values of the intra particle rate constant illustrate an enhancement in the rate adsorption whereas larger values illustrate a better adsorption mechanism<sup>42</sup>. The value of  $k_p$  determined from the plot drawn between  $a$  and  $t^{1/2}$  as shown in Fig. 8 has been calculated to be  $2.6 \times 10^{-2} \text{ mg g}^{-1} \text{ s}^{-1/2}$ .

#### Pore diffusion co-efficient

The pore diffusion co-efficient for the interparticle transport of  $\text{Cr}^{+6}$  ions was calculated assuming

spherical geometry of microspheres by the following equation,

$$t_{1/2} = (0.03 r_o^2)/D \quad \dots(17)$$

where  $r_o$  is the radius of the microspheres,  $D$  is the pore diffusion constant, and  $t_{1/2}$  is the time for half-sorption<sup>43</sup>. The calculated value of  $D$  is found to be  $56.18 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ .

#### Effect of pH

The pH value of the solution is an important controlling parameter in the adsorption process as a small variation in pH influences both the adsorbent surface and ionic species of metal in water<sup>44</sup>. The pH affects the network of negative charge on the surface of the biosorbing cells and the chemistry of the walls, as well as physicochemistry and hydrolysis of the metal<sup>45,46</sup>. The effect of pH on the adsorbed amount of Cr(VI) ions has been investigated in the range 1.8 to 11.5 (Fig. 9).

Results clearly reveal that the removal of chromium (VI) ions from aqueous solution was more efficient with decreasing pH and was highest at pH 1.8.

The results may be explained on the basis of the charge developed over the biosorbent surfaces and chromium ions due to variation in pH of the solution.

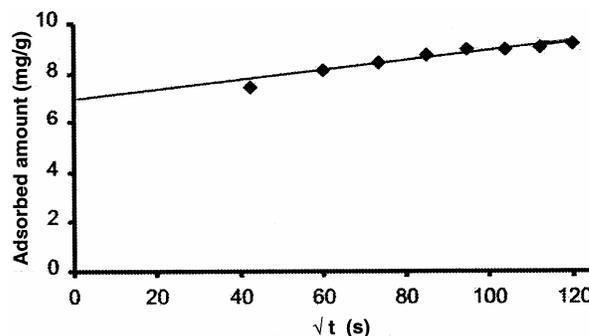


Fig. 8—A plot between the adsorbed amount and  $\sqrt{t}$  for adsorption of  $\text{Cr}^{+6}$  ions onto microspheres.

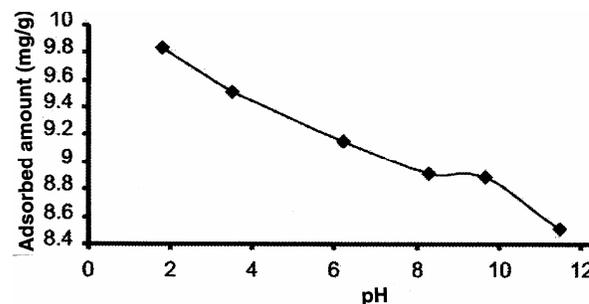


Fig. 9—Effect of pH on the adsorbed amount for adsorption of  $\text{Cr}^{+6}$  ions onto microspheres.

It is well known that the point of zero charge ( $pH$ ) of chitosan and gelatin are in the range 6.2 to 6.8 and 4.8 respectively. Here, below this  $pH$ , the biomass surfaces are positively charged while at the same time  $Cr(VI)$  ions form stable complexes such as  $Cr_2O_7^{-2}$ ,  $HCrO_4^{-2}$ ,  $HCr_2O_7^{-7}$ . Thus at lower  $pH$  values different anionic species of chromium adsorb preferentially on the positive charge active sites of biomass<sup>47</sup>.

Therefore, an optimum adsorption is noticed at  $pH$  1.8. However, upon further increasing the  $pH$  the biomass surface acquires increasing negative charge and due to the repulsion between the negative charge of biomass and metal ions, the adsorption decreases<sup>48</sup>.

#### Effect of temperature

Temperature exerts a significant influence on the adsorption of metal ions as a small change in temperature produces a large effect on interactive forces between metal ion and adsorbent. In the present work the effect of temperature on adsorption was studied in the range 5 to 80°C. It was observed that the extent of sorption of metal ion by the sorbent increased with increase in temperature up to 60°C and further increase in the temperature showed a reduction in biosorption<sup>49</sup> (Fig. 10). It has been known that higher temperature leads to higher affinity of metal for binding sites on the biosorbent. Energy of the system facilitates attachment of  $Cr(VI)$  to the cell surface<sup>50</sup>.

The decrease of biosorption capacity at higher temperature may be due to loss of active binding sites in the biomass<sup>51</sup>. Furthermore at higher temperature the binding force between microspheres and metal ions weakens and therefore the adsorption decreases.

The following thermodynamic parameters were calculated by using the equation<sup>52</sup>.

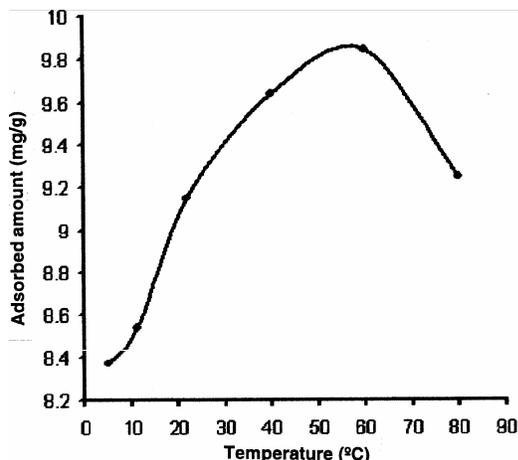


Fig. 10—Effect of temperature on the adsorbed amount for adsorption of  $Cr^{6+}$  ions onto microspheres.

(i) The standard free energy  $\Delta G^\circ$  (kcal/mol) was calculated by using the relation

$$\Delta G^\circ = -R T \ln K \quad \dots(18)$$

where  $K$  being the equilibrium constant of the adsorption process. The value of  $\Delta G^\circ$  has been calculated to be -4.28 kca/mol.

(ii) The apparent heat of reaction enthalpy  $\Delta H_o$  (k cal/mol) was estimated using equation

$$\ln k_1/k_2 = \Delta H^\circ/R (1/T_1 - 1/T_2) \quad \dots(19)$$

The value of  $\Delta H^\circ$  has been calculated to be 9.09 kcal/mol. The positive value of  $\Delta H^\circ$  suggest for the endothermic nature of adsorption process.

(iii) The entropy  $\Delta S^\circ$  (kcal/mol) of the adsorption process was calculated using the following relationship

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad \dots (20)$$

The value  $\Delta S^\circ$  was found to be 0.045 kcal/mol which indicates that the adsorption process is spontaneous in nature.

#### Solid liquid ratio

The solid to liquid ratio is an important parameter for adsorption. A change in solid to liquid ratio changes the number of active site available on the solid but also brings about a change in the number of ions of solute invading the solid surface for adsorption. In the present study the solid to liquid ratio has been varied in two ways: (i) The solid to liquid ratio was varied by increasing the volume of potassium dichromate solution of define concentration from 6 to 25 mL keeping mass of the adsorbent constant as shown in Fig. 11a. (ii) Solid to liquid ratio may also be varied by increasing the amount of adsorbent from 0.025 to 0.20 g for the fixed volume of metal ion solution (Fig. 11b).

The results depicted in Fig. 11a and 11b clearly reveal that in the former case adsorbed amount of  $Cr(VI)$  ion increases when solid-liquid ratio decreases from 3.34 to 0.8 while on the contrary, in the later case a decrease in the adsorbed amount is noticed with increasing solid to liquid ratio in the range of 2 to 10. This observation may be explained as below.

When the volume of metal ion solution increased keeping the amount of adsorbent as constant, the increase observed in the amount of adsorbed metal ions may be explained by the fact that as the volume

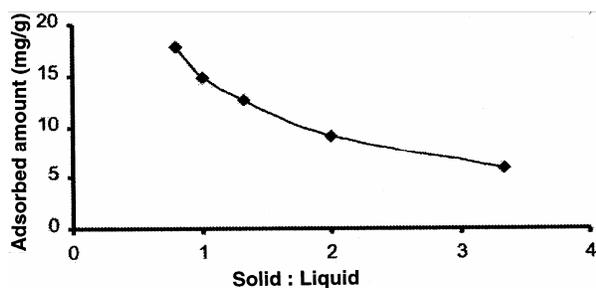


Fig. 11—(a): Effect of solid to liquid ratio (by varying the volume of Cr<sup>6+</sup> ions solution of definite concentration) on the adsorbed amount for adsorption of Cr<sup>6+</sup> ions onto microspheres.

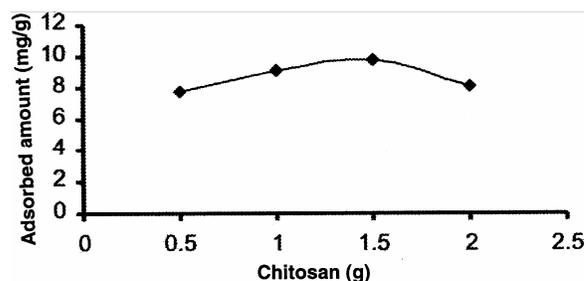


Fig. 12—Effect of chitosan on the adsorbed amount for adsorption of Cr<sup>6+</sup> ions onto microspheres.

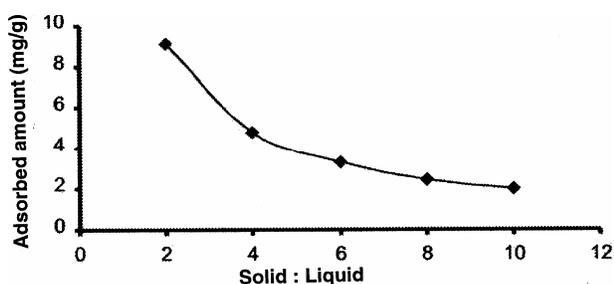


Fig. 11—(b): Effect of solid to liquid ratio (by varying the amount of microspheres) on the adsorbed amount for adsorption of Cr<sup>6+</sup> ions onto microspheres.

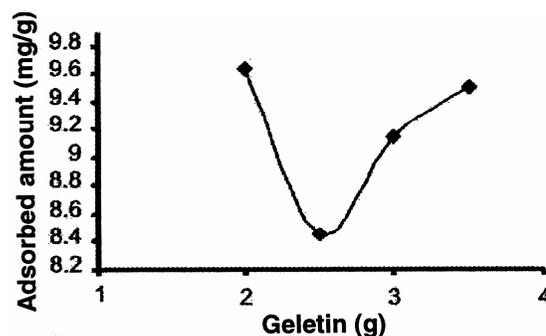


Fig. 13—Effect of gelatin on the adsorbed amount for adsorption of Cr<sup>6+</sup> ions onto microspheres.

of metal ions solution increases, the mobility of both metal ions and microspheres increases and thus get more space for rapid interaction. On the other hand on increasing the amount of adsorbent while keeping volume of metal ion solution constant, the adsorbed amount (per gram of the adsorbent) decreases due to crowding of adsorbent and, consequently, increase in competition between the active sites of adsorbent for adsorbing metal ions.

#### Effect of composition

##### Effect of chitosan

In the present case when the amount of chitosan was varied in the range 0.5 to 2.0 g adsorption of Cr (IV) ion varies as shown in Fig. 12. The figure clearly shows that with increasing concentration of chitosan the adsorption of chromium ions also increases and then beyond a definite concentration the adsorption decreases. The results may be explained by the fact that amino sugar of chitosan and chitin are major effective binding sites for metal ions and form stable complex with metal ions by co-ordination. The amino group (-NH<sub>2</sub>) on chitosan has been suggested as the active site for metal ion co-ordination because the lone pair of electrons present on the nitrogen can establish dative bonds with transition metal ion<sup>53</sup>.

Thus, with increasing chitosan content in the microspheres the adsorption of metal ions also increases, whereas beyond an optimum concentration of chitosan (1.5 g), the adsorption decreases. This may be due to the fact that at higher chitosan concentration diffusion of Cr (VI) ions may be hindered due to compactness and shrinkage of the pore size of the microspheres.

##### Effect of gelatin

In case of gelatin the amount was varied in the range 2.0 to 3.5 g and its influence on the adsorption of metal ions was noticed. The results shown in Fig. 13 indicate that adsorption of Cr (VI) decreases with increasing gelatin concentration up to 2.5 g and then increase in gelatin concentration results in an increase in the adsorption. The decrease in the adsorption could be due to the clogging of the biomass. Further increase in the amount of gelatin brings about an increase in removal capacity due to the greater availability of exchangeable sites for the ions<sup>54</sup>.

##### Effect of yeast

In the present case the amount of yeast was varied in the range 1.0 to 2.5 g. The results are shown in Fig 14 which reveals that adsorption of Cr (VI) ions decreases with increasing yeast concentration up to

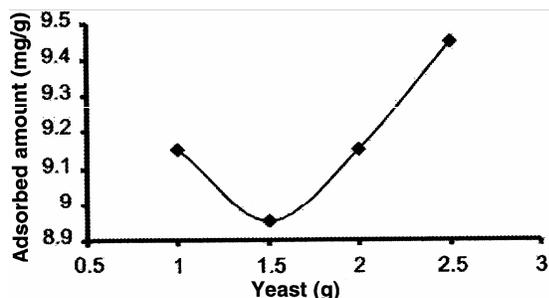


Fig. 14—Effect of yeast on the adsorbed amount for adsorption of  $\text{Cr}^{6+}$  ions onto microspheres.

1.5 g and then upon further increase in yeast concentration the adsorption decreases. The results may be explained by the fact as the yeast concentration increases the volume fraction of the polymer in the microspheres also increases which causes the microspheres to become more dense. However, after certain limit as yeast concentration in the polymer is increased and more active sites become available for metal ion adsorption this consequently results in an enhanced removal.

### Conclusions

Biosorption of chromium from aqueous solution using ternary microspheres (152  $\mu\text{m}$ ) of yeast, gelatin, and chitosan as adsorbent was studied. FTIR spectra show that the OH,  $>\text{C}=\text{O}$ , amine groups are the main functional groups of the adsorbent which are responsible for binding of chromium ions onto the surface. The adsorption of Cr(VI) ions onto the water-swollen microspheres increases with increasing initial metal ion concentration in the range 0.0050 to 0.040 mg/mL. The absorbed amount attains nearly constant values at definite contact time of 4 h. The Freundlich and Langmuir adsorption models were applied for mathematical description of biosorption equilibrium data. The present results demonstrate that the Langmuir model fits fairly well than the Freundlich model to the adsorption equilibrium data in the examined concentration range. The arrival of plateau is further confirmed by surface coverage concentration plot, which also exhibits more than 90 percent coverage. The pH of the solution when varied in the range 1.8 to 11.5 the adsorption is found to decrease. It is also noticed that an optimum adsorption occurs in acidic medium. Adsorption is also found to increase upto to 60°C and at much higher temperature it falls.

The adsorption of Cr(VI) ions exhibits a significant change with changing concentration of the

biopolymer constituents of the microspheres. It is observed that at definite concentrations of chitosan, gelatin and yeast the adsorption becomes optimum.

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