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Microbial sorption studies for removal of trivalent chromium from model tanning bath

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Abstract: Out of the industrial waste streams/effluents entering in the aquatic system containing metallic species, tanneries release high amounts of chromium, an anthropogenic pollutant because of use of basic chromium sulphate in the tanning processes. Trivalent chromium, Cr(III) is the targeted ionic species for removal by biosorption on a fungal species in this work, as the technique has inherent merit of easy adsorbent regeneration and lower capital costs. The study involves the use of *Aspergillus niger* (*A. niger*), to remediate chromium from a model tanning bath with Cr(III) concentration of 500 mg L^{-1}. The fungal species was grown in Czapek Dox media at pH 2.5 and 35^{o}C temperature and its biomass was used in various forms such as live, autoclaved and alkali treated. With 1% (w/v) alkali treated biomass, the biosorption of chromium reached a maximum of 91% for a feed concentration of 500 mg L^{-1} in 2 h time at pH 2.5, temp 35^{o}C and A/R (adsorbent : solution volume) ratio of 1/100. The lower biosorption of metal (42 - 44%) was observed with live and autoclaved biomass. The biosorption of chromium (III) on the fungal biomass was explained with various isotherms and fitted to the kinetic model involving first order expression. The study focuses on establishing the mechanism of bioremediation of chromium on *A. niger*.

Introduction

Rapid industrialization coupled with exponential growth in population has led to many fold increase in emanating toxic heavy metals in environment. Heavy metals like mercury, cadmium, lead, nickel, and chromium are toxic even in extremely minute quantities [1, 2, 3]. Of these, chromium is considered as an anthropogenic pollutant produced from industrial units viz., electroplating, leather tanning, metal finishing, chemical industries, and many others [4]. Chromium exists in several oxidation states out of which Cr(III) and Cr(VI) are most stable. Cr(III) is toxic at higher concentration with its permissible limits of 0.05 and 0.1 mg L^{-1} concentration in potable and tannery effluents respectively [5,6,7,8].

Physicochemical method such as reduction and precipitation, reverse osmosis, ion exchange and activated carbon adsorption suffers from several constraints which include incomplete metal removal, high reagent consumption and generation of toxic sludge [9,10]. The application of algae, fungi and bacterial biomass for removal of metal ions (biosorption) is poised to emerge as a potential alternative to the conventional method [11,12,13,14]. The major advantage of biosorption is its *in-situ* operability for industrial process operations. The technological merit of this process lies in the ability of negatively charged cell surface of microorganisms to bind the metal cations [15,16,17]. The interaction of metallic ions with microbe cell surface depends not only on the nature of biosorbent used but also on the solution chemistry of the metal to be removed [18,19,20]. The solubility diagram [21] of chromium in water at 25^{o}C is given in **Figure 1**. It is widely known that the most stable valence state of chromium, in aqueous media, is the trivalent species. Chromium exists in its trivalent form predominantly at lower pH. As the pH rises, Cr(III) precipitates as $Cr(OH)_3$.

In most previous studies, biosorption of chromium was investigated with the synthetic solutions without any compositional similarity to the actual stream/effluent. Whereas, the present study is based on the experiments mostly conducted at pH 2.5 unless stated otherwise [22], containing all the ingredients as that obtained in actual stream, which has the pH in the range 2.0-2.5. A pure culture of *Aspergillus niger* grown in Czapek Dox broth was adapted on Cr(III) in the

range 100-1000 mg L^{-1} at 2.5 pH and 35°C temperature and was examined for biosorption. The biomass of the adapted species was pre-treated also and subsequently used for the Cr(III) uptake.

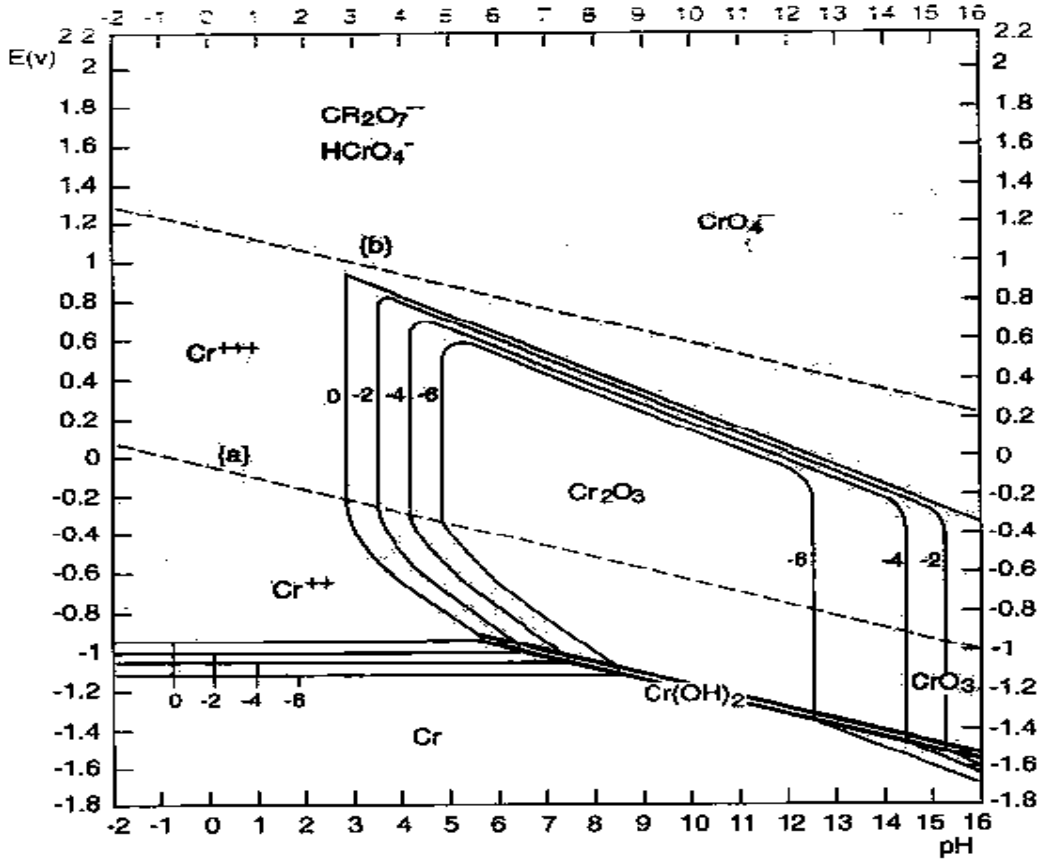

Fig. 1: Pourbaix diagram of chromium in water at 25°C, Conc.=1M [21]

Materials and methods

Composition of tanning bath: The model tanning bath contained Cr(III) with the following composition: SO_4^{2-}–12.0 g L^{-1}, C– 1.8 g L^{-1}, Cl^- - 60 g L^{-1}, Cr(VI)- 0.005 g L^{-1}, Fe(III) - 0.1 g L^{-1}, Al(III) - 0.15 g L^{-1}, pH 2-2.5. The pH of the solution was maintained to 2.5 by using 0.1 M H_2SO_4 and 0.1 N NaOH and varying concentration of Cr(III) ion (solution) was prepared from the stock solution.

Microorganism and biosorption experiments: Pure culture of *Aspergillus niger* (MTCC-281 obtained from IMTECH, Chandigarh) was cultivated in Czapek Dox broth [8,17] (Composition: Sucrose - 30 g L^{-1}, Sodium Nitrate - 3.0 g L^{-1}, Di-potassium Phosphate -1.0 g L^{-1}, Magnesium Sulphate - 0.50 g L^{-1}, Potassium Chloride - 0.50 g L^{-1}, Ferrous Sulphate - 0.01 g L^{-1}). Experiments for production of *A. niger* biomass was carried out using Czapek-Dox medium (200 mL in 500 mL volumetric flask) with the addition of 1 percent (volume per volume; 2×10^7 spores mL^{-1}) inoculum, pH 2.5, agitated at 120 rpm, and incubated at 35°C. The biomass was adapted over a wide range of Cr(III) concentration (100-1000 mg L^{-1}) at 35°C and 2.5 pH. The fully grown biomass was sonicated [*Model*- SONICS™, Vibracell] to release electro-statically bound Cr(III) on cell surfaces and centrifuged at 10,000 rpm for 10 min. to separate the biomass from the solution. The biomass settled after centrifugation was further air dried for 24 h (total 6.8 g of biomass L^{-1} of culture media) and used in biosorption experiments.

Fungal strain (100 mg Cr(III) L^{-1} adapted biomass) was used in different forms in the biosorption studies viz., live, autoclaved and alkali-treated. The pre-treatment was done as follows:-

a) Live biomass: Fungal cells adapted on Cr(III) was filtered and washed several times with distilled/deionised water so as to free it from the media components. It was air dried for 24 h and 1.0 g biomass was used for 100 ml of tanning bath.
b) Autoclaved biomass: Known aliquot of Cr(III) adapted *A. niger* was taken in excess and autoclaved at 1.07 bar pressure (15 psi) and 121^{o}C temperature for 15 min, then it was filtered and washed several times with distilled/deionised water to free the biomass from ionic components of media. The biomass obtained was air dried for 24 h; 1% (w/v) (1 g 100 ml^{-1} of solution) of this was used in the experiments [19,20].
c) Alkali treated biomass: The adapted fungal species were boiled in 50 ml of 0.5 N NaOH for 15 min, filtered and washed several times with distilled/deionised water. Washing with deionised water was meant to bring down the pH to neutral range. It was then air dried for 24 h and 1.0 g of this biomass was used per 100 ml of tanning bath [19,20].
Batch experiments were carried out in Erlenmeyer flasks by adding known amount of fungal biomass in different forms in 500 mg L^{-1} Cr(III) solution under rotary shaker. Samples drawn at pre-determined time intervals were filtered using Whatman No.42 filter paper and diluted in HCl for estimation of Cr(III) ions by AAS (*Model*- GBC-980™). The uptake of Cr(III) by the sorbent was then calculated by the equation [23-27] from the difference between the C_i {initial Cr(III)} and C_f {final Cr(III)} at specified time interval.

$$q_e = \frac{V(C_i - C_f)}{m} \tag{1}$$

Where q_e is the Cr(III) uptake by biomass (mg g^{-1}), V is the Cr(III) solution volume in L and m is the weight of biomass in g.

Evaluation of isotherms and kinetics in biosorption: The experimental results obtained for the biosorption of chromium on alkali treated biomass of *A. niger* at pH 2.5 and 35^{o}C temperature were analyzed using different isotherms [27]. *Langmuir sorption model* assumes that the uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction with the sorbed species. The model can be represented in the linearised form as:-

$$\frac{1}{q_e} = \left[\left(\frac{1}{K_1.q_m}\right)\left(\frac{1}{C_e}\right)\right] + \left[\frac{1}{q_m}\right] \tag{2}$$

Where,
C_e = equilibrium concentration of metal in solution (mg L^{-1})
q_e = amount of metal sorbed on the surface at equilibrium.
K_l = equilibrium constant related to the affinity of the binding sites for the metal or the Langmuir constant.
q_m = the biosorption capacity (maximum amount of metallic ion sorbed per unit mass of sorbent)

Whereas, *Freundlich model* assumes that the uptake or sorption of metal ions occurs on a heterogeneous surface by monolayer sorption and is described as:

$$q_e = K_f(C_e)\frac{1}{n} \tag{3}$$

$$\log(q_e) = \left(\frac{1}{n}\right)\log(C_e) + \log K_f \tag{4}$$

Terms in the equation carry the meaning as described above. The K_f and n are Freundlich constants that can be related to the biosorption capacity and intensity respectively. The plot of log q vs *log Ce* should give a straight line with a slope of *1/n* and intercept of *log k*.

Dry *A. niger* samples, before and after metal cation biosorption, were glued onto 10 mm diameter metal mounts and coated with gold under vacuum in an argon atmosphere. The coated samples were put in to a JEOL JSM-5400 SEM/ EDS unit, and different sections in the samples were examined. The voltage used was 10 keV. This technique was used to examine the fungal cell surface. Scanning electron microscopy was used to examine samples of *A. niger* biomass, both before and after metal binding.

Results and discussion

Adaptation of A. niger on Cr (III): Fungus grown in Czapek Dox medium at pH 2.5 and 35°C were adapted to Cr(III) ranging from 100-1000 mg L^{-1} rendering the cellular metabolism to increase its affinity for that ionic species. **Figure 2 (a-d)** shows the microscopic observation of fungal cells which infers the growth of biomass and also indicates successful adaptation of *A. niger* upto 1000 mg L^{-1} in 96 h. The biomass grew to the concentrations of 3.8 and 1.6 g L^{-1} for 100 and 1000 mg L-1 Cr(III) adapted sets, respectively. The adapted masses in different forms were then used for biosorption experiments.

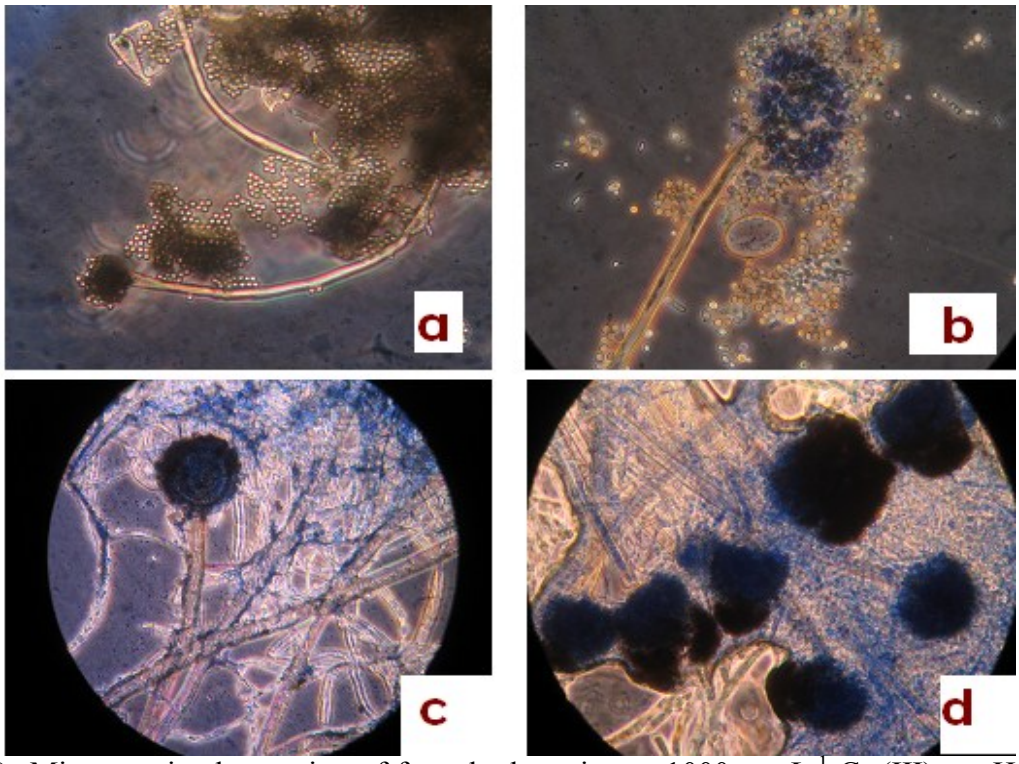

Fig. 2(a-d): Microscopic observation of fungal adaptation to 1000 mg L^{-1} Cr (III) at pH = 2.5 and 35°C (1000X) (**a** – *A. niger* adapted in 24 h, **b** – adapted in 48 h, **c** – adapted in 72 h and **d** – adapted in 96 h)

Effect of pH of bio-sorption of chromium (III): Live *A. niger* biomass (1% w/v) was inoculated at different pH (pH 2.0 - 5.0) with 500 mg L^{-1} of Cr(III) in the tanning bath. As shown in **Figure 3**, biosorption efficiency was low at pH 2.0, which increased with increase in pH from 2.5 to 4.5 with almost similar results (45 - 47%). The sorption of the metal was low at still higher pH (5.0). The effluents of the tanning waste streams [24] have chromium predominantly in Cr(III) state in acidic conditions.

Low uptake of chromium at lower pH is because of competition of proton (H_3O^+) with the trivalent chromium [18]. The predominant species in the moderate pH range between 2.0 and 5.0 are $CrOH^{2+}$ and $Cr(OH)_2^+$. However, chromium forms increased amount of $Cr(OH)_3$ at higher pH. Therefore, the decrease in chromium uptake by the biomass is attributed to the sorption of $Cr(OH)_3$ species from the solution at pH above 4.5. Thus, further experiments for fungal adaptation and biomass production for biosorption studies using tanning bath were carried out at pH 2.5.

Biosorption of Cr(III) by different forms of biomass: Uptake of chromium versus time was examined for aqueous feed of 500 mg L^{-1} Cr(III) using different forms of fungal strain (*A. niger*). Results presented in **Figure 4** show that the alkali-treated fungus was most effective for removal of Cr(III) from the solution. A maximum biosorption of 91% (45.5 mg g^{-1}) was observed with alkali

treated bio-mass as compared to 68% (34 mg g^{-1}) and 61% (30.5 mg g^{-1}) biosorption using autoclaved and live biomass in 2 h.

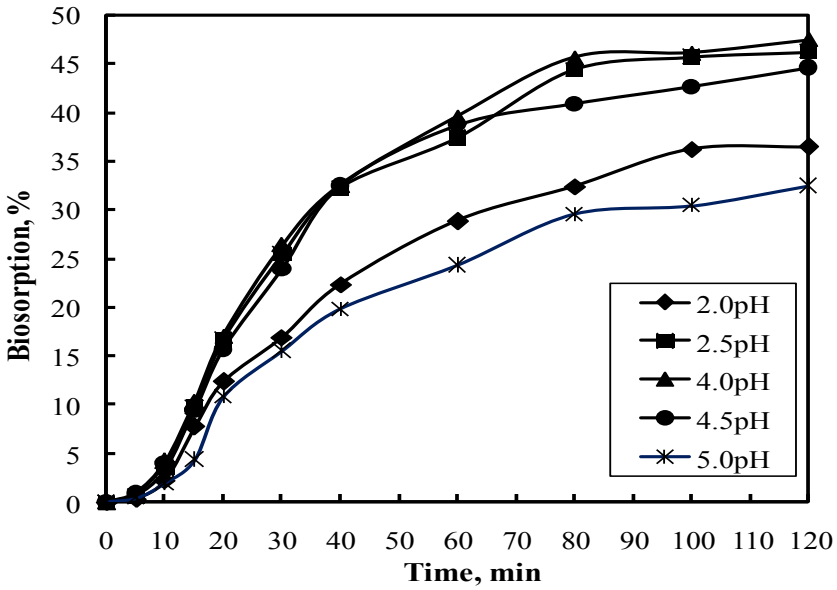

Fig. 3: Effect of pH on biosorption of 500 mg L^{-1} Cr(III) solution with live *A.niger* [1% (w/v) biomass, 35°C]

The higher uptake with alkali-treated material might be attributed to the exposure of chitin and chitosan content of the fungus cell wall, after alkali treatment and release of polysaccharide in the solution to form metal complexes. Sodium hydroxide appears to remove amorphous polysaccharides from the cell wall, generating accessible space within the *ß*-glucan-chitin skeleton thus permitting metal ion complexation on the surface [19,20]. A lower biosorption with live and autoclaved biomass exhibited reduced capacity of the binding sites for chelating ions. This reduction is attributed to the saturation of reactive sites on the cell wall. Living cells are likely to be more sensitive to metal ion concentration and adverse operating conditions of pH and temperature [19]. Furthermore, a constant nutrient supply is required for living cells. The non-viable cells frequently exhibit a higher affinity for metal ion uptake as compared to the viable (live species) biomass due to the absence of competing protons produced during metabolism [20].

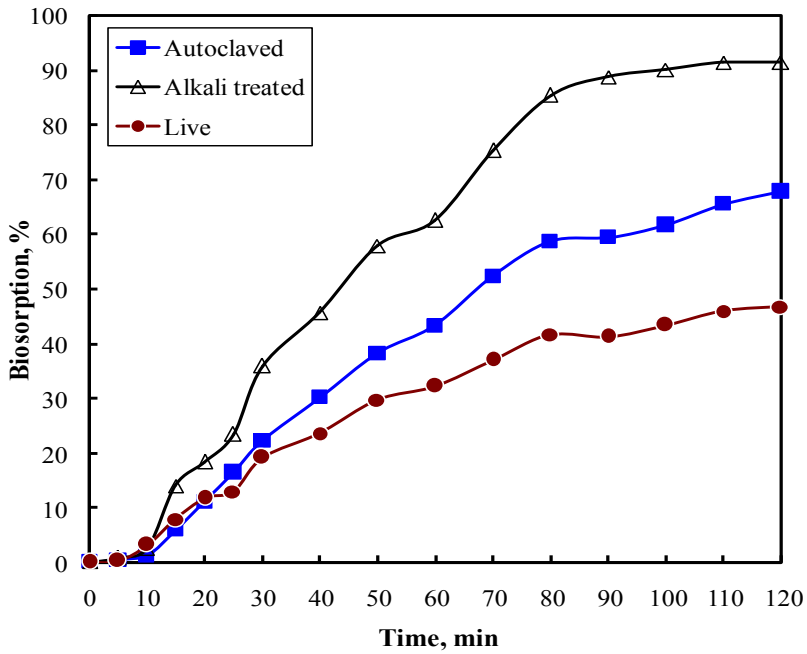

Fig. 4: Biosorption of Cr(III) by various forms of *A.niger* at pH 2.5 and 35°C temp.

Adsorption isotherms: The equilibrium data on sorption of trivalent chromium at pH 2.5 and 35°C was plotted for evaluating the Langmuir isotherm (**Fig. 5**) with less fit and very low value of K_1 for 500 mg L^{-1} feed (**Table 1**) indicating limited physical interaction of *A. niger* with chromium (III). The equilibrium data on Cr(III) sorption at pH 2.5 was also applied on Freundlich isotherm (**Fig. 6**).

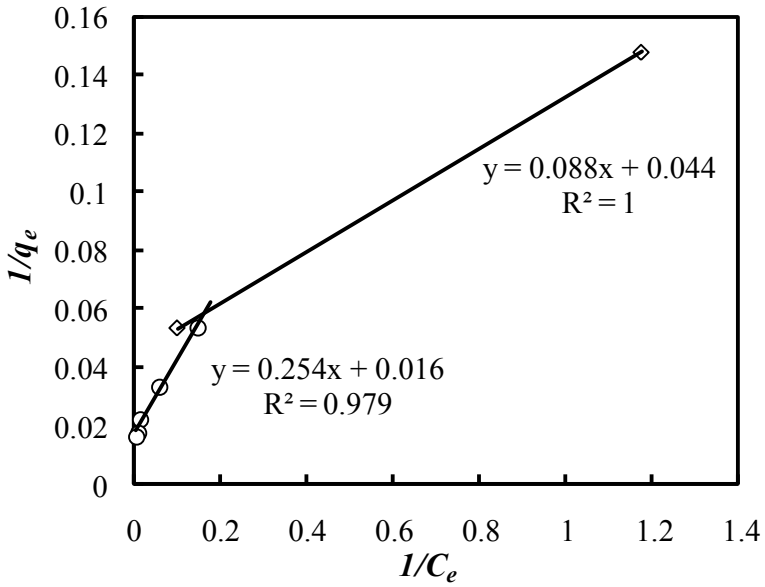

Fig. 5: Langmuir Isotherm for 500 mg L^{-1} Cr (III) biosorption on alkali treated *A. niger*

In this case, the sorption data showed good fit (R^2 value close to unity) to the isotherm (**Table 1**) with a break in the straight line thus giving two straight lines instead of one. The presence of two straight lines with different slopes viz. 0.254 and 0.088 clearly indicate the possibility of two distinct binding sites. It may thus be assumed that the interaction of the positively charge chromium ion with the negatively charged functional groups such as carboxyl, amine, hydroxyl, phosphate and sulphydryl in the cell wall, gives rise to the sorption process by involving ionic, physical and chemical forces [28,29]. The exact prediction of the group binding the metal ion is difficult because of presence of multifunctional groups in the cell wall, different metal ions in the aqueous feed and complex chemistry of the metals. The value of K_f is found to be very high and so is the interaction intensity ($1/n$ = 2.7) indicating strong chemical complexation of Cr(III) on to the functional groups of *A. niger*.

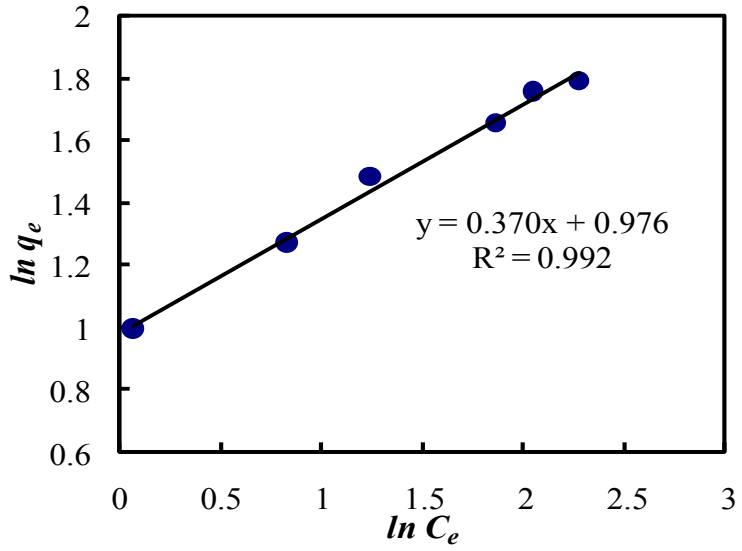

Fig. 6: Freundlich isotherm for Cr (III) biosorption on alkali treated *A. niger*

Table 1: R^2 values and equilibrium constants obtained for Langmuir and Freundlich isotherm for biosorption of 500 mg L^{-1} Cr(III) concentration

Freundlich Model			Langmuir Model			
R^2	K_f	*1/n*	R^2a	R^2b	K_l a	K_l b
0.992	9.47	2.7	0.979	1	0.0632	0.018

Kinetics of Cr (III) biosorption: About 1.0 g of biomass was taken for sorption of metal [100 mL solution of 500 mg L^{-1} Cr(III)]. In order to study the kinetics of sorption, Lagergren expressions, (first and second order) were considered [27].

The Lagergren *first order rate expression* is generally described as

$$\left(\frac{dq}{dt}\right) = k_1(q_e - q) \tag{5}$$

Where, q_e and q are the amounts of Cr(III) ion, (mg g^{-1}) adsorbed on the sorbent at equilibrium and at time t, respectively and k_1 is the rate constant. Integrating and applying the boundary conditions, t = 0 and q = 0 to t = t and $q = q_e$ at maximum sorption, equation (5) takes the form:

$$\log(q_e - q) = \log(q_e) - \left(\frac{k_1}{2.303}\right)t \tag{6}$$

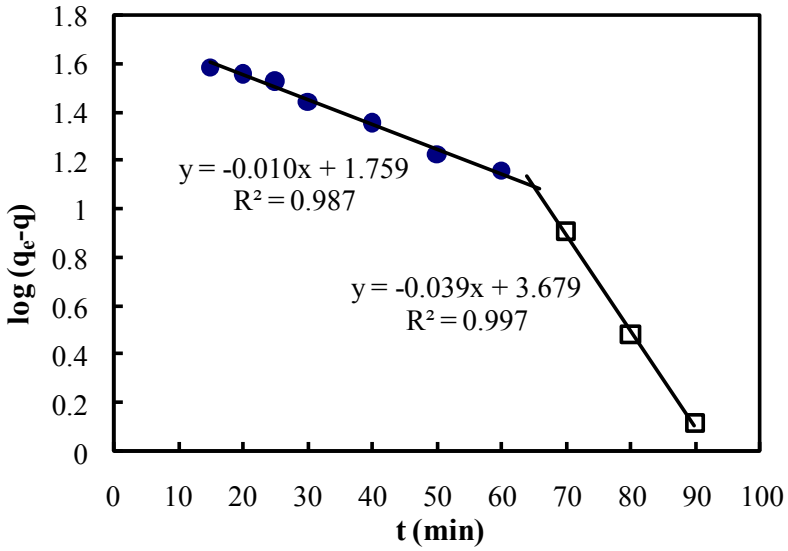

Fig. 7: First order kinetics of alkali treated biomass for the sorption of Cr (III)

Sorption data were also fitted to the *second order expression* represented as:

$$\left(\frac{dq}{dt}\right) = k_2(q_e - q)^2 \tag{7}$$

Where, k_2 is the rate constant of second order sorption (g mg^{-1}.h). Integrating and applying boundary conditions t = 0 and q = 0 to t = t and $q = q_e$, equation (7) can be presented in the linear form as

$$\left(\frac{t}{q}\right) = \left(\frac{1}{h}\right) + \frac{t}{q_e} \tag{8}$$

Where, $h = k_2 q_e^2$ is the initial sorption rate.

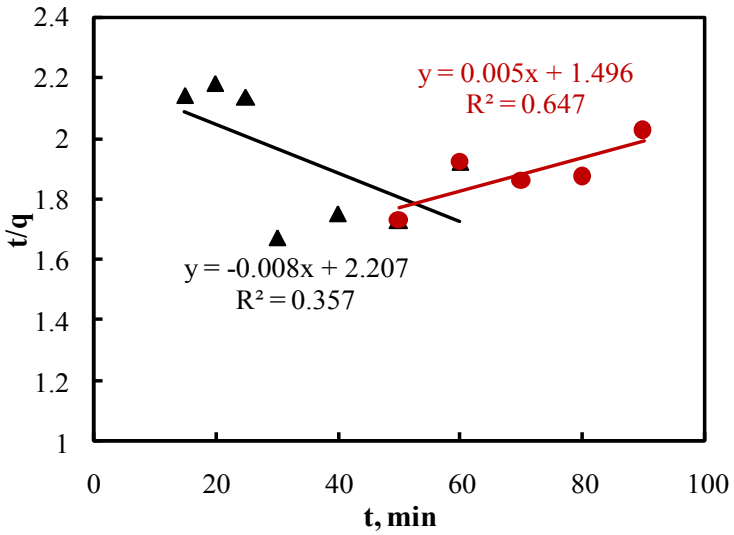

Fig. 8: Second order kinetics of alkali treated biomass for the sorption of Cr (III)

The data on the kinetics of first order reaction (**Fig. 7**) showed two distinct stages of biosorption. The time period from 0-60 min has the R^2 value 0.987 and the second stage has a R^2 value of 0.997 (**Table 2**). The whole biomass was not properly wetted initially up to 60 min thus showing low kinetic rate (k_1^a) (2.34×10^{-2}). After 60 min., the sorption rate (k_1^b) increased significantly indicating the use of almost complete surface for metal uptake. **Figure 8** shows poor fit of data to second order kinetic model. The high values of k_1 (k_1^a & k_1^b) and relatively very lower values of k_2 showed that the biosorption of chromium (III) on *A. niger* follows first order kinetics at room temperature.

Table 2: R^2 values and rate constants for 500 mg L^{-1} Cr(III) concentration

1st order		2nd order		
R^2_a	k_1^a	R^2_a	k_2^a	h
0.987	2.34×10^{-2}	0.357	3.055	0.64
R^2_b	k_1^b	R^2_b	k_2^b	h
0.997	8.22×10^{-2}	0.647	1.37×10^{-3}	2.88

Intraparticle diffusion model: The data was also fitted to the intraparticle diffusion equation [30] which can be described as:

$$q_t = k_i t^{0.5} \quad (9)$$

Where k_i is the intraparticle diffusion rate constant (mg g^{-1}). q_t is the amount of adsorbed Cr(III) concentrations on adsorbent (mg g^{-1}) at equilibrium and at time t.

The plot of q_t versus $t^{0.5}$ may present multilinearity. With the <0.149 mm (+100 mesh) particle size of *A. niger* biomass, three shapes of the straight line are seen (**Fig. 9**): the first shape portion may be attributed to the external surface biosorption stage due to the extremely low particle size as reported [30]. The second shape is the gradual biosorption stage, where the intraparticle diffusion may be the rate-controlling. The third shape is the final equilibrium stage where the intraparticle diffusion starts to slow down due to extremely low solute concentrations in the solution [31]. When the adsorption has reached saturation at exterior surface, the Cr(III) ions might have entered in the pores within the alkali treated biomass of *A. niger* for interaction of interior surface of fungal biomass [30].

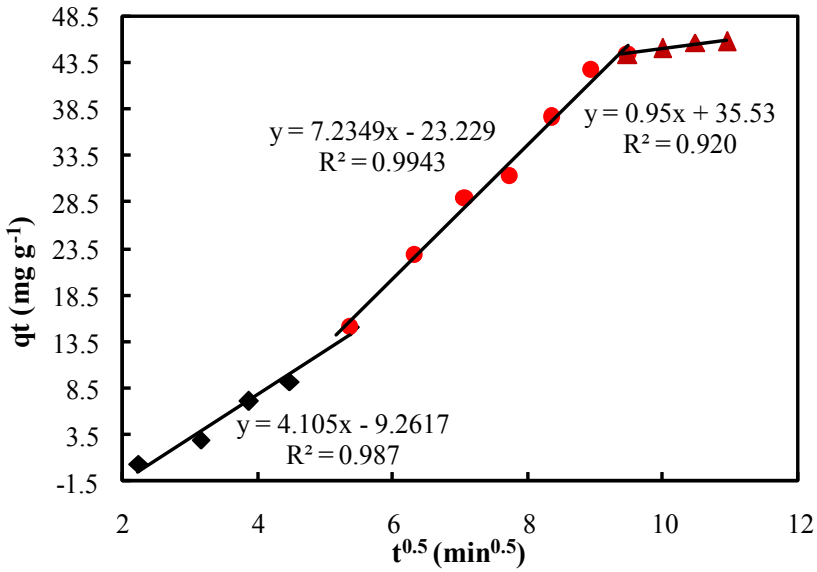

Fig. 9: Intraparticle diffusion kinetics at pH 2.5 and 35°C from 500 mg L^{-1} Cr(III) model tanning solution.

The intraparticle diffusion rate constants (k_i1, k_i2 and k_i3) and R^2 values are given in **Table 3**. If intraparticle diffusion rate constants are compared, it is easy to see that:

k_i1 (first stage) < k_i2 (second stage) > k_i3 (third stage)

Table 3: Intraparticle diffusion constants and R^2 values at <0.149 mm particles

1st stage		2nd stage		3rd stage	
k_i1	4.105	k_i2	7.23	k_i3	0.95
$R^2$1	0.987	$R^2$2	0.994	$R^2$3	0.920

The variation in biosorption rate may depend upon the kinetics of metal uptake. As mentioned above, the biosorption followed first order kinetics in two stages: first stage was from 0-60 min of time and second one was from 60-90 min of time period. A look at the intraparticle diffusion kinetics also showed a similar trend. In the first stage, the external surface interaction is seen in 0-60 min whereas the second stage the intraparticle diffusion is apparently followed for the period 60min - 90 min. The low sorption beyond 90 min may be accounted for decreased rate of metal uptake as discussed above.

SEM-EDS quantification for biosorption: An electron micrograph of alkali treated *A. niger* biomass, both before and after Cr(III) binding is depicted in **Figure 10 (a,b)**. After completion of the metal binding (**Fig. 10b**), obvious morphological changes were seen in the cell well matrix, such as shrinking and sticking of layers. The morphological changes in the cell wall electron micrographs after cation adsorption were very small, as compared to the structure in Fig.10a. EDS analysis indicates Cr(III) bound on cell surface based on the presence of Cr(III) detected with respect to its intensity (by Kα orbital), which can be referred as $Cr(OH)_3$ precipitates under the above experimental conditions.

Conclusions

- *Aspergillus niger* adapted over chromium (III) and used in different forms, are found suitable for removing Cr(III) from model tanning bath. Alkali treated biomass is observed to be a better adsorbent than live and dead fungus for Cr(III).
- For the alkali (NaOH) pretreated biomass, a maximum biosorption of 91% for a feed concentration of 500 mg L^{-1}, at pH 2.5 in 2 h time. The high chromium(III) uptake (45.5 mg g^{-}

[1]) on the alkali treated biomass is attributed to the exposure of available binding sites, due to the release of polysaccharides for binding Cr(III) chemically through complexation.

- The chromium (III) sorption on the bio-mass follows Langmuir isotherm. The near to unity value of correlation coefficient expresses a good fit to Freundlich isotherm further indicating the chemical complexation of Cr(III) with the functional group on fungal surface.
- Sorption of Cr(III) on the alkali treated bio-mass of *A. niger* follows first order kinetics. The adsorption of chromium is characterized by intraparticle diffusion with three distinct stages and the intraparticle diffusion being the rate controlling process. The pattern was corroborated with SEM-EDS quantification.

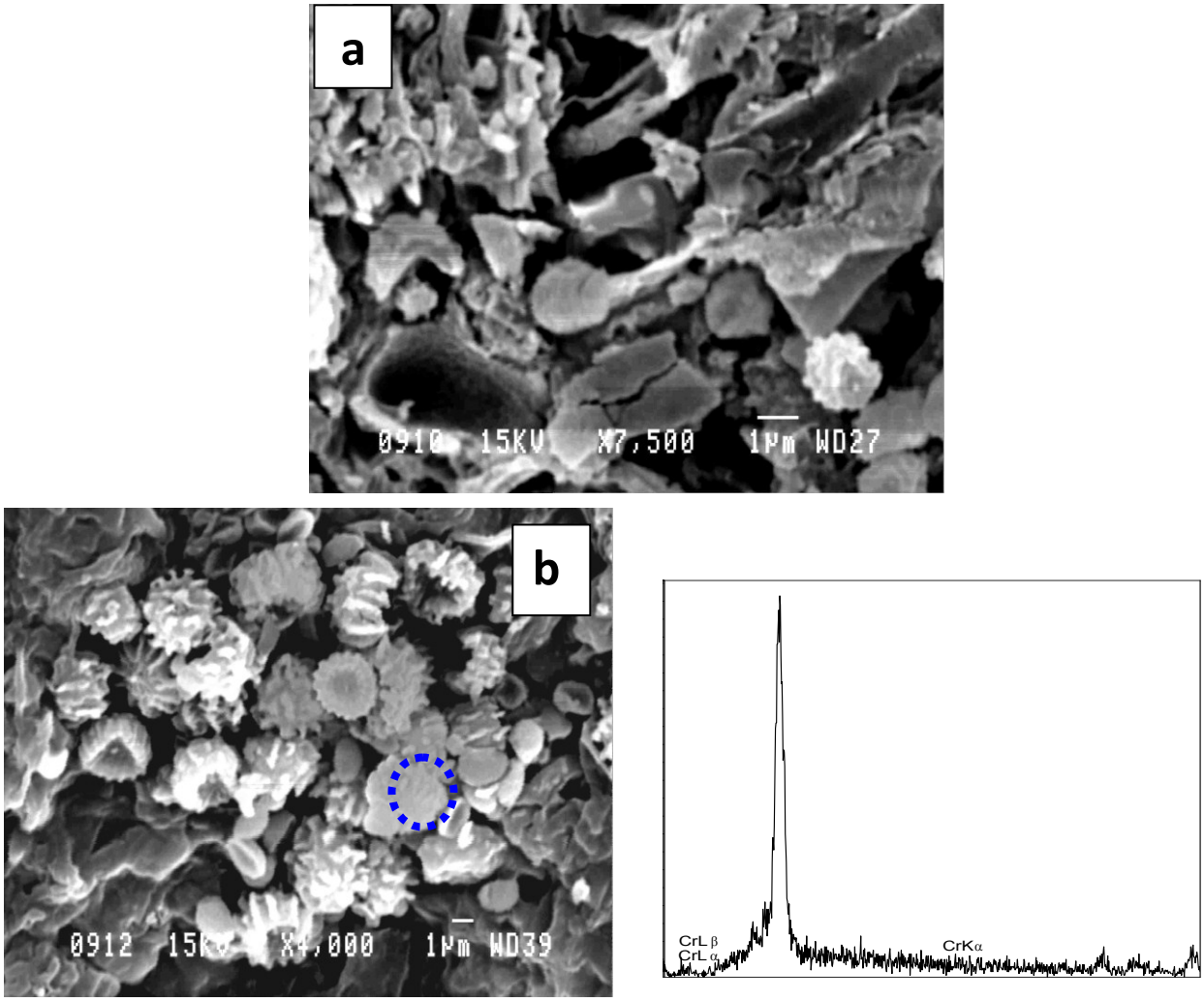

Fig. 10: SEM details of *Aspergillus niger* cell wall: **(a)** before adsorption and **(b)** after adsorption with EDX (point marked in dotted circle), of Cr(III) from model tanning solution

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