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Bioremoval of Chromium (Iii) from Model Tanning Effluent by Novel Microbial IsolatE

Abhilash Divya G Nair*, Kirtal Hansdah, B. Dhal, K. D. Mehta, B. D. Pandey

CSIR-National Metallurgical Laboratory (CSIR), 831007, Jamshedpur
biometnml@gmail.com

Abstract Tanneries have always been under the scanner of Pollution Control Boards with respect to the amount of effluents and solid wastes that they generate. Wastewater from tanneries usually contains high concentration of chlorides, sodium sulfide, aliphatic sulfonates, sulfates and several other organic components including fatty acids, proteins and soluble carbohydrates. Chromium is present in the wastewater because of its use as a tanning agent in the form of basic chromium sulfate. In this paper, our efforts on isolation of Penicillium sp. from a tannery effluent sample and its use as a sorbent to remove Cr(III) from a model solution are described. Various parameters such as pH, temperature, biomass dose, particle size of the biosorbent and initial metal ion concentration have been optimized. With a model solution of 100ppm Cr(III), about 84% sorption is achieved with 1%(w/v) biomass of <150μm size Penicillium species at 4.0pH and 35°C temperature.

Keywords Tannery Effluent, Chromium, Ground Water Pollution, Toxicity, Penicillium Species

1. Introduction

Since the invention of chrome tanning in 1858 by Knapp, the leather industry has undergone a makeover change. Around 90% of the leather produced globally is by chrome tanning, let alone, in India 80% of the leathers are produced by chrome tanning[1,2]. Large amounts of Cr (III) can also be hazardous to health and its natural oxidation to hexavalent state further complicates the issue. Hence, stringent discharge limits have been specified for chromium into inland water (0.1-5.0 mg/L); sewer (1-10 mg/L); and surface water (1.0mg/L)[3,4]. In order to bring down the level of chromium in the effluents to an acceptable limit, various physicochemical methods such as ion-exchange, precipitation and reverse osmosis are employed but these methods have certain constraints such as incomplete metal removal, high reagent consumption, and generation of toxic sludge[5]. Amongst the alternate options, use of biotechnological approach viz., biosorption is finding acceptability which involves the utilisation of microorganisms such as algae, fungi, bacteria as biosorbents for the removal of metal ions. The technological merit of this process lies in the ability of negatively charged cell surface of microorganisms to bind the metal cations. 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[6,7]. The stability diagram of chromium in water[8,9] at 25oC is given in Fig. 1, which shows the presence of different species at varying pH and potential.

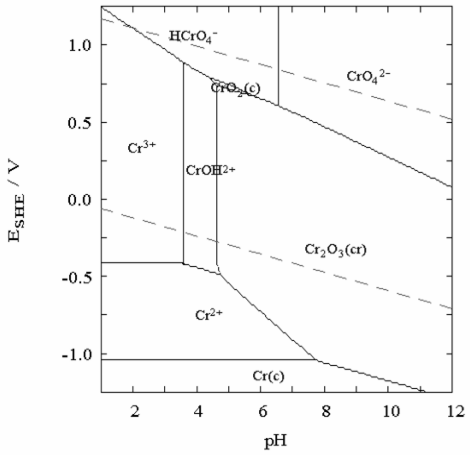

Figure 1. Pourbaix Diagram of Chromium in water at 25 ℃ [Concentration=1M]

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 $Cr(OH)_3$[8,9].

In the present investigation, a fungus, *Penicillium sp*. was isolated from a tannery effluent sample and was used for biosorption of Cr(III) from model tanning effluent.

2. Materials and Methods

* Corresponding author:
biometnml@gmail.com (Abhilash Divya G Nair)
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2.1. Microbial Isolate

Penicillium sp. was isolated from a tannery effluent sample procured from Chennai and was cultivated in Czapek Dox broth[Composition: Sucrose: 30g/L; Sodium nitrate: 3.0g/L; Di-potassium phosphate: 1.0g/L; Magnesium sulphate: 0.50g/L; Potassium chloride: 0.50g/L; Ferrous sulphate: 0.01g/L] at 35° C and pH 2.5 in an orbital shaker[10]. Citric acid produced by the fungus was estimated on a daily basis, by titrating 10 mL of broth culture without the fungal pellets against 0.5N NaOH using bromothymol blue as indicator. The pure isolate was studied for its growth characteristics in absence of various nutrients of the artificial media. The purified isolate was preserved as culture slants for biochemical and molecular characterization.

Fully grown culture was filtered using Whatman filter paper No.1 and rinsed thoroughly with de-ionised water for 5-6 times and dried at room temperature to a constant weight lessening moisture content. The dried biomass was passed through a sieve to get particle size of <150µm.

2.2. Model Tanning Effluent Solution

A model tanning effluent[11] (MTE)[Composition: $CaCl_2$:0.319g/L;$MgCl_2.6H_2O$:0.962g/L;Na_2S:0.234g/L; $Na_2SO_4.10H_2O$:6.205g/L; NaCl:1.119g/L] was prepared with 200 ppm Cr(III) using $CrCl_3.6H_2O$ as source. All chemicals used were of AR grade. The pH of the solution was maintained at 4.0, unless stated otherwise, by using 10N H_2SO_4 and 2N NaOH.

2.2. Biosorption Experiments

The factors that affect the biosorption rate and uptake capacity of the biosorbent were examined in a batch mode. Unless stated otherwise, all experiments were carried out with 1%(w/v) biomass having particle size <150µm in 250 ml Erlenmeyer flasks containing 100 mL of MTE with 100ppm Cr(III) on a horizontal shaker, operating at 100rpm set at 35°C. The effect of pH, temperature, biosorbent dose, particle size of the sorbent and effect of initial metal ion concentration on removal of Cr(III) ions was examined. Samples were withdrawn at periodic intervals. Concentration of Cr(III) ions was estimated by AAS. The percent adsorption (%) and distribution constant (K_d) were calculated by:

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

where C_i and C_f are the concentration of the metal ions in the initial and final solutions (mg/L), respectively:

$$K_d = \frac{\text{Amount of metal in adsorbent}}{\text{Amount of metal in solution}} \times \frac{V}{m} \quad (2)$$

where V is the volume of the solution (mL), m is the weight of the adsorbent (g).

3. Results and Discussions

3.1. Growth Characteristics of Penicillium Species

Change in morphology of the fungus with respect to variation in nutrient sources showed that *Penicillium* could grow in the absence of potassium chloride (Table 1).

Table 1. Influence of media components of CZB on fungal growth

Media Comp. absent	Days	Observations
Sucrose	2	Growth of conidia, thin mycelia
	4	Thin mycelia, less vacoules
	6	Less growing stage, little branching
	8	Degraded mycelia, hyphae budded
$NaNO_3$	2	Bud formed, growth started
	4	Slow growth compare to normal
	6	Loose mycelium, less spores
	8	Scattered budded hyphae
K_2HPO_4	2	Conidiophores with thick mycelia
	4	Less growth, short filamentous
	6	Rapidly growing mycelia
	8	Weak forming mycelia wall
$MgSO_4$	2	Growing stage appeared
	4	Well developed mycelia with spores
	6	Budded hyphae at the terminal
	8	Vertical growth in budded hyphae
KCl	2	No branching, vacuole present
	4	Bifurcate hyphae, growth appeared
	6	Conidiophores present, spore present
	8	Buds in pre proliferation stage.

Citric acid is a metabolite produced by the fungus during its growth stage. At the end of 8 days, amount of citric acid produced by the fungus was found to be 4.02 g/L correlating it to the full growth of fungal cells.

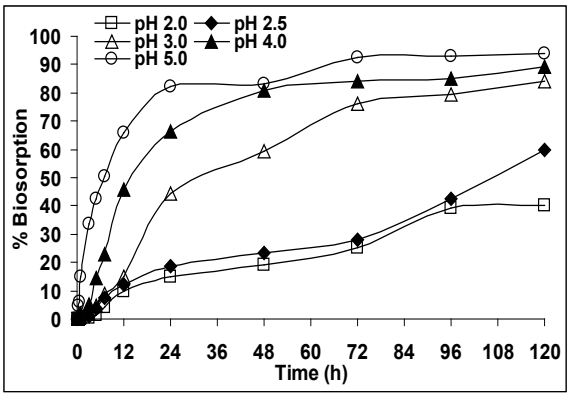


Figure 2. Effect of pH on Cr(III) biosorption at 35°C, 1%(w/v) biomass of <150µm size

3.2. Effect of pH

pH is a critical parameter for biosorption studies as it not only influences the speciation of the metal ion in solution but also can change the state of the active binding sites, which are usually acidic[7]. The effect of pH on Cr(III) biosorption was studied in the range 2.0- 5.0. As shown in Figure.2, biosorption efficiency was low at pH 2.0 because of competition for sorption sites between the highly available hydrogen ions and metal ions. The sorption capacity increased gradually with an increase in pH[12]. Maximum

biosorption of 84% and 93% was obtained respectively at pH 4.0 and 5.0. As at pH above 4.5, Cr(III) is likely to be precipitated as $Cr(OH)_3$, the value at pH 4.0 may be taken as the optimum[8,9].

3.3. Effect of Initial Metal Ion Concentration

The results on variation of Cr(III) concentration are shown in Fig.3.A decrease in biosorption beyond 100 ppm Cr(III) in feed was observed.

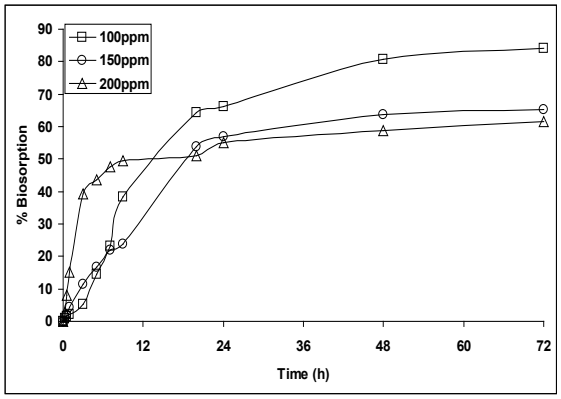


Figure 3. Effect of initial metal ion concentration on Cr(III) biosorption at pH 4.0, 35°C, 1%(w/v) biomass of <150µm size

3.4. Effect of Particle Size

Four different particle sized biomass of >150µm, 150-75µm, 75-53µm and <53µm was used to study biosorption of Cr(III). Maximum sorption (67.2%) was observed (Fig.4) with 150-75µm sized biomass. Finer size particles were found to agglomerate and thus decreasing the sorption to 55.5% with <53µm size biomass. The mixed size material < 150µm was however, most effective with 84% sorption (Figure 2).

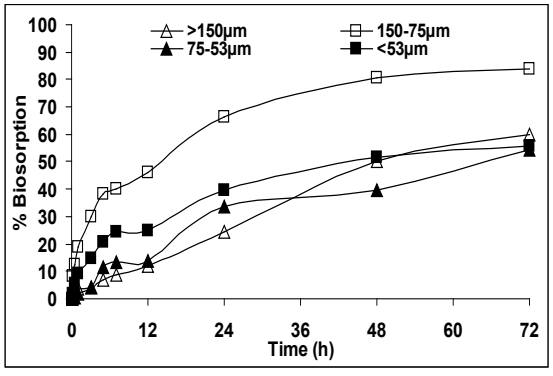


Figure 4. Effect of particle size on Cr(III) biosorption at pH 4.0,35°C, 1%(w/v) biomass

3.5. Effect of the Sorbent Dose

On varying the biomass from 0.1%- 5.0% (w/v), it was found that maximum biosorption occurred with 1% biomass as shown in Figure.5. The biosorption capacity increased as the concentration of the biomass increased from 0.1% to 1% as a result of availability of more binding sites. A minor decrease in the biosorption capacity was observed on increasing the biomass dose from 1% to 5% because of its agglomeration resulting in unavailability of binding sites for metal ions.

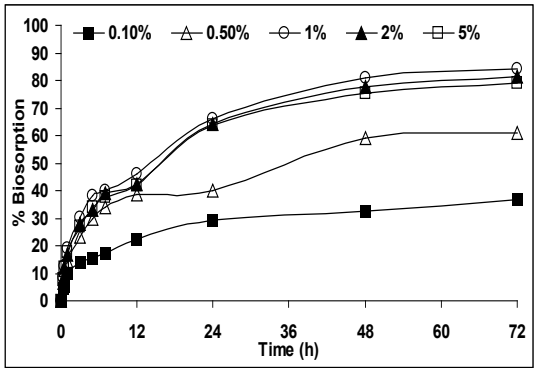


Figure 5. Effect of biosorbent dose on Cr(III) biosorption at pH 4.0, 35°C, biomass of <150µm size

3.6. Effect of Temperature

The effect of temperature on the sorption of Cr(III) was also studied (Fig.6). The percentage biosorption increased with increase in temperature till 35°C, thereafter it decreased because of greater degree of hydrolysis of the cell wall constituents[13] at 40°C.

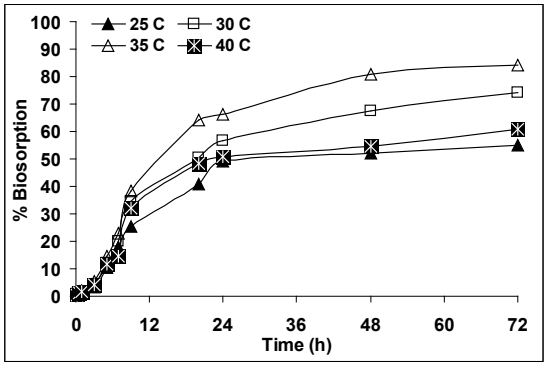


Figure 6. Effect of temperature on Cr(III) biosorption at pH 4.0,1%w/v biomass of <150µm.

The distribution coefficient (K_D) is related to the Gibbs free energy change ($\Delta G°$) as:

$$\Delta G° = -RT \ln K_D = \Delta H° - T\Delta S° \quad (3)$$

$$\log K_D = \Delta S°/2.303R - \Delta H°/2.303RT \quad (4)$$

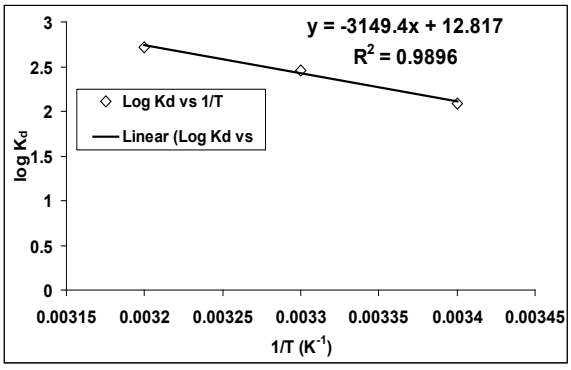


Figure 7. Log K_d vs 1/T graphs for the biosorption of 100ppm Cr(III) onto *Penicillium* at pH 4.0; *m*: 1.0 g; *t*: 72h; *size:* <150µm

Table 2. Thermodynamic parameters for the biosorption of 100ppm Cr(III) on *Penicillium sp*

Temp (K)	ΔH° (kJ/mol)	ΔS° (J/K mol)	R^2	ΔG° (kJ/mol)
298	60.3	245.4	0.989	-12.8
303				-13.9
308				-15.1

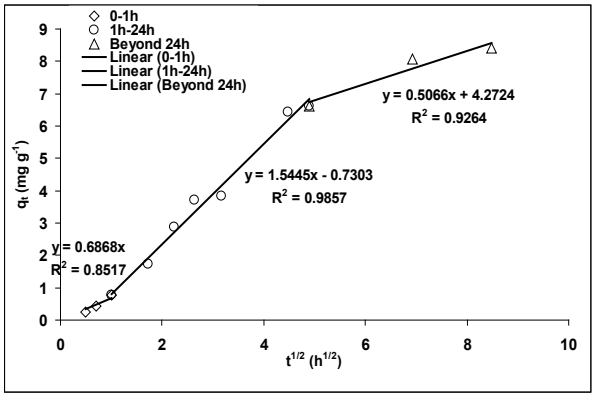
The plot (Fig.7) of log K_D versus 1/T shows linearity and the calculated thermodynamic values are given in Table-2. ΔH° value was found to be 60.3 kJ/mol indicating endothermic nature of Cr(III) chemisorption[14]. Negative values of ΔG° indicates the spontaneous nature of the reaction. The reaction is favored and getting easier as temperature rise from 25 to 35°C.

3.7. Intraparticle Diffusion

The adsorption process on porous sorbents can be described by intraparticle diffusion; where in mass transfer within the sorbent particles may involve a short-range diffusion in both the fluid and adsorbed phases[14]. In the aqueous phase, pore surfaces are hydrated, resulting in both pore and surface diffusion of metals playing a role in the liquid phase adsorption on macroporous sorbents like fungal biomass. Intraparticle diffusion model is expressed as :

$$q_t = k_{id} t^{1/2} \quad (5)$$

where q_t is the amount of metal ions adsorbed at time t and k_{id} is the intraparticle diffusion rate constant. A plot of qt versus t1/2 is shown in Figure. 8.



Figuer 8. Intraparticle diffusion plot for biosorption of 100ppm Cr(III) from MTE on 1%(w/v) biomass of <150µm size at 35°C

With the biomass of <150µm size, three slopes of the straight lines are seen (Fig.8): the first portion for 0-1h may be attributed to the external surface sorption due to the extremely low particle size as reported[14]. The second is the gradual sorption stage in 1-24h time, where the intraparticle diffusion may be the rate-controlling stage. The third and final equilibrium stage beyond 24h corresponds to the slowing down of intraparticle diffusion because of low solute concentrations in the solution. When the adsorption has reached saturation at exterior surface, the Cr(III) ions might have entered in the pores within the biomass.

A comparison of intraparticle diffusion rate constants (mg/g.h) viz. (k_i1-0.68, k_i2-1.54 and k_i3-0.50) values and R^2 values obtained from Fig.8 follows the sequence:

$$k_i1 < k_i2 > k_i3$$

4. Conclusions

1. *Penicillium sp.* isolated from the waste tanning solution shows promise to remove Cr(III) from model tanning effluent. Maximum Cr(III) sorption of 84% is achieved at pH 4.0, 35°C temperature with 1%(w/v) biomass of <150µm size from a Cr(III) solution of 100 ppm.

2. At higher temperature of 40°C the sorption of Cr(III) decreases due to instability of the fungal structure. The increase in metal ion concentration beyond 100 ppm, decreases the biosorption efficiency. THE coarser particle size (>150-75µm) shows high metal uptake as compared to the fine size particles which gets agglomerated easily obstructing the binding sites of the pores. The mixed size material <150µm removes Cr(III) most effectively(84%) at 4.0 pH.

3. The Cr(III) sorption on the live biomass of *Penicillium sp.* is an endothermic process and is thermodynamically favourable with ΔG° value of 12.8- 15.1kJ/mol.

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