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Comparitive Study On Biosorption Of Hexavalent Chromium Using Aspergillus Oryzae NCIM 637 And Aspergillus Sojae NCIM 1198 From Electroplating Effluent

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Abstract: The biosorption of chromium (VI) ions on *Aspergillus oryzae* NCIM 637 and *Aspergillus sojae* NCIM 1198 were investigated. Biosorption studies were carried out by varying initial metal ion concentration, pH, and biosorbent dosage. A contact time of 330 min was required to reach equilibrium. Percentage removal increased as the biosorbent dosage increased. A maximum of 89% and 85% chromium removal was observed at 5 mg/L concentration using *Aspergillus oryzae* and *Aspergillus sojae* respectively. Better adsorption was seen in the case of *A.oryzae*. Adsorption isotherm studies were carried out. The equilibrium data were analyzed using Langmuir, Freundlich and Tempkin isotherms. The parameters of each isotherm were determined. Freundlich isotherm provided the best correlation for chromium on to *Aspergillus oryzae*. The kinetics of chromium biosorption has been evaluated for *A.oryzae* with respect to pseudo first order and pseudo second order kinetic equations. The characterization studies were carried out using SEM for both organisms. The Cr (VI) metal was found to desorb effectively using EDTA and removal efficiency was found to be 94 % and can be recycled.

Key words: Aspergillus, biosorption, Langmuir, Freundlich and equilibrium.

INTRODUCTION

Technological processes involved in extraction of metals and their productive cycle generate significant amounts of effluents contaminated with heavy metal. These include mining, mineral processing and extractive metallurgical operations, electroplating, painting, dying, surface treatment industry and many others. The presence of heavy metals in aquatic environments is known to cause severe damage to aquatic life, beside the fact that these metals kill microorganisms during biological treatment of wastewater with a consequent delay of the process of water purification. Most of the heavy metal salts are soluble in water and form aqueous solutions and consequently cannot be separated by ordinary physical means of separation. These metals exert a deleterious effect on the flora and fauna that grow in lakes and streams[1]. Chromium is one of the major concern because of its non- degradability nature.

Chromium, a highly reactive element with an oxidation state of 6 exhibits stability as Cr (III) and Cr (VI). But hexavalent chromium is more toxic to living organisms than the trivalent chromium[2]. Trivalent chromium has limited hydroxide solubility making it relatively immobile and less available for biological uptake. Cr (VI) being powerfully carcinogenic modifies DNA transcription process thereby causing important chromosomic aberration as quoted by the International Agency for Research on Cancer[3].

The Cr (VI) has also been classified as a group A carcinogen by USEPA based on its chronic effects [4]. Strong exposure of Cr (VI) causes cancer in the digestive tract and lungs [5] and may cause epigastric pain, nausea, vomiting, severe diarrhea and hemorrhage [6]. Chromium has adverse impacts on aquatic species. It accumulates in fish tissues and at higher concentration causes reduction in fish production[7]. Use of chromium species is commonly found in many industries such as steel production, leather tanning, aluminum productions, nuclear power production, metal processing, electroplating, iron sheet cleaning, chrome plating, wood preservation, water cooling, pigments, inorganic chemical production, galvanometric, electric, mining industries, battery manufacturing, mine drainage etc.,[8,9,10].

There are some chemical methods for the separation of these heavy metals such as the ion exchange, chemical precipitation, reverse osmosis, membrane separation process, oxidation-reduction, filtration, adsorption, lime coagulation, solvent extraction, incineration, recovery by evaporation, neutralization, electro dialysis and electrochemical treatment[11,12,13,14,15]. All of these methods have many disadvantages, for instance, elevated capital investment as well as recurring expenses, high reagents, incomplete metal removal, high energy requirements, generation of the toxic sludge or other waste products that required safe disposal etc., [16, 17].

Many aquatic microorganisms, such as bacteria, yeast and algae can take up dissolved metals from their surroundings onto their bodies and can be used for removing heavy metal ions successfully[18]. Furthermore, biosorption processes have a major potential alternative for detoxification and recovery of toxic and valuable metals from industrial wastewater. Fungi are known to tolerate and detoxify metals by several mechanisms including valence transformation, extra and intracellular precipitation and active uptake. The high surface to volume ratio of microorganisms and their ability to detoxify metals are the reasons they are considered as potential alternative to synthetic resins for remediation of dilute solutions of metals and solid wastes [19].

Considering the above mechanisms of metal resistance in fungi, it is expected that screening of metal tolerant fungi may provide strains with improved metal accumulation. Only limited studies have been conducted in our country to systematically screen filamentous fungi from metal polluted sites for their metal tolerance and their biosorption potential [20]. Fungal biomass has strong metal binding capacities that contain polysaccharides, proteins or lipid on the surface of their cell walls by may functional groups of carboxyl, hydroxyl, sulfydryl, amino and phosphate group of lipids [21]. Dead fungal biomass has been used in a number of studies because it does not require nutrients and can solve the environment problems of high toxicity. The immobilization of biomass within the polymeric matrix used for many studies because of several advantages such as separation of solid biomass from the bulk liquid, recovery of metals, control of particle size, fast growth and multiplication, lowest level density, high separation ability, low costing application of microbial absorbents and high biomass loading. When biomass is immobilized, support material should be rigid, chemically inert, cheap, high loading capacity and increasing diffusion[22].

In the present work, we have studied the effect of contact time, initial metal ion concentration, pH, biosorbent dosage and pretreatment. The experimental data were fitted to adsorption isotherms followed by its kinetic studies. The reusuability of biosorbents were also analysed after desorption studies

MATERIALS AND METHODS

Biosorbent preparation

Aspergillus oryzae NCIM 637 and *Aspergillus sojae* NCIM 1198 were collected from National Collection of Industrial Microorganisms, Pune, India. The obtained fungal cultures were then sub cultured on readymade Potato dextrose agar and incubated at 37°C for 4 to 5 days. Sub cultured fungus was then used for Mass culturing. Mass culturing was done for 10-15 days and mate obtained was taken and dried 80°C for about 3 hrs. Dried fungal mate was powdered and used for further studies.

Preparation of stock solution

Aqueous chromium solution of concentration 1000mg/L prepared by dissolving 2.83 g of potassium dichromate salt in 1000 ml distilled water. Concentration of chromium was varied from 5 mg/L to 25 mg/L.

Biosorption studies

Biosorption studies were carried out using dead *Aspergillus oryzae* and *Aspergillus sojae*. The experiments were carried out in Erlenmeyer flask by adding 1 g of dead *Aspergillus oryzae* and *Aspergillus sojae* in two different flask containing 100 ml of aqueous chromium solution of desired concentration. The samples were taken at regular intervals, analysed using DPC assay and absorbance values are noted at 540 nm. The above procedure is repeated until the equilibrium is reached[23].

Effect of contact time

The effect of contact time was carried out for different contact times (15, 30, 45, 60, 120, 180, 240,270,300 and 330 min) at an initial concentration of 5 mg/L of Cr (VI) ion at pH 2.0. The adsorbent dosage was 1 g in 100 ml solution in 250 ml conical flask at37^{0}C and pH 2.0. The flasks were then agitated in a shaker at 150 rpm and at regular intervals the samples were withdrawn, filtered and analyzed using DPC assay and absorbance values are noted at 540 nm. Each experiment was repeated three times in order to get accurate results.

Effect of initial metal ion concentration

The effect of initial chromium concentrations were carried out for the initial chromium (VI) concentration (5, 10, 15, 20 and 25 mg/L) at pH 2.0 The adsorbent dosage was 1 g in 100 ml solution in 250 ml conical flask at 37^{0}C and pH 2.0. The flasks were then agitated in a shaker at 150 rpm and at regular intervals the samples were withdrawn, filtered and analyzed using DPC assay.

Effect of pH

The effect of pH was carried out for the initial chromium (VI) concentration with 5 mg/L. The 5 mg/L concentration chromium solution was adjusted to various pH (1, 2, 3, 4, 5, 6, 7, 8 and 9) and 1g of biomass at 37^{0}C was added. The flasks were then agitated in a shaker at 150 rpm and at regular intervals the samples were withdrawn, filtered and analyzed using DPC assay. Each experiment was repeated three times in order to get accurate results.

Effect of biomass loading

The effect of biomass loading studies was carried out with 100 ml of 5 mg/L concentration of chromium solution and the solution was loaded with different biosorbent dosages (1, 2, 3, 4 and 5 g) by keeping pH and temperature as 2.0 and 37^{0}C respectively. The flasks were then agitated in a shaker at 150 rpm and at regular intervals the samples were withdrawn, filtered and analyzed using DPC assay.

Effect of pretreatment

Fungal biomass was modified by various pretreatment like acid treatment, alkali treatment, doping and sterilization. Percentage removal of metal ion with this pretreated fungal biomass was studied spectrometrically at 540 nm using DPC assay.

Desorption studies

Desorption studies were carried out using desorping agents like HCl, NaOH and EDTA. The fungal biomass that has been used for biosorption is collected and weighed before desorption. The desorbing reagents were prepared and the adsorbed fungal biomass was added and kept in shaker overnight. Then the solution was centrifuged. The supernatant obtained was subjected to DPC assay to estimate the amount of chromium desorbed and the desorbed fungal biomass obtained as pellet was weighed.

Characterization of the Biosorbent- SEM Analysis

Scanning Electron Microscope was done for the characterization of the biosorbent. A Scanning Electron Microscope (SEM) is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography. For SEM, a specimen is normally required to be completely dry, since the specimen chamber is at high vacuum[24]. The sample for SEM analysis was prepared by drying and powdering the fungal mat obtained from mass culturing. The surface of the fungal biomass was analyzed before and after Cr (VI) biosorption. The change in the surface morphology was studied for both *Aspergillus oryzae* and *Aspergillus sojae.*

RESULTS AND DISCUSSION

Effect of contact time

Effect of contact time using dead *Aspergillus oryzae* and *Aspergillus sojae* were studied and results were shown in Figure 1. Initially there was a rapid increase in the adsorption and as the time increases it reaches equilibrium and remains constant after the equilibrium time. The percentage removal was around 89% and 85% for *Aspergillus oryzae* and *Aspergillus sojae* respectively with equilibrium time of 330 mins. As time passes the metal uptake by the sorbent surface slows down as the competition for the decreasing availability of active sites intensifies by the metal ions remaining in the solution[25].

Effect of Initial Metal Ion Concentration

Effect of initial metal ion concentration using dead *Aspergillus oryzae* and *Aspergillus sojae* were studied and results were shown in Figure 2. The percentage removal of chromium was around 89% and 85% with initial metal ion concentration of 5mg/L for *Aspergillus oryzae* and *A.sojae* respectively. The percentage removal decreased as the concentration increased and it is due to lack of active sites.

Effect of pH

Effect of pH using dead *Aspergillus oryzae* and *Aspergillus sojae* were studied and results were shown in Figure 3 and it was observed that the percentage removal of chromium was maximum at pH 2.0 and was found to be 89% and 85% for *Aspergillus oryzae* and *Aspergillus sojae* respectively. As the pH increases from pH 1.0 to pH 2.0 there is increase in the removal efficiency and when it reaches pH 3.0 it starts to decrease[26]. The cell wall of *Aspergillus* species contains a large number of surface functional groups. Biomass has active sites capable of binding metal ions and such bond formation could be done by displacement of protons which can be determined by pH[27].

Effect of biosorbent dosage

The concentration of biosorbent is also one of the significant factor to be considered for effective biosorption. It determines the sorbent/sorbate equilibrium of the system[28]. Biosorption of chromium with varying biosorbent dosage is shown in Figure 4. From the figure it has been observed that as the concentration of biosorbent increases from 1 g to 5 g there is increase in the percentage removal. This may be due increase in the binding sites in the biomass.

Effect of pre-treatment

Metal affinity to biomass can be manipulated by pre-treating the biomass with alkaline, acid, and heat which may increase the amount of metal sorbed[29].The comparison for chromium adsorption capacities of *Aspergillus oryzae* and *Aspergillus sojae* were shown in Figure 5. It showed that the fungus pre-treated with nitric acid has better adsorption efficiency followed by alkali treated dry and wet biomass and then sterilized wet biomass. Adsorption of chromium varies because of the modifications in the cell wall.

Figure 1: Effect of contact time on biosorption of Cr (VI) using *A.oryzae* and *A.sojae*

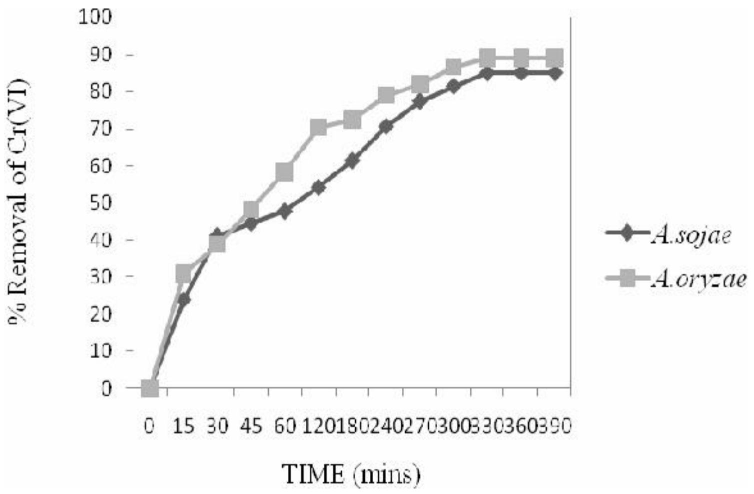


Figure 2: Effect of initial metal ion concentration on biosorption of Cr (VI) using *A.oryzae* and *A.sojae*

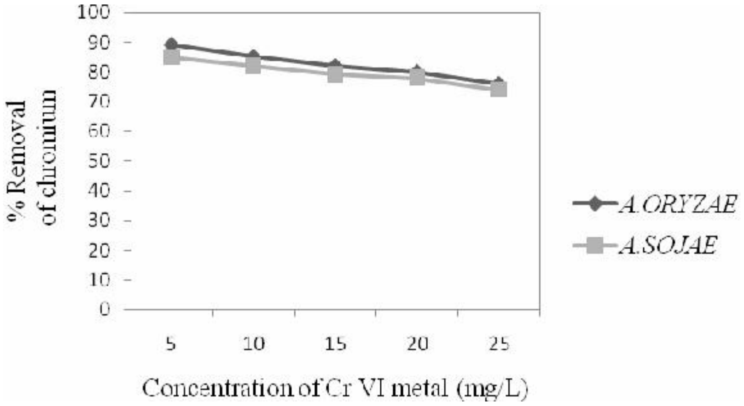


Figure 3: Effect of pH on adsorption of chromium using *A. oryzae* and *A.sojae*

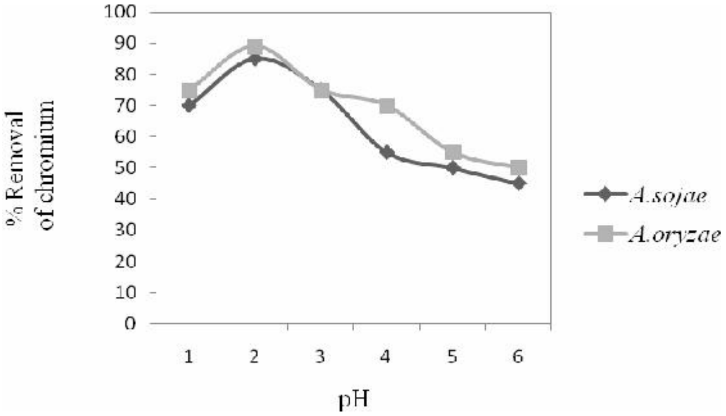


Figure 4: Effect of biomass loading on adsorption of chromium using *A. oryzae* and *A.sojae*

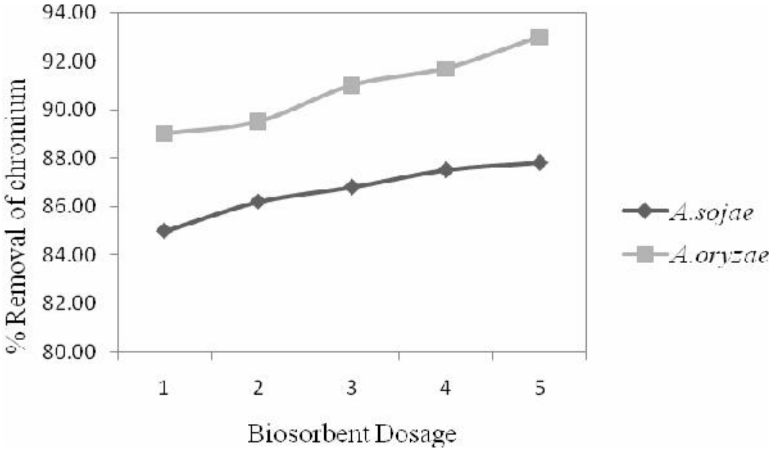
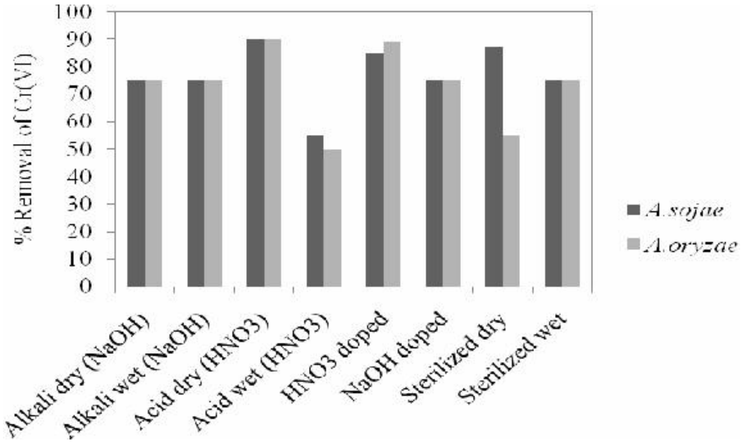


Figure 5: Effect of pretreatment of fungal biomass on adsorption of chromium using variously pre-treated *A. oryzae* and *A.sojae*



SEM Analysis

Scanning Electron Microscope has been used for the characterization of biosorbent. Aspergillus oryzae and Aspergillus sojae are subjected to characterization before and after adsorption and is showed in Figure 6 and Figure 6a respectively. The surface of the fungal biomass showed that the biomass appeared scattered before adsorption to Cr (VI) and the biomass appeared complexed with Cr (VI) after adsorption.

Figure 6: SEM image of *Aspergillus oryzae* after and before adsorption

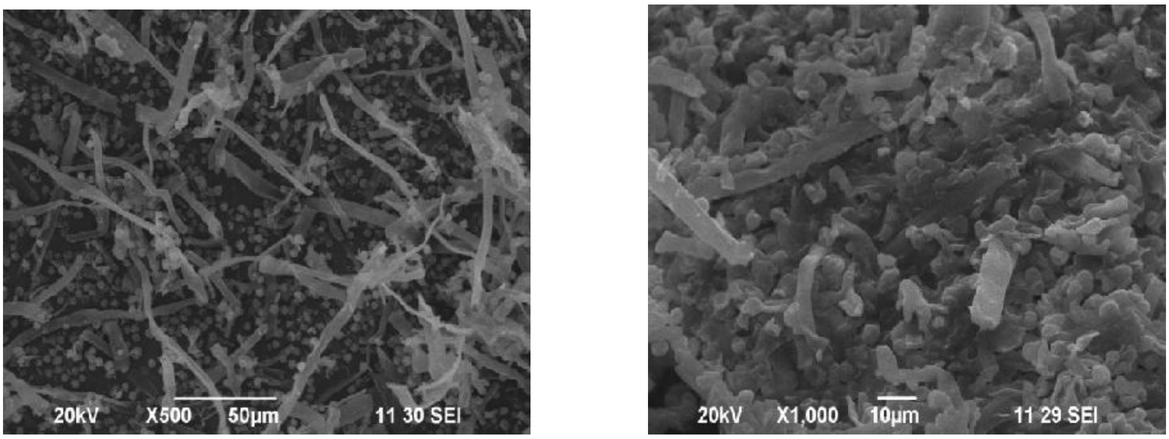
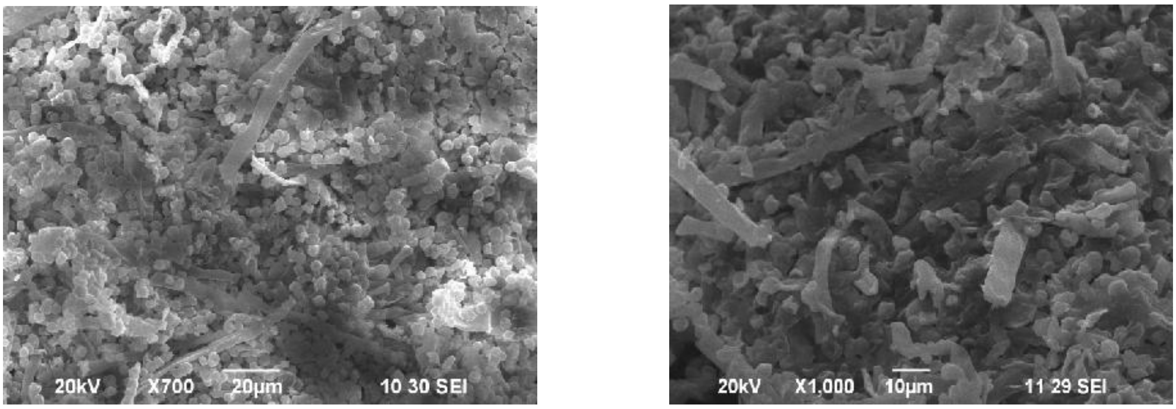


Figure 6 (a): SEM image of *Aspergillus sojae* after and before adsorption



Adsorption isotherms

Adsorption isotherms are used to predict the adsorption behaviors of chromium metal ion solution on to the biosorbent. Langmuir and Freundlich isotherms are most commonly used.

Langmuir isotherm[30] is represented by the equation-

$$q_e = \frac{q_{max} b\, C_{eq}}{1 + bC_{eq}}$$

Where, q_e and C_{eq} are the amount of adsorbed metal per unit weight of biosorbent at equilibrium (mg/g) and unadsorbed metal concentration in solution at equilibrium (mg/L), respectively. q_{max} is the maximum amount of metal per unit weight of biomass to form a complete monolayer on the surface bound (mg/g) and b is a constant related to the affinity of the binding sites (L/mg). The values of b, $q_{max,}$ nonlinear regression correlation (R^2) for Langmuir isotherm is given in Table 1.

The characteristics of Langmuir constant can be determined by Seperation factor R_L,

$$R_L = \frac{1}{(1 + bCo)}$$

Where b is the Langmuir constant (L/mg) and C_o is the initial metal ion concentration (mg/L), R_L values between 0 and 1 indicate that adsorption is favourable for all concentrations[31].

The next isotherm used for fitting the data using Freundlich equation[32] is given below:

$$q_e = K_F C_e^{\frac{1}{n}}$$

Where, q_e is the amount of metal ion adsorbed per gram of adsorbent (mg/g), C_e is the equilibrium concentration of metal ion in solution (mg/L). K_F and n values indicating the adsorption capacity and adsorption intensity respectively are given in Table 1. The Freundlich constant n value between 1 and 10 indicates good adsorption. The value of n and correlation coefficient for adsorption of Cr (VI) by *A.oryzae* were found to be 1.616 and 0.6554 respectively, which indicates that this isotherm is best fitted and is favourable.

Tempkin isotherm is also used to explain the adsorbing species adsorbate interactions[33].In this isotherm it is assumed that heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate repulsions, and the adsorption is a uniform distribution of maximum binding energy[34]. The data was fitted to the isotherm and the constants calculated from Figure 9 are tabulated in Table 1. Based on the correlation coefficient the adsorption was found to be less efficient than Langmuir and Freundlich Isotherms.

$$q_e = \frac{RT}{b_T} \ln A_T C_e$$

Where, B_T = RT/$b_{T,}$ T is the absolute temperature (K), and R is the universal gas constant (8.314 mol^{-1} K^{-1}). The constant b_T is related to the heat of adsorption, A_T is the equilibrium binding constant (1 min^{-1}) corresponding to the maximum binding energy.

Isotherm studies

Figure 7: Linearized Langmuir isotherm plot for Cr (VI) adsorption into *Aspergillus oryzae*

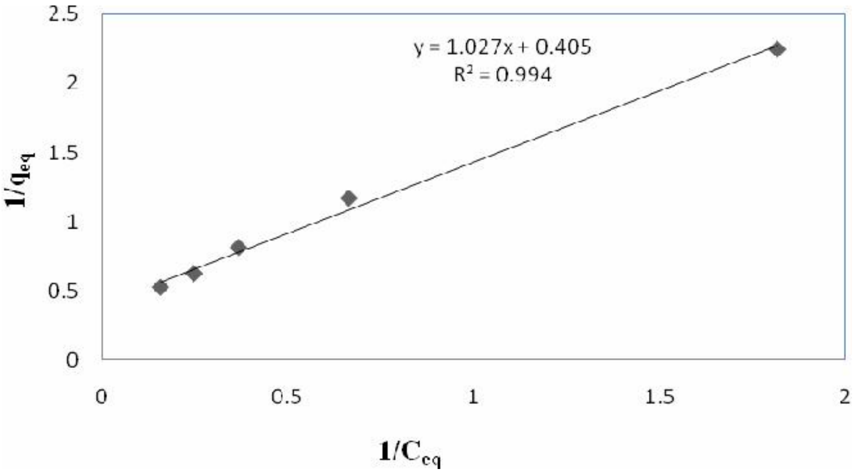


Figure 8: Linearized Freundlich isotherm plot for Cr (VI) adsorption into *Aspergillus oryzae*

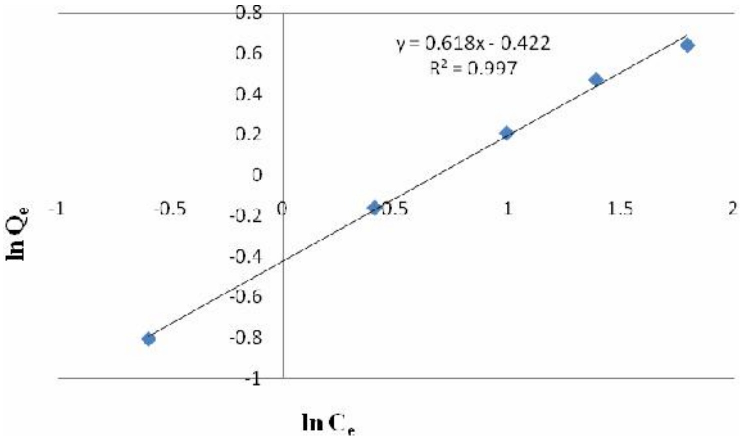


Figure 9: Linearized Tempkin isotherm plot for Cr (VI) adsorption into *Aspergillus oryzae*

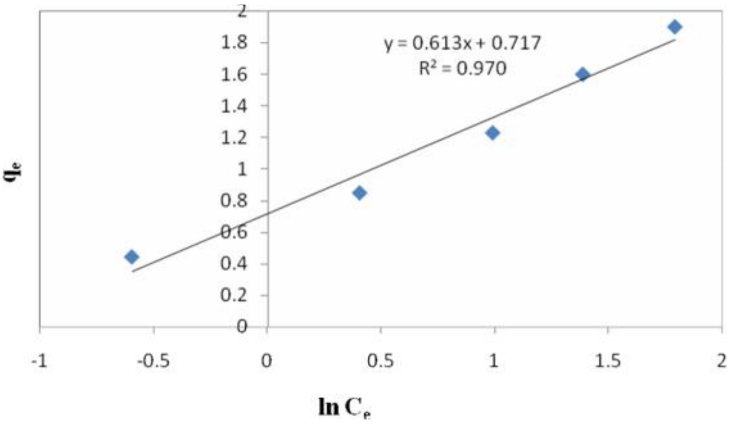


Table 1: Adsorption Isotherm Parameters

Adsorption Isotherm	Adsorption Isotherm Parameters		
Langmuir	**q_{max} (mg/g)**	**b (L/mg)**	**R^2**
	2.4648	0.3950	0.9943
Freundlich	**K_F**	**n**	**R^2**
	0.6554	1.616	0.9971
Tempkin	**A_T (L/min)**	**B_T (J/mol)**	**R^2**
	3.22	0.6131	0.9708

Adsorption Kinetics:

Mostly Pseudo first order kinetic model issued for the biosorption of chromium. The present Cr (VI) sorption data of *Aspergillus oryzae* at various initial metal ion concentrations are tested for kinetic modelling using pseudo first order equation and pseudo second order equation by linear regression plots and are shown in Figure 10 and Figure 11 respectively. The estimated statistical parameters of the model equations are presented in Table 2. Based on linear regression values, the kinetics of Cr (VI) adsorption onto non-growing *Aspergillus oryzae* indicates that the pseudo second order kinetics followed by pseudo first order model fits progressively well with increasing sorbate concentration.

Desorption studies:

The biosorbed fungus was then weighed which showed increase in weight from 1 g to 1.4 g. then after desorption using EDTA, the weight of fungal biomass decreased to 1.13 g indicating the efficiency of desorption process. The values of DPC assay of the desorbed supernatant showed 94 % removal of Cr (VI) from the biosorbent. The values for effect of desorption and the effects of desorbed *A.oryzae* on adsorption are tabulated in Table 3 and Table 4 respectively.

Biosorption of Chromium from electroplating effluent:

The AAS results showed that the electroplating effluent had 0.85 mg/L concentration of Cr (VI). So 100 ml of effluent was taken, 1 g of dried *Aspergillus oryzae* was added and the pH was adjusted to 2.0 at 37°C. The OD values obtained after 330 mins showed that a maximum removal of 88.2 %. The removal performed using Nitric acid treated dry fungal biomass also showed a maximum Cr (VI) removal of 89 %. The percentage adsorption using the dry and pre-treated fungal biomass is shown in Figure 12.

Adsorption Kinetics

Figure 10: Pseudo First order kinetics plot for biosorption of various initial concentrations of Cr (VI) into *Aspergillus oryzae*

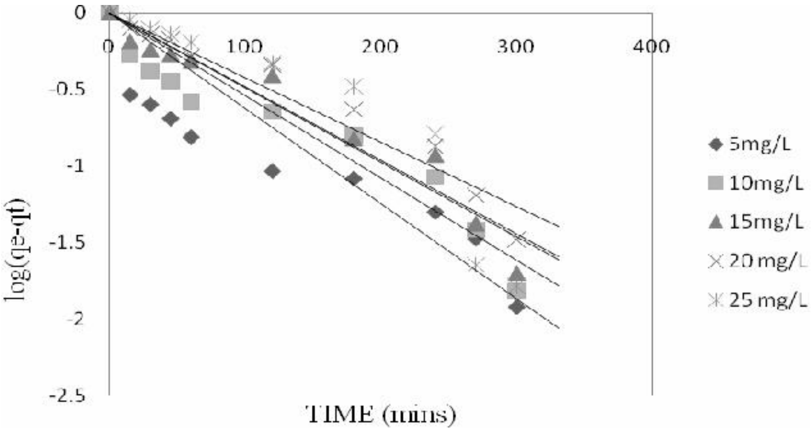


Figure 11: Pseudo Second order kinetics plot for biosorption of various initial concentrations of Cr (VI) in to *Aspergillus oryzae*

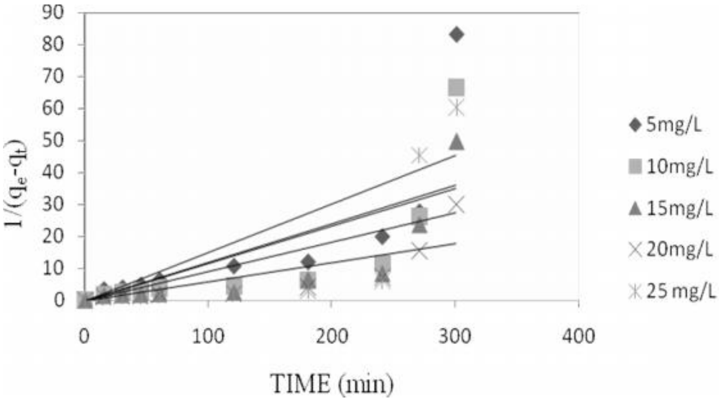


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Table 2: Estimated Kinetic Parameters for pseudo first order and pseudo second order kinetics

Kinetic Model	Parameters	Concentration of Chromium (mg/L)				
		5	15	10	20	25
Pseudo1st order equation $\log(q_e-q_t)=-K_1t$	$K_1(min^{-1})$	0.0062	0.0054	0.0049	0.0042	0.0048
	R_1^2	0.6615	0.8843	0.9379	0.95	0.8471
Pseudo 2nd order equation $1/(q_e-q_t)=K_2t$	K_2(g/mg min)	0.1514	0.1167	0.0919	0.0596	0.1202
	R_2^2	0.6044	0.57	0.6069	0.666	0.573

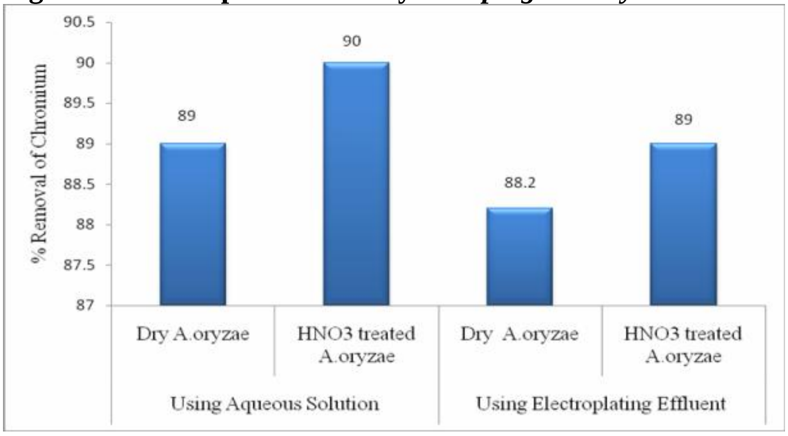
Table 3: Effect of desorption

Reagents	Chromium Removal (%)	
	Aqueous solution	Electroplating effluent
1 N HCl	85	84.1
1 N NaOH	83	81.9
0.1 N EDTA	94	93.2

Table 4: Effect of Recycled fungal biomass on biosorption

Reagents	Chromium Removal (%)	
	Aqueous solution	Electroplating effluent
1 N HCl	86	84.8
1 N NaOH	85	83.6
0.1 N EDTA	88	86.9

Figure 12: Biosorption efficiency of *Aspergillus oryzae* from electroplating effluent.



CONCLUSION:

The results show that the hexavalent chromium can be effectively removed upto 89 % and 85% from the aqueous solution using 1 g dried *Aspergillus oryzae* and *Aspergillus sojae* respectively from 5 mg/L concentration chromium solution at pH 2.0 and 37°C. The results also showed that when the biosorbent dosage was increased the removal was also found to increase linearly. Further when the fungus was pre-treated using various chemicals the efficiency of their chromium metal removal increased. Maximum Cr (VI) removal of about 90 % was obtained when the biosorbent treated with nitric acid at 37ºC, pH 2.0 and 150 rpm. The desorption studies showed that 94 % of the chromium was effectively desorbed from the biosorbent using EDTA and the reuse of the biosorbent showed a maximum of 88 % chromium removal. The correlation coefficients obtained from the isotherm studies for Langmuir, Freundlich and Tempkin are 0.9943, 0.9971 and 0.9708 respectively indicating that the data's fit well in the following order: Freundlich > Langmuir > Tempkin isotherms. The kinetic studies show that pseudo second order fits well followed by pseudo first order. The optimized conditions like 5 mg/L chromium concentration, pH 2.0, 1 g biomass was used for biosorption in electroplating effluent. The removal efficiency was checked after 330 mins at which removal efficiency reached equilibrium. A maximum removal of about 88.2 % was obtained using dry *Aspergillus oryzae*. Further pre-treated biomass was used for removal from electroplating effluent. Maximum Cr (VI) removal of about 89 % was obtained when the biosorbent treated with nitric acid was used.

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