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RESEARCH ARTICLE

BIOSORPTION OF HEXAVALENT CHROMIUM ION AQUEOUS SOLUTION USING FREE AND IMMOBILIZED FUNGAL BIOMASS

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ABSTRACT

Ganoderma lucidum and *Mucor hiemalis* adsorption efficiency for chromium (VI) was studies by free and immobilized biomass. Both the fungus was incubated for the uniform growth at 30°C for 2 days. The results showed that immobilized biomass were more efficient for Cr(VI) removal from the aqueous solution. The effects of biosorbent dose, Cr ion concentration, pH and contact time were investigated. On increasing Cr (Vi) concentration biosoption capacity decreases in both the cases. Adsorption of Cr (VI) ion on the free and immobilized *G.lucidum* and *M. hiemalis* showed highest values at around pH 6.0 and pH 4.0.The maximum uptake for Cr (93.27 mg/g) occurred at 20 mg/l concentration. The Langmuir, Freundlich and Dubinin–Radushkevich models have been applied and according to results Langmuir model fit better for biosorption of Cr (VI) at concentration ranges (20-150mg/l).The pseudo first order, pseudo second order kinetic and intra particle diffusion models were used to describe the time dependent adsorption of Cr(VI).

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INTRODUCTION

The discharge of heavy metals into environment has become a matter of concern over the last few decades. The heavy metals like lead, mercury, zinc, aluminum, arsenic, nickel, chromium, cobalt etc. are the common pollutants present in the environment from various natural and industrial sources [1]. Chromium is a toxic metal of widespread industrial use and exists in several oxidation states. The most stable and common forms are the trivalent Cr (III) and the hexavalent Cr (VI) species, which display quite different chemical properties. Cr (VI) is designated and widely recognized to be a human inhalation carcinogen. High doses of Cr (VI) compounds are also associated with nephrotoxicity [2]. Chromium and its compounds are extensively used in industry with the most common and important sources coming from the electroplating, tanning, water cooling, pulp production, dyes and pigments, film and photography, wood preservation and alloy manufacture industries. Petroleum refining processes have resulted in introduction into soil, air and water [3].

The use of microbial biomass to remove Cr(VI) ions from aqueous solution has gained great interest in place of other conventional methods which include precipitation and coagulation, ion-exchange, membrane processes and electrolytic technologies [4].Fungal and other microbial biomass have been used to remove and recover Cr(VI) ions from aqueous solution [5]. According to the different fungal species and the origin of the biomass the adsorption mechanism differs quantitatively and qualitatively [6]. Application of fungal biomass to remove heavy metals from industrial wastewater and to recover economically valuable metals is attractive for industry [7-11].

In the present study macro-fungi *Ganoderma lucidum* and *Mucor hiemalis* free and immobilized biomass was identified as a promising biosorbent for the removal of Cr (VI) ions from aqueous solution. There are several advantages of these macro fungi such as: biomass can beretained on support under the working environment, adsorbed metal ions can be easily desorbed [12, 13]. Natural polymers such as alginate, chitosan, chitin and cellulose derivatives have been mostly used for the immobilization of microbial cells viaentrapment technique [14]. *Ganoderma lucidum* and *Mucor hiemalis* were immobilized using Na-alginate beads as the natural polymeric matrix. After uniform growth on the surface of the matrix, the free and immobilized fungal biomasses were used for the biosorption of chromium ions from aqueous solutions in a batch system.Equilibrium studies were also conducted with isotherm modeling.

MATERIALS AND METHODS

Biomass production of test fungal species

The fungi(fruiting bodies) used in present study were collected during the post monsoon period(September-October) from forests in uttarakhand (India) and identified in Mushroom Research & Training Centre, G.B.P.U.A. & T., Pantnagar. The fruiting bodies were detached from the rotting wood, washed with deionised water for several times in order to remove dust, cut into small pieces and then dried in an oven at 70°C until constant weight. These pure cultures were maintained on 2% MEA, both in 250 mL conical flasks by taking active inocula from preserved stock culture. Inoculated flasks were incubated for 15 days under controlled temperature of 30±1 °C in stationary phase for utilization in biosorption studies.

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For immobilization studies, live fungal cells (dry weight = 1g) were suspended in 50 ml of sodium alginate (Na-alginate, Sigma) (4% w/v). The mixture was then introduced into 200 mL of 3% w/v $CaCl_2$solution, in a drop-wise manner and with constantstirring, to avoid aggregation of alginate beads. The beads (4 mm diameter) were further cured in this solution for 1 h at room temperature (27 ± 3°C) prior to filtration to remove the $CaCl_2$ solution [15].

Metal Solution

All the reagents were of Analytical Reagent Grade and were prepared in Double Distilled H_2O. An aqueous stock solution (1000 mg/l) of Cr (VI) ions was prepared using potassium dichromate ($K_2Cr_2O_7$) salt. This was used as the source of Cr (VI) in the synthetic wastewater. pH of the solution was adjusted using 0.1 N HCl or NaOH. Fresh dilutions were used for each study [16].Stock solution was diluted to produce Cr (VI) solutions of different concentrations.

Biosorption study

Batch biosorption experiments were conducted in 150 ml Erlenmeyer flasks containing 50 ml chromium solution. Equilibrium studies were performed using known biomass per 50 ml of chromium solution. The test solutions were agitated on shaker at 30°C. The experiments were conducted to evaluate the influence of pH (2–7), biosorbent dose (0.1–0.2 g/50 ml), initial metal ion concentration (20–120 mg/l), contact time (15- 75 h) Samples were centrifuged at 10,000 rpm for 5 min to remove the biomass and analyzed for residual metal ion concentrations. Chromium ions adsorbed on to the biosorbent was calculated from the difference between the metal ion concentration in the solution before and after the biosorption process. The Cr(VI) uptake by free and immobilized biomass of *G.lucidum* , and *M. hiemalis* was calculated from the difference between the initial and final chromium concentration as follows,

$$q=(Ci-Ce)V/W \quad (1)$$

where q is the amount of metal ions biosorbed onto the unit mass of the biomass (mg/g), C_i and C_e are the concentrations of the metal ions before and after biosorption (mg/l), V is the volume of the aqueous phase (L), and W is the amount of the adsorbent (g)[17].

Determination of uptake capacity and % removal

The Cr(VI) percentage sorption and uptake capacity were calculated as follows:

$$\text{Sorption efficiency}(\%)=(Ci-Ce)100/Ci \quad (2)$$

$$qe=(Ci-Ce)V/1000w \quad (3)$$

Where V is the volume of the solution in mL and W is the mass of the sorbent

RESULT AND DISCUSSION

Effect of solution pH

Fig. 1 shows the effect of pH on biosorption of Cr (VI) by *G. lucidum* and *M. hiemalis.* In sorption, the pH affects two aspects viz. metal ion solubility and biosorbent total charge [18]. This behavior depends on the functional group present on the fungal cell wall, which in turn determine the acidity constant. Therefore the pH of the medium affects the system's equilibrium state, as per following equations:

$$B\text{-}H=B^-+H^+ \quad (4)$$

Ionization of functional groups present on cell wall of biomass is strongly related to solution pH [19].Adsorption of Cr(VI) by *G. lucidum* free and immobilized had been found to increase with increase in pH up to pH2.0-6.0. For free (63.56%) and immobilized (93.27%) biomass of *G. lucidum* the maximum removal of Cr (VI) was observed at pH 6.0. As shown in Fig.1, sorption efficiency of Cr (VI) were higher under acidic and neutral pH and decrease with the increase of under alkaline pH conditions.

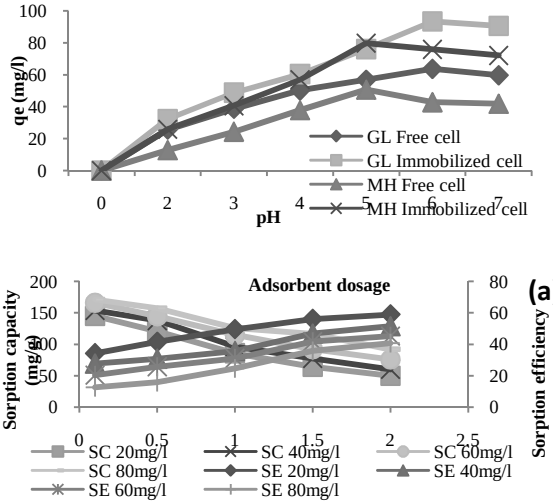
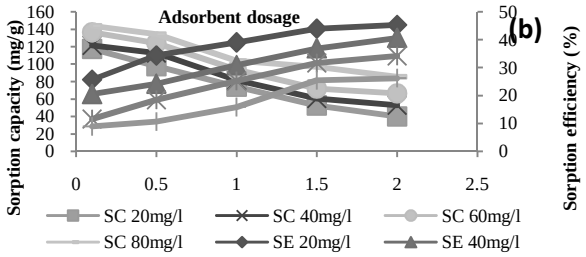
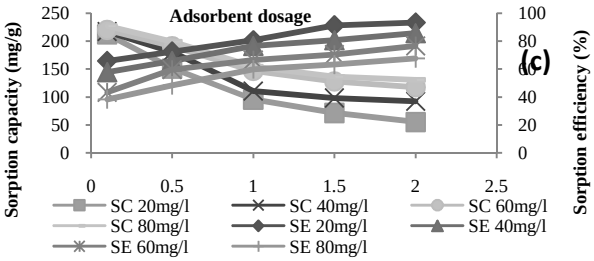
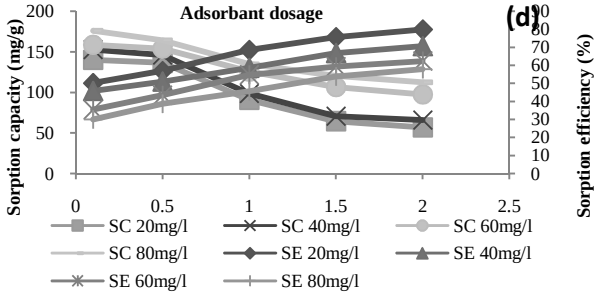


Fig. No 1 Effect of pH on the Cr(VI) uptake by free and immobilized biomass of *Ganoderma lucidum* and *Mucor hiemalis* Cr(VI) conc. 20ppm,biomass concentration=2g/l, Temperature=30°C.







At low pH the cell surface of the biomass becomes positively charged due to high concentration of protons and this inhibits

the binding of metal ions owing to columbic repulsion. Uptake of Metal uptake was low at lower pH as hydrogen ions effectively compete with metal ions to bind the sorption site [20]. The sorption capacity of Cr (VI) at pH 4.0 by free and immobilized *M. hiemalis* 50.67 %& 75.76% and it reduces when pH increases gradually. Cr (VI) occurs in the form of oxy anion as $HCrO_4^-$, $Cr_2O_7^{2-}$, CrO_4^{2-}, $Cr_4O_{13}^{2-}$, $Cr_3O_{10}^{2-}$ [21]. The lowering of pH causes the surface of the sorbent to be protonated to a higher extent. This results in a stronger attraction for negatively charged Cr (VI) complex ions in the solution.

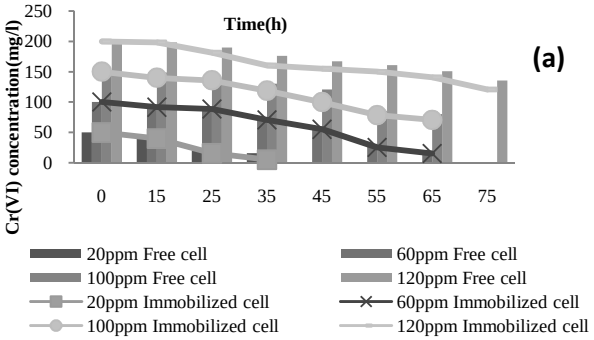
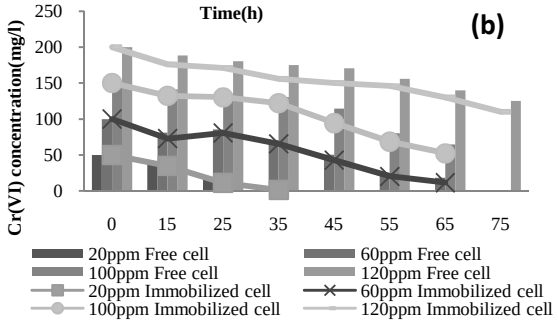


Fig. No 2 Effect of the adsorbent dosage (a) effect of free *Ganoderma lucidum dosages* at pH6.0 (b) effect of free *Mucor hiemalis* at pH4.0 (c) effect of Immobilized *Ganoderma lucidum* at pH6.0 (d) effect of Immobilized *Mucor hiemalis* at pH4.0 on Cr(VI) adsorption at different Cr(VI) concentrations(biomass concentration=2g/l, Temperature=30°C). SE represents *Sorption efficiency* and SC represents *Sorption capacity*.



Effect of biosorbent dose

The adsorbent dosage is an important factor for sorption capacity of Cr (VI). The number of available sites and exchanging ions for adsorption depends upon the amount of adsorbent in the biosorption process. Both the organisms showed an increase in percentage removal and decline in biosorption capacity on increasing biomass from 0.1g to 0.2g and decreasing metal concentration from 20 to 80mg/l (Fig. 2). Similar results were obtained by immobilized cells of both *G. lucidum* and *M. hiemalis.* Maximum biosorption capacities (and efficiencies) were 227 and 93.27respectively by *G. lucidum* at 0.2 g dose. Higher biomass concentration can exert a shell effect, protecting the active sites which is occupied by metal (Cr) and results a lower specific Cr (VI) uptake [22].

Effect of initial metal concentration and contact time

The initial concentration of Cr (VI) in the solution remarkably influenced the equilibrium uptake of Cr (VI) at all the time studied (15-75 min). Cr (VI) concentration of 20, 60,100,120 mg/l were taken for study in different time interval. As shown from Fig.3 66% Cr(VI) removal in 20 mg/l, 41% removal in 60 mg/l , 33% removal in 120 mg/l and 87.54% in 20mg/l, 55% in 60 mg/l, 40% in 120 mg/l by free and immobilized biomass of *M. hiemalis.* Free and immobilized biomass of *G. lucidum* shows 88.66% Cr (VI) reduction in 20 mg/l, 49.66% in 60 mg/l, 37.50% in 120mg/l and 96.20% in 20mg/l, 57.09% in 60mg/l, 45.50% in 120mg/l respectively. Immobilized biomass of both the fungus shows higher biosorption capacity. The low metal concentrations result in a higher ratio of the surface binding sites on the adsorbent to the total metal ions available, and virtually all the metal ion could be sorbed and removed [23].

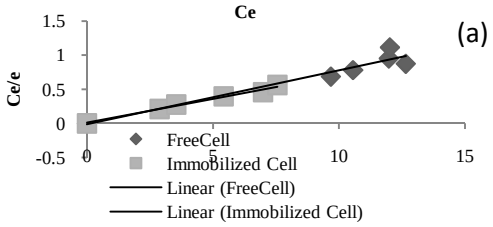
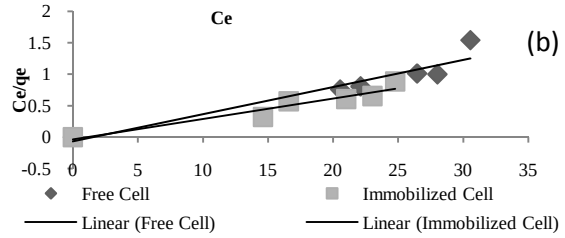
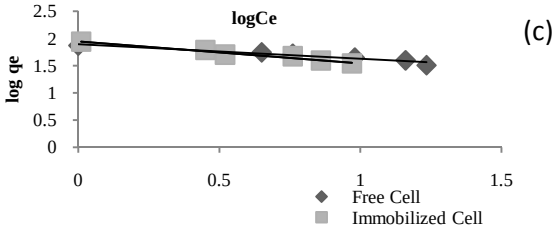
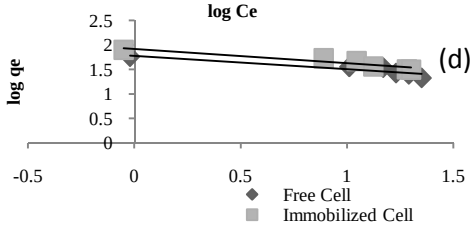
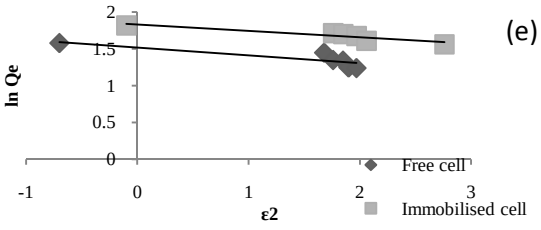


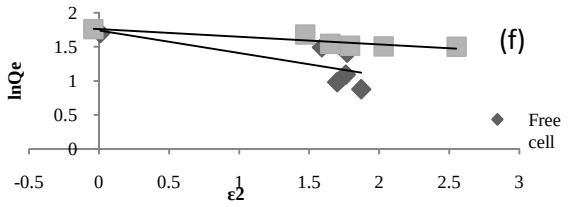
Fig. No 3 Effect of initial chromium concentration 20, 60, 100 and 120ppm with (a) free and immobilized biomass of *Ganoderma lucidum* (b) free and immobilized biomass of *Mucor hiemalis* at different contact time (15-75 h) on Cr(VI) reduction.











Equilibrium isotherm models

Langmuir, Freundlich and Dubinin – Radushkevich models were used to determine the sorption equilibrium between the solid biosorbent and metals ions. The isotherm equations for all models proposed are listed in Table 1. The Langmuir model assumes that a monomolecular layer is formed when biosorption takes place without any interaction between the adsorbed molecules [24, 25].The Langmuir adsorption model is given by

$$C_e/q_e=1/Q_{max}b+C_e/Q_{max} \quad (5)$$

Table 1 Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm model constant and correlation coefficient for sorption of Cr(VI) by Free and Immobilized biomass of *Ganoderma lucidum* and *Mucor hiemalis.*

Langmuir isotherm		b	Q_{max}		R^2
	Free	0.879	23.20		0.933
	Immobilized	0.673	30.67		0.985
	Free	0.136	12.67		0.902
Ganoderma lucidum	Immobilized	0.142	14.24		0.919
Mucor hiemalis		K_f	n		R^2
	Free	1.895	3.74		0.929
Freundlich isotherm	Immobilized	1.947	2.47		0.968
	Free	1.776	3.66		0.853
Ganoderma lucidum	Immobilized	1.915	3.45		0.885
Mucor hiemalis					
Dubinin–Radushkevich (D–R) isotherm		q_m	k	E	R^2
Ganoderma lucidum	Free	1.518	0.106	9.433	0.733
	Immobilized	1.829	0.086	11.627	0.861
Mucor hiemalis	Free	1.732	0.331	3.021	0.529
	Immobilized	1.760	0.113	8.849	0.803

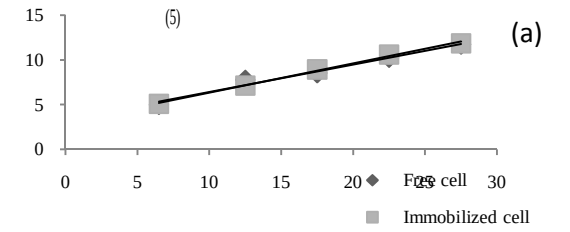


Fig. No 4 Langmuir (a, b) for free and immobilized *Ganoderma lucidum* and *Mucor hiemalis,* Freundlich (c, d) for free and immobilized *Ganoderma lucidum* and *Mucor hiemalis* and free and immobilized Dubnin- Redushkevich (e, f) for *Ganoderma lucidum* and *Mucor hiemalis.*

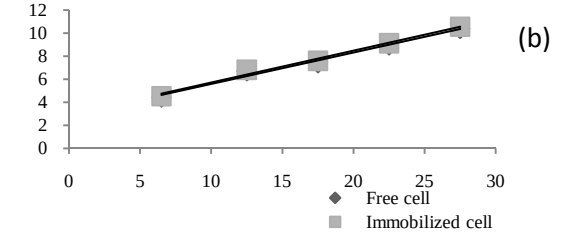


Fig. No 5 Weber-Morris/ Intraparticle diffusion for adsorption of Cr (VI) ions by free and immobilized (a) *Ganoderma lucidum* (b) *Mucor hiemalis.*

Where q_e (in milligram per liter) and C_e (in milligram per liter) are the amount of adsorbed per unit mass of adsorbent and unabsorbed absorbate concentration in the solution at equilibrium, respectively., and Q_{max} *and b* are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. When C_e/q_e is plotted against C_e, straight line with slope1/Q_{max} indicates that adsorption follows the Langmuir isotherm [26]. Freundlich isotherm is an empirical equation based on a heterogeneous surface [27, 28]. Freundlich isotherm model is a most popular model for a single solute system, based on the distribution of solute between the solid phase and aqueous phase at equilibrium.

$$\log q_e = \log K_f + 1/n \log C_e \quad (6)$$

Table 2 Comparison of the pseudo first-order, pseudo Secound-order and Intra-particle diffusion sorption rate constant, qe values obtained at different initial Cr (VI) concentration.

First order kinetics		$k_1(min^{-1})$	q_{eq} (mmol/g)	R^2
	Free	0.0067	1.833	
Ganoderma lucidum	Immobilized	0.0099	1.848	
	Free	0.0032	1.582	0.964
Mucor hiemalis	Immobilized	0.0045	1.595	0.98
				0.932
Secound order kinetics		k_2 (g/mmol/min)	q_{eq} (mmol/g)	0.983
Ganoderma lucidum	Free	0.1344	0.297	
	Immobilized	0.1738	0.797	R^2
Mucor hiemalis	Free	0.2824	0.086	0.981
	Immobilized	0.4289	0.124	0.996
Intra-particle diffusion		k_{id} (mmol/g $min^{0.5}$)	R^2	0.977
	Free		0.981	0.981
Ganoderma lucidum	Immobilized	0.3071	0.999	
	Free	0.3265	0.986	
Mucor hiemalis	Immobilized	0.2729	0.988	
		0.2764		

where$q_e$and C_e are the equilibrium adsorption capacity of the biosorbent and the equilibrium concentration in the aqueous solution, respectively. K_f and n are Freundlich constants related to sorption capacity and sorption intensity of adsorbents. The value of n falling in the range of 1– 10 indicates favorable sorption [29].

The Dubinin–Radushkevich (D–R) isotherm is more general than the Langmuir isotherm since it does not assume a homogeneous surface or constant biosorption potential. It was applied to distinguish between the physical and chemical biosorption of Cr (VI) ions. (D–R) isotherm model is expressed by the following equation [30]

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \quad (7)$$

ε is the Polanyi potential, which is related to the equilibrium concentration as follows:

$$\varepsilon = RT\ln(1 + 1/C_e) \quad (8)$$

qe,is the amount of Cr(VI) ions sorbed at equilibrium per unit weight of biosorbent (mol g^{-1}), β is aconstant related to the biosorption energy (mol^2 kJ^{-2}), q_m is the theoretical saturation capacity (mol g^{-1}), C_e is the equilibrium concentration of Cr(VI) ions in solution (mol L^{-1}), R is the gas constant (J mol^{-1} K^{-1}), and T is the absolute temperature (K).Value of q_m are calculated from the intersept and slope of the plot by plotting in qe versus ε^2 . The value of E can be calculated from D-R parameter as follows:

$$E = 1/2\beta^{1/2} \quad (9)$$

The value of mean sorption energy gives information about the chemical ion-exchange or physical biosorption. If its value is in the range of 8–16 $kJmol^{-1}$ the biosorption process follows chemical ion-exchange mechanism , while for the values of E <8 kJ mol^{-1} the biosorption process is of a physical nature [31].

As shown in Fig.4 Langmuir, Freundlich and Dubinin–

Radushkevich (D–R) adsorption constants evaluated from the isotherms at different concentration along with the correlation coefficients. From Table 1, higher correlation coefficient, R^2, was obtained for Langmuir isotherm in compare to Freundlich and Dubinin–Radushkevich (D–R). The immobilized biomass showed better affinity to Cr (VI) than free biomass but low capacity may be attributed due to loss of some homogenous.The best fit of equilibrium data for Langmuir expression confirms the monolayer adsorption occurred over a surface containing a finite number of adsorption sites [32].

Kinetic studies

Langergren's pseudo first order, pseudo second order, and diffusion models were use for analysis of sorption kinetics. The Langergren's pseudo first order kinetics can be written in Eq.(10) as follows [33].

$$\log(q_e - q_t) = \log q_e - k_1/2.303 \times t \quad (10)$$

where q_e and q_t are the amounts of Cr(VI) ion, (mg/g) adsorbed on the sorbent at equilibrium, and at time t, respectively, and k_1 is the rate constant (min^{-1}). The values of the rate constants k_1 obtained for various concentrations are given in Table 2 along with the corresponding correlation coefficients.

If the rate of sorption is a second-order mechanism, the pseudo-second-order chemisorption kinetic rate equation is expressed as [34].

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (11)$$

The rate constant k_2 can be obtained from the intercept of the linearized pseudo-second-order rate equation. If the pseudo second- order equation can fit the sorption data, there should be good linearity between t/q and t.The values of the rate constant are presented in Table 2 along with the correlation coefficient.

As shown from Table2 R^2 value of Langergren's pseudo first order is less than pseudo second order. The rate of sorption on free and immobilized biomass of both the organism follows the pseudo-second order kinetics because the correlation coefficient of the second order was slightly higher than that of the first order. This suggests that the rate-limiting step may be the chemical adsorption not the mass transport limitation [35,36].

Intra-particle diffusion studies

If the movement of the metal ion from the bulk liquid film surrounding the particle is ignored, the adsorption process can be divided into boundary layer diffusion, sorption of ions onto sites and intra-particle diffusion. Intra-particle diffusion will be a rate limiting step inmany cases and can be determined using the following equation [37].

$$q_t = k_{id}^{1/2} + C \quad (12)$$

where k_{id} is the interpartical diffusion rate constant (in miligram per gram per (hour)1/2) and C is the intercept. Figure 5 a, b represents the plot of q_t versus $t^{1/2}$. If the regression of q_t versus $t^{1/2}$ is liner and passes through the oregin, then the intraparicle diffusion is the sole rate limiting step. Table2 shows the value of k_{id} and corelation coefficient**.** Increasing metal ion concentration in the aqueous solutions seems to reduce the external diffusion of the adsorbate and enhances intra-particular diffusion [38]. As seen from the figure, the intra-particle diffusion rate equation provided the best correlation coefficient, i.e. 0.981,0.999 for free and immobilized *G. lucidum* and 0.986, 0.988 for free and immobilized *M. hiemalis* for all the process of Cr(VI) adsorption.

CONCLUSION

G.lucidum shows higher biosorption capacity at pH 6.0. Concentration was most affacting parameter in present study. The biosorption capacity decreases wih increasing concentration. Comparative analysis of biosorption indicated that immobilized biomass of both *G. lucidum* and *M. hiemalis* showed better Cr(VI) adsorption capacity than free biomass from aqueous environment up to 96 %, therefore the fungus is proposed as an effective biosorbent for removal of heavy metals in waste water treatment [39]. As the pH increased, the metal biosorption capacity increased significantly up to pH 6.0 for *G. lucidum* and pH 4.0 for *M. hiemalis*. The equilibrium adsorption data showed better correlation with the Langmuir adsorption data in concentration ranges (20-150mg/l). The maximum adsorption capacity (q_{max}) for immobilized biomass of *G. lucidum* was upto 30.67mg/g. The sorption kinetic data fit the intra particle diffusion and pseudo-second order rate equation better in compare to pseudo first order equation. According to [40-42] the biosorbents can be regenerated and reused by acid treatment.

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