

Biosorption of Chromium(VI) by immobilized mixed biosorbent: Equilibrium and Kinetic Modelling

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Abstract

Due to their extreme toxicity towards aquatic life and humans, the removal of heavy metal ions from waste water is significant. Microorganisms (*Aspergillus niger*) and low cost natural biosorbents (*Annona squamosa* peel powder) are increasingly being studied to remove aqueous solution from heavy metal ions. Batch shaking sorption experiments have been performed in this study to investigate the sorption ability of mixed biosorbents (*Aspergillus niger* and *Annona squamosa* peel powder) at different initial concentrations of chromium, initial pH, temperature and biomass load. Equilibrium reached after 24 h of touch time.

The optimal value for initial concentration was found to be 100mg/l. A maximum percentage removal of 97 percent and specific uptake of 7mg/g for Cr(VI) sorption were obtained under this optimized environment. Equilibrium model suits well with isotherms for adsorption in Langmuir and Freundlich. The kinetic analysis showed that at the initial stage the sorption process was very quick and after 24 h of contact time equilibrium was reached. Chromium sorption on mixed biosorbents is achieved by a second-order kinetic approach from Lagergren. The overall sorption cycle was regulated by processes of intraparticle and external diffusion.

Keywords: Biosorption, mixed biosorbent, adsorption isotherms, equilibrium model, kinetic model.

Introduction

The growth of industrial production in recent years contributes significantly to the rise in environmental heavy metal levels, particularly in aquatic system³. Chromium (VI) is commonly used in manufacturing processes such as tanning leather and metal plating and is present in oil refining and mining wastewater. Chromium is toxic at higher levels; Due to its toxicity, drinking water requirements allow chromium concentrations in inland surface water below 0.1mg/l and below 0.5mg/l in potable water¹⁶.

Many physico-chemical methods for extracting them from industrial effluents have been suggested. Such methods are however frequently unsuccessful and/or expensive when used for extracting heavy metal ions at low concentrations¹⁹. Therefore, low-cost, readily available materials need to be

produced which could adsorb chromium. Biosorption is a method used to sequester harmful heavy metals and extract toxins from industrial effluents using inexpensive dead biomass. Fungal cell walls and their constituents play a major role in the biosorption process.

Fungal biomass may also suck up significant quantities of heavy metals from aqueous solution through adsorption or a similar mechanism, even if physiological activity is not present. Several fungal species such as *Rhizopus arrhizus*, *Aspergillus niger* and *Penicillium spinulum* have been studied extensively for biosorption of heavy metals and the process mechanism seems to depend on the species^{8,11}.

Previous work shows an increasing interest in the quest for a variety of materials such as low-cost adsorbents like sawdust, cocoa shell, rice husk, modified walnut sawdust, papaya wood, maize leaf, rice husk ash and neem bark, fly ash and tea-industry waste¹⁵. Therefore, the use of such materials as low-cost adsorbents is recognized as a feasible and economical wastewater treatment method.

Equilibrium based kinetic modelling: Sorption equilibrium is generally defined by an isothermic equation whose parameters express the sorbent's surface properties and affinity at a fixed temperature, pH and initial concentration of metals. The simplest examples of such isotherms are the isotherms Freundlich and Langmuir which are often used to achieve optimum biosorption efficiency of the biosorbent. The Langmuir model suggests as a hypothesis that the absorption occurs by monolayer sorption on a homogeneous surface without the interaction of sorbed molecules. The basic assumptions on which the model is based are: 1) metal ions are chemically adsorbed at a fixed number of well-defined sites; 2) each site can carry one sorbate ion; 3) all sites are energetically equivalent and 4) adjacent sites do not interact with ions. This model is described by the equation²⁰:

$$q_{eq} = \frac{Q^0 b C_{eq}}{1 + b C_{eq}} \quad (1)$$

where q_{eq} and C_{eq} are the amount of adsorbed metal per unit weight of biosorbent and un adsorbed metal concentration in solution at equilibrium respectively. Q^0 is the maximum amount of metal per unit weight of biomass to form a complete monolayer on the surface bound and b is a constant related to the affinity of the binding sites. Q^0 and b can be determined from a plot of $1/q_{eq}$ and $1/C_{eq}$.

Freundlich model proposes a monolayer sorption with a heterogeneous energy distribution of active sites as defined in the equation:

$$q_{eq} = K_F C_{eq}^{1/n} \quad (2)$$

where K_F and n are device properties of the Freundlich constants. K_F and n are the adsorption power and adsorption strength measures respectively. Eq. (2) can be linearized in logarithmic form and Freundlich constants can be determined. A single-layer metal sorption is designed for both models²⁰.

Sorption kinetic data and Modelling: Sorption kinetics is important because it regulates the efficiency of the process and the prediction of sorption rate gives important information for the design of batch sorption systems. Biosorption kinetics is analysed using the chemical kinetic model based on reaction and the kinetic model based on diffusion.

Chemical reaction – based kinetic modelling: First-order and second-order kinetic models from Lagergren are the most common models used to study heavy metal biosorption kinetics and to measure the extent of biosorption kinetics uptake. These models are experimentally tested and used to predict the biosorption rate of heavy metals during biosorption²⁰.

In order to investigate the mechanism of biosorption and potential rate controlling steps, the first and second order kinetic models have been used. The first order rate expression of Lagergren is:

$$\log(q_{eq} - q) = \log q_{eq} - \frac{K_{1,ad}t}{2.303} \quad (3)$$

where $K_{1,ad}$ is the rate constant of first order biosorption (min^{-1}), q_{eq} is the adsorbed quantity of the metal ion per g of dried fungal biomass at equilibrium (mg/g) and q is the amount of metal adsorbed by sorbent (mg/g) at any time and is calculated from the following equation:

$$q = \frac{(C_o - C)V}{W} \quad (4)$$

where C_o is the initial concentration of metal ions (mg/l), V is the volume of metal solution (l), W is the weight of biosorbent (g) and C is the final concentration of metal ions (mg/l). Linear plots of $\log(q_{eq} - q)$ versus time indicate the applicability of this model as in eq. (3):

The integrated form of second order kinetic model is expressed as:

$$\frac{t}{q} = \frac{1}{K_{2,ad}q_{eq}^2} + \frac{t}{q_{eq}} \quad (5)$$

where $K_{2,ad}$ is the rate constant of second order biosorption (g/mg/min). If the second order kinetics is applicable, the plot of t/q versus time should give a linear relationship⁷.

Diffusion – based kinetic modelling: Diffusion of sorbate has a significant effect on sorption. Sorption of any sorbate molecule on sorbent particles necessarily involves the following steps: (i) bulk diffusion, (ii) external mass transfer of sorbate molecules across the external liquid film around the sorbent particles, (iii) binding of sorbate molecules on the active sites distributed on the outer surface of the sorbent particles, (iv) intra-particle diffusion of sorbate molecules into macro, meso and micropore and (v) sorption of sorbate molecules onto active sites distributed within the sorbent particles. The steps (iii) and (v) are very rapid and hence they do not have much role in determination of the rate of sorption process. Thus, only external mass transfer and intra-particle diffusion play important role in rate determination⁹.

Weber and Morris have defined that the sorption capacity will vary with the square root of time if the intra-particle diffusion is the control stage of the cycle.

$$q_t = K_{id}t^{1/2} + I \quad (6)$$

where K_{id} is the intra-particle diffusion rate constant and I is the intercept. Plot of q_t versus $t^{1/2}$ should be straight line when sorption mechanism follows the intra-particle diffusion process¹⁴.

The external mass transfer model is represented by eq. (7):

$$\left[\frac{d\left(\frac{C_t}{C_i}\right)}{dt} \right]_{t=0} = -K_{ES} \quad (7)$$

where C_i and C_t , respectively represent the concentration in the beginning and at time (mg/l). The rate constant of external mass transfer model K_{ES} (min^{-1}) is calculated by the slope of the plot of C_t/C_i versus time.

Boyd plot: Boyd's model determines whether the main resistance to mass transfer is in the thin film (boundary layer) surrounding the adsorbent particle, or in the resistance to diffusion inside the pores. Boyd plot predicts the actual slow step involved in the adsorption process. Boyd kinetic expression is given by Vadivelan et al¹⁸:

$$F = \frac{q_t}{q_o} \quad (8)$$

where q_o is the amount of adsorbates adsorbed at infinite time (mg/g) and q_t represents the amount of metal adsorbed at any time t (min), F represents the fraction of solute adsorbed at any time t and B_t is a mathematical function of F and is expressed by the following equation. The Boyd plot is obtained by plotting B_t versus time.

$$B_t = -0.4977 - \ln(1 - F) \quad (9)$$

The goal of the present work was the development of an efficient and cheap biotechnological system for the removal of chromium(VI) using immobilized mixed biosorbent. In the present study, batch shaking sorption experiments were performed to investigate the sorption capacity of immobilized mixed biosorbent at different initial chromium concentration, initial pH, temperature and biomass loading.

Material and Methods

Preparation of sorbate solution: Dissolving 2.83 g of potassium dichromate in double distilled water has produced a 1000 mg/l stock solution of chromium. The required concentrations of chromium ions were prepared by dilution method from stock solution.

Preparation of the biosorbent: In this study we used *Annona squamosa* (custard apple) peel powder. The custard apple peel was obtained from the local market; materials were washed, dried and crushed for several days in primary crusher and air dried in the sun until their weight remained constant. It had been crushed in roll crusher and hammer mills after drying. Material obtained by crushing and grinding was screened through BSS meshes. Finally, the items collected were kept for further use in glass bottles.

Aspergillus niger MTCC-132, a filamentous fungus obtained from the Institute of Microbial Technology, Chandigarh, was also used in this study. The culture was grown at 30°C in an agitated liquid media containing potato extract (200 g/l) and dextrose (20 g/l). Before sterilization the medium's pH was adjusted to 5.5 with dilute sulphuric acid. Then, the cell suspension was separated, dried, homogenized and stored for subsequent studies of biosorption.

Preparation of immobilized mixed biomass beads: Immobilized mixed biomass beads are prepared using sodium alginate from 8 per cent (w/v). A known equivalent amount of biomass (peel powder and *A. niger*) is combined with sodium alginate and the mixtures under warm condition are continuously stirred until the alginate is dissolved. The suspension is dripped into 2% (w/v) calcium chloride solution through a syringe. The beads are stored in calcium

chloride solution for about 30 min before being rinsed in double distilled water.

Batch biosorption studies: Batch tests were performed in Erlenmeyer flasks by inserting proven amounts of immobilized mixed biomass beads in 100 ml of aqueous potassium dichromate. The flasks were shaken gently on a shaker at a steady rate of shaking at 150 rpm for 240 min before sorption for equilibrium was obtained. Samples for the residual concentration of metal ions in the solution were taken from the solution at regular time intervals. The residual concentration of chromium ions in the solutions was spectrophotometrically calculated at 547 nm using the complexing agent diphenylcarbazide².

The effect of the initial concentration of chromium ion on the percentage removal of chromium is studied by conducting experiments with different initial concentrations of chromium ion, namely 100 mg/l, 200 mg/l, 300 mg/l, 400 mg/l and 500 mg/l under the same temperature, pH and biomass loading conditions and the experiment was carried out as mentioned.

Characterization of the Biosorbent

FTIR Analysis: The FTIR spectra of raw *Annona squamosa* peel powder and chromium-loaded *Annona squamosa* peel powder in the range of 400-4000 cm⁻¹ are taken to gather information on the existence of potential interactions between the functional groups of natural biosorbents and the metal ions as shown in fig. 1.

The FTIR spectrum of fresh biosorbent showed several individual and narrow adsorption bands of different wavelength. The infrared spectrum of fresh *Annona squamosa* peel powder has large bands based at 3400 cm⁻¹ for O-H and N-H stretching, C-H stretching vibrations at 2924 cm⁻¹, stretching carboxylate groups at 1639 cm⁻¹, C-O stretching of oxygen containing compounds at 1062 cm⁻¹ and polysulfide groups at 500 cm⁻¹^{13,17}.

The FTIR spectra of metal-loaded biomass showed some shifts in some of characteristic bands as shown in fig. 2. The overlapping region for N-H and O-H stretching in the range of 3200-3600 cm⁻¹ presents some changes in the spectrum of biomass. It has been recommended that the binding of metal ions microorganisms relates to the oxygen and nitrogen containing compounds as functional groups on the cell walls of microbial biomasses⁵. The stretching vibration of carboxylate groups is shifted from 1639 cm⁻¹ to slightly higher wave number 1654 cm⁻¹, which could be attributed to an interaction between the both metal ions and carboxylate groups. The peak of C-O group of the raw biomass is shifted from 1100 cm⁻¹ to 1019 cm⁻¹ for metal loading biomass.

The result indicates that some frequency change is observed which suggests that this group did not participate in the biosorption of metal ions and only sulphur compounds are involved in the metal biosorption.

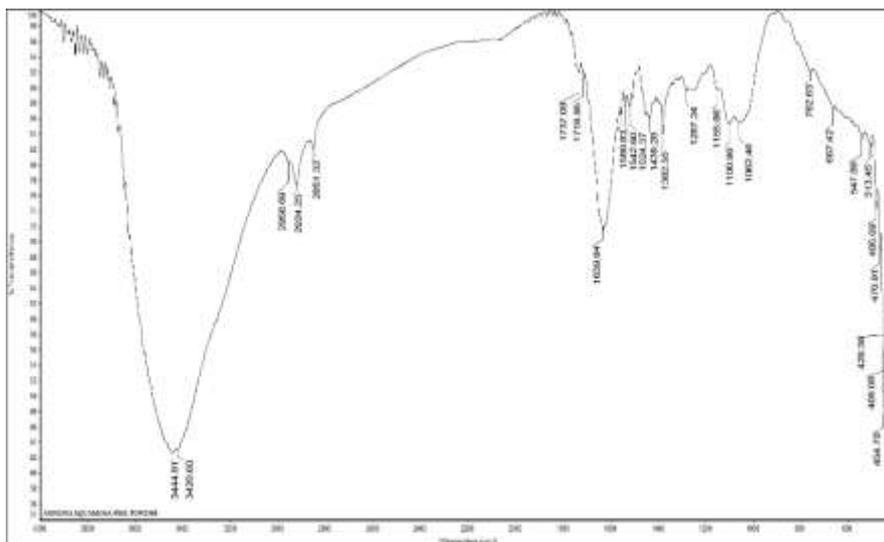


Fig. 1: FTIR Spectra of Raw *Annona squamosa* Peel Powder

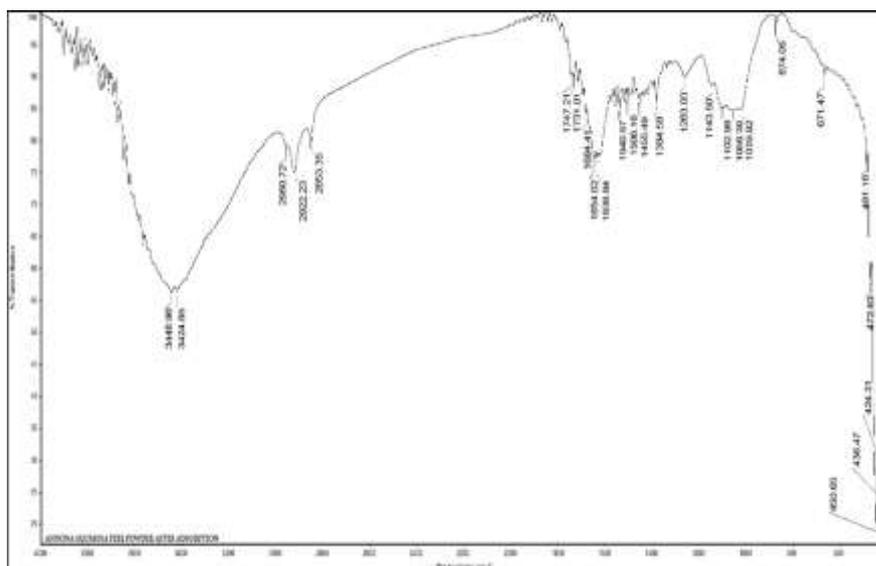


Fig. 2: FTIR Spectra of Chromium Loaded *Annona squamosa* Peel Powder

Change in the spectrum represents change in functional groups of biomass after metal adsorption. It is noted that shifting of wave number depends on the concentration of the metal present in the given sample and changes in functional groups of biomass after metal adsorption are approved by literature survey¹⁰.

Results and Discussion

The biosorption of metals using immobilized mixed biosorbent in a batch process depends on both contact time between the adsorbate and adsorbent particles and initial metal ion concentration. The effect of initial metal ion concentration on contact time, percentage removal and specific uptake of chromium was given in fig. 3 and fig. 4 respectively. Fig. 3 shows that equilibrium was attained in 24 h, also the sorption of chromium on immobilized mixed biosorbent increases with increasing contact time.

Chromium removal efficiency was affected by the initial metal ion concentration with decreasing removal

percentages as concentration increases from 100 mg / l to 500 mg / l. As the initial chromium concentration increases from 100 mg/l to 500 mg/l, the percentage removal of chromium decreases from 97 percent to 74 percent and the specific uptake of chromium increases from 7 mg/g to 26 mg/g respectively. Adequate adsorption sites are essential for the adsorption of metal ions at lower initial metal ion concentrations. However, the number of metal ions are relatively higher in higher concentrations compared to the availability of adsorption sites.

The functional groups involved in metal absorption and the metal chemistry may explain the pH-dependence of biosorption capacity. The proportion of metal sorption varies with the pH of the medium specified in fig. 5. Chromium's percentage reduction falls from 93 per cent to 65 per cent as the pH rose from 2.0 to 6.0. With a higher pH, the biosorbent surface will have hydroxyl groups that do not impact the chromate ions that are interacting with the hydroxyl ions.

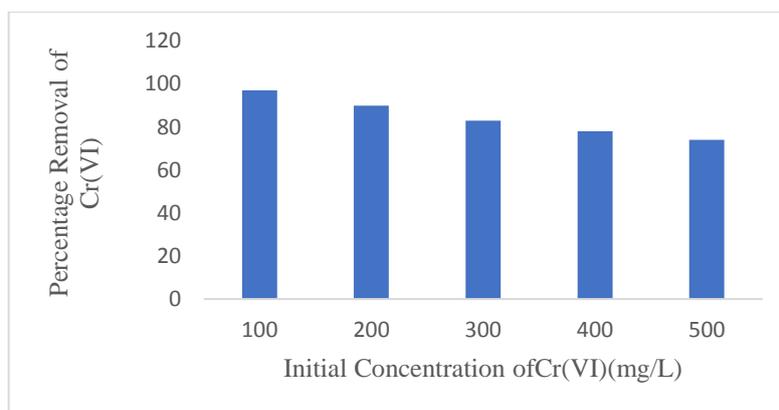


Fig. 3: Effect of Initial Chromium concentration on Percentage Removal of Chromium by Immobilized mixed biosorbent

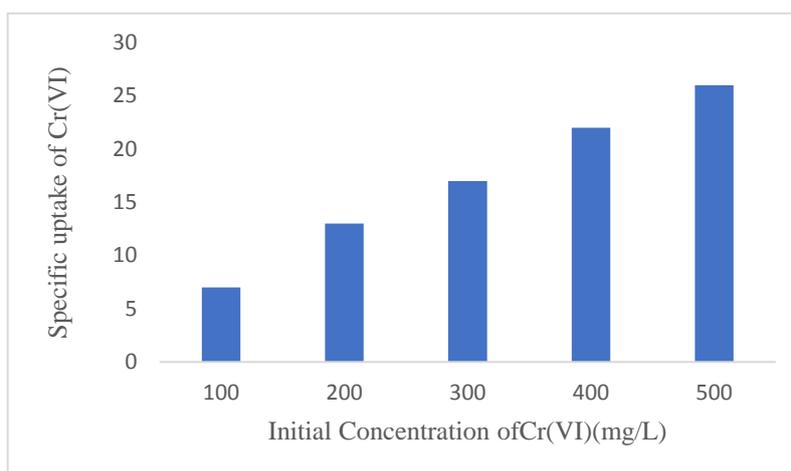


Fig. 4: Effect of Initial Chromium concentration on Specific uptake of Chromium by Immobilized mixed biosorbent

Table 1
Langmuir and Freundlich Constants-Biosorption of Chromium by immobilized mixed biosorbent

Langmuir constants		
Q_0 (mg/g)	b (l/mg)	R^2
22.53	0.169	0.9456
Freundlich constants		
K_F	n	R^2
4.835	2.761	0.9923

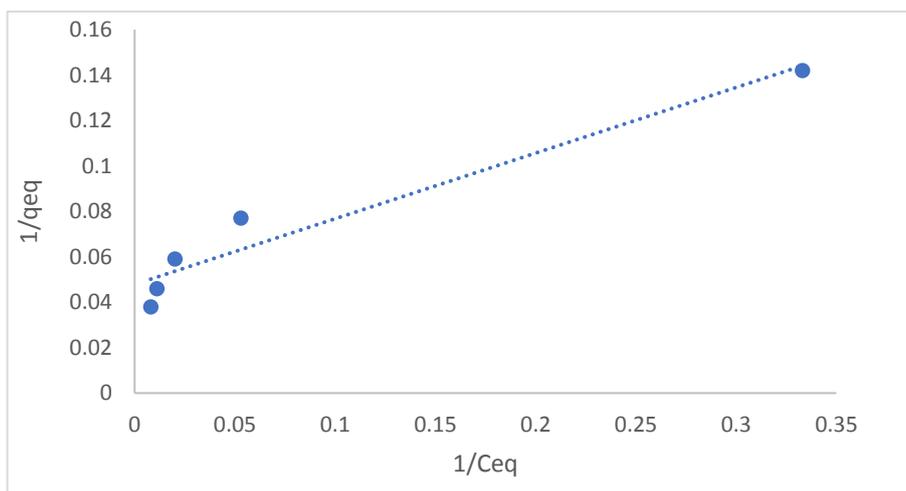


Fig. 5: Langmuir Adsorption Isotherm for the Biosorption of Chromium by Immobilized mixed biosorbent

The linearized Langmuir and Freundlich adsorption isotherms of chromium were given in fig. 5 and fig. 6. The higher correlation coefficients showed that the biosorbent was very suitable to characterize the equilibrium of biosorption in the concentration ranges studied. The Langmuir and Freundlich constants were used to compare the biosorptive capacity of the biosorbent for chromium. The constants were evaluated and tabulated in table 1.

Chromium's sorption on immobilized mixed biosorbent data was plotted as per eq. 3 and the results are shown in fig. 7. The first-order kinetic model does not provide a good fit for the chromium sorption experimental data as well as the

theoretical q_e values obtained from the kinetic model did not provide appropriate values.

The t/q plot against t of eq. 5 appears in fig. 8. The linearity is strong for the second-order sorption model with the correlation coefficients shown in table 2. The correlation coefficients are extremely high (> 0.99) and the theoretical q_e values for the second-order model have also been found to be in strong agreement with the experimental q_e values.

The second-order kinetics predicts the behaviour across the entire range of studies supporting a second-order equation and is in agreement with the rate-controlling phase being chemisorption (diffusion).

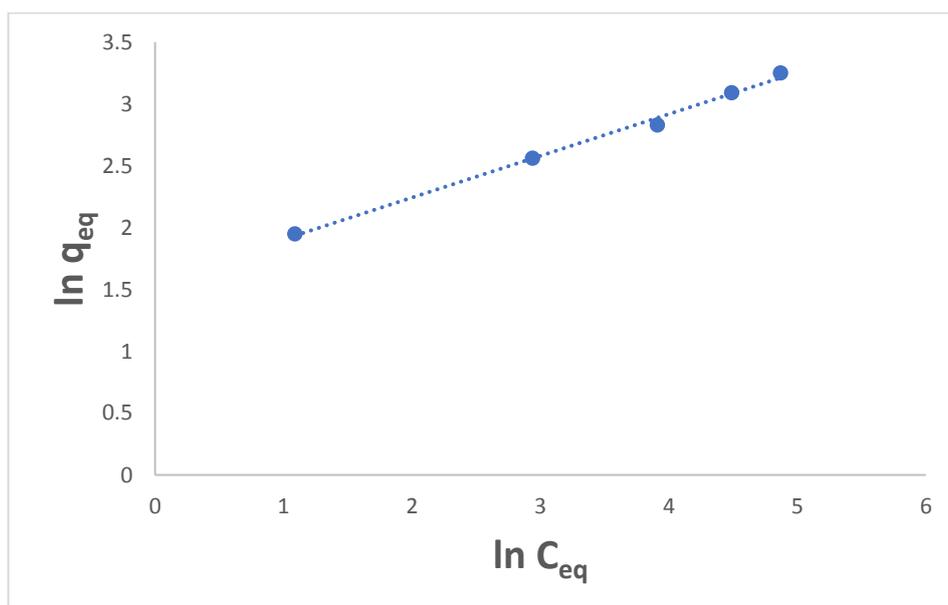


Fig. 6: Freundlich Adsorption Isotherm for the Biosorption of Chromium by Immobilized mixed biosorbent

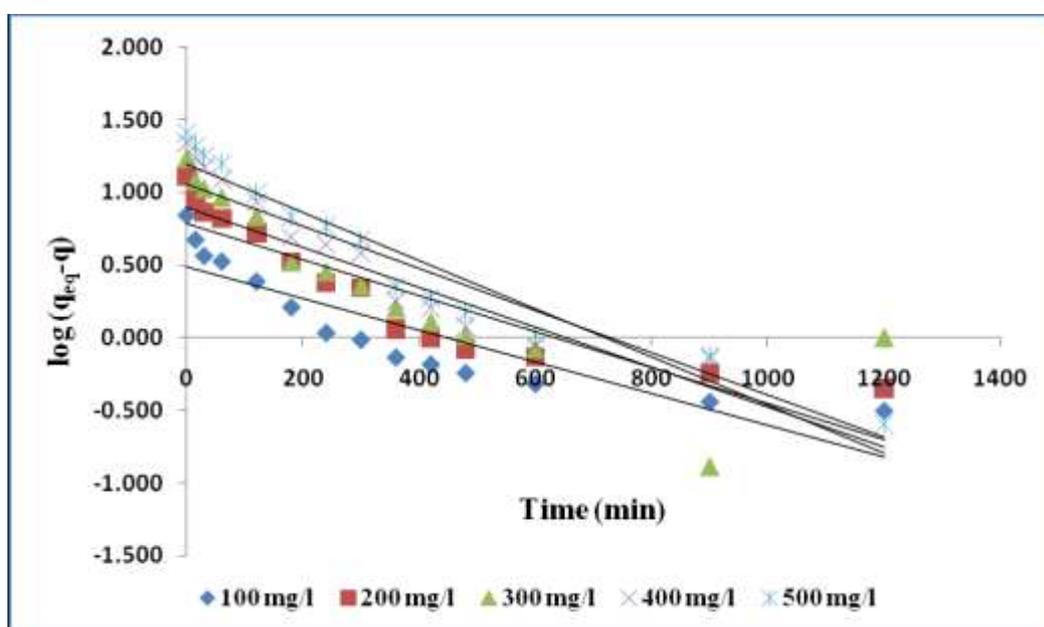


Fig. 7: First-order Lagergren Plot for the Biosorption of Chromium by Immobilized Mixed Biosorbent

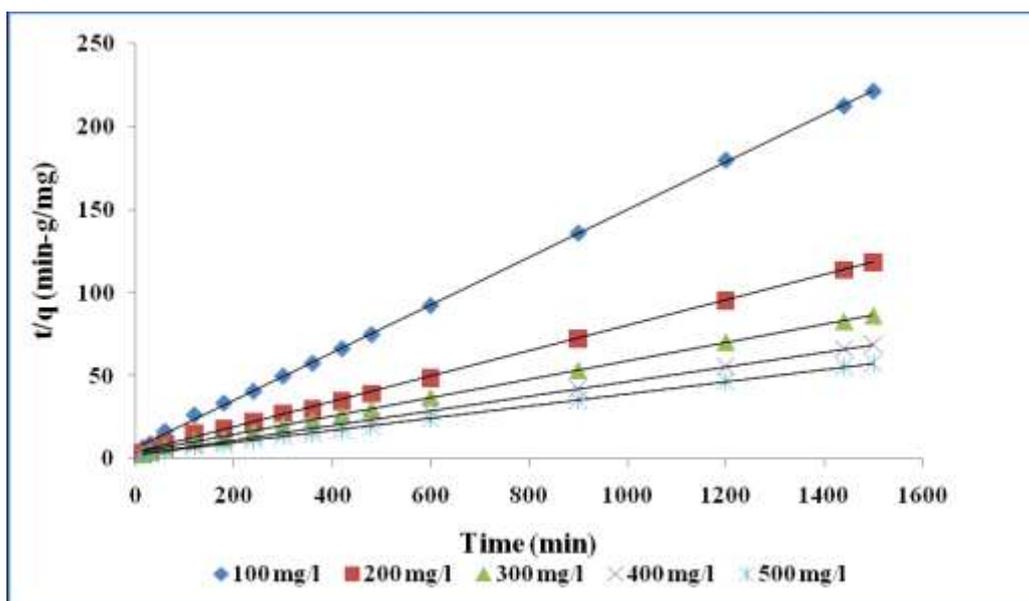


Fig. 8: Second-order Lagergren Plot for the Biosorption of Chromium by Immobilized Mixed Biosorbent

Table 2

Comparison of first- and second- order sorption rate constants obtained at different initial Chromium concentrations

Initial Concentration of Chromium (mg/l)	$q_{eq}(exp)$ (mg/g)	First order rate constant $K_{1,ad}$ (min^{-1})	$q_{eq}(theo)$ (mg/g)	R^2	Second order rate constant $K_{2,ad}$ (g/ mg-min)	$q_{eq}(theo)$ (mg/g)	R^2
100	7	0.0023	3.05	0.784	0.0031	6.99	0.999
200	13	0.0023	6.11	0.812	0.0015	13.16	0.999
300	17	0.0023	7.89	0.707	0.00083	18.18	0.999
400	22	0.0023	11.32	0.850	0.00071	22.73	0.999
500	26	0.0023	15.63	0.925	0.00048	27.78	0.999

Table 3

Kinetic parameters of the intraparticle diffusion model for the sorption of Chromium by immobilized mixed biosorbent.

S.N.	Initial (Chromium) concentration (mg/l)	Kinetic parameters		
		I (mg/g)	K_{id} (mg/g-min)	R^2
1	100	3.486	0.136	0.852
2	200	5.069	0.325	0.872
3	300	7.552	0.388	0.805
4	400	8.902	0.543	0.886
5	500	9.729	0.671	0.932

Sorption rate limiting phase prediction is an important feature for the sorption process analysis. Generally, the sorption can be controlled by film diffusion and/or intraparticle diffusion processes in batch mode sorption experiments. In order to evaluate the relative importance of these two processes, time-course metal sorption data proceeds through one or more than one steps or combination of two steps. The role of pore diffusion as the single rate controlling steps is tested by the aid of 'Weber and Morris' intraparticle diffusion model.

Table 3 shows the kinetic parameter data obtained for the sorption time period involving intraparticle diffusion process. Fig. 9 shows the plot of specific uptake versus $t_{1/2}$

for five different initial concentrations of chromium. The first linear portion referred to film diffusion of 0-60 min for the sorption era, the second linear portion represented intraparticle diffusion of 60-900 min for the sorption era and the last linear portion indicated sorption-desorption equilibrium of 900-1440 min for the length. A high coefficient of regression value indicates an significant link between q and $t_{1/2}$. The linearity of the plot indicates that the diffusion of intra particles plays a significant role in the taking up of metals. The value of intercept I from table 3 increased in solution with increased concentration of metal ions. The values of the intraparticle diffusion rate constant K_{id} decrease as the concentration of chromium increases.

Higher metal ion concentrations have provided stronger driving force to the mechanism of external mass transfer. It is clear from fig. 9 that the process of biosorption is jointly regulated by film (outer) diffusion and intraparticle (inner) diffusion respectively for the sorption of Chromium by immobilized mixed biosorbent^{1,6}. This non-linear relationship was also stated by other researchers that there was both boundary diffusion and intraparticle diffusion¹².

Figure 10 displays the external chromium sorption diffusion plot for the initial rapid process on immobilised mixed biosorbent. Table 4 shows the external mass transfer rate constant at different initial chromium concentrations for the initial rapid process. For an external mass transfer time of 60 min, the external diffusion model shows excellent correlation with the sorption results with strong correlation coefficients ($R^2 = 0.952 - 0.959$).

The external mass transfer rate constant decreased with increasing concentration of metal ions in the solution. This will suggest that the metal sorption at high concentration is presumably a surface process occurring on the outside of the sorbent atom which in effect decreases the intrinsic resistance to the transfer of mass for the sorption of chromium. Earlier research for the adsorption of lauryl benzyl sulfonate on algae has also identified similar patterns⁴.

Film diffusion and intraparticle diffusion are distinguished by using the Bt versus t plots and are shown for specific initial concentrations of chromium in fig. 11. Boyd plot shows the linearity for external mass transit time (0-60 min) for all the chromium concentration measured. The plot did not move through the origin in all cases, thus confirming that external particle film diffusion is a dominant rate of sorption cycle¹⁴.

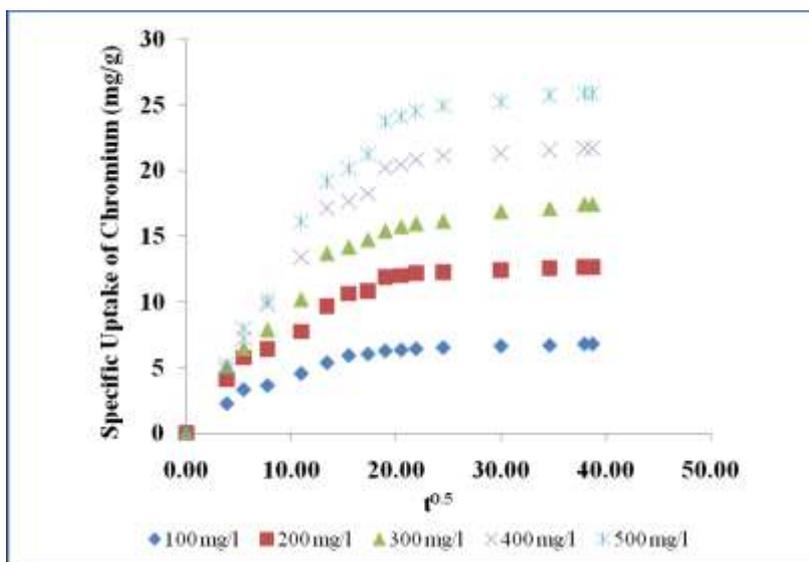


Fig. 9: Intra particle Diffusion Plot for the Sorption of Chromium by Immobilized Mixed Biosorbent

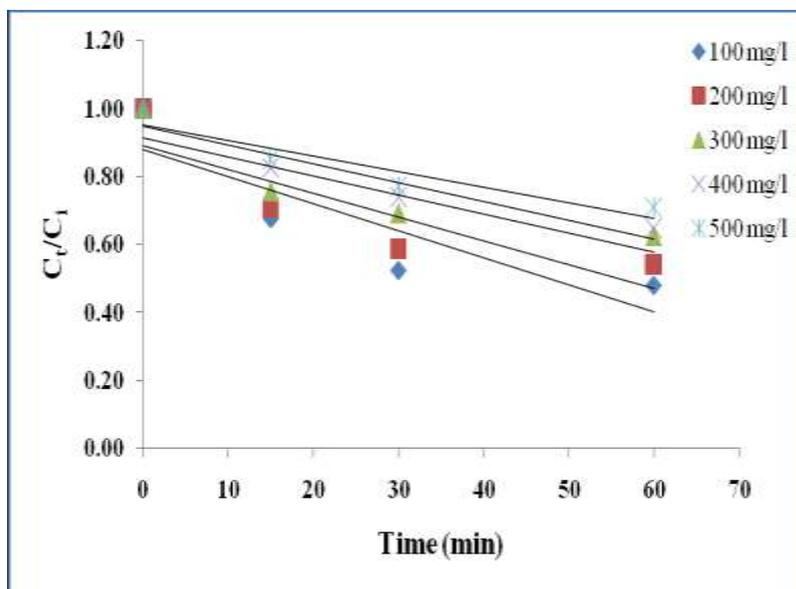


Fig. 10: External Diffusion Plot for the Sorption of Chromium by Immobilized Mixed Biosorbent

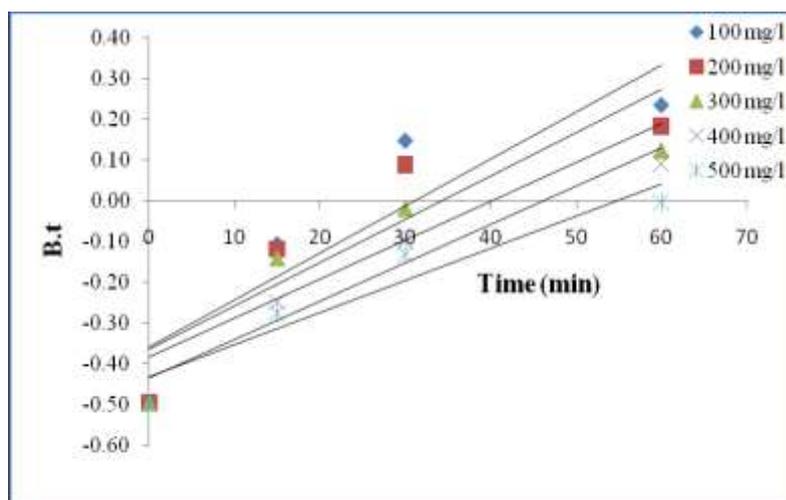


Fig. 11: Boyd Plot for the Sorption of Chromium by Immobilized Mixed Biosorbent

Table 4
Estimated external mass transfer rate constant for the initial rapid phase at different initial concentration of Chromium.

S. N.	Initial Chromium concentration (mg/l)	K_{ES} (min^{-1})
1	100	0.008
2	200	0.007
3	300	0.006
4	400	0.005
5	500	0.004

Conclusion

This study suggested that the immobilized mixed biosorbent (*Annona squamosa* + *Aspergillus niger*) can be used as an effective biosorbent in a batch reactor to extract Chromium from aqueous solution. Biosorption was affected by initial concentrations of chromium ions and it was noticed that as the initial concentration of chromium rises from 100 mg / l to 500 mg / l, the percentage of chromium removal decreases from 97% to 74% and the actual chromium uptake rises from 7 mg / g to 26 mg / g respectively. A second order mechanism regulates the kinetics of the sorption cycle.

The chromium adsorption phenomenon undergoes the processes of external (bulk to solid surface mass transfer) and intraparticle diffusion. It was found that the sorption rate is regulated by film diffusion for a short period of time and that pore diffusion regulates the sorption rate at longer sorption times.

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