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Challenges in Biochemical Engineering and Biotechnology for Sustainable Environment

Kinetics and Equilibrium Studies on Biosorption of Chromium (VI) By Mixed Biosorbents

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Abstract : Biosorption is a process, which represents a biotechnological innovation as well as a cost effective excellent tool for removing heavy metals from aqueous solutions. The kinetics and equilibrium of the biosorption of Chromium (VI) from aqueous solution were investigated using immobilized mixed biosorbents of *Annona squamosa* seeds and *Aspergillus niger* in a batch system. The biosorption characteristics of Chromium (VI) ions were studied with respect to well-established effective parameters including initial metal ion concentration, pH, temperature and biosorbent dosage. Biosorption equilibrium was established in about 24 h. The Chromium (VI) sorption data were analyzed using the Lagergren first and second order kinetic models. The Lagergren second-order rate equation was the most appropriate equation to predict the biosorption capacities of immobilized mixed biosorbents. The equilibrium data were analyzed using the Langmuir adsorption isotherm. The characteristic parameters of Langmuir sorption isotherm provided the best correlation for Chromium (VI) onto immobilized mixed biosorbents.

Keywords: Biosorption, mixed biosorbents, kinetic modeling, equilibrium modeling.

1. Introduction

Agricultural runoff, industrial and domestic effluents and acid mine drainage have all greatly contributed to the metal loads in our natural water systems¹. As a result of their toxicity, environmental mobility and complex chemical forms, increasing attention is directed towards studying their removal and recovery from metal bearing waste streams. Chromium is a priority metal pollutant introduced into the water bodies from many industrial processes such as tanning, electroplating, metal processing, paint manufacturing, steel fabrication and agricultural runoff. A number of treatment methods for the removal of metal ions from aqueous solutions have been reported, mainly ion exchange, electrochemical reduction, evaporation, solvent extraction, reverse osmosis, chemical precipitation, membrane filtration and adsorption. Most of these methods involve high capital cost and are not suitable for small-scale industries². The use of biological materials for removing and recovering heavy metals from contaminated industrial effluents has emerged as a potential alternative method to conventional techniques. Biosorption is becoming an important component in the integrated approach to the treatment of aqueous effluents. Microbial biomass types investigated for their biosorptive potential include bacteria, yeasts, filamentous fungi and marine and freshwater algal flora³⁻⁹. Microbial biomass in its native form is not suitable for large-scale process utilization because of its small particle size, low mechanical strength, and difficulty of separation from the liquid stream due to relatively low density. As for immobilized whole cells or enzymes, the use of immobilized biomass as a biosorbent has many advantages over

the use of native biomass. Immobilized biomass appears to have greater potential in packed-or fluidized-bed reactors, with benefits including control of particle size, more efficient regeneration of biomass, easy separation of biomass and effluent, high biomass loading, and minimal clogging under continuous – flow conditions^{10, 11}.

1.1 Kinetic modeling

In order to investigate the mechanism of biosorption and potential rate controlling steps the first – and second – order kinetic models have been used.

The linearized form of first – order Lagergren equation is given below:

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

Linear plots of $\log (q_{eq} - q)$ versus time indicate the applicability of this model Eq. (1).

The second order kinetic model is expressed as

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

If the second order kinetics is applicable, the plot of t/q versus time should give a linear relationship^{12, 13}.

1.2 Equilibrium Modeling

The equilibrium of the process is often described by fitting the experimental points with models usually used for the representation of adsorption isotherms. The Langmuir model suggests, as a hypothesis, that uptake occurs on a homogeneous surface by monolayer sorption without interaction between 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 hold one sorbate ion 3) all sites are energetically equivalent 4) there is no interaction between ions adsorbed on neighboring sites. This model is described by the equation¹³⁻¹⁵.

$$q_{eq} = \frac{Q^{\circ}bC_{eq}}{1 + bC_{eq}} \quad \dots (3)$$

Q° and b can be determined from a plot of q_{eq}^{-1} and C_{eq}^{-1} .

2. Experimental

A 1000 mg/l stock solution of Chromium was prepared by dissolving 2.83 g of Potassium dichromate in double distilled water. The required concentrations of Chromium ions were prepared from the stock solution by dilution method.

2.1 Preparation of the biosorbent

Annona squamosa (custard apple) seeds were also used in this study. The seeds separated from the fruit were thoroughly washed with tap water, followed by rinsing in distilled water and dried at 40°C for a period of 24 h. The seeds were then crushed, powdered and stored for subsequent biosorption studies.

Aspergillus niger MTCC-132, a filamentous fungus obtained from the institute of microbial technology, Chandigarh, was 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). The pH of the medium was adjusted to 5.5 with dilute sulphuric acid before sterilization. The cell suspension was then separated, dried, homogenized and stored for subsequent biosorption studies.

2.2 Preparation of immobilized mixed biosorbent beads

Immobilized biomass beads were prepared using 8% (w/v) sodium alginate. A known amount of biosorbents (*Aspergillus niger* & *Annona squamosa* seeds) was mixed with sodium alginate and the mixtures

were constantly stirred under warm condition until the alginate gets dissolved. The suspension was dripped into 2% (w/v) calcium chloride solution through a syringe. The beads were stored in calcium chloride solution for about 30 min before being rinsed in double distilled water.

2.3 Batch studies on biosorption of Chromium

Batch experiments were carried out in Erlenmeyer flasks by adding immobilized mixed biosorbents in 100 ml aqueous potassium dichromate solution. The flasks were gently agitated on a shaker with a constant shaking rate at 150 rpm for 240 min until equilibrium sorption was obtained. Samples were taken from the solution at regular time intervals for the residual metal ion concentration in the solution. The residual concentration of Chromium ions in the solutions was determined Spectrophotometrically at 540 nm using Diphenylcarbazide as the complexing agent ¹⁶. The effect of initial Chromium (VI) concentration, pH, temperature and biosorbent dosage on percentage removal of Cr (VI) was carried out as described above.

3. Results and Discussion

3.1 Effect of Biosorbent dosage

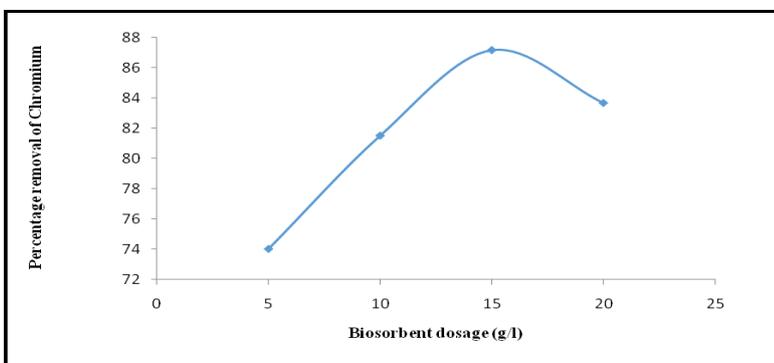


Fig 1 Effect of Biosorbent dosage on percentage removal of Chromium

The biosorbent dosage is varied between 5g/l and 20 g/l in this set of experiments while the initial Chromium while the initial Chromium concentration, pH and temperature are constant at 500 mg/l, 5.7 and 30°C respectively. Chromium removal by mixed adsorbent as a function of adsorbent dose is shown in Fig 1. An increase in Chromium removal is observed from 5g/l to 15g/l; thereafter decrease in Chromium removal is observed with increasing biosorbent dosage. The reason might be attributed to the fact that the high biomass concentration could make a `screen` effect on the dense outer layer protecting the binding sites from metal and thereby lowering the Chromium removal at higher biomass loading.

3.2 Effect of Temperature

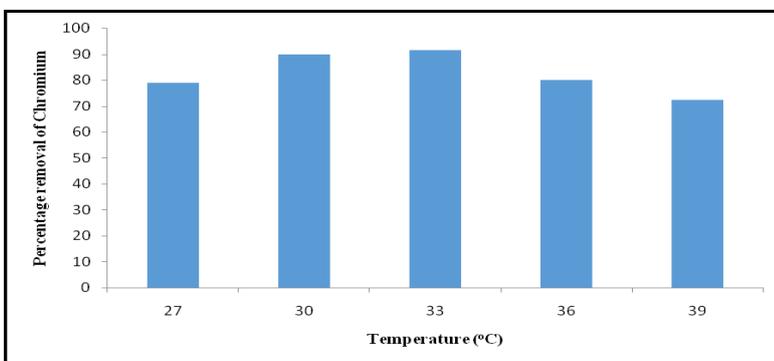


Fig 2 Effect of temperature on percentage removal of Chromium

The effect of temperature (27 to 39°C) is evaluated on the biosorption of 500 mg/l of Chromium on to 15g/l of mixed adsorbent at pH 5.7 (Fig 3.2). Removal of Chromium by mixed adsorbent appeared to be temperature dependent over the temperature range tested. The experimental results (Fig 2) indicated that the

percentage removal of Chromium increased from 79% to 91.5% with an increase in temperature from 27°C to 33°C and thereafter, biosorption is found to decrease at higher temperature (39°C). The decreasing Chromium removal at higher temperature may possibly due to the damage of active binding sites in the biomass, the weakening of adsorptive force between active sites of the adsorbent and the adsorbate species and also between the adjacent molecules of adsorbed phase.

3.3 Effect of pH

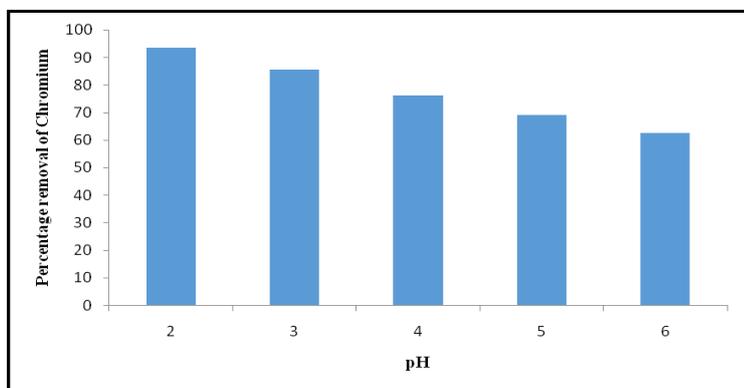


Fig 3 Effect of pH on percentage removal of Chromium

pH is an important parameter affecting the rate and the extent of biosorption of metal ions onto biosorbents such as mixed sorbents. It is clear from Fig 3 the maximum percentage removal of Chromium (93.5%) is observed at pH 2.0. In the pH range 2.0-6.0, HCrO_4^- and Cr_2O_7^- ions are in equilibrium whereas, at lower pH ($\text{pH} > 2.0$), there is formation of more polymerized Chromium oxide species such as $\text{Cr}_3\text{O}_{10}^{2-}$ and $\text{Cr}_4\text{O}_{13}^{2-}$, which results in decrease in Chromium removal high adsorption capacity is observed at low pH 2.0; value may be attributed due to presence of large number of H^+ ions, which in turn neutralize the negatively charged adsorbent surface thereby, reducing hindrance to the diffusion of the dichromate ions at lower pH.

3.4 Effect of Initial Chromium Concentration

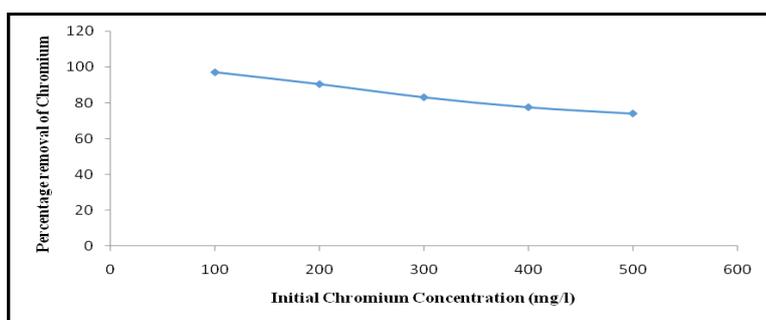


Fig 4 Effect of initial Chromium concentration on percentage removal of Chromium

The biosorption of Chromium on mixed biosorbent in a batch process is dependent on initial metal concentration. It is observed from Fig 4, the percentage removal of Chromium decreases with increase in initial Chromium concentration. The percentage removal of Chromium decreased from 97 % (at 100mg/l) to 74 % (at 500mg/l) respectively. The decrease in the extent of removal of Chromium(in %) with the increase in the initial concentration may be due to the reduction in immediate adsorption due to the lack of available binding active sites for the high concentration of Chromium.

3.5 Kinetic modeling

The sorption of Cr (VI) onto mixed biosorbent data were plotted according to Eq.2 and the results are shown in Fig. 5. The first- order kinetic model does not provide a good fit to the experimental data for the sorption of Cr (VI) also the theoretical q_e values found from the kinetic model did not give reasonable values. The plot of t/q against t of Eq.4 is shown in Fig.6. For the second- order sorption model, the linearity is good with the correlation coefficients shown in Table.1. The correlation coefficients are extremely high (>0.99) and

also the theoretical q_e values were found to be in good agreement with the experimental q_e values for the second-order model. The second-order kinetics predicts the behavior over the whole range of studies supporting a second-order equation and is in agreement with chemisorption (diffusion) being the rate-controlling step.

Table 1 comparison of first and second order biosorption rate constants, calculated and experimental q_{eq} values obtained at different initial Chromium concentrations by immobilized mixed biosorbents

Initial Chromium concentration (mg/l)	$q_{eq}(exp)$ (mg/g)	$K_{1,ad}$ (min^{-1})	$q_{eq}(cal)$ (mg/g)	R^2	$K_{2,ad}$ (g/mg-min)	$q_{eq}(cal)$ (mg/g)	R^2
100	0.65	0.0081	0.472	0.950	0.0423	0.66	0.999
200	1.21	0.0080	1.33	0.958	0.0204	1.24	0.999
300	1.67	0.0069	1.044	0.922	0.0124	1.70	0.999
400	2.08	0.0078	0.662	0.940	0.0094	2.15	0.999
500	2.48	0.0074	0.511	0.944	0.0066	2.58	0.999

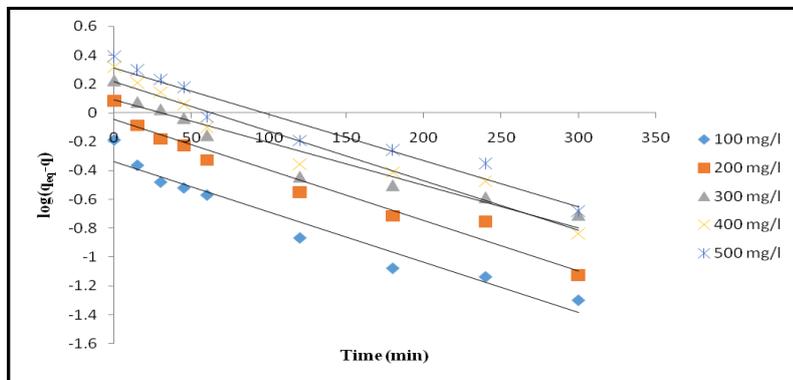


Fig 5 First order Lagergren plot for the biosorption of chromium by mixed biosorbents

3.6 Equilibrium modeling

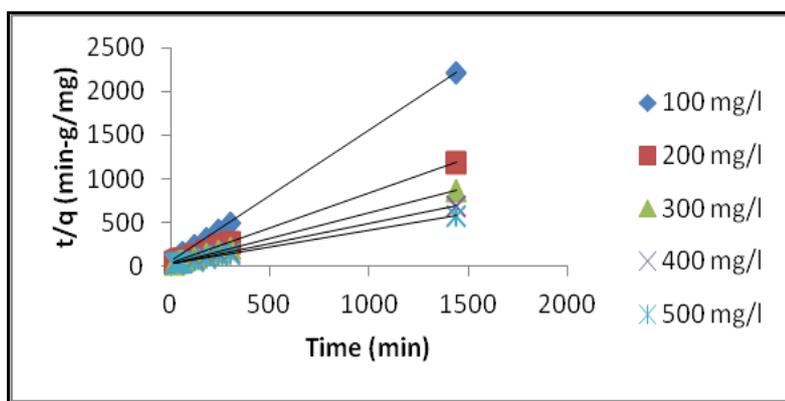


Fig 6 Second order Lagergren plot for the biosorption of chromium by mixed biosorbents

The linearized Langmuir adsorption isotherm of Chromium obtained were given in Fig 7. The higher correlation coefficients showed that chromium was very suitable for describing the biosorption equilibrium in the studied concentration ranges. The Langmuir constants were used to compare the biosorptive capacity of the mixed biosorbent for Chromium. The maximum capacity Q^0 determined from the Langmuir isotherm defined the total capacity of the biosorbent as 2.709 mg/g for the Chromium. A large value of b (0.048) also implied strong bonding of Chromium to the mixed biosorbent.

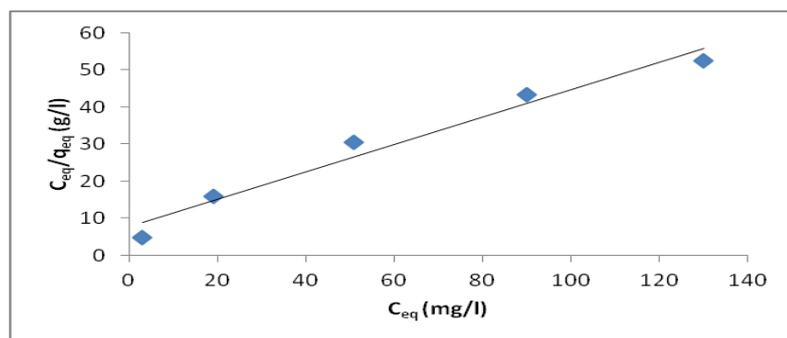


Fig 7 Langmuir plot for the biosorption for chromium

4. Conclusions

Biosorption experiments were performed as a function of initial metal ion concentration, pH, temperature and biosorbent dosage. The obtained results showed that immobilized mixed biosorbents of *Annona squamosa* seeds and *Aspergillus niger* was a good adsorbent for the removal of metal ions and had high adsorption yields for the treatment of aqueous solutions containing chromium ions. The sorption process followed a second- order rate kinetics indicating that the process to be diffusion controlled. The equilibrium data fitted very well to Langmuir adsorption isotherm model.

Nomenclature

- $K_{1,ad}$ = Rate constant of first- order biosorption (min^{-1})
 q_{eq} = Adsorbed quantity of the metal ion per g of dried fungal biomass at equilibrium(mg/g)
 C_o = Initial concentration of metal ions (mg/l)
 V = Volume of metal solution (l)
 W = Weight of biosorbent (g)
 C = Final concentration of metal ions (mg/l)
 $K_{2,ad}$ = Rate constant of second – order biosorption (g/mg/min)
 Q^o = Maximum amount of metal per unit weight of biomass
 b = Langmuir constant

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