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Biosorption Kinetic Studies and High Yield Recovery of Cr (VI) Through Liquid Solid Fluidised Bed Reactors from Industrial Effluents

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Abstract

The present investigation is the recovery of highly toxic heavy metals of chromium from waste effluents using beads *Spirulina platensis*. The effluent has been subjected to batch operation of Liquid solid Fluidized bed reactors (LSFB) with varied concentrations of stock solutions, time, pH, and pressure drop for bio-treatment studies. LSFB processes using dead *Spirulina platensis* beads followed by characterization of UV screened toxic chromium ions are recovered for the time interval of 120 minutes at constant 5 pH. The results indicated that the high recovery of chromium ions with hydrodynamic constraints of high efficiency of 82.3% at 150 LPH is recorded. Thus, the sustainable and eco-friendly way for the removal of toxic chromium ions is also examined under the linear isotherm model of the BET, Langmuir and Freundlich isotherm models. The best fit is BET Isotherm as compared with Langmuir and Freundlich isotherm model with maximum efficiency in recovery chromium ions of experimental value of B (Constant) of 1.346×10^{6} was also reported.

Keywords: Waste water; Heavy metals; LSFB; *Spirulina platensis* beads; Isotherm; Kinetics

Introduction

Industrialization has led to serious environmental degradation and emits more industrial pollution and effluents to the environment. Industrial effluents consist of various chemical components, but the presence of heavy metals of density more than $5gm/cm^3$ causes more environmental disturbance [1-3]. Heavy metals are the metals that are more toxic, but they contribute a major role in medical and engineering fields. Emission of these heavy metals leads to environmental danger for both the biotic and abiotic species [3-5]. Among the heavy metals from the industrial effluents, chromium is the one of the most hazardous heavy metals and has widened application in metal finishing, electroplating, tanning, textile, dying and many more industries. Chromium in industrial effluents exists either in Its hexavalent Cr (VI) and trivalent Cr (III) form in which Chromium (VI) is more toxic, carcinogenic and acts mutagenic in the bio system [6-7]. It is necessary to remove Cr (VI) from the industrial effluents. Toxic levels of chromium can be reduced by converting them to its oxidized form. Moreover, chromate can be reduced to the less toxic Cr (III) by several methods to oxidize Cr (VI) namely Ion Exchange, Chemical Precipitation, Carbon adsorption and much more [7-9]. However, these methods are found to be expensive and they also deal with secondary fluid disposal. Several reports have been reported earlier in use of micro-algal biomass were successfully employed as a adsorbing agent by the biosorption processes for both the biomass of Living and Non-Living cells as adsorbent. Unlike other oxidation methods, biosorption is cost effective, it can be used for a wide range of metal selectivity for adsorption, and can be regenerated easily [10-12] no secondary waste disposal is needed. Biosorption is a surface phenomenon in which living or dead microorganisms [13-14]. But the living cell is very difficult to sustain the high toxic level of industrial effluents

with the suitable parameters and conditions. This case is not adaptable when use of dead cells as an adsorbent, since dead cells need less care and they can be easily regenerated and consecutively the process gets cheaper. There are various reports [14-16] which are already available for the heavy metal adsorption, among which algae plays a vital role in extraction of heavy metals in an effective manner. Thus, the micro-algae were *Spirulina platensis*, *dunaliella* and *chlorella* vulgaris for the extraction of the Cr (VI) in the effluent treatment plants [17-20]. In this research work recovery of Cr (VI) by using dead *Spirulina platensis* beads as an adsorbent in a cheaper way in a fluidized bed reactor [21]. The efficiency and the cost of regeneration are also discussed by several kinetic studies and isotherm models for the better recovery of the heavy metals from the industrial effluents with biomass.

2. Materials and Methods

2.1. Microorganisms

The microorganism for the work *Spirulina platensis* was purchased from OFER in an NGO cultivating *Spirulina* on commercial grounds. The algae were harvested from a medium solution by plankton of 20' cloth mesh. The collected algae were completely dried in sunlight for 3 weeks and kept in an oven for a week at 60 °C. The dried algae were ground using a laboratory mill. Obtained power is then soaked in distilled water and mixed at low temperature of less than 5 °C. Then it was filtered using micra cloth, thereby the insoluble *Spirulina platensis* is obtained as powdered and stored at laboratory refrigerator at 4 °C.

2.2. Preparation of metal solution

The original stock solution was prepared by mixing metal salts of metal concentration of 50,100,150 mg/L [21-22]. The high-end recovery of chromium is done by Potassium Dichromate in mixed salt of double distilled water. All the chemicals used were of analytical grade with MERCK purity and were used for preparation of stock solutions. All glass wares were sterilized before and after completion of the experiments. The concentration of Cr ions present in the stock solution was determined using UV-Visible Spectrophotometer.

2.3. Beads and its strength

2.3.1. Preparation of beads

Plain alginate solution was prepared by mixing Sodium dodecyl sulphate (0.5 % w/w) and sodium alginate (0.5 % w/w) in double distilled water. The mixture was then agitated for 15 minutes at 70 °C. Cross linking solution for internal gelation process was prepared by dissolving $CaCO_3$ (2% w/w) in double distilled water. *Spirulina* powder obtained in 2.1 is mixed with the cross-linking solution until it reaches 15% w/w concentration. The mixture of *Spirulina* and cross-linking solution was taken into a syringe, the size of the needle was 26 G and dropped into the alginate solution. The height difference between needle and the alginate solution is kept constant as 4 cm. After completion of the dropping process, the cross-linking solution is cooled to 4 °C in the laboratory refrigerator for 10hrs. Thus, the beads formed were filtered using a strainer and tested to determine its compression strength. Further the pH studies of the beads were also analysed in the range of 3 to 7.

2.4. Analysis of Adsorption of the developed beads

The adsorption capacity of the developed beads and the dead *Spirulina* powder for a batch test was examined between two adsorbents with an equal amount of chromium stock solution. Equal weight of the adsorbents is added selectively in two different Erlenmeyer flasks containing the same concentrations of the metal stock solutions. Two flasks were stirred at constant speed of 150rpm in rotary shaker for 120 minutes, and adsorption capacity q_t of these two adsorbents were calculated using the equation 1 and C_i and C_t are the initial and final concentrations of the Chromium in the stock solution (mg/L), V_s is the volume of the stock solution (L), W is the weight of the adsorbent added(g).

$$q_t = \frac{C_i - C_t}{W} v_s \quad \text{---------- (1)}$$

2.5. Biosorption Kinetics for adsorption Isotherm and its models

The kinetic study for the adsorption is developed by 0.1g of beads in 2.3.1 being added to 100 ml Cr(VI) stock solution (0.1mg/mL); pH is kept constant. The experiments were conducted with 5 samples at different time intervals. To obtain the isotherm, adsorption experiments were conducted in 100ml of Cr (VI) stock solution for different concentrations of 50, 100 ,150 mg/L in the Erlenmeyer flask. Flask was subjected to agitation in a rotary shaker at a constant speed of 150 rpm at room temperature (Controlled) 25°C for 24 hrs. Using Langmuir, Freundlich and BET adsorption isotherms, the obtained equilibrium data is analyzed. Langmuir adsorption isotherm is defined by equation 2.

$$q_t = \frac{q_m K_l C_t}{1 + K_l C_t} \quad \text{---------- (2)}$$

Where q_t is the adsorption capacity of the adsorbent (mg/g), K_l is the Langmuir constant (L/mg), q_m is the adsorption capacity in the monolayer of the adsorbent (mg/L), C_t is the metal concentration in the solution at equilibrium. Similarly, Freundlich isotherm can also be defined as the equation 3.

$$q_t = K_f C_t^{1/n} \quad \text{---------- (3)}$$

Where q_t is the adsorption capacity of the adsorbent (mg/g), K_f is the Freundlich constant (L/mg), $1/n$ is the empirical parameter. Value of $1/n$ varies with respect to the heterogeneity nature of the material used.

The BET adsorption model is also used to analyse the equilibrium data. The BET isotherm is represented by equation 4.

$$\frac{C_t}{(C_s - C_t)} = \left(\frac{1}{B q_m}\right) + \left(\frac{B-1}{B q_m}\right)\left(\frac{C_t}{C_s}\right) \quad \text{-------- (4)}$$

Where B is the energy of the interaction with the surface (Constant value) (g/mg), C_s is the saturated concentration of the solute (mg/L), q_m is the adsorption capacity in monolayer (mg/L).

2.6. Biosorption studies in LSFB

For the batch flow study in Liquid Solid Fluidized Bed, the immobilized beads are filled in the fluidized bed column till $1/3^{rd}$ of its height with 40 liters of heavy metal stock. Distilled water is pumped to the fluidized bed at different speeds to understand the pressure drop. The heavy metal concentration is then checked using UV-Visible spectrophotometer at different time intervals. pH value is kept constant at 5 and the experiment was done at room temperature. The effect of pressure drop and bed height is studied using variable flow rate.

3. Results and discussion

3.1. Batch sorption studies

Batch process carried out at constant room temperature of 25 °C by influence of widal parameters like pH, contact time, Pressure drops, LSFB reactor efficiency and studies.

3.1.1 Effect of pH

The effect of pH and the percentage of adsorption while using the prepared beads are shown in Fig. 1. The study was done between the pH values of 3 to 7. Three different concentrations of Cr metal ions were used for the study. Maximum biosorption of Cr (VI) is found to be 86.7% at the pH 5. Biosorption gradually started to decrease after the pH scale of 5.

3.1.2. Effect of contact time

The results based on contact time and the Cr metal sorbedaz are shown in Fig. 2. This experiment was carried out using three different Cr stock solutions and samples were tested at different time intervals. At t=120 minutes maximum recovery of material was 87.27%. With increase in time, the percentage of adsorption rapidly increases and remains the same for 130 minutes.

3.1.3. Adsorption isotherm

The study of equilibrium of the biosorption of heavy metal chromium ions from waste water by using Spirulina *platensis* was carried out by using Langmuir, Freundlich and BET models. Equilibrium of biosorption of heavy metal using dead *Spirulina platensis* is plotted against q_t and residual Cr concentration in the stock solution. The resultant effect and the R values are shown in Fig. 3. The high recovery of Cr metal ions is obtained in the contact time of 120 minutes and also no Chromium recovery ions after this time interval. Linear regression data for the Langmuir and Freundlich Isotherms is shown in Table 1. By comparing the R^2 value, BET isotherm is found to be the best fit as compared with Langmuir and Freundlich isotherm models.

3.2. Biosorption studies in fluidized bed reactor

3.2.1. Studies of Hydrodynamic Constraints

3.2.1.1. Pressure drops

The pressure drop inside the fluidized bed reactor is passed by distilled water in a bead filled ratio 1/3 of the volume inside the tube of the reactor. For the measurement of the flow-rate we used a rota-meter, and for the pressure measurement mercury manometer was used. Fig. 4 shows the change in pressure-drop inside the reactor with respect to the flow rate. Minimum fluidization velocity was around 55 (LPH).

3.2.2 Fluidized bed reactor studies

The reactor studies are conducted in a Fluidized type bed reactor which is packed with laboratory synthesized *Spirulina beads* to the *1/3* of its total volume. The stock metal solution is pumped to the reactor at a flow rate of 150 LPH. For every 15 minutes an outlet sample is taken and its metal concentration is checked using UV-Visible Spectrophotometer. Concentration change of chromium (VI) metal with respect to time is shown in Fig. 5. The corresponding bio sorption efficiency with respect to residence time is shown in Fig. 6. Thus, the Cr (VI) recovery was found to be 82.3% for a time period of 120 minutes and this is the maximum amount of Cr (VI) recovered and it shows widened applications in heavy metal removal methods.

4. Conclusion

The removal of chromium ions from waste effluents yields significant results after subjecting the LSFB *Spirulina beads* to 1*/3* of its total volume. The maximum recovery of chromium metals recorded in this work was about 82,3% by the selected *Spirulina platensis* dead beads to 1*/3* of its total volume. The best fit of the recovery of chromium ions and with efficiency in a flexible point of BET isotherm as on par with the Langmuir model and Freundlich models were also discussed and the results are reported in this work. The concurrent treatment for the recovery of toxic heavy metals at low economic and high regenerations of *Spirulina beads* and conversion by LSFB reactors with minimum time interval were also analysed in this work.

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Table 1. Correlation coefficients and Isotherm constant.

Biomass	Langmuir isotherm			Freundlich isotherm			BET isotherm		
	q_t (mg/g)	K_l (L/mg)	R^2	n	K_f (L/mg)	R^2	q_t (mg/g)	B (g/mg)	R^2
Bead type *Spirulina plantesis*	89.23	0.348	0.9764	1.45	8.76	0.9577	91.32	1.346×10^5	0.9927
RMSE	0.0985			3.456			0.1941		
SSE	0.0789			0.2674			0.02		

Fig.1 Effect of pH with respect to the percentage of biosorption by using a prepared bead type *Spirulina platensis*.

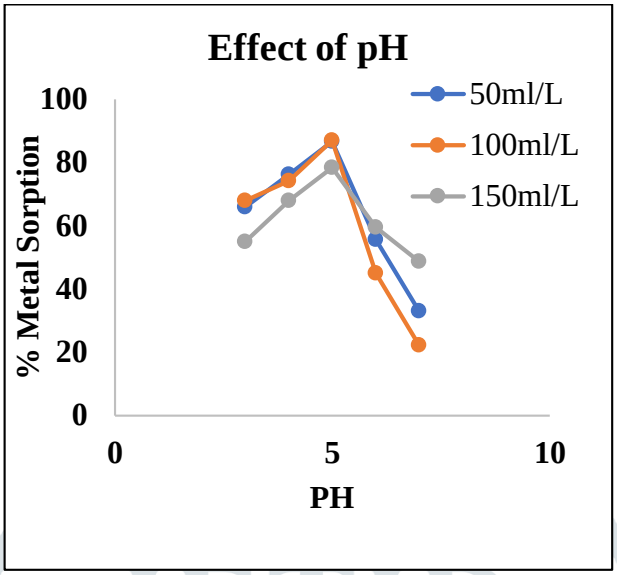

Fig.2 Effect of contact time for the different concentration of heavy metal using bead type dead *Spirulina platensis.*

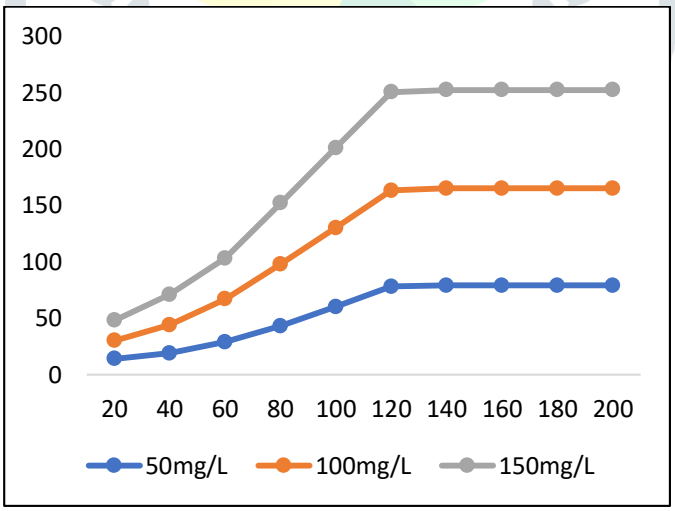

Fig. 3 Experimental data obtained by using Langmuir, Freundlich and BET Isotherms

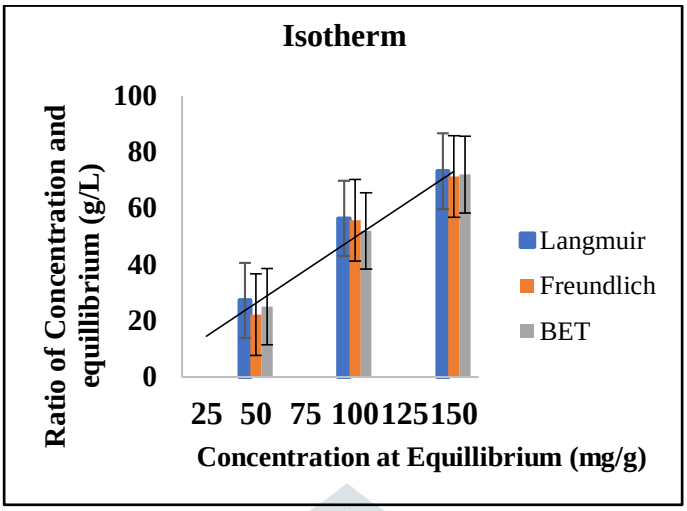

Fig. 4 Pressure drop vs Flow rate

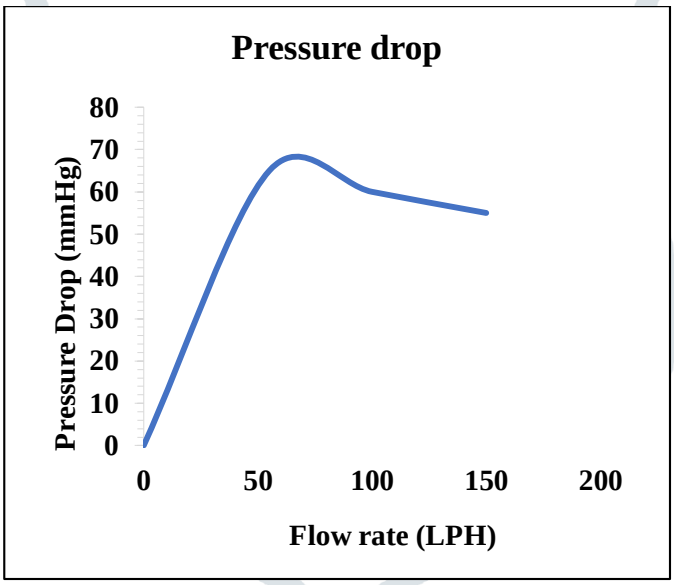

Fig. 5 Removal of Cr(VI) with respect to time in the bioreactor.

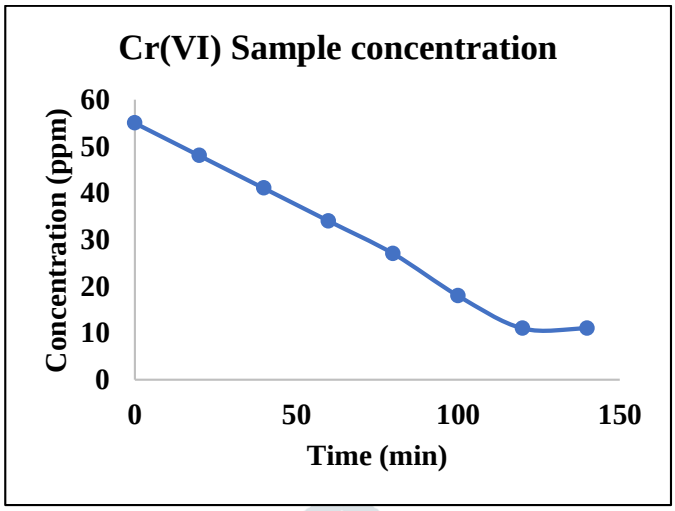

Fig. 6 Biosorption efficiency of recovery of Heavy metal Cr(VI) in a bioreactor.