

Chromium (VI) Adsorption and its Kinetic Studies Using Industrial Spent Biomass

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Abstract — *Biosorption is mass transfer phenomenon by which a substance can be transferred from liquid phase to the surface of a solid. The substance becomes bound, by physical and/or chemical interactions. Availability of large surface area, surface reactivity, high sorption capacity and low cost makes it feasible over other traditional methods of treatment. In this study important sorption parameters were investigated as a function of time, pH, initial chromium (VI) concentration, temperature and biomass dosage. Kinetics and equilibrium data were obtained from batch experiments. The biosorption kinetics were checked for both first order and second order models and it was found that the sorption process followed the pseudo - second order kinetics. Adsorption equilibria was checked for Langmuir, Freundlich, Redlich- Peterson and Tempkin models and the process was well described by Freundlich isotherm ($R^2=0.9992$), Redlich-Petersen isotherm ($R^2=0.961$) and Tempkin Isotherm ($R^2=0.9592$) models as compared to Langmuir Isotherm ($R^2=0.5702$) model. The maximum adsorption capacity of the biomass was 14.2 mg/g at a temperature of 298K and pH of 2.0. The scanning electron micrograph revealed the surface texture and morphology of multilayer adsorption. Surface and pore size analysis through BET revealed that industrial spent has a specific surface area of 4.8477 m²/g and pore diameter 56.865^oA. The present work reveals that spent biomass can be effectively used for Chromium (VI) removal at low concentrations.*

Keywords: Chromium (VI), biosorption, kinetics, isotherm, industrial spent

1. Introduction

Removing and recovering heavy metals from industrial effluents using biological materials has emerged as a potential alternative to conventional treatment methods. Economy of environmental remediation necessitates the biological material to be naturally available, involve less processing, is abundant in nature or is a by- product or waste from other industry. Microorganisms, algae, fungi, yeast, agricultural wastes among other biomaterials have been tested for metal sorption and have performed well. These biosorbents contain variety of functional sites like carboxyl, imidazole, sulphhydryl, amino, phosphate, sulfate, thioether, phenol, carbonyl, amide and hydroxyl groups [i] which have experimentally proved to adsorb heavy metals in effluents, even at very low concentrations. This applicability of biosorbents has been

utilized in removal of Chromium (VI) metal ions in this study. The biosorbent used is herbal spent, devoid of its active components (extracted for medicinal purposes) and discarded as waste. Chromium finds wide application in the making of steel and other alloys, manufacture of dyes, pigments, leather, textile, wood - preservation and in treatment of cooling tower water. Hexavalent chromium is one of the most toxic heavy metals and may cause a series of health effects, ranging from shortness of breath to lung cancer [ii]. The removal and recovery of these heavy metals from industrial effluents is very important for the environmental protection and by large, human health. Different alternatives are available in literature, including chemical precipitation, carbon adsorption, ion exchange and membrane separation process among others. However there are limitations in these processes, such as high cost, low efficiency, labor intensive operation, and lack of selectivity of the precipitation process [iii]. In the present work, the influence of several parameters, such as time, pH, initial chromium (VI) ion concentration, temperature and biomass dosage were investigated. The kinetics and adsorption equilibria were obtained from batch experiments. The biosorbent was analyzed for its porosity and surface area characteristics through BET analysis and also scanned through the scanning electron microscope.

II. Material and Methodology

Preparation of biomass

Spent biomass of plant origin, whose active components were extracted under super critical conditions, was discarded as an industrial waste in the form of dry powder. This was used as biosorbent and was obtained from Ms. Sami Labs Pvt Ltd, Bangalore. The spent biomass was sieved through a 100 μ m mesh, dried at a temperature of 60 $^{\circ}$ C and used directly without any pre-treatment.

Chemicals

All chemicals used in this study were of analytical grade and the solutions were prepared using distilled water. A stock solution of Cr (VI) (100ppm) was prepared by dissolving potassium di chromate. Cr (VI) solutions of different concentrations were obtained by diluting the stock solution. To adjust pH, 0.1N hydrochloric acid and 0.1N sodium hydroxide solutions were used.

Kinetic experiments

Kinetic experiments were performed using 100ml Cr (VI) solutions at different concentrations (20-100ppm) and 0.5g of biosorbent at a pH of 2.0. Samples were collected at different intervals of time and analyzed for residual Cr (VI) concentration by atomic absorption spectrometer (GBC932 plus).

Effect of pH on Cr (VI) adsorption

Experiments were conducted under different pH to investigate the effect on adsorption. The pH was adjusted to a designated value from 2.0 to 11.0 using 0.1N hydrochloric acid or 0.1N sodium hydroxide solution for the study.

Effect of temperature on Cr (VI) adsorption

Experiments were conducted at different temperatures using an incubator (10-40 °C) to investigate the effect on biosorption of Cr (VI) ions.

Effect of biomass variation on Cr (VI) adsorption

Varying biomass dosage, experiments were conducted to investigate its effect on the removal of chromium metal ions. Biomass dosage was varied from 0.1 to 2.5 grams.

Adsorption equilibrium

Equilibrium studies were conducted by varying the concentration of Cr (VI) solutions from 20ppm to 100ppm with the biosorbent dosage being varied from 0.1 to 2.5g. The pH was adjusted to 2.0 using 0.1N hydrochloric acid solution. The mixture was constantly shaken on a shaker at 150rpm for different time intervals at room temperature. Then the biosorbent was centrifuged at 10,000rpm in a cooling centrifuge (REMI C-24) for a period of 10 minutes. The supernatant was collected and filtered through Whatman 41 filter paper. The amount of Cr (VI) uptake by biosorbent was estimated by checking for residual Cr (VI) ion concentration using AAS, correspondingly through the mass balance equation

$$q = \frac{C_0 - C_e}{W} \quad (1)$$

Where q is the adsorption amount at equilibrium (mg/g), C₀ the initial concentration of heavy metal (mg/l), C_e the concentration remaining in solution at equilibrium (mg/l) and W is the biosorbent dosage (g/l)[ix].

Characterization of the adsorbent

The biosorbent was characterized using BET analysis. It was found that the biosorbent had a specific surface area of 4.8477 m²/g and pore diameter 56.865°A. The surface feature and morphology of the biosorbent was analyzed using Scanning Electron Microscope.

III. Results and Tables

Kinetics of biosorption

Figure 1 depicts Cr (VI) percentage removal with time (t) profile by extract spent, at constant initial metal ion

concentration. The removal rate was high in the first 60 min and then the rate significantly decreased and eventually reached a stationary phase after 90 min. The result was the same for all the initial Cr (VI) concentrations. The uptake capacities increased with increasing initial Cr (VI) concentrations as a result of higher probability of collision between the ions and the biosorbent particles. Many models have been developed to describe the kinetics of heavy metal biosorption [iv-ix]. The pseudo-second order kinetic model based on sorption capacity of the solid phase can be used, assuming that measured concentrations are equal to the cell surface concentrations. The pseudo – second order kinetic rate equation is expressed as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2)$$

At boundary conditions q_t=0 at t=0 and q_t at time t, the linearized form of pseudo-second order model is obtained.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

Where k₂ is the second order biosorption rate constants (g/mg min⁻¹), q_e and q_t are the amounts of the sorbed metal ions on the biosorbent at equilibrium, at any time t. The kinetic data analyzed were in terms of pseudo-second order. Figure 2 shows the variation of t/q_t with respect to time. The values of parameters k₂, q_e and correlation coefficients are presented in Table -1. The correlation coefficients obtained were greater than 0.9753 and suggests that the sorption of Cr (VI) onto extract spent followed the second order model very well and based on the assumption; the rate limiting step may be chemisorption involving forces through the sharing of electrons between sorbent and sorbate [x].

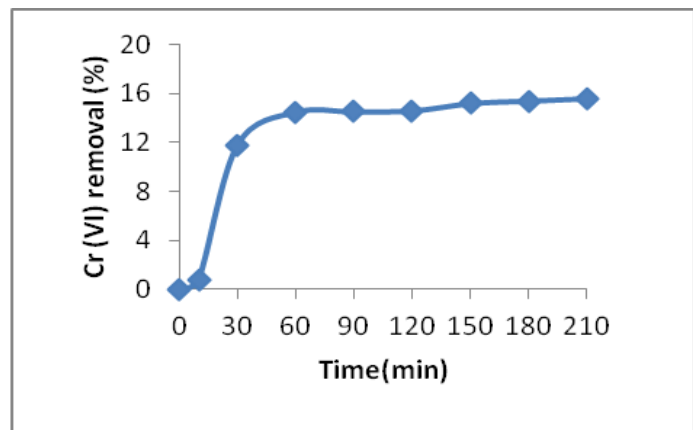


Figure 1: Adsorption of Cr (VI) on the extract spent biosorbent at different time(min) at pH 2 and 298K

Effect of pH and biomass on Cr (VI) adsorption

The effect of pH was significant on biosorption of heavy metals as it affects the protonation of the functional groups on the biomass as well as their interaction chemistry [x]. The effect of

pH on the Cr (VI) adsorption was studied and the results are shown in Figure 3. The percentage adsorption at pH 2 was 39.61% and with the increase in pH, the percentage removal with biosorbent decreased as the pH moved towards the higher range. Percentage adsorption also varied with varying biomass dosage. There was an increase in adsorption of heavy metal ions linearly, up to 2g and with further increase; it was observed that the adsorption rate was constant as shown in Figure 4.

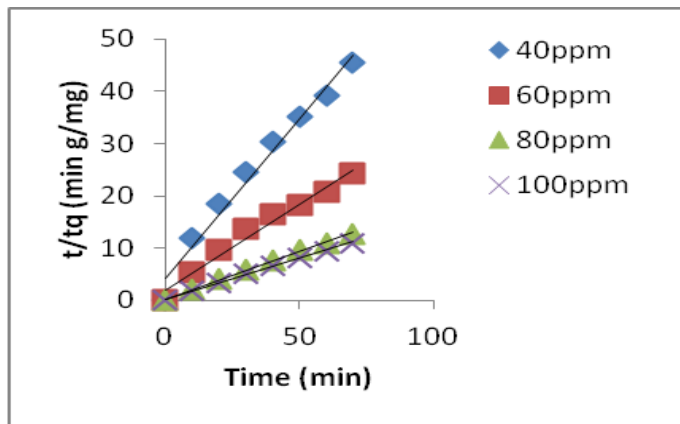


Figure 2: Variation of t/t_q with time at different initial Cr (VI) concentrations at a pH of 2 and 298K

Effect of Temperature

The effect of temperature on the equilibrium sorption capacity were conducted within a temperature range of 10-40°C. The pH of each metal solution was fixed at the optimum value determined from the pH study i.e., at pH 2.0. Figure 5 show the variation of percentage removal with temperature. It was observed that the maximum percentage removal occurred at room temperature. Earlier experiments conducted, explain our observations that with further increase in temperature (above 30°C) there is marked decrease in the percentage removal [xi].

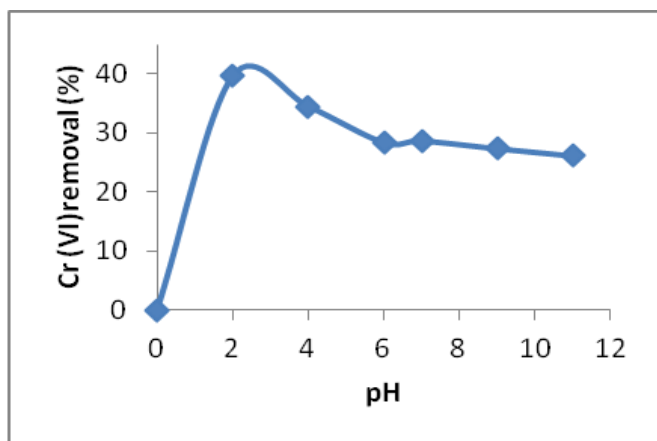


Figure 3: Adsorption of Cr (VI) on the spent biosorbent at different pH, 50ppm and 298K

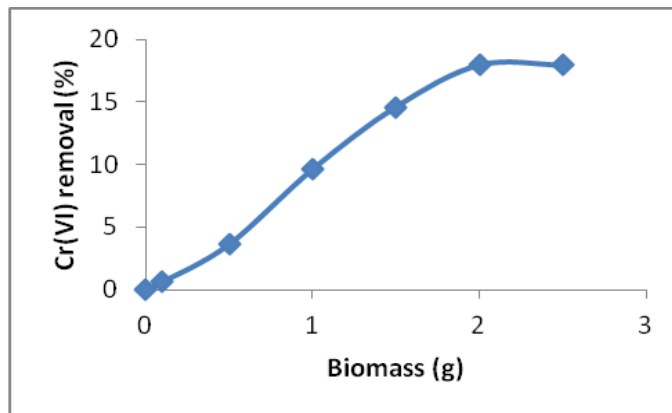


Figure 4: Adsorption of Cr (VI) on the spent biomass at different biomass dosage

This decrease in biosorption efficiency may be due to an increase in the relative desorption of the heavy metals from the solid phase to the liquid phase, destruction of active sites on the biosorbent surface due to bond disruption, or due to the weakness of the sorbent active site binding forces and the sorbate species and also between the adjacent molecules of the sorbed phase. from Figure 5, it is evident that the variation of temperature from 20-30°C has minimal effect on biosorption process and experiments can be carried out at room temperature without adjustments.

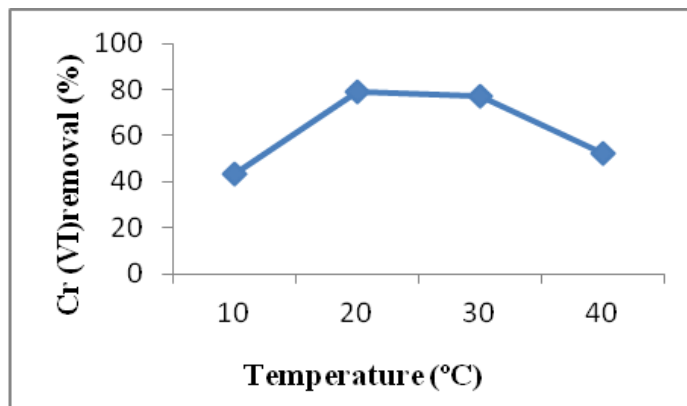


Figure 5: Adsorption of Cr (VI) on the spent biomass at different temperature and at pH 2.0.

Table 1: Pseudo second order adsorption constants

| C_o (ppm) | q_e (mg/g) | $K_2(x10^3/g/mg\ min^{-1})$ | R^2 |
|-------------|--------------|-----------------------------|--------|
| 40 | 1.534 | 0.098 | 0.9774 |
| 60 | 2.892 | 0.057 | 0.9753 |
| 80 | 5.492 | 0.120 | 0.9975 |
| 100 | 6.336 | 0.095 | 0.9978 |

Adsorption Isotherms

Equilibrium sorption isotherms describe the capacity of an adsorbent, characterized by certain constants whose values express the surface properties and affinity of the adsorbent. The Langmuir sorption isotherm has been the most widely used adsorption isotherm and has been successfully applied to many pollutant adsorption processes for the adsorption of a solute from a liquid solution. Langmuir theory's basic assumption is that the adsorption takes place at a specific homogeneous site within the adsorbent. The saturated monolayer adsorption isotherm can be represented as:

$$q = \frac{q_m b C_e}{1 + b C_e} \quad (4)$$

Where q_m is the maximum adsorption capacity and b is an affinity constant related to the energy of adsorption. The value of b indicates the strength or affinity of the sorbate for the solute.

Freundlich isotherm is an empirical isotherm that is used for non-ideal adsorption and is represented by the equation:

$$q = K_f C_e^{1/n} \quad (5)$$

Where K_f and n are Freundlich constants and b is the affinity constant related to the adsorption capacity and the adsorption intensity of the adsorbent respectively.

Redlich- Peterson Isotherm incorporates features of both the Langmuir and Freundlich equations, given by the equation:

$$q_e = \frac{A C_e}{1 + B C_e^g} \quad (6)$$

A linear analysis is not possible for a three parameter isotherm and the three isotherm constants can be evaluated from the pseudo –linear plot using a trial and error optimization method.

Tempkin Isotherm assumes that the fall in the heat of sorption is a linear rather than the logarithmic, as implied in the Freundlich equation. The equation is given by

$$q_{eq} = \frac{RT}{b_T} \ln(A_T C_{eq}) \quad (7)$$

Biosorption isotherms are characterized by certain constants, the values of which express the surface properties and affinity of the sorbent and can also be used to compare the adsorption capacity of biomass for different metal ions. Out of several isotherm equations available, four have been applied for this study, the Langmuir, Freundlich, Redlich-Peterson and Temkin isotherms. The equilibrium constants and correlation co-efficient (R^2) are represented in the Table -2. The maximum adsorption capacity increased with increase in metal ion concentration. The value of q_m at room temperature were 14.92 mg/g at 298 K at pH of 2.0.

Table 2: The Langmuir, Freundlich, Redlich- Peterson and Tempkin sorption constants for biosorption of Cr (VI) at 298K and at pH of 2

| Langmuir constants | | | Freundlich constants | | |
|--------------------|------------------|--------|----------------------|--------|--------|
| $q_m(\text{mg/g})$ | $b(\text{l/mg})$ | R^2 | K_F | n | R^2 |
| 14.92 | 0.067 | 0.5702 | 0.1887 | 1.1376 | 0.9992 |

| Redlich-Petersen constants | | | Tempkin constants | | |
|----------------------------|------|-------|-------------------|--------------|--------|
| A | G | R^2 | A_T | $b_t * 10^3$ | R^2 |
| 0.001 | 0.14 | 0.961 | 3.4403 | 1.58 | 0.9592 |

Morphological changes and surface structure of the adsorbent:

The surface texture of the biosorbent after adsorption was imaged using scanning electron microscope (SEM, JEOL, JSM-6490LV) with magnification of 2000x. It was clearly observed (Figure: 6) that the surface tearing takes place after metal biosorption, confirming the site participation in biosorption. Analysis through BET (NOVA 1000) indicates the biosorbent to be mesoporous with a specific surface area of 4.8477 m²/g and pore diameter 56.865°A.

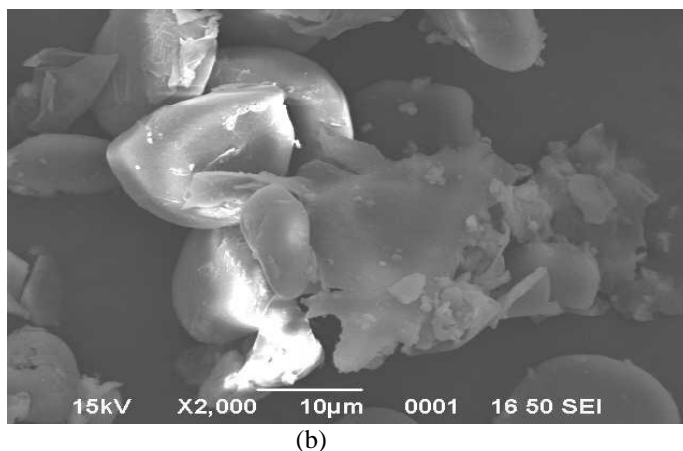
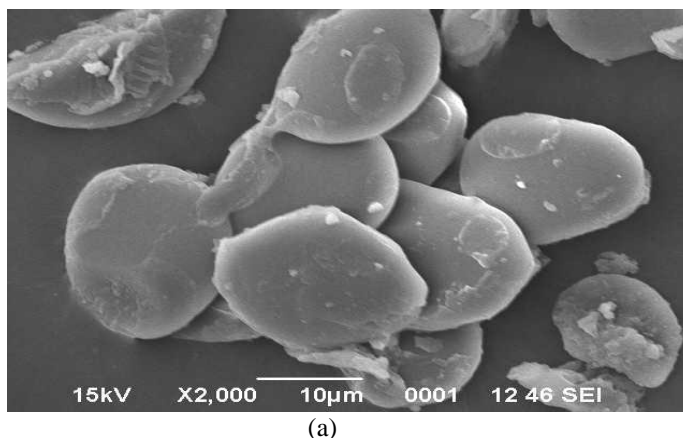


Figure 6: Scanning electron microscopy (SEM) micrographs of spent biomass before (a) and after (b) biosorption of Cr (VI).

IV. Conclusion

This adsorption study indicates that the spent industrial biomass which is usually discarded as waste, in large quantities, can be used as an efficient adsorbent material for the removal of Cr(VI) ions from industrial effluents of various origin. The rate of adsorption was very fast in the first 60 minutes and then showed a steady phase. The biosorption process was endothermic and followed pseudo-second order kinetic model and the adsorption isotherms were well described by Freundlich, Redlich-Peterson and Tempkin isotherm models. The maximum adsorption was 14.12 mg/g at 298K and pH 2.0. This study led to the conclusion that the industrial spent biomass with their rapid adsorption rate, makes them well suited for the removal of chromium (VI) from wastewater.

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References

i. Jianlong Wang, Can Chen (2009), "Biosorbents for heavy metals removal and their future", *Biotechnology Advances* 27(2009)195-226.

ii. T. R. Muraleedharan, Leela Iyengar and C. Venkobachar, "Biosorption, An alternative for metal removal and recovery", *General article*.

iii. Ahalya N., Kanamadi R D and Ramachandra T V., 2008. *Biosorption of Chromium (VI) Tamarindus indica pod shells, Journal of Environmental Science Research International*, 1 (2):77-81

iv. Eric Guibal, Javier Guzman, Ricardo Navarro, Montserrat Ruiz, Ana Sastre, (2004), "Influence of the speciation of metal ions on the sorption on Chitosan", *Fundamentals and applications of anion separations*. pp 225-247.

v. Volesky B. Holan ZR (1995), "Biosorption of Heavy Metals". *Biotech, Prog* 11:235-259.

vi. J. Yang, B. Volesky, "Biosorption of Uranium on Sargassum biomass", (1999) *water Res.*33

vii. M. A. Hashim, K. H. Chu, "Biosorption of cadmium by brown, green and red sea weeds", *Chem. Engg. J.* 97 (2004) 249-255.

viii. V. K. Gupta, A. K. Shrivastava, N. Jain, "Biosorption of chromium (VI) from aqueous solutions by green *Spirogyra* species, *Water Res.* 35 (2001) 4079-4085.

ix. V. K. Gupta, A. Rastogi, V. K. Saini, N. Jain, "Biosorption of Cu (II) from aqueous solutions by green *Spirogyra* species", *J. Colloid Interf. Sci.*296 (1) (2006) 59-63.

x. Liping Deng, Yingying Su, Hua Su, Xinthing Wang, Xiaobin Zhu, "Sorption and desorption of lead (II) from waste water by green algae *Cladophora fassicularis*", *Journal of Hazardous Materials* 143 (2007) 220-225.

xi. Z. R. Holan, B. Volesky, I. Prasetyo, "Biosorption of cadmium by biomass of marine algae", *Biotech, Bioeng.* 41(1993)819-825

xii. Sulaymon AH, Mohammed AA, Al-Musawi TJ (2013) "Column Biosorption of Lead, Cadmium, Copper, and Arsenic ions onto Algae." *J Bioprocess Biotech* 3: 128.