Removal of Hexavalent Chromium from Aqueous Solution using Wheat (*Triticumaestivum*) Bran as Biosorbent

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Abstract: In this paper, removal of Cr (VI) from aqueous solution by wheat bran as a biosorbent has been presented. Effect of pH, contact time, adsorbent dose, initial metal concentration and agitation speed on the removal of Cr (VI) in batch mode were studied. At pH 2, 35°C, contact time of 180 min., adsorbent dose of 0.4 g/100 ml, an initial metal conc. of 100 ppm and stirring speed of 200 rpm, maximum biosorption capacity of Cr (VI) was found to be 8.43 mg/g and removal efficiency was 80.04%. The biosorption process was found to follow pseudo second order kinetics and the equilibrium data fitted well to the Langmuir isotherm. The kinetic and isotherm study of the adsorption process can be useful in designing and fabrication of wastewater treatment plants using wheat bran as biosorbent, where major contaminants are heavy metals and use of standard material such as activated carbon is economically not viable.

Keywords: Biosorption, Chromium (VI), Wheat bran, Triticumaestivum, Kinetics, Isotherms.

1. INTRODUCTION

Rapid industrialization is one of major causes of extensive heavy metal pollution of environment. Out of several heavy metal pollutants, Cr (VI) compounds are found to have adverse effects on biological systems and human health [1]. Major cause of chromium release into our ecosystem is through the discharge of various industrial processes including electroplating, tannery, alloy making, wood preservation etc. [2]. Chromium exists in trivalent and hexavalent forms in aqueous systems. The trivalent form is innocuous and desired for various processes [3], but hexavalent form is toxic, carcinogenic in nature. The toxicity of hexavalent form is 500 times more than the trivalent form [4]. Its overexposure can cause lung cancer, as well as kidney, liver, and gastric damage [5, 6]. Industrial effluents contain 40 to 1000 mgl⁻¹ of Cr (VI) [7, 8]. Permissible limit of Cr (VI) for industrial waste water is 0.1mgl⁻¹, thus removal of Cr (VI) is necessary before discharge of the effluents in environment [9]. Though various physio-chemical methods for the treatment of Cr (VI) are employed like precipitation, reverse osmosis, ion-exchange, reduction, electro dialysis [10] but these are high energy consuming and thus expensive techniques which often generates of toxic sludge [11].

The use of commercially available activated carbon for the treatment of heavy metal laden waste water is limited in developing countries like India because of being costly. Several types of low-cost biosorbents like wool, pine needle, cactus leaves, waste tea, sawdust, rice hulls, olive cake, soybean hulls, cotton seed hulls, etc. have been investigated for their use in heavy metal removal in wastewater treatment [12-17]. Although their sorption capacity is usually lesser than activated carbons but these materials could be an inexpensive substitute for wastewater's treatment [2].

Wheat bran, a byproduct of flour mills is generated in large quantities in India and used for cattle food. In the present study an attempt has been made to explore the use of wheat bran adsorbents for chromium removal from aqueous systems under different experimental condition.

2. MATERIALS AND METHODS

2.1. Adsorbent

Wheat bran is a by-product of a flour milling plant. It was collected from Tarambkam Flour Mills Pvt. Ltd, Ravindrapuri, Varanasi, Uttar Pradesh. It was washed twice with distilled water to remove soluble lighter materials. Thereafter, it was dried in an oven at 60° C for 2 hour. After that, it was crushed and sieved to less than 60 mesh size [18].

2.2. Adsorbate

Stock solutions of Chromium (VI) were prepared by dissolving accurately weighed amount of analytical grade $K_2Cr_2O_7$ in distilled water. The test solutions were prepared by diluting 1g/l of stock solution of Cr (VI) to the desired concentrations. Before mixing the adsorbent, the pH of each test solution was adjusted to the required value with 0.1N HCl and NaOH solutions, respectively [19]. Insignificant decreases in the final equilibrium pH were recorded, so during the uptake pH was assumed constant.

2.3. Biosorption studies

Batch experiments were carried out 35° C (room temp.). 100 ml of Cr (VI) solution with initial concentration C₀ (10-100 ppm) were shaken in the shaker incubator at an agitation speed (10-220 rpm) with fixed amount of biosorbent dose (0.1-0.6 g/100 ml) for a specified period of contact time (10-220 min), varying the initial pH (1-10).The pH of the Cr (VI) solution

was adjusted by adding 0.1N HCl or 0.1N NaOH solutions. After attaining equilibrium, 10 ml sample of the adsorbate was withdrawn and centrifuged to remove the adsorbent particles present. Final concentration of Cr in the adsorbate was determined spectro photometrically [UV-Vis Spectrophotometer ELICO SL 173]by diphenyl carbazide method [20]. The percentage removal of Cr (VI) were calculated by the difference in Cr (VI) conc. before and after biosorption i.e. C_i and C_e and presented by given equation:

$$\% \text{ Removal} = \frac{C_{i} - Ce}{C_{i}} \times 100 \tag{1}$$

The amount of adsorbed Cr (VI) per gram biosorbent was obtained using equation [21]:

$$q_e = \frac{(C_i - C_e) V}{m}$$
(2)

3. RESULTS AND DISCUSSIONS

3.1. Effect of pH

In order to establish the effect of pH on the sorption of Cr (VI) ions by wheat bran, experiments were performed at different initial solution pH value. It was found that uptake of free Cr (VI) depends on pH and decreases from 70% to 35% with increasing pH (Fig. 1).These results are consistent with previous works in this area[12-14, 21, 22]. The Cr (VI) uptake was found to be maximum at pH 2. The pH dependence of metal uptake is largely related to surface functional group and metal solution chemistry.Dichromate ion $(Cr_2O_7^{2-})$ gets reduced to Cr³⁺under acidic conditions

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

However in basic environment, it exists as Cr (OH)₃

$$\operatorname{Cr}_2\operatorname{O}_7^{2-} + 4\operatorname{H}_2\operatorname{O} + 3e^- \rightarrow \operatorname{Cr}(\operatorname{OH})_3 + 5\operatorname{OH}^-$$

More adsorption at lower pH indicates that there is strong electrostatic attraction between chromate ions and positively charged adsorbent surface. Lesser adsorption of Cr(VI) at high pH values greater than 6.0 may be due increased competition of both the anions ($\text{CrO}_4^{2^-}$ and OH^-) to get adsorbed on the surface of the adsorbent of which OH^- predominates. This is in accordance with the earlier studies that have reported the removal of Cr(VI) by different adsorbents [22–25].

2.2. Effect of contact time

Equilibrium time is the maximum time taken by the sorption experiment to achieve equilibrium after which no further metal uptake is observed. It can be noticed from Fig.2 that contact time significantly affects the metal uptake; the metal sorption increases sharply in first 150 minutes and then tapers off thereafter, as the equilibrium is approached. The uptake of Cr (VI) ions by biosorbent has often been observed to occur in two stages: (i) rapid and quantitatively predominant and (ii) slower and quantitatively insignificant. The rapid stage is probably due to abundant availability of active sites on the biomass. With gradual occupancy of these sites, the sorption becomes less efficient in slower stages. According to the results, it was concluded that 180 min was sufficient for the sorption to attain equilibrium. The percentage removal of Cr (VI) was found to be maximum 80.8% at 35°C and equilibrium capacity obtained after two hour of sorption was 7.9 mg/g.

2.3. Effect of adsorbent dose

The experiments were carried out under the

Conditions described earlier and varying biosorbent mass from 0.1gm/100ml to 0.6 gm/100 ml .From Fig. 3, it can be observed that Cr (VI) removal efficiency increases with increase in adsorbent dose, since contact surface of adsorbent particles increased and it would be more probable for $HCrO_4^-$ and $Cr_2O_7^-$ ions to be adsorbed on adsorption sites. Similar results are also reported by other researchers [26-30].Maximum adsorption was observed at 0.4gm /100 ml i.e. 80.34%.

2.4. Effect of Initial Cr (VI) concentration

Experiments were carried out with different initial Cr (VI) concentrations at pH 2 of the metal solution and 0.4 g biosorbent dose. It can be observed from Fig.4 that specific metal uptake increased with an increase in the Cr (VI) ion concentration. The highest uptake by Wheat bran was around 8.14 mg g⁻¹ at an initial Cr (VI) concentration of 100 mg I^{-1} .The enhancement in metal uptake could be due to an increase in electrostatic interactions involving the sites of progressively lower affinity for metal ions. At higher concentrations, the mass transfer resistance of metal ions between the aqueous and solid phases was reduced which resulted in higher probability of collision between the metal ion and biosorbent.

2.5. Effect of agitation speed

To study the effect of agitation on biosorption capability of wheat bran for removing Cr (VI), There was sharp increase in metal uptake with increasing the agitation speed from 50 to 200 rpm and thereafter it almost reached saturation. These results can be associated to the fact that with increasing the agitation speed, the rate of diffusion of Cr (VI) ions towards the surface of the adsorbent increases. It also depicts that an agitation speed of 200 rpm is sufficient to assure that all the surface binding sites are made readily available for Cr (VI) uptake. Experiments were conducted at different agitation speed (50–200 rpm).It can be inferred from Fig.5 that Cr (VI) uptake was increasing with the increase in agitation speed.



Fig. 1. Effect of pH on adsorption (biosorbent dose:0.3 g/100 ml;35°C;Initial conc.: 100 ppm; particle size: 60 meshes; agitation speed:180 rpm)



Fig. 2. Variation of % removal and uptake of Cr (VI) ions with time (biosorbent dose: 0.3 g/100 ml; Temp.:35°C; Initial conc.:100 ppm; particle size: 60 meshes; pH:2; agitation speed:180 rpm)



Fig. 3. Effect of biosorbent mass on % removal and uptake (Initial conc.:100 ppm; particle size: 60 meshes; temp.: 35⁰C; contact time: 180 min; pH: 2; agitation speed: 180 rpm)



Fig. 4. Effect of initial Cr (VI) concentration on metal uptake (biosorbent dose:0.4 g/100 ml; particle size: 60 meshes; temp.: 35⁰C;contact time: 180 min; pH: 2; agitation speed:180 rpm)



Fig. 5. Effect of agitation on Cr (VI) uptake (biosorbent dose: 0.4 g/100 ml; initial conc.:100 ppm; particle size: 60 meshes; temp.: 35^oC; contact time: 180 min; pH: 2)

4. KINETIC STUDY

The study of sorption kinetics describes the adsorbate uptake rate and evidently this rate controls the residence time of adsorbate at the solid liquid interface [31]. The kinetics of Cr (VI) sorption on thewheat bran powder as adsorbents was analyzed using two kinetic models i.e. pseudo-first order and pseudo-second order models.

The integrated pseudo-first order equation [32] is generally expressed as:

$$Log (q_e - q_t) = log q_e - k_1 t / 2.303$$
(3)

Where q_e and q_t are the sorption capacities at equilibrium and at time t, (mgg^{-1}) and K_1 is the rate constant of pseudo-first order sorption (min^{-1}) .

The pseudo-second-order sorption kinetics [33]can be expressed as:

$$\frac{t}{h_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$
(4)

Where q_e and q_t are the sorption capacity at equilibrium and at time t, (mgg^{-1}) respectively and K_2 is the rate constant of the pseudo-second order sorption $(g.mg^{-1}.min^{-1})$.

Experimental data were fitted to pseudo-first order equation (Fig. 6) and pseudo-second order equation (Fig. 7) and related parameters are summarized in Table 1.

Parameter	Pseudo-first order model	Pseudo-second order model
Equi. sorption capacity, q _e	12.302	8.621
Rate constant	0.0299	0.0028
Correlation coefficient, R	0.867	0.976

Table 1. Kinetic parameters of fitting of experimental data

The correlation coefficients (R^2) for the pseudo second-order kinetic model fits are much higher than ones derived from the pseudo first-order kinetic model which means good agreement between model and experimental data. This suggests that the chemical sorption as rate-limiting step of adsorption mechanism.

5. ADSORPTION ISOTHERMS

In this study, two empirical adsorption models, namely Langmuir and Freundlich equations were used to fit the experimental data at various temperatures.

Langmuir adsorption isotherm relation [34] is given by:

$$\frac{C_{e}}{q_{e}} = \frac{C_{e}}{q_{M}} + \frac{1}{bq_{M}}$$
(5)

Table2. Lagmuir and Freundlich model regression constants at different temperatures

Temperature	Langmuir isotherm parameters				Freundlich isotherm parameters		
	q _m	b	R _L	R ²	K _F	1/n	R ²
20 ⁰ C	5.53	0.175	0.0540	0.974	1.61	0.208	0.938
30 ⁰ C	6.06	0.1227	0.0753	0.989	1.745	0.224	0.98
40^{0} C	10.30	0053	0.1587	0.984	2.14	0.342	0.950

Where q_M (mg/g) and b are Langmuir constants related to adsorption capacity and the energy of biosorption respectively.



Fig. 6. Pseudo-first-order kinetic model for removal of Cr (VI) (pH:2; Dosage: 0.4g/100 ml; agitation speed 180 rpm; Initial metal conc. 100 ppm)



Fig. 7. Pseudo second-order kinetic model for removal of Cr (VI) (Initial metal conc.: 100 ppm; pH:2;Dosage:0.4g/100 ml; agitation speed: 180 rpm)

The Freundlich adsorption isotherm model [35] is expressed as:

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

where q_e is the metal ion sorbed (mg/g), Ce the equilibrium concentration of metal ion solution (mg/L). K_f is adsorption capacity and n is adsorption intensity and are dimensionless.

From Fig. 7.1, Fig. 7.2 and Table 2, it is evident that the high value of correlation coefficient ($R^2 = 0.989$) obtained for Langmuir model indicates a good agreement between the experimental values and isotherm parameters and this confirms the monolayer adsorption of Cr(VI) onto the wheat bran surface.

The equilibrium parameter,
$$R_{\rm L}$$
 is defined as,

$$R_{\rm L} = \frac{1}{1+bC_0}$$
(7)

is a measure of adsorption favorability.



Fig.7.1 Langmuir isotherm for adsorption of Cr (VI) on wheat bran at different temperature (pH: 2; Dosage: 0.4g/100 ml; agitation speed 180 rpm, contact time 180 min)



Fig.7.2 Freundlich adsorption isotherm for Cr (VI) on wheat bran at different temperatures (pH: 2; Dosage: 0.4g/100 ml; agitation speed: 180 rpm, contact time: 180 min)

In the present study, value of R_L is found in the range of 0.0550 and 0.1587 (0 < R_L < 1) which confirms the favorable adsorption process for Cr (VI) removal. Hence the sorption process was very favourable and the adsorbent employed exhibited a good potential for the removal of Cr (VI) from aqueous solution [36].

6. CONCLUSION

The present study shows wheat bran as an effective adsorbent of Cr(VI). The experimental parameters such as pH, adsorbent dose, contact time, initial metal concentration and agitation speed were found to have an effect on the adsorption efficiency and uptake of Cr (VI) on biosorbent. At an initial metal conc. of 100 ppm, pH 2, 35° C, agitation speed of 180 rpm, particle size of 60 meshes, adsorbent dose of 0.4 g/100ml, contact time of 180 minutes, maximum biosorption of Cr (VI) was found to be 8.54 mg/g. The Freundlich and Langmuir isotherm models were used to study the adsorption process and it was found that the experimental data fitted well for Langmuir isotherm model confirming monolayer adsorption. The kinetic sorption data fitted well to the pseudosecond order kinetic model. Thekinetic data obtained from the adsorption studies will be useful for fabrication and design of heavy metal laden wastewater treatment plants using wheat bran as biosorbent, where use of standard material such as activated carbon is economically not viable.

REFERENCES

- R.S. Bai, T.E. Abraham, Studies on chromium (VI) adsorption–desorption usingimmobilized fungal biomass, Bioresour. Technol. 87 (2003) 17–26.
- [2] H.S. Altundogan, Cr(VI) removal from aqueous solution by iron (III)hydroxide-loaded sugar beet pulp, Process Biochem. 40 (2005) 1443–1452.
- [3] G. Rojas, J. Silva, J.A. Flores, A. Rodriguez, M. Ly, H.Maldonado, Adsorption of chromium onto crosslinked chitosan, Sep. Purif. Technol. 44 (2005).
- [4] Z. Kowalski, Treatment of chromic tannery wastes, J. Hazard. Mater. 37 (1994) 137–144.
- [5] US Department of Health and Human Services, Toxicological Profile for Chromium, Public Health Services Agency for Toxic substances and Diseases Registry, Washington, DC, 1991.
- [6] M. Cieslak-Golonka, Toxic and mutagenic effects of chromium(VI). A review, Polyhedron 15 (1995) 3667– 3689.
- [7] S. Srivastava, I.S. Thakur, Isolation and process parameter optimization of *Aspergillussp.* for removal of chromium from tannery effluent, Bioresour. Technol. 97 (2006) 1167–1173.
- [8] A. Ganguli, A.K. Tripathi, Survival and chromate reducing ability of *Pseudomonasaeruginosa*in industrial effluents, Lett. Appl. Mcrobiol. 28 (1999) 76–80.
- [9] N. Goyal, S.C. Jain, U.C. Banerjee, Comparative studies on microbial adsorption of heavy metals, Adv. Environ. Res. 7 (2003) 235–250.
- [10] Eccles, Treatment of metal-contaminated wastes: why select a biological process, Process Biotopic 17 (1999) 462–465.
- [11] Demir, M. Arisoy, Biological and chemical removal ofCr (VI) from wastewater: cost and benefit analysis, J. Hazard. Mater. 147 (2007) 275–280.
- [12] A. Kapoor, T. Viraraghavan, D.R. Cullimore, Removal of heavy metals using the fungus *Aspergillusniger*, Bioresour. Technol. 70 (1999) 95–104.
- [13] Z. Aksu, Equilibrium and kinetic modelling of cadmium (II) biosorptionby*C*. *vulgaris* in a batch system: effect of temperature, Sep. Purif. Technol. 21 (2001)285–294.

- [14] L. Zhang, L. Zhao, Y. Yu, C. Chen, Removal of lead from aqueous solution by non-living *Rhizopusnigricans*, Water Res. 32 (1998) 1437–1444.
- [15] M. Dakiky, M. Khamis, A. Manassra, M. Mer'eb, Selective adsorption of chromium (VI) in industrial wastewater using low-cost abundantly available adsorbents, Adv. Environ. Res. 6 (2002) 533–540.
- [16] H.M. Amir, N. Dariush, V. Forugh, N. Shahrokh, Teawaste as an adsorbent for heavy metal removal from industrial wastewaters, Am. J. Appl. Sci. (2005) 372–375.
- [17] N. Ahalya, R.D. Kanamadi, T.V. Ramachandra, Biosorption of chromium (VI) from aqueous solutions by the husk of Bengal gram (*Cicerarientinum*), Electr. J. Biotechnol. 3 (2005) 258–264.
- [18] R. Elangovan, L. Philip, K. Chandraraj, Biosorption of hexavalent and trivalent chromium by palm flower (*Borassusaethiopum*), Che. Eng. J. 141 (2008)99–111.
- [19] X. Han, Y. S. Wong, M. H. Wong, N. F. Y. Tam, Biosorption and bioreduction of Cr(VI) by a microalgal isolate, *Chlorella miniata*, J. of Haz. Mat. 146 (2007) 65–72.
- [20] L. Zhang, L. Zhao, Y. Yu, C. Chen, Removal of lead from aqueous solution by non-living *Rhizopusnigricans*, Water Res. 32 (1998) 1437–1444.
- [21] J. Goel, K. Kadirvelu, C. Rajagopal, V.K. Garg, Removal of lead (II) by adsorption using treated granular activated carbon: batch and column studies, J. Hazard. Mater. B125 (2005) 211–220.
- [22] K. Mohanty, M. Jha, B.C. Meikap, M.N. Biswas, Biosorption of Cr(VI) from aqueous solutions by *Eichhorniacrassipes*, Chem. Eng. J. 117 (2006)71–77.
- [23]] N.K. Hamadi, X.D. Chen, M.M. Farid, M.G.Q. Lu, Adsorption kinetics for the removal of chromium(VI) from aqueous solution by adsorbents derived from used tyres and sawdust, Chem. Eng. J. 84(2001)95–105.
- [24] T. Karthikeyan, S. Rajgopal, L.R. Miranda,

Chromium(VI) adsorption fromaqueous solution byHeveaBrasilinesis sawdust activated carbon, J. Hazard.Mater. B124 (2005) 192–199.

- [25] C.P. Huang, M.H.Wu, The removal of chromium (VI) from dilute aqueoussolution by activated carbon, Water Res. 11 (1977) 673–679.
- [26] E. Pehlivan, T. Altun, 2008. "Biosorption of chromium (VI) ion from aqueous solutions usingwalnut, hazelnut and almond shell", Journal of Haz. Materials., 155, 378-384.
- [27] E. Demirbas, M. Kobya, A.E.S. Konukmanc, 2008. "Error analysis of equilibrium studies forthe almond shell activated carbon adsorption of Cr(VI) from aqueous solutions", Journal ofHazardous Materials.154, 787–794.
- [28] G. Moussavi, B. Barikbin, 2010. "Biosorption of chromium (VI) from industrial wastewateronto pistachio hull waste biomass", Chemical Engineering Journal.162, 893–900.
- [29] A. Ahmadpour, M. Tahmasbi, T. RohaniBastami, J. AmelBesharati, 2009. "Rapid removal ofcobalt ion from aqueous solutions by almond green hull", Journal of Hazardous Materials. 166, 925–930.
- [30] S. Tunali, I. Kiran, T. Akar, 2005. "Chromium (VI) biosorption characteristics of Neurosporacrassa fungal biomass", Min. Eng. 18 (7) 681–689.
- [31] Ofomaja A., UkpeborE.andUzoekwe S., Biomass and Bioenergy, **35**, 4112 (2011).
- [32] S. Lagergren, About the theory of so-called adsorption of soluble substances, K.Sven. Vetenskapsakad. Handl. 24 (1898) 1–39.
- [33] Y.S. Ho, G. McKay, Kinetics of pollutant sorption by biosorbents: review, Sep.Purif. Methods 29 (2000) 189–232.
- [34] Langmuir I., J. Am. Chem. Soc., 40, 1361 (1918)
- [35] Freundlich H., J. Phys. Chem., 57, 385 (1907)