

## Adsorption Studies of Cr (VI) on Rice Husk Ash (Rha)

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**Summary:** In the present investigation, the adsorption of Cr (VI) was studied by making use of batch-technique. Percentage adsorption was calculated for RHA-Chromium solution system as a function of i) contact time, ii) pH, iii) adsorbate concentration and iv) temperature. Adsorption is interpreted in terms of Freundlich and Langmuir equations. The value of  $\Delta H^0$  was found to be -16.4708 KJ/mole. The desorption studies especially with 0.1M CaCl<sub>2</sub> and 10 % HCl at given Chromium loadings on RHA give significant percent desorption of Cr (VI).

### Introduction

Heavy metal contamination exists in aqueous waste streams of many industries. Most of the effluents discharge by the industries are contaminated with heavy metals. The effluents produced during the electroplating, leather tanning, cement clinkering, mining, dyeing, fertilizer and photography industries contain hexavalent chromium which pose environmental and public health problems. Hexavalent chromium has been reported to be toxic not only for animals and but also for humans and is a known carcinogen [1]. Cr (VI) concentration in industrial waste waters required between 0.5 to 270.00 mg.l<sup>-1</sup> [2]. The tolerance limit of Cr (VI) for discharge into inland surface waters is 0.1 mg.l<sup>-1</sup> where as, in potable water it is 0.05 mg.l [3]. In order to comply with this limit, it is essential that industries treat their effluents to reduce the Cr (VI) to acceptable levels. A number of treatment methods for the removal of metal ions from aqueous solutions have been reported which include reduction, ion exchange, electro dialysis, electrochemical precipitation, evaporation, solvent extraction, reverse osmosis, chemical precipitation and adsorption [2]. Most of these methods are expensive due to their high capital and operational costs for the disposal of the residual metal sludge. Many reports have appeared on the development of low-cost activated carbon adsorbents developed from cheaper and readily available materials [4-6].

The adsorption technique of Cr (VI) by leaf mould [7], activated groundnut husk carbon [8, 9], coconut shell activated carbon [10], phosphate treated saw dust [1], rice husk carbon [8, 11], coconut husk and palm pressed fibers [12], sugar beet pulp and cane bagasse [7] have been reported in the literature.

In the present study rice husk ash (RHA), prepared from rice husk incineration [13] was used for the removal of Cr (VI) from aqueous solution.

### Results and Discussion

The adsorption of Cr (VI) on the rice husk ash (RHA) was studied as a function of shaking time, pH, adsorbate concentration and temperature for known Cr (VI) concentration at  $34 \pm 0.5$  °C. The results are interpreted in terms of percentage adsorption as shown in (Table-1A, 1B, 1C). The rapid adsorption of Cr (VI) on rice husk ash (RHA) at room temperature and establishing equilibrium instantaneously after mixing indicate that surface precipitation as well as ion exchange may be the possible adsorption mechanisms. The investigations indicate that adsorption is pH dependent [14]. A much greater adsorption capacity of RHA for Cr (VI) was observed in acidic solution *i.e.*, pH 1.02 to 5.5 (Table-1A, Fig. 1) thus more acidic conditions have favored a shift to induce density of available charged sites at which adsorption could occur. The span of adsorption will therefore depend upon experimental parameters that could affect the surface charge [15, 16]. Desorption studies at given Cr (VI) loadings on rice husk ash (RHA) showed that significant percentage of the element is reversibly desorbed. 0.1M CaCl<sub>2</sub> and 10 % HCl solution was used for the elution of chromium (Table-1D).

The adsorption isotherms at two different temperatures ( $34 \pm 0.5$  °C and  $50 \pm 0.5$  °C) were obtained by plotting the amount of chromium adsorbed on rice husk ash (RHA) (g/g) against metal equilibrium concentration (Fig. 2). Adsorption of Cr

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Table-1A: Effect of pH on adsorption of Cr (VI) on rice husk ash at  $34 \pm 0.5^\circ\text{C}$ .

pH	Amount of Cr (VI) Taken (ppm)	Amount of Cr (VI) in Soln. at Equilibrium (ppm)	Amount of Cr (VI) Adsorbed (ppm)	Adsorption (%)
1.02	10.00	0.0556	9.9444	99.444
3.25	10.00	2.6600	7.3400	73.400
5.12	10.00	3.4640	6.5360	69.360
7.20	10.00	3.7650	6.2350	66.320
9.00	10.00	4.3280	5.6720	56.720

Table-1B: Effect of temperature on adsorption of Cr (VI) on rice husk ash at pH = 7.20.

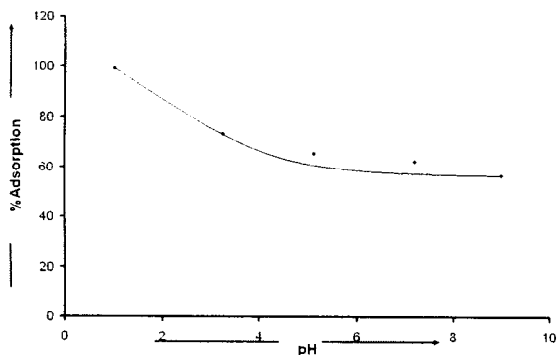
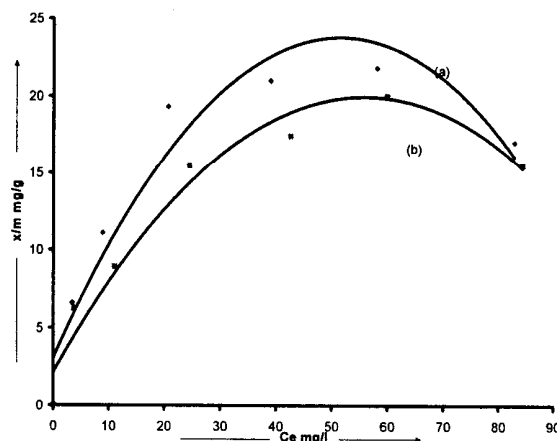
Temperature $^\circ\text{C}$	Amount of Cr (VI) Taken (ppm)	Amount of Cr (VI) in soln. at Equilibrium (ppm)	Amount of Cr (VI) adsorbed (ppm)	Adsorption (%)
$34 \pm 0.5$	10.00	3.400	6.600	66.000
$50 \pm 0.5$	10.00	3.740	6.260	62.600
$70 \pm 0.5$	10.00	3.850	6.150	61.500

Table-1C: Dependence of adsorbate concentration relative to Cr (VI) adsorption on rice husk ash at  $34 \pm 0.5^\circ\text{C}$  at pH 7.20.

Amount of Adsorbent Taken (mg)	Amount of Cr (VI) Taken (ppm)	Amount of Cr (VI) in Soln. at Equilibrium (ppm)	Amount of Cr (VI) Adsorbed (ppm)	Adsorption (%)
1000.00	10.00	3.400	6.600	66.00
1000.00	20.00	8.910	11.09	55.45
1000.00	40.00	20.68	19.32	48.30
1000.00	60.00	39.00	21.00	35.00
1000.00	80.00	58.18	21.82	27.27
1000.00	100.0	83.00	17.00	17.00

Table-1D: Desorption studies of Cr (VI) with 10 % HCl & 0.1M  $\text{CaCl}_2$ .

Amount of Adsorbent Taken (mg)	Amount of Cr (VI) Taken (ppm)	Adsorption of Cr (VI) (%)	Desorption of Cr (VI) with 10 % HCl (%)	Desorption of Cr (VI) with 0.1M $\text{CaCl}_2$ (%)
1000.00	20.00	55.45	98.20	98.00
1000.00	40.00	48.30	96.00	95.76
1000.00	60.00	35.00	93.10	94.50
1000.00	80.00	27.27	93.50	94.60
1000.00	100.0	17.00	92.10	93.99

Fig. 1: Effect of pH on adsorption of Cr (VI) on Rice Husk Ash at  $34 \pm 0.5^\circ\text{C}$ .Fig. 2: Adsorption isotherms of  $\text{Cr}^{6+}$  on rice husk ash at different temperature: (a) 307K, (b) 323K.

(VI) decreases with increasing temperature. The straight lines were obtained for Freundlich isotherms, which gave the comparable values of Freundlich constant *i.e.*  $1/n = 0.6229$  and  $0.8952$  (Fig. 3). Similarly straight lines were obtained for Langmuir adsorption isotherms (Fig. 4).

#### Calculations of Thermodynamic Parameters

Thermodynamic parameters such as Gibbs free energy  $\Delta G^\circ$  (KJ/mol) change in enthalpy  $\Delta H^\circ$  (KJ/mol) and change in entropy  $\Delta S^\circ$  (KJ mol $^{-1}$ K $^{-1}$ ) for Cr (VI) adsorption were calculated from the distribution constant  $K$  [16] by using the following relations:

$$\Delta G^\circ = -RT \ln K \quad (1)$$

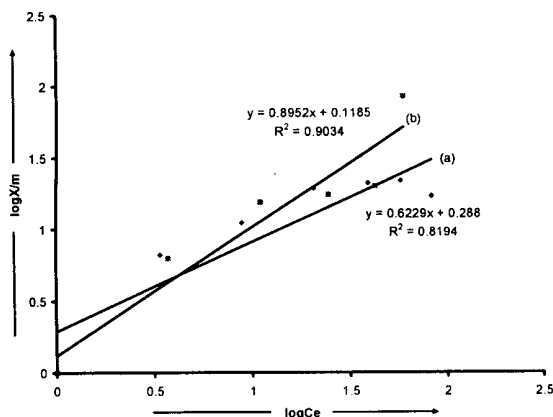
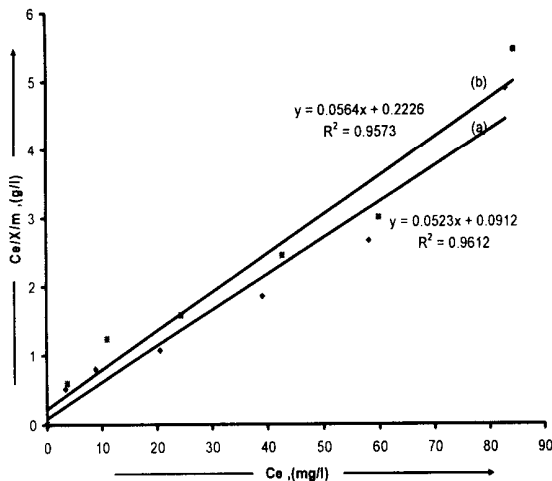
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (2)$$

$$\text{And } \ln K = T\Delta S^\circ - \Delta H^\circ / RT + \text{Constant} \quad (3)$$

Table-2 shows the values of thermodynamics parameters  $\Delta H^\circ$ ,  $\Delta S^\circ$ ,  $\Delta G^\circ$ . The negative value of  $\Delta H^\circ = -16.4708$  KJ/mole, which is calculated from the slope of  $\ln K$  vs.  $1/T$  [15]. Fig. 5 confirms the exothermic nature of the overall adsorption process. The positive value of  $\Delta S^\circ$  suggests increased randomness at the solid/solution interface with some structural change in the adsorbate and adsorbent and also affinity of the RHA towards Cr (VI). A negative value of  $\Delta G^\circ$  indicates the feasibility and spontaneity of the adsorption process, where higher negative value reflects a more energetically favorable adsorption process.

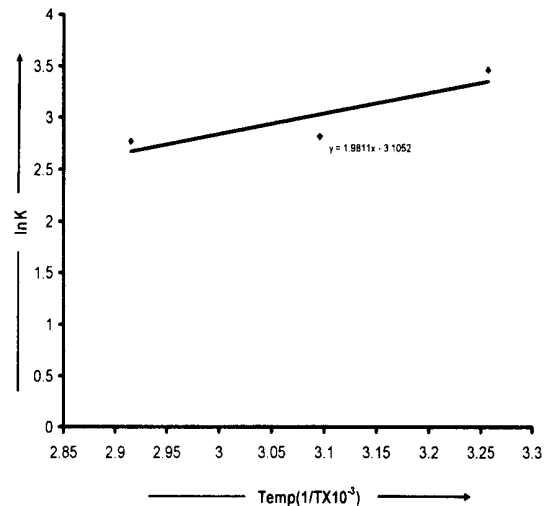
Table-2: Value of thermodynamic data for Cr<sup>+6</sup> adsorption on rice husk ash.

Temperature K	$\Delta H^0$ (KJ/mole)	$\Delta G^0$ KJ/mole	$\Delta S^0$ (KJK <sup>-1</sup> mol <sup>-1</sup> )
307	-16.4708	-8.8310	0.0824
323	-16.4708	-7.5590	0.0740
343	-16.4708	-7.8990	0.0710

Fig. 3: Freundlich plots of Cr<sup>+6</sup> adsorption on rice husk ash at solution to rice husk ash ratio 10:1 at different temperature (a) 307K, (b) 323K.Fig. 4: Langmuir plots of Cr<sup>+6</sup> adsorption on rice husk ash at solution to rice husk ash ratio 10:1 at different temperature (a) 307K, (b) 323K.

### Experimental

Redox titration was employed for the determination of Cr (VI) initial and equilibrium concentrations [17].

Fig. 5: Plot of lnK vs. 1/T for Cr<sup>+6</sup> adsorption on rice husk Ash.

All reagents used were of analytical grade (E. MERCK)<sup>TM</sup>; the following reagents were employed: 0.01M Ferrous ammonium sulphate standard solution, sodium diphenylamine sulphonate (as indicator) in the presence of mixture of concentrated sulphuric acid and phosphoric acid. 1000 ppm K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> stock solution was prepared by the standard procedure [17]. Various spiked standard solutions were prepared by taking a known aliquot of the stock solution in borosilicate 250 ml measuring flasks, making the volume up to the mark with deionized water.

RHA was prepared from rice husk (which was obtained from Daroghewala Rice Mills, Lahore) by incineration at 750 °C in Muffle furnace (Make: PCSIR, 2005). By heating at 750°C a carbon free sample of ash was obtained, which was ground to -200 mesh and was used without any heat or chemical treatment for the adsorption studies reported here. A complete chemical analysis Table-3 and (SEM) S2700 Hitachi-JAPAN (Fig. 6) of rice husk ash is given showing the presence of SiO<sub>2</sub> which is > 90 %.

Table-3: Chemical analysis of rice husk ash.

Metal Oxides	% age
SiO <sub>2</sub>	94.7520
Fe <sub>2</sub> O <sub>3</sub>	0.9000
MgO	0.6400
CaO	0.4980
Na <sub>2</sub> O	1.0852
K <sub>2</sub> O	2.0300

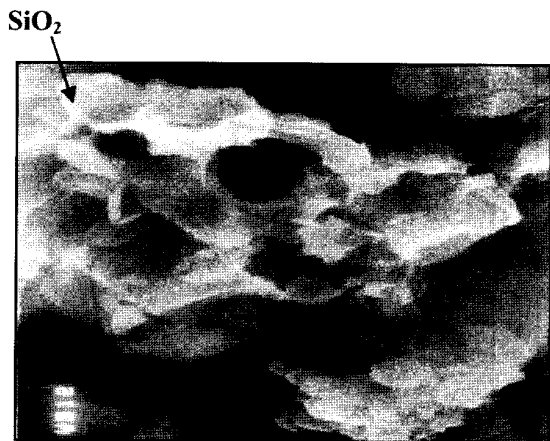


Fig. 6: Scanning electron microgram of rice husk ash at 750 °C.

The adsorption of Cr (VI) on rice husk ash (RHA) was studied through batch-technique [15]. All adsorption experiments except variable pH were undertaken at pH 7.20, which was obtained naturally at solution to adsorbent ratio of 10:1 and measured by using pH meter (Model: 8417 Hanna Instruments). The pH of the suspension in one set of experiments was adjusted by using NaOH/NH<sub>4</sub>OH and HNO<sub>3</sub> [15]. The pH of solution was that of supernatant, which was obtained after equilibration. After attaining of equilibrium the suspension was centrifuged in a stoppered tube for 5 minutes at 4500 rpm and was then filtered through Whatman 41 filter paper. The amount of Cr (VI) adsorbed "X" and equilibrium Cr (VI) concentration in the solution "Ce" was determined by Oxidation-Reduction titration [17]. Adsorption of Cr (VI) on rice husk ash (RHA) was determined in terms of percent extraction. Amount adsorbed per unit weight of the rice husk ash (RHA), X/m was calculated from the initial and final concentration of the solution. Adsorption capacity for the adsorption of Cr (VI) species was evaluated from the Freundlich and Langmuir adsorption isotherms [16] were studied at two different temperatures (*i.e.*, 34 ± 0.5 °C and 50 ± 0.5 °C). The Cr (VI) concentration studied was in the range of 10 ppm to 100 ppm for 10:1 (solution to rice husk ash (RHA) ratio).

### Conclusion

Rice husk ash (RHA) is proven to be potentially good scavenger and low-cost adsorbent

for the removal of Cr (VI) from aqueous solution, at optimum parameters more specifically pH, as adsorption of Cr (VI) was highly pH dependent. The optimum pH was found to be .1, at which Cr (VI) exists mostly as the most easily adsorbed form, HCrO<sub>4</sub> [14]. In the isotherm studies the experimental adsorption data fitted reasonably well the Langmuir and Freundlich isotherms.

### References

1. M. R. R. Ajmal and B. A. Siddiqui, *Water Research*, **30**, 1478 (1996).
2. J. W. Patterson, *Waste Water Treatment Technology*, 2<sup>nd</sup> ed. Butterworth-Heinmann, London, p. 1134 (1998)
3. EPA (Environment Protection Agency), *Environmental Pollution Control Alternatives*. EPA/625/5-90/025, EPA/625/4-89/023, Cincinnati, US (1990).
4. S. Babel and T. A. Kuraniawan, *A Review; Journal of Hazardous Materials*, **97**, 219 (2003).
5. S. E. Bailey, T. J. Olin, R. M. Brick and D. D. Adrian, *Water Research*, **33**, 2469 (1999).
6. S. H. Pollard, G. F. Flower, S. C. Jollars and R. Perry, *A Review; Science of the Total Environment*, **116**, 31 (2002).
7. D. C. Sharma and C. F. Forster, *Bioresource Technology*, **49**, 31 (1994a).
8. K. Srinivassan, N. Balasubramanianand, T. V. Ramakrishnan, *Indian Journal of Environmental Health*, **33**, 433 (1991).
9. K. Periasamy, K. Srinivassan and P. R. Murugan, *Waste Management*, **15**, 256 (1995).
10. G. J. Alaerts, V. Jitjaturant and P. Kelderman, *Water Science and Technology*, **21**, 1701 (1989).
11. K. S. Low, T. S. T. OOI and C. K. Lee, *Bioresource Technology*, **68**, 205 (1999).
12. W. Tan, T. S. T. OOI and C. K. Lee, *Environmental Technology*, **14**, 277 (1988).
13. Z. Uzma, Z. Samreen, N. Sumra and S. F. Mahmood, *Pakistan Journal of Science*, **57**, 84 (2005).
14. D. Erhan, K. Mehmet, S. Elif and O. Tuncay, *Water SA*, **30**, 533 (2004).
15. A. K. Saad, U. R. Riaz and M. A. Ali, *Waste Management*, **14**, 125 (1994).
16. Z. Uzma, I. K. Izhar, J. Farhat and S. Naeem, *Journal of the Chemical Society of Pakistan*, **24**, 92 (2002).
17. A. I. A. Vogel, *A text book of Quantitative Inorganic Analysis* (3<sup>rd</sup> ed.), Rickard Cloy Company, Ltd. Great Britain, p. 645 (1961).