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Full Length Research Paper

Removal of chromium ion from leather industrial wastes by activated pure rice hulls

Mahejabeen Mukhtar

Department of Chemistry, University of Karachi, Pakistan. E-mail: prime1@super.net.pk.

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The removal of Cr ions from industrial wastage by adsorption on rice hulls was investigated based on activated pure rice hulls dosage, stay time, metal concentration and solution temperature. The optimum values of activated pure rice hulls dosage and stay time were determined to be 0.5 gm/50 ml solution and 60 min, respectively, for the adsorption of Cr ions. The constant for the Freundlich, D-R and Langmuir isotherms were calculated at (293 – 323 K). The adsorption of Cr from industrial wastage was found to be exothermic. Thermodynamic parameters such as free energy (∆G°), enthalpy (∆H°) and entropy (∆S°) of adsorption was also calculated and interpreted from the slope and intercept of the plots of ln K_D vs I/T. The ∆G° value decreases with rise in temperature and the negative values of ∆H° indicate that the adsorption of Cr from industrial wastage was an exothermic process while positive values of change in entropy (∆S°) were also observed.

Key words: Adsorption, Cr metal, activated pure rice hulls.

INTRODUCTION

Rice hull is a waste product from different agricultural industries. Rice hulls which are a waste substance can be converted into a adsorbent material (Marshall and Johns, 1996; Marshall et al., 1999; Ahmedna et al., 1997) This product exhibits very good adsorption for "Cr" ion from industrial wastage, and the quest for cheap treatment alternative has compelled the researches (Ahmedna et al., 1998; Johns et al., 1998; Marshall et al., 1999, 1996). Rice hull is gene-rated during the first stage of rice milling, when rough rice or paddy rice is husked, that is, husk is separated from the rest of the grain. In general, 100 kg of paddy rice will generate 20 kg of hulls.

Moisture content of rice hulls is about 10%; the equilibrium moisture content is lower then that of paddy or rough rice. Bulk density of rice hull is 100 to 150 kg/m^3. If rice hull is grind, bulk density increases to 200 to 250 kg/m^3. Rice hulls have excellent adsorption properties (Prabhu et al., 1981; Sen and De, 1987); the main organic compounds of the dry hull are cellulose and hemicelluloses (50%) and lignin (26%) with the remaining 4% represents other compounds such as oil, protein, etc (Huang and Ostovic, 1993; Reed and Matsumoto, 1993; Khattak et al., 1999).

A high concentration removal of such metal ion is more effective by ion exchange or adsorption on solid sorbents such as activated pure rice hulls (Qadeer et al., 1995). In this study, pure rice hulls which is a solid waste matter was used as an adsorbent for the removal of Cr metal from industrial wastage (Khattak et al., 2000; Khattak et al., 2002). The aim was to investigate the optimum condition of metal uptake and to calculate the adsorption capacity and some thermodynamic constants at different temperatures.

Nomenclature: **C** = concentration of adsorbate ions at equilibrium, ∆**G°** = Gibbs free energy of adsorption (KJ/mol), ∆**H°** = enthalpy of adsorption (KJ/mol), **K and n** = Freundlich isotherm coefficient, **K** = equilibrium constant (L/mol), **m** = the amount of adsorbent (g), ∆**S°** = entropy of adsorption (KJ/mol), **X** = the amount of adsorbate ions (mg), and **Xm** = the adsorption maxima (mol/g).

EXPERIMENTAL

Apparatus and chemicals

Shimadzu atomic adsorption spectrophotometer (AA 2380) with

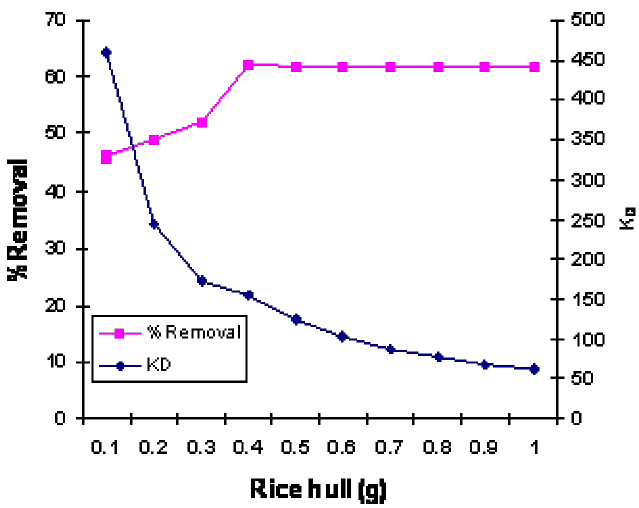

Figure 1. Effect of activated pure rice hulls concentration (amount) on adsorption of Cr metal at 300K (500 ppm, contact time 60 min).

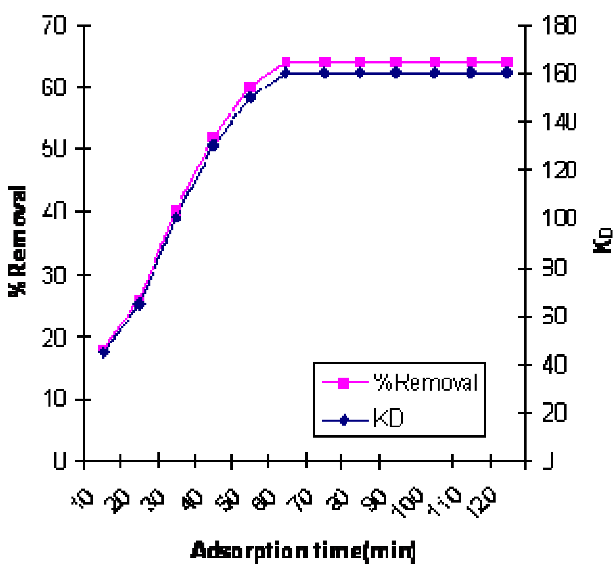

Figure 2. Effect of contact time on adsorption of Cr metal at 300 K (500 ppm, dosage 0.5 g/50 ml) using activated pure rice hulls.

automatic background correction capability and flame photometer (400) was used for the determination of Cr metal. An air-acetylene flame was used for Cr ion. The pH measurement was made with digital pH meter (METTLER TOLEDO.MP220 PH meter). Hot plate (78 Hw-1) serial constant temperature magnetic was also used. PUG Mills was used for shaking at constant speed of 120 revolutions per minute at different temperatures for activation of adsorbent electric oven (W.T.C. binder, 7200, Tuttlinger /Germany-type 'E' 28 No. 89248) with a precision of ± 0.1°C. All the reagent and chemicals used in the present investigation were of spectroscopy grade. Standard stock solutions of mentioned elements were prepared from titrisol concentrates (Merck). Reference solutions were prepared as required by further dilution with distilled water.

Preparation of activated pure rice hulls (cellulosic adsorbent)

The rice hulls obtained from M. Rice factory, Karachi. The fine powered of rice hulls was washed by repeated immersion in distilled water; there was no change in its pH. This was done to remove anion and cation present in the rice hulls lattice. The washed rice hull was dried in an elective oven, at high temperature for several hours and kept in a desicator.

Adsorption experiments

Batch adsorption experiment were carried out in which aliquots of 50 ml of Cr solution of known concentration were pour into beaker glasses (100 ml) containing accurately weighed amounts of the adsorbents. The activated rice hulls weight ranged from 0.01 to 1.0 g per 50 ml of solution. The beaker glasses were shaken at 120 rpm using an electric shaker for a prescribed length of time to attain equilibrium at 293 to 323 K, separately. The adsorbent was then removed by filtration. After filtration through the filter paper the solutions were analyzed for residual metal content by AAS.

Adsorption isotherm equation

To quantify the adsorption capacity of rice hulls for the removal of Cr from industrial wastage the Freundlich equation (Glasstane, 1981) in the form,

$$\log \frac{x}{m} = \text{Log}\, k + \frac{1}{n} \log$$

And the arranged Langmuir equation (Srivastava and Tyagi, 1989), and Dubinin - Redushkevich (D-R) in the from,

$$\frac{C}{X/m} = \frac{1}{k.\, x_m} + \frac{C}{x_m}$$

The linearized D-R equation

$\ln x = \ln Xm - kE^2$

$E = (-2k)^{-1/2}$

were applied where k was the assumed equilibrium constant or binding energy. Langmuir, Fruenhlich and D-R isotherms were obtained from the experiment at 293 – 323 K.

RESULTS AND DISCUSSION

The dependence of adsorption of Cr on activated rice hulls is given in Figure 1. The figure indicates that the adsorption increased with increasing activated pure rice hulls amount up to a certain value and then there was no further increase in adsorption for either metal ions. Therefore, the optimum activated pure rice hulls amount was selected as 0.5 g/50 ml. The effect of the contact time on the adsorption of Cr is shown in Figure 2. The equilibrium was attained after shaking for 60 min. Therefore, in each experiment the shaking period was selected as 60 min.

The effect of Cr metal concentration on its adsorption was studied under the optimized condition of contact time

Table 1. D-R parameters for the removal of Cr metal from standard $Cr(NO_3)_2$ and from leather industrial waste sample (LEL5) using activated pure rice hulls at 293 – 323 K.

Temperature (K)	$Cr(No_3)_2$				(LEL5)			
	K (mol^2Kg^{-2})	x_m ($mol.gm^{-1}$)	E ($KgJ.mol^{-1}$)	R^2	K (mol^2Kg^{-2})	x_m ($mol.gm^{-1}$)	E ($KgJ.mol^{-1}$)	R^2
293	-1.15	3.949	0.659	0.961	-1.076	3.813	0.681	0.98
303	-1.155	4.037	0.657	0.976	-0.982	3.264	0.713	0.98
308	-0.978	3.685	0.714	0.975	-0.835	3.142	0.773	0.973
313	-0.867	3.305	0.759	0.982	-0.756	2.885	0.812	0.978
318	-0.769	2.866	0.806	0.98	-0.69	2.7	0.85	0.98
323	-0.709	2.799	0.839	0.98	-0.503	1.914	0.997	0.891

Table 2. Langmuir parameters for the removal of Cr metal from standard $Cr(NO_3)_2$ and from leather industrial waste sample (LEL5) using activated pure rice hulls at 293 – 323 K.

Temperature (K)	$Cr(N0_3)_2$			LEL5		
	V_m ($mol.L^{-1}$)	K ($mol^{-1}.L$)	R^2	V_m ($mol.L^{-1}$)	K ($mol^{-1}.L$)	R^2
293	1.857	92.84	0.511	1.452	146.4	0.849
303	1.673	112.7	0.702	1.247	211.0	0.932
308	1.509	140.9	0.83	1.197	245.5	0.94
313	1.28	205.5	0.935	1.125	306.3	0.953
318	1.186	255.3	0.953	1.096	350.6	0.957
323	1.116	308.8	0.963	0.953	582.3	0.942

Table 3. Freundlich parameters for the removal of Cr metal from standard $Cr(NO_3)_2$ and from leather industrial waste sample (LEL5) using activated pure rice hulls at 293 – 323 K.

Temperature (K)	$Cr(NO_3)_2$			LEL5		
	N	K(lit/gm)	R^2	n	K (lit/gm)	R^2
293	1.1364	65.62	0.9416	1.223	47.97	0.963
303	1.163	60.17	0.954	1.336	34.3	0.968
308	1.21	51.7	0.961	1.394	30.22	0.967
313	0.001	35.98	0.971	1.477	24.94	0.967
318	1.399	29.78	0.97	1.536	22.17	0.97
323	1.482	24.5	0.97	1.993	10.02	0.893

and dosage of activated pure rice hulls. The concentration of Cr from industrial wastage sample was varied from 25 – 500 mg l^{-1}. In certain practical application, equilibrium between ions per gramme of solid and concentration of metal ion per ml of aqueous solution is most conveniently expressed in terms of the distribution coefficient of the counter ions. The distribution coefficient increases with the dilution of the solution. It is depicted that percentage removal and distribution coefficient (k_D) value are correlated at various concentration and temperature ranging from 2936 to 323 K as shown in Figures 1 and 2. At higher temperature (323K), as the Cr metal concentration increases the percentage removal and K_D value decreases. This indicates that energetically more active site has been occupied earlier and less favorable sites became available with increasing concentration.

The adsorption data obtained with the adsorbent correlates well with the Freundlich's, Langmuir and D-R adsorption isotherm equation. The D-R, Freundlich and Langmuir constants calculated from the adsorption datas are given in Tables 1 - 3. The values of k decreased as temperature increased indicating that adsorption decreased with increasing temperature. The thermodynamic parameters calculated from the adsorption data are shown in Table 4. Standard molar or Gibbs free energy for the process is calculated as:

$$\Delta G^o = \Delta H^o - T\Delta S^o.$$

Table 4. Thermodynamic parameters for the removal of Cr metal from standard $Cr(NO_3)_2$ and from leather industrial waste sample using activated pure ricehulls at 293 – 323 K.

Concentration $(mol.L^{-1}) \times 10^3$	ΔH^0 $(KJ\ mol^{-1})$	ΔS^0 $(KJ.deg^{-1}mol^{-1})$	$\Delta G^0 (KJ\ mol^{-1})$ 293 K	303 K	308 K	313 K	318 K	323 K
$Cr(NO_3)_2$	Ricehull adsorbent							
10.4	-0.794	5.373	-1575	-1629	-1656	-1683	-1710	-1736
8.33	-0.086	6.130	-1797	-1889	-1889	-1920	-1950	-1981
6.25	-1.715	9.100	-2669	-2805	-2805	-2851	-2896	-2942
4.16	-2.274	12.53	-3667	-3864	-3864	-3927	-3990	-4052
2.08	-3.403	15.43	-4527	-4758	-4758	-4835	-4913	-4990
1.04	-6.578	26.93	-7897	-8301	-8301	-8436	-8570	-8570
0.52	-11.13	40.78	-1196	1237	-1257	-1277	-1298	-1318

Concentration $(mol.L^{-1}) \times 10^3$	ΔH^0 $(KJ\ mol^{-1})$	ΔS^0 $(KJ.deg^{-1}mol^{-1})$	$\Delta G^0 (KJ\ mol^{-1})$ 293 K	303 K	308 K	313 K	318 K	323 K
Sample	Ricehull adsorbent							
10.4	-0.872	5.717	-1676	-1733	-1761	-1790	-1819	-1847
8.33	-1.1182	7.031	-2061	-2131	-2166	-2201	-2237	-2272
6.25	-2.330	11.32	-3319	-3433	-3489	-3546	-3602	-3659
4.16	-3.455	16.73	-4907	-5074	-5158	-5241	-5325	-5409
2.08	-3.675	16.70	-4898	-5066	-5149	-5233	-5316	-5400
1.04	-19.18	69.49	-2038	-2107	-2142	-2177	-2211	-2246
0.52	-13.96	51.61	-1513	-1565	-1591	-1617	-1642	-1668

And the standard enthalpy change is ΔH^o and entropy change ΔS^o for Cr metal were calculated from distribution coefficient

$$\ln k_D = \Delta S^o/R - \Delta H^o/RT.$$

The adsorption capacity (Xm) of activated pure rice hulls for the uptakes of Cr metal decrease with increasing temperature from 293 to 323 K indicating that the process is exothermic (Table 4). The negative Gibbs free energy value indicates the feasibility of the process and the spontaneous nature of adsorption. The amount of adsorption decreased with temperature and the negative ΔH° value indicates the exothermic nature of the process. A positive entropy of adsorption also reflects the affinity of adsorbent material for Cr metal under consideration.

Conclusion

Pure rice hulls, which are waste substances, can be used as adsorbent material. This product exhibits very good adsorption for Cr from industrial wastage. Adsorption of Cr ions by activated pure rice hulls was shown to depend significantly on the activated pure rice hulls dosage, contact time and metal ions concentration. The data thus obtained will be of full help in the design and performance of a fixed-bed adsorption.

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