



## PROCESS FOR REMOVAL OF CHROMIUM ION FROM LEATHER INDUSTRIAL WASTES BY ACTIVATED PURE RICE HUSK

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### ABSTRACT

The removal of (Cr) ions from industrial wastage by adsorption on rice husk was investigated based on activated pure rice husk dosage, stay time, metal concentration and solution temperature. The optimum values of activated pure rice husk dosage and stay time were determined to be 0.5gm/50ml solution and 60 mins, respectively, for the adsorption of (Cr) ions. The constant for the Freundlich, D-R and Langmuir isotherms were 50%, calculated at 50°C. The adsorption of (Cr) from industrial wastage was found to be exothermic. Thermodynamic parameters such as free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) of adsorption also calculated and interpreted from the slope and intercept of the plots of  $\ln k_D$  vs  $1/T$ . The  $\Delta G^\circ$  value decreases with rise in temperature and the negative values of  $\Delta H^\circ$  indicate that the adsorption of (Cr) from industrial wastage was an exothermic process while positive values of change in entropy ( $\Delta S^\circ$ ) were also observed.

**Keywords:** Adsorption, (Cr) metal ion, activated pure rice husk, leather industrial waste.

### INTRODUCTION

Rice husk is a waste product from different rice production industries. Rice husk is a waste substance that can be converted into an adsorbent material (Marshall and Johns, 2016; Marshall et al., 2019; Ahmedna et al., 2017) This product exhibits very good adsorption for “(Cr)” ion from industrial waste, and the quest for cheap waste treatment alternative has compelled the researches (Ahmedna et al., 2018; Johns et al., 2018; Marshall et al., 2019, 2016). Rice husk is generated 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 husk.

Moisture content of rice husk is about 10%; the equilibrium moisture content is lower than that of paddy or rough rice. Bulk density of rice husk is 100-150 kg/m<sup>3</sup>. If rice husk is grinded, bulk density increases to 200-250 kg/m<sup>3</sup>. Rice husk have excellent adsorption properties (Prabhu et al., 2011; Sen and De, 2017); the main organic compounds of the dry husk are cellulose and hemicelluloses (50%), protein (20%) lignin (26%) with the remaining (4%) represents oil. (Huang and Ostovic, 2013; Reed and Matsumoto, 2013; Khattak et al., 2019).

A high concentration removal of such metal ion is more effective by ion exchange or adsorption on solid sorbents such as activated pure rice husk (Qadeer et al., 2015). In this study, pure rice husk which is a solid waste matter was used as an adsorbent for the removal of (Cr) metal ion from industrial waste (Khattak et al., 2000; Khattak et al., 2002). The aim was to investigate the optimum condition of metal ion uptake and to calculate the adsorption capacity and some thermodynamic constants at different temperatures.

### Parameters:

**C** = concentration of adsorbate ions at equilibrium,  $\Delta G^\circ$  = Gibbs free energy change of adsorption (Kcal/mol),  $\Delta H^\circ$  = enthalpy change of adsorption (Kcal/mol), **K** and **n** = Freundlich isotherm coefficient, **K** = equilibrium constant (L/mol), **m** = the amount of adsorbent (g),  $\Delta S^\circ$  = entropy change of adsorption (Kcal/mol), **X** = the amount of adsorbate ions (mg), **X<sub>m</sub>** = the adsorption maxima (mol/g), **Q<sub>o</sub>** = constant related to the area occupied by a monolayer of adsorbate (mg/g) and **K<sub>L</sub>** = direct measure of the intensity of the sorption (L/mg).

**EXPERIMENTAL**

**Apparatus and chemicals**

Shimadzu atomic adsorption spectrophotometer (AAS 2380) with 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 (78Hw-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, Tuttlingers/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 husk (cellulosic adsorbent)**

The rice husk was obtained from local rice factory in Challawa industrial area Kano. The fine powdered of rice husk 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 husk lattice. The washed rice husk was dried in an electric oven, at high temperature for several hours and kept in a desiccator.

**Adsorption experiments**

Batch adsorption experiment were carried out in which liquor of 50 ml of (Cr) solution of known concentration were poured into five beakers (100 ml) containing accurately weighed amounts of the adsorbents. The activated rice husk weight

ranged from 0.01-1.0 g / 5 ml of solution. The beakers were shaken at 120 rpm using an electric shaker for a prescribed length of time to attain equilibrium at 30-50°C, 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 husk for the removal of (Cr) from leather industrial waste the Freundlich equation (Glasstane, 1981) in the form,

$$\log \frac{X}{m} = \log K + \frac{1}{n} \log C_e \dots \dots (1)$$

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

$$\frac{C}{X_m} = \frac{1}{Q_0 \cdot K_l} + \frac{C}{Q_0} \dots \dots (2)$$

Where k was the assumed equilibrium constant or binding energy. Langmuir, Fruenhlich and D-R isotherms were obtained from the experiment at 30-50°C.

**RESULTS AND DISCUSSION**

The dependence of adsorption of (Cr) on activated rice husk is given in Figure 1. The figure indicates that the adsorption increased with increasing activated pure rice husk amount up to a certain value and then there was no further increase in adsorption for Cr metal ion.

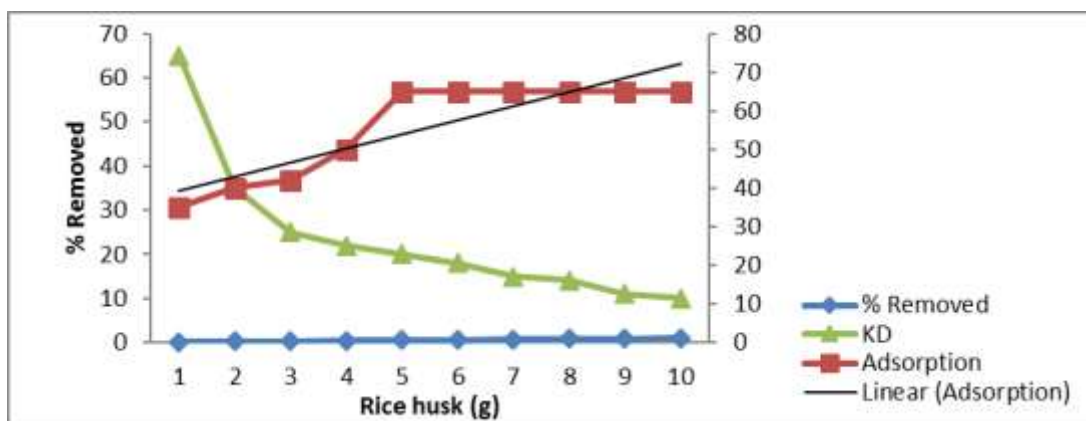


Fig. 1: Effect of activated pure rice husk concentration (amount) on adsorption of (Cr) metal at 37°C (500 ppm, contact time 60 mins).

Therefore, the optimum activated pure rice husk 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 mins. Therefore, in each experiment the shaking period was selected as 60 mins.

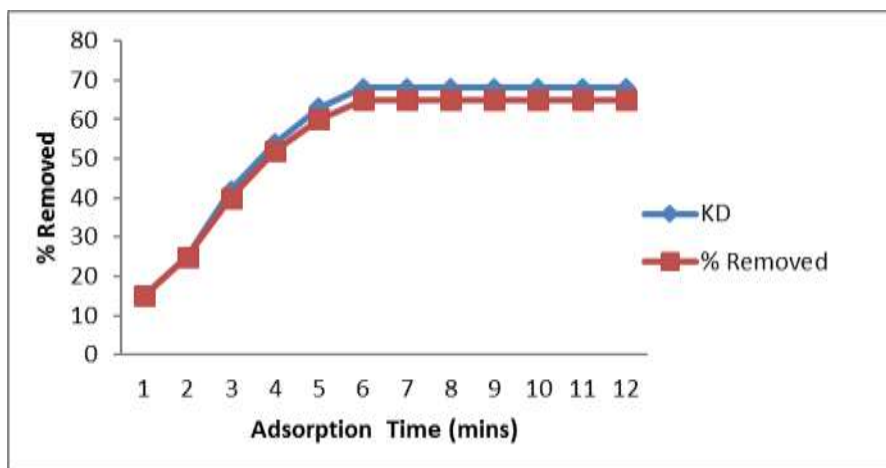


Fig. 2: Effect of contact time on adsorption of (Cr) metal at 37°C (500ppm, dosage 0.5 g/ 50 ml) using activated pure rice husk.

The effect of (Cr) metal ion concentration on its adsorption was studied under the optimized condition of contact time and dosage of activated pure rice husk. The concentration of (Cr) from industrial wastage sample was varied from 25-500 mg/l. In practical application, equilibrium between ions / g 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 30-50°C as shown in Figures 1 and 2. At higher temperature 50°C, as the (Cr) metal ion concentration increases, the percentage removal and  $k_D$  value decreases. This indicates that energetically more active sites have 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 data are given in Tables 1-3. The values of  $k$  decreased as temperature increased indicating that adsorption decreased with increasing temperature.

**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 husk at 30-50°C

Temperature °C	Cr(NO <sub>3</sub> ) <sub>2</sub>				(LEL5)			
	K(Kg <sup>-1</sup> mol <sup>-1</sup> )	Xm (mol.gm <sup>-1</sup> )	E(KgJ.mol <sup>-1</sup> )	R <sup>2</sup>	K(Kg <sup>-1</sup> mol <sup>-1</sup> )	Xm (mol.gm <sup>-1</sup> )	E(KgJ.mol <sup>-1</sup> )	R <sup>2</sup>
30	-1.150	3.949	0.659	0.96	-1.076	3.813	0.681	0.98
35	-1.155	4.037	0.657	0.98	-0.982	3.264	0.713	0.98
40	-0.978	3.685	0.714	0.98	-0.835	3.142	0.773	0.97
45	-0.867	3.305	0.759	0.98	-0.756	2.885	0.812	0.98
50	-0.769	2.866	0.806	0.98	-0.690	2.700	0.85	0.98

**Table 2:** Langmuir parameters for the removal of (Cr) metal ion from standard Cr(NO<sub>3</sub>)<sub>2</sub> and from leather Industrial waste sample (LEL5) using activated pure rice husk at 30-50°C

Temperature °C	Cr(NO <sub>3</sub> ) <sub>2</sub>			(LEL5)		
	Vm(mol / L)	K(mol / L)	R <sup>2</sup>	Vm(mol / L)	K(mol / L)	R <sup>2</sup>
30	1.673	112.7	0.511	1.247	211.0	0.849
35	1.509	140.9	0.702	1.197	245.5	0.932
40	1.280	205.5	0.83	1.125	306.3	0.940
45	1.186	255.3	0.935	1.096	350.6	0.953
50	1.116	308.8	0.953	0.953	582.3	0.957

**Table 3:** Freundlich parameters for the removal of (Cr) metal from standard Cr(NO<sub>3</sub>)<sub>2</sub> and from Leather industrial waste sample (LEL5) using activated pure husk at 30-50°C

Temperature °C	N	Cr(NO <sub>3</sub> ) <sub>2</sub>		n	(LEL5)	
		K(lit/gm)	R <sup>2</sup>		K (lit/gm)	R <sup>2</sup>
30	1.1364	65.62	0.942	1.223	47.97	0.963
35	1.163	60.17	0.954	1.336	34.30	0.968
40	1.210	51.7	0.961	1.394	30.22	0.967
45	0.001	35.98	0.971	1.477	24.94	0.967
50	1.399	29.78	0.97	1.536	22.17	0.97

The thermodynamic parameters calculated from the adsorption data are shown in Table 4. Standard molar or Gibbs free energy change for the process is calculated as:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \dots \dots (5)$$

And the standard enthalpy change is ΔH° and entropy change ΔS° for (Cr) metal ion were calculated from distribution coefficient.

$$\ln kD = \Delta S^\circ R - \Delta H^\circ / RT \dots (6)$$

The adsorption capacity (Xm) of activated pure rice husk for the uptake of (Cr) metal decrease with increasing temperature from 30 to 50°C indicating that, the process is exothermic (Table 4).

**Table 4:** Thermodynamic parameters for the removal of Cr metal from standard Cr(NO<sub>3</sub>)<sub>2</sub> and from leather industrial waste sample using activated pure rice husk at 30-50°C

Concentration Cr(NO <sub>3</sub> ) <sub>2</sub> (mol.L <sup>-1</sup> )x10 <sup>3</sup>	ΔH°( KJ.mol <sup>-1</sup> )	ΔS°(KJ.mol <sup>-1</sup> )	ΔG°(KJ.mol <sup>-1</sup> )				
			30°C	35°C	40°C	45°C	50°C
10.40	-0.794	5.373	-1575	-1629	-1656	-1683	-1710
8.33	-0.086	6.130	-1797	-1889	-1889	-1920	-1950
6.25	-1.715	9.100	-2669	-2805	-2805	-2851	-2896
4.16	-2.274	12.53	-3667	-3864	-3864	-3927	-3990
2.08	-3.403	15.43	-4527	-4758	-4758	-4835	-4913
1.04	-6.578	26.93	-7897	-8301	-8301	-8436	-8570

**Table 5:** Thermodynamic parameters for the removal of Cr metal from standard (LEL<sub>5</sub>) and from leather industrial waste sample using activated pure rice husk at 30-50°C

Concentration (LEL <sub>5</sub> ) (mol.L <sup>-1</sup> )x10 <sup>3</sup>	$\Delta H^\circ$ (KJ.mol <sup>-1</sup> )	$\Delta S^\circ$ (KJ.mol <sup>-1</sup> )	$\Delta G^\circ$ (KJ.mol <sup>-1</sup> )				
			20°C	35°C	40°C	45°C	50°C
10.40	-0.872	5.717	-1676	-1733	-1761	-1790	-1819
8.33	-1.1182	7.031	-2061	-2131	-2166	-2201	-2237
6.25	-2.330	11.32	-3319	-3433	-3489	-3546	-3602
4.16	-3.455	16.73	-4907	-5074	-5158	-5241	-5325
2.08	-3.675	16.70	-4898	-5066	-5149	-5233	-5316
1.04	-19.18	69.49	-2038	-2107	-2142	-2177	-2211

The negative Gibbs free energy change value indicates the feasibility of the process and the spontaneous nature of adsorption. The amount of adsorption decreased with temperature and the negative  $\Delta H^\circ$  value indicates the exothermic nature of the process. Positive entropy change of adsorption also reflects the affinity of adsorbent material for (Cr) metal under consideration.

## CONCLUSION

Pure rice husk, which are waste substances, can be used as adsorbent material. This product exhibits very good adsorption for (Cr) from industrial waste. Adsorption of (Cr) ions by activated pure rice husk was shown to depend significantly on the activated pure rice husk dosage, contact time and metal ions concentration at 30-50°C. The data thus obtained will be of assistance in the design and performance of a fixed-bed adsorption.

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