Adsorptive Removal of Cr(VI) from Aqueous Solution Using Abundantly Available Rice Waste - Kinetic, Equilibrium and Thermodynamic Studies

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Abstract— *Hexavalent chromium is a major water pollutant from industrial effluent whose concentration is to be reduced within permissible limits. Rice waste, a cheaply available adsorbent used for the removal of Cr(VI) from aqueous solution. Present study reports a systematic evaluation of rice straw and rice bran as low cost silica based adsorbent for the removal of Cr(VI). Studies were carried out at 303 K to find out the effect of initial pH, initial metal ion concentration, adsorbent dosage and equilibrium contact time for the adsorption process. The optimum pH for the adsorption was 2 for both rice straw and rice bran. Maximum adsorption capacities assuming monolayer adsorption were 12.172 and 12.341 mg/g for rice straw and rice bran respectively. Rate kinetics for the adsorption was studied to understand the mechanistic steps for the adsorption process. Kinetic data was better described by pseudo second order model. Adsorption isotherm of Cr(VI) was better described by Freuindlich adsorption isotherm model. The thermodynamic studies indicated that the process of adsorption was spontaneous and endothermic in nature.*

Keywords— **Rice straw, Rice bran, Freundlich, Pseudo second order, Gibbs free energy.**

1. INTRODUCTION

Cr(VI) is considered to be non biodegradable and have great environmental, public health and economic impacts. Cr(VI) is present in the effluent produced during the electroplating, leather tanning, cement, mining, dyeing, fertilizer and photography industries etc. Cr(VI) has been reported to be toxic to animals and humans. It is also known to be carcinogenic [1].

The concentration of Cr(VI) in industrial waste water varies in the ranges from 0.5 to 270 mg/L [2]. The maximum permissible limit of Cr(VI) for discharge into inland surface water is 0.1mg/L and in potable water is 0.05 mg/L [3], [4]. In order to comply with this limit, it is essential that industries treat their effluents to reduce the Cr(VI) concentration in water and waste water to acceptable levels before its transport and cycling into the natural environment. Several methods are utilized to remove Cr(VI) from industrial waste water. The advantage and disadvantage of these methods are shown in Table 1[5]-[12].

Adsorption is by far most versatile and effective method for such removal, especially, if combined with appropriate regeneration steps. In this study rice straw and rice bran, agricultural wastes were used to remove Cr(VI) from aqueous solution. Factors affecting the adsorption characteristics such as initial pH, contact time, adsorbent dosage and initial Cr(VI) ion concentration were studied. Rate kinetics and isotherm models were also investigated to know the adsorption behavior of the adsorbents considered for study.

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2. EXPERIMENTAL

Adsorbents used and preparation

Rice straw and Rice bran - The adsorbents were collected from Shyampur, Howrah, West Bengal, India. All the adsorbents were boiled with distilled water for 7 hr to remove colored materials from it and filtered. Then the adsorbents were dried at 105^0 for 6 hr to remove the adherent moisture, sieved to obtain particle size of 250-350µm and them kept in desicators.

Adsorbent and reagent

All the chemicals used were of analytical grade and purchased from E. Merck Limited, Mumbai, India. The stock solution containing 1000 mg/L of Cr(VI) was prepared by dissolving 3.73 g of AR grade K_2CrO_4 , $2H_2O$ in 1000 ml of de-ionized, double distilled water. Required initial concentration of Cr(VI) standards were prepared by appropriate dilution of the above stock Cr(VI) standard solution.

Batch adsorption studies

The quantitative amount of adsorbents were taken in a 250 ml stopper conical flask containing 100 ml of desired concentration of the test solution at the desired pH value, contact time and adsorbent dosage level. The pH of the solution was measured with a EUTECH make digital microprocessor based pH meter previously calibrated with standard buffer solutions. The contents in the flask were shaken for the desired contact time in an electrically thermostated reciprocating shaker @ 110-125 strokes/minute at 30^0C. The contents of the flask were filtered through filter paper and the filtrate was analyzed for remaining Cr(VI) ion concentration by UV visible spectrophotometer (Model No. U-4100 spectrophoto-meter, Hitachi, Japan) [13].

3. RESULTS AND DISCUSSION

Effect of pH on Cr(VI) adsorption

Figure1 shows the percentage removal of Cr(VI) as a function of pH. It is clearly evident that the adsorption characteristics of the adsorbents are highly pH dependent. The percentage removal reached a maximum value at an initial pH of the solution at 2.

Effect of contact time

The influence of contact time on the batch adsorption of Cr(VI) ion at 30^0C, optimum pH and adsorbent dosage is shown in Figure 2. It is obvious that increase in contact time, the percent removal of Cr(VI) enhanced significantly. This figure is indicated that the equilibrium was reached at 3 hr. for rice straw and 5 hr. for rice bran.

Effect of adsorbent dosage

Figure 3 shows the variation of adsorbent dosage on the percentage removal of Cr(VI) from aqueous solution using initial metal ion concentration at 25 mg/L. The efficiency of Cr(VI) removal was found to increase rapidly at adsorbent dosage from 1g/L to 7.5 g/L. Further increasing the adsorbent dosage above 10 g/L, the removal efficiency almost remained constant. It was evident that for all the aforesaid adsorbents maximum removal efficiency was achieved at an adsorbent dosage level of 10 g/L which may be considered as an optimum adsorbent dosage level.

Effect of initial Cr(VI) ion concentration

The effect of initial metal ion concentration on the removal of Cr(VI) is shown in Figure 4. Percent removal of Cr(VI) ion decreases with increasing in initial Cr(VI) ion concentration. At the lower concentration, all the Cr(VI) ions in the solution would react with the binding sites and thus facilitated almost complete adsorption.

Adsorption kinetics study

The rate kinetics of Cr(VI) adsorption were analyzed using different kinetic model as follows

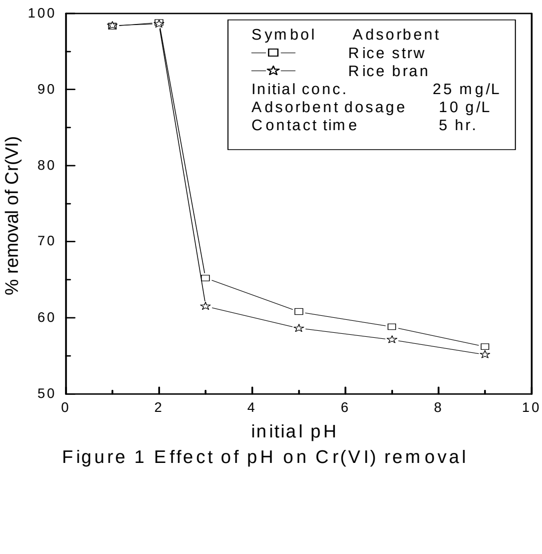

Figure 1 Effect of pH on Cr(VI) removal

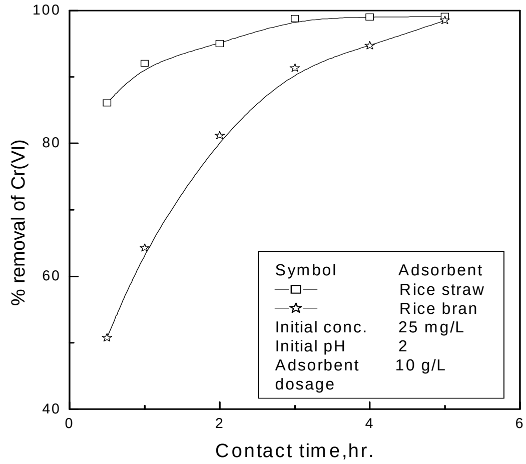

Figure 2 Effect of contact time on Cr(VI) removal

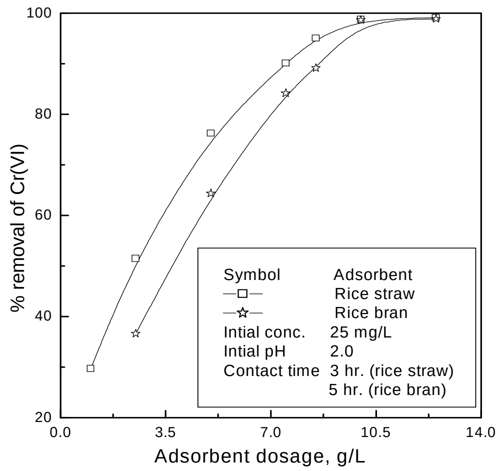

Figure 3 Effect of adsorbent dosage on Cr(VI) removal

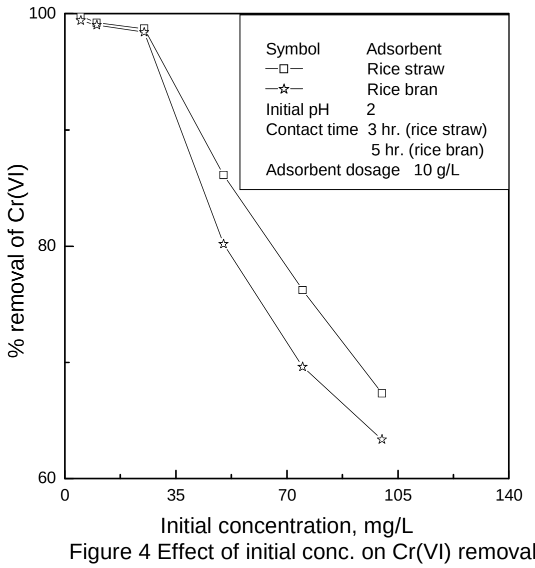

Figure 4 Effect of initial conc. on Cr(VI) removal

Table 1: Some Conventional method of removal of heavy metal (Advantage/ Disadvantage)

Removal process	Advantage	Disadvantage
Coagulation-precipitation-filtration	Comparatively cheap	i) Process is complicated ii) Disposal of precipitated heavy metal hydroxides poses a major problem iii) Insufficient to meet requirement when present in low concentration
Resin ion exchange	i) Removal of metal at low concentration ii) Simplifies the equipment and operation	i) Low selectivity of metal ion except using chelating resins ii) Resins are expensive
Membrane separation	i)Effective simple technique ii) Greater selectivity	Very much expensive
Cementation	Greater selectivity	i) Production of toxic sludge or waste product ii) High operational cost
Sedimentation	i) Simple technique ii) Greater selectivity	i) Incomplete removal ii) Production of toxic sludge or waste product
Adsorption using activated carbon	i) High adsorption capacity ii) Greater selectivity iii) Fairly uniform	i) High capital investment ii) High regeneration cost
Adsorption using natural adsorbents	i) High adsorption capacity ii) Low cost iii) Local availability	

Table 2 Rate Kinetics for adsorption of Cr(VI) ion by different adsorbents

Adsorbents	Lagergren 1st Order model		Pseudo 2nd Order model	
	K_{ad} (min^{-1})	r^2	K_2 [(mg/g)min]	r^2
Rice straw	0.027	0.975	0.072	0.999
Rice bran	0.019	0.957	0.009	0.998

Pseudo first order Lagergren model

The pseudo first order kinetic model was proposed by Lagergren [14]. The integral form of the model generally expressed as follows

$$\log(q_e - q) = \log q_e - \frac{K_{ad} t}{2.303} \qquad (1)$$

Pseudo second order model

The linearized form of pseudo second order kinetic equation [15] is expressed as

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \qquad (2)$$

Lagergren and Pseudo second order models are presented in Figures 5 and 6 respectively. The values of rate constants and correlation coefficients for each model are shown in Table 2. The high correlation coefficients (r^2) values were indicated that the adsorption of Cr(VI) onto rice straw and rice bran follow pseudo second-order model than that of pseudo first-order model.

Isotherm model

For the analysis of equilibrium data for Cr(VI) adsorption onto rice straw and rice bran, the following isotherm models are used

Langmuir isotherm model

The data obtained from adsorption study was fitted to the Langmuir adsorption isotherm as [16]

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \qquad (3)$$

The values of Langmuir constants and correlation coefficients (r^2) obtained from Figure 7 are shown in Table 3. Linearity of the plots indicated the applicability of the adsorption isotherm. The maximum adsorption capacities for the adsorption onto rice straw and rice bran were 12.172 mg/g and 12.341mg/g respectively.

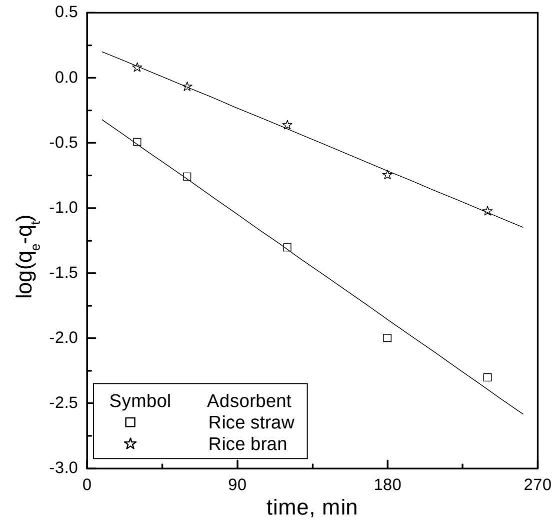

Figure 5 Lagergren plot for adsorption of Cr(VI)

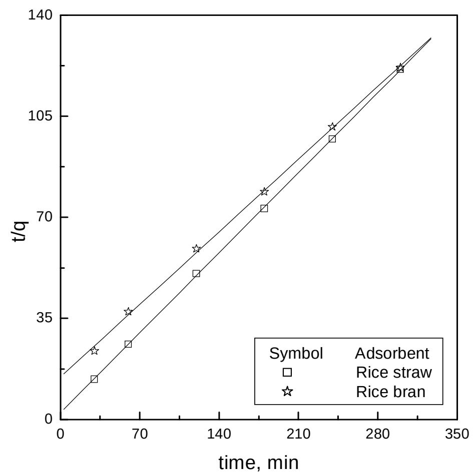

Figure 6 Pseudo second order plot for adsorption of Cr(VI)

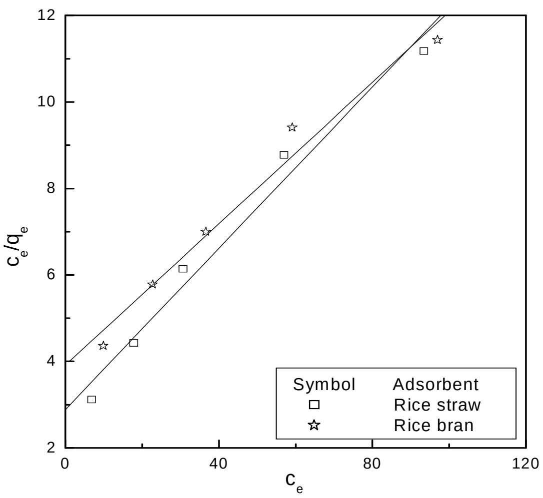

Figure 7 Langmuir plot for adsoption of Cr(VI)

Freundlich isotherm model

The adsorption data obtained was also fitted to the Freundlich adsorption isotherm as [17]

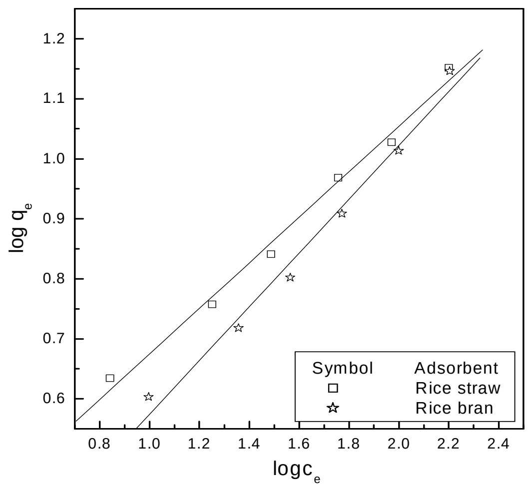

Figure 8 Freuindlich plot for adsorption of Cr(VI)

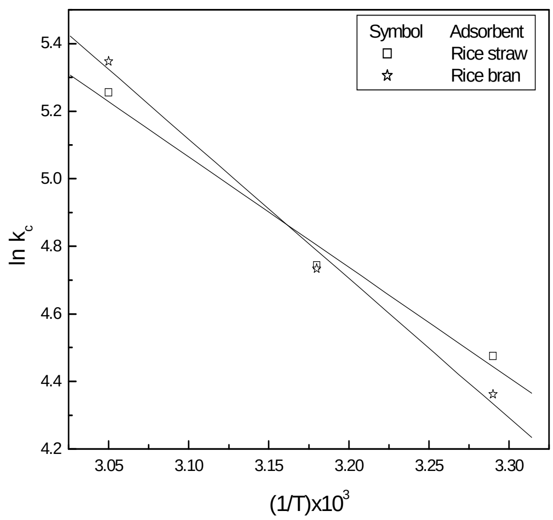

Figure 9 Determination of thermodynamic parameter

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad (4)$$

The values for Freundlich constants and correlation coefficients (r^2) obtained from Figure 8 are shown in Table 3. From the value of correlation coefficients (r^2), it can be concluded that the adsorption of Cr(VI) onto rice straw and rice bran follow Freundlich adsorption isotherm model.

Thermodynamic parameters for adsorption

The effect of temperature was investigated at 30, 40 and 55^0C at optimum pH value of 2 and adsorbent dosage level 10 g/L.

The thermodynamic equilibrium constant (K_c^0) for each adsorbent was calculated by determining the apparent equilibrium constant, $K_c^{'}$ at different initial concentration of Cr(VI) and extrapolating to zero.

Table 3 Langmuir and Freundlich adsorption isotherm constants for Cr(VI) on different adsorbents

Adsorbents	Langmuir Constants			Freundlich Constants		
	q_{max} (mg g^{-1})	B (L mg^{-1})	r^2	K_f (mg/g)/$(mg/L)^{1/n}$	n	r^2
Rice straw	12.172	0.183	0.980	2.713	3.018	0.993
Rice bran	12.341	0.064	0.947	2.136	3.041	0.954

Table 4 Thermodynamic parameters for the sorption of Cr(VI) onto adsorbents

Adsorbent	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol)	T (K)	$-\Delta G^0$ (kJ/mol)
Rice straw	26.124	0.104	303	5.538
			313	6.407
			328	8.131
Rice bran	38.547	0.144	303	5.248
			313	6.385
			328	8.828

Table 5 Comparison of adsorption capacities of the adsorbents

Serial no.	Adsorbents	Adsorption capacities for Cr(VI) (mg/g)	Reference
1	Leaf mould	43.1	[18]
2	Beech sawdust	16.1	[18]
3	Sugarcane bagasse	13.4	[18]
4	Eucalyptus bark	45.00	[19]
5	Rice straw	3.15	[20]
6	Sawdust	20.70	[21]
7	Neem bark	19.60	[21]
8	Rice husk	8.5	[22]
9	Rice straw	12.172	[Present study]
10	Rice bran	12.341	[Present study]

$$K_c^{'} = \frac{C_a}{C_e} \tag{5}$$

The Gibbs free energy, ΔG^0, enthalpy, ΔH^0, and entropy, ΔS^0 were computed using following equation

$$\Delta G^0 = -RT \ln k_c \tag{6}$$

$$\ln k_c = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{7}$$

The value of standard free energy, ΔG^0, was calculated using Equation (6). The value of slope and intercept of the plot $\ln k_c$ vs 1/T (Figure 9) gave standard enthalpy, ΔH^0, and standard entropy, ΔS^0, respectively (Table 4). Negative value of, ΔG^0, at all temperatures indicated the spontaneous nature of the adsorption. Positive values of enthalpy change suggested the endothermic nature of the adsorption process. Positive values of entropy change also indicated the increased randomness at solid/solution interface during the adsorption process.

Comparison of adsorption capacity with different adsorbents reported in literature

The adsorption capacity of Cr(VI) onto rice straw, rice bran were compared with other adsorbents reported in literature and is shown in Table 5. The adsorption capacity varies and it depends on the characteristics of the individual adsorbent, the extent of surface modification and initial concentration of the adsorbate.

4. CONCLUSIONS

The optimum pH for the removal of Cr(VI) was found to be 2. Increase in the concentration of adsorbent dosage and contact time, the percentage removal of Cr(VI) were increases whereas increase in initial Cr(VI) concentration, percentage removal decrease. The kinetics of the Cr(VI) adsorption on different adsorbents was found to follow pseudo second order rate mechanism. Adsorption isotherm of Cr(VI) was better described by Freuindlich adsorption isotherm model. The negative values of Gibbs free energy for the adsorption process reveal that the process is spontaneous. The standard enthalpy change for the adsorption indicated that the process is endothermic. Rice waste can be used as an effective natural adsorbent for the economic treatment of waste water containing Cr(VI).

NOMENCLATURE

b Langmuir constant(L/ mg)

C_a concentration of Cr(VI) after certain period of time (mg/L)

C_e concentration of Cr(VI) in solution at equilibrium (mg/L)

ΔG^o Gibbs free energy (kJ/mol)

ΔH^o enthalpy of adsorption (kJ/mol)

K_{ad} Lagergren rate constant (min^{-1})

$K_c^{'}$ apparent equilibrium constant

K_f measure of adsorption capacity(mg/g)

K_c^0 thermodynamic equilibrium constant

K_2 pseudo second order rate constant [(mg/g)min]

n Freundlich constants, intensity of adsorption

q amount adsorb per gm of the adsorbent (mg/g)

q_e amount adsorb per gm of the adsorbent at equilibrium (mg/g)

q_{max} maximum adsorption capacity(mg/g)

r^2 Correlation coefficient

R universal gas constant (kJ/mol/K)

ΔS^o entropy of the adsorption (kJ/mol)

t time (min)

T absolute temperature (K)

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