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Adsorption Dynamics: Comparison of Adsorption Potentials of Fibrous Keratinous Materials, *viz.*, Human Black and White Hairs

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Industries, such as tanneries, textile mills and chromium plating industries discharge effluents containing chromium and they generate serious disorders and diseases. Several methods of removal, such as precipitation, reverse osmosis and ion-exchange were known, but they involve high capital investments. Hence, adsorption method was chosen using human black and white hairs as adsorbents by the authors. Batch-type experiments were conducted. Contact time for attaining equilibrium and pH suitable for study were found to be 4 h and 1.5 respectively. The equilibrium data are analysed in the light of Langmuir and Freundlich isotherm models and a comparative study is made with a view to exploring the adsorption potentials of these two keratinous adsorbents.

INTRODUCTION

Chromium is essential for plant and animal metabolism, but when accumulated at high levels, it generates serious disorders and diseases[1,2]. The maximum tolerance[3] for total chromium for public water supply and bathing ghats has been fixed at 0.05 mg dm^{-3} as per Indian Standards IS-2296–1974.

Some of the major industries which discharge the effluents containing chromium(VI) species are tanneries, chromium plating industries, textile mills and industries manufacturing photographic dyes, ink, pigments and chemicals. Effluents from metallurgical and metal finishing industries also contain chromium in high concentrations.

There are two predominant forms of chromium, *viz.*, trivalent and hexavalent and the latter is more hazardous to biological activities. Since chromium(VI) is lethal to both aquatic and animal life, its removal from waste water is considered very essential[4]. The conventional methods, often followed to remove metal ions from waste water, include hydroxide precipitation, sulphide precipitation, reaction with silica, evaporation, reverse-osmosis, solvent extraction and ion-exchange. Since these methods involve high capital investments and regeneration costs, researches are seriously directed towards finding out various low cost adsorbents.

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Adsorption technique was shown to be highly effective and very cheap. The removal of chromium by physico-chemical techniques has been reviewed[5]. Coupal and Jean[6] have used peat moss as the adsorbent. Grover and Narayans-wamy[7] have reported the use of fly ash for the removal of hexavalent chromium. Pandey *et al.*[8] have used clay ash-china clay for the removal of chromium(VI) from its aqueous solutions. The chemically treated human hair has been used by Tan *et al.*[9] for the uptake of heavy metal ions. Srinivasan *et al.*[10] have made a detailed study on chromium removal by rice husk carbon. Use of bituminous coal for the removal of chromium has also been reported[11]. Deepak and Gupta[12] have reported the method of removal of chromium(VI) from waste water. Lignite coal[13] and rice hush ash[14] have also been reported as adsorbents for the removal of chromium. Singh and Lal[15] have made a study on removal of chromium(VI) from aqueous solutions using waste tea leaves carbon.

EXPERIMENTAL

In the present investigation, two kinds of hair, *viz.*, human black and white hairs, were collected from local barber shops and ladies' beauty parlours. After washing well with a detergent, it was rinsed thoroughly with deionised water and dried in an air oven at 100°C. Standard potassium dichromate solutions containing different initial concentrations of chromium(VI) were prepared. The concentration of chromium(VI) in a given solution was estimated potentiometrically by titrating with potassium permanganate solution after adding excess ferrous sulphate solution of known concentration. All chemicals used in the present study were of analytical reagent grade.

Batch-type experiments were conducted[16] to construct adsorption isotherm. A known weight of the adsorbent was added to a well stoppered bottle and a known volume of potassium dichromate solution of known concentration was pipetted out. The pH of the solution was measured using a digital LI-120 model pH meter and was kept in the temperature controlled mechanical shaker. Preliminary experiments indicated that the contact time to reach equilibrium is 4 h. At the end of the prescribed length of time, the bottle was removed and it was then kept in a water bath at room temperature for 30 min. After filtration, concentration of chromium(VI) in the filtrate was estimated. Experiments were repeated in order to examine the applicability of Langmuir and Freundlich models. The pH dependence on adsorption potential was also examined with a view to fixing the pH for comparative study of adsorption potentials of these two adsorbents.

RESULTS AND DISCUSSION

Initial studies on adsorption of chromium using hair as the adsorbent suggested that the system needs 4 h of contact time for attaining equilibrium and the percentage of adsorption is high in the pH range 1.2 to 1.7. It has also been observed that the equilibrium time remained almost same for varying concentrations of chromium(VI).

The tables (Table 1 and 2) present the effect of initial concentration of chromium(VI) on the percentage of adsorption with black and white hairs respectively. The figures (Fig. 1 and 2) represent the relation between the initial and equilibrium concentrations of chromium(VI) in waste water with black and white hairs respectively. Analysis of these tables and figures indicates that removal of chromium(VI) decreases with the increase of initial concentration.

TABLE-1
EFFECT OF INITIAL CONCENTRATION OF THE PERCENTAGE OF ADSORPTION OF CHROMIUM

Adsorbent = Black hair pH = 1.5 Mean $W_{adsorbent}$, g = 0.5025
Temp., °C = 29.5 t_{shaken}, h = 4.0

S. No.	$[Cr(VI)]_{ini}$, C_0, mg dm^{-3}	$[Cr(VI)]_{eq}$, C_{eq}, mg dm^{-3}	Removal of chromium x, mg dm^{-3}	Removal of chromium, %
1	202	128	74	36.63
2	293	197	96	32.77
3	383	293	90	23.50
4	490	383	107	21.84

TABLE-2
EFFECT OF INITIAL CONCENTRATION ON THE PERCENTAGE OF ADSORPTION OF CHROMIUM

Adsorbent = White hair pH = 1.5 Mean $W_{adsorbent}$, g = 0.5025
Temp., °C = 29.5 t_{shaken}, h = 4.0

S. No.	$[Cr(VI)]_{ini}$, C_0, mg dm^{-3}	$[Cr(VI)]_{eq}$, C_{eq}, mg dm^{-3}	Removal of chromium x, mg dm^{-3}	Removal of chromium, %
1	199	129	70	35.18
2	306	210	96	31.37
3	392	296	96	24.49
4	489	398	91	18.61

The equilibrium data for the removal of chromium are presented in the tables (Table 3 and 4) and they are analysed in the light of Langmuir isotherm model.

$$\frac{1}{q_e} = \frac{1}{\theta_0 b} \cdot \frac{1}{C_{eq}} + \frac{1}{\theta_0} \tag{1}$$

where,

q_e = amount of metal ion adsorbed per unit weight of the adsorbent, mg g^{-1},
x = amout of metal ion adsorbed, mg,
m = weight of the adsorbent, g
C_{eq} = equilibrium concentration of the metal ion, mg dm^{-3}
θ_0 = Langmuir constant, mg g^{-1}, related to the capacity of adsorption, and
b = Langmuir constant dm^3 mg^{-1} related to the energy of adsorption.

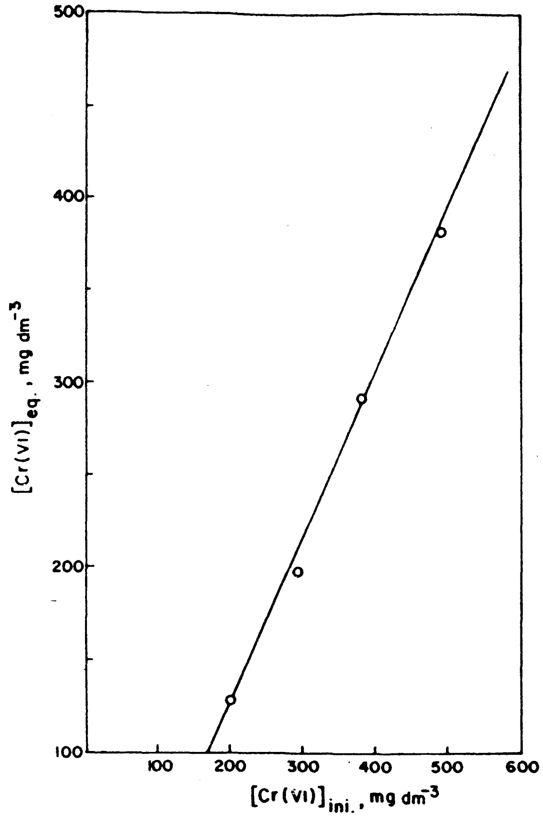

Fig. 1. Effect of initial concentration of chromium(VI) on $C_{eq}X$ adsorbent: Black hair

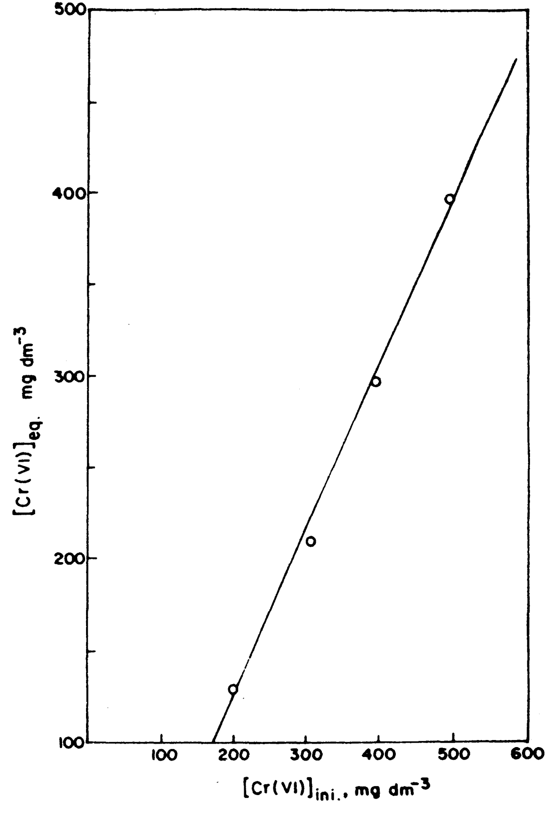

Fig. 2. Effect of initial concentration of chromium(VI) on $C_{eq}X$ adsorbent: White hair

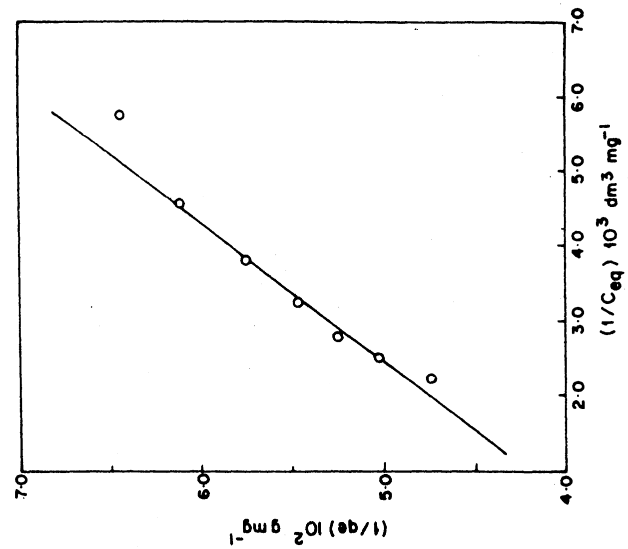

Fig. 4. Langmuir isotherm model for the removal of chromium(VI) adsorbent: White hair

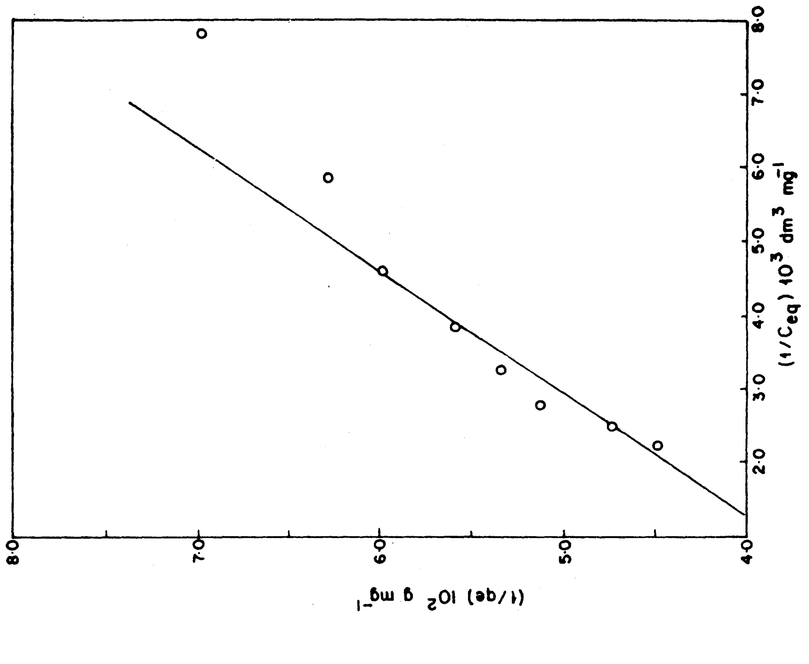

Fig. 3. Langmuir isotherm model for the removal of chromium(VI) adsorbent: Black hair

TABLE-3
LANGMUIR ISOTHERM MODEL FOR THE REMOVAL OF CHROMIUM

Adsorbent = Black hair pH = 1.5 Mean $W_{adsorbent}$, g = 0.5025
Temp., °C = 29.5 t_{shaken}, h = 4.0

S. No.	$[Cr(VI)]_{ini}$, C_0, mg dm^{-3}	$[Cr(VI)]_{eq}$, C_{eq}, mg dm^{-3}	Removal of chromium x, mg dm^{-3}	$\left(\frac{1}{q_e}\right)10^2$, g mg^{-1}	$\left(\frac{1}{C_{eq}}\right)10^3$, dm^3 mg^{-1}
1	300	216	84	5.98	4.63
2	350	260	90	5.58	3.85
3	400	306	94	5.35	3.27
4	450	352	98	5.13	2.84
5	500	394	106	4.74	2.54
6	550	438	112	4.49	2.28

TABLE-4
LANGMUIR ISOTHERM MODEL FOR THE REMOVAL OF CHROMIUM

Adsorbent = White hair pH = 1.5 Mean $W_{adsorbent}$, g = 0.5025
Temp., °C = 29.5 t_{shaken}, h = 4.0

S. No.	$[Cr(VI)]_{ini}$, C_0, mg dm^{-3}	$[Cr(VI)]_{eq}$, C_{eq}, mg dm^{-3}	Removal of chromium x, mg dm^{-3}	$\left(\frac{1}{q_e}\right)10^2$, g mg^{-1}	$\left(\frac{1}{C_{eq}}\right)10^3$, dm^3 mg^{-1}
1	300	218	82	6.13	4.59
2	350	262	88	5.71	3.82
3	400	308	92	5.47	3.25
4	450	354	96	5.24	2.82
5	500	400	100	5.03	2.50
6	550	444	106	4.75	2.25

The plots of $(1/q_e)$ against $(1/C_{eq})$ were drawn for the both the systems. They are shown in figures (Fig. 3 and 4) and these figures represent black and white hairs as adsorbents respectivley. The observed linearity suggests the applicability of this isotherm model for both the systems, studied presently. The adsorption capacity, θ_0 in mg g^{-1} and the adsorption energy, $b \times 10^3$, dm^3 mg^{-1} for white hair are found to be 27.75 and 6.47 respectively and the respective values for black hair are 30.78 and 5.35 (Table-5).

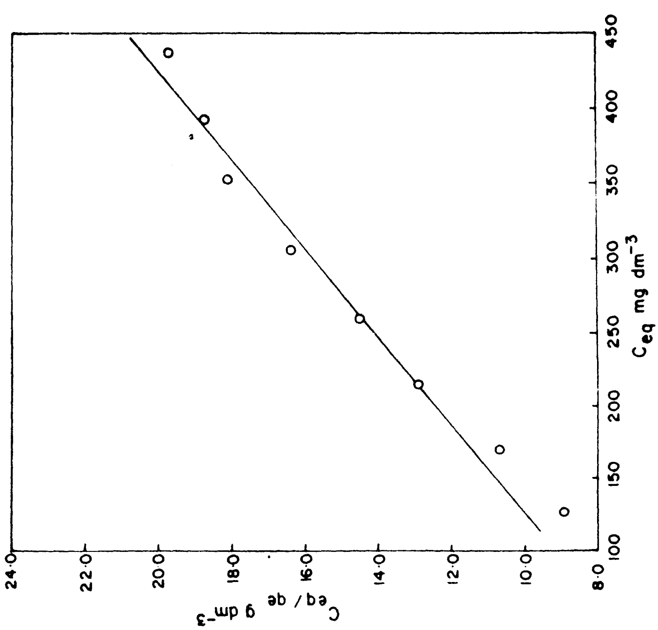

Fig. 5. Rearranged langmuir model for the removal of chromium adsorbent: Black hair

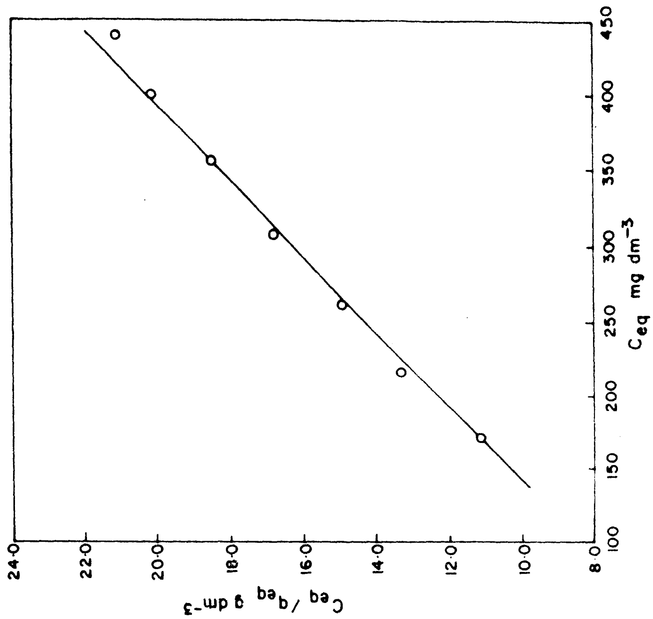

Fig. 6. Rearranged langmuir model for the removal of chromium adsorbent: White hair

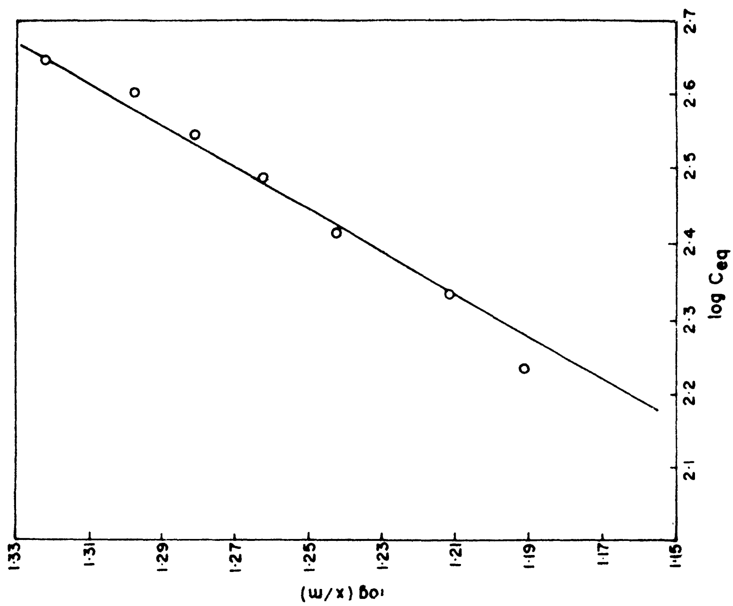

Fig. 8. Freundlich model for the removal of chromium(VI) adsorbent: White hair

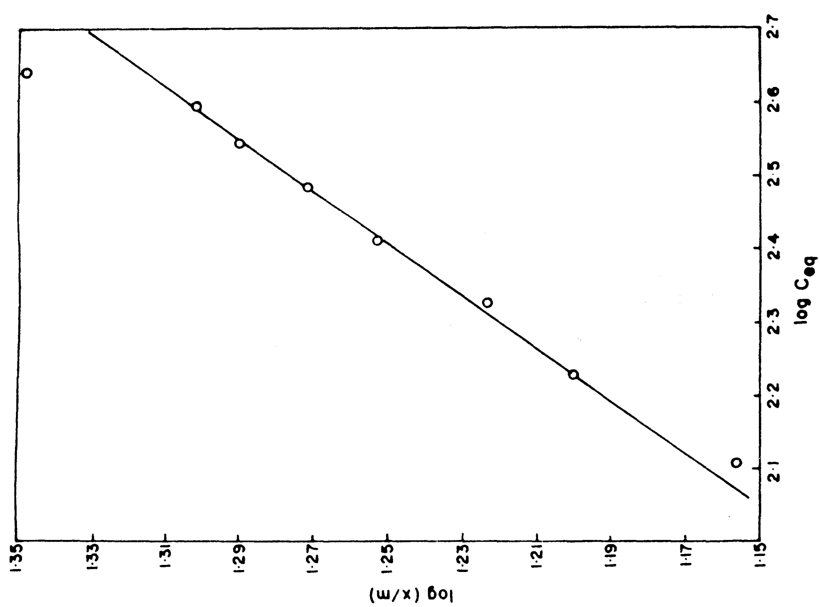

Fig. 7. Freundlich model for the removal of chromium(VI) adsorbent: Black hair

TABLE-5
LANGMUIR AND FREUNDLICH ISOTHERM PARAMETERS

pH = 1.5 t_{shaken}, h = 4.0 Temp., °C = 29.5

Absorbent	Langmuir Isotherm		Rearranged Langmuir Isotherm		Freundlich Parameters	
	θ_0, mg g^{-1}	$b \times 10^3$ $dm^3\ mg^{-1}$	θ_0, mg g^{-1}	$b \times 10^3$ $dm^3\ mg^{-1}$	$\frac{1}{n}$	k
Black hair	30.78	5.35	29.76	5.76	0.321	3.02
White hair	27.75	6.47	25.51	8.49	0.344	2.56

Rearranged Langmuir isotherm[17] model (Equation 2) was also applied to these systems.

$$\frac{C_{eq}}{q_e} = \frac{C_{eq}}{\theta_0} + \frac{1}{\theta_0 b} \tag{2}$$

The linear plots of (C_{eq}/q_e) against C_{eq} for black hair (Fig. 5) and white hair (Fig. 6) confirm the authors' previous inference of the applicability of Langmuir model to these systems. The θ_0 and b values were calculated and are tabulated (Table 5).

The data in the tables (Table 1 and 2) were also analysed in the light of Freundlich isotherm model (Equation 3).

$$\log (x/m) = \log k + 1/n \log C_{eq} \tag{3}$$

where k is related to adsorption capacity and (1/n) to adsorption intensity.

The plots of log (x/m) against log C_{eq} were drawn and are shown in figures (Fig. 7 and 8) for black and white hairs respectively. The linearity suggests that the isotherms are of the empirical Freundlich type. The calculated Freundlich parameters are listed in the Table-5. It is worthy to note that even though the applicability of Freundlich isotherm does not indicate the heterogeneous nature of the surface, it serves well for practical design purposes.

Analysis of results in the Table-5 shows that θ_0 values for adsorption of chromium are larger for black hair than for white hair, suggesting that the adsorption potential of black hair is higher than that of white hair and a similar result could also be inferred from the values of Freundlich (1/n) parameters.

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