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Removal of Chromium (VI) from aqueous solutions onto *Lagerstroemia Indica* Seeds activated carbon by adsorption

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Abstract-The aim of this investigation was to determine the adsorption behaviour and kinetics of Chromium (VI) in aqueous solution on activated carbon prepared from *Lagerstroemia indica* seeds (LIS) by Phosphoric acid activation. Surface study of LIS was investigated using Fourier Transform Infrared (FTIR) and Scanning Electron Microscopy (SEM). The effect of operational parameters such as adsorbent dosage, initial dye concentration, pH and temperature onto metal removal was studied. The intraparticle diffusion model, the pseudo-first order and the pseudo-second order were used to describe the kinetics data. Equilibrium isotherms were analyzed using Langmuir, Freundlich and D-R adsorption models. Thermodynamic parameters of dye adsorption were obtained. The experimental data fitted well to the pseudo-second order kinetics model for metal. The results indicated that isotherm data of Cr (VI) followed Langmuir isotherm. The thermodynamic data indicated that the adsorption was exothermic process. Metal adsorption studies in aqueous solution at pH 11 showed that maximum adsorption of 96.26%, were achieved for Cr (VI). It can be concluded that LIS could be effectively employed as an effective biosorbent for the removal of metals from aqueous solutions.

Keywords-Adsorption; activated carbon;Kinetics; Isotherms.

1. INDRODUCTION

Water is very essential for human beings and other living things to survive as no life is possible on earth without water. It has been reported that water pollution is the leading cause of deaths and diseases observed globaly[1,2]. It accounts for the death of more than 14000 people daily[2]. In India, it is estimated that everyday about 580 people die due to illness related to water pollution[3]. Chemical industries utilise reagents of varied nature and composition, ranging from inorganic compounds to polymers and organic compounds. Water pollution mostly occurs when effluents containing these harmful chemicals are discharged from these industries directly or indirectly into water bodies without adequate treatment to remove the harmful substances. Dyes and Heavy metals are identified as the most prominent pollutants, as they pollute water to a greater extent[4-6].

Metals and metal like compounds with density more than 5 g/cm^3 and atomic numbers above twenty are collectively known as heavy metals[7]. These are natural constituents of the earth crust and their presence in the environment is mainly due to the weathering of rocks[8].Various sources of heavy metals in water are the effluents from battery manufacture, paint, coating, smelting, alloy preparation, wood preservation, plating, tanning and mining etc., These heavy metals cause serious health problems in animals, plants and human beings as they are toxic and have a tendency to accumulate in the environment and in food chains[9, 10].

The industrial effluents therefore are to be treated to reduce their pollutant content to the desired limits before they are discharged into any aquatic receiving bodies. In the past, several physical, chemical and biological methods of decolourisation like coagulation, flocculation, ion-exchange, membrane separation, electrochemical treatment, oxidation, etc., have been tried for treating effluents containing heavy metals and dyes.

In this context, adsorption process has proved itself to be more convenient because of the benefits like removing wide variety of target pollutants even when present in low concentrations, high capacity, easy to operate with low operational cost, short operation time, fast kinetics, simplicity of design, possibly selectively depending on adsorbent and effectiveness[11, 12].

The objective of this study is to prepare activated carbon from *Lagerstroemia indica* seed by chemical activation with Phosphoric acid. Large availability of this material around our city attracted us to utilize it as potential adsorbent for the removal of toxic metals. The adsorption capacity of *Lagerstroemia indica* seed used as the adsorbent for the removal of metals varying with process factors including initial metal ion concentration, contact time,

initial pH, adsorbent dose and temperature.

2. METHODS AND MATERIALS

2.1 Adsorbent preparation

The *Lagerstroemia indica* seeds (LIS) used in this study was collected from local fields. The collected seeds were extensively washed with tap water to remove soil and dust, sprayed with distilled water then dried, charred with excess quantity of phosphoric acid for 10h. Then the resultant carbon is washed with excess quantity of distilled water and dried at 110°C for 1 hour and stored in air tight lid container for further studies. It is then screened through a mesh sieve with a particle size range of 180-300 µm.

2.2 Determination of Chromium (VI)[13]

Hexavalent Chromium was determined spectrophotometrically by diphenylcarbazide method. To a series of standard solutions of Chromium (VI) (5.50µg) 3mL of 2N sulphuric acid, 2 drops of phosphoric acid and 0.5mL of diphenylcarbazide solution (0.5% in acetone) were added and made up to 25mL with doubly distilled water. After few minutes the absorbance was measured at 540nm after against a reagent blank. A calibration graph with absorbance vs Chromium (VI) concentration was prepared. The concentration in the sample was determined using the calibration graph.

2.2.1 Chromium (VI) stock solution (1000ppm):

A stock solution of (1000mg/L) of Chromium (VI) was prepared by dissolving 5.658g of dried potassium dichromate ($K_2Cr_2O_7.H_2O$) in doubly distilled water and making up to 1000mL.

2.3 Adsorption dynamics

In order to predict the mechanism of the present biosorption process and evaluate the performance of the biosorbent for metal removal, three well-known kinetic models were used to fit the experimental data; pseudo-first-order, pseudo-second-order and intraparticle diffusion models.

2.3.1. Pseudo first order model

For a batch contact time process, where rate of sorption of metal on to given adsorbent is proportional to amount of metalsorbed from solution, first order Langergren kinetic equation may be expressed as[14],

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \text{.....(1)}$$

where,
qe= amount of dye adsorbed at equilibrium (mg/g),
qt= amount of dye adsorbed at time t (mg/g) and
k1 = rate constant for first order adsorption(min-1).

Hence a linear trace is obtained between the two values log (qe– qt) and t, provided the adsorption follows first order kinetics. In order to examine the efficiency of an adsorbent, this study is useful in removal of adsorbate species from aqueous solution by an adsorbent.

2.3.2 Pseudo second order model

The pseudo-second order equation in its linear form proposed by Ho and Mckay[15]can be represented as

$$dq_t/dt = k_2 (q_e - q_t) \quad \text{.... (2)}$$

Integration ofeqn (13) and subsequent rearranging gives

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e2}} + \frac{1}{q_e} t \quad \text{.... (3)}$$

Where,
qe= amount of dye adsorbed at equilibrium (mg/g),
qt= amount of dye adsorbed at time t (mg/g) and
k2 = rate constant for pseudo second order adsorption, (g/mg/min).
For the boundary conditions t=0 to t=1 &qt= 0, qt= qt

The above equation it leads to the calculation of k_2 and qe, without knowing any parameters beforehand, from the slope and intercept of the plot of t/qtvs t[16]

2.4. Isotherm models

Langmuir, Freundlich, Tempkin and D-R isotherms are used to determine the relationship between the amount of metal adsorbed and its equilibrium concentration was analyzed.

2.4.1 Langmuir adsorption isotherm

The Langmuir isotherm model commonly used for the adsorption of a solute from a aqueous solution[17]in its linear form can be represented as

$$C_e / q_e = i / bq_0 + C_e / q_0 \quad \text{.....(4)}$$

Where $C_e$is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of dye adsorbed per unit mass of adsorbent (mg/L) and q_0 and 'b' are Langmuir constants related to adsorption capacity and rate of adsorption respectively.

2.4.2 Freundlich model

The Freundlich isotherm, in its logarithmic form can be represented as

$$\log q_e = \log K_f + 1/n \log C_e \text{..... (5)}$$

Where K_f and 1/n are Freundlich constants related to adsorption capacity and adsorption intensity of the sorbent respectively. q_e is the amount adsorbed

at equilibrium (mg/g); C_e is the equilibrium concentration of the adsorbate.

2.4.4 Dubinin -Radushkevich isotherm model

Dubinin –Radushkevich (D-R)[18]equation can be represented as

$$\ln q_e = \ln q_d - \beta\varepsilon^2 \ldots\ldots\ldots\ldots (6)$$

Where, q_d is the D-R constant, β is the constant related to free energy and ε is the Polanyi potential which is defined as;

$$\varepsilon = RT \ln(1+1/Ce) \quad \ldots\ldots\ldots\ldots (7)$$

The constant β is pertained to the mean free energy of adsorption per mole of the adsorbate as it is transferred to the surface of the solid from infinite distance in the solution.

This energy can be computed using the following relationship.

$$E = 1/\sqrt{2Q} \quad \ldots\ldots\ldots\ldots (8)$$

3. RESULT AND DISCUSSION

3.1 Effect of contact time and initial dye concentration

In the present investigation batch adsorption experiments were conducted to consider the impact of these factors by agitating 50 mL of respective metal ion solutions mixed with a fixed weight of adsorbent (100 mg) at various initial concentrations (10, 20,30 and 40 mg/L) at 301K in 100mL conical flasks. The adsorbent and the adsorbate were separated at predetermined time intervals and the residual concentrations of the metal ions in solution were analysed spectrophotometrically as discussed under experimental section. Initially the adsorbents adsorption capacity was high finally it becomes constant showing the attainment of equilibrium. An increased percentage removal of Chromium (VI) from 55.15.00 to 99.15% observed with 100 mg of the adsorbent in agitation time of 90 minutes and results are shown in Fig. 1. From the Figure the curves shows monolayer coverage on the adsorbent surface.

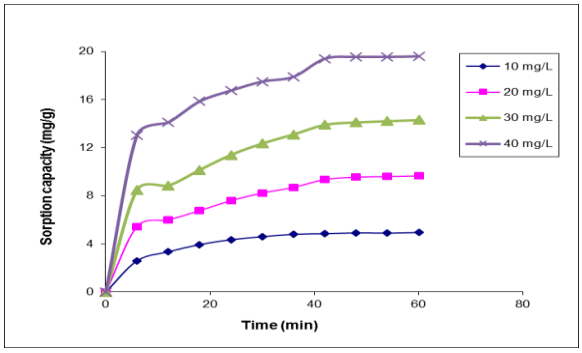

Fig.1. Effect of initial dye concentration

3.2. Effect of pH

Effect of pH on adsorption was carried out at various pH values ranging from 5 to 11 maintaining the required pH by adding necessary HCl (0.5N) /NaOH (0.5N) . The initial pH of solution was varied from 5 to11 with the adsorbate concentration varying from 10-40 mg/L maintaining the adsorbent dose at 0.1g and the contact time as 2 hours. From Fig.7 indicates that maximum dye removal had occurred in basic medium and also observed that as the pH increases the Sorption capacity also increases. The pHzpc for the nanocomposite was determined as 11.0

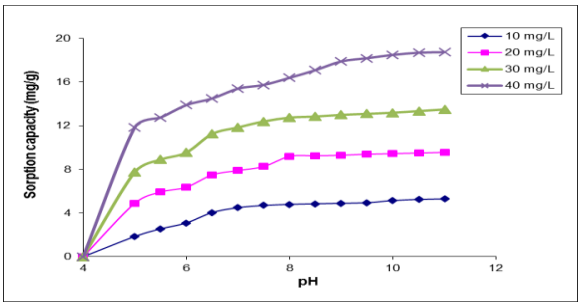

Fig.2. Effect of pH

3.3. Effect of temperature

The adsorption of Chromium (VI) with temperature has an important effect on the adsorption on adsorbent. The result from Fig.3 revealed the exothermic nature of adsorption of metal ion onto LIS adsorbent. This may be due to the fact that as the temperature increases, rate of diffusion of adsorbate molecules across the external boundary layer and internal pores of adsorbent particle increase**.** The data likewise revealed that the impact of temperature was not that much significant as there was just a slight decrease in uptake of metal studied with the raise in temperature.

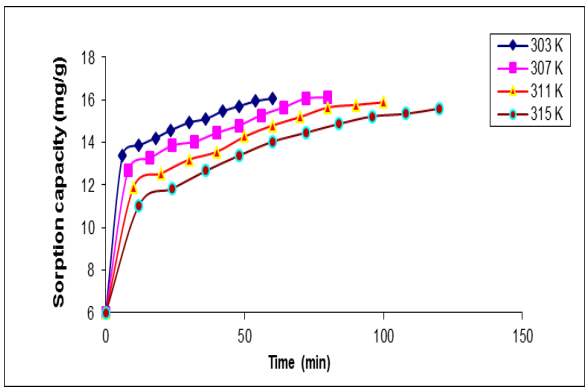

Fig.3. Effect of temperature

3.4. Adsorption kinetics

3.4.1. First order kinetics

Langergren first order plot for the adsorption of chromium (VI) at various initial concentrations is given in the Fig 4. The applicability of Lagergren model suggests the formation of a monomolecular layer of dye species onto surface of adsorbent. The study of influence of initial metal ion concentration on Lagergren rate constant from Table 1 shows a increase in rate constant with increase in initial metal ion concentration.

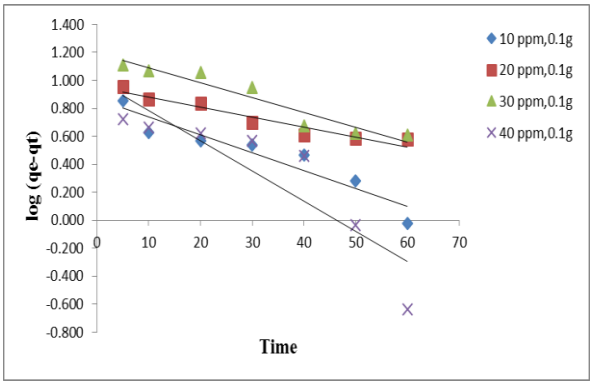

Fig.4. Pseudo first order model for adsorption of Chromium

3.4.2. Pseudo second order model

Fig. 5 shows that pseudo second order equation at various initial metal ion concentrations (10, 20, 30 & 40 mg/L). These plots show that data had good correlation coefficients when pseudo second order equation was employed and was possible to ascertain from them whether rate determining process is a chemical reaction. Thus increasing metal ion concentration from 10 to 40 mg/L, equilibrium sorption capacity qe increases metal ion sorbed at any contact time increases.

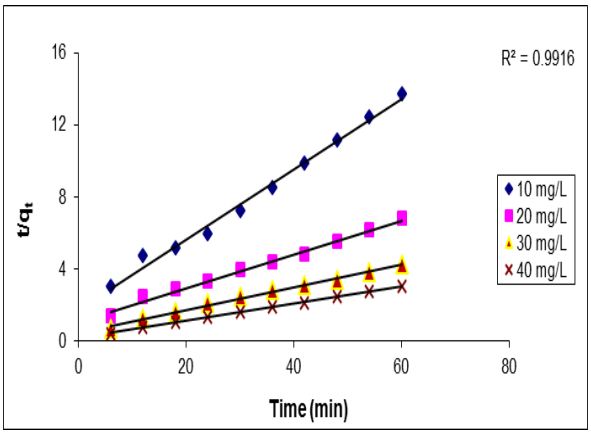

Fig.5. Pseudo second order model for adsorption of Chromium

Table 1. Kinetic model values for adsorption of Chromium (VI) onto activated LIS carbon

Pseudo First Order				
Metal ion conc.mg/L	**$q_{e\,(exp.)}$ mg/g**	**$q_{e\,(cal.)}$ mg/g**	**$k_1 \times 10^2$ min^{-1}**	**R^2**
10	5.109	1.542	5.251	0.5121
20	6.985	2.766	4.281	0.7954
30	8.390	3.110	3.014	0.8909
40	11.782	4.781	2.917	0.3227
Pseudo Second Order				
Metal ion conc.mg/L	**$q_{e\,(exp.)}$ mg/g**	**$q_{e\,(cal.)}$ mg/g**	**$k_2 \times 10^3$ min^{-1}**	**R^2**
10	5.109	5.237	7.901	0.9998
20	6.985	7.167	4.003	0.9914
30	8.390	8.689	3.811	0.9916
40	11.782	11.966	2.277	0.9960

3.5. Adsorption isotherms

3.5.1. Langmuir adsorption isotherm

The plots of C_e/q_e vs C_e, as required by Langmuir equation[17] for the adsorption of the metal ion considered on adsorbent were shown in Fig. 6 and data were presented in Table 2. The linearity of the plots indicated the applicability of Langmuir isotherm for the adsorption process. The calculated values of Langmuir adsorption capacities Q^o, and the constant b for all the four metal ions studied were presented in Table 2.

To confirm the favourability of the adsorption process the separation factor (R_L) was calculated using the relation[19].

$$R_L = 1/1+b\,C_0 \qquad \ldots. (9)$$

In the present investigation, $R_L$valuesobtained were observed to be less than unity indicating that the adsorption processwas favorable. The results were represented in Table 2. The regression coefficient values in the range 0.9462-0.7458 indicate that the adsorption data for all the metal ion onto LIS adsorbent fit well with Langmuir isotherm.

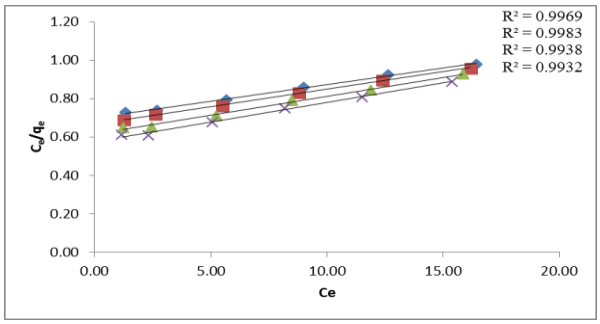

Fig.6. Plot of Langmuir adsorption isotherm

Table 2: The values of Langmuir constant Q^0 and b in addition to R_L

Metal ion Concentration mg/L	Langmuir Parameters			
	R_L	Q^O	b	R^2
20	0.9462			
40	0.8979			
60	0.8544			
80	0.8148	6.10	0.00284	0.9927
100	0.7788			
120	0.7458			

3.5.2 Freundlichadsorption isotherm

Freundlich plot for the adsorption of chromium on to LIS activated carbon is given in the Fig. 7 and the results of Freundlich plot are given in the Table 3. It shows that the values of adsorption intensity 1/n > 1 reveal that applicability of Freundlich adsorption is not good compared to Langmuir Adsorption Isotherm.

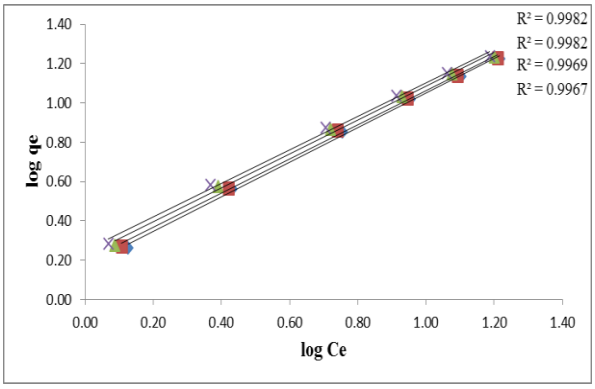

Fig.7. Plot of Freundlich adsorption isotherm

Table 3: The values of Freundlich constant K_f and n

Metal ion	K_f (L/mg)	n (mg/g)	R^2
Chromium (VI)	6.025	1.91	0.9982

3.5.3. D-R isotherm model

The D-R isotherm[20] can be used to distinguish between the physical and chemical adsorption. The adsorption isotherm constants q_m and B can be determined experimentally by plotting $\ln q_e$ vs ε^2. The plots are shown in Fig 8 and data in Table 4.

The values of E in the present examination are observed to be in the range of 22.72 kJ/mol (Table 4) which show that the chemisorption process[21] play a significant role in the adsorption of metal ion utilised on the LIS adsorbent. The R^2 values in the range 0.9269 (Table 4) demonstrate that the adsorption data fits fairly well with D-R isotherm.

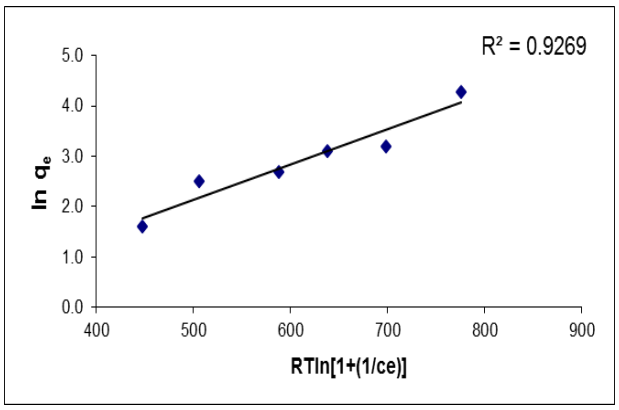

Fig.8.D-R model for adsorption of Chromium

Table 4. The values of D-R constant

q_d	B	E	R^2
9.51	0.008	22.72	0.9269

3.6 Thermodynamic parameters

The thermodynamic parameters for the adsorption process such as free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were evaluated using the following equations:

$$\ln K_C = \Delta S^0 / R - \Delta H^0 / RT \quad \text{.....(10)}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad \text{.....(11)}$$

Where K_C is the Langmuir constant related to the energy of adsorption, R is the gas constant and T is the absolute temperature (K). The values of ΔH^0 and ΔS^0 can be calculated, respectively, from the slope and intercept of the Van't Hoff plot of ln K_C versus 1/T.

The calculated values of ΔH^0, ΔS^0 and ΔG^0 for adsorption of Chromium (VI) on LIS were given in Table 5. Negative values of ΔH^0 confirms that the adsorption process to be exothermic. The negative value of ΔG^0 at various temperatures indicates the feasibility and spontaneity of the adsorption process. The positive value of ΔS^0 shows the affinity of adsorbent for Chromium and it further confirms a spontaneous increase in the randomness at the solid-solution interface during the adsorption process.

Table 5: Thermodynamic parameters for adsorption of Chromium (VI) on LIS

Name of the Metal ion	$-\Delta G^0$ kJ/mol			
	303 K	307 K	311 K	315 K
Chromium (VI)	16.4	16.9	17.7	18.1
	ΔS°J/k/mol		−ΔH° kJ /mol	
	23.2		41.3	

4. CONCLUSION

The present study showed that *Lagerstroemia indica* seed (LIS) activated carbon modified with Phosphoric acid can be used as an effective adsorbent for the removal of Chromium (VI) from aqueous solution. The maximum adsorption capacity was obtained (96.92%) by using carbonaceous *Lagerstroemia indica* seed at pH 11 with adsorbent dose of 100 mg and with agitation time of 90 minutes. The adsorption followed pseudo second order kinetics and data fitted the Langmuir and D-R adsorption isotherms. Thermodynamic studies indicated that the metal ion adsorption onto LIS was as spontaneous, exothermic, and feasible in nature. Based on the data of present study, LIS is an eco-friendly adsorbent for metal ion removal from colored aqueous solution.

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