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Adsorption of Chromium (VI) by using HCl modified *Lagenaria siceraria* peel (HLSP)

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Abstract

An attempt has been made to test the potential of HCl modified *Lagenaria siceraria* (bottle gourd) peel (HLSP) towards Cr^{6+} uptake. 120 minutes contact time and pH 4-5 is the optimum condition. Negative activation energy shows ease and exothermic nature of the adsorption process. The maximum uptake of Cr^{6+} is 1.17 mg/g of HLSP. The adsorption of Cr^{6+} by HLSP is well explained by different isotherms like Ho & Mc-Kay equation (Pseudo 2nd order kinetics), Langmuir and Morris-Weber equation.

Keywords: Cr^{6+} adsorption, pzc, separation parameter, Ho & Mc-Kay equation.

1. Introduction

Among all the natural resources water is the most vital one and it is very much crucial for the survival of all the living beings. Presently, this important natural resource is getting contaminated due to rapid industrialization and population growth. Industries are the main source of heavy metal contamination in drinking water. The waste water of various industries such as electroplating, leather tanning, paints, pigments etc. contains different toxic heavy metal ions such as chromium, copper, lead, cadmium, mercury, zinc etc. Due to improper treatment process, non-biodegradable nature of the heavy metal ions and disposal problem, it contaminates drinking water sources [1, 2]. These heavy metal ions are very much toxic to the living beings including human beings and they cause various diseases. Chromium is one of the most common toxic heavy metal ions which are discharged to water sources through almost all the industries. In aqueous solution Cr exists in two forms i.e., Cr^{3+} and Cr^{6+}. Chromium is a micronutrient required by our body in the form of Cr^{3+} ion but Cr^{6+} ion is poisonous and it causes cancer, anuria, nephritis, gastrointestinal ulceration etc. [3]. So, it is very much essential to treat Cr^{6+} contaminated waste water before disposal.

The various methods used to remove Cr^{6+} from waste water are chemical precipitation, electrochemical reduction, sulphide precipitation, cementation, ion-exchange, reverse osmosis, electro dialysis, solvent extraction, and evaporation etc. [4]. For large scale treatment of Cr^{6+} rich waste water the above methods are expensive and are unaffordable. Therefore, adsorption technology is being given more priority for removal of metal ions like Cr^{6+} because of its low cost and efficiency. An adsorbent must be eco-friendly, cost-effective, industrially viable and efficient. So, in recent years, various low cost natural materials have been proposed as potential bio sorbents. These include moss peat, algae, leaf mould, sea weed, coconut husk, sago waste, peanut hull, hazelnut, baggage, rice hull, sugar beet pulp, plant biomass and bituminous coal [5-8] etc.

Materials derived from plants can also be effective adsorbents because of its easy availability and low cost. Plant materials are mainly composed of cellulose that can adsorb heavy metal ions from aqueous solution [9]. The heavy metal ions adsorption occur as a result of physicochemical interaction, primarily ion exchange or complex formation between metal ions and the functional groups present on the surface of the adsorbents. Different plant materials like leaves, roots, seeds, barks, fruit pulps, fruit peels have been used as bio sorbents for the sequestration of heavy metal ions from aqueous solution [10-12].

So, in the present paper, an attempt has been created to measure the potential of *Lagenaria siceraria* (bottle gourd) peel as adsorbent for the removal of Cr^{6+} ion from aqueous solution.

2. Materials and methods

2.1. *Preparation of adsorbents*

Lagenaria siceraria was collected from the local market, emptied manually. The peels were washed thoroughly to remove dust using distilled water, sun dried for 2 days, and then dried in an oven at 60°C for 24h, ground in mortar and pestle. This powder was modified by soaking it in 0.1M HCl/0.1 M H_2SO_4 for 24 hrs. It was filtered and washed with distilled water to remove acid contents. The washing was continued till neutral pH of the filtrate. The residue was first dried at room temperature and then in an oven at 105ºC to remove moisture. This modified bottle gourd peel adsorbent was stored in air tight glass bottles to protect it from humidity.

2.2. *Preparation of adsorbates*

Stock solution of 1000 mg/dm^3 of Cr^{6+} was prepared using required amount of $K_2Cr_2O_7$ of analytical grade in acidified distilled water. During batch adsorption experiments, the stock solution was diluted to desired concentration level required for the adsorption studies.

2.3. *Characterization of the sample*

Fourier Transform Infrared Spectroscopy (FTIR) spectra of the modified adsorbent before adsorption were obtained using JASCO FTIR instrument-4100. The sample was pressed into spectroscopic quality KBr pellet with a sample/KBr ratio of about 1/100. The FTIR spectra were recorded in the region 4000−400 cm^{-1} frequency.

The pH at point of zero charge (pzc) of the adsorbent was determined by the solid addition method [13]. Initial pH of 0.1 N KNO_3 solutions (pH_i) was adjusted from pH 2 to 8 by adding either 0.1 N HCl or 0.1 N NaOH. Adsorbent dose (1 g/L) was added to 50 mL of 0.1 N KNO_3 solutions in 250 mL conical flasks and stirred for 30 min of contact time and final pH (pH_f) of solutions was measured. The difference between the initial and final pH (pH_f - pH_i) was plotted against the initial pH (pH_i) and the pH where $pH_f - pH_i = 0$ was taken as the pzc. Other physicochemical parameters such as surface area, percentage moisture content, loss of mass on ignition, pH and density were determined by following the methods reported earlier [14].

2.4. *Batch Adsorption Study*

Batch experiments were conducted in 250 mL stoppered conical flasks containing 100mL of test solution. pH of the solution was maintained by adding 0.1 N HCl/0.1N NaOH solution. Stirring was carried out by a temperature controlled magnetic stirrer. Samples were withdrawn at regular time intervals, filtered through Whatman no.1 filter paper and filtrate was analyzed for remaining Cr^{6+} concentration. Most of the adsorption experiments were conducted in the following conditions: pH – 5.0, Initial Cr^{6+} concentration – 10 mg/dm^3, Temperature – 30°C, Adsorbent concentration – 0.5 g. The temperature experiments were carried out by using a temperature controlled thermostat.

The loading was calculated according to equation (1) as follows:

$$q = (C_o - C_e)\ V/M \qquad (1)$$

Where,
q = Adsorbent phase concentration after equilibrium, mg adsobate /g adsorbent or loading
C_o = Initial concentration of Cr^{6+}, mg/dm^3
C_e = Equilibrium concentration of Cr^{6+}, mg/dm^3
V= Volume of the liquid in the reactor, dm^3
M= Mass of the adsorbent, g.

$$\text{Sorption (\%)} = [(C_o-C_e)/C_o]*100 \qquad (2)$$

2.5. *Analysis*

The concentration of Cr^{6+} in the solution before and after equilibrium was determined by Elico SL-244 double beam UV-Visible spectrophotometer following diphenyl carbazide (DPC) method [15].

3. Results and discussion

3.1. *The physico-chemical parameters of HLSP*

3.1.1. *Determination of surface functional groups by FTIR*

The surface functional groups on the adsorbent (HLSP) were analysed by Fourier Transform Infrared Spectroscopy (FTIR). The FTIR graph is shown as Figure 1. The strong and broad peak at 3414.35 cm^{-1} wave number indicates O-H stretch bond and H-bonded structure like alcohols and phenols. Cr^{6+} is present as $HCrO_4^-$ and CrO_4^{2-} in natural water. Therefore, the interaction between Cr^{6+} and alcoholic or phenolic linkage can be interpreted according to Jones oxidation [16] as follows.

$$4\ HCrO_4^- + 3\ RCH_2OH + 16\ H^+ + 11\ H_2O \rightarrow 4\ [Cr(H_2O)_6]^{3+} + 3\ RCOOH$$

In this reaction H$^+$ ions are being consumed according to the above equation. In adsorption of Cr^{6+} on HLSP, it has also been observed that the pH of the solution increases after the reaction is over. Similarly, in presence of CrO_4^{2-} also alcohol is oxidized to carboxylic acid [17]. Medium peak at 1053.91 cm^{-1} indicates the existence of stretching vibrations of C-O of alcoholic groups and carboxylic acids [18]. If this is the case, a surface complexation reaction between surface functional group and Cr^{6+} species (as $HCrO_4^-$ and CrO_4^{2-}) may be assumed.

$$S\text{-}OH + H^+ + HCrO_4^- \leftrightarrow S\text{-}OH_2^+\text{-}HCrO_4^-$$
$$2S\text{-}OH + 2H^+ + CrO_4^{2-} \leftrightarrow (S\text{-}OH_2^+)_2\text{-}CrO_4^{2-}$$

Where, S-OH is the surface containing hydroxyl group and $S\text{-}OH_2^+\text{-}HCrO_4^-$ and $(S\text{-}OH_2^+)_2\text{-}CrO_4^{2-}$ are the surface complexes [19]. Similarly, other different functional groups present on HLSP surface are found to be alkanes, alkenes and alkynes etc..

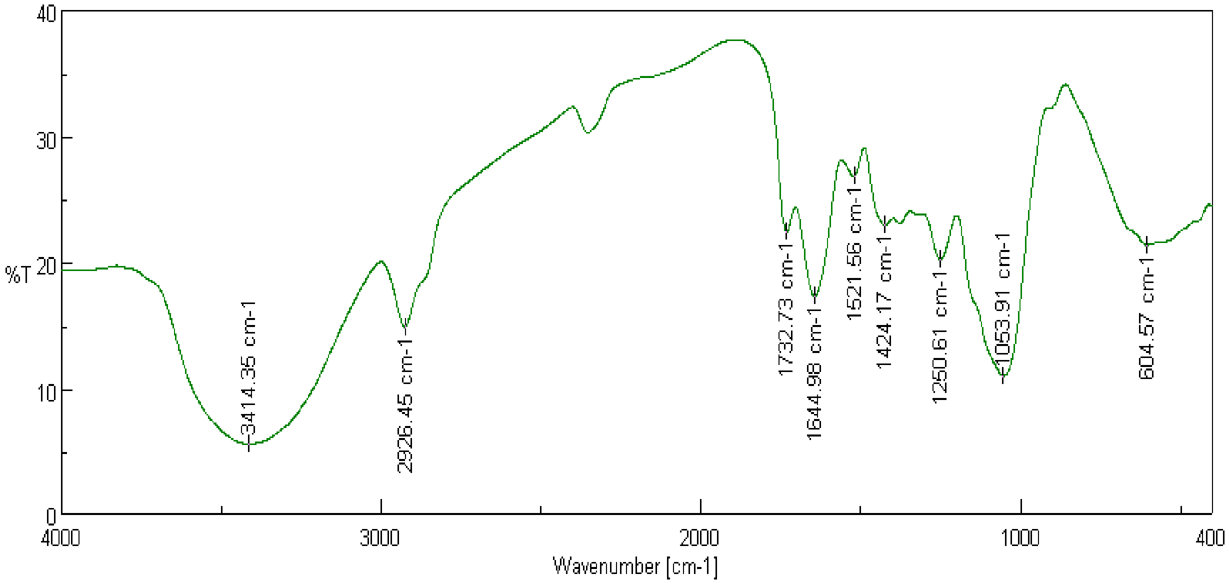

Figure 1 : FTIR spectra of HLSP

3.1.2. *Determination of Point of Zero Charge (pzc)*

Point of zero charge (pzc) describes the condition when the electrical charge density on a solid surface (adsorbent) is zero. The value of pH is used to describe pzc only for systems containing H$^+$/OH$^-$ ions. Below pzc, the acidic water donates more protons than hydroxide groups and the adsorbent surface becomes positively charged whereas, above pzc the surface is negatively charged. As a result, below pzc negatively charged ions or anions are attracted more towards adsorbent and above pzc the cations are attracted more towards adsorbents [20]. The graph of ($pH_{final} - pH_{initial}$) vs. $pH_{initial}$ is shown as Figure 2. The pzc of HLSP is found to be 3.4. That means below pH 3.4, the surface of HLSP is positively charged whereas above pH 3.4 surface of HLSP is negatively charged.

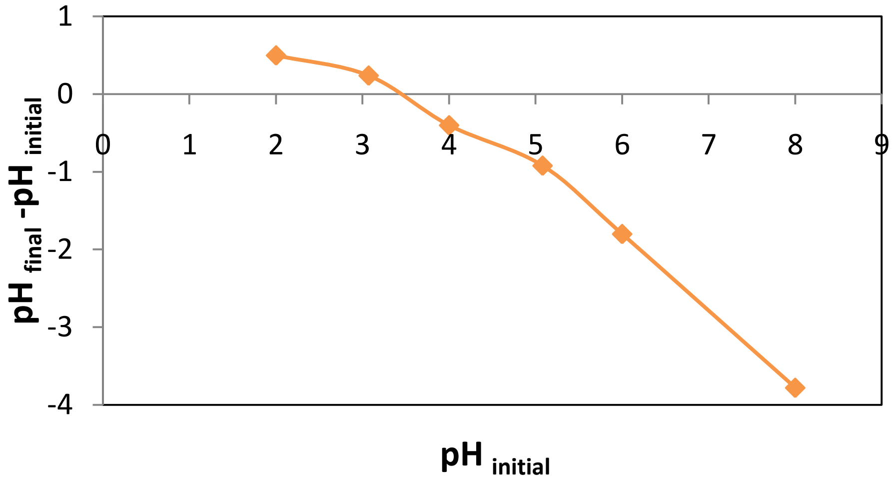

Figure 2 : The plot of ($pH_{final} – pH_{initial}$) vs. $pH_{initial}$

3.1.3. *Determination of other physico-chemical parameters*

All the other physico-chemical parameters such as pH, % moisture content, % loss of mass on ignition, bulk density and surface area are shown in Table 1 and are comparable to the other reported data [14].

Table 1 : Different physico-chemical parameters

Properties	**HLSP**
pH	6.3
% Moisture Content	2.22
% Loss of mass on ignition	90
Bulk density (g/cm^3)	0.386
Surface Area (m^2/g)	44.6

3.2. *Modification of the adsorbent*

Experiments were conducted with raw *Lagenaria siceraria* peel. But Cr^{6+} up take was very less (only 7%). So, basing on the literature the surface of the bio sorbent was modified by treating it with either 0.1 M HCl/0.1M H_2SO_4 [21]. Modification by HCl gave better result (62%) in comparison to H_2SO_4 modification (54%). The result is shown as Figure 3.

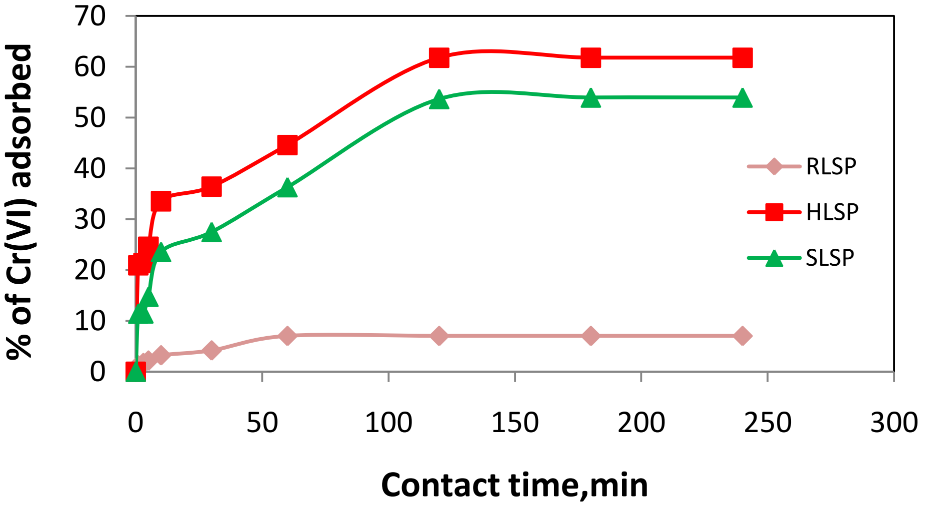

Figure 3 : Effect of contact time on percentage of Cr^{6+} adsorption (RLSP – Raw *Lagenaria siceraria* peel, HLSP – Hydrochloric acid modified *Lagenaria siceraria* peel, SLSP – Sulphuric acid modified *Lagenaria siceraria* peel)

The genus *Lagenaria* mainly composed of cellulose and lignin [22]. Cellulose is rich in hydroxyl groups and lignin is mainly an alcohol. After modification with acid, hydroxyl group may react with H^+ ion of the acid and may produce $-OH_2^+$ according to the following reaction:

$-OH + H^+ \rightarrow -OH_2^+$

Cr^{6+} exists mainly as $HCrO_4^-$ or CrO_4^{2-} in natural water. These negatively charged Cr ions then react with positively charged $–OH^{2+}$ by electrostatic force of attraction and the formation of the surface complexes [$S-OH_2^+-HCrO_4^-$ and $(S-OH_2^+)_2-CrO_4^{2-}$] described in section 3.1.1 may get accelerated in presence of acids. So, adsorption of Cr^{6+} becomes more after acid treatment. The increase in Cr^{6+} uptake after acid treatment may also be due to the removal of alkaline and alkaline earth metals present on the bio sorbent surface [22]. So, HCl modified bottle gourd peel (HLSP) was taken for the further studies.

3.3. *Effect of contact time*

It has been observed from Figure 3 that % of adsorption increases with the increase of contact time up to 120 minutes and then remains constant. Initially, all the functional groups present on the adsorbent surface remain free. As time passes the functional groups are satisfied with Cr^{6+} and when all the adsorption sites/functional groups get satisfied, there is no more adsorption with the increase in contact time. So, 120 minutes is taken to be the optimum contact time.

3.4. *Effect of pH*

The adsorption capacity of the adsorbent as a function of hydrogen ion concentration (pH) was determined. The result of the adsorption of Cr^{6+} with the variation in pH is shown in Figure 4. The uptake of Cr^{6+} is pH dependent as seen in the Figure 4. This could be because pH affects the solubility of metal ions in solution and the ions of the functional groups of the adsorbent [23]. The pH of the solution was varied from 3 to 7. The % of Cr^{6+} removal at pH 3 was 32%. But, when pH was raised to the range 4 to 5, % of Cr^{6+} removal became almost double. With the further increase in pH to 7, the % of metal removal again decreased. This result is in agreement with the other reported results [24]. The surface of bottle gourd contains mainly carboxyl and hydroxyl groups [25]. At low pH, Cr^{6+} occurs as dichromate ($Cr_2O_7^{2-}$) ion. Since it is a strong oxidizing agent, it hardly exists in natural water. So, at lower pH, H^+ is the most predominant one and the adsorption percentage is less. After pH 4, Cr^{6+} exists as $HCrO_4^-$ and CrO_4^{2-}. These ionic forms of Cr^{6+} compete with H^+ for the adsorption sites present on the adsorbent surface. So, adsorption percentage increases after pH 4. Surface of bottle gourd mainly contains functional groups like carboxyl and hydroxyl, pzc of HLSP is 3.4 and in natural water Cr^{6+} is present mainly in anionic forms like negatively charged $HCrO_4^-$ and CrO_4^{2-}. So, it can be concluded that electrostatic force of attraction or ion exchange mechanism is not only the key factor in this adsorption process. Decrease of Cr^{6+} adsorption after pH 6 may be due to the dual competition of $HCrO_4^-$ /CrO_4^{2-} and OH^- on the surface of the adsorbent and probability of precipitation of Cr^{6+} metal ions.

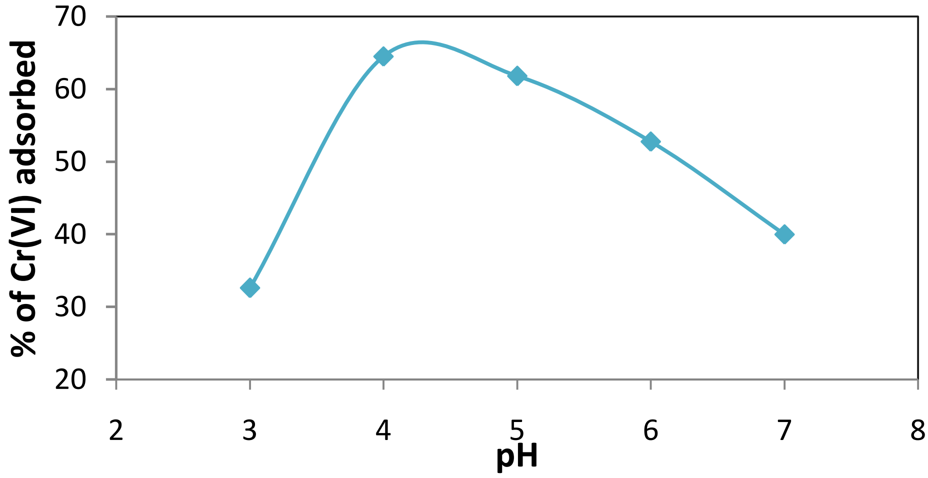

Figure 4: Effect of pH on percentage of Cr^{6+} adsorbed

3.5. *Effect of adsorbent dose*

The adsorbent dose was varied from 5 g/dm^3 to 30 g/dm^3. The percentage of adsorption increases from 62 to 70% with the increase in adsorbent dose whereas, Cr^{6+} up take per g of adsorbent decreases from 0.75 to 0.23 mg/g. This observation implies that at lower concentration, the adsorbents are more exposed to the adsorbates so, better up take takes place compared to higher adsorbent concentrations.

3.6. *Effect of metal ion (Cr^{6+}) concentration*

It has been observed that, the amount of Cr^{6+} ion uptake per unit weight of adsorbent increases from 0.75 to 1.15 mg/g with increasing initial Cr^{6+} ion concentration, but the percentage of adsorption decreases from 75 to 25% with the same. This is because at higher initial metal ion concentrations, the ratio of initial concentration of metal ions to the available adsorption surface area is high. This also may be due to the increase in the driving force of the concentration gradient with the increase in the initial Cr^{6+} ion concentration [26].

3.7. *Effect of temperature*

Effect of temperature on adsorption of Cr^{6+} was studied by conducting different sets of experiments at different temperatures i.e. 30, 40, 50 and 60°C. It was observed that adsorption of Cr^{6+} ion decreased from 62 to 25% when the temperature increased from 30 to 60°C. The negative effect of temperature is due to exothermic nature of the reaction and the greater degree of hydrolysis of the functional groups present on the adsorbent surface.

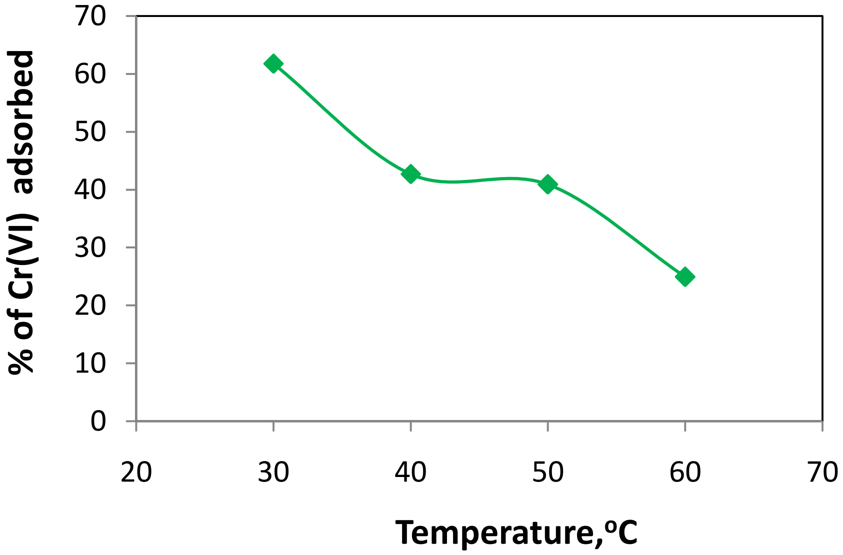

Figure 5 : Effect of temperature on percentage of Cr^{6+} adsorbed

Arrhenius equation was used to determine activation energy. The equation is as follows:

$$k=Ae^{-Ea/RT} \quad (3)$$

Where, k = Reaction rate constant
A = Frequency factor
E_a = Activation energy
T = Temperature, K
R = Universal gas constant

Activation energy was determined from the slope of Arrhenius plot (a plot between lnk versus 1/T). The activation energy was found to be - 69.34kJ/mol. The negative activation energy indicates the ease and exothermic nature of sorption reaction.

The value of ΔH and ΔS were calculated from the slope and intercept of the plot of $\ln K_D$ versus 1/T [27] as shown in Figure 6 by using the relation.

$$\ln K_D = \Delta S/R - \Delta H/RT \quad (4)$$

Where,

K_D = Distribution coefficient = $\frac{\textbf{Concentration of Cr6+ on adsorbent (mg/g) at equilibrium}}{\textbf{Concentration of Cr6+ in solution (mg/dm3) at equilibrium}}$

T = Temperature, K
ΔS = Entropy change
ΔH = Enthalpy change
R = Universal gas constant

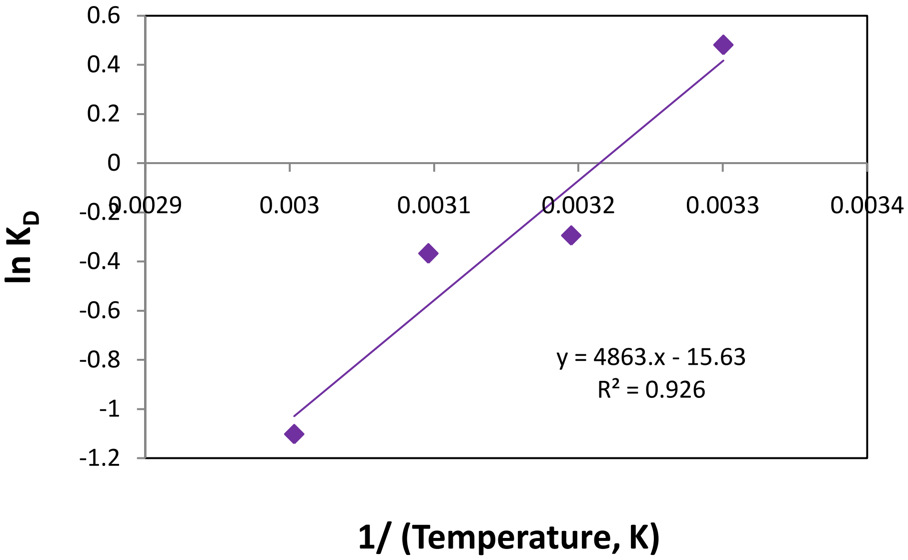

Figure 6 : A plot of ln K_D versus 1/T to determine thermodynamic properties

By using the values of ΔS and ΔH, the values of free energies of specific adsorption, i.e., ΔG were calculated as

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

The ΔG, ΔH and ΔS values are shown in Table 2. The negative value of enthalpy change suggests that the reaction is exothermic in nature. It has been observed that free energy change at 30°C is only negative. So, adsorption of Cr^{6+} only at 30°C is spontaneous, whereas at other temperatures, adsorptions are non spontaneous.

Table 2: Thermodynamic Parameters

Temp, K	Activation Energy, kJ/mol	ΔH, kJ/mol	ΔS, kJ/K.mol	ΔG, kJ/mol
303	-69.34	-40.43	-0. 13	-1.04
313				0.26
323				1.56
333				2.86

3.8. *Adsorption Isotherm*

The two well known models Freundlich and Langmuir were fitted to the adsorption of Cr^{6+} on HLSP. These two isotherms were studied by using initial Cr^{6+} concentration between 5 and 25 mg/dm^3 at an adsorbent dose of 5 g/dm^3.

The Langmuir adsorption isotherm is as follows:

$$C_e/q_e = 1/q_m b + C_e/q_m \quad (6)$$

Where the constants b and q_m relates to the energy of adsorption and adsorption capacity respectively. Their values were obtained from the intercept and slope of a straight line plotted between C_e/q_e and C_e. The value of b i.e., heat of adsorption was used to calculate a dimensionless constant, i.e., separation parameter R_L [28].

$R_L = 1/(1+bC_o)$ (7)

Where, C_o=Initial concentration of Cr^{6+}.

According to Mc kay et al. [29] $R_L>1$ means unfavourable, $R_L=1$ means linear, R_L= 0-1 means favourable and $R_L=0$ means irreversible adsorption. R_L value 0.22 to 0.49 indicates that the sorption of Cr^{6+} on HLSP is favourable in nature.

The adsorption data was also fitted to Freundlich isotherm. This isotherm gives the relationship between loading (q_e) and equilibrium concentration (C_e).

The Freundlich equation is:

$$\log q_e = \log K + 1/n \log C_e \quad (8)$$

Where, K and n are Freundlich constants which correspond to adsorption capacity and adsorption intensity respectively. The slope (1/n) and intercept (log K) can be obtained from a straight line plotted between log q_e versus log C_e. The result shows that Langmuir adsorption isotherm is a better fit for the experimental data in comparison to Freundlich isotherm as is evidenced from R^2 values shown in Table 3.

Table 3: Freundlich and Langmuir isotherm constants

Isotherm models	**Various constants**		
Langmuir	R^2	q_m (mg/g)	b
	0.98	1.17	0.21
Freundlich	R^2	K(mg/g)	n
	0.62	0.76	24.39

3.9. *Adsorption Kinetics*

The mechanism and the rate of adsorption depend upon various factors like physical and chemical properties of adsorbents. In order to study the adsorption of Cr^{6+} ions on the surface of HLSP, several kinetic models are proposed to examine the controlling mechanism of adsorption process. Data was fitted to Lagergren's equation (Pseudo 1st order kinetics), Ho & Mc-Kay equation (Pseudo 2nd order kinetics), Morris-Weber, Dubinin-Radushkevich (D.R.) and Temkin's isotherms as follows.

3.9.1. *Lagergren's equation:*

The pseudo first – order rate equation of Lagergren is given as:

$$\log(q_e - q_t) = \log(q_e) - (k_1/2.303)\,t \quad (9)$$

Where q_t and q_e are the amounts of Cr^{6+} ions adsorbed (mg/g), at time t and equilibrium respectively, and k_1 is the pseudo first order rate constant of the adsorption process.

3.9.2. *Ho & Mc-Kay equation:*

The pseudo second – order rate equation of Ho & Mc-Kay is given as follows:

$$t/q_t = 1/(k_2 q_e^2) + (1/q_e)t \quad (10)$$

Where, k_2 is the equilibrium rate constant of pseudo second order equation.

Cr^{6+} adsorption on HLSP obeys pseudo second order kinetics in comparison to pseudo first order kinetics which is evidenced from correlation coefficient (R^2) values listed in table 4.

Table 4: Comparison of different constants (rate constant for pseudo 1st order kinetics, pseudo second order kinetics, Morris-Weber equation, D-R Isotherm, Temkin's isothem) along with their R^2 values at pH 5.0 and temperature 30°C.

Sl No	**Cr^{6+} a)**	**HLSP b)**	**L R^2 c)**	**H k_2 d)**	**H R^2 e)**	**M R_{id} f)**	**M R^2 g)**	**D-R X'_m h)**	**D-R K' i)**	**D-R R^2 j)**	**E_{Ad} kJ/mol k)**	**T B J/mol l)**	**T R^2 m)**
1	5	5	0.89	0.059	0.90	0.022	0.95	0.84	4×10^{-8}	0.57	3.5	0.034	0.60
2	10	5	0.79	0.103	0.96	0.025	0.95						
3	15	5	0.76	0.471	0.99	0.067	0.85						
4	20	5	0.87	0.497	0.99	0.02	0.77						
5	10	5	0.79	0.103	0.96	0.025	0.95	0.85	9×10^{-6}	0.68	0.23	0.553	0.72
6	10	10	0.52	0.786	0.99	0.009	0.87						
7	10	15	0.84	0.362	0.97	0.014	0.96						
8	10	20	0.82	0.421	0.97	0.011	0.96						

a) Initial Cr^{6+} *concentration, mg/dm^3*
b) HLSP, g/dm^3
c) Lagergren's (L) equation (Pseudo 1st order kinetics), $R^{2.}$
d) Ho & Mc-Kay (H) equation (Pseudo 2nd order kinetics), k_2 *, g/mg/min*
e) Ho & Mc-Kay (H) equation (Pseudo 2nd order kinetics), R^2
f) Morris- Weber (M) equation, R_{id}
g) Morris- Weber (M) equation, R^2
h) Dubinin-Radushkevich(D.R.) isotherm, X'_m *, mg/g*
i) Dubinin-Radushkevich(D.R.) isotherm , K'*, mol^2/kJ$^{2.}$*
j) Dubinin-Radushkevich(D.R.) isotherm , R^2
k) Dubinin-Radushkevich(D.R.) isotherm , E, kJ /mol
l) Temkin (T) isotherm, B, J/mol
m) Temkin (T) isotherm, R^2

3.9.3. *Morris-Weber Equation*

Intra particle diffusion model and sorption kinetics of Cr^{6+} by HLSP was examined by using Morris-Weber equation. The equation is [30]

$$q_t = R_{id}\, t^{1/2} \qquad (11)$$

Where, q_t = Sorbed Cr^{6+} concentration at time t;
R_{id} = Rate constant of intra particle transport,
t= Time.

R_{id} can be obtained from the slope of a graph plotted between q_t and $t^{1/2}$. The R_{id} values for each experiment are shown in Table 4. High R^2 values led to the conclusion that the intra particle diffusion process is the rate limiting step. Higher R^2 values indicate the higher rate of adsorption and better adsorption mechanism through intra particle diffusion process.

3.9.4. *The Dubinin-Radushkevich (D.R.) isotherm*

D.R. isotherm is generally applied to heterogeneous surface and is expressed as

$$q_e = X'_m \exp(-K' \epsilon^2) \qquad (12)$$

Where,
ϵ= Polanyi potential =RT ln (1+ 1/C_e)
q_e= Amount of Cr^{6+} ions adsorbed per unit weight of adsorbent (mg/g)
X'_m = Adsorption capacity of the adsorbent (mg/g)
C_e = Equilibrium concentration of metal ions in solution (mg/dm^3)

K’ = Constant related to adsorption energy (mol^2/ kJ^2)
R= Gas constant (kJ/K /mol)
T = Temperature (K)

In linear form, D.R. isotherm can be expressed as

$$\ln q_e = \ln X'_m - K'\epsilon^2 \quad (13)$$

A straight line is obtained if ln q_e is plotted against ϵ^2. Slope and intercept give K’ and X'_m values respectively for different experiments, which are listed in Table 4.
The mean adsorption energy (E_{Ad}, kJ/mol) can be obtained from K’ (from D.R. isotherm) using the following equation.

$$E_{Ad} = (2\ K')^{-1/2} \quad (14)$$

Adsorption is generally classified as physiosorption and chemisorption. In physiosorption the sorbate and sorbent molecules are held by weak van der Waals forces whereas, in chemisorption they are held together by covalent bonding or electrostatic attraction [31]. For physiosorption the value of adsorption energy E_{Ad} is less than 8kJ/mole and for chemisorption this value varies from 8 – 16 kJ/mol. In case of Cr^{6+} adsorption using HLSP, E_{Ad} were found to be within the range 0.23-3.5 kJ/ mol. So, physiosorption dominates the sorption mechanism [32].

3.9.5. *Temkin isotherm model*

This isotherm explains interaction between adsorbate and adsorbent. The equation is given by

$$q_e = B \ln A_T + B \ln C_e \quad (15)$$

Where,
q_e= Amount of Cr^{6+} ions adsorbed per unit weight of adsorbent (mg/g)
B = Constant related to heat of sorption (J/mol)
A_T = Temkin isotherm equilibrium binding constant (L/g)
C_e = Equilibrium concentration of metal ions in solution (mg/dm^3)

So, the slope of a straight line drawn between q_e and $\ln C_e$ gives heat of sorption. The heat of sorption for initial Cr^{6+} concentration and adsorbent variation are found to be 0.034 and 0.553 J/mol respectively, which is an indication of physical adsorption process [33]. The heat of adsorption values along with R^2 values are shown in Table 4.

Conclusions

1. HCl treated *Lagenaria siceraria* peel (HLSP) gave better Cr^{6+} uptake in comparison to raw one and H_2SO_4 treated.
2. 120 minutes and pH 4 to 5 were found to be the optimum contact time and pH respectively.
3. Adsorption process was found to be exothermic in nature and the activation energy was found to be -69.34kJ/mol.
4. This adsorption was found to be favourable and only at 30°C the process is spontaneous.
5. Electrostatic force of attraction or ion exchange mechanism is not only the key factor in this adsorption process.
6. Physio sorption dominates sorption mechanism and intra particle diffusion process is the rate limiting step.
7. The sorption data is a better fit to Ho & Mc-Kay equation (Pseudo 2nd order kinetics), Langmuir and Morris-Weber isotherms in comparison to Lagergren, Freundlich, Dubinin-Radushkevich(D.R.) and Temkin’s isotherms.

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