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Removal of Cr(VI) from electroplating wastewater using fruit peel of Leechi (*Litchi chinensis*)

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ABSTRACT

Fruit peel of *Litchi chinensis* showed remarkable adsorption capacity towards Cr(VI) ions. The effect of temperature, pH, initial Cr(VI) concentration and time was investigated using batch process. The adsorption of Cr(VI) was maximum at pH 2. Fourier transform infrared spectroscopy (FTIR) was used to explore number and position of active functional groups available for the binding of Cr(VI) ions. Thermodynamic parameters like change in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) indicated the spontaneous, endothermic and increased randomness nature of Cr(VI) adsorption. Equilibrium data were well fitted in Langmuir isotherm at 40°C.The value of mean free energy ($E = 8.28\,\mathrm{kJ\,mol^{-1}}$) indicated that adsorption process was chemical in nature. The breakthrough and exhaustive capacities were found to be 30 and $50\,\mathrm{mg\,g^{-1}}$ respectively. The results indicated that the adsorbent could be used effectively for the removal of Cr(VI) from electroplating wastewater by batch process.

Keywords: Cr(VI); Adsorption; Thermodynamic parameters; Breakthrough capacity; Electroplating wastewater

1. Introduction

Presence of heavy metals in water systems is hazardous to the environment and human health because they are easily bio-accumulated through the food chain. Ingestion of heavy metals like copper, chromium, and zinc beyond permissible quantities causes various chronic disorders [1]. Chromium is one of the toxic substances which occur in aqueous systems in both trivalent [Cr(III)] and hexavalent forms [Cr(VI)] [2]. Chromium and its compounds are widely used in many industries such as metal finishing, dyes, pigments, inks, glass, ceramics, and certain glues. It is also used in chromium tanning, textile, dyeing, and wood preserving industries [3]. Cr(VI) is considered by IARC (International Agency for Research on Cancer) as powerful carcinogenic agent that modifies the DNA transcription process causing important chromosomic aberrations [4]. Cr(VI) is corrosive in nature and causes chronic ulceration and perforation of the nasal septum as well as chronic ulceration of the other skin surfaces. The mechanism of Cr(VI) carcinogenicity in the lung is believed to be its reduction to Cr(III) and generation of reactive intermediates. The maximum acceptable limit for the total chromium in drinking water recommended by World Health Organization is $0.05\,\mathrm{mg\,L^{-1}}$ [5].

Various techniques are available for the removal of Cr(VI) from industrial wastewaters like ion-exchange, precipitation, membrane filtration, and solvent-extraction with amines, electro-deposition, and various biological processes [6–11]. These methods have certain drawbacks like high capital and operational cost and

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lack of skilled personnel. Adsorption is a versatile treatment technique practiced widely in fine chemical and process industries for wastewater treatment. Nowadays various low-cost adsorbents such as agriculture wastes and activated carbon prepared from agriculture wastes have been used for the removal of toxic metals and organic pollutants from aquatic environment [12–19]. Ghaedi et al. [20] have proposed an spectrophotometric method for the determination of Cr(III) in surfactant media using α-benzoin oxime. Sunflower (*Helianthus annuus*) stem [21], rice straw [22], *Ficus religiosa* leaf powder [23], spent activated clay [24] have been studied during the past two decades as new adsorbents for the removal of Cr(VI) from water and wastewater.

In the present study, fruit peel of *Litchi chinensis* has been used as a new low-cost adsorbent for the removal of Cr(VI) from wastewater. Leechi tree (*Litchi chinensis*) belongs to Sapindaceae family and is a tropical and subtropical fruit tree native to China. It is evergreen, reaches 10–20 m in height and found in northern parts of India especially in the state of Bihar. The Leechi fruit is 2 inch long and 1.5 inch wide and contains white fleshy edible portion, surrounding the dark brown inedible seed. The fruit cover with thin, tough inedible skin is green when immature, ripening to red or pink-red, and is smooth or covered with small sharp protuberances. The fruition period is from April to June. Ingested in moderate amounts, the Leechi is said to relieve coughing and to have a beneficial effect on gastralgia, tumors, and enlargements of the glands. Leechi roots have shown activity against one type of tumor in experimental animals in the United States Department of Agriculture/National Cancer Institute Cancer Chemotherapy Screening Program. Leechi fruit pericarp extract have anticancer activity against human breast cancer [25].

The fruit peel of Leechi is a waste material therefore the aim of the work was to utilize it as an economical adsorbent for the removal of heavy metals from water and wastewater. Preliminary studies showed that Leechi peel exhibited remarkable adsorption capacity towards Cr(VI) ions and the effect of various parameters such as pH, contact time, temperature, adsorbent amount and initial Cr(VI) concentration was studied in detail to optimize maximum removal of Cr (VI) ions from water and electroplating wastewater.

2. Materials and methods

2.1. Preparation of adsorbent

Leechi Fruits were collected in the month of April. The ripped fruits were peeled and the peel was washed several times with double distilled water (DDW) to remove dirt and dust particles and then dried in air oven at 60°C for 24 h. The dried peel of Leechi was then crushed and sieved through 100–300 μm sieve. The powder obtained was used as adsorbent for following experiments.

2.2. Adsorbate

Stock solution of Cr(VI) was prepared (1,000 mg L^{-1}) by dissolving 2.8288 g of $K_2Cr_2O_7$ (AR grade) in one liter double distilled water (DDW). The working solutions of different concentrations were prepared by diluting the stock solution in DDW.

2.3. Point of zero charge (pHpzc)

Solid addition method [26] was used to determine zero surface charge characteristics of the Leechi fruit peel. 40 mL of 0.1 N KNO_3 solution was transferred to five different 250-mL conical flasks. The initial pH (pH_i) of the solution in each flask was roughly adjusted to 2, 4, 6, 8, and 10 respectively by adding either 0.1 N HCl or 0.1 N NaOH. The total volume of the solution in each flask was adjusted exactly to 50 mL by adding KNO_3 of the same strength. Initial pH (pH_i) of the solutions was then accurately noted with the help of pH meter. 0.5 g of sorbent was then added to each flask and allowed to equilibrate for 24 h with intermittent manual shaking. The final pH (pH_f) of the supernatant liquid was noted. The difference between the initial pH (pH_i) and final pH (pH_f) values ($\Delta pH = pH_i - pH_f$) was plotted against pH_i. The point of intersection of the resulting curve with abscissa, at which $\Delta pH = 0$, gave pHpzc.

2.4. Adsorption studies

The batch experiments were carried out in 250-mL conical flask by agitating 0.5 g of adsorbent with 50 mL of Cr(VI) solution with different Cr(VI) concentrations (10, 20, 50, 60, 80 and 100 mg L^{-1}) for 24 h. The adsorbent was separated from the solution using Whatman filter paper No. 41 and final concentration of metal ions was determined in the filtrate by atomic adsorption spectroscopy (AAS) (Model GBC 902, Australia). The amount of metal ions adsorbed was then calculated by subtracting the final concentration from initial concentration [27].

2.5. Effect of pH

The effect of pH on the adsorption of Cr(VI) ions was studied as follows. 100 mL of Cr(VI) solutions of 50 mg L^{-1} concentration were taken in five different conical flasks. The pHs of these solutions were adjusted to 2, 4, 6, 8, and 10 after 15 min by adding 0.1 N HCl or NaOH solution. Thereafter 50 mL solution from each flask was withdrawn and taken in a series of conical flasks each containing 0.5 g of adsorbent. The suspensions were shaken at room temperature for 24 h in shaker incubator and the amount of chromium adsorbed was determined after filtration by AAS.

2.6. Effect of time

Kinetics studies were carried out by shaking the adsorbent (0.5 g) with 50 mL of Cr(VI) solution (10, 20, 50, 60, 80, and 100 mg L^{-1}) at room temperature for the predetermined intervals (5,10, 15, 30, 60, 120, 180, and 240 min); the solution of the specified flask was taken out and filtered. The concentration of Cr(VI) in the filtrate was determined by AAS and the amount of Cr(VI) adsorbed in each case was then calculated as described above.

2.7. Effect of adsorbent dose

The effect of adsorbent dose on the adsorption of Cr(VI) ions was performed by shaking various adsorbent doses (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, 0.9, and 1 g) with 50 mL of Cr(VI) solution of 50 mg L^{-1} initial concentrations for 24 h at 30℃, individually. The solutions were then filtered and amount of Cr(VI) adsorbed in each case was calculated as described above. The same procedure was repeated at 40 and 50℃.

2.8. Breakthrough capacity

0.5 g of adsorbent was placed in a glass column (0.6 cm internal diameter) with glass wool support. 1 Litre of Cr(VI) solution with 50 mg L^{-1} initial concentration was taken in a flask and the pH of this solution was adjusted to 2. It was then passed through the column at flow rate 1 mL min^{-1}. The effluent was collected in 50 mL fractions and the amount of Cr(VI) was determined in each fraction (C) with the help of AAS. The breakthrough curve was obtained by plotting C/Co vs. the volume of effluent.

2.9. Analysis of electroplating wastewater

The electroplating wastewater was collected from one of the lock factory in Aligarh. The pH of electroplating wastewater was found to be 5.6 at the time of collection. Presence of heavy metals ions in the wastewater was determined by AAS. The amount of total dissolved salts (TDS) was determined by evaporating 100 mL wastewater in a china dish.

2.10. Treatment of electroplating wastewater by batch process

The electroplating wastewater showed high concentration of Cr(VI) (114 mg L^{-1}). It was diluted to acquire 50 mg L^{-1} Cr(VI) concentration. The pH of this solution was adjusted to 2 before treatment then 50 mL wastewater was added to a series of conical flasks (250 mL) and treated with increasing adsorbent dose. The flasks were shaken in a shaker incubator for 24 h and then filtered. The amount of Cr(VI) remained unabsorbed was determined by AAS. The amount of Cr(VI) removed was then calculated by subtracting final concentration from initial concentration.

3. Results and discussion

3.1. Characterization of adsorbent

FTIR spectra of Leechi fruit peel before and after Cr(VI) adsorption are shown in Fig. 1a and b, respectively. The band at 3,403 cm^{-1} was due to bounded hydroxyl (–OH) and amine (–NH) groups. The band at 2,922.4 cm^{-1} was due C–H vibrations of aliphatic acid [28]. The peak observed at 2,361.84 could be assigned to vibration of C–H groups. The two peaks at 1,435 and 1630.2 cm^{-1} indicated the presence of COO and C=C groups. The peaks at 1,375.7 and 1,264.4 cm^{-1} were due to aliphatic C–H and amide groups [28]. The peak at 898.6 cm^{-1} represented C–H stretching of alkenes. The change in the position of peaks due to C–O, C=C, COO, and M–O (metal-oxide

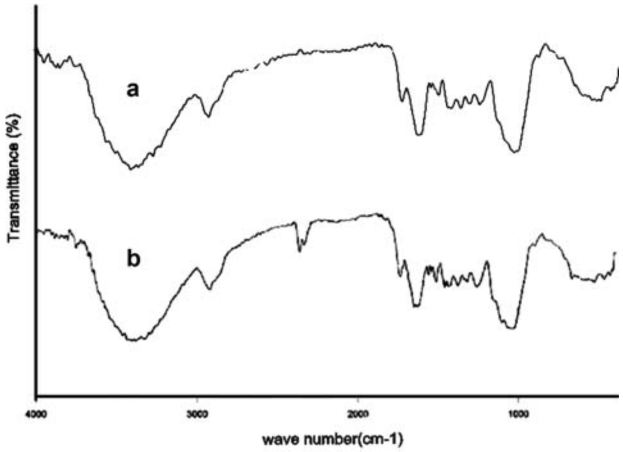

Fig. 1. FTIR of Leechi fruit peel (a) before, and (b) after Cr (VI) adsorption.

from 453 to 461 cm^{-1}) indicated the interaction of Cr (VI) with these binding sites (Table 1).

3.2. *Effect of initial concentration, contact time, and doses*

The initial concentration of metal provides an important driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid phases. Hence, a higher initial concentration of Cr(VI) will increase the adsorption rate. The relationship between contact time and Cr(VI) adsorption at different initial concentrations (10–100 mg L^{-1}) at pH 2 is shown in Fig. 2. Adsorption increased rapidly at initial stage and then gradually reached towards equilibrium. The contact time needed for Cr(VI) solutions with initial concentrations of 10 and 20 mg L^{-1} to reach equilibrium was found to be 20 and 30 min while solutions with initial Cr(VI) concentrations of 50, 60, 80, and 100 mg L^{-1} needed more than 30 min to attain equilibrium .The fast adsorption at the initial stage was probably due to increased concentration gradient between the adsorbate in the solution and adsorbate in adsorbent, followed by slower internal mass transfer within the adsorbent particles. The adsorption capacity of Cr(VI) at equilibrium was found to be 0.23, 1.04, 2.5, 3.6, 5.0, and 6.7 mg g^{-1} respectively at 10, 20, 50, 60, 80, and 100 mg L^{-1} initial Cr(VI) concentrations. The effect of adsorbent dosage (Fig. 3) at 30˚C indicated increased adsorption from 68 to 93.4% and decrease in adsorption density from 17 to 2.33 mg g^{-1} at pH 2. The decrease in adsorption density with increased adsorbent dose might be attributed to increased surface area of the adsorbent and availability of more adsorption sites due to increased adsorbent dose at fixed Cr(VI) concentration (50 mgL^{-1}) and fixed solution volume (50 mL) [38]. The % adsorption increased with increase in temperature initially at lower adsorbent dose but the effect was not significant at 40 and 50˚C when adsorbent dose was increased above 0.5 g. Similarly decrease in adsorption density with temperature was not significant above 0.5 g adsorbent dose. The higher adsorbent/Cr(VI) ratio produced lower metal concentration in the solution because a fixed amount of adsorbent could remove only a certain amount of metal ions. Therefore higher the adsorbent dose larger is the volume of effluent that can be treated.

Table 1
FTIR peak values for different functional groups present in fruit peel of Leechi before and after adsorption

Functional groups	Before adsorption	After Cr(VI) adsorption
–OH (water)	3,403.58	3,407.56
Aliphatic C–H	2,922.5	2,922.47
C–H vibration	–	2,361.84
C=C	1,630.24	1,642.17
COO^{-}	1,435.41	1,427.46
Phenolic OH	1,375.7	1,320.10
Amide groups	1,264.44	1,260.46
C–H bending	–	1,105
C–O	1,053.7	1,033.82
Alkenes	898.63	898.63
C–H stretching		
Bending mode of	–	668.02
Aromatic compound	544.76	520.90
Metal–O	453.31	461.26

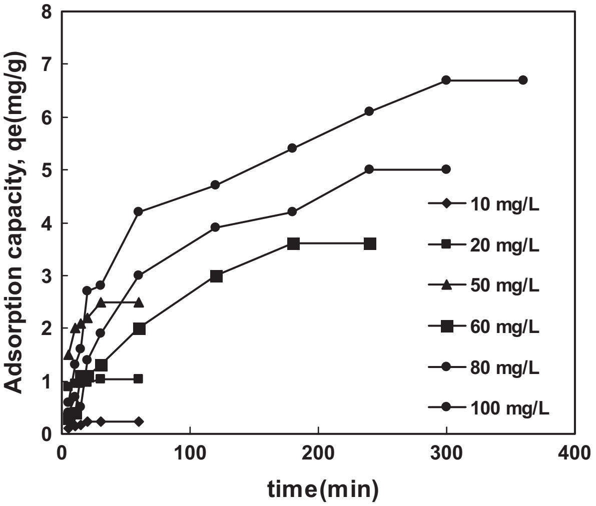

Fig. 2. Effect of time on the adsorption of Cr(VI) at different concentrations at 30°C (pH 2).

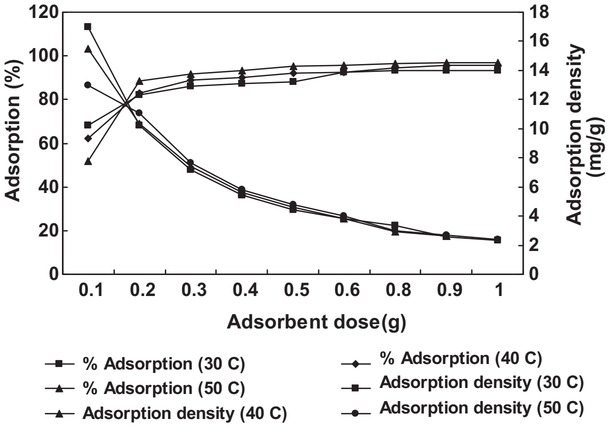

Fig. 3. Effect of adsorbent doses on the adsorption of Cr (VI) at different temperatures (pH 2).

3.3. Effect of pH

The adsorption of Cr(VI) at various controlled pH values is represented in Fig. 4. Adsorption increased from 54 to 96% when pH decreased from 10 to 2. The increase in Cr(VI) adsorption (%) with decrease in solution pH was also observed on peat [29], fungal biomass [30], and bacterium biomass [31]. At optimal acidic condition (pH 2), the dominant species of Cr(VI) ions in solution are ($HCrO_4^-$, $Cr_2O_7^{2-}$, $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$ [32]. These anionic species could adsorb on protonated active sites of the adsorbent, though at highly acidic pH (pH = 1), Cr(VI) anions are likely to get reduced to Cr(III) ions which due to electrostatic repulsive forces are poorly adsorbed [33]. At very low pH values, the surface of the adsorbent is surrounded by hydronium ions which enhanced the Cr(VI) interaction with binding sites of adsorbent by greater attractive forces [34]. Fig. 4 also showed how equilibrium pH or final pH changed after Cr(VI) adsorption. When initial pH of the solution was adjusted to 2, there was no change in the final pH indicating that surface of the adsorbent remained protonated due to high concentration of H^+ ions hence adsorption of Cr(VI) was maximum at this pH due to electrostatics attraction. However, when initial pH was adjusted to 4, the final pH increased to 6, perhaps due to exchange of Cr(VI) ions with OH^- ions and adsorption of Cr(VI) decreased slightly from 96 to 88% but when initial pH was adjusted to 6, the final pH became almost constant (6.45) which might be due to complete exchange of OH^-. The surface therefore became less protonated and caused further decrease in Cr(VI) adsorption (72% at pH 6). Further increase in initial pH resulted in a decrease in final pH due to release of H^+ ions from the adsorbent and% adsorption of Cr(VI) decreased further at and above pH 8. It has also been observed that % adsorption of Cr(VI) was strongly affected in the presence of high concentration (0.1 M NaCl) of electrolyte. Fig. 5 indicated that there was no common point of intersection of the two curves (0.1 M NaCl and DDW) at $\Delta pH = 0$, hence second charge reversal could not be considered as pHpzc. However, ΔpH values at pH = 2 were not affected in the presence of electrolyte (0.1 M NaCl) therefore first-charge reversal observed at pH ~ 1.7 (calculated by extrapolation of the two curves) may be considered as pHpzc [35]. The surface of the adsorbent is positive at pH < pHpzc, neutral at pH = pHpzc, and negative at pH > pHpzc and therefore adsorption of Cr(VI) was maximum at pH 2 due to electrostatic attraction since charge of adsorbent surface is positive at this pH.

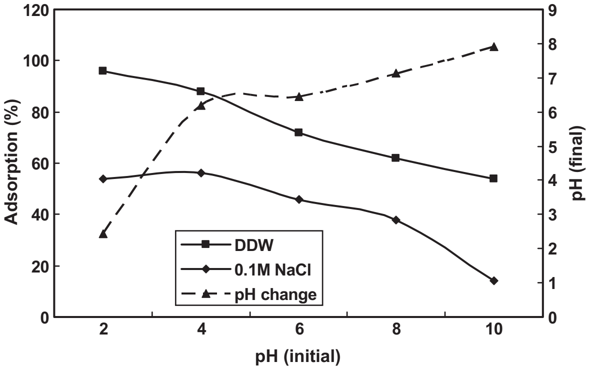

Fig. 4. Effect of pH and Electrolyte on the adsorption of Cr (VI) (Cr(VI) = 50 mg/L; temp = 30°C; adsorbent = 0.5 g).

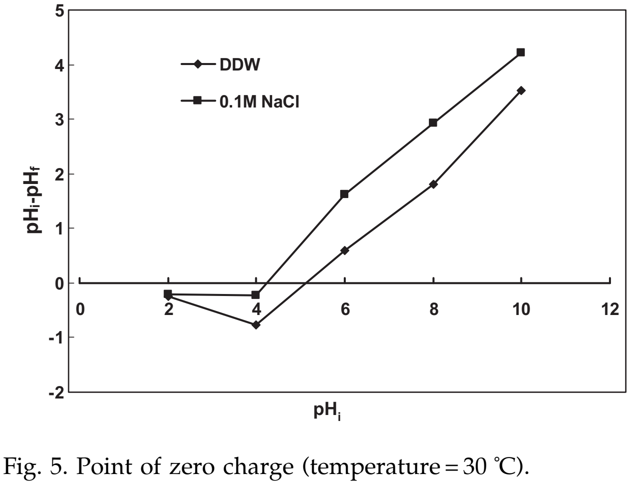

Fig. 5. Point of zero charge (temperature = 30 ℃).

3.4. Adsorption isotherms

Several models have been used by researchers to describe the experimental data. The Langmuir, Freundlich, Dubinin, and Radushkevich (D–R) models are the most frequently employed models.

The Langmuir isotherm is applicable when the extent of adsorbate coverage is limited to molecular layer. The linear form of this isotherm equation may be represented as

$$\frac{1}{q_e} = \frac{1}{q_m \times b} \times \frac{1}{C_e} + \frac{1}{q_m} \tag{1}$$

where q_e is the amount adsorbed on the unit mass of the adsorbent (mg g^{-1}) when the equilibrium concentration is C_e (mg L^{-1}), q_m is the quantity of adsorbate required to form a single monolayer on the unit mass of adsorbent (mg g^{-1}), q_e is the amount of metal ions adsorbed per unit weight of adsorbent and b is related to bonding energy associated with pH dependent equilibrium constant. Plots of $1/q_e$ vs. $1/C_e$ at 30, 40, and 50℃ gave straight lines [36] and values of b and q_m were calculated from the slope and intercept of the plots. The values of b and q_m at different temperatures are reported in Table 2. A chi-square test (χ^2) was also applied to this model. The advantage of χ^2 test is that $q_{e(cal)}$ from the model and q_e determined experimentally ($q_{e(exp)}$) can be compared on the same abscissa and ordinate [37]. If data from model were similar to the experimental data, χ^2 would be small and vice versa. Values of χ^2 were calculated using the following relation.

$$\chi^2 = \frac{\sum\left(q_{e(exp)} - q_{e(cal)}\right)^2}{q_{e(exp)} - q_{e(cal)}} \tag{2}$$

The least χ^2 value and high regression coefficient ($R^2 > 0.977$) indicated that Langmuir model was best fitted at 40℃ (Table 2).

Freundlich isotherm was proposed by H.M.F. Freundlich in 1906 for multilayer adsorption from solution. The linear form of the Freundlich isotherm is expressed as follows:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{3}$$

where, K_f is the Freundlich constant, which indicates the relative adsorption capacity of the adsorbent related to bonding energy and n is the heterogeneity factor representing the deviation from linearity of adsorption and is also known as Freundlich coefficient. Plots of log q_e vs. log C_e generated straight lines at 30, 40, and 50℃ and values of n and K_f were calculated from the slope and intercept of these plots (Table 2). The least value of χ^2 and high correlation coefficient ($R^2 = 0.967$) at 40℃ indicated that Freundlich isotherm was also obeyed at 40℃.

A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L, also known as the separation factor, given by Eq. (4):

$$R_L = \frac{1}{(1+b \times C_0)} \tag{4}$$

where b is the Langmuir constant and C_0 is the initial concentration of Cr(VI) (mg L^{-1}). R_L value predicts the shape of the isotherm. If $R_L > 1$ unfavorable, $R_L = 1$ linear, $0 < R_L < 1$ favorable and $R_L = 0$ for irreversible

Table 2
Adsorption isotherm parameters for the adsorption of Cr(VI) on fruit peel of Leechi

Isotherms	Parameters	30℃	40℃	50℃
Langmuir	q_m (mg g^{-1})	−34.48	101.10	75.98
	b (L mg^{-1})	−0.020	0.012	0.024
	R_L	−10.00	0.625	0.454
	R^2	0.894	0.977	0.956
	χ^2	1.142	0.907	8.627
	RSE	0.043	0.020	0.027
	P-value	<0.05	<0.05	<0.05
Freundlich	K_f ((mg/g)(L/mg)$^{1/n}$)	0.686	1.330	2.450
	n	0.599	1.125	1.580
	R^2	0.947	0.967	0.837
	χ^2	0.825	0.979	4.237
	RSE	0.069	0.054	0.837
	P-value	<0.05	<0.05	<0.05
D–R	q_m (mol g^{-1})	0.022	0.007	0.003
	K (mol^2/J^2))	1.02×10^{-8}	0.73×10^{-9}	4.875×10^{-9}
	E (kJ mol^{-1})	7.00	8.28	10.13
	χ^2	1.57×10^{-5}	1.55×10^{-3}	2.42×10^{-3}
	RSE	0.162	0.319	0.870
	R^2	0.946	0.782	0.8701
	P-value	<0.05	<0.05	<0.05

Table 3
Comparison of the adsorption capacities for Cr(VI) onto various adsorbents

Adsorbent	Adsorption capacity (mg g^{-1})	References
Spirogyra sp	14.70	[39]
Coconut shell based activated carbon	20.00	[40]
Palm pressed-fibers	5.00	[41]
Almond	10.00	[42]
Distillery sludge	5.70	[43]
Walnut shell	1.33	[44]
Soya cake	0.28	[45]
Cactus	7.08	[42]
Pine needle	21.5	[42]
Activated neem leaves	62.97	[46]
Ficus glomerata	46.73	[47]
Litchi chinensis	101.10	Present study

adsorption [38]. The R_L values at 30, 40 and 50°C are shown in Table 2. The values of R_L in the range 0–1 at 40° showed favorable adsorption of Cr(VI). The maximum monolayer adsorption capacity of Leechi fruit peel for Cr(VI) was compared with other adsorbents reported earlier (Table 3). The adsorption capacity of Leechi fruit peel was comparable or higher than those reported in the literature [39–47].

Dubinin and Radushkevich [48] have proposed another model that does not assume a homogeneous surface or constant sorption potential. It is applied to estimate the free energy change when one mole of ion is transferred from infinity in the solution to the surface of the adsorbent. The mean free energy (E) is used to predict the physical or chemical nature of the adsorption process. The D–R equation may be given as

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \tag{5}$$

where q_e is the adsorption capacity (mol g^{-1}) and q_m is the maximum adsorption capacity (mol g^{-1}), β is the activity coefficient constant, and ε is the Polyanyi potential which is given as:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{6}$$

where R is the gas constant (kJ mol^{-1}) and T is the temperature in Kelvin. C_e is the equilibrium concentration (mol L^{-1}). The values of q_m and β were be obtained from the intercept and slope of the linear plots of $\ln q_e$ vs. ε^2 at different temperatures. The mean free energy of adsorption E can be calculated from the following equation:

$$E = \frac{1}{\sqrt{(-2\beta)}} \tag{7}$$

The D–R parameters and mean free energy along with correlation coefficients (R^2) are given in Table 2. The values of E obtained were in the range 7.00–10.13 kJ mol^{-1} indicating that adsorption process was chemisorption in nature [49].

3.5. Thermodynamic studies

Thermodynamic parameters such as standard free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) change of adsorption can be evaluated from the following Eqs. (9) and (10). The temperature range used in this study was 30–50°C. The equilibrium constants (K_c) at 30, 40, and 50°C were calculated from the following relation [50]:

$$K_c = \frac{C_{AC}}{C_e} \tag{8}$$

where K_c is the equilibrium constant and C_{AC} and C_e (both in mg L^{-1}) are equilibrium concentrations for solute on the absorbent and in the solution respectively and T is the absolute temperature and R is gas constant. The K_c values obtained from Eq. (9) at different temperatures were used to determine ΔG°, ΔH°, and ΔS° by using the following relations.

$$\Delta G^\circ = -RT \ln K_c \tag{9}$$

$$\ln K_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{10}$$

ΔS° and ΔH° were calculated from the slope and intercept of linear plot of $\ln K_c$ vs. $1/T$ [50]. The values of K_c, ΔH°, ΔS° and ΔG° are reported in Table 4. The positive values of ΔH° indicated that process was endothermic, the negative values of ΔG° indicated the spontaneous nature of the process and more negative value with increase of temperature showed that an increase in temperature favored the adsorption process. The positive value of ΔS° suggested increased randomness at the solid–liquid interface during adsorption.

3.6. Adsorption kinetics

In order to analyze the adsorption rate, the kinetic data were modeled using Lagergren pseudo-first-

Table 4
Thermodynamic parameters for the adsorption of Cr(VI) at pH 2

Temperature (°C)	K_c	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1}K^{-1})	R^2
30	14.15	−6.67			
40	22.8	−8.14	21.88	0.0941	0.9884
50	32.33	−9.32			

Table 5
Kinetics parameters for adsorption of Cr(VI) on Leechi fruit peel

Concentration	Pseudo-first-order kinetics				Pseudo-second-order kinetics			
(mg L^{-1})	K_1 (min^{-1})	$q_{e(cal)}$ (mg g^{-1})	R^2	$q_{e(exp)}$ (mg g^{-1})	$q_{e(cal)}$ (mgg^{-1})	K_2 (g mg^{-1} min^{-1})	h (mg g^{-1} min^{-1})	R^2
10	0.060	0.17	0.9868	0.23	0.26	0.660	0.04	0.9852
20	0.060	0.19	0.9227	1.04	1.06	0.750	0.84	0.9996
50	0.070	1.28	0.9293	2.50	2.67	0.100	0.73	0.9983
60	0.014	3.41	0.9857	3.60	3.64	0.003	0.05	0.9357
80	0.010	4.49	0.9610	5.00	6.78	0.001	0.06	0.9078
100	0.008	5.38	0.9668	6.70	7.59	0.002	0.14	0.9915

order [51] and pseudo-second-order [52] equations. The pseudo-first-order expression is given by equation:

$$\log(q_e - q_t) = -\left(\frac{K_1}{2.323}\right) \times t + \log q_e \qquad (11)$$

where q_t and q_e are the amounts of Cr(VI) adsorbed (mg g^{-1}) at time t and at equilibrium respectively, and K_1 (min^{-1}) is the pseudo-first-order adsorption rate constant. Linear plots of log $(q_e - q_t)$ vs. t were observed at different initial Cr(VI) concentrations. The regression coefficients (R^2) and rate constants at various concentrations are reported in Table 5. The pseudo-second-order adsorption kinetics rate equation is given as:

$$\frac{t}{q_t} = \frac{1}{K_2 \times q_e^2} + \frac{1}{q_e} \times t \qquad (12)$$

where h is the initial adsorption rate (mg g^{-1} min^{-1}), which is given as $h = K_2 \times q_e^2 K_2$ (mg g^{-1} min^{-1}) is the adsorption rate constant for pseudo-second-order reaction. The values of K_2 were calculated from the slope of the linear plots of t/q_t vs. t. These values are reported in Table 5. A comparison of the experimental adsorption capacities ($q_{e(exp)}$) and calculated values ($q_{e\ (cal)}$) obtained from Eqs. (12) and (13) showed that pseudo-second order model was better obeyed than pseudo-first order.

3.7. Breakthrough capacity

Determination of breakthrough capacity is important in process design because it directly affects the feasibility and economics of the process [53]. It was found that 300 mL of Cr(VI) solution containing 50 mg L^{-1} Cr(VI) could be passed through the column without detecting Cr(VI) in the effluent. The breakthrough capacity and exhaustive capacities were found to be 30 and 50 mg g^{-1} respectively.

3.8. Removal of Cr(VI) from electroplating wastewater

The analysis of electroplating wastewater (Table 6) showed high concentration of Cr(VI). The wastewater was therefore diluted properly to bring down Cr(VI) concentration from 114 to 50 mg L^{-1} before treatment. 50 mL of this solution (pH = 2) was then treated separately with increasing adsorbent dose (0.2–1.0 g) for 24 h. it was found that 5 removal of Cr(VI) increased with increasing adsorbent dose and reached maximum (100%) at 6.0 g adsorbent dose (Fig. 6) there fore It can be concluded that 6 g adsorbent was sufficient to remove 100% Cr(VI) from electroplating wastewater.

Table 6
Analysis of electroplating wastewater (pH 5.6; temperature 40˚C)

Parameters	Concentration (mg L^{-1})
TDS	700.00
Cu(II)	1.50
Ni(II)	1.20
Cr(VI)	114.00

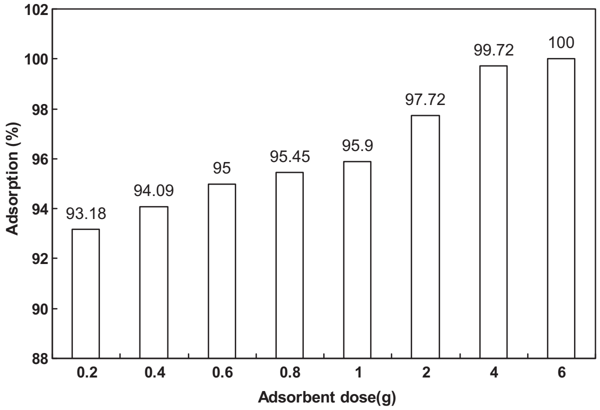

Fig. 6. Removal of Cr(VI) From electroplating wastewater by batch process (Cr(VI) conc = 50 mg/L; pH = 2; temp = 30˚C.

4. Conclusions

The present investigation showed that fruit peel of Leechi (*Litchi chinensis*) is an effective adsorbent for the removal of Cr(VI) from water and electroplating wastewater. The adsorption properties have been explored using batch process. The adsorption process was pH dependent and the optimum pH was 2.0. Thermodynamic parameters indicated endothermic and spontaneous nature of adsorption. The mean free energy value showed that adsorption was chemical in nature. Langmuir and Freundlich isotherm models were better obeyed at 40˚C as indicated by regression coefficient and chi-square test values. The kinetic data proved that pseudo-second-order kinetics was applicable model since q_e values calculated from the model were very close to q_e determined experimentally. The analytical applicability has been demonstrated by removing 100% Cr(VI) from electroplating wastewater by batch process hence fruit peel of Leechi could be utilized to reduce Cr(VI) concentration from electroplating wastewater before its disposal.

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List of symbols

AAS — atomic absorption spectrophotometer
AR Grade — analytical reagent grade
b — Langmuir constant for energy of adsorption (L/mg)
C_0 — initial concentration of adsorbate in the solute (mg/L)
C_e — equilibrium concentration of adsorbate in the solution (mg/L)
C_{Ae} — the amount adsorbed on solid at equilibrium (mg/L)
DDW — double distilled water
E — mean free energy (kJ/mol)
FTIR — Fourier Transform Infrared radiation
h — hours
K_f — Freundlich adsorption constant
K_1 — pseudo first-order rate constant (1/min)
K_2 — pseudo second-order rate constant (g/mg-min)
K_c — equilibrium constant
χ^2 — Chi-square Test
β — activity coefficient constant
n — Freundlich exponent
ε — polyaniyi potential
ΔG° — standard Gibb's free energy change (kJ/mol)
ΔS° — standard entropy change (kJ/mol-K)
ΔH° — standard enthalpy change (kJ/mol)
q_e — adsorption capacity (mg/g)
q_m — the maximum sorption capacity determined by the number of reactive sites in an ideal monolayer system (mg/g)
q_t — adsorbed amount at time t (mg/g)
$q_{e(exp)}$ — adsorption capacity determined experimentally (mg/g)
$q_{e(cal)}$ — adsorption capacity calculated from the model (mg/g)
R — Universal gas constant (8,314 J/mol K)
R_L — separation constant
R^2 — coefficient of determination
RSE — residual standard error
t — time (min)
T — absolute temperature (K)

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