

Sorption studies on removal of Cd²⁺ from the aqueous solution using fruit-peels of *Litchi chinensis* Sonn.

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ABSTRACT

In this work fruit-peel of *Litchi chinensis* have been used to remove Cd²⁺ ions from the aqueous medium. The untreated and alkali-treated peels were used to study different optimization factors and conduct isothermal, kinetic and thermal studies on the biosorption of Cd²⁺ ions. The optimum conditions found were pH 7, 100 rpm shaking speed, 50°C temperature and 20 min contact time with 0.1 g peel-powder in 200 ppm solution of Cd²⁺ ions. Linear, Langmuir, Freundlich and Temkin isotherms were applied. The maximum quantity of sorbed Cd²⁺ was 81.97 mg/g with alkali-treated *Litchi chinensis* fruit-peels and 77.52 mg/g was with untreated peels. The pseudo-second-order model was more applicable and predicted the process as chemisorption. Intraparticle and film diffusion mechanisms were controlling the rate of sorption. Thermodynamic studies revealed the process as physisorption contrary to the kinetic studies but the process can be treated as physicochemical in nature because the rates of reactions are not a good criterion for discriminating between physisorption and chemisorption processes. Scanning electron microscopy analysis showed a very porous surface of the fruit-peels of *Litchi chinensis* responsible for the maximum removal of Cd²⁺ ions. Boehm titration showed the phenolic group to be in abundance.

Keywords: *Litchi chinensis*; Cd²⁺; Langmuir isotherm; Pseudo-second-order; SEM/EDX; Physicochemical

1. Introduction

The heavy metals have always been of concern to environmental sustainability and human health. These heavy metals are industrially important but their exposure to life forms is ignored and not addressed seriously despite that many environmental organizations all over the world are continuously shedding light on the hazards related to these heavy metals. Many processes such as chemical precipitation, filtration, ion exchange, membrane technology, chemical oxidation-reduction etc. have been developed to remove heavy metal ions and other effluents from the wastewater, but these techniques are not efficient when metal concentrations are in

the range of 1–100 mg/dm³ [1–3]. These techniques are also complicated and costly so the industrialists are not much interested in the removal of effluents from the wastewater. The other problems related to these techniques are rigorous monitoring, sludge production and high energy consumption. So, a process that is efficient as well as cheap will make it easier for all the stakeholders to become agreed on solving this problem seriously. Biosorption is such a cost-effective technique in which live or dead plant, animal or microbial mass is used to remove the heavy metal ions, dyes and other effluents from the waste water [4,5].

Plant material is available in huge quantity so it can be used for the purpose of biosorptive removal of different

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pollutants. Different plant-based materials have been used in many studies for the removal of heavy metal ions such as Cd^{2+} , Cr^{3+} , Pb^{2+} , Ni^{2+} etc. In this work, we have used fruit-peels of *Litchi chinensis* for the sorptive removal of Cd^{2+} from the aqueous solution.

Cadmium comes into the aquatic environment through anthropogenic activities. The industries of batteries, paints and pigments, electroplating, plastics, mining and refining processes are responsible for the drain out of cadmium to the environment [6]. It is estimated that cadmium is being released at a rate of 22,000 metric tons per year to the environment [7]. WHO has recommended a limit of 3.0×10^{-6} mg/L in water. It is also a carcinogenic metal. It affects the kidneys and causes hypertension, anaemia, etc. It causes disturbance in calcium metabolism leading to kidney stones, softening of bones and osteoporosis. Its higher concentration causes Itai-itai disease. It also affects lungs causing acute pneumonitis with pulmonary edema and even lung cancer [8,9].

Litchi chinensis Sonn. belongs to soapberry family, *Sapindaceae*. Its fruit is edible and is harvested in China and in some parts of India, Bangladesh South East Asia, and Pakistan. Its fruit has many beneficial effects. The peel of its fruit has no specific use so it can be used as a biosorbent for the removal of pollutants. Its peels' and seeds' powder have been used for the removal of Cr^{3+} , Ni^{2+} , Pb^{2+} and Cu^{2+} ions from the aqueous media [10–13]. Litchi peels have been shown in Fig. 1.

2. Materials and methods

Fruit of *Litchi chinensis* was purchased from the local market of Lahore and the peels were separated, washed and dried under the sun. Then the dried peels were ground to powder in a grinder and 80 mesh powder was separated from the rest of the mass. This 80 mesh powder was then soaked in 0.1 M NaOH and rotated for an hour at 100 rpm speed. Then the filtrate was removed and the alkali-treated powder was washed with distilled water several times to remove the un-reacted base from the peel-powder. Then



Fig. 1. Dried peels of *Litchi chinensis*.

this powder was dried in an oven at 60°C and stored in an airtight bottle [14]. Alkali treatment was selected keeping in view the mercerization process in textiles in which the cellulosic fibers are treated with alkali to increase their dye adsorption efficiency.

All the chemicals were purchased from Sigma Aldrich. $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ was used to prepare 1,000 ppm stock solution of Cd^{2+} . Standard solutions from 1 to 10 ppm were prepared from 100 ppm solution. The calibration curve was plotted between the concentrations and the absorbance values which were taken from analyzer atomic absorption spectrophotometer by Perkin Elmer (USA). The Eqs. (1) and (2) were used in calculating the amount of metal adsorbed per gram (q_e) of the peel and percentage removal respectively.

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$\text{Percentage Removal} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

Here C_0 is the initial concentration of a metal ion in solution, C_e is the equilibrium concentration in solution, V is the volume of solution in dm^3 and m is mass of the Litchi-peels in grams.

Cary 360 FTIR Spectrometer by Agilent technologies (USA) was used for Fourier transform infrared spectroscopy (FTIR) study and Nova Nano scanning electron microscopy (SEM) 450 by Thermo Fisher Scientific (USA) was used in SEM analysis. The pH meter pH 211 by Hanna, orbital shaker by SkyLine Analog (Germany), Electric grinder by Kenwood (UK) and Balance ER-120A by AND were used in these studies.

3. Results and discussion

3.1. FTIR analysis

In the FTIR spectrum of untreated peels of *Litchi chinensis*, the broad peak at $3,310.7 \text{ cm}^{-1}$ was associated with O–H stretching vibrations of cellulose, hemicellulose, and lignin. This frequency was decreased after Cd^{2+} loading. The peak appearing at $2,920.4 \text{ cm}^{-1}$ was related to $-\text{CH}_2-$ stretching of alkanes. The frequency at $1,735.1 \text{ cm}^{-1}$ was related to C–O stretching of an ester group. This peak disappeared after alkali treatment in spectrum of alkali-treated (AT) Fruit Peels of *Litchi chinensis* FPLC. The medium peak at $1,397.1 \text{ cm}^{-1}$ was related to free O–H in-plane bending. The intensity and frequency of this peak were decreased after alkali treatment and metal loading. The peak at $1,013.8 \text{ cm}^{-1}$ corresponded to C–O stretching. This peak also disappeared after alkali treatment which might be due to the hydrolysis of the ester bond. The peak for the deformation of cellulose appeared at 894 cm^{-1} . This frequency decreased to 882 cm^{-1} in metal loaded FPLC. This study revealed that mainly carboxyl and hydroxyl groups were involved in metal ion binding [15].

3.2. SEM/EDX analysis

SEM analysis with Nova Nano SEM 450 showed a very porous structure of fruit-peels of *Litchi chinensis* as shown in

Fig. 2. SEM technique showed an etched surface of the alkali-treated peel as compared to that of the untreated peel. This etched surface area was due to the degradation of the surface with alkali which resulted in increased surface area. This porous structure with a large surface area and hollow spaces allowed the maximum removal of Cd^{2+} ions. Backscattered imaging (BSI) technique was used for greater contrast to detect the presence of Cd^{2+} adsorbed on the surface as bright spots as shown in Fig. 3. The energy-dispersive X-ray spectroscopy (EDX) analysis confirmed the adsorption of Cd^{2+} in the form of peaks as shown in Fig. 4.

3.3. Boehm titration

The Boehm titration was developed in 1994 by Hans Petre Boehm for the purpose of quantification of oxygen-containing functional groups on carbon black surface. The principle behind this is that a particular base neutralizes oxo-acids of a particular range of pKa values. It is considered that NaOH neutralizes phenolic, lactonic and carboxylic functional groups, Na_2CO_3 neutralizes both the lactonic and carboxylic groups while NaHCO_3 neutralizes only carboxylic group [16].

The standardized base solutions used were 0.05 M NaOH, 0.05 M NaHCO_3 and 0.05 M Na_2CO_3 along with 0.05 M HCl solution. Three samples of 0.25 g of the biosorbent were mixed with separate 25 ml of each base solution and kept rotating for 96 h at 100 rpm agitation speed. Then the filtrates of these mixtures were titrated with a standardized 0.05 M HCl solution. The blanks were also run and the amounts of the functional groups were calculated by the method of difference. The results given in Table 1 indicated that the phenolic content was abundant on the surface, making it more acidic in nature. The phenolic content in the solution increased due to the breaking down of cellulosic fibers after drying the peels under sun or heat treatment which resulted in setting free of phenols [17]. The pink color of the peels was also turned brown due to heating process [18]. The point of zero charge (PZC) for the untreated peels was also determined which was 6.1 as shown in Fig. 5.

3.4. Effect of pH

The pH factor is the most important factor which controls the sorption efficiency of the biosorbent due to surface modification. It was observed that with an increase in pH, there was an increase in percentage removal of Cd^{2+} ions. At lower pH due to competition with H^+ ions, the Cd^{2+} ions were not able to fully adsorb on the surface of the biosorbent. At higher pH due to neutralization and removal of

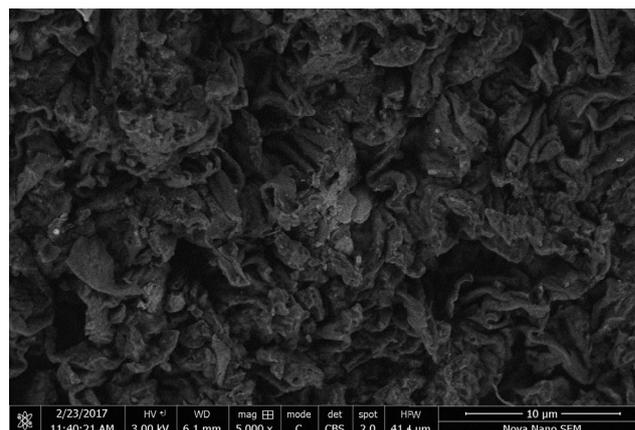


Fig. 3. SEM-BSI micrograph of Cd^{2+} adsorbed surface of FPLC.

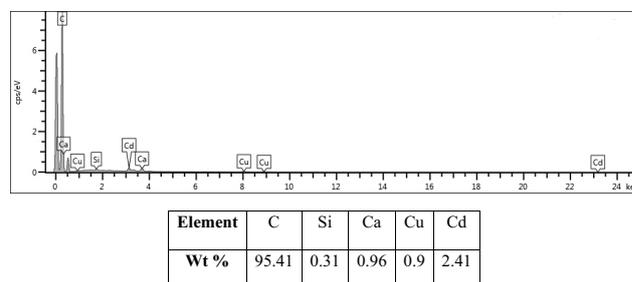


Fig. 4. EDX analysis of Cd^{2+} adsorbed on peel-surface of Litchi chinensis.

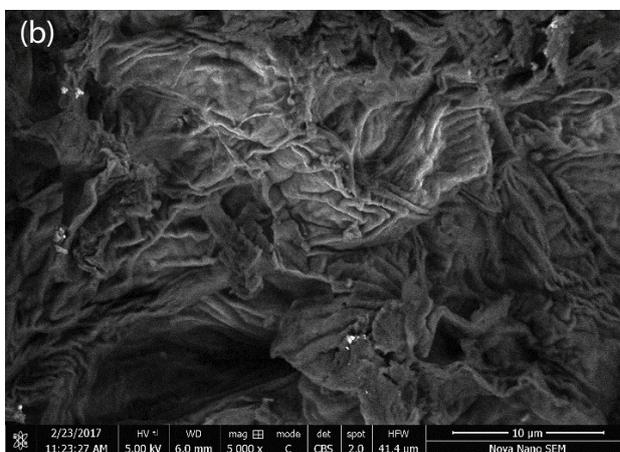
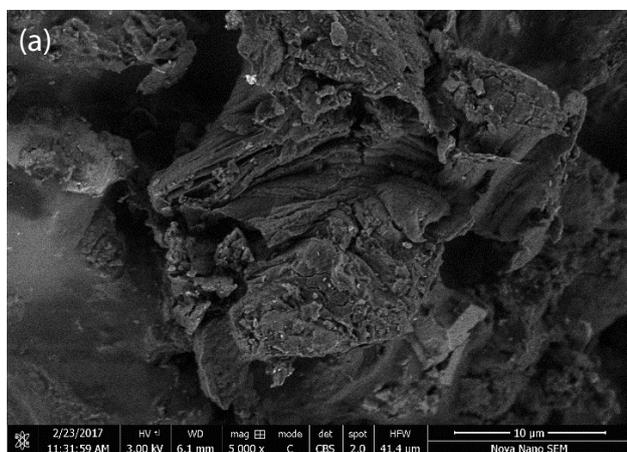


Fig. 2. SEM-BSI micrographs of untreated (a) and alkali-treated (b) FPLC.

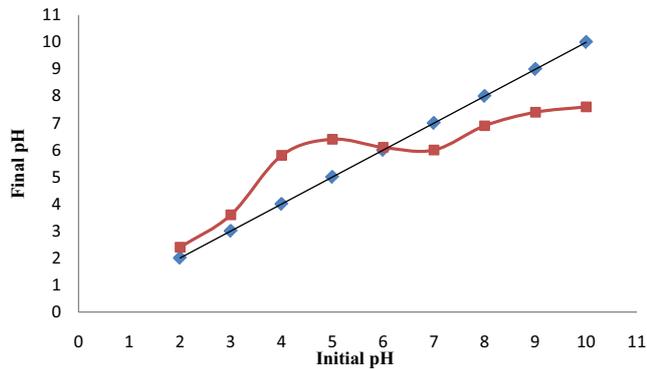


Fig. 5. PZC determined for the surface of fruit-peels of *Litchi chinensis*

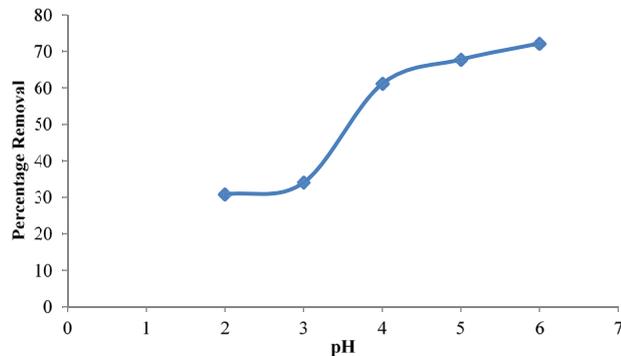


Fig. 6. Effect of pH on removal (%) of Cd^{2+} by AT FPLC.

acidic protons from the biosorbent surface, Cd^{2+} ions were able to be adsorbed on the surface of the peel-particle at a maximum amount. Maximum removal was 72.2% at pH 6 as shown in Fig. 6. This indicated the electrostatic attraction of Cd^{2+} ions with the surface functional groups and the possibility of ion exchange process [10,19]. The pH was not increased beyond the neutral pH due to precipitation of Cd^{2+} ions as hydroxide.

3.5. Effect of rotational speed

The rotational speed affected the number of contacts of peel-particles with Cd^{2+} ions. The percentage removal increased from 51% to 77% with an increase in rotational speed from 25 to 100 rpm due to overcoming the liquid-solid interface barrier as shown in Fig. 7. But on further increasing the speed, the percentage removal decreased due to dominance of shear forces over the adhesive forces. The weak interactions between the ions and the biosorbent surface vanished with an increase in rotational speed.

3.6. Effect of temperature

The temperature also plays a key role in the favourability of the sorption process. The interaction between the adsorbing species and the surface functional groups can be exothermic or endothermic. Temperature control can explain these interactions and the stability of the bonds. As the temperature was raised up to 50°C, percentage

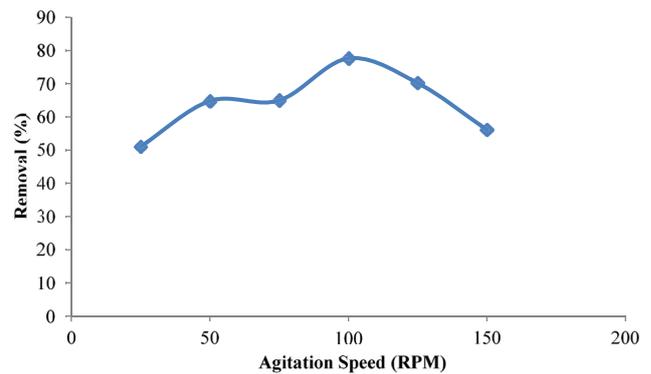


Fig. 7. Effect of rotation speed on removal (%) of Cd^{2+} by AT FPLC.

removal increased due to an increase in effective collisions as shown in Fig. 8. Then, it decreased at a higher temperature due to higher kinetic energies. Therefore, the ions were unable to make stable bonds with the surface functional groups.

3.7. Effect of biosorbent dosage

Biosorbent dosage is also a crucial factor that determines the sorption efficiency of a biosorbent. With an increase in the peels' dosage, the percentage removal increased. This happened due to an increase in surface area available for the sorption. As the dosage increased from 0.05 to 0.175 g; percentage removal also increased from 51% to 88% as shown in Fig. 9.

3.8. Effect of contact time

The contact time also demonstrates the efficiency of a biosorbent, the lesser the time required for maximum removal, greater is the efficiency of the biosorbent. It can be seen in Fig. 10 that the time required for maximum removal of 78.11% of Cd^{2+} with alkali-treated biosorbent was 20 min while in case of untreated peels, it took 25 min to remove 81.03% Cd^{2+} from the solution. At the initial stages, the alkali-treated peels removed a greater amount of Cd^{2+} as compared to untreated peels which made it a better biosorbent. The time factor is also important for studying kinetics of the sorption process.

3.9. Effect of initial concentration of Cd^{2+}

To study the effect of different initial concentrations of Cd^{2+} ; 50, 100, 150, 200 and 250 ppm solutions of Cd^{2+} were prepared. 0.05 g powder of 80 mesh size was used for each concentration. The rotational speed was 100 rpm, pH was around 6.7 and temperature was 30°C in studying the effect of initial concentration. It is shown in Fig. 11 that 99.78% maximum removal occurred with alkali-treated and 98.44% maximum removal occurred with the untreated peels using 50 ppm Cd^{2+} ion solution. With an increase in Cd^{2+} ion concentration, the percentage of removal decreased due to the availability of a limited number of active sites.

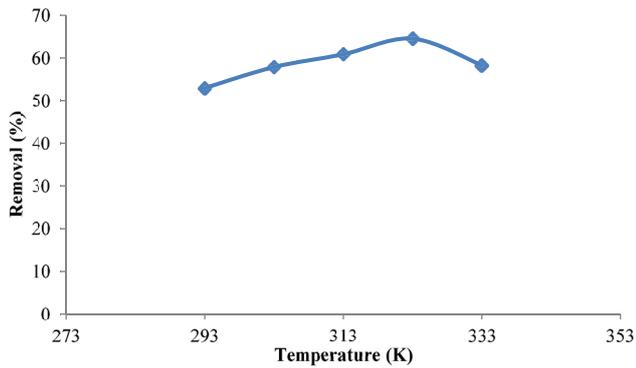


Fig. 8. Effect of temperature on removal (%) of Cd²⁺ by AT FPLC.

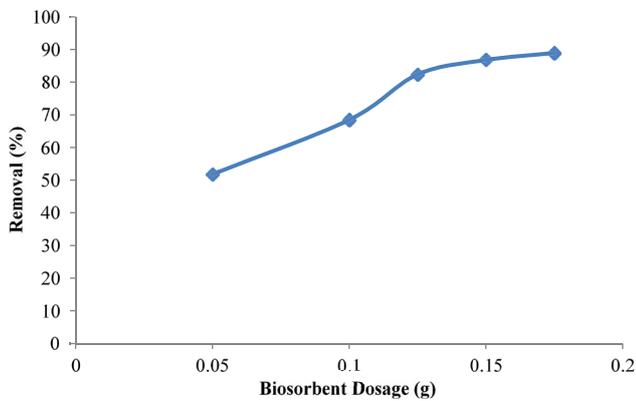


Fig. 9. Effect of biosorbent dosage on removal (%) of Cd²⁺ by AT FPLC.

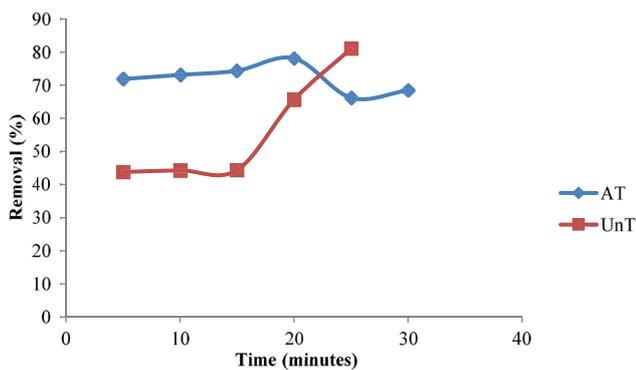


Fig. 10. Effect of contact time on removal (%) of Cd²⁺ by UnT and AT FPLC.

3.10. Isothermal studies

In isothermal studies, alkali-treated and untreated peel-powder of *Litchi chinensis* were used to ascertain on which surface the maximum amount of Cd²⁺ could be adsorbed. To study the adsorption behavior, different isothermal models have been proposed. These isotherms help in understanding the solute and surface interactions and nature and mechanism of the adsorption process. When the equilibrium is

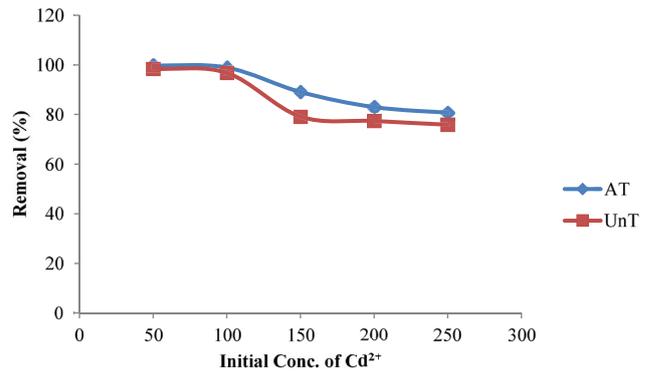


Fig. 11. Effect of initial conc. on removal (%) of Cd²⁺ by UnT and AT FPLC.

established between the two phases, the isotherm explains the distribution of sorbent on the sorbate. The common isothermal models of Langmuir, Freundlich and Temkin were applied. The linear isotherm was also possible as shown in Eq. (3) [20].

$$q_e = a + bC_e \quad (3)$$

Here q_e is the amount of Cd²⁺ adsorbed in mg/g on the biosorbent, C_e is the equilibrium concentration of Cd²⁺ in the solution while a and b are the constants. The linear relationship between q_e and C_e depicted that with increase in concentration of Cd²⁺ ions, the q_e value also increased linearly as shown in Fig. 12. The adsorption increased with increase in concentration due to availability of adsorbent sites.

The Langmuir isotherm assumes monolayer adsorption with thickness not more than one layer. It also assumes that there is no interaction among the adsorbed Cd²⁺ ions and the energy distribution on the surface is homogeneous [21]. The linear form of the Langmuir isotherm is shown as Eq. (4).

$$\frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m} \quad (4)$$

Here q_e represents the concentration of Cd²⁺ ions adsorbed in mg/g at equilibrium, C_e is the equilibrium concentration of Cd²⁺ in the solution, q_m represents the maximum amount of Cd²⁺ that can be adsorbed on the adsorbent in mg/g and K_L represents the Langmuir constant. A graph was plotted between $1/C_e$ and $1/q_e$ values representing the Langmuir isotherm as shown in Fig. 13. The maximum amount of Cd²⁺ adsorbed was 81.97 and 77.52 mg/g with alkali-treated and untreated peels respectively. Another factor which tells about the feasibility of the adsorption process is separation factor R_L . It was calculated by knowing the value of the Langmuir constant K_L using Eq. (5).

$$R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

If the value of $R_L = 1$ then the adsorption process is linear, if R_L value is $0 < R_L < 1$ then the process is favorable, if

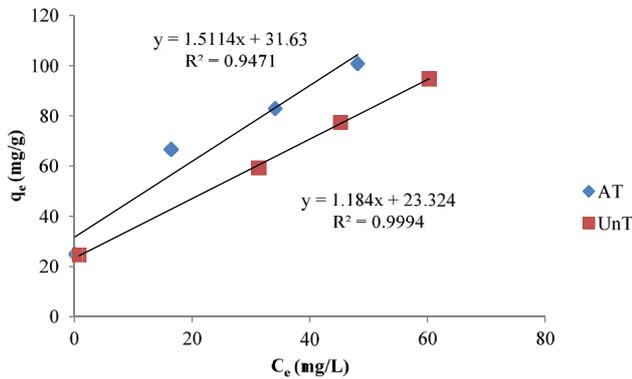


Fig. 12. Linear isotherms for the biosorption of Cd²⁺ by UnT and AT FPLC.

$R_L = 0$ then it is irreversible and if $R_L > 1$ then the process of adsorption is not favorable [22]. The values of the Langmuir isotherm parameters are shown in Table 2. In Table 3 a comparison has been shown of maximum quantities of Cd²⁺ absorbed by different biosorbents with q_m values of the untreated and alkali-treated peels of *Litchi chinensis*. It can be seen that litchi peels are more efficient than many other biosorbents in removing Cd²⁺ ions from water.

The Freundlich model, on the other hand, proposes a heterogeneous energy distribution with multilayered adsorption [23]. Mathematically it can be expressed as Eq. (6).

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (6)$$

A graph was plotted between $\log C_e$ and $\log q_e$ as shown in Fig. 14. Here q_e represents the equilibrium concentration of Cd²⁺ adsorbed on the surface, C_e represents the equilibrium concentration of Cd²⁺ in the solution while K_f and n are the constants. The value of n tells us about adsorption efficiency or heterogeneity. A value of n greater than 1 will support the heterogeneous energy distribution [24]. K_f shows the adsorption capacity or relative adsorption of Cd²⁺ at equilibrium. The values of these parameters are shown in Table 2.

Temkin isotherm is related to the heat of adsorption. This isotherm states that sorption energy decreases linearly with an increase in coverage of the surface [25]. This isotherm is applicable for intermediate-range of concentrations [26].

$$q_e = B \ln A + B \ln C_e \quad (7)$$

Where

$$B = \frac{RT}{b} \quad (8)$$

In Eqs. (7) and (8), q_e is the amount of cadmium adsorbed in mg/g, C_e is the equilibrium concentration of Cd²⁺ in the solution, T is the temperature in Kelvin, and R is ideal gas constant while A , B and b are the Temkin isotherm constants. B and b are related to the heat of adsorption. A graph was plotted between q_e and $\ln C_e$ as shown in Fig. 15. R^2 value was closer to 1.00 in the case of alkali-treated peels as compared

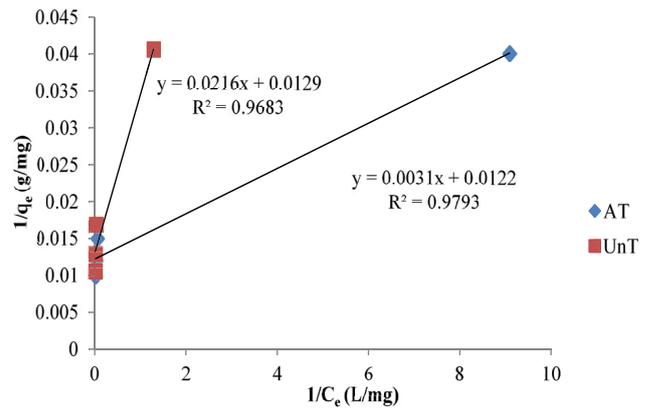


Fig. 13. Langmuir isotherms for the biosorption of Cd²⁺ by UnT and AT FPLC.

Table 1
Amounts of different oxygen-containing functional groups from Boehm titration

Functional group	Amount
Lactonic, mEq/g	0.05
Carboxylic, mEq/g	1.73
Phenolic, mEq/g	11.67

Table 2
Different isothermal parameters for the biosorption of Cd²⁺ by FPLC

Isotherm	Treatment	Linear
		Treated $b = 1.51 \text{ L/g}$ $R^2 = 0.947$ Untreated $b = 1.18 \text{ L/g}$ $R^2 = 0.999$
Langmuir	Treated	$q_{\max} = 81.97 \text{ mg/g}$ $K_L = 3.94 \text{ L/g}$ $R_L = 0.007\text{--}0.003$ $R^2 = 0.9797$
	Untreated	$q_{\max} = 77.52 \text{ mg/g}$ $K_L = 0.6 \text{ L/g}$ $R_L = 0.001\text{--}0.005$ $R^2 = 0.9683$
Freundlich	Treated	$K_f = 39.62 \text{ mg/g}$ $n = 4.6$ $R^2 = 0.9853$
	Untreated	$K_f = 25.86 \text{ mg/g}$ $n = 3.5$ $R^2 = 0.9618$
Temkin	Treated	$A = 73.36 \text{ L/g}$ $B = 10.95 \text{ J/mol}$ $R^2 = 0.9174$
	Untreated	$A = 6.61 \text{ L/g}$ $B = 13.73 \text{ J/mol}$ $R^2 = 0.8679$

Table 3
Comparison of sorption capacity of Cd²⁺ with some biosorbents reported in literature

Biosorbent	q _{max} (mg/g)	Reference
Banana peel	35.52	Memon et al. [27]
Sugarcane bagasse	14.80	Garg et al. [28]
Grapefruit peel	42.09	Torab-Mostaedi et al. [29]
Chemically modified (HNO ₃) wheat straw	3.833	Mahmood-ul-Hassan et al. [30]
Compost	7.15	Ahmad et al. [31]
Lentil husk	107.31	Basu et al. [32]
<i>Araucaria heterophylla</i>	9.25	Sarada et al. [33]
Modified <i>Auricularia Auricular</i> matrix waste	35.51	Song et al. [34]
Immobilized <i>Pleurotus ostreatus</i> spent substrate	100	Jin et al. [35]
Alkali treated <i>Litchi chinensis</i> peels	81.97	Present study

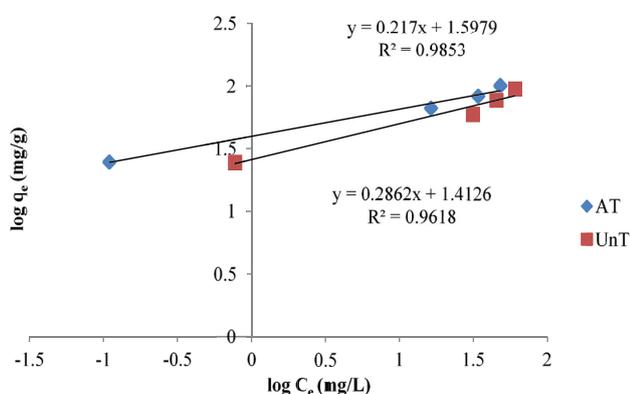


Fig. 14. Freundlich isotherms for the biosorption of Cd²⁺ by UnT and AT FPLC.

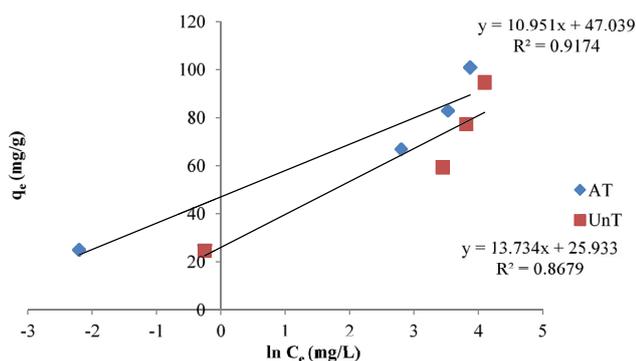


Fig. 15. Temkin isotherms for the biosorption of Cd²⁺ by UnT and AT FPLC.

to that of untreated peels. The values of the Temkin constants have been shown in Table 2.

3.11. Kinetic studies

The rate of sorption process was studied by pseudo-first-order and pseudo-second-order models and intraparticle diffusion and film diffusion models were used to

study the sorption mechanism. The pseudo-first-order, also known as Lagergen’s model, is shown as Eq. (9) [36].

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{9}$$

Here q_e represents the concentration of Cd²⁺ adsorbed at equilibrium, q_t shows the concentration of Cd²⁺ sorbed at any instant and k_1 is the pseudo-first-order rate constant. A linear graph was obtained between $\ln(q_e - q_t)$ against time t as shown in Fig. 16. R^2 value with alkali-treated peels was closer to 1.00 as compared to that with untreated peels. This model is applicable only for the initial stages and deviates at later stages.

The pseudo-second-order model in the adsorption process is also known as Ho’s model [37]. This model is applicable to the whole range of time. The linear form of this model is shown as Eq. (10).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{10}$$

Here q_e^2 represents the concentration of Cd²⁺ sorbed at equilibrium, q_t shows the concentration of Cd²⁺ sorbed at any instant and k_2 is pseudo-second-order rate constant. A linear graph was plotted between t/q_t and $1/q_e$ as shown in Fig. 17. The values of R^2 were greater than those of Lagergen’s model which shows the dominance of Ho’s model in applicability to the experimental data. Another thing that shows the dominance of Ho’s model is the agreement in experimental and model-calculated q_e values. It is evident from Table 4 that experimentally collected q_e values are closer to the theoretical values in both cases of treated and untreated fruit-peels as compared to q_e values calculated from the pseudo-first-order model. So, the pseudo-second-order model was more applicable which suggested chemisorption of Cd²⁺ ions on the peel-surface.

The intraparticle diffusion model tells us about the mechanism of the sorption process. It signifies the boundary layer and the mass transfer effect. The Weber–Morris form was used to inspect the intraparticle diffusion as shown in Eq. (11) [38].

$$q_t = K_{ip} t^{1/2} + C \tag{11}$$

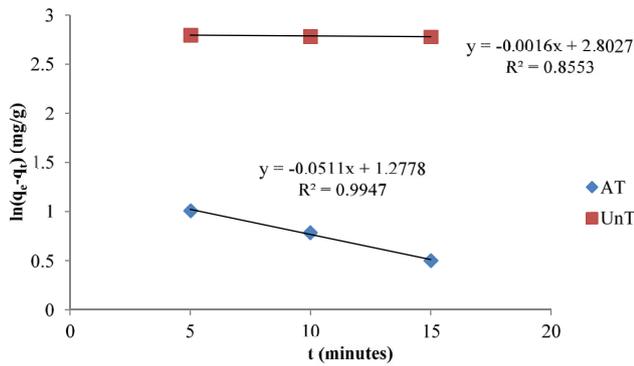


Fig. 16. Pseudo-first-order model for the biosorption of Cd²⁺ by UnT and AT FPLC.

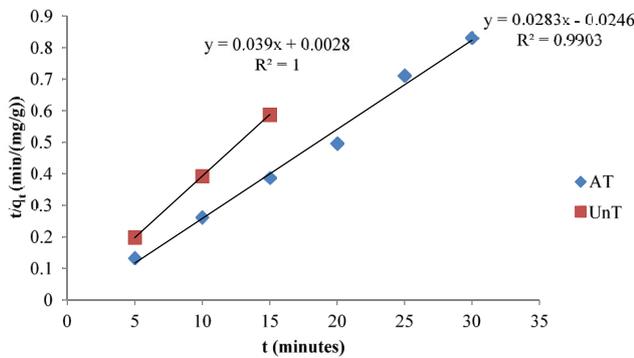


Fig. 17. Pseudo-second-order model for the biosorption of Cd²⁺ by UnT and AT FPLC.

Here q_t represents the quantity of Cd²⁺ adsorbed in mg/g at any instant, K_{ip} is intraparticle diffusion constant and C is the thickness of the boundary layer. The values of these parameters are shown in Table 4. If the graph between $t^{1/2}$ and q_t was a straight line passing through the origin then it could be following the Weber–Morris model. But in Fig. 18 multilinearity suggested that there were other factors also which controlled the sorption of Cd²⁺ ions instead of intraparticle diffusion alone. Multilinearity was more pronounced in the case of untreated fruit-peels of *Litchi chinensis*. The first linear part was related to mesoporous diffusion which was faster than the second linear portion which represented the macroporous diffusion [39].

The film diffusion model or Boyd’s model was also applied according to Eq. (12) [40]. According to this model, a film surrounding the particle controls the sorption process. Cd²⁺ ions diffuse from the film and enter into the particle through intraparticle or interparticle diffusion [41].

$$\ln(1 - F) = -K_{fd}t \quad (12)$$

Here F is fractional attainment in equilibrium and is equal to q_t/q_e . K_{fd} is the liquid film diffusion constant. A graph was plotted between $-\ln(1-F)$ and time t as shown in Fig. 19. In the case of untreated fruit-peels, it can be seen that R^2 value is closer to 1.00 as compared to that of the

Table 4

Different parameters of kinetic models of biosorption of Cd²⁺ by FPLC

Model	Parameter	Value
Pseudo-first-order	q_e (Exp)	38.72 mg/g
	q_e (Theor)	3.59 mg/g
	k_1	0.0511 min ⁻¹
	R^2	0.9947
Pseudo-second-order	q_e^2 (Exp)	38.72 mg/g
	q_e^2 (Theor)	35.33 mg/g
	k_2	0.03 g mg/min
	R^2	0.9867
Intraparticle diffusion	C	34.79 mg/g
	K_{ip}	1.14 mg/g/min ^{0.5}
	R^2	0.9
	C	8.90 mg/g
Film diffusion	K_{fd}	0.047 min ⁻¹
	R^2	0.805
	K_{fd}	0.024 min ⁻¹
	R^2	0.9415

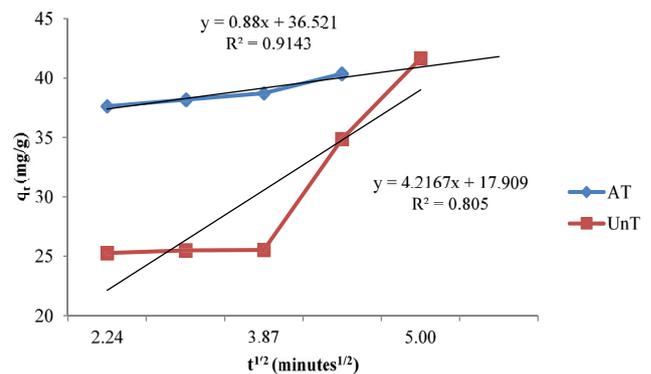


Fig. 18. Intraparticle diffusion model for biosorption of Cd²⁺ by UnT and AT FPLC.

intraparticle diffusion model which suggests that the film diffusion process is the main rate-controlling step in case of untreated peels. In the case of alkali-treated fruit-peels, the intraparticle diffusion process is dominant due to greater R^2 value. This difference in mechanisms in the case of untreated and alkali-treated peels can be related to surface modification with alkali treatment. Boyd’s model seems similar to Lagergen’s model but Boyd’s model also depends upon the

speed of agitation which helps in overcoming the boundary layer and mass transfer effects [42].

3.12. Thermodynamic studies

In temperature-controlled experiments, it was observed that the rate of Cd²⁺ adsorption increases with an increase in temperature. This showed the endothermic nature of the process. Eqs. (13)–(16) were employed in thermodynamic studies. A graph was plotted between ln K_d and 1/T representing Van't Hoff plot as shown in Fig. 20 and from the values of slope and intercept ΔH and ΔS were calculated. The values of ΔH and ΔG were positive and greater than –40 and –80 KJ mol⁻¹ respectively which indicated the endothermic and non-spontaneous nature of the process [43,44]. This pointed out physisorption or van der Waals

types of forces present between Cd²⁺ ions and the surface functional groups. Table 5 shows the calculated values of ΔG, ΔH and ΔS.

$$\ln K_d = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{13}$$

$$-\Delta G^\circ = -RT \ln K_d \tag{14}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{15}$$

where

$$K_d = \frac{C_e}{q_e} \tag{16}$$

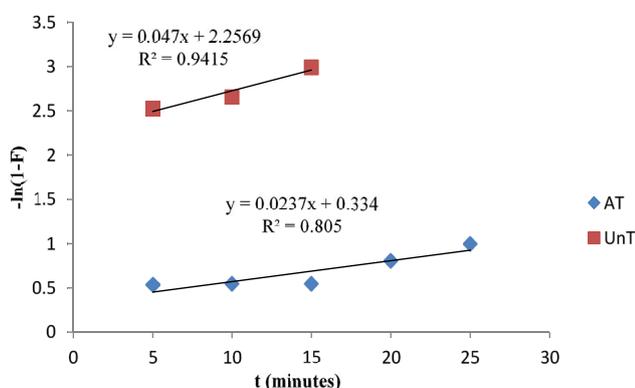


Fig. 19. Film diffusion model for biosorption of Cd²⁺ by UnT and AT FPLC.

Table 5
Different thermal parameters for the adsorption of Cd²⁺ on FPLC

ΔG (KJ/mol)					ΔG (KJ/mol)	ΔS (J/mol/K)
293 K	303 K	313 K	323 K	333 K		
2.81	2.51	2.21	1.90	1.60	11.37	30.25

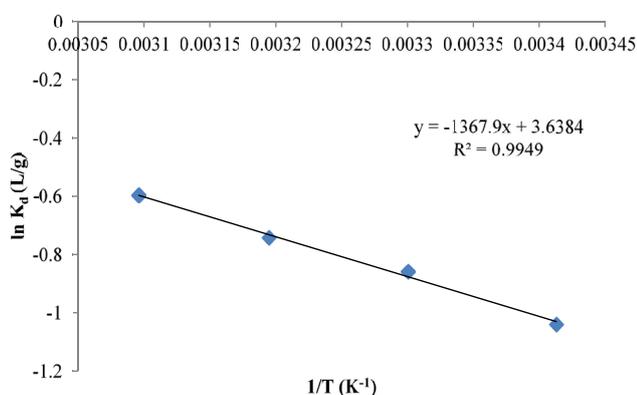


Fig. 20. Van't Hoff plot for the adsorption of Cd²⁺ on alkali-treated FPLC.

4. Conclusion

In this work, it was observed that fruit-peels of *Litchi chinensis* are a very efficient biosorbent in removing Cd²⁺ from the aqueous solution as compared to some other biosorbents reported in the literature. Different optimizing values of the factors such as pH, shaking speed, temperature, biosorbent dosage, and initial Cd²⁺ ion concentration were determined. Isothermal studies showed that linear isotherm was more dominant. Kinetic studies revealed the pseudo-second-order was more applicable which suggested the process as a chemisorption process. Both Intraparticle and Film diffusion mechanisms were involved in controlling the sorption of Cd²⁺. Thermal studies provided evidence that the sorption process was a non-spontaneous, endothermic and a physical process. Kinetic and thermal studies differ in concluding the process as a physical or a chemical process but it can be considered as a physicochemical process as the rates of reactions are not a good criterion of distinguishing the physical or chemical nature of the process [45].

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