



Cadmium(II) removal from aqueous solution using a novel magnetic nanoparticle impregnated onto *Citrus hystrix* leaves

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ABSTRACT

The Cd(II) adsorption capacity of magnetic nanoparticle loaded activated carbon synthesized from *Citrus hystrix* leaves (MCHLAC), which is a novel agricultural waste material, was evaluated regarding contact time, pH, adsorbent dose, and temperature during batch adsorption process with raw material (*Citrus hystrix* leaves (CHL)). The optimum contact time and pH for the adsorption of cadmium(II) ions onto CHL and MCHLAC were found to be 120 min and 4.0–7.0. The functionality, textural, surface morphology, and elemental analysis of the CHL and MCHLAC before and after the adsorption were characterized by Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscope, and energy dispersive X-ray analysis. The experimental data were analyzed using the Freundlich, Langmuir, Temkin, and Dubinin–Radushkevich adsorption isotherm equations using nonlinear regression analysis. The equilibrium data agreed well with the Langmuir model, which confirmed the monolayer coverage of cadmium(II) ions. Based on Langmuir isotherm the adsorption capacity was found to be 257.45 mg g⁻¹ for MCHLAC which was significantly 4.4 times greater than that of CHL (58.75 mg g⁻¹) at 300 K. The thermodynamic parameters indicated that the adsorption process was spontaneous and exothermic in nature. The kinetic data followed by the pseudo-second-order model with a film diffusion process. The spent adsorbent was regenerated and recycled by batch mode process over five cycles of operation and MCHLAC showed a better result than CHL.

Keywords: Cadmium(II); Isotherm; *Citrus hystrix* leaves

1. Introduction

Water is one of the essential requirements for life. Water is used for a variety of purposes, including drinking, food preparation, irrigation, and manufacturing. Industries are a major source of water pollution and it produces heavy metals

that are extremely harmful to people and the environment. Cadmium is one of the toxic heavy metals and released into the environment by electroplating, alloy manufacturing, smelting, pigments, battery, plastics, mining, and refining processes [1]. Acute poisoning of cadmium causes flu-like symptoms and can damage the lungs. Chronic exposure

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results in kidney, bone, and lung disease. According to World Health Organization (WHO) has been recommended the maximum permissible level of cadmium in drinking water is 0.005 mg L^{-1} . Therefore, the cadmium contaminated wastewater should be properly treated prior to their discharge into receiving water bodies.

A variety of technologies have been developed to remove cadmium(II) ions from an aqueous solution such as ion exchange, membrane process, chemical precipitation, electrochemical treatment, and reverse osmosis. However, most of these above technologies are sometimes restricted owing to technical or economical constraints [2]. Nowadays, researchers have been focused a new technology like adsorption is one of the most promising approach for the removal of metallic pollutants from wastewater.

Many researchers reported that a low cost and high efficiency of adsorbent prepared from several raw and chemically modified different types of agricultural waste such as bamboo charcoal [3], olive stone wastes [4], *Leucaena leucocephala* biomass [5], Brewery spent barley husk [6], Cherry kernel [7], Olive fruit stone [8], and *Albizialebeck* pods [9] have been successfully applied for the removal of cadmium(II) ions from aqueous solution. However, separation of these adsorbents from wastewater is a nontrivial task due to their low specific gravity and tendency to agglomerate. Hence, scientists have been explored a magnetic separation is a convenient technique in which separation of solid particles from the suspension can be achieved by the application of an external magnetic field. This technique has recently gained prominence in the water treatment process and is now recognized as a prospective technique for resolving the aforementioned issues [10]. However, little work has been done on the preparation of magnetic adsorbents based directly on agricultural waste for application to the removal of heavy metals from aqueous solution.

The aim of the present research is to prepare Fe_3O_4 magnetic nanoparticles loaded activated carbon are prepared from the *Citrus hystrix* leaves to develop a new magnetic adsorbent (MCHLAC) and evaluated with raw *C. hystrix* leaves for the removal of cadmium(II) ions from aqueous solution and wastewater. The synthesized magnetic adsorbents were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray analysis (EDX). The adsorption capacity of *C. hystrix* leaves (CHL) and MCHLAC for Cd(II) ions are investigated by assessing the impact of contact time, pH, adsorbent dose, and temperature using batch experiment. The adsorption isotherms, kinetics, and thermodynamic parameters for the adsorption Cd(II) ions onto CHL and MCHLAC are also determined in order to estimate the adsorption process. The suitability of adsorbent at field conditions was checked by collecting the wastewater sample from nearby industrial areas in Perundurai.

2. Materials and methods

2.1. Reagents

The stock solution containing $1,000 \text{ mg L}^{-1}$ of cadmium(II) was prepared by dissolving 2.282 g of cadmium sulfate in 1,000 mL distilled water. The stock solutions are

used to dilute the preparation of the desired concentration of cadmium(II) solution. The real cadmium electroplating wastewater was collected from Perundurai in Erode district, Tamilnadu.

2.2. Synthesis of raw *C. hystrix* leaves

C. hystrix leaves were collected from Gnanamani Educational Institutions campus, Namakkal, Tamil Nadu, India, and washed thoroughly with deionized water to remove dust particles and other impurities. The materials were dried in a hot air oven at 100°C for 8 h and crushed into powder and stored in a bottle.

2.3. Synthesis of magnetic *C. hystrix* leaves based activated carbon

About, 12 g of anhydrous ferric chloride (FeCl_3) and 6 g of hydrated ferrous chloride ($\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$) were dissolved in 200 mL of distilled water with vigorous stirring at 80°C for 30 min. Then 10 g of powered *C. hystrix* leaves were added and the mixture was stirred for 1 h. Then 20 mL of 25% NaOH solution was added in drop wise and stirring was continued until the black-colored precipitate was obtained. The precipitate was filtered and dried at 100°C for 12 h. The resultant impregnated samples were activated at 450°C for 3 h in a muffle furnace. After cooling, the activated sample were washed with deionized water until the pH of the filtrate was about 6–7, and dried in a hot air oven for 6 h at 110°C . The obtained samples were named as magnetic *C. hystrix* leaves based activated carbon (MCHLAC) and stored in a bottle then used for further experiments.

2.4. Batch mode adsorption experiments

Batch adsorption studies have been carried out in plastic bottles of 300 ml capacity containing 100 mL of 20 mg L^{-1} initial cadmium(II) concentration and 0.1 g of adsorbent at pH 7.0. Then the reaction mixture was shaken in a temperature controlled shaker at a constant speed of 200 rpm at room temperature for varying time intervals. The influence of solution pH was identified and the pH of the solution was adjusted to the required value by using 0.1 N of HCl/NaOH solutions. The isotherm studies were carried out by varying the initial Cd(II) concentrations of $10\text{--}60 \text{ mg L}^{-1}$ at 27°C , 37°C , and 47°C . The kinetic studies were conducted for various Cd(II) concentrations in the range of 5, 10, 20, and 30 mg L^{-1} at an optimum pH and at room temperature. Each experiment was repeated for three times, and the average results are taken in this work.

At the end of equilibrium time, the solution was centrifuged, filtered, and the amount of Cd(II) concentrations were obtained by an atomic absorption spectrophotometer (Elico Model-SL 163). The cadmium(II) removal percentage and adsorption capacity was estimated by using the following Eqs. (1) and (2):

$$\% \text{ Removal of cadmium} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$\text{Adsorption capacity } (q_e) = \frac{C_0 - C_e}{M} \times V \quad (2)$$

where C_e and C_0 are the equilibrium and initial concentrations of Cd(II) (mg L^{-1}); V is the volume of Cd(II) solution (L); M is the mass of the adsorbent used (g); q_e is the adsorption capacity at equilibrium (mg g^{-1}), respectively.

3. Results and discussion

3.1. Fourier transform infrared spectroscopy

The FTIR spectroscopy is an important tool for the identification of various functional groups associated with the surface of the adsorbent. The FTIR spectrum of CHL and MCHLAC before and after the adsorption of cadmium(II) ions are shown in Figs. 1a–d and their corresponding data are presented in Table 1. The bands within the range of $3,448\text{--}3,474\text{ cm}^{-1}$ correspond to OH group (alcohols, phenols, and carboxylic acids) which is responsible for the metal binding process [11]. The peak at about the range of $2,926\text{--}2,846\text{ cm}^{-1}$ indicates the aliphatic C–H groups [12]. The peaks observed at $1,701\text{--}1,744\text{ cm}^{-1}$ could be assigned the C=O stretching vibration of carboxyl groups [13]. The presence of Fe–O group in MCHLAC was observed at a frequency range of 551.64 cm^{-1} [14]. The FTIR spectrum of cadmium(II) ions loaded CHL and MCHLAC showed that the peak values are shifted slightly from their original position and their intensity are also changed. From the above results clearly indicated that the hydroxyl and carboxylic acid groups in CHL, in addition to that Fe–O groups are present in MCHLAC, which is responsible for the adsorption of cadmium(II) ions from aqueous solutions.

3.2. Scanning electron microscopy and energy dispersive X-ray spectroscopy studies

The surface morphology and the adsorption of metal ions were confirmed by SEM and EDX. SEM images of CHL and MCHLAC before and after the adsorption of cadmium(II) ions are shown in Figs. 2a–d. The SEM image indicates that the surface of CHL and MCHLAC is relatively smooth and contains many pores. It shows very distinguished dark spots that can be taken as a sign for effective adsorption of cadmium(II) ions in the cavities and pores of these adsorbent.

EDX analysis of the CHL and MCHLAC before and after the adsorption of cadmium(II) ion is shown in Figs. 3a–d. The elemental analysis of the CHL and MCHLAC surface is determined by EDX showed that the presence of Ca and Fe (Fig. 3c) are considered to be an effective binding adsorption sites. According to the EDX result in Fig. 3d shows that after the adsorption Cd(II) ions, the Ca and Fe elements containing peaks are disappeared and are replaced by cadmium(II) on the surface CHL and MCHLAC (Figs. 3b and d).

3.3. XRD analysis

Fig. 4 shows that the XRD pattern for the adsorbents such as CHL and MCHLAC before and after the adsorption of cadmium(II) ions. The well-defined peaks present in both adsorbent were examined by XRD analysis shows that the crystalline phase of carbon. This crystalline nature of the

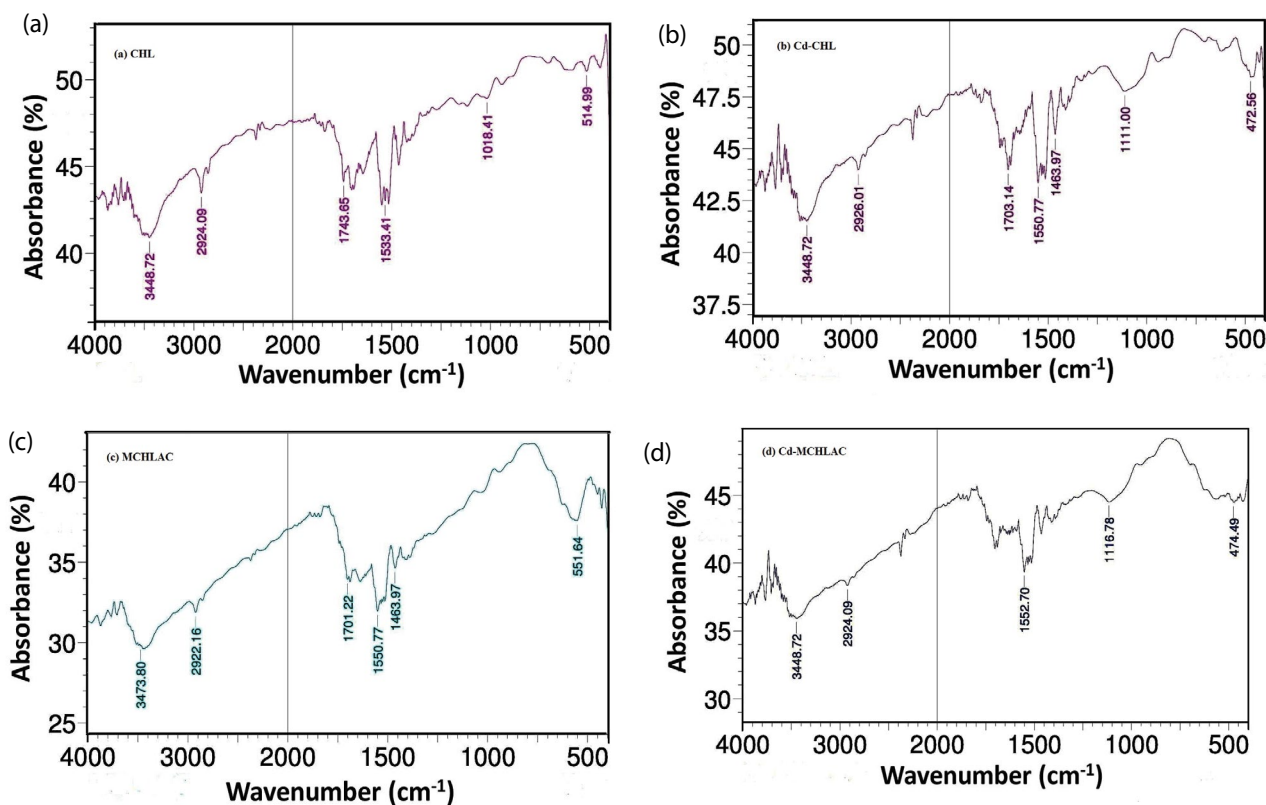


Fig. 1. (a–d) FT-IR image of CHL and MCHLAC before and after the adsorption of cadmium(II) ions.

Table 1
FTIR spectra of absorption band and corresponding functional groups on CHL and MCHLAC before and after the adsorption of Cd(II) ions

CHL		MCHLAC		Corresponding functional groups
Before adsorption	After adsorption	Before adsorption	After adsorption	
3,448.72	3,448.72	3,473.80	3,448.72	Bonded –OH groups
2,924.09	2,926.01	2,925.16	2,924.09	CH ₂ stretching vibrations
1,743.65	1,703.14	1,701.22	Disappear	C=O stretching in carboxylic acid group
1,533.41	1,550.77	1,550.77	1,552.70	C=C stretching (aromatic)
1,457.78	1,463.97	1,463.97	1,465.78	C–H groups in the plane deformation (CH ₃ , CH ₂ , and OCH ₃ groups)
1,018.41	1,111.00	Disappear	1,116.8	C–O stretching (alcohol)
514.99	472.56	–	–	C–H bending (aromatic)
–	–	551.64	474.49	Fe–O group

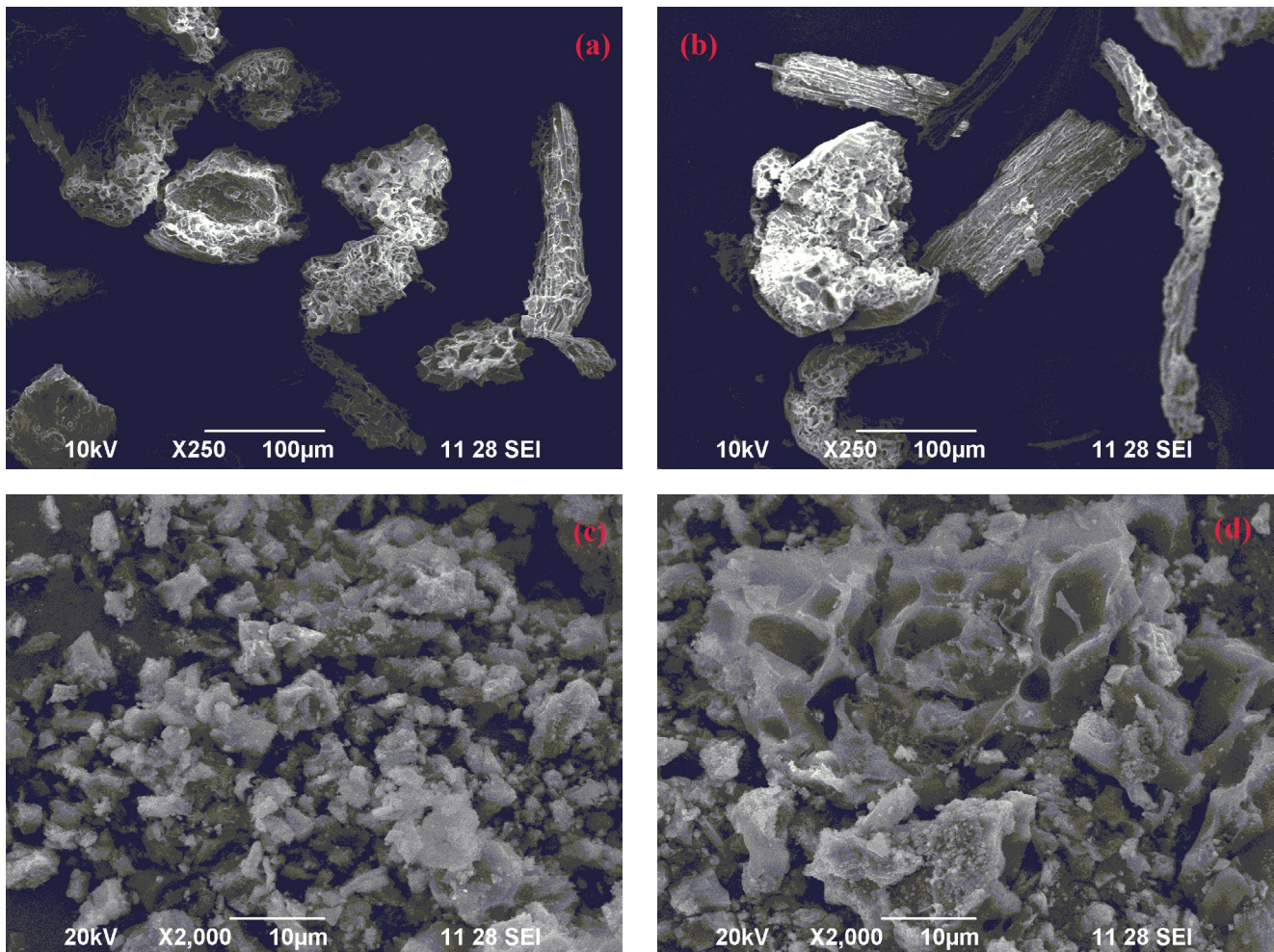


Fig. 2. (a–d) SEM micrographs of CHL and MCHLAC before and after the adsorption of cadmium(II) ions.

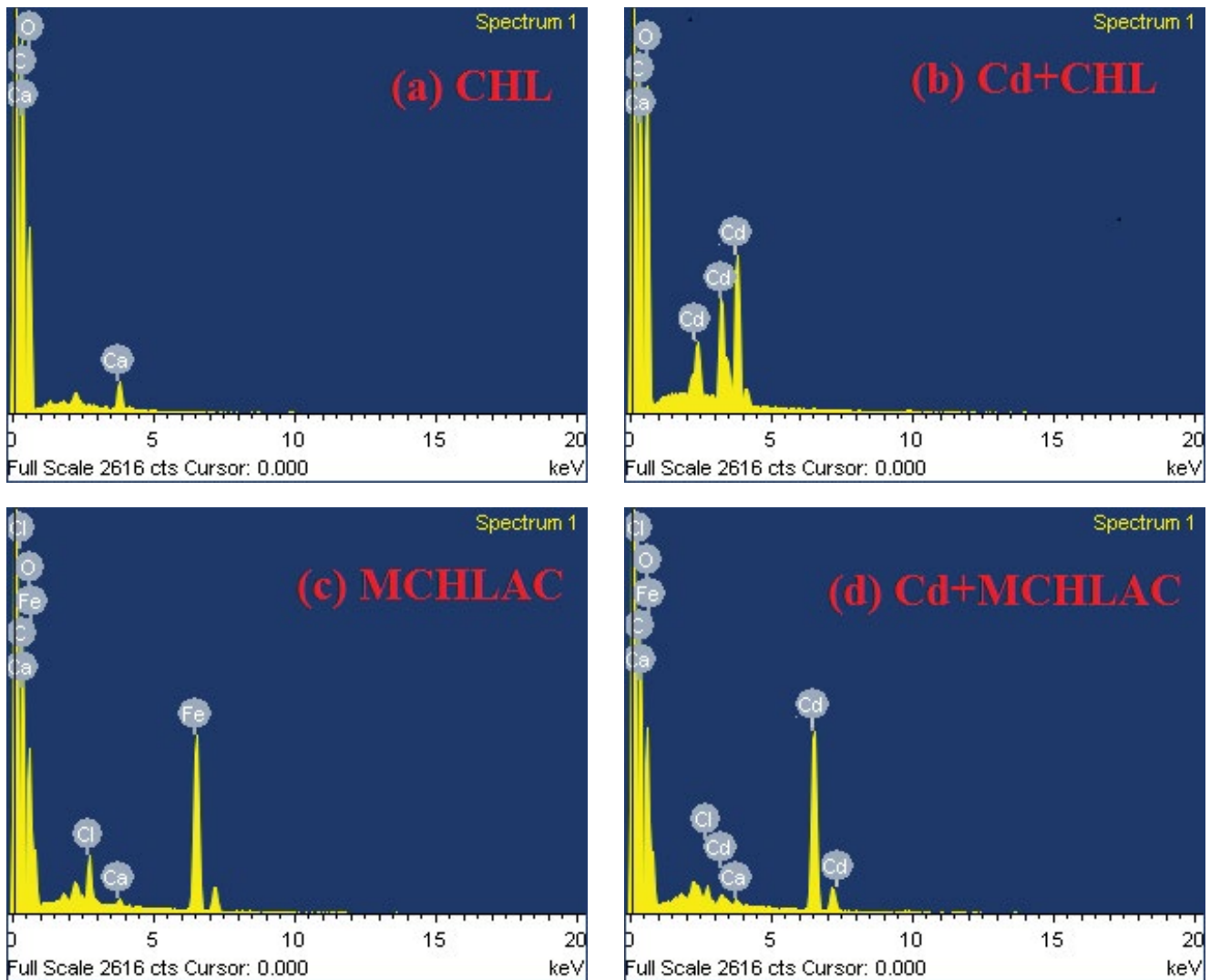


Fig. 3. (a–d) EDX image of CHL and MCHLAC before and after the adsorption of cadmium(II) ions.

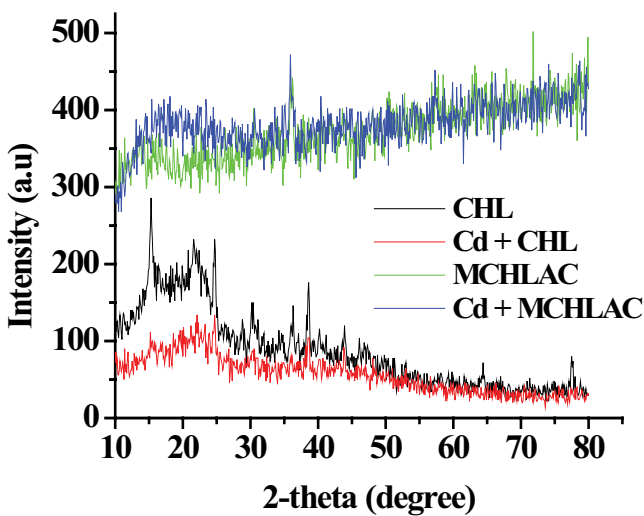


Fig. 4. XRD patterns for CHL and MCHLAC before and after the adsorption of Cd(II) ions.

beads are facilitated to more effective for the adsorption cadmium(II) ions.

3.4. Effect of agitation time and initial metal ion concentration

The equilibrium time is one of the important parameters for economical wastewater treatment applications. Fig. 5 shows the effects of agitation time on the adsorption of Cd(II) ions by CHL and MCHLAC at various metal ion concentrations using pH 7.0 and at constant adsorbent dose of 0.1 g L⁻¹. The results obtained from Fig. 5 reveal that the removal of cadmium(II) ions increased rapidly over time and attaining equilibrium for 120 min for both CHL and MCHLAC. The rate of adsorption is higher at the initial stage; due to the larger number of adsorption sites are present in the CHL and MCHLAC. Therefore, the optimum contact time was taken as 120 min for the subsequent experiments. Furthermore, the removal of cadmium(II) ions is decreased with increasing the metal ion concentrations is due to more number of Cd²⁺ ion is available at the

higher initial concentration which in turn may have provided higher driving force is supplied for the metal ions from the solution to the sorbents.

3.5. Effect of solution pH

The pH of the solution has been recognized as the most important parameter which influences the adsorption process as well as it affects the surface of the adsorbent and the degree of ionization of the cadmium(II) ions present in the solution. The effect of pH on the removal of 100 mL of 20 mg L⁻¹ cadmium(II) ions by CHL and MCHLAC were studied over the pH range of 3.0–11.0, while maintaining all other parameters are constant. From the Fig. 6 clearly shows that the percentage removal of cadmium(II) increases with increasing pH and attained the maximum percentage adsorption of 55% ± 0.4% and 99% ± 0.5% for CHL and MCHLAC at pH 5.0–7.0 and 4.0–8.0, respectively. At low pH values, the uptake of Cd²⁺ is decreased because the adsorbent surface may become highly protonated due to the presence of H⁺ ions which started competing with positively charged cationic cadmium(II) ions for the adsorption sites. The possible sorption mechanism that may takes place at different pH condition represented as follows:

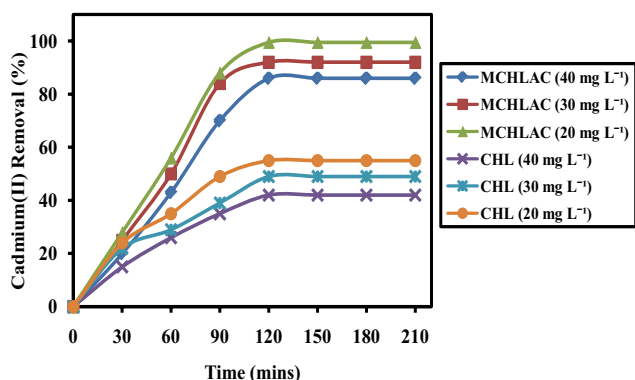


Fig. 5. Effect of contact time for the removal of cadmium(II) onto CHL and MCHLAC at different cadmium(II) concentrations.

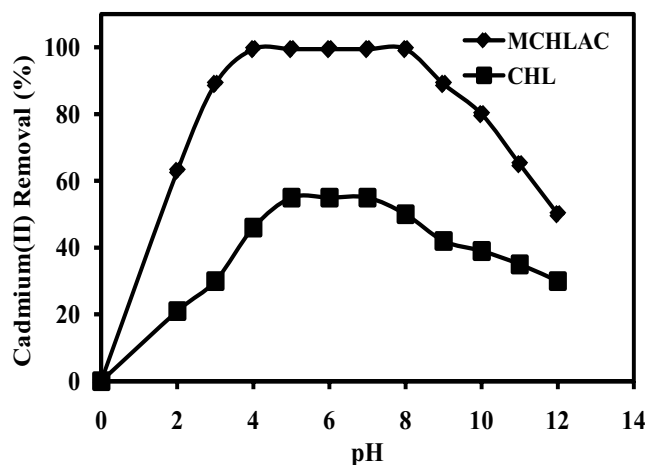
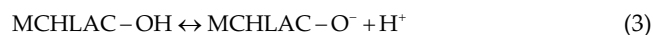


Fig. 6. Effect of pH for the removal of cadmium(II) onto CHL and MCHLAC.



At higher pH, the surface of the adsorbents acquires negative charge due to the dissociation of surface functional group and thereby causing repulsions to the negatively charged adsorbate species namely Cd(OH)₃⁻ and Cd(OH)₄²⁻ and hence, the removal of cadmium(II) is less favored. In the intermediate pH, it was found that the number of H⁺ ions is decreased and the surface of magnetic *C. hystrix* leaves based activated carbon (MCHLAC) becomes negatively charged and favors the sorption of positively charged metal ion due to electrostatic force of attraction [15].

3.6. Effect of adsorbent dose

Adsorbent dose is an essential parameter for the determination of adsorption capacity of the adsorbent for the extraction of polluted ions from the wastewater. The number of available sites and exchanging ions for the adsorption depends upon the amount of adsorbent in the adsorption process [16]. The effect of the CHL and MCHLAC dose on the removal of cadmium(II) ions are shown in Fig. 7. It could be observed from Fig. 7 that initially the removal of metal ion increases very sharply with the increase in adsorbent dose but after a certain value (0.3 g/100 mL for CHL and 0.1 g/100 mL for MCHLAC) the removal was found to be almost constant. It is evident that 100 mL of cadmium(II) solution containing 20 mg L⁻¹ of cadmium(II) ions, a minimum adsorbent dose of 0.1 g MCHLAC is required for the maximum removal of 99.6% ± 0.5% and in the case of CHL, 0.3 g is required for the removal of 80% ± 0.4% only. The data clearly indicate that MCHLAC is nearly 3.0 times more effective than CHL and this may be due to moderate ion-exchange capacity exhibited by MCHLAC as compared to CHL.

3.7. Adsorption isotherms

The equilibrium data is a vital piece of information to design a particular adsorption process. At equilibrium

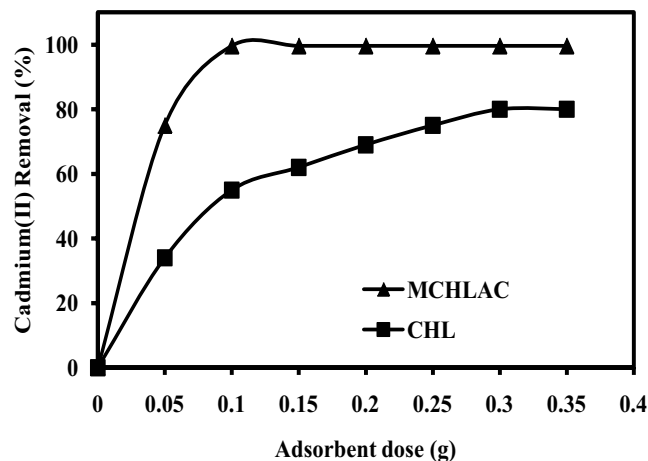


Fig. 7. Effect of adsorbent dose for the removal of cadmium(II) onto CHL and MCHLAC.

condition, the chemical potential of the solute in liquid phase is equal to that in solid phase. The equilibrium data for the adsorption of cadmium(II) ions onto CHL and MCHLAC were correlated by applying the nonlinear forms of four different isotherm equation such as Freundlich, Langmuir, Temkin, and Dubinin–Radushkevich at different temperatures (27°C–47°C) using MATLAB R2010b.

The Freundlich adsorption isotherm is a commonly used an empirical equation and is applicable to assume the formation of multilayer of adsorbates on the adsorbent's surface and is expressed as follows [17]:

$$q_e = K_F C_e^{1/n} \quad (5)$$

where K_F is the Freundlich constant ((mg g⁻¹) (L mg⁻¹)^(1/n)) related to the bonding energy and n (g L⁻¹) is a measure of the deviation from linearity of adsorption. The n value indicates the degree of non-linearity between solution concentration and adsorption as follows: if $n = 1$, adsorption is linear; if $n < 1$, adsorption is a chemical process; if $n > 1$, adsorption is a physical process.

The Langmuir adsorption isotherm model is based on monolayer adsorption onto a homogeneous structure without any reaction between the adsorbed molecules and is represented as follows [18]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (6)$$

where q_m (mg g⁻¹) is the maximum monolayer adsorption capacity, and K_L (L mg⁻¹) Langmuir constant relating to adsorption energy. The essential characteristics of the Langmuir isotherm parameters can be expressed to predict the affinity between the sorbate and sorbent using dimensionless equilibrium parameter, " R_L " expressed as in the following equation [19]:

$$R_L = \frac{1}{1 + K_L C_0} \quad (7)$$

where K_L is the Langmuir sorption constant and C_0 is the initial Cd(II) ion concentration. Adsorption is favorable when the value of R_L is between 0 and 1. The value of R_L classifies the isotherm to be either irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$).

The Temkin isotherm assumes linear rather than logarithm decrease of heat of adsorption while ignoring extremely low and very high concentration and applied in the following form [20]:

$$q_e = B \ln(AC_e) \quad (8)$$

where A (L mg⁻¹) is the equilibrium binding constant that corresponds to the maximum binding energy, B is a constant related to the heat of adsorption (kJ mol⁻¹).

Dubinin–Radushkevich (D–R) model assumes that the heterogeneous surface of the adsorbent and used to identify the nature of the adsorption process and expressed mathematically by the following equation [21]:

$$q_e = q_{mD} e^{-\beta \epsilon^2} \quad (9)$$

where q_{mD} (mg g⁻¹) is the Dubinin–Radushkevich monolayer capacity, β is a constant related to sorption energy, and ϵ is the Polanyi potential which is related to the equilibrium concentration as follows [22]:

$$\epsilon = RT \ln \left[1 + \frac{1}{C_e} \right] \quad (10)$$

where R is the gas constant (8.314 J mol⁻¹ K) and T is the absolute temperature. The constant β is the activity coefficient useful to calculate the mean adsorption free energy E , and expressed as follows:

$$E = \left[\frac{1}{\sqrt{2\beta}} \right] \quad (11)$$

The magnitude of E is used to determine the type of adsorption mechanism. If E value is lesser than 8 kJ mol⁻¹, the adsorption is regarded as physical in nature [23]. The value of E lies between 8 and 16 kJ mol⁻¹, indicates the adsorption process follows ion-exchange [24], while its value in the range of 20–40 kJ mol⁻¹ indicates chemisorptions [25].

The result of the isotherm constants such as correlation coefficients (R^2), sum of squares error (SSE), and root mean squared error (RMSE) values were calculated from the plot of q_e vs. C_e (Figs. 8a and b) and are represented in Table 2. As summarized in Table 2, results shows that the better fitting of the data by the Langmuir model compared with other three isotherm models based on the greater R^2 values and small SSE, RMSE values. This observation confirms the homogeneous monolayer coverage of cadmium(II) ions onto CHL and MCHLAC. The maximum monolayer adsorption capacity of Cd(II) ions onto MCHLAC was found to be 257.45 mg g⁻¹, which was about 4.4 times greater than that of CHL (58.75 mg g⁻¹). The R_L values for the Langmuir isotherm fall between 0 and 1, indicating a favorable adsorption of Cd(II) ions onto CHL and MCHLAC. From this study, the uptake of Cd(II) ions onto CHL and MCHLAC from aqueous solution is decreased with increasing temperature indicating that the adsorption process is exothermic in nature.

The comparison of maximum monolayer adsorption capacity of cadmium(II) ions onto various adsorbents are listed in Table 3. The value of cadmium(II) ions sorption observed in the present study is in good agreement with the values found by other researchers. Differences in metal uptake are due to the properties of each adsorbent such as structure, functional groups, and surface area. Therefore, it could be concluded that MCHLAC has a promising adsorbent for the removal of cadmium(II) ions from aqueous solution.

3.8. Thermodynamic studies of Cd(II) adsorption onto CHL and MCHLAC

The effect of temperature on cadmium(II) adsorption onto CHL and MCHLAC was studied at 100 mL of 20 mg L⁻¹ of cadmium(II) solution containing an adsorbent dose of 0.3 g for CHL and 0.1 g for MCHLAC was added at pH 5.0 by varying temperature range of 27°C–47°C (Fig. 9a).

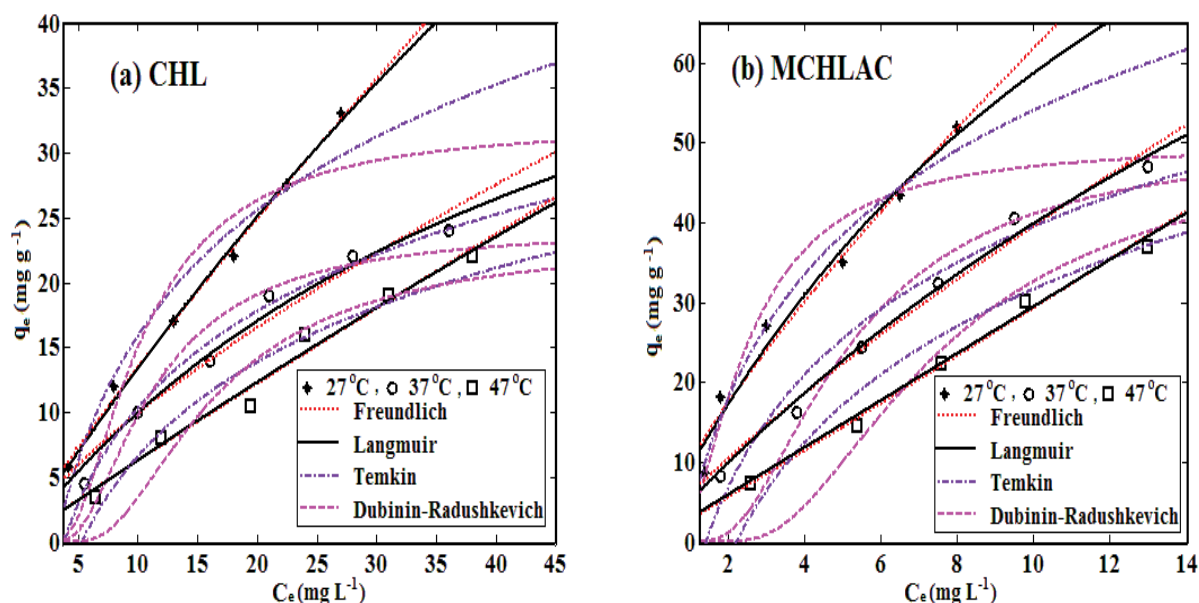


Fig. 8. (a and b) Nonlinear adsorption isotherm for the adsorption Cd(II) ions onto CHL and MCHLAC at different temperatures.

Table 2

Adsorption isotherm constants and thermodynamic parameters for the removal of cadmium(II) ions onto CHL and MCHLAC at 27°C, 37°C, and 47°C

Isotherm model	Parameters	Adsorbents					
		CHL			MCHLAC		
		27°C	37°C	47°C	27°C	37°C	47°C
Freundlich	K_f (mg g ⁻¹)	1.742	1.815	0.6871	10.09	5.894	2.745
	n (g L ⁻¹)	1.125	1.356	1.041	1.270	1.209	0.972
	SSE	1.827	9.926	5.355	35.65	17.52	5.426
	RMSE	0.6758	1.575	1.157	2.985	2.093	1.165
	R^2	0.969	0.965	0.978	0.972	0.979	0.981
Langmuir	q_m (mg g ⁻¹)	98.75	73.45	52.80	257.45	221.20	181.60
	K_L (L mg ⁻¹)	0.167	0.128	0.102	0.187	0.140	0.125
	SSE	2.131	3.082	4.096	1.835	2.234	1.429
	RMSE	0.620	0.815	0.312	0.275	0.346	0.228
	R^2	0.995	0.991	0.990	0.996	0.992	0.997
Temkin	A (L mg ⁻¹)	0.313	0.262	0.188	1.107	0.699	0.452
	B	3.051	3.661	4.537	2.066	3.124	4.121
	b (kJ mol ⁻¹)	0.818	0.704	0.586	1.207	0.825	0.646
	SSE	26.19	13.27	14.19	30.42	44.14	69.82
	RMSE	2.559	0.898	1.884	2.758	3.322	4.178
Dubinin–Radushkevich	q_{mD} (mg g ⁻¹)	32.15	24.18	23.32	49.75	50.72	50.84
	$\beta \times 10^{-7}$ ((mol K kJ ⁻¹) ²)	4.393	5.985	6.450	1.880	2.241	2.879
	E (kJ mol ⁻¹)	1.075	0.909	0.769	1.636	1.493	1.316
	SSE	68.45	19.76	27.99	89.75	79.60	77.62
	RMSE	4.137	2.222	2.645	4.737	4.461	4.405
Thermodynamic	R^2	0.864	0.929	0.887	0.931	0.926	0.923
	ΔG° (kJ mol ⁻¹)	-2.113	-1.317	-2.662	-11.461	-5.663	-3.293
	ΔH° (kJ mol ⁻¹)	-3.735			-16.800		
	ΔS° (kJ mol ⁻¹ K ⁻¹)	-0.011			-0.051		

Table 3
Comparative monolayer adsorption capacities of various low-cost adsorbents for the adsorption of cadmium(II) ions

Adsorbents	Adsorption capacity, q_m (mg g ⁻¹)	References
Olive stone	7.80	[4]
<i>Leucaena leucocephala</i> biomass	70.42	[5]
Brewery spent barley husk	6.64	[6]
Cherry kernel	198.7	[7]
Olive fruit stone	24.83	[8]
<i>Albizialebeck</i> pods	21.22	[9]
Silk cotton hull	100.00	[26]
Hazelnut husk	61.35	[27]
Saffron leaves	68.75	[28]
Bamboo powder	8.57	[29]
Sunflower stem carbon	4.40	[30]
Sulfonated magnetic nanoparticle	80.90	[31]
Magnetite/carbon nanocomposites	76.67	[32]
CHL (Present study)	58.75	Present study
MCHLAC (Present study)	257.45	Present study

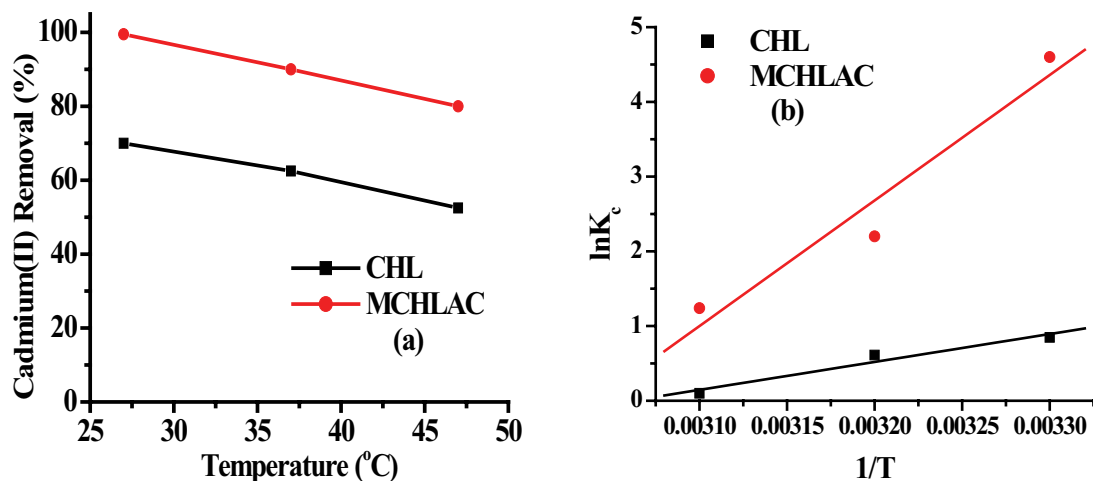


Fig. 9. (a and b) Effect of temperature and thermodynamic plots for the adsorption Cd(II) ions onto CHL and MCHLAC.

The various thermodynamic parameters such as ΔG° , ΔH° , and ΔS° were estimated from the experimental data using the van't Hoff equation as expressed as follows [33]:

$$\ln K_c = \frac{\Delta G^\circ}{RT} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (12)$$

where T is the temperature in Kelvin, R is gas constant (8.314 kJ mol⁻¹ K) and K_c is the thermodynamic equilibrium constant can be calculated by the following equation:

$$K_c = \frac{q_e}{C_e} \quad (13)$$

where q_e and C_e (mg L⁻¹) are the equilibrium adsorption capacities and concentration of cadmium(II) ions. The ΔH° and ΔS° values can be calculated from the slope and intercept of

a plot of $\ln K_c$ vs. $1/T$ (Fig. 9b), respectively [34]. The values of ΔG° at different temperatures were calculated from Eq. (14).

$$\Delta G^\circ = -RT \ln K_c \quad (14)$$

As shown in Table 2, the negative values of ΔG° indicate that the adsorption of cadmium(II) ions onto CHL and MCHLAC was spontaneous and feasible. The negative value of ΔH° suggests that the adsorption process is exothermic and the ΔS° can be used to describe the randomness at the adsorbent-solution interface during the sorption.

3.9. Adsorption kinetics

The various adsorption kinetic models such as pseudo-first-order, pseudo-second-order, intra-particle diffusion,

and Boyd models were used to determine the mechanism of Cd(II) adsorption and the rate-determining step during adsorption process.

3.9.1. Pseudo-first order-kinetics

The Lagergren's pseudo-first-order model is based on the binding of each metal ion to only one sorption site on the surface of the adsorbent. In this model, the rate of adsorption sites are occupied is proportional to the number of unoccupied sites. The linear pseudo-first-order equation is generally expressed as [35]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (15)$$

where q_e (mg g⁻¹) and q_t (mg g⁻¹) are the adsorbed amount at equilibrium and at time t (min), respectively. k_1 (min⁻¹) is the pseudo-first-order rate constant and determined experimentally by plotting of $\log(q_e - q_t)$ vs. t .

3.9.2. Pseudo-second-order kinetics

The linearized form of the pseudo-second-order equation can be expressed as [36]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (16)$$

where k_2 (g mg⁻¹ min⁻¹) is the pseudo-second-order rate constant. By plotting a curve of t/q_t against t , q_e and k_2 can be evaluated. The initial adsorption rate, h_0 (mg g⁻¹ min⁻¹) is defined as [37]:

$$h_0 = k_2 q_e^2 \quad (17)$$

In order to compare quantitatively the applicability of kinetic models in fitting to data, the percentage relative deviation (P %) was calculated by the following equation:

$$P (\%) = \frac{100}{N} \sum \left[\frac{q_{e(\text{exp})} - q_{e(\text{theo})}}{q_{e(\text{exp})}} \right] \quad (18)$$

where $q_{e(\text{exp})}$ and $q_{e(\text{cal})}$ are experimental and calculated value for the adsorption cadmium(II) ions onto CHL and MCHLAC, N is the number of measurements made. Ayranci and Duman [38] reported that the lower value of percentage deviation (P % < 5), is considered to be an excellent fit of the kinetic model.

The different kinetic parameters, correlation coefficients, and P (%) are given in Table 4. The correlation coefficient (R^2) values of the pseudo-second-order model are higher than those of the pseudo-first-order model. In addition, the calculated q_e values for the pseudo-second-order model is much closer to the experimental q_e values. Furthermore, the percent relative deviation (P %) is also found to be less than 5% in the case of pseudo-second-order model suggested that the rate-limiting step of Cd(II) ions onto CHL and MCHLAC is mainly governed by may be chemisorptions.

3.9.3. Adsorption mechanism

The pseudo-first-order and pseudo-second-order kinetic models were not able to explain the diffusion mechanism and also the rate-determining step for the adsorption of cadmium(II) ions onto CHL and MCHLAC. It is explained by intra-particle diffusion and Boyd kinetic model. For a solid-liquid sorption process, the solute transfer is usually characterized by either external diffusion (boundary layer diffusion) or intraparticle diffusion or both. The following three steps can describe adsorption dynamics.

- The movement of adsorbate molecules from the bulk solution to the external surface of the adsorbent (film diffusion).
- Adsorbate molecules move to the interior part of the adsorbent particles (particle diffusion).
- Sorption of the solute on the interior of the pores and capillary spaces of adsorbent (sorption).

The Weber and Morris intra-particle diffusion model and Boyd kinetic model is expressed by the following equation [39,40].

$$q_t = k_d t^{1/2} + C \quad (19)$$

Table 4

Pseudo-first order and Pseudo second order constants for Cd(II) adsorption onto CHL and MCHLAC at different initial concentrations

Adsorbent	C_0 (mg L ⁻¹)	$q_{e(\text{exp})}$ (mg g ⁻¹)	Pseudo-first-order				Pseudo-second-order				
			k_1 (min ⁻¹)	$q_{e(\text{cal})}$ (mg g ⁻¹)	R^2	P (%)	k_2 (g mg ⁻¹ min ⁻¹)	$q_{e(\text{cal})}$ (mg/g)	h_0	R^2	P (%)
CHL	30	16.9	0.023	19.70	0.942	16.57	0.0027	16.20	0.709	0.999	4.14
	20	9.90	0.025	11.67	0.973	17.88	0.0029	9.60	0.267	0.997	3.03
	10	6.30	0.023	5.35	0.981	15.10	0.0025	6.10	0.093	0.996	3.17
	5	4.20	0.023	5.90	0.989	40.48	0.0038	4.00	0.061	0.998	4.76
MCHLAC	30	29.9	0.030	24.10	0.983	19.40	0.0009	30.30	0.826	0.999	1.34
	20	19.2	0.030	22.11	0.984	15.17	0.0010	19.00	0.361	0.998	1.04
	10	9.20	0.023	11.67	0.983	26.85	0.0026	8.99	0.210	0.999	2.28
	5	4.60	0.032	5.90	0.981	28.26	0.0114	4.45	0.226	0.999	3.26

$$F = 1 - \frac{6}{\pi^2} \exp(-B_i) \quad (20)$$

where k_d is the intra-particle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{1/2}$) and C is the intercept, which can be calculated from the slope of the linear plot of q_t vs. $t^{1/2}$ as shown in Figs. 10a and b. $F = q_t/q_e$, F represents the amount of Cd(II) adsorbed at any time t , and B_i is a mathematical function of F . Eq. (20) can be rearranged by taking the natural logarithm to obtain the equation:

$$B_i = -0.4977 - \ln(1-F) \quad (21)$$

The plot of B_i vs. t can be employed to test the linearity of the experimental values. If the plots are linear and the lines are passed through the origin, then the intra-particle

diffusion and Boyd kinetic model are the rate-controlling step [41]. From Figs. 10c and d show that the plots are linear but do not pass through the origin. This deviation from the origin may perhaps be due to the difference in the rate of mass transfer in the initial and final stages of adsorption suggesting that the adsorption process is controlled by film diffusion. The B values from Boyd kinetic models were used to calculate the effective diffusion coefficient, D_i ($\text{cm}^2 \text{s}^{-1}$) using the following relationship:

$$B = \frac{\pi^2 D_i}{r^2} \quad (22)$$

where D_i is the effective diffusion coefficient of cadmium(II) ions in the adsorbent surface and r is the radius of the adsorbent particle. The D_i values were found to be 4.192×10^{-8} ,

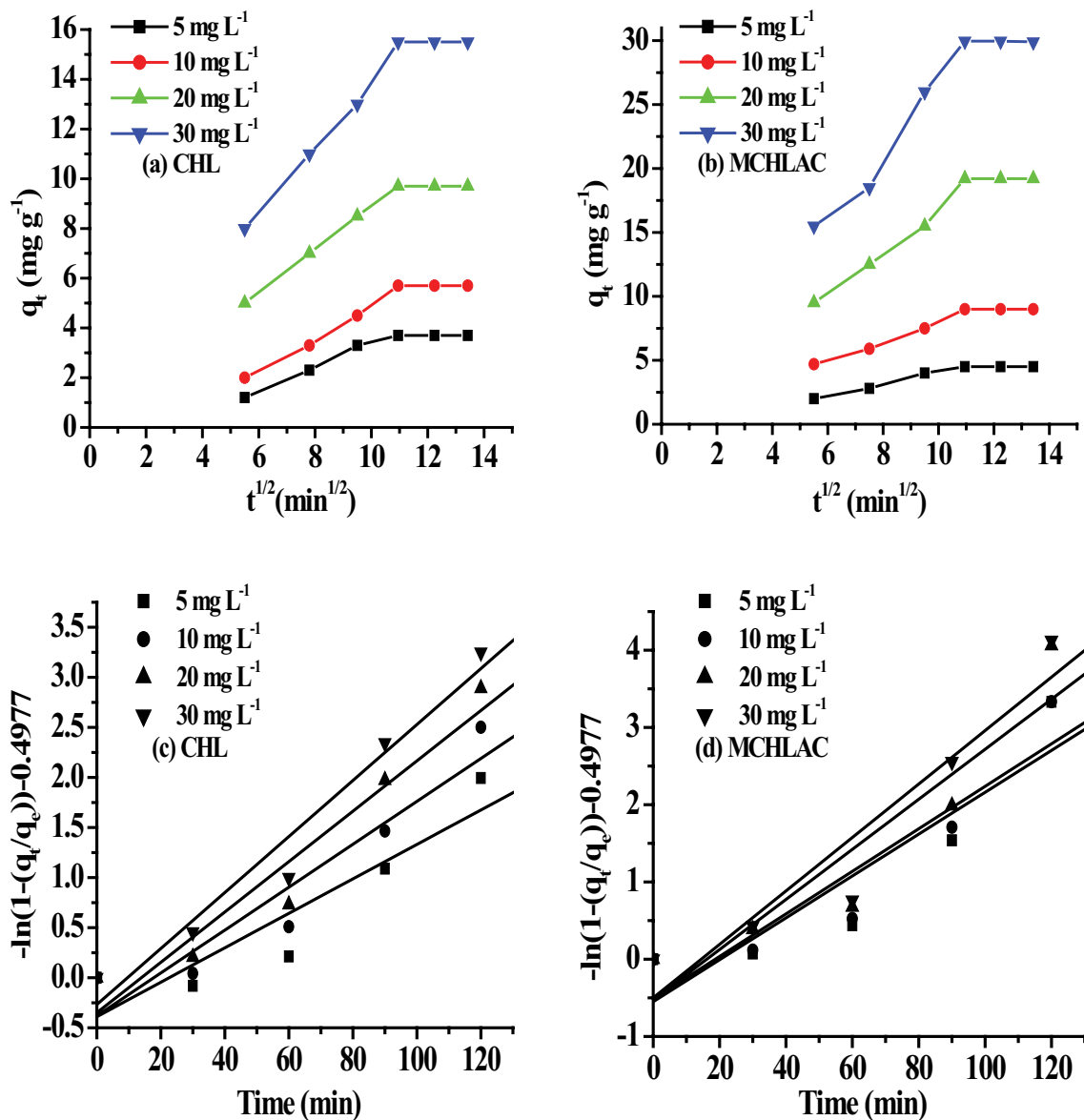


Fig. 10. (a–d) Intraparticle diffusion and Boyd kinetic plot for the removal Cd(II) ions onto CHL and MCHLAC.

Table 5
Physical and chemical characteristics of the electroplating wastewater in real sample

Parameter	Concentration of cadmium-plating industry wastewater before treatment	Concentration of cadmium-plating industry wastewater after treatment with MCHLAC
pH	2.00	6.7
Total solid, mg L ⁻¹	3,500.00	250.00
Turbidity, NTU	26.00	3.00
Conductivity, mS cm ⁻¹	8.85	1.15
Chloride, mg L ⁻¹	750.00	50.00
Sulfate, mg L ⁻¹	190.00	100.00
Cd, mg L ⁻¹	255.00	0.10
COD, mg L ⁻¹	98.00	25.00
Sodium, mg L ⁻¹	90.00	40.00
Calcium, mg L ⁻¹	85.00	20.00
Magnesium, mg L ⁻¹	108.00	25.00

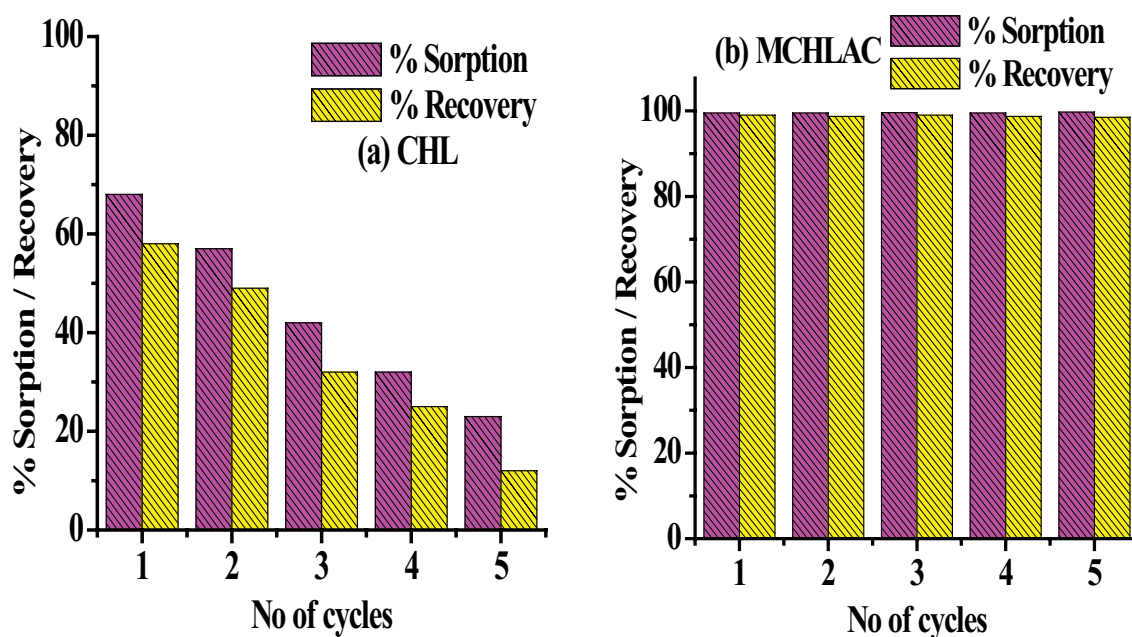


Fig. 11. (a and b) Regeneration and recycling by a batch process for the removal Cd(II) ions onto CHL and MCHLAC.

4.052×10^{-8} , 4.052×10^{-8} , and 3.772×10^{-8} cm² s⁻¹ for CHL and 5.449×10^{-8} , 5.030×10^{-8} , 4.890×10^{-8} , and 3.912×10^{-8} cm² s⁻¹ for MCHLAC at an initial cadmium(II) ions concentration of 30, 20, 10, and 5 mg L⁻¹, respectively.

4. Removal of cadmium(II) from electroplating wastewater and regeneration studies

Batch experiments with cadmium electroplating wastewater have been carried out to elucidate the applicability of both sorbents under batch mode operations. The electroplating wastewater was collected from local electroplating industry in Tirupur district, Tamilnadu, India. The chemical and physical parameters of real electroplating wastewater are listed in Table 5. It could be observed that 1 L

wastewater containing 255 mg L⁻¹ cadmium(II) ions, a minimum MCHLAC dose 1 g L⁻¹ is required for the maximum removal of 99.5% ± 0.4%, but in the case of CHL, the optimum CHL dose of 3 g L⁻¹ was used to achieve the maximum removal of 65% ± 0.4% only. Therefore, MCHLAC is 3 times more effective than CHL for the removal of cadmium(II) ions from electroplating wastewater.

In order to explore the practical efficiency of the adsorbent over repeated uses, 0.3 N HCl was used to regenerate the adsorbent for five cycles of operation. It could be observed from Figs. 11a and b show that MCHLAC could be used repeatedly for more than five cycles without affecting the cadmium(II) ion adsorption capacity. However, in the case of CHL, both adsorption and desorption values decreased rapidly. The above results confirmed that the

prepared MCHLAC has a greater potential for repeated use and recovery of cadmium(II) ions from electroplating wastewater.

5. Conclusion

The present study shows that the magnetic activated carbon synthesized (MCHLAC) from a novel *C. hystrix* leaves, is effectively to remove 99.6% of cadmium(II) ions from aqueous solution. The FT-IR studies showed that the presence of hydroxyl and carboxylic acid groups in CHL, in addition to that Fe–O groups are present in MCHLAC, which is responsible for the adsorption of cadmium(II) ions. Equilibrium data agreed well with Langmuir isotherm and the monolayer adsorption capacity of cadmium(II) ions onto MCHLAC was found to be 4.4 times greater than that of CHL. The negative value of change in free energy and enthalpy showed that the sorption process was spontaneous and exothermic in nature. The adsorption is followed by pseudo-second-order kinetics, which indicates the chemisorptions with film diffusion process being essential rate-controlling step. Experiments with Cd(II) electroplating wastewater showed that MCHLAC is more effective than CHL. Regeneration study shows that MCHLAC can be effectively utilized for the removal of cadmium(II) ions up to five cycles of operation when compared with CHL. Therefore, the conclusion of the present research reveals that the magnetic activated carbon derived from CHL is a very effective and inexpensive adsorbent for the removal of organic, inorganic, and heavy metal ions from aqueous solution.

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