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Cadmium(II) removal from an aqueous solution using CSCMQ grafted copolymer

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ABSTRACT

In this work, an approach was developed to synthesize copolymer by grafting 5-Chloromethyl-8-Hydroxyquinoline on to Cassava starch for removal of Cd(II). Characterization experiments were done by scanning electron microscopy and Fourier transform infrared analysis. The study was performed under different experimental conditions of initial metal ion concentration, adsorbent dose, time, pH and temperature. Batch adsorption experiment showed that grafted copolymer had strong adsorption capacity of 51.546, 53.191, and 55.249 mg/g at 298, 308, and 318 K for Cd(II) removal. The kinetics data were analyzed using pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. The pseudo-second-order model best described the adsorption of Cadmium(II) ions onto copolymer. Langmuir model fitted well and thermodynamics parameters were analyzed where results revealed that the adsorption process was a spontaneous and endothermic in nature.

Keywords: Cassava starch; Copolymer; Cadmium(II); Adsorbate; Adsorbent

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1. Introduction

Agile industrialization with uncontrolled anthropogenic fluxes related to mining, refining, plating, ammunition, storage cells, metal smelting, and finishing, engine exhausts, industrial emissions and effluents, heavy metal enrichment of agricultural products, etc. has lead heavy metal break in and pollute the environment. Cadmium is in limelight because it has been recognized as hazardous heavy metal pollutant that cannot be tolerated due to its long biological half-life, non-biodegradability, teratogenicity, and latent poisoning. Today, the quest to remove heavy metals from both industrial and drinking water has heightened proportional interest in the possible water treatment technologies [1]. Various conventional technologies have been used for cadmium removal, among which adsorption has an inevitable place [2].

Recently, with an ability to remove cadmium ions from an aqueous solution, modified cellulose [3,4], chitin and its derivative [5] and modified starch [6] has been studied. Among these, starch is important and good because of its low cost, renewability, and biodegradability. Various starches are obtainable like potato, maize, sago, cassava, etc. But the reason behind choosing cassava starch (CS) [7] (Manihotesculenta, also known as manioc or yucca) was its promising characteristics like high paste viscosity, high paste

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clarity, and high freeze—thaw stability, which are advantageous [8–10]. The present research focuses upon adsorption of cadmium metal ion from its aqueous solution by substitution of starch with 5-choloromethyl-8-hydroxyquinoline (CMQ), which forms chelates with metal ions in aqueous medium [11].

2. Materials and method

CS was procured from Sigma Aldrich, India and all other chemicals used were obtained from ACS Chemicals Pvt. Ltd (Ahmadabad). All the chemicals used for this particular research were of analytical grade. The stock solution of cadmium metal ion (1,000 mg/L) was prepared in double-distilled water and working solutions were obtained by apt dilution. In order to prevent metal contamination, glassware was kept overnight in a 10% (V/V) HNO_3 solution.

Adsorbent was prepared by blending of dried CS (10 g) with an appropriate amount of Triethyl amine and Tetra hydro Furan. After the agitation of 30 min, CMQ, which was synthesized, purified and characterized by previously reported routes [12] was added with constant stirring. Then the mixture was allowed to heat for 6 h at 60°C. The product synthesized was dried. This product was further used for the adsorption of cadmium metal ion from an aqueous solution (Fig. 1).

For the determination of metal ion concentrations before and after adsorption, atomic absorption spectrophotometer (Model novAA® 400 P, Analytic Jena, Germany) was used and to analyze the functional groups present on the adsorbent FT-IR (Nicolet IR-200, USA) was utilized. Scanning electron micrographs were obtained by using scanning electron microscopy (SEM) (SNE-15 00 M, Korea and CarlZeiss, EVO MA 15, England).

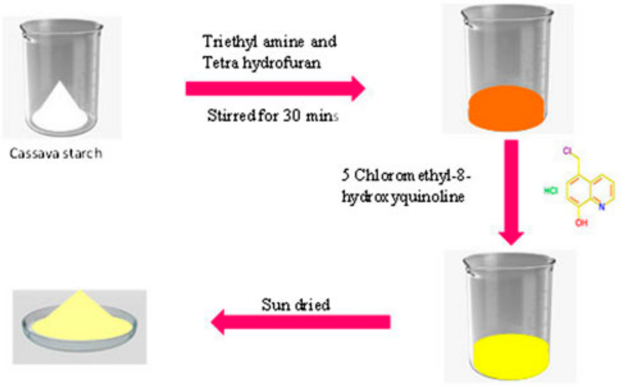

Fig. 1. Synthetic pathway for the preparation of CSCMQ.

2.1. Batch adsorption experiments

The CSCMQ was used to adsorb Cd(II) from an aqueous solution. Batch adsorption experiments were enforced at room temperature to scrutinize the effect of pH, adsorbent dosage, contact time and initial concentration of Cd(II) on adsorption over CSCMQ adsorbent. Posterior to agitation of flasks, the content of each flask was filtered and the filtrate was analyzed by atomic adsorption spectrometer (AAS). The calculation of removal efficiency (%) of the adsorbent and the metal concentration (mg/g) pertaining on the adsorbent was done using following equations:

$$R\% = \frac{(C_i - C_e)}{C_i} \times 100\,\% \tag{1}$$

$$q_e = \frac{(C_i - C_e)V}{W} \tag{2}$$

where q_e is the adsorption capacity (mg/g), C_i is the initial concentration of Cadmium(II) in the solution (mg/L), C_e is the equilibrium concentration of Cadmium(mg/L), V is the volume of metal ion solution (mL), and W is the weight of the adsorbent (mg).

Investigation of pH effect (1.0–9.0) and initial concentration of metal ion (10–50 mg/L) were also carried out in order to conclude its influence on the adsorption rate and also to obtain the adsorption isotherm.

3. Results and discussion

3.1. Scanning electron microscopy

SEM analysis seen in Fig. 2, was conducted to explicate the surface morphology of CSCMQ before and after adsorption of Cd(II). Results depicted that SEM images of CSCMQ had intercellular voids. In 1.50 KX magnification of SEM micrograph seen in Fig. 2(a), some fissure and irregularities were observed. Such fissure and irregularities are congenial for adsorption of metal ions in the solution because dispersion of Cd(II) can take place towards the interior portion of the adsorbent. It also showed the rough surface texture and porous structure which provides new adsorption site from interior cavities to participate in binding of metal ions, while in Fig. 2(b) having 1.50 KX magnification reveals that the surface of copolymer becomes smooth after the adsorption process, while the filtered liquid is still clear, meaning that thus modified copolymer has the acceptable resistance to the possible solubility in the aqueous solution.

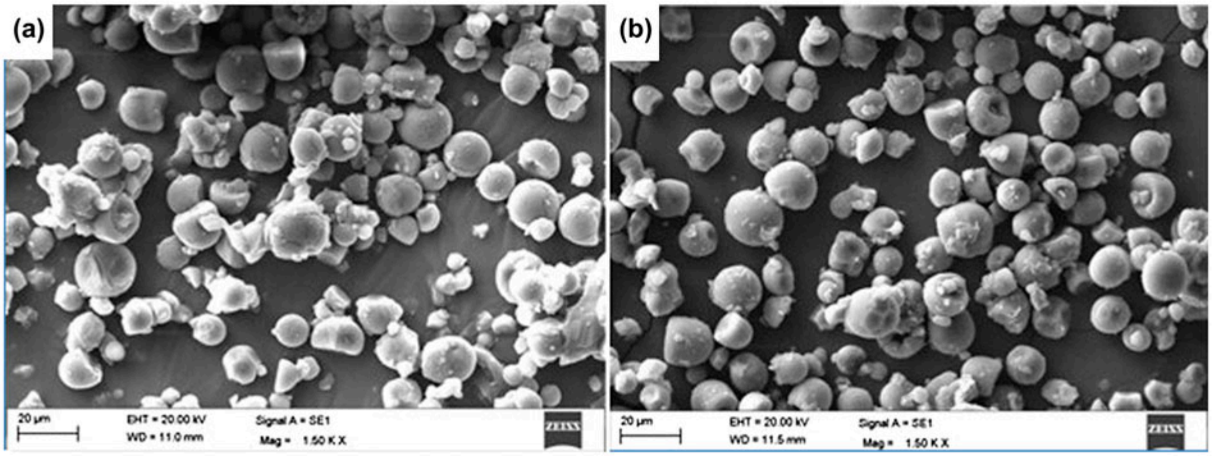

Fig. 2. Scanning electron microscopic images. (a) Starch–CMQ copolymer before Cd(II) adsorption at 1.5 KX magnification and (b) Starch–CMQ copolymer after Cd(II) adsorption at 1.5 KX magnification.

3.2. Fourier transform infrared spectroscopy

The characterization of grafted copolymer, non-grafted starch and CMQ were done by IR spectrophotometer. The IR spectrum of CS in Fig. 3(a) (Starch**)** showed that the IR spectra displays the O–H stretching adsorption in the region 3,550–3,200 cm^{-1} (broad) and single intermolecular polymeric band C–H stretching at 2,930 cm^{-1} (m) and 1,076 cm^{-1}. The bending mode of water is shown at 1,800–1,600 cm^{-1}. The wave number at 1,658 cm^{-1} was assigned as a peak of the first overtone of OH bending. On the other hand, 1,150 cm^{-1} was assigned as C–O–C stretching.

In Fig. 3(b), (CMQ) a sharp peak is seen at 1,491 cm^{-1} which confirms C=N aromatic nitro compound in CMQ. The broad band at 3,283 cm^{-1} observed in the case of ligand was shifted at 3,343 cm^{-1}, which was attributed to (O–H) of coordinated water molecule. In the investigated metal complexes, the bands observed in the regions of 1,267–1284 cm^{-1} and 865–875 cm^{-1} are attributed to –OH stretching, bending, rocking, and wagging vibrations, respectively, due to the presence of water molecules.

The spectra of grafted copolymer showed the existence of sharp peak at 785 cm^{-1} as observed in Fig. 3(c) CSCMQ copolymer which arises from the stretching vibration mode of C–Cl bond and a small peak is observed at 1,500 cm^{-1} which confirms the presence C=N aromatic nitro compound and a weak symmetrical stretching band 1,431–1,396 cm^{-1}, characteristics of C=O group indicated the occurrence of grafting it is evidence of grafting. Most other peaks are related to polymer backbone (starch).

3.3. Effect of pH

pH is one of the eminent environmental factor because it influences the adsorption of metal ions from an aqueous solution. It affects adsorbent surface charge, the degree of ionization and the species of adsorbates [13]. Thus, to determine the optimum pH for metal adsorption, the adsorption was studied at various pH.

The results in Fig. 4 showed that the adsorption capacities increase with the increase in pH. At a lower pH range of 1.0–4.0 inconsequential adsorption was been found. With pH increasing from 5.0 to 6.0, the adsorption then escalated gradually. The observed lower capacity in an acidic medium may attribute to the partial protonation of the active groups which causes repulsion of groups bearing positive charge. The increase in Cd(II) adsorption at higher pH values (5.0–6.0) can be explained by the ionization of the reaction sites on the chelate surface which involves competitive reactions of protonation and complex binding [14]. The maximum sorption efficiency is found in alkaline zone from Fig. 3. This is because precipitation plays main role in removing Cd(II) attributed to the formation of precipitation of Cd(OH). Therefore, pH 6 was preferred to be the optimum pH for advance studies [15].

3.4. Effect of initial metal ion and contact time concentration

For developing a sorbent-based water technology, removal rate of metal ion is of great significance. As seen, in Fig. 4 the adsorption of Cd(II) by CSCMQ copolymer was carried out considering the contact

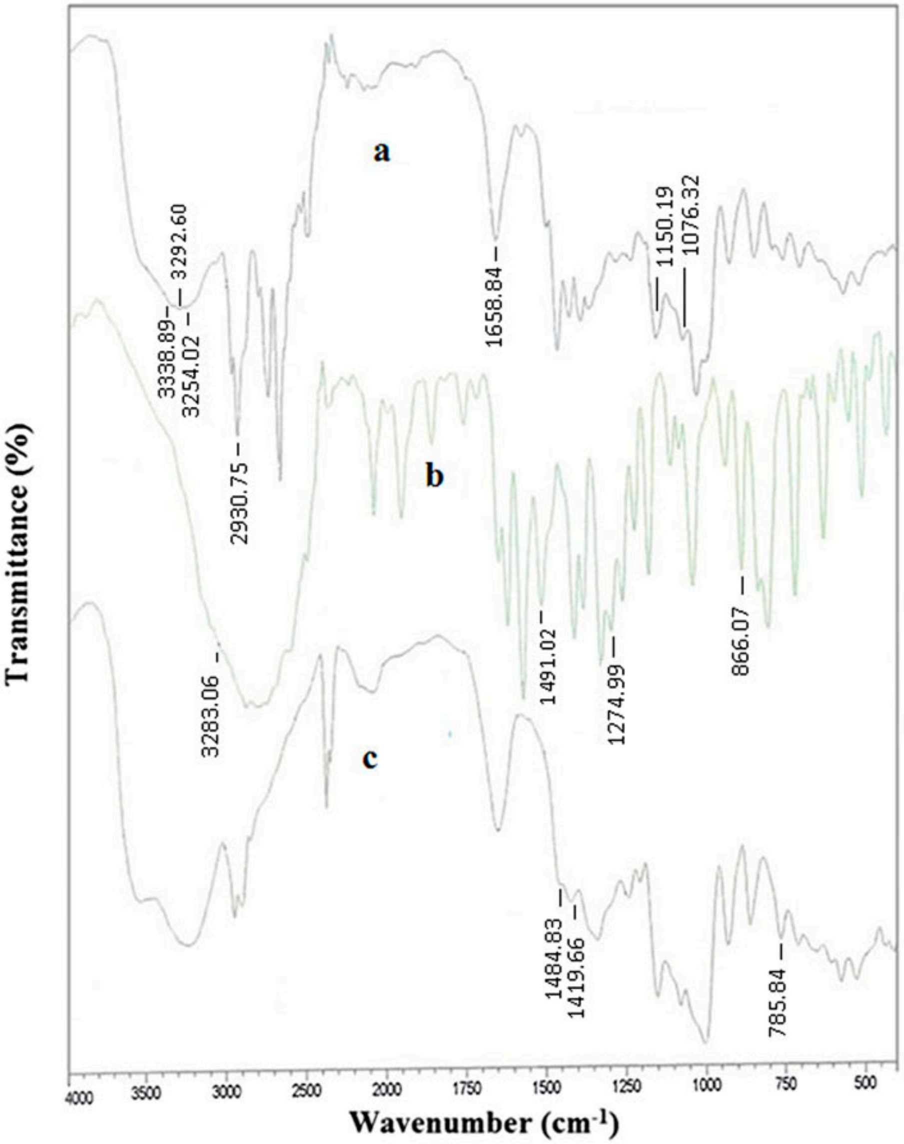

Fig. 3. FTIR spectra: (a) Starch, (b) CMQ, and (c) Starch–CMQ Copolymer.

time from 0 to 120 min for establishing the formulation of equilibrium time for maximum uptake and to know the kinetics of the sorption process. The adsorption efficiency of Cd(II) gradually reaches plateau with increasing contact time. Now, it was also observed that with an increase in initial concentration, there is also an increase in sorption capacity of cadmium. Over the range of experimental concentration there is increase in equilibrium uptake with increase in the initial metal ion concentration. Reason found behind such elevation is the driving force of the concentration gradient, with an increase in the metal ion initial concentration. Hence, from Fig. 4 it can be portrayed that with the increasing initial metal ion concentration from 10 to 50 ppm, there is also increase in the amount of metal ion adsorption from 9.417 to 42.014 mg/g at room temperature.

3.5. Effect of adsorbent dosage

Absorbent dosage is important factor because it determines the adsorbent–adsorbate equilibrium of the system for adsorption process [16]. The plot of the sorption curve is seen in Fig. 5. It is observed that the removal of Cd(II) enhances as the dosage of CSCMQ copolymer increases till 0.1 g. The reason behind the upsurge in adsorption rate is that there is more

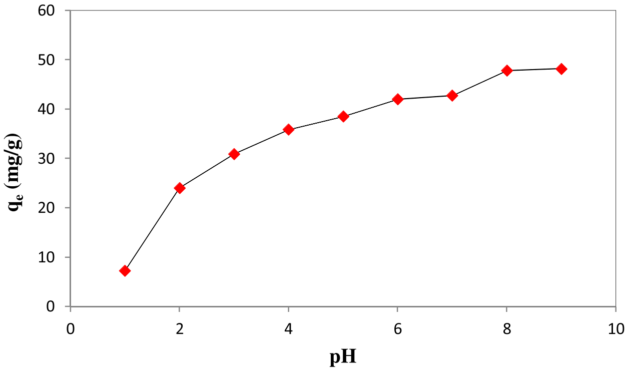

Fig. 4. Effects of pH on the adsorption of Cd(II) by Starch–CMQ Copolymer. ($C_0 = 50$ ppm; contact time = 120 min; agitation speed = 200 rpm).

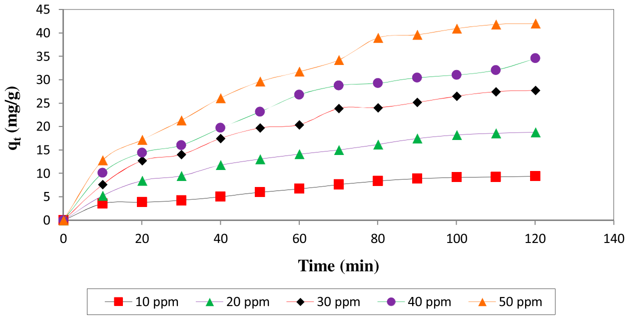

Fig. 5. Effects of initial metal ion concentrations and contact time on the adsorption of Cd(II) by Starch–CMQ Copolymer. (pH 6.0; dosage of adsorbent = 0.1 g/100 mL; agitation speed = 200 rpm).

surface area available and hence more active sites are accessible for binding of metal ions. For a given initial concentration of cadmium, further increment of the adsorbent dosage practically has no impact on the rate of adsorption of cadmium.

3.6. Effect of temperature

Researchers have been much attracted towards effect of temperature because it may influence reaction rate and process. Thus, for removal of Cd(II) in an aqueous medium, the effect of temperature was studied by varying temperature (25, 35, and 45°C). Results observed from thermodynamic study depicted that the rate of adsorption increases with the increase in temperature indicating the adsorption process to be endothermic. Positive values of ΔH° and with that change in ΔS°, shown in Table 3, it was suggested that the endothermic nature of adsorption is present. There is also increase in randomness at the solid-solution interface during the adsorption of Cd(II) ions on CSCMQ copolymer, respectively. The adsorbed solvent molecules, in the adsorption are displaced by adsorbate species by gaining more translational entropy and then they are lost by adsorbate ions. Thus, this allows the prevalence of randomness in the system [17].

3.7. Isotherm studies

3.7.1. Adsorption isotherms

Equilibrium adsorption isotherms are basic mechanism for designing of adsorption systems. The correlation of equilibrium data by either theoretical or empirical equations is important for predicting the adsorption capacity of the adsorbent [18]. The most widely used isotherm models for solid–liquid adsorption are the Langmuir, Freundlich and Temkin.

3.7.1.1. Langmuir model. Langmuir model assumes that sorption occurs on a structurally homogenous adsorbent and all the sorption sites are energetically identical. Hence, it anticipates the formation of a monolayer of the adsorbate on the homogenous adsorbent surface and does not consider surface heterogeneity of the adsorbent. The saturated monolayer curve can be represented [19]:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} \cdot C_e \qquad (3)$$

where C_e (in milligrams per liter) is the equilibrium concentration of the Cd(II) in the solution. q_e (in milligrams per gram) is the equilibrium adsorption capacity per gram dry weight of the adsorbent corresponding to complete coverage of the adsorptive sites. a_L (in liter per milligram) and K_L (in liter per gram) are the Langmuir isotherm constants. The values of a_L and K_L are calculated from the slope (a_L/K_L) and intercept ($1/K_L$) of the plot of C_e/q_e vs. C_e. The value of monolayer sorption capacity of the adsorbent q_m (in milligrams per gram) is given by ratio of a_L/K_L. Table 1 indicates that the maximum adsorption capacity of CSCMQ copolymer were 51.546, 53.191, and 55.249 mg/g at 298, 308, and 318 K, respectively, which is equivalently high and can be compared with previously reported adsorbents (Table 2).

The imperative attribute of Langmuir isotherm can be articulated in terms of "R_L", a dimensionless constant referred to as "separation factor" or "equilibrium parameter". The value of R_L is calculated using the following equation:

Table 1
Equilibrium isotherm models parameters with error analysis values for the adsorption of Cd(II) onto Starch–CMQ copolymer

Experimental conditions	Adsorption isotherm parameters												
	Langmuir					Freundlich				Tempkin			
	q_m (mg/g)	K_L (L/g)	R_L	R^2	χ^2	K_F (mg^{1-n} L^n/g)	$1/n$	R^2	χ^2	K_T (L/mg)	b_T (J/mol)	R^2	χ^2
T = 298 K	51.546	34.014	0.132–0.0294	0.994	0.195	18.578	0.484	0.954	1.408	6.89	97.558	0.995	135.22
T = 308 K	53.191	22.272	0.193–0.0456	0.984	0.553	15.066	0.529	0.929	1.909	4.068	93.915	0.987	131.52
T = 318 K	55.249	16.75	0.248–0.0619	0.98	0.475	13.001	0.557	0.955	1.031	3.06	94.89	0.987	128.55

$$R_L = \frac{1}{(1 + a_L \cdot C_0)} \tag{4}$$

The value of R_L lies between 0 and 1 for favorable adsorption, while $R_L > 1$ represents unfavorable adsorption, and $R_L = 1$ represents linear adsorption while the adsorption process is irreversible if $R_L = 0$ [15]. R_L values of CSCMQ copolymer for the initial Cd(II) concentration from 10 to 50 mg/L indicated in Table 1 was found favorable for adsorption of Cd (II) onto CSCMQ copolymer.

3.7.1.2. *Freundlich model.* Freundlich equation is derived to model the multilayer sorption and for the sorption on heterogeneous surfaces. The Freundlich isotherm theory says that the ratio of the amount of solute adsorbed onto a given mass of sorbent to the concentration of the solute in the solution is not constant at different concentrations. The linear form of Freundlich isotherm model is as follows [30]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{5}$$

where K_F (in liter per gram) is the Freundlich adsorption isotherm constant, relating to the extent of adsorption. n (in grams per liter) is the Freundlich exponent. The values of K_F and $1/n$ are calculated from the slope and intercept of the plot of log q_e vs. log C_e and are listed in Table 1.

The equilibrium adsorption of Cd(II) using CSCMQ polymer (q_e vs. C_e) is shown in Fig. 6 and the isotherms are plotted together with the experimental data points.

3.7.1.3. *Temkin model.* The Temkin isotherm model [31] shown in Table 1 contains a factor that accurately takes into account the interaction of adsorbing species and adsorbate. Following are the assumption done based on this model: (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The derivation of the Temkin isotherm presumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm has commonly been applied in the following form:

$$Q_e = b_T \ln K_T + b_T \ln C_e \tag{6}$$

Table 2
Adsorption capacity of cadmium by different adsorbents reported in other studies

	Adsorbent	q_m (mg/g)	Refs.
1	Granulometric soil fractions	0.50	[20]
2	Cyanobacterium metallothionein	7.70	[21]
3	Na- and Fe-modified zeolitic tuffs and carbonaceous material	15.13	[22]
4	Exhausted coffee by an aqueous solution	17.3	[23]
5	Shellac-coated iron oxide nanoparticles	18.80	[24]
6	Indigenous halomonas bvr1 strain	23.28	[25]
7	Activated carbon	25.00	[26]
8	Humic acid coated titanium dioxide	28 ± 0.5	[27]
9	*S. cerevisiae* cell	42.63	[28]
10	Biochar derived from municipal sewage sludge	42.80 ± 2.38	[29]
11	CSCMQ	55.249	Present study

where K_T and b_T are the Temkin isotherm constants. The isotherm constant K_T is the equilibrium binding constant (L mg^{-1}) corresponding to the maximum binding energy and constant b_T is related to the heat of adsorption.

Langmuir, Freundlich and Temkin isotherms for the Cd(II) were calculated and shown in Table 1 with Isotherm parameters and the correlation coefficients R^2.

For the adsorbent, Langmuir isotherm model fitted well with the experimental data though R^2 value of Temkin was nearer to 1. Because according to error analysis given below the value of χ^2 was very large for Temkin isotherm as compared to Langmuir isotherm.

3.8. Kinetic studies

Adsorption kinetics provides the rate of metal ion uptake by CSCMQ copolymer, which is highly dependent on their interaction and operating conditions [32]. Rate of adsorption uptake can be described with adsorption kinetics as it is enforced for selecting optimum operating condition for the full-scale batch process [33]. Three most common kinetic models were performed to evaluate the rate constants.

Pseudo-first-order expression is given by the following equation [34]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (7)$$

where q_e is the amount adsorbed at equilibrium, q_t the amount adsorbed at time t and k_1 (per min) is the adsorption rate constant. The linear plot of $\log(q_e - q_t)$ vs. t is observed in Fig. 7.

The linear pseudo-second-order kinetic equation is given as [35]:

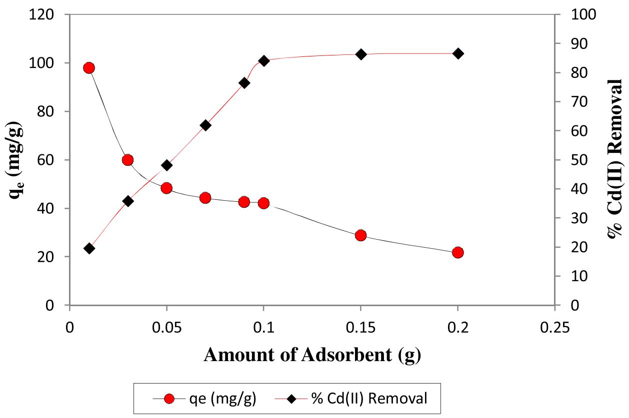

Fig. 6. Effects of amount of adsorbent on the percentage removal (a) and adsorption capacity (b) of Cd(II) by Starch–CMQ Copolymer. (C_0 = 50 ppm; contact time = 120 min; agitation speed = 200 rpm).

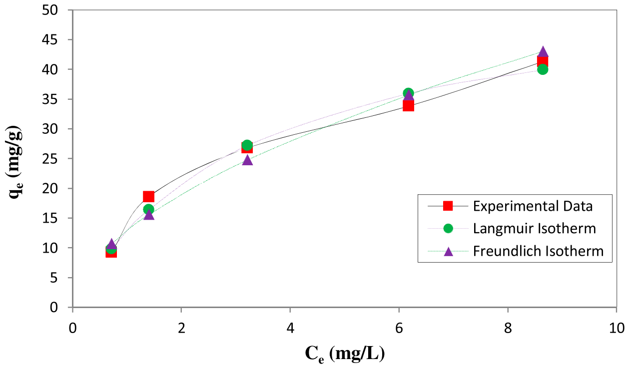

Fig. 7. Plot of q_e vs. C_e for the adsorption of Cd(II) onto Starch–CMQ Copolymer. (pH 6.0; contact time = 120 min; dosage of adsorbent = 100 mg/100 mL; temperature = 318 K; agitation speed = 200 rpm).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

where k_2 (in grams per milligram per minute) is the pseudo-second-order rate constant. The values of k_2 and q_e for pseudo-second-order rate model calculated from intercept and slope of the t/q_t vs. t plots are given in Table 3. The plot of second-order was shown in Fig. 8.

It is detected that the values of the correlation coefficient for both the pseudo-first-order and pseudo-second-order rate models were adjacent to unity. The description of pseudo-second-order model was very sound for the adsorption of Cd(II) onto CSCMQ copolymer since the experimental q_e values were very nearer to the calculated q_e values for pseudo-second-order rate model. As demonstrated in table the values of the rate constant k_2 declines with the inclination in initial concentration of Cd(II) metal ion because higher metal ion concentration corresponds to higher surface loading which decreases the diffusion efficiency.

Table 3
Kinetic parameters with error analysis values for the adsorption of Cd(II) onto Starch–CMQ Copolymer

		Initial concentration of Cd(II) ion solution				
Adsorption kinetics rate models	Kinetic parameters (318 K)	10 mg/L	20 mg/L	30 mg/L	40 mg/L	50 mg/L
Pseudo-first-order model	$q_{e(exp)}$ (mg/g)	9.286	18.602	26.793	33.829	41.358
	k_1 (1/min)	0.0371	0.0299	0.0311	0.0375	0.0253
	q_e (mg/g)	11.995	26.1216	29.2281	55.4626	45.9198
	R^2	0.916	0.813	0.971	0.873	0.944
	χ^2	18.389				
Pseudo-second-order model	k_2 (g/mg min)	0.0031	0.00081	0.00057	0.00044	0.00038
	q_e (mg/g)	11.4025	25.0627	37.7358	47.1698	55.5556
	R^2	0.984	0.941	0.966	0.973	0.971
	χ^2	17.33				
Intraparticle diffusion model	K_{id} (mg/g min$^{1/2}$)	0.725	1.678	2.583	3.206	3.753
	I (mg/g)	1.687	0.127	0.441	0.104	0.516
	R^2	0.989	0.983	0.918	0.987	0.992

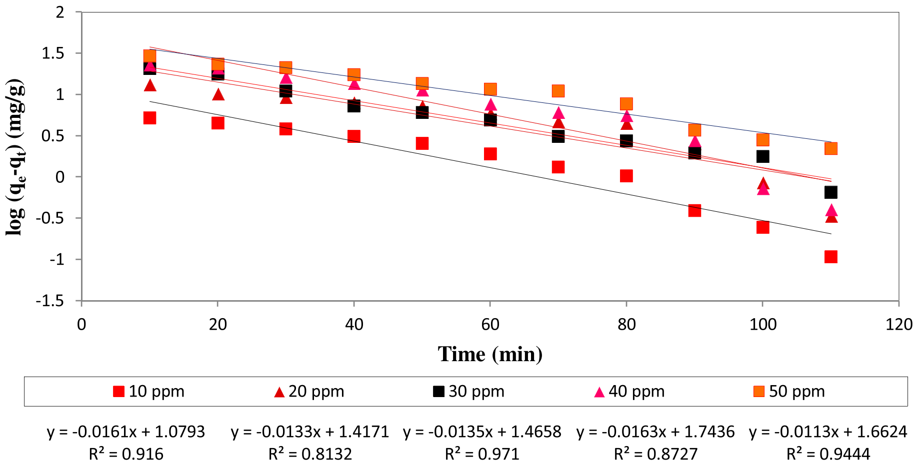

Fig. 8. Pseudo-first-order model for the adsorption of Pb(II) onto Starch–CMQ Copolymer. (pH 6.0; temperature = 45℃; dosage of adsorbent = 0.1 g/100 mL; agitation speed = 200 rpm).

3.9. Intraparticle diffusion model

The rate constant for intraparticle diffusion (k_{id}) is given by Weber Morris:

$$q_t = k_{id}\, t^{\frac{1}{2}} \tag{9}$$

where q_t is the amount adsorbed (mg/g) at time t (min).

Plot of q_t vs. $t^{1/2}$ is shown in Fig. 9 for Cd(II) ions. The initial curved portion is attributed to the bulk diffusion of the linear portion to the intraparticle diffusion and the plateau to the equilibrium. This indicates that transport of Cd(II) ion from solution through the particle solution interface, into the pores of the particle as well as the adsorption on the available surface of CSCMQ copolymer are both responsible for the uptake of heavy metal ions. Rate constants (k_{id}) characteristic of the adsorption in the region where intraparticle diffusion is rate-controlling. Extrapolation of the linear portions of the plots back to the axis provides intercepts which are proportional to the extent of the boundary layer thickness, i.e. the larger the intercept is, greater is the boundary layer effect. The deviation of the curves from the origin also indicates that intraparticle transport is not the only rate-limiting step (Fig. 10).

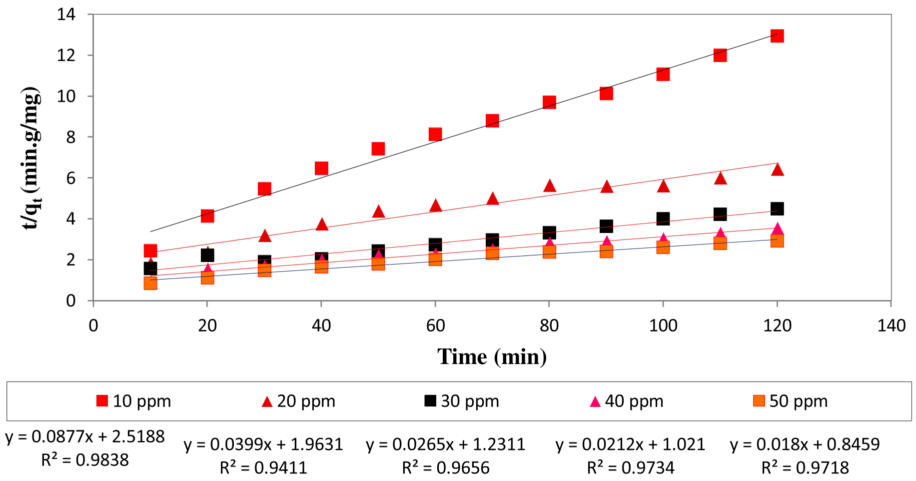

Fig. 9. Pseudo-second-order model for the adsorption of Cd(II) onto Starch–CMQ Copolymer. (pH 6.0; temperature = 45℃; dosage of adsorbent = 0.1 g/100 mL; agitation speed = 200 rpm).

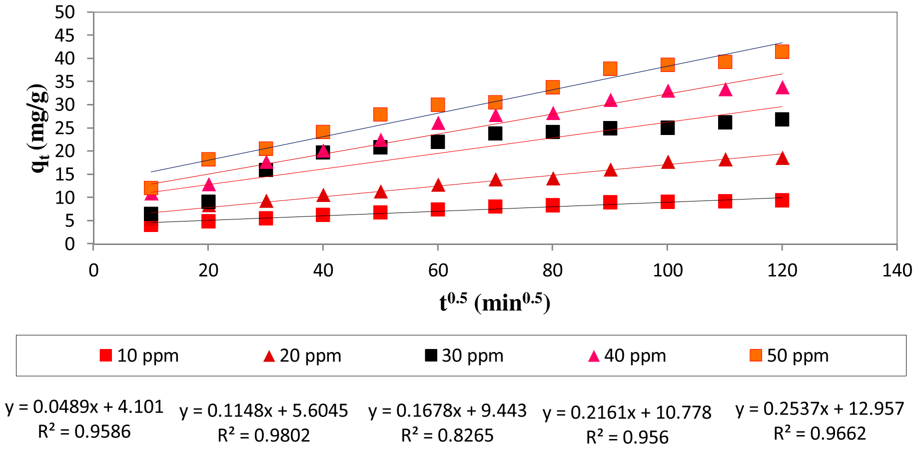

Fig. 10. Intraparticle diffusion model for the adsorption of Cd(II) onto Starch–CMQ Copolymer. (pH 6.0; temperature = 45℃; dosage of adsorbent = 0.1 g/100 mL; agitation speed = 200 rpm).

3.10. Error analysis

In the single component isotherm studies, the optimization procedure requires an error function to be defined in order to be able to evaluate the fit of the isotherm equation to the experimental equilibrium data. In this study, linear coefficient of determination (R^2) and a non-linear Chi-square test (χ^2) were performed for both the isotherms.

The χ^2 test statistics is basically the sum of the squares of the differences between the experimental data and the data obtained by calculating from models, with each squared difference divided by the corresponding data obtained by calculating from models. The mathematical equation can be represented as:

$$\chi^2 = \sum \frac{\left(q_{\mathrm{e(exp)}} - q_{\mathrm{e(cal)}}\right)^2}{q_{\mathrm{e(cal)}}} \tag{10}$$

where $q_{\mathrm{e(exp)}}$ (in milligrams per gram) is the experimental data of the equilibrium capacity; $q_{\mathrm{e(cal)}}$ (in milligrams per gram) is the equilibrium capacity obtained by calculating from the model. If data from the model are similar to the experimental data, χ^2 will be a smaller number, and if they differ, χ^2 will be a bigger number.

Therefore, it is necessary to analyze the data using the non-linear χ^2 test to confirm the best fit isotherm for this adsorption system and also for kinetic rate model. Thus, from results shown in Tables 1 and 4, of non-linear χ^2 test, it was confirmed the Langmuir adsorption isotherm and pseudo-second-order kinetic rate model were best fitted models.

3.11. Thermodynamics study

Thermodynamic parameter like affiliation of temperature dependence of the adsorption process is affiliated with several thermodynamic parameters. In order to delineate the thermodynamic behavior of the adsorption of Cd(II) ions onto CSCMQ polymer, the standard Gibbs free energy of adsorption ΔG° is calculated from the following equation:

$$\Delta G^\circ = -RT \ln K_C \tag{11}$$

where R is the universal gas constant (8.314 J/mol/K), T is the temperature in Kelvin, and K_c is the adsorption equilibrium constant. The value of K_c is calculated from the following equation:

$$K_c = \frac{C_{ae}}{C_e} \tag{12}$$

where C_{ae} is the equilibrium metal ion concentration on the adsorbent (mg/L) and C_e is the equilibrium metal ion concentration in solution (mg/L).

The negative values of ΔG° given in the Table 4 indicate the spontaneous and favorable nature of the adsorption process. Standard enthalpy (ΔH°) and standard entropy (ΔS°) of adsorption can be estimated from Van't Hoff equation and were calculated from the slope and intercept of Van't Hoff plot (Fig. 11) of K_c vs. $1/T$ and are shown in Table 3.

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

As shown in Table 3, positive values of ΔH° suggested the endothermic nature of the adsorption and reaction was spontaneous as ΔG° was found to be negative. The positive value of ΔS° suggested that there is increase in randomness at solid/solution interface during adsorption process. The adsorbed water molecules, which are displaced by the adsorbate species gain more translational energy than lost by the adsorbate ions. This allows the prevalence of randomness in the system. Enhancement of adsorption capacity at higher temperature may be attributed to the enlargement of pore size and/or activation of the adsorbent surface [36].

Table 4
Thermodynamic parameters for the adsorption of Cd(II) onto Starch–CMQ Copolymer

S. no.	C_o (mg/L)	ln K_c	ΔG° (kJ/mol)	$1/T$ (K^{-1})	ΔS° (kJ/mol/K)	ΔH° (kJ/mol)	R^2
1	20	1.57513	−8.9875	0.00336	0.0549332	7.38888	0.999
2	20	1.61493	−9.5238	0.00325			
3	20	1.65663	−10.087	0.00314			

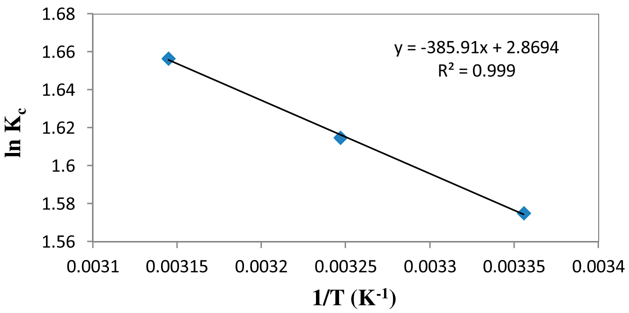

Fig. 11. Van't Hoff plot for the adsorption of Cd(II) onto Starch–CMQ Copolymer. (C_0 = 20 ppm; pH 6.0; contact time = 120 min; agitation speed = 200 rpm).

4. Conclusion

This study demonstrated that CSCMQ copolymer can be effectively used as an adsorbent due to higher number of active binding sites after modification. The sorption process was spontaneous, endothermic and favored pseudo-second-order kinetic model. The adsorption capacities of CSCMQ copolymer at pH 6 were 51.546, 53.191, and 55.249 mg/g at 298, 308, and 318 K. Further the best fitted adsorption isotherm model was Langmuir for the experimental data obtained from the non-linear χ^2 statistic test. The high efficiency of CSCMQ copolymer and its rapid uptake indicated it to be an excellent adsorbent for scavenging Cadmium(II) from water and waste water.

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Abbreviations

CSCMQ	—	cassava starch 5-chloromethyl 8-Hydroxyquinoline
TEM	—	transmittance electron microscopy
SEM	—	scanning electron microscopy
EDX	—	energy dispersive X-ray spectroscopy
FT–IR	—	Fourier transform infrared spectroscopy
UV–vis	—	ultraviolet–visible spectrophotometer

List of symbols

R %	—	removal percentage of metal ion
q_e	—	the equilibrium adsorption capacity per gram (dry weight) of the adsorbent (mg/g)
C_0	—	the initial concentration of Cadmium in the solution (mg/L)
C_e	—	the equilibrium concentration of Cadmium in the solution (mg/L)
V	—	the volume of the solution (mL)
W	—	the dry weight of CSCMQ (mg)
t	—	time (min)
a_L	—	the Langmuir isotherm constant (L/mg)
K_L	—	the Langmuir isotherm constant (L/g)
q_m	—	the monolayer sorption capacity of the nanocomposite (mg/g)
R^2	—	the linear coefficient of determination
R_L	—	separation factor or equilibrium parameter (dimensionless)
K_F	—	the Freundlich adsorption isotherm constant (L/g)
n	—	the Freundlich exponent (g/L)
χ^2	—	a non-linear Chi-square test
$q_{e,exp}$	—	the experimental data of the equilibrium capacity (mg/g)
$q_{e,cal}$	—	the equilibrium capacity obtained by calculating from the model (mg/g)
T	—	absolute temperature (K)
q_t	—	the amounts of metal adsorbed on adsorbent at time t (mg/g)
k_1	—	the pseudo-first-order rate constant (per min)
k_2	—	the pseudo-second-order rate constant (g/mg/min)
K_c	—	the equilibrium constant at temperature T (dimensionless)
C_{ae}	—	the equilibrium metal concentration on the adsorbent (mg/L)
ΔH°	—	change in enthalpy (kJ/mol)
ΔS°	—	change in entropy (J/mol/K)
ΔG°	—	Gibbs free energy (kJ/mol)
R	—	universal gas constant (8.314 J/mol/K)
K_T	—	equilibrium binding constant (L mg^{-1})
b_T	—	the heat of adsorption

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