



Kinetic and equilibrium studies for cadmium biosorption from contaminated water using *Cassia fistula* biomass

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Abstract

Cadmium (Cd) contamination of the water resources is one of the serious environmental issues. The present study aims to (1) evaluate the biosorption potential of *Cassia fistula* biomass for the removal of Cd from contaminated water and validate the experimental results with kinetic and equilibrium sorption models, (2) assess the removal of Cd from groundwater samples in the presence of other competing ions in the solution. The *C. fistula* biomass was characterized using Fourier transform infrared spectroscopy, Brunauer–Emmett–Teller technique and scanning electron microscopy to understand the role of its physical properties in Cd biosorption and removal. The effects of biosorbent dose, initial Cd concentrations, contact time and presence of competing cations in groundwater samples at constant pH and temperature (27 ± 1.5 °C) were studied. At equilibrium (90 min), Cd removal (98–16%) and biosorption (6.26–0.34 mg/g) were recorded depending on the experimental conditions. The Langmuir model yielded a better approximation of the experimental data at equilibrium ($Q_{\max} = 7.24$ mg/g, $R^2 = 0.99$) rather than Freundlich model. The pseudo-second-order kinetic model explained well the kinetic behavior of Cd biosorption. Results revealed a decline in the Cd removal (12.7 and 6% at 0.25 and 1.0 g/100 mL, respectively) in the presence of cations in the water samples. The results proved that *C. fistula* is a very effective and environment friendly alternative adsorbent for the removal (98%) of Cd from the aqueous system.

Keywords *Cassia fistula* · Cadmium · Sorption · Removal · Characterization · Coexisting ions · Kinetics

Introduction

Human exposure to heavy metals is one of the major environmental problems that pose a serious threat to human health (Ahmad et al. 2017; Xiong et al. 2014). Heavy metals are inorganic pollutants that have received considerable attention due to their toxicity and adverse health impacts. Industrial effluents contain various heavy metals including cadmium, copper, lead, iron, arsenic and chromium (Zhou and Haynes 2010). Cadmium (Cd) is considered to be among

the most toxic heavy metals and is oxyphilic in natural environment. Moreover, it is considered unnecessary for living organisms (Norouznia and Hamidian 2014). Cd has become a considerable concern due to its high mobility, solubility and accumulation in food chain (Moore and Ramamoorthy 2012; Peralta-Videa et al. 2009). Human exposure to heavy metals can cause acute and chronic diseases along with detrimental effects on the development of the nervous system and severe lungs, kidney and bone problems (Sud et al. 2008; Babarinde and Onyiaocha 2016). Cd contamination is the cause of extremely adverse consequences for plants, animals and humans (Duruibe et al. 2007).

Weathering of the geological materials and volcanic events are considerable contributors to Cd mobilization from the earth's anterior (Choppala et al. 2014; Zhao et al. 2015). Approximately 150–2600 tons of Cd per year is released into the air by natural sources. Cadmium is generally emitted into the environment from paints, metal refineries, corrosion of galvanized pipes, rechargeable Ni–Cd batteries, textile, alloys preparation and other industrial processes

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(Karunanayake et al. 2018, Ahmad et al. 2017). An important Cd-flux to the biogeosphere originates from leakage of open landfills (Agnieszka et al. 2014; Amarasinghe and Williams 2007). It is reported that every year about 600 metric tons of Cd are manufactured in the USA, and about 150 metric tons are imported (USGS 2011).

The food chain is the main route of Cd ingestion by humans (Shahid et al. 2015). The non-degradable nature of heavy metals results into its accumulation in living organisms. The use of Cd has been confined in many European countries due to its prospective adverse effects on human population (Shahid et al. 2015).

A variety of traditional and non-traditional strategies is employed for remediation of Cd contaminated water. The generally used techniques for remediation of heavy metals are coagulation/flocculation, solvent extraction, ion exchange, reverse osmosis, filtration and chelation/complexation, electrolytic recovery (Anastopoulos et al. 2013; Bilal et al. 2013; Sen-Gupta et al. 2009). The choice of the most desired remediation strategy relies on the type of the pollutant, the site characteristics, the concentrations to be removed and the end use of the contaminated medium (Ahmad et al. 2017). These approaches have limitations due to high cost, low efficiency, excessive use of chemicals and concentrated sludge production. Adsorption is an efficient and environment friendly strategy for the removal of metals and dyes as compared to other techniques in terms of the initial cost, simplicity, cost effectiveness and availability of the material. Agricultural waste is an economical material that can be used efficiently for the remediation of Cd from aqueous systems through biosorption.

Biosorption is a low-cost non-conventional remediation technique that is eco-friendly and easily accessible with minimum sludge production and commonly used technique in the recent past because of its outstanding results (Sud et al. 2008; Ahmad et al. 2017). It is also a domestic remediation strategy for wastewater even for the elimination of heavy metals from highly contaminated wastewater (Chandrasekhar et al. 2001; Bishnoi et al. 2004; Ghimire et al. 2002). Literature shows that biosorption of heavy metals and dyes has been extensively and effectively studied for wastewater and aqueous systems using various fruits and vegetables, rice husk, sugarcane bagasse and wheat straw (Abid et al. 2016; Shakoor et al. 2015; Yao et al. 2012; Tofan et al. 2011; Wang et al. 2010; Saikaew et al. 2009). Biosorption is a low-cost alternative technique with possibility for biosorbent regeneration and metals recovery, high removal capability and minimal poisonous waste production (Fu and Wang 2011). Biosorption is influenced with many factors such as concentration of the target contaminant, solution pH, ionic charges, size and nature of the biosorbent, biosorbent dose and temperature (Gupta et al. 2010; Chojnacka 2010), number of the active sites at the surface of the biosorbent

and their accessibility (Hanif et al. 2007; Paradhan et al. 2007).

Cassia fistula is a very famous deciduous tree in the world and contains a very high amount of ionizable groups such as C=O, -OH, C-H, C-C, C=C. The *C. fistula* has been very rarely used for biosorption of heavy metals. It belongs to genus: *Cassia*, family *Fabecea*, species *Fistula*. Literature shows that *C. fistula* is identified as a good biosorbent to eliminate Ni from a synthetic aqueous solution (Hanif et al. 2007) but has not been applied so far for removing other metals from aqueous solutions. Therefore, this study was conducted to evaluate the biosorption potential of *C. fistula* biomass (leaves) for the removal of Cd from contaminated water, characterize the biomass and validate the experimental results with kinetic and equilibrium sorption models.

Materials and methods

Preparation and characterization of the biosorbent from *C. fistula*

Biomass of *C. fistula* leaves was harvested from COMSATS Vehari Campus. The collected leaves from *C. fistula* were washed thoroughly thrice with distilled water to remove dirt and other adhering particulate material from the surface of the leaves. The washed leaves were first air-dried and then oven dried at 75 °C for 24 h and subsequently ground to fine particles with a blender, sieved and stored in air tight plastic container for further application.

The characteristics of the prepared particles of the biosorbent were measured to get insight into the biosorption by these particles. The distribution of the main active functional groups possibly involved in removal of the Cd was determined with FTIR in the range of 500–4000 cm^{-1} . The micrographs for the morphology of the particles surface were made with SEM (TESCAN Vega TS5136LM) at working distance (WD) 12.21 mm, electron energy 15 kV and magnification of 5 kx. Brunauer–Emmett–Teller (BET) was used to measure pore volume, average particle size, BET surface area and particle density.

Chemicals and equipments

All the chemicals used in the experiment were of analytical reagent grade. A stock solution of 1000 mg/L of Cd was prepared by dissolving salt $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ in distilled water. Cd working solutions of five different concentrations (10, 20, 40, 80 and 100 mg/L) were prepared by dilution of the Cd stock solution with distilled water for the batch study. Due to optimum pH for Cd biosorption as shown in our preliminary experiments and literature (Ahmad et al. 2017), all the experimental cases were carried out at pH 6. The pH of



the water used for Cd biosorption was maintained by using 1 M HCl and NaOH solutions. The concentration of Cd in the water samples was measured by using atomic absorption spectrophotometer (AAS, Thermo AA[®], Solar-Series).

Batch scale studies

A series of batch scale biosorption experiments was conducted at room temperature 27 ± 1.5 °C and pH 6. All the experiments were carried out in duplicate and the mean values were used for measuring biosorbed metal q (mg/g), removal R (%) and fitting kinetic and equilibrium adsorption isotherm models. Batch adsorption tests were conducted in conical flasks of 250 mL. A 1000 mg/L stock solution was prepared by dissolving 1.79 g of hydrated cadmium chloride in 1 L distilled water. Various initial concentrations of Cd solution ranging from 10 to 100 mg/L were obtained by dilution of 1000 mg/L stock solution to evaluate their impact on biosorption potential of the *C. fistula* biomass. The effects of adsorbent dosage, contact time and initial concentration of Cd were studied by taking 100 mL of cadmium chloride solution in conical flasks. Four different doses of the biosorbent (0.25, 0.5, 1.0 and 1.5 g/100 mL) were used and samples were constantly mixed using a rotary shaker at 150 rpm. The samples were collected after 15, 30, 90 and 240 min) from start to investigate the kinetic behavior and equilibrium stage of Cd biosorption. The samples were centrifuged at 3500 rpm, 25 °C for 10 min and filtered for Cd analysis. The filtrate was saved in 10 mL plastic bottles and analyzed for Cd.

Effect of inorganic ions

To quantify the impact of inorganic ions on the removal and biosorption of Cd with *C. fistula* biomass in aqueous system, two groundwater samples [GW1 (29.9569°N, 72.3031°E) and GW2 (29.9556°N, 72.3042°E)] were collected from electric pumps used for drinking purposes in Vehari. The chemical characteristics (EC, TDS, Na, K, Ca, Ca+Mg, Mg and Cd) of both water samples were measured (see Table 1). In this scenario, two doses of the biosorbent (0.25 g and 1 g/100 mL of Cd solution) and four levels of Cd (10, 20, 40 and 100 mg/L) were used diluting the stock solution. The water samples containing Cd, biosorbent and inorganic ions were shaken at 150 rpm and samples were taken at same times (15, 30, 90 and 240 min) similar to the batch experiments carried out in distilled water containing Cd and biosorbent (no other ions).

Table 1 Concentration of cations (mg/L), EC (dS/m), TDS (mg/L) and Cd (µg/L) in the groundwater samples for ionic effect on the removal and biosorption of Cd

Water	EC	TDS	Na	K	Ca	Ca + Mg	Mg	Cd
GW1	0.56	290	20.4	4.93	19.4	44.5	25.1	15.76
GW2	0.7	345	27.15	5.78	29.6	62.8	43.2	25.4

Both groundwater samples were used to explore the efficiency of *C. fistula* biomass for Cd removal in the presence of different cations in solution. The pH of the groundwater samples was also maintained to 6 for comparative analysis carried out in distilled water.

The amount of biosorbed Cd per unit mass of the *C. fistula* leaves (mg/g) was determined by measuring the final concentration of the Cd (mg/L) in the solution C_f , volume (L) of the solution V_w , initial concentration of Cd (C_0) (mg/L) in the solution and mass of the biosorbent material M_b (g) using following relation (1):

$$q = \frac{(C_0 - C_f)}{M_b} \times V_w \quad (1)$$

The metal ion removal R (%) by the biosorbent was calculated with the following relation

$$R(\%) = \left(\frac{C_0 - C_f}{C_0} \right) \times 100 \quad (2)$$

Modeling of the Cd biosorption

The experimental results were validated with adsorption isotherm models. The Langmuir and Freundlich models were employed for equilibrium adsorption isotherms, and for kinetic effects, first-order and second-order kinetic models were applied.

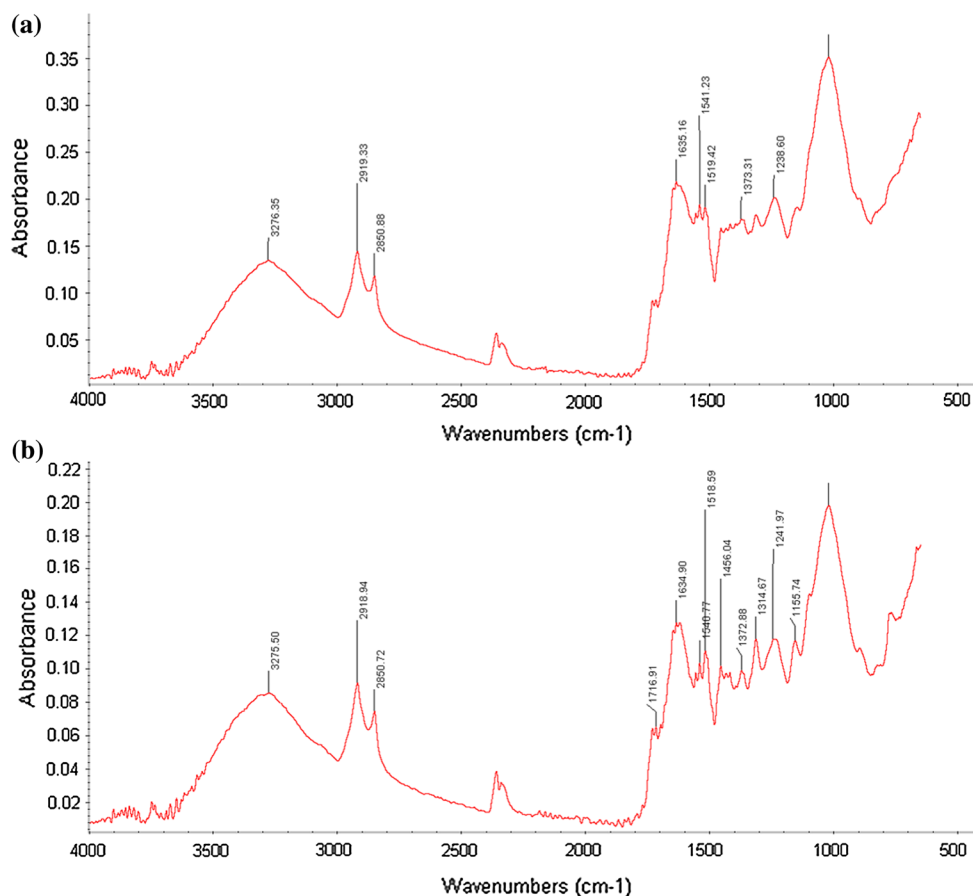
Results and discussion

Characterization of the *C. fistula* biomass

FTIR analysis

The presence of different functional groups on the adsorbent surface and their interaction with the contaminant Cd was detected with IR spectroscopy. Based on stretching and bending vibrations detected by FTIR analysis, potential applicability of an adsorbent for the removal of pollutants is ensured. Figure 1 presents FTIR analysis of the adsorbent prepared from the leaves of *C. fistula* before and after removal of the Cd. The FTIR spectra of absorbance were recorded between wavenumbers 4000 and 500 (cm^{-1}). There are clear shifts in the peak values of the absorbance and decline in intensity at 3276, 2919, 2850, 1635, 1541,

Fig. 1 FTIR of the biosorbent prepared from *Cassia fistula* biomass: **a** biomass loaded with Cd at the particles surface and **b** unloaded biomass



1591, 1373, 1238 and 1030 cm^{-1} as function of the functional groups found at the surface of *C. fistula* biomass. The wide band observed at 3276 wavenumber indicated alcoholic groups (OH) and a band at 2919.33–2850.88 cm^{-1} indicates aliphatic groups (C–H). The peak at 1635 wavenumber (cm^{-1}) is in harmony with carbonyl (C=O) vibrations stretching of ester and O–H (Gan et al. 2015). The peak at 1541 cm^{-1} is for secondary amine while the peak at 1373.31 cm^{-1} is assigned to the symmetric deformation band of CH_3 . The one observed at 1238.6 cm^{-1} corresponds to sulfite stretching ($-\text{SO}_3$). The band at 1030 cm^{-1} reflects C–O bonds of ether, ester or phenol (Bello et al. 2015). The shifts in FTIR spectrum proved that a *C. fistula* is very useful in removing heavy metals like Cd from aqueous solutions.

The absorbance peaks between 1635 and 1236 cm^{-1} are shifted upward in case of Cd loaded biomass of the *C. fistula* due to the attachment of Cd at particles surface. The shifting of peaks explains the biosorption of Cd that might be due to complexation or ion exchange with the surface moieties present on adsorbent surface. The presence of cellulose and hemicellulose in plant materials may give hydroxyl, carboxyl and amide, which could be responsible for Cd removal from aqueous systems (Lupea et al. 2012).

BET surface area analysis

The particle size and surface area of the biomass derived from agricultural waste or medicinal plants is important for the adsorption of the target contaminants. The BET surface area of the particles prepared from *C. fistula* leaves was 116.6 m^2/g with average particle size of 36.19 μm and mass density of 0.75 g/cm^3 , which make it a better biosorbent. A large surface area and porous nature of the adsorbent material provide more active sites for the interaction of the contaminant (Naushad et al. 2017).

Scanning electron micrographs of *C. fistula* biomass

The surface characteristics of the particles play a critical role in the attachment of pollutants at the surface of the adsorbent. Removal of the target contaminants by adsorbent depends on the surface homogeneity and heterogeneity. The surface morphology of the particles derived from *C. fistula* leaves has been shown in Fig. 2a, b before adsorption and after removal of Cd, respectively. As can be observed in Fig. 2 that before biosorption, the surface has shown some roughness, groves and pores which provided large surface



area for Cd interaction and surface became smooth with the Cd attached to the surface (Grieco et al. 2015).

Cd biosorption and its removal from aqueous system

Cd biosorption and removal at equilibrium

The behavior of Cd biosorption and removal is different depending on the contact time. Usually, there is more change in the adsorption and removal in first few minutes and with increase in time, this difference is minimized. An equilibrium stage is reached when there is no further change in the adsorption and removal, even when samples are allowed to remain for long time (Potgieter et al. 2006; Ali et al. 2016; Zhou et al. 2016)

Effect of the initial concentration and biosorbent dose

Biosorbent doses and the initial concentrations of the target contaminant are important variables to determine the effective biosorption. Different initial Cd levels in the solutions were developed to assess the sorption characteristics of *C. fistula*. The initial Cd level was changed from 10 to 100 ppm, while the mass of *C. fistula* was varied from 0.25 to 1.5 g. Figure 3 shows biosorption of Cd induced by different initial concentrations of the target contaminant under the influence of biosorbent dose. As adsorbent dose increases, biosorption is significantly influenced by the material. With increasing biomass, removal efficiency increases. This

increase is gradual and reaches maximum at the highest dose of the biosorbent. However, for the last two doses 1.0 and 1.5 g, there is less difference in removal efficiency as compared to biomass 0.25 and 0.5 g in the Cd solution. Furthermore, increase in biomass increases number of active

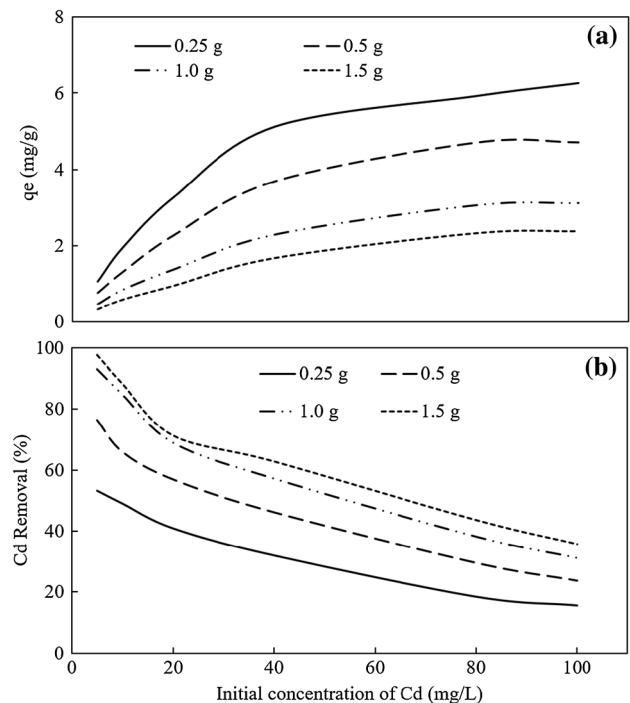


Fig. 3 Effect of the initial concentrations of Cd and biosorbent dose on the **a** biosorption and **b** removal of Cd from aqueous system to the surface of biosorbent material at equilibrium

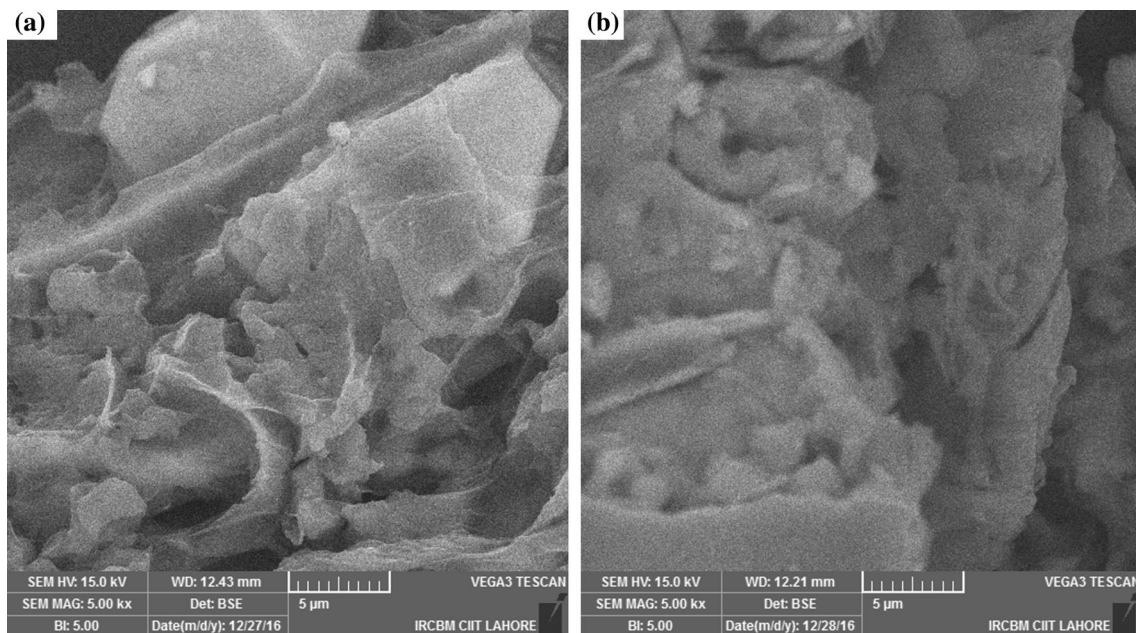


Fig. 2 Micrographs of the particles of *Cassia fistula* leaves using scanning electron microscope: **a** before biosorption and **b** after biosorption of Cd

sites thereby decreasing metal uptake. This trend could be the result of possible increase in diffusional route yielding reduced Cd uptake (Gupta and Rastogi 2008). Ahmad et al. (2017) obtained a similar trend for Cd removal by compost derived from fruits and vegetables using biosorbent dose of 0.5–1.5 g/100 mL. As adsorbent dosage increased, chromium uptake was also decreased (Vinodh et al. 2011). It is because of the increased surface area of the biosorbent and availability of more functional groups at higher dose (Chowdhury and Saha 2010). In the literature, *Moringa oleifera* seed was also demonstrated as a good biosorbent for the removal of cobalt, copper, lead, cadmium and silver (Ndibewu et al. 2011).

Increase in the dose of biosorbent material from 0.25 to 1.5 g decreased adsorption from 6.26 to 1.06 mg/g. As a result Cd, removal (R%) was increased from 53 to 98% at the initial Cd concentration of 10 mg/L (highest removal at maximum dose of the biosorbent) but Cd removal decreased with increase in its initial concentration. At maximum concentration of Cd (100 mg/L), the removal attained with maximum biosorbent dose is 50%.

Kinetic behavior of Cd biosorption and its removal by *C. fistula*

The kinetic study is important to control the process of metal removal by the material (Verma and Quraishi 2017). The change in biosorption of Cd as a function of time by *Cassia fistuala* biomass is shown in Fig. 4. The Cd biosorption seems to be a two-step process. At the start of experiment during first 30 min, there was rapid increase in biosorption capacity. After the initial fast adsorption period, the uptake of Cd by *Cassia fistuala* reaches equilibrium in approximately 90 min. Similar behavior of Cd sorption was observed by Yaacoubia et al. (2014), where they investigated the adsorption of Cd as a bi-phasic process and found an increase in the adsorption capacity during the first 20 min using nanoparticles (NPs). After this initial fast adsorption in their results, the Cd adsorption by NPs reached equilibrium.

To assess kinetic behavior of the Cd removal characteristics of *C. fistula*, at different initial concentrations of working solution, Cd removal is presented in Fig. 4b. The Cd removal was enhanced with increase in contact time and biosorbent dose. For the both initial concentrations and biosorbent dose, Cd removal increases rapidly at an initial stage of the process (about 95% in 90 min) and after 90 min, equilibrium was attained. There was no further increase in Cd removal after equilibrium. The biosorption of heavy metal Cd(II), Pb(II) and Cu(II) with the fungal biomass as function of time was studied by Say et al. (2001). In their case, the amount of adsorbed metal ions was very high at the beginning of adsorption (more than 60% metal ions species adsorbed within the initial 2 h), and saturation levels were

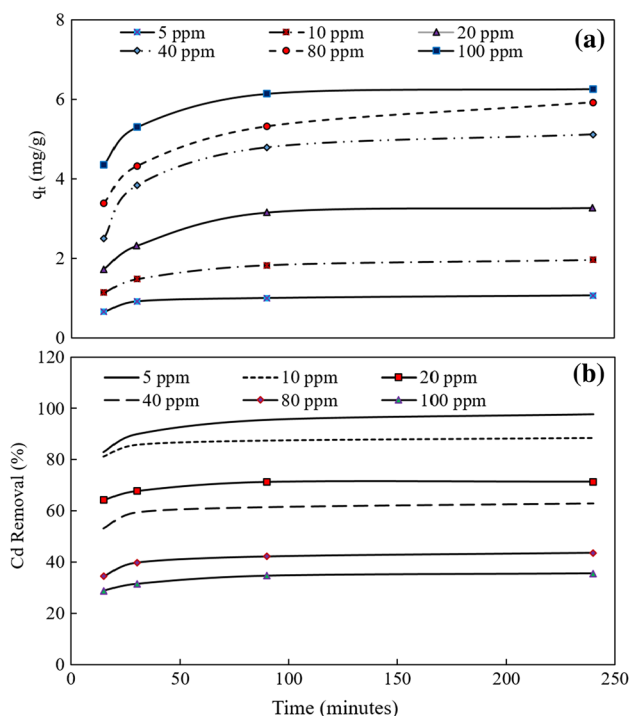


Fig. 4 Effect of contact time on the **a** biosorption and **b** removal of Cd at different initial concentrations of Cd

gradually reached at about 6 h for all metals ions. After this equilibrium period, the amount of adsorbed metals ions did not significantly change with time.

Effect of the inorganic ions on metal removal by the biosorbent

The presence of cations in wastewater and groundwater due to high salt concentrations may interfere with the metal removal by biosorbents (Vilvanathan and Shanthakumar 2015). Therefore, it is important to investigate the influence of cations like sodium, calcium, magnesium, EC and TDS on the removal of Cd from the solution by the biosorbent. Two groundwater samples (GW1 and GW2) with characteristics given in Table 1 were used to analyze the impact of cations (Ca, Na, K, Mg), EC and TDS on the biosorption and removal of Cd from the solution. Figure 5 shows the adsorption capacity and removal of Cd by the biosorbent in the presence of cations at equilibrium. It reveals that increasing the concentration of cations, EC and TDS in the groundwater samples, there is change in biosorption potential (Fig. 5a) and removal (Fig. 5b) of Cd. The biosorbent dose 0.25 g showed more differences in biosorption and removal as compared with dose 1.0 g. This may be attributed to the poor affinity of Na, K and more affinity of Ca, Mg as compared to Cd (Meseguer et al. 2016). The biosorption of Cd is affected strongly by divalent cations like Ca, Mg as compared to Na and K in aqueous solution.

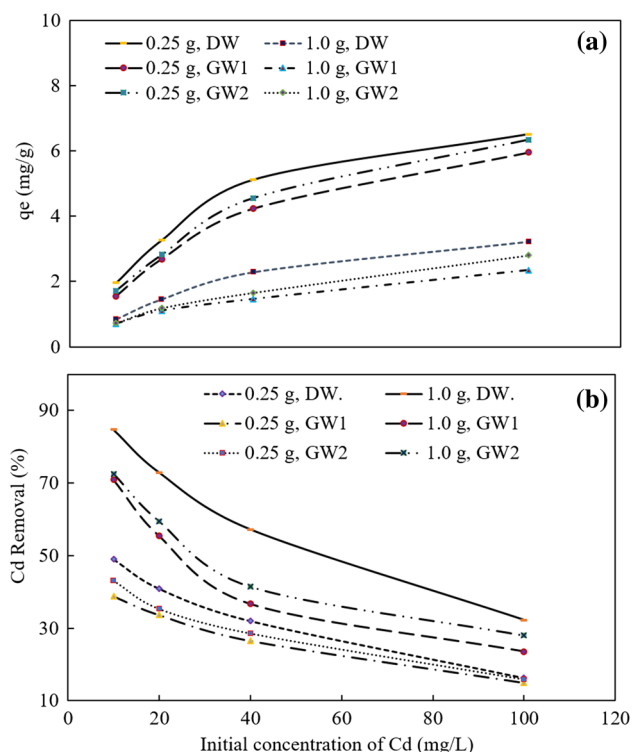


Fig. 5 Effect of inorganic cations at different initial concentrations of Cd present in two natural groundwater samples on the biosorption and removal of Cd at equilibrium isotherms and pH 6

Although, differences in cations, EC and TDS between the two groundwater samples were not significant, however, the values of these parameters were relatively greater for GW2 than GW1. The results revealed that a more decline in adsorption and removal of Cd was observed for the former as compared to the latter water type. This finding corroborates with Meseguer et al. (2016) who also reported similar results by developing cationic levels separately in the solution. Moreover, Schiewer and Wong (2000) observed swelling of the biosorbent at higher ionic strength, which affects metal uptake by the biosorbent due to variation in electrostatic attraction.

Equilibrium modeling of the biosorption isotherms

Adsorption isotherm shows distribution of the molecules between liquid and solid phases at equilibrium state (Zhou et al. 2017). There are several adsorption isotherm equations for analysis of experimental adsorption equilibrium data. In the present study, Langmuir and Freundlich adsorption isotherm models were applied to validate the Cd sorption through *C. fistula* biomass. The Langmuir model is based on few assumptions. It considers that the surface of the adsorbent material is homogeneous with localized attachment and each active site can accommodate one molecule of the target contaminant. The Langmuir model is valid for monolayer adsorption with limited

number of identical sorption sites on the surface of the biosorbent, which depends on the active sites with a uniform energy for adsorption and is given by Eq. (3).

$$q_e = \frac{K_L Q_{\max} C_e}{1 + K_L C_e} \quad (3)$$

where q_e is the equilibrium adsorption capacity of the biosorbent (mg/g), $K_L [L^3 M^{-1}]$ is a Langmuir sorption equilibrium constant related to affinity of the binding sites, $Q_{\max} [mg/g]$ is the maximum amount of the Cd adsorbed on *C. fistula* biomass when the surface of the biosorbent is saturated with Cd ions and C_e is metal concentration in the solution (mg/L) at equilibrium. In the Langmuir model, all adsorption sites are equally capable for holding the adsorbate (Cd).

In Eq. (3), the two parameters Q_{\max} and K_L are unknown and their values can be calculated from the linearized form (Eq. 4a) of Eq. 3 (Subramani and Thinakaran 2017; Shim et al. 2015)

$$\frac{C_e}{q_e} = \frac{1}{Q_{\max} K_L} + \frac{C_e}{Q_{\max}} \quad (4a)$$

A plot of C_e/q_e versus C_e gives values of Q_{\max} and K_L from the slope and intercept of the curve, respectively (Fig. 6). The estimated model parameters and corresponding correlation coefficients are given in Table 2. The $Q_{\max} [mg/g]$ ranged between 7.24 and 2.56 mg/g and K_L varied from 0.07 to 0.19.

The favorability of the biomass for adsorption can be expressed by a dimensionless separation factor R_L , which is defined as

$$R_L = \frac{1}{1 + K_L C_0} \quad (4b)$$

where C_0 is the initial concentration of the metal ion in the solution. The calculated values of R_L in the present study were $0 < R_L < 1$, which shows that *C. fistula* strongly favors biosorption (Mirghaffari et al. 2015).

Another generally employed model for equilibrium adsorption isotherm is the Freundlich isotherm model, which is given by Eq. (5)

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

where K_F is the Freundlich distribution coefficient or adsorption capacity and $1/n$ is Freundlich constant representing the medium heterogeneity and adsorption intensity (Kamal et al. 2010). The value of n is usually larger than unity. More the value of n is in Freundlich model, more favorable is the adsorption and more will be the heterogeneity on the surface of the particles and more nonlinearity in the adsorption isotherm.

The Freundlich parameters K_F and n are determined by rewriting Eq. (5) in linearized (6) and logarithmic form as (Shim et al. 2015)

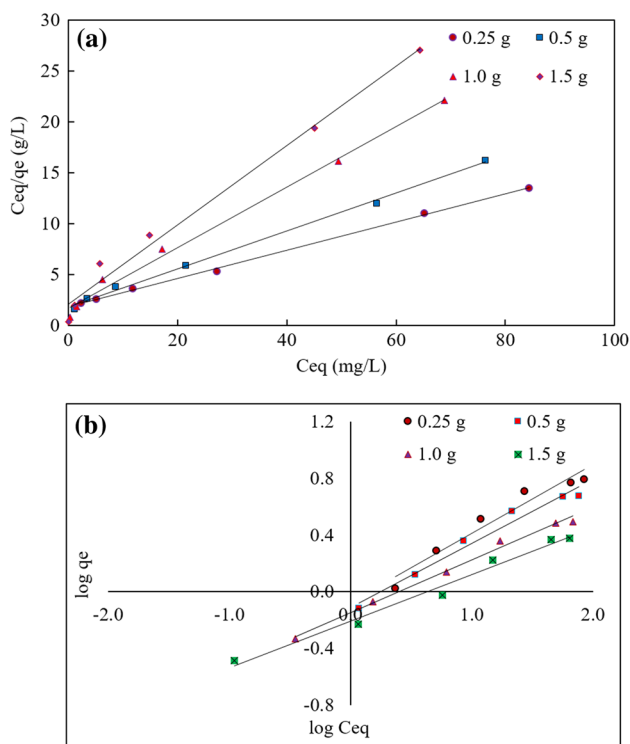


Fig. 6 Equilibrium adsorption isotherm models: **a** Langmuir isotherm at biosorbent dose 0.25 g/100 mL, and **b** Freundlich isotherm models at 0.5 g/100 mL, pH 6 and room temperature $27 \pm 1.5^\circ\text{C}$

$$\log q_e = \log K_F + 1/n \log C_e \tag{6}$$

The slope and intercept of the plot of $\log q_e$ versus $\log C_e$ give the values of n and K_F , respectively. The n changed from 2.06 to 3.04 and K_F varied from 0.62 to 0.85 as biosorbent dose was changed from 0.25 to 1.5 g/100 mL (Table 2). The Freundlich model is widely used in water/wastewater treatment but provides no information about the monolayer adsorption capacity (Kamal et al. 2010; Raouf et al. 2010). In comparison with the Langmuir model, the Freundlich model considers that the material surface energy and active sites are heterogeneous in nature. It considers that the stronger adsorption sites are filled first and there is decline in the binding energy of the adsorption sites with degree of site occupation. The correlation coefficient values suggested Langmuir model fitted well with the experimental data.

Table 2 Adsorption isotherm parameters at equilibrium and their kinetic behavior

Biosorbent dose (g)	Langmuir parameters			Freundlich parameters			First-order kinetic			Second-order kinetic		
	Q_{\max}	K_L	R^2	K_F	n	R^2	$k_{1,\text{bio}}$	q_e	R^2	$k_{2,\text{bio}}$	q_e	R^2
0.25	7.24	0.07	0.999	0.85	2.06	0.948	0.027	2.28	0.968	0.035	4.24	0.998
0.5	5.36	0.1	0.997	0.78	2.22	0.973	0.029	1.46	0.99	0.11	3.08	0.998
1.0	3.36	0.18	0.992	0.71	2.7	0.99	0.024	0.6	0.932	0.22	1.85	0.999
1.5	2.56	0.19	0.986	0.62	3.04	0.981	0.0291	0.299	0.94	0.60	1.39	0.999

Kinetic modeling of the biosorption isotherms

The kinetics of the experimental data were analyzed with pseudo-first-order and pseudo-second-order kinetic models. The pseudo-first-order rate equation based on the capacity of the adsorbent is generally given as

$$\frac{dq_t}{dt} = k_{1,\text{bio}}(q_e - q_t) \tag{7}$$

where $k_{1,\text{bio}}$ is the rate constant for first-order biosorption, q_e and q_t are the amounts of biosorbed Cd at the surface of the biosorbent at equilibrium, and at time t , respectively.

The integrated form of Eq. (7) between the limits, $q=0$ at $t=0$ and $q=q_t$ when $t=t$ yields (Sivasamy et al. 2012)

$$\log(q_e - q_t) = \log q_e - \frac{k_{1,\text{bio}}}{2.303} t \tag{8}$$

The pseudo-second-order model is represented by Eq. (9)

$$\frac{dq_t}{dt} = k_{2,\text{bio}}(q_e - q_t)^2 \tag{9}$$

Integration and rearrangement of Eq. (9) for its linearized form yields

$$\frac{t}{q_t} = \frac{1}{k_{2,\text{bio}}q_e^2} + \frac{1}{q_e} t \tag{10}$$

where $k_{2,\text{bio}}$ indicates equilibrium rate constant for pseudo-second-order biosorption (g/mg min). The kinetic biosorption data were evaluated with the linearized forms of pseudo-first-order and pseudo-second-order equations (Fig. 7). The constant parameters of pseudo-first order and pseudo-second order were calculated from the slope and intercept values of linear plots of $\log(q_e - q_t)$ versus t (Eq. 8) and $\frac{t}{q_t}$ versus t (Eq. 10), respectively, given in Table 2. The values of $k_{1,\text{bio}}$ varied from 0.024 to 0.029 for biosorbent dose (0.25–1.5 g/100 mL) while in case of pseudo-second order $k_{2,\text{bio}}$ changed from 0.035 to 0.6. It is clear from Fig. 7 that data points of pseudo-first-order plot were not fitted well with the solid trend lines. The lower values of correlation coefficient (≥ 0.932) also indicated the limited applicability of pseudo-first-order kinetic model as compared with correlation coefficients (≥ 0.998) of pseudo-second-order kinetic model.

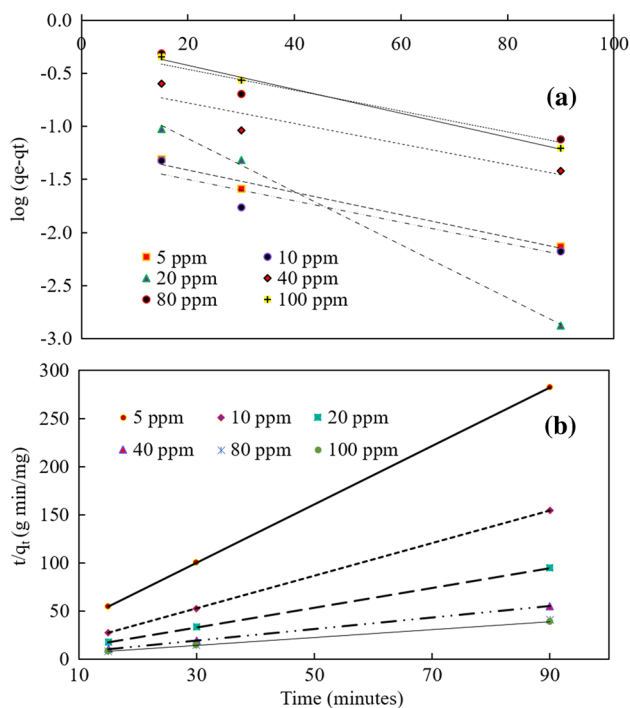


Fig. 7 Pseudo-first-order (a) and pseudo-second-order kinetic models (b) at different initial concentrations of Cd, mass 1.5 g/100 mL, pH 6 and room temperature

Conclusion

Results revealed that the *C. fistula* biomass (leaves) is very effective for the removal of Cd from the aqueous system. Its biosorption potential was evident with FTIR, BET and SEM analysis. Maximum removal (98%) of Cd was attained at the highest dose 1.5 g of the biosorbent while maximum biosorption (6.26 mg/g) was achieved at minimum biosorbent dose (0.25 g). Langmuir model yielded better approximation of the experimental data at equilibrium ($Q_{\max} = 7.24$ mg/g and $R^2 = 0.99$) and kinetic behavior was well explained with pseudo-second-order kinetic model. Results revealed a decline (12.7 and 6% at 1.0 and 0.25 g/100 mL, respectively) in the removal of Cd in the presence of cations in the water samples. The FTIR spectrum proved *C. fistula* as a low-cost and eco-friendly material in removing Cd from aqueous solutions due to the presence of alcoholic groups (OH), aliphatic groups (C–H), carbonyl vibrations (C=O), stretching of ester and O–H, secondary amine and C–O bonds of ether or phenol.

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