Sorption profile of Cd(II) ions onto beach sand from aqueous solutions

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Abstract

Sorption of traces of Cd(II) ions onto beach sand is investigated as a function of nature and concentration of electrolyte (10^{-4} to 10^{-2} M nitric, hydrochloric and perchloric acids, pH 2–10 buffers and deionized water), shaking time 5–40 min, shaking speed 50–200 strokes/min, dosage of sand (50–1000 mg/15 cm^3), concentration of sorbate (1.04×10^{-6} to 1.9×10^{-4} M) and temperature (293–323 K). Maximum sorption of Cd(II) ions ($\sim$66%) is achieved from deionized water using 300 mg/15 cm^3 sand in 20 min. The data are successfully tested by Langmuir, Freundlich and Dubinin–Redushkevich (D–R) sorption isotherms. The values for characteristic Langmuir constants $Q = 13.31 \pm 0.20$ µmol/g and of $b = (6.56 \pm 0.53) \times 10^3$ dm^3/mol, Freundlich constants $A = 2.23 \pm 1.16$ mmol/g and $1/n = 0.70 \pm 0.05$ of (D–R) constants $\beta = -0.005068 \pm 0.000328$ kJ^2/mol^2, $X_m = 46.91 \pm 11.91$ µmol/g and energy $E = 9.92 \pm 0.32$ kJ/mol have been estimated. Kinetics of sorption has been studied by applying Morris–Weber, Richenberg and Lagergren equations. The sorption follows first order rate equation resulting 0.182 ± 0.004 min^{-1} The thermodynamic parameters $\Delta H = 32.09 \pm 2.92$ kJ/mol, $\Delta S = 111.0 \pm 9.5$ J/mol K and $\Delta G = -1.68 \pm 0.02$ kJ/mol are evaluated. The influence of common ions on the sorption of Cd(II) ions is also examined. Some common ions reduce the sorption while most of the ions have very little effect. It can be concluded that beach sand may be used as an alternative for the expensive synthetic sorbents.
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1. Introduction

In recent years public awareness has increased toward the toxic effects of water containing dissolved metal ions. Numerous industrial processes produce effluents containing heavy metal contaminants. These pollutants concentration must be reduced to meet ever increasing legislative standards, and recovered where feasible. According to World Health Organization the metals of most immediate concern are aluminium, chromium, manganese, iron, cobalt, nickel, copper, cadmium, mercury and lead [1]. Cadmium is a toxic element; it has been recognized as carcinogen for human [2]. Elevated environmental level of Cd(II) ions arises from a variety of sources such as wastewater from metal plating industries, cadmium–nickel batteries, phosphate fertilizer, mining, pigments, stabilizers and alloys [3]. The acute cadmium poisoning in humans causes high blood pressure, kidney damage and destruction of testicular tissue and red blood cells [4]. Small amounts of Cd(II) ions are associated with hypertensive diseases. A relation has been found between occupational exposure to cadmium and lungs cancer and possibly prostate cancer [5]. The tolerance limits of Cd(II) ions for air are 0.05–0.2 mg/m^3, for water 5 µg/dm^3 and for food 50–50 µg/day [6]. The search for efficient and economical methods to eliminate or recycle the heavy metals present in industrial effluents has become a necessity [7].

Chemical precipitation, ion-exchange, membrane separation, reverse osmosis, solvent extraction, electrodeposition, electro-coagulation, cementation, adsorption and biosorption have been employed to remove toxic metals from water systems [8]. Most of these techniques are of high cost, produce toxic waste, and inability to meet the government legislation.

The adsorption of heavy metals by a variety of substances has been the subject of many studies, but high cost of the commercially available sorbents makes their large scale applications difficult. Efforts have been made to develop methods for the removal of heavy metals from effluents using natural and waste materials as sorbents which are abundant and inexpensive, such as zeolite for lead, cadmium, zinc, chromium, nickel, copper and

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cobalt [9], flyash for lead [10], goethite for chromium, nickel, zinc, copper and cadmium [11], lignite for copper, cadmium and zinc [12], kaolin and ballclay for cadmium, zinc, chromium, nickel and copper [13]. Haro river sand for antimony [14], cadmium [15], and zinc [16], bed sediment for cadmium [17], blast furnace waste for zinc and cadmium [18].

The objective of this study is to determine the sorption characteristics of Cd(II) ions onto beach sand from Hawks Bay, Karachi, Pakistan, a locally available cost effective material as a potential sorbent for the removal of Cd(II) ions more economically from water bodies.

2. Materials and methods

All reagents were of analytical or equivalent grade and all solutions were made in doubly distilled deionized water having conductivity $(0.5 \pm 0.1\,\mu\text{S/cm})$ and pH (6.5 ± 0.2). The beach sand was sieved with Ro-tap type mechanical shaker. The mesh size of $300\,\mu\text{m}$ was selected as a sorbent because of its larger proportion (45%) in the total sand. The other mesh sizes separated from the total beach sand were $150\,\mu\text{m}$ 25.1%, $600\,\mu\text{m}$ 17.5%, $900\,\mu\text{m}$ 8.4% and $1950\,\mu\text{m}$ 5.6%. The surface area of mesh size of $300\,\mu\text{m}$ using BET method [19] was found to be $\sim1\,\text{m}^2\,\text{g}^{-1}$, which is of the same order of magnitude as reported for Haro river sand, $1.47\,\text{m}^2\,\text{g}^{-1}$ [16].

The X-rays diffraction analysis of the beach sand $(300\,\mu\text{m})$ gives calcite 70%, quartz 26% and aragonite 3% in percentage by weight. A portion of beach sand $(300\,\mu\text{m})$ was treated with doubly distilled deionized water, stirred occasionally and left for 2–3 h. After stirring the water was decanted and fresh deionised water is added. This procedure was repeated until a colorless supernatant is obtained.

The pH of the distilled deionized water was 6.5 ± 0.2, and after washing its pH was monitored frequently. It was noticed that after washing pH rises to 8.0. But when used in the experiments with $300\,\text{mg}/15\,\text{cm}^3$ of the solution, there was no change in pH after shaking. The treated sand is heated for 8–10 h at $110\,^\circ\text{C}$. After complete removal of moisture, the sand has been stored in a vacuum desiccator.

3. Procedure

A fixed volume $(15\,\text{cm}^3)$ of analyte containing Cd(II) ions $(1.78 \times 10^{-5}\,\text{M})$ is agitated with beach sand $(100\,\text{mg})$ in a mechanical shaker for 10 min, in a 50 ml polypropylene vessel. The concentration of the analyte solution is determined before and after shaking by Metrohm VA trace analyzer model 747 with VA stand 746. An aliquot $(10\,\text{cm}^3)$ is taken into the VA stand and concentration of Cd(II) ions is determined on hanging mercury drop electrode at a peak potential of 480 mV. The percent sorption and distribution coefficient (R_d) are calculated using the following equations:

$$\% \text{ sorption} = \left(\frac{C_i - C_e}{C_i}\right) \times 100 \tag{1}$$

$$R_d = \frac{C_i - C_e}{C_e} \times \frac{V}{W}(\text{cm}^3\,\text{g}^{-1}) \tag{2}$$

where C_i is the initial concentration of Cd(II) ions, C_e the equilibrium concentration of Cd(II) ions in solution, V the volume of Cd(II) ions solution $(15\,\text{cm}^3)$ and W is the mass of sorbent (300 mg). The results are the average of at least triplicate measurements at $30 \pm 2\,^\circ\text{C}$ unless specified otherwise. In most cases the precision is around $\pm 2\%$.

4. Result and discussion

The sorption of traces of metal ions is influenced by the amount of sorbent, shaking time, shaking speed, concentration of sorbate and nature of electrolytes [20]. Firstly, the shaking speed is optimized from 50 to 200 strokes/min from deionized water using arbitrarily chosen Cd(II) ions concentration at $1.78 \times 10^{-5}\,\text{M}$, shaking time 10 min, amount of beach sand $100\,\text{mg}/15\,\text{cm}^3$, Maximum sorption is achieved around 100 strokes/min. For further investigations 100 strokes/min is used as optimized shaking speed.

The influence of the amount of sorbent is examined from 100 to 1000 mg using 10 min shaking time and 100 strokes/min shaking speed and $1.78 \times 10^{-5}\,\text{M}$ concentration of Cd(II) ions from deionized water. The percent sorption first increases and attains a maximum value ($\sim58\%$) around 300 mg and remains almost constant up to 1000 mg. The distribution ratio, R_d, increases up to 300 mg of sorbent. The volume to mass ratio (V/W) has an appreciable effect on the sorption upto 300 mg where after a decline in sorption is observed. Increasing the V/W ratio results in a better dispersion of sand particles and the inner surfaces are more exposed. Therefore, for further investigations 300 mg sorbent is used, the results are depicted in Fig. 1. A similar trend is observed in the sorption of Zn(II) ions onto Haro river sand while changing the amount of sorbent under optimized conditions [16].

The sorption of Cd(II) ions $(1.78 \times 10^{-5}\,\text{M})$ is also investigated as a function of nature and concentration of electrolytes. Initially, the sorption is monitored as a function of pH (2–10) of
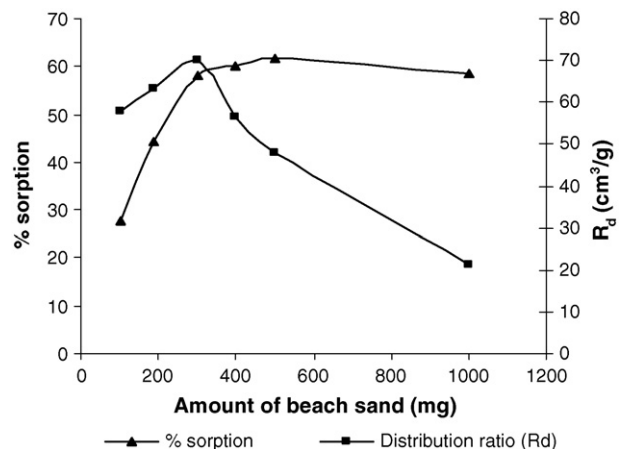

Fig. 1. The effect of beach sand dose on the sorption of Cd(II) ions $(1.78 \times 10^{-5}\,\text{M})$ employing 100 rpm shaking speed and 10 min shaking time.
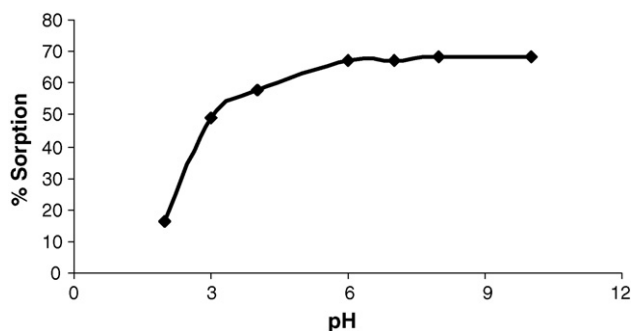
Fig. 2. Variation of % sorption of Cd(II) ions onto beach sand with pH (amount of beach sand 300 mg/15 cm³, shaking time 10 min, shaking speed 100 rpm). *Buffer of pH (2–3) KCl/HCl, pH (4–6) CH₃COONa/CH₃COOH and pH (8–10) NaCO₃/NaHCO₃.

Fig. 4. Effect of pH on Ca(II) ions removal from and Cd(II) ions sorption onto beach sand.

sorptive solution under the experimental conditions listed. The results are shown in Fig. 2. The percent sorption registers an increase with an increase in pH. The maximum sorption around 66% is noticed at pH 6. At low pH < 3 unfavorable high concentration of protons affect detrimentally the uptake of Cd(II) ions onto beach sand. The solutions of nitric acid, hydrochloric acid and perchloric acid (10^{-4} to 10^{-2} M), along with deionized water have also been investigated as sorptive medium as a function of agitation time. The dilute solutions (10^{-4} M) of all three acids gave maximum sorption 57.6% from HNO_3, 58.6% from HCl and 58.6% from $HClO_4$, and 66.7% from deionized water in 20 min shaking. The results are shown in Fig. 3. Maximum sorption is noticed from deionised water. The sorption of Cd(II) ions decreases with increasing molarity of the acid solutions. Therefore in all subsequent experiments, deionised water is used as a sorptive medium and 20 min as optimized shaking time. Cd(II) would be present as Cd^{2+} ions up to pH 8. However, at pH 10 the dominant species would be Cd^{2+} (~60%), $Cd(OH)^+$ (~24%) and $Cd(OH)_2$ (~11%) [21].

The results revealed that pH is the dominant parameter controlling the adsorption of Cd(II) ions (Fig. 2). The sorption first increases with the pH up to around pH 6, thereafter a no change in noticed. The variation of surface charge with pH is determined, particularly the point of zero charge (pH_{pzc}) of specific crystal surfaces. The pH_{pzc} is fundamentally important to many
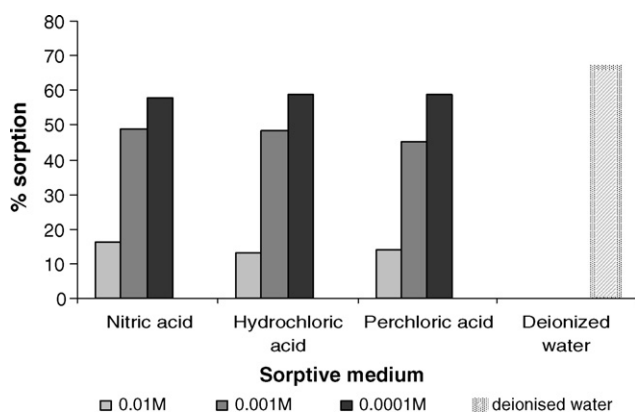

Fig. 3. Sorption of Cd(II) ions in different media as a function of acid concentration using 20 min shaking time and 100 strokes/min shaking speed.
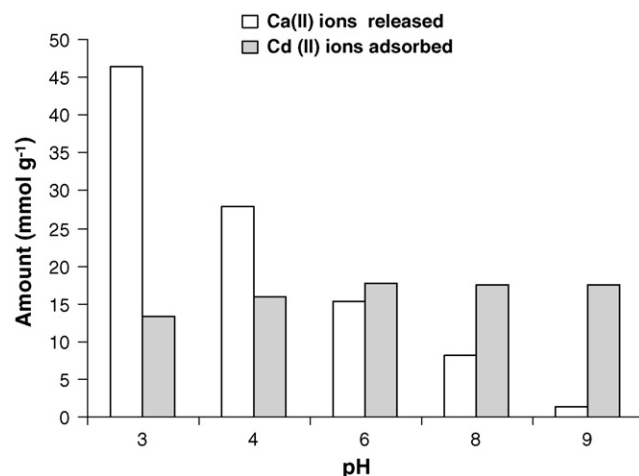
processes occurring at the mineral–water interface, including dissolution rates [22] and adsorption processes [16]. Above the pH_{pzc}, minerals display negative surface charge, whereas below the pH_{pzc} a positive charge occurs. Quartz, for example, accumulates pH-dependent surface charge through the dissociation of silanol (SiOH) groups [23]. The most common method for determining the pH_{pzc} of a mineral is acid-base titration. The pH_{pzc} of the beach sand is 8.2 calculated using computer software protofit, where as the reported valves of pH_{pzc} of calcite and quartz are 9.5 and 2.8, respectively [24]. Adsorption of Cd(III) ions onto beach sand may be explained on the basis of the fact that (a) quartz is present in 26% by weight of the sorbent which has a pH_{pzc} of 2.8, the surface of the quartz is dominated by negative charge on the surface above its pH_{pzc}. Due to the excess of negative sites metal ions are easily adsorbed on the surface. (b) Calcite which is 70% by weight of the total beach sand has a pH_{pzc} 9.5, and may be the dominating factor for the total properties of the beach sand. Calcite surface should be dominated by positive site below its pH_{pzc}. But maximum sorption of Cd(II) ions is noticed around pH 4–6, this may be explained on the basis of the fact that, calcite is a carbonate mineral with a rhombohedral structure. The surface of calcite in water is assumed to be dominated by the uncharged sites =CaOH and =CO₃H, but ionic sites are also present in the form of =Ca(OH₂)⁺ and =CO₃(OH₂)⁻ [25], The presence of negative site on the surface may also be demonstrated by the removal of Ca(II) ions into the solution from the sorbent surface at low pH values as shown in Fig. 4. The removal of Ca(II) ions from sorbent surface resulted in an increase in the number of negative sites which ultimately provides electrostatic attraction for the Cd(II) ions present in the aqueous environment. As the Cd^{2+} and Ca^{2+} ions are of nearly the same size 1.09 and 1.14 Å, respectively [26]. It may be expected that Cd^{2+} ions replaces Ca^{2+} from the mineral surface. This may be an important mechanism for the removal of trace concentrations of Cd(II) ions from water bodies in contact with $CaCO_3$ [20].

Studies on the adsorption of amino acids on calcite [27] reveal that calcite, even below its pzc of 9.5; will have both positive
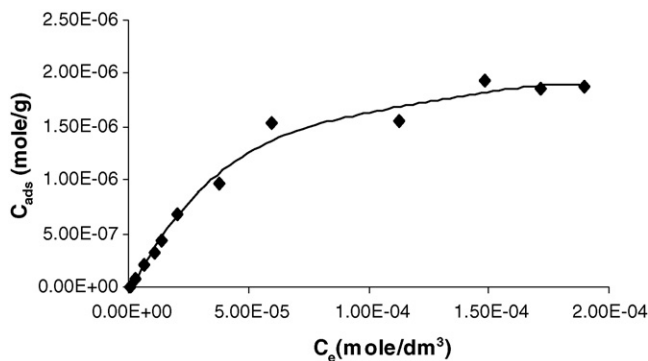
Fig. 5. Influence of concentration of Cd(II) ions on its own sorption onto beach sand (amount of beach sand 300 mg, shaking time 20 min, shaking speed 100 spm from deionized water as sorptive medium).

and negative regions of surface charge. Consequently, there are sites near exposed oxygen atoms of the CO_3 groups that might take up heavy metal cations. Models of the quartz surface suggest a relatively uniform distribution of terminal oxygen atoms, which achieve a neutral surface charge through hydration. Calcite, by contrast, has both oxygen and calcium atoms at surfaces. Such calcite surfaces likely possess an array of both positive and negative charge centers at any pH.

The concentration of sorbate ions is examined over a 100-fold concentration of Cd(II) ions in the range of 1.04×10^{-6} to 1.90×10^{-4} M under the experimental condition given in Fig. 5. Dilute aqueous solution of Cd(II) ions have been employed as models for low metal concentration wastewater. The sorbed concentration increases with initial concentration of sorbate and attains a constant value around 10^{-4} M. A similar trend has been noticed for the sorption of Cd (II) ions onto Haro river sand [15] while monitoring the concentration of sorbate onto sorbent surface.

5. Sorption isotherms

The sorption data at different temperatures have been subjected to different sorption isotherms namely Langmuir, Freundlich and Dubinin–Radushkevich (D–R) to assess sorption capacity of Cd(II) ions. The Langmuir sorption isotherm envisages that all sites are equal and uniform, there is no interaction between neighboring sorbed molecules and there is no steric hindrance between sorbed molecules and incoming ions and monolayer is formed at maximum sorption capacity [28]. The Langmuir sorption isotherm is tested in the following form:

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q} \tag{3}$$

where C_e is the residual concentration of sorbate in solution (mol/dm^3) at equilibrium, C_{ads} the amount sorbed (mol/g), Q the sorption capacity corresponding to complete monolayer coverage and b is the enthalpy dependent sorption equilibrium constant relating to the affinity of binding sites for metal ions. C_e/C_{ads} is plotted against C_e at different temperatures and straight lines are obtained. The Langmuir parameters (Q and b) calculated using slope and intercept of the linear plots are tabulated in Table 1. Maximum value of Q and minimum value of b is obtained at 323 K. The value of Q increases as the sorptive solution temperature is raised indicating the process to be endothermic. This can further be explaining by thermodynamic parameters in subsequent section. A dimensionless constant R_L [29], as given by the Eq. (4) may be evaluated employing Langmuir constant b and initial concentration of sorbate, C_i. R_L is estimated in the range of 0.45–0.99. This higher value of R_L indicates reasonable sorption of Cd(II) ions onto beach sand:

$$R_L = \frac{1}{1 + bC_i} \tag{4}$$

The Freundlich isotherm, the most widely used mathematical description of sorption in aqueous solutions, is an empirical expression that encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies [30]. The Freundlich equation is tested in following linearized form:

$$\log C_{ads} = \log A + \frac{1}{n} \log C_e \tag{5}$$

where C_{ads} and C_e have same meaning as defined earlier, $1/n$ is the Freundlich characteristic constant related to energy or intensity and A is the maximum sorption capacity. $\log C_{ads}$ is plotted against $\log C_e$ at different temperatures, and linear plots are obtained. From the slope and intercept of the plots values of $1/n$ and A have been estimated using linear regression analysis. The results are listed in Table 1. A and $1/n$ are minimum at lowest temperature investigated. The value of Freundlich parameters at 303 K are comparable to $A = 1.38 \pm 1.14 \, \text{mmol g}^{-1}$ and of $1/n = 0.67 \pm 0.05$ reported for Cd(II) ions sorption onto Haro river sand [15].

A general correlation of sorption equilibrium for microporous sorbent has been developed by Dubinin and co-workers [31] from the ideas put forward by Polanyi [32]. The Dubinin–Redushkevich (D–R) model is tested in the following form [33]:

$$\ln C_{ads} = \ln X_m - \beta \varepsilon^2 \tag{6}$$

where C_{ads} is the amount sorbed in mol g^{-1}, X_m the sorption capacity in the same unit, β the a constant related to free energy

Table 1
Langmuir and Freundlich constants of Cd(II) ions sorption onto beach sand

T (K)	Q (μmol/g)	b (dm^3/mol)	R^2	$1/n$	A (mmol/g)	R^2
293	5.37 ± 0.13	$(1.41 \pm 0.31) \times 10^4$	0.9698	0.64 ± 0.06	0.39 ± 0.09	0.9424
303	7.51 ± 0.15	$(1.98 \pm 0.63) \times 10^4$	0.9593	0.54 ± 0.05	0.37 ± 0.16	0.8856
313	10.4 ± 0.15	$(1.49 \pm 0.16) \times 10^4$	0.9785	0.62 ± 0.05	1.30 ± 0.65	0.9301
323	22.96 ± 0.28	$(1.76 \pm 0.14) \times 10^4$	0.9908	0.64 ± 0.04	3.73 ± 1.70	0.9625

Table 2
(D-R) characteristic constants for Cd(II) ions onto beach sand

T	β (kJ^2/mol^2)	X_m (μmol/g)	E (kJ/mol)	R^2
293	-0.0049 ± 0.00044	20.40 ± 6.30	10.13 ± 0.45	0.9595
303	-0.0051 ± 0.00032	29.45 ± 8.85	10.43 ± 0.44	0.9256
313	-0.0041 ± 0.00026	36.30 ± 8.55	11.06 ± 0.35	0.9514
323	-0.0038 ± 0.00019	83.30 ± 15.71	11.48 ± 0.28	0.9775

and ε is the Polanyi potential, which is expressed as

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \tag{7}$$

where R is a gas constant in kJ/mol K, T the temperature in Kelvin and C_e as defined earlier. The Polanyi model postulates 'sorption space', close to the sorbent surface where sorption takes place. The Polanyi defines the sorption potential 'ε' for any molecule within the attractive force field of the solid surface as the work required to removing a molecule to infinity from its location in the sorption space. From the plots of $\ln C_{ads}$ versus ε^2 at different temperatures the values of β, X_m are determined by the slope and intercept of the linear lines and energy of sorption E is calculated [34] using following equation. The results are registered in Table 2. The calculated value of X_m at 303 K is very much higher as compare 0.23 μmol g^{-1} reported for the sorption of Cd(II) ions onto Haro river sand [15]. The mean sorption energy E is found to vary within a narrow range of 10.13–11.48 kJ/mol which are in the range of 8–16 kJ/mol reported for ion exchange mechanism [35]:

$$E = \frac{1}{\sqrt{-2\beta}} \tag{8}$$

The experimental equilibrium data fit all three sorption models. The variation in the sorption capacities estimated in three sorption isotherms may be explained due to assumptions taken into account while deriving these sorption models. In general, the sorption capacities appear to increase with temperature. This can be interpreted that at higher temperature number of activated sites have increased, providing more space for Cd(II) ions to occupy on the sorbent surface.

6. Kinetics of sorption

Mass transfer process can be understood by kinetics and thermodynamics of sorption. Therefore, the change in the sorbed concentration onto sorbent with shaking time is tested by Morris–Weber equation [36] in the following form:

$$q_t = R_{id} \sqrt{t} \tag{9}$$

where q_t is the sorbed concentration at time 't', and R_{id} is the rate constant of intraparticle transport. The plot of q_t versus $t^{1/2}$ is given in Fig. 6. This is a linear plot with a correlation factor of 0.9352. The value of R_{id} calculated from the slope is 80 ± 3.3 μmol g^{-1} min$^{-1/2}$.
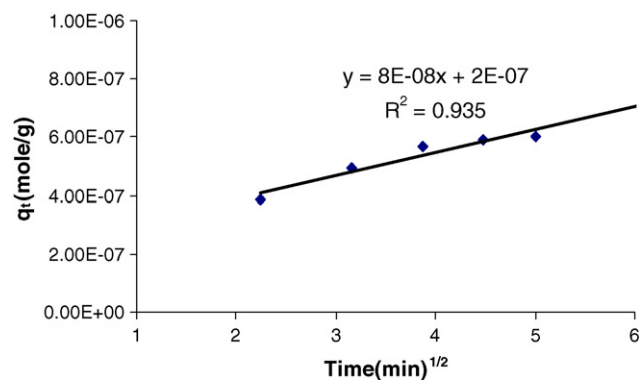

Fig. 6. Validation of Morris–Weber equation of Cd(II) ions sorption onto beach sand.

The kinetics of Cd(II) ions sorption is subjected to Reichenberg equation [37]:

$$F = \left(\frac{1-6}{\pi^2} \right) e^{-Bt} \tag{10}$$

where Bt can be calculated for each value of F by the relationship [16] $Bt = -0.4977 - \ln(1 - F)$ where

$$F = q_t/q_e$$

where q_e is the sorbed concentration at equilibrium and q_t is the sorbed concentration at time 't'. The linearity test of Bt versus 't' is illustrated in Fig. 7 is employed to distinguish between film and particle diffusion-controlled mechanisms. The linear Bt versus t plot does not pass through the origin suggesting a film diffusion sorption process.

The validity of Lagergren equation [38] is also tested using the kinetic data [16]:

$$\log(q_e - q_t) = \log q_e - \frac{kt}{2.303} \tag{11}$$

where 'k' is the first order rate constant. The equation is tested by plotting $\log(q_e - q_t)$ against time 't' in Fig. 8, yielding a straight line with a correlation factor of 0.9858. The rate constant $k = 0.17 \pm 0.004$ min^{-1} is computed from the slope of the linear plot. This is of the same order of magnitude of 0.18 min^{-1} estimated for Ag(I) ions sorption onto polyurethane foam [39].
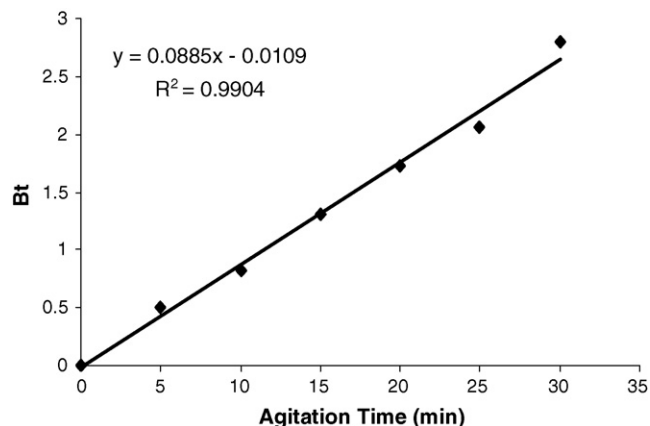

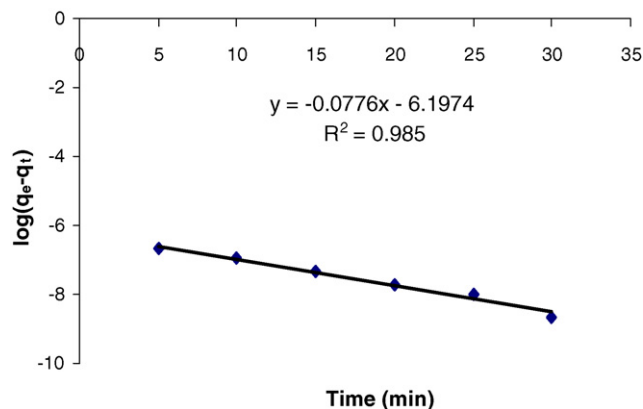Fig. 7. Reichenberg plot of Cd(II) ions sorption onto beach sand.

Fig. 8. Lagergren plot of Cd(II) ions sorption onto beach sand.

7. Thermodynamic studies

The variation in temperature also affects the sorption of trace metal ions onto solid surfaces. The sorption of Cd(II) ions onto beach sand is monitored over a temperature range of 293–303 K under the optimized conditions already chosen. The values of ΔH and ΔS are calculated from the slope and intercept of the Van't Hoff plot of $\log K_c$ versus $1/T$ (T in Kelvin) using Eq. (13) [33]:

$$K_c = \frac{F_e}{1 - F_e} \quad (12)$$

where F_e is the fraction sorbed at equilibrium:

$$\log K_c = \frac{-\Delta H}{2.303RT} + \frac{\Delta S}{2.030R} \quad (13)$$

The plot shown in Fig. 9 is linear over the entire range of temperature investigated. The values of ΔG are calculated using the Eq. (14):

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

The results are listed in Table 3. The positive value of ΔH indicates that process is endothermic in nature and negative ΔG suggests the spontaneity of the sorption of Cd(II) ions onto beach

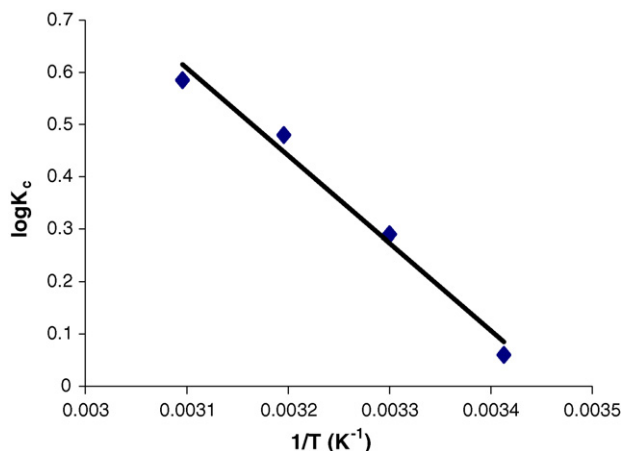

Fig. 9. Variation of sorption of Cd(II) ions with temperature.

Table 3
Thermodynamic parameters for Cd(II) ions sorption onto beach sand

ΔG (kJ/mol)	
293 K	-0.34 ± 0.06
303 K	-1.68 ± 0.15
313 K	-2.88 ± 0.21
323 K	-3.62 ± 0.26
ΔH (kJ/mol)	32.10 ± 2.95
ΔS (kJ/mol K)	111 ± 9.6

sand. The positive value of entropy change (111 J/mol K) suggests the increased randomness at the solid–solution interface during sorption. The endothermic nature of the sorption process have also been reported in [16].

The increase in sorption capacity with an increase in temperature is noticed in Tables 1 and 2 which suggests a temperature dependent sorption of Cd(II) ions onto beach sand.

8. Influence of diverse anions and cations

The influence of different anions and cations on the sorption of Cd(II) ions is very important because in the environmental samples the ions other than the targeted ions greatly effect the sorption of the required ion in aqueous medium. Sorption of Cd(II) ions is studied in the presence of different anions and cations. The anions have been added as their sodium or potassium salts, whereas cations are included as their nitrates or chlorides. The results are shown in Table 4. The nil result refers to the sorption of Cd(II) ions from sorptive medium without additional diverse anion or cation. Co(II), Fe(II), Cr(III), Pb(II) and Ni(II) ions suppress the sorption of Cd(II) ions appreciably. This may be due to strong affinity of these cations toward the sorbent surface. Sulphate, thiosulphate, iodide, acetate and EDTA cause substantial decrease in the sorption of Cd(II) ions onto beach sand. This may be due to higher affinity of anionic complexes of Cd(II) ions with these ions to Cd(II) ions themselves. Strong complexes of Cd(II) ions with sulphate, thiosulphate, acetate, iodide and EDTA have been reported in the literature [40–42].

Table 4
Sorption of Cd(II) in the presence of diverse cations and anions

Cations	% Sorption	Anions	% Sorption
Nil	66.42	Nil	66.42
Li(II)	51.23	SO_4^{2-}	55.49
Na(I)	47.98	S^{2-}	62.58
K(I)	47.89	$S_2O_3^{2-}$	42.58
Ca(II)	61.25	CO_3^{2-}	64.58
Fe(II)	26.84	HCO_3^-	61.02
Co(II)	23.89	Cl^-	63.25
Ni(II)	50.25	Br^-	59.24
Zn(II)	55.68	I^-	53.78
Pb(II)	40.58	CH_3COO^-	30.58
Cr(III)	38.59	EDTA	30.65

Nil result indicate sorption of Cd(II) ions without any diverse ion.

Table 5
The sorption of other metal ions onto beach sand (300 mg) after 20 min shaking from deionized water

Element	% Sorption	R_d (cm^3 g^{-1})	$\propto = R_d$ Cd(II)/R_d (M)
Cd(II)	66.4	98.8	
Pb(II)	85.5	294.8	0.225
Ni(II)	62.2	82.5	1.198
Zn(II)	67.2	102.7	0.962
Cr(III)	75.4	150.8	0.655
Co(II)	34.8	26.7	3.694
Fe(II)	55.6	62.6	1.579

9. Selectivity of the sorbent

The selectivity of beach sand is investigated by measuring the sorption of other metal ions under optimized condition chosen for the sorption of Cd(II) ions. The results are including separation factor ($\propto$) with respect to Cd(II) ions are presented in Table 5. The difference in the affinity of beach sand towards other metal ions can be provide a foundation for the effective separation of these ions from aqueous solution. There is very little difference in the separation factor for the metal ions investigated, though Pb(II) and Cr(III) ions showed higher affinity as compare to Co(II) and Fe(II) ions.

10. Reaction and mechanism

The beach sand is composed of calcite, quartz, and aragonite. Calcite is rhombohedral in shape where carbonate ions are arranged in a triangular manner, the oxygen of each carbonate ions occupied three corners of a triangle, whereas calcium remained there in the center of the two planes of the triangles. The triangular carbonate groups are the basic building units of all carbonate minerals and are largely responsible for the properties peculiar to the group. The quartz has a tetrahedral structure with oxygen atoms occupying the four corner of a tetrahedron. The aragonite is also calcium carbonate with a orthorombic shape; the properties of this component of beach sand also depend upon the carbonate [43]. A possible sorption mechanism is proposed for Cd(II) ions onto beach sand. The presence of negative sites in the structure of the calcite, quartz and aragonite in the form of carbonates and oxides provides affinity for the positively charged Cd(II) ions in the aqueous solutions as shown below: the electrostatic attractive forces between cadmium cation and the negatively charged surface of the beach sand is likely to dominate the accumulation of Cd(II) ions onto sorbent surface:

$$Cd^{2+} + O^{2-} \rightarrow \ O^- \cdots Cd^{2+} \cdots O^-$$
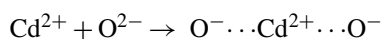
11. Conclusions

The beach sand can be used as a potential sorbent to remove Cd(II) ions from aqueous solutions. The sorption is quiet selective because Cd(II) ions can easily be removed in the presence of common diverse ions from aqueous solutions. Very few of these ions tested have an effect on the sorption. The sorption of Cd(II) ions followed all three sorption isotherms. Sorption capacity generally increased with an increase in temperature. Thermodynamics suggest that the sorption is endothermic and spontaneous in nature. The cost effective beach sand may be used to remove traces of Cd(II) ions or to preconcentrate its very minute amounts from the aqueous media. This sorbent has a potential to treat industrial effluents containing Cd(II) ions or to clean large volume of solutions contaminated with traces of Cd(II) ions.

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