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Fate of cadmium at the soil-solution interface: a thermodynamic study as influenced by varying pH at South 24 Parganas, West Bengal, India

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Abstract A study on the sorption kinetics of Cd from soil solution to soils was conducted to assess the persistence of Cd in soil solution as it is related to the leaching, bioavailability, and potential toxicity of Cd. The kinetics of Cd sorption on two non-contaminated alkaline soils from Canning (22° 18′ 48.02″ N and 88° 39′ 29.0″ E) and Lakshmikantapur (22° 06′ 16.61″ N and 88° 19′ 08.66″ E) of South 24 Parganas, West Bengal, India, were studied using conventional batch experiment. The variable soil suspension parameters were pH (4.00, 6.00, 8.18, and 9.00), temperatures (308, 318, and 328 K) and Cd concentrations (5–100 mg L^{-1}). The average rate coefficient (k_{avg}) and half-life ($t_{1/2}$) values indicate that the persistence of Cd in soil solution is influenced by both temperature and soil suspension pH. The concentration of Cd in soil solution decreases with increase of temperature; therefore, Cd sorption on the soil-solution interface is an endothermic one. Higher pH decreases the $t_{1/2}$ of Cd in soil solution, indicating that higher pH (alkaline) is not a serious concern in Cd toxicity than lower pH (acidic). Based on the energy of activation (E_a) values, Cd sorption in acidic pH (14.76 ± 0.29 to 64.45 ± 4.50 kJ mol^{-1}) is a surface control phenomenon and in alkaline pH (9.33 ± 0.09 to 44.60 ± 2.01 kJ mol^{-1}) is a diffusion control phenomenon The enthalpy of activation ($\Delta H^{\mp}$) values were found to be between 7.28 and 61.73 kJ mol^{-1}. Additionally, higher positive energy of activation ($\Delta G^{\mp}$) values (46.82 ± 2.01 to 94.47 ± 2.36 kJ mol^{-1}) suggested that there is an energy barrier for product formation.

Keywords Enthalpy · Entisols · Entropy · Free energy · Half-life · Sorption

Abbreviations

$\Delta H^{\mp}$	Enthalpy of activation
$\Delta G^{\mp}$	Free energy of activation
$\Delta S^{\mp}$	Entropy of activation
A	Pre-exponential factor
CG	Canning
E_a	Energy of activation
k_{avg}	Average rate coefficient

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LKPR	Lakshmikantapur
k_{obs}	Observed rate coefficient
$t_{1/2}$	Half-life

Introduction

Additions of potentially toxic heavy metals (HMs), e.g., Cd, Cu, Cr, Pb, Hg, As, Se, Zn, and Ni, to soils either through sewage sludge application or some other source of pollution, e.g., atmospheric deposition and use of agri-chemicals, pose a threat to the environment and human health (Kanbar et al. 2014). Of these potentially toxic metals, Cd is considered one of the most hazardous from an environmental viewpoint (Islam et al. 2014). Thus, concern about soil and water pollution has emphasized the need for understanding the processes or factors controlling the retention of Cd in soils. The mobility and fate of Cd in soils and sediments are governed to a large extent by adsorption reactions at solid-water interfaces of minerals (Sayadi et al. 2014). Adsorption reaction is due to chemical bond formation, complex formation, and ion exchange which are mostly dependent on soil solution pH (Duc et al. 2013; Robson et al. 2014) and fraction of the surface of adsorbed soil that is bare. Several studies have demonstrated that pH is the most influential factor controlling sorption-desorption processes of heavy metals in soils (e.g., Anderson and Christensen 1988; Naidu et al. 1994). Sauvé et al. (2000) reviewed and compiled data from more than 70 soils and found by multiple linear regression analysis that approximately 50 % of the overall variation in the distribution coefficient for Cd and Pb could be explained by variations in pH. The steep increase in HM sorption with rising pH is usually illustrated by means of sorption edges (Zan et al. 2013). Lindsay (1979) reported the formation of different insoluble compounds of HMs influenced by the pH of the soil suspension (e.g., at values above 7.5, depending on CO_2, Cd^{2+} activity is limited by octavite). McBride (1980, 1989) concluded that calcite ($CaCO_3$) serves as a site for adsorption of Cd^{2+} at low concentrations of Cd, while $CdCO_3$ precipitation, possibly as a coating on the calcite, occurs only at higher Cd concentrations.

Increasing temperature has been shown to increase both the rate and the amount of trace metal sorption by soil particles (Jayasiri et al. 2014). At the same time, trace metal uptake by plants is reported to increase with increasing temperature (Hooda and Alloway 1998; Fritioff et al. 2005), indicating that a temperature-induced retention of metals in soil is not necessarily limiting the plant uptake. As noted by Barrow (1986), increasing temperature tends to change both the reaction rate and the equilibrium point. Indeed, in studying the sorption of Cd^{2+} by goethite, Brümmer et al. (1988) demonstrated a shift of the sorption edge to a lower pH as temperature increased from 5 to 35 °C. Furthermore, while the initial reaction was more rapid at the higher temperature, it appeared that some type of secondary reaction caused an extended drift toward equilibrium (Sundaray et al. 2012). A 10 °C temperature difference can substantially alter (i) the sorption kinetics, (ii) the solution metal content at equilibrium, and (iii) the time required for equilibrium to be achieved (Harter and Naidu 2001). Such temperature variation may have contributed to variability in experimental results. Therefore, the concentration of metals in the soil solution, at any given time, is governed by a number of interrelated processes, including inorganic and organic complexation, precipitation/dissolution reactions, and adsorption reactions (Li et al. 2013). These reactions are presumably determined and constrained by soil properties like soil texture; content of organic matter; content and type of clay minerals and Al, Fe, and Mn oxides; and prevailing physicochemical conditions in the soil such as pH (Appel and Ma 2002; Collins et al. 2003; Hodgson et al. 1964) and soil temperature (Adhikari and Singh 2003).

In the literature, attention has been mainly given to equilibrium processes in soils, but soil processes are never at equilibrium because most of HM reactions on soils mainly follow first-order kinetics (Sparks 1989). Most studies of the behavior of HMs in soils also have been carried out under equilibrium conditions with fixed temperature and pH (generally in acidic range) to explore the sorption and partition coefficients (Collins et al. 2003) of HMs. However, the time dependence disappearances of HMs from soil solution to soil are also a major factor to control the solution-phase HMs. The study of chemical kinetics is concerned with the rates and mechanistic pathways of chemical reactions (Laidler and Meiser 1985). There is also a dearth of information on the rate constant (k), half-life ($t_{1/2}$), activation energy (E_a), Gibbs free energy of activation ($\Delta G^{\mp}$), enthalpy of activation ($\Delta H^{\mp}$), entropy of activation ($\Delta S^{\mp}$), and the thermodynamic parameters related to Cd reaction kinetics in the soil-solution interface as a thermodynamic approach can predict the final state of metals in the soil system from an initial nonequilibrium state. Similarly, an understanding of change in enthalpy and entropy helps in determining the free energy change and disorders occurring during the sorption process. Such information on Cd sorption is lacking for the soils at the coastal regions of West Bengal, India.

Since most of the laboratory experiments were conducted at room temperature (T = 293–298 K), data generated from such experiments are limited in understanding reactions at higher temperatures that often undergo seasonal temperature changes mainly in subtropical countries like India. Accordingly, the objectives of this study were to observe the influence of temperature and pH upon the kinetics of Cd reaction in soil and to determine the rate coefficient (k), the half-life ($t_{1/2}$) of Cd retention in the soil solution phase applying different nonequilibrium rate equations, and the E_a, A, $\Delta G^{\mp}$, $\Delta H^{\mp}$, and $\Delta S^{\mp}$ through application of the Arrhenius (1889) and Eyring (1935) equations.

Theoretical approaches

Reaction kinetics

The kinetics of the first-order reaction can be written as

$$\ln C_t = \ln C_0 - k_{\mathrm{obs}} t \qquad (1)$$

where t = time (h, min, or s); C_0 = initial concentration of the reactant (mg L^{-1} or mol L^{-1}); C_t = concentration of the reactant (mg L^{-1} or mol L^{-1}) at time t; and k_{obs} = observed overall rate constant or the rate coefficient.

Half-life ($t_{1/2}$), the time required for half of the original concentration of the reactant to disappear (Bhon et al. 1985), of the first-order reaction is

$$t_{1/2} = \frac{0.693}{k_{\mathrm{obs}}} \qquad (2)$$

$t_{1/2}$ is a useful semi-quantitative indicator of the reaction rate and of how long a solute persists in the soil-solution interface.

Temperature effects on reaction kinetics

Of great importance was van't Hoff's (1884) development of the general thermodynamic relationship between the heat of conversion and the displacement of the equilibrium as a result of temperature variation.

$$\frac{\partial \ln(K)}{\partial\left(1/T\right)} = \frac{-E_a}{R} \qquad (3)$$

where K is the equilibrium constant, T is the reaction temperature in absolute scale (K), E_a is the empirical calorimetric parameter called the activation energy, and R is the universal gas constant (8.31 J mol^{-1} K^{-1}). van't Hoff (1884) also pointed out that a similar relationship should hold for the observed rate coefficient k_{obs} of a reaction.

$$\frac{\partial \ln(k_{\mathrm{obs}})}{\partial\left(1/T\right)} = \frac{-E_a}{R} \qquad (4)$$

Drawing upon the work by van't Hoff (1884), Arrhenius (1889) concluded that most of the observed reaction rate (k_{obs}) obeyed the integrated form of Eq. 4:

$$k_{\mathrm{obs}} = A e^{\frac{-E_a}{RT}} \qquad (5)$$

where A is a frequency or pre-exponential term with the same units as k_{obs}. A is related to the frequency of collisions and the probability that the collisions are favorably oriented for reaction which is also often qualitatively correlated with the entropic component of the activation barrier. Equation 5 is generally referred to as the Arrhenius law (Arrhenius 1889).

Taking the natural log of both sides of Eq. 5, one obtains

$$\ln k_{\mathrm{obs}} = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln A \qquad (6)$$

By plotting $\ln k_{\mathrm{obs}}$ vs. $1/T$, a linear relationship is obtained and one can determine E_a from the slope ($-E_a/R$) and A from the y-intercept. Although the Arrhenius equation (Eq. 5) is an empirical approach to determining the activation energy (E_a) values, one can calculate the enthalpy, entropy, and free energy of activation for metal sorption kinetics by applying the Eyring equation (Eyring 1935). In the Arrhenius (1889) equation form, the Eyring (1935) equation in its thermodynamic version becomes

$$k_{\mathrm{obs}} = \frac{\kappa \mathrm{T}}{h} e^{-\frac{\Delta G^{\mp}}{RT}} \qquad (7)$$

where κ is the Boltzmann constant (1.38 × 10^{-23} J K^{-1}), h is Planck's constant (6.63 × 10^{-34} J s), and $\Delta G^{\mp}$ is the

Gibbs free energy of activation. Since the Gibbs free energy of activation may be written in terms of entropy of activation $\Delta S^{\mp}$ and enthalpy of activation $\Delta H^{\mp}$,

$$\Delta G^{\mp} = \Delta H^{\mp} - T\Delta S^{\mp} \tag{8}$$

Therefore, Eq. 7 may be written as

$$\ln\frac{k_{\text{obs}}}{T} = \left(\ln\frac{\kappa}{h} + \frac{\Delta S^{\mp}}{R}\right) - \frac{\Delta H^{\mp}}{RT} \tag{9}$$

By plotting $\ln(k_{\text{obs}}/T)$ vs. $1/T$, a linear relationship is obtained and one can determine $\Delta H^{\mp}$ from the slope $(-\Delta H^{\mp}/R)$ and $\Delta S^{\mp}$ from the y-intercept $[\ln(\kappa/h) + (\Delta S^{\mp}/R)]$.

Materials and methods

Soil samples and analyses

The soils used in this study were collected from the non-contaminated surface horizon (0–15 cm) of two agricultural fields at Canning (sample ID: CG at 23° 25′ 22.5″ N and 85° 50′ 10.3″ E) and Lakshmikantapur (sample ID: LKPR at 23° 49′ 32″ N and 87° 21′ 08.3″ E) of South 24 Parganas, West Bengal, India. Soil samples were collected, pretreated for analysis, and preserved according to the protocol described by Rubio and Ure (1993). We used the non-contaminated soil for kinetic study to lessen the complications that may arise from the release of Cd from soil on the kinetic study.

pH was carried out on soil slurries having a soil to water ratio of 1:2.5, and exchangeable acidity was measured by using neutral 0.1 N KCl solution maintaining the same soil-solution ratio (Jackson 1973) using a pH meter (Systronics India Ltd. model 239). Organic carbon content was found by $K_2Cr_2O_7$ at digestion (Nelson and Sommer 1982). Cation exchange capacity (CEC) of the soil sample was determined by the NH_4OAc exchange method (Rhoades 1982). The particle size distribution was determined by sieving and the pipette method after removal of organic matter with 30 % H_2O_2 and 0.002 M sodium pyrophosphate (Jackson 1973). PO_4^{3-} was determined colorimetrically (Varian Cary 50 Bio spectrophotometer, Australia) according to the method described by Peachey et al. (1973). The methodology of van Raij and Peech (1972) was used to measure PZC (point of 0 charge). Assessment of potentially phyto-available elements (Al, Ca, Cd, Co, Cu, Fe, Mg, Mn, Ni, Pb, and Zn) was conducted using the DTPA/TEA method developed by Lindsay and Norvell (1978). Briefly, 10 mL of 0.005 M diethylene triamine pentaacetic acid (DTPA), 0.1 M triethanolamine (TEA), and 0.01 M $CaCl_2$ solution (pH = 7.3) was added to 5 g of soil and the sample was shaken for 2 h. After centrifugation (4000 rpm for 10 min), the supernatant was filtered through a 0.2-μm Whatman filter paper in a 25-mL polycarbonate volumetric flask and diluted to 25 mL with deionized water.

For the determination of total concentrations of aluminum (Al), cadmium (Cd), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), and zinc (Zn) in experimental soils, 1 g of each sample was weighed into a 100-mL Erlenmeyer flask and wetted with a few drops of deionized water. The three-acid (HCl 4 mL, HNO_3 2 mL, and HF 2 mL) dissolution method was applied and described by Cappuyns et al. (2002). Approximately 2 mL of the tri-acid mixture was added into the flask and carefully mixed with the soil. The mixture was gently heated on a hot plate until half dried and subsequently reattacked with the same three acids and heated until the reaction died down. The residue was redissolved with 20 mL of 2.5 N HCl and filtered (Whatman 45). Finally, the solution was collected in a 25-mL polycarbonate volumetric flask and diluted to 25 mL with deionized water. A blank digest was carried out in the same way. Elements were determined using an atomic absorption spectrophotometer (Model No.: AA240, Australia). The detection limit, defined as 3 standard deviations above the mean for 25 analyses of blank solutions, was 0.860 μg L^{-1} for Al, 1.274 μg L^{-1} for Ca, 0.081 μg L^{-1} for Cd, 0.074 μg L^{-1} for Co, 0.349 μg L^{-1} for Cr, 0.990 μg L^{-1} for Cu, 0.871 μg L^{-1} for Fe, 2.507 μg L^{-1} for K, 1.559 μg L^{-1} for Mg, 1.003 μg L^{-1} for Mn, 0.071 μg L^{-1} for Ni, 0.306 μg L^{-1} for Pb, and 0.738 μg L^{-1} for Zn. To check the accuracy of analytical results, standard reference materials (SRM-2710 and BCR-144) were analyzed following the same digestion and analytical procedure as those of soils. The obtained values were in good agreement with the certified values. All the aforementioned analyses were made on the basis of three replicates.

Kinetics of cadmium (Cd) sorption

The Cd^{2+} sorption kinetics on two alkaline soils was investigated at 298, 308, and 318 K by the conventional batch method within the pH range from 4 to 9 including native soil pH. Cadmium nitrate tetrahydrate [$Cd(NO_3)_2{\cdot}4H_2O$] was used and all the experiments were performed in triplicate. 2.5 g soil sample (triplicate) was added to a 150-mL Pyrex stopper bottle containing 25 mL 0.5 M neutral $NaNO_3$ of double-deionized water and mixed using a temperature control orbital shaker. The pH of the suspension was adjusted to reaction pH range (4.00, 6.00, 8.18, and 9.00) using freshly prepared 0.1 M HNO_3 or 0.1 M NaOH. The suspension was then shaken for 24 h in a constant-temperature water bath with another interim adjustment of pH. After shaking for 24 h, the suspension pH was readjusted to the range of reaction pH and the volume of water was adjusted to 25 mL by weighing the reaction vessel.

A measured quantity of stock solution of 500 mg L^{-1} Cd^{2+} solution (having pH 4.0–9.0) was then carefully added to the suspension to maintain the Cd^{2+} concentration within the range of 5–100 mg L^{-1}. The final volume of the soil suspension was 150 mL and the reaction vessel was weighed. After that, the reaction vessel was then immediately transferred to the temperature control orbital shaker from the variation of temperature 298–318 K. Any evaporation loss was compensated by adding a measured quantity of distilled deionized Cd^{2+}-free water on an hourly basis. The pH was readjusted in every hour of progress of the reaction.

To prevent the thin water layer on the soil colloid surface, the soil suspension was shaken every half an hour at 120 rpm. Chloroform (50 μL) was also added at the time of the batch experiment to minimize bacterial activity in the soil (Collins et al. 2003). At various times between 1 and 125 h (1, 5, 10, 20, 30, 40, 50, 75, 100, and 125 h), the sample was centrifuged at 2500×*g* for 15 s. Next, the solution was filtered using a 0.2-μm Millipore filter paper and the filtrate was fridged by addition of two drops of chloroform to prevent microbial growth in the filtrate. After completion of all experiments, the cadmium concentration in the filtrate was determined using an atomic adsorption spectrophotometer (Model No.: AA240, Australia). All the chemical and standard solutions were purchased from Merck Chemicals, Mumbai, India.

The amount sorbed after a particular reaction period was determined from the difference between the concentration of Cd^{2+} in the parent solution and that remaining in the filtrate. Two of the three replicates were analyzed. If the data of the two replicates were not within an acceptable range of precision (relative error <5 % for high concentrations and <15 % for low concentrations), the third sample was analyzed. This was necessary when the analyte was near the detection limit of the analytical procedure. The sorption data were applied to an array of kinetic models (zero–third-order models, parabolic diffusion, Elovich, and power function). The first-order kinetic model provided a better fit of sorption data set in terms of R^2 and standard error; the best fits of the data and observed rate constants (k_{obs}) and half-life ($t_{1/2}$) of Cd^{2+} were calculated. The Arrhenius and Eyring equations were applied to the data to determine the E_a, A, $\Delta G^{\mp}$, $\Delta H^{\mp}$, and $\Delta S^{\mp}$.

Graphical presentation and statistical analysis

Graphical representation of data sets was done using the Excel software package, and the statistical analyses were performed using the SPSS 15.0 statistical package (SPSS Inc., Chicago, USA) (Norusis 2000).

Results and discussion

Physical and chemical properties of soils

Selected physicochemical properties of the investigated soils are given in Table 1, together with their mean values and standard errors of the mean. Experimental soils were dominant of entisols and a major soil group was Typic Fluvaquents. All the experimental soils were alkaline in nature (pH 8.18 ± 0.04 to 8.83 ± 0.02). Organic carbon ranged from 0.97 ± 0.02 to 1.31 ± 0.01 % in soils from CG and LKPR, respectively. The range of CEC values (16.51 to 17.84 cmol kg^{-1}) in the soils was partly within the range of a typical clay loam texture, i.e., from 15 to 30 cmol kg^{-1} soil. This might be due to the presence of montmorillonite that has high CEC values. Linear regression analysis was carried out between CEC and clay contents within soil profiles: a good correlation (r^2 = 0.889 to 0.921) was found between these two parameters. The mean values of DTPA-extractable selected elements showed that soil LKPR was considerably higher than soil CG. Heavy

Table 1 Selected physicochemical characteristics of soil samples collected from LKPR and CG for the present investigations (values represent the mean of three replications ± standard error of the mean)

Soil properties	Soil	
	LKPR	CG
Taxonomy	Typic Haplumbrept	Typic Haplaquest
pH (H_2O)	8.83 ± 0.02	8.18 ± 0.04
pH (KCl)	8.72 ± 0.04	8.03 ± 0.01
PZC	7.94 ± 0.01	8.02 ± 0.01
Clay content (%)	8.97 ± 0.03	11.21 ± 0.02
CEC (cmol kg^{-1})	17.84 ± 0.09	16.51 ± 0.01
Total carbon (%)	1.82 ± 0.01	0.98 ± 0.01
Organic carbon (%)	1.31 ± 0.01	0.97 ± 0.02
PO_4^{3-} (mg kg^{-1})	673 ± 9.87	529 ± 2.05
Sand (%)	38.27 ± 1.96	51.12 ± 3.49
Silt (%)	20.25 ± 1.22	22.83 ± 2.09
Clay (%)	41.48 ± 2.01	26.05 ± 1.27
Texture	Clay	Sandy clay loam
Calcium carbonate equivalent (g kg^{-1})	360 ± 7.99	412 ± 6.03
Water-soluble carbonate content (g kg^{-1})	98 ± 1.00	120 ± 1.26
DTPA-extractable elements (mg kg^{-1}, unless otherwise stated)		
Aluminum (%)	2.22 ± 0.10	9.22 ± 0.21
Cadmium	BDL[*] ± –	0.02 ± –
Calcium (%)	0.27 ± 0.01	1.14 ± 0.02
Cobalt	BDL ± –	0.02 ± –
Copper	1.16 ± 0.01	1.01 ± 0.02
Chromium	BDL ± –	BDL ± –
Iron (%)	2.29 ± 0.08	3.36 ± 0.08
Lead	BDL ± –	BDL ± –
Manganese	4.22 ± 0.03	5.21 ± 0.08
Magnesium (%)	1.23 ± 0.01	2.03 ± 0.01
Potassium(%)	6.22 ± 0.19	8.87 ± 0.09
Nickel	BDL ± –	BDL ± –
Zinc	22.21 ± 1.09	20.24.09 ± 0.97
Total elements (mg kg^{-1}, unless otherwise stated)		
Aluminum (%)	9.83 ± 0.25	9.22 ± 0.21
Cadmium	0.03 ± –	0.02 ± –
Calcium (%)	6.86 ± 0.04	5.36 ± 0.02
Cobalt	1.36 ± 0.04	1.36 ± 0.04
Copper	4.42 ± 0.04	3.96 ± 0.03
Chromium	2.21 ± 0.01	2.01 ± 0.01
Iron (%)	8.86 ± 0.11	9.27 ± 0.11
Lead	0.42 ± 0.01	0.38 ± 0.02
Manganese	11.52 ± 1.01	14.56 ± 1.20
Magnesium (%)	4.48 ± 0.07	5.52 ± 0.09
Potassium (%)	8.28 ± 0.17	9.11 ± 0.10
Nickel	2.98 ± 0.01	2.98 ± 0.03
Zinc	34.91 ± 2.46	41.09 ± 1.03

[*] *BDL* below detectable limit

metal concentrations in investigated soils are found to be relatively low, as the total amount of HMs was within the range prescribed by Alloway (1995). Furthermore, low Mn in experimental soils could be regionally specific.

Cd sorption

A time dependence decrease in solution-phase Cd^{2+} was observed for both soils under different temperature and pH values of the soil suspension, indicating the occurrence of reactions leading to Cd^{2+} disappearance from solutions. Cd^{2+} sorption on the soil-solution interface in this study exhibited a typical metal sorption behavior. Figure 1a, b shows the percent of Cd sorbed on the soil CG with time for the three experimental temperatures at pH 4.00 where initial concentrations of Cd^{2+} were 100 and 5 mg L^{-1}, respectively. As the temperature of the reaction increased from 298 to 318 K, with all other reaction conditions (i.e., pH and C_0) remaining constant, the rate of Cd sorption increased. For the soil CG, the percent of Cd sorbed from soil solution to soil varied with pH, i.e., in the order $9.00 \gg 8.18 > 4.00 > 6.00$. Increasing soil pH increases the mobility of Cd^{2+} from soil solution to soil via adsorption, inner sphere complexation, and/or precipitation and multinuclear-type reactions (Sparks 1989). Increasing the pH to greater than the PZC (a point where the net total charge on the particle is 0) in soil systems increases negative charge (Marcano-Martinez and McBride 1989). The PZC of CG was 8.02 (Table 1). Therefore, soil particles mainly carry a negative charge on the pH > 8.02 and positive charge on the pH < 8.02. At low pH values, the sorption of metal ions was low due to electrostatic repulsion between the soluble positively charged metal ions. The sorption of metal ions with an increase of pH was due to an increase in the negative charge of soil particles and in

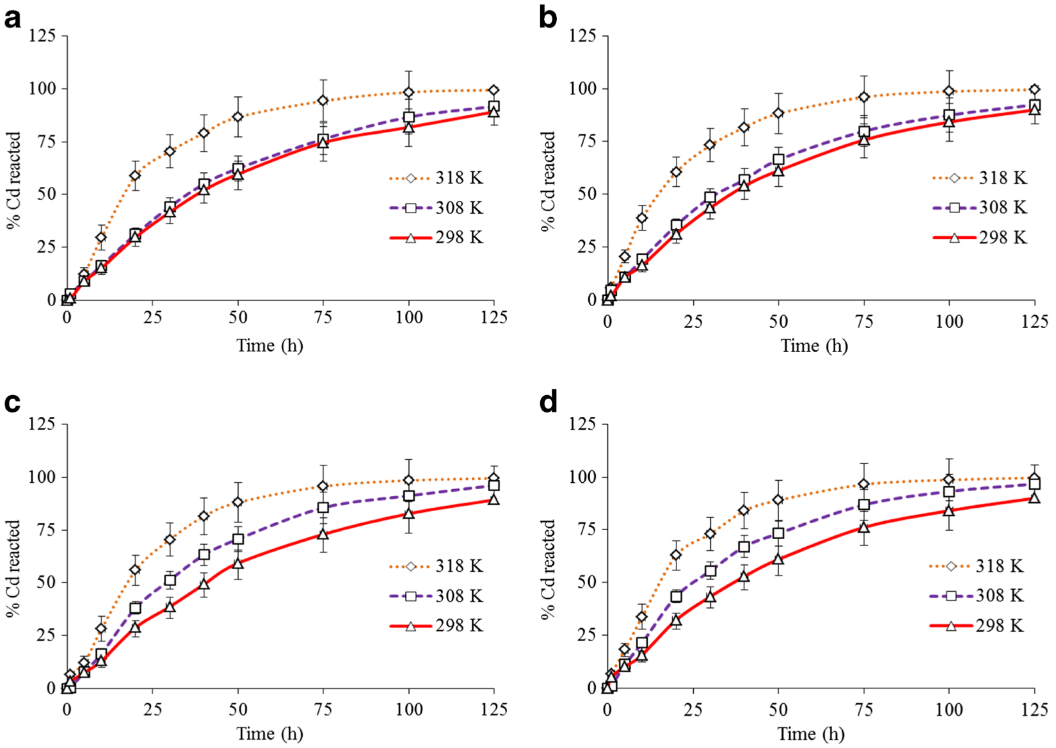

Fig. 1 Percent of Cd^{2+} sorbed on CG at different temperatures vs. time: **a** $C_0 = 100$ mg L^{-1} and pH = 4.0, **b** $C_0 = 5$ mg L^{-1} and pH = 4.0, **c** $C_0 = 100$ mg L^{-1} and pH = 6.0, and **d** $C_0 = 5$ mg L^{-1} and pH = 6.0

the number of dissociated carboxylic and phenolic functional groups. Several studies have demonstrated that increasing pH can increase Cd sorption in tropical soils or in pure oxide mineral systems (i.e., goethite; Appel and Ma 2002; Brümmer et al. 1988; Tiller et al. 1984). Figure 1c, d represents the percent of Cd sorbed from soil solution onto soil CG at pH 6.0 within the range of reaction temperatures and initial concentrations of 100 and 5 mg L^{-1} Cd^{2+}, respectively. An interesting observation was found in the percent of Cd sorbed at pH 4.0 within the range of reaction temperatures. The percent of Cd sorbed at pH 4.0 was greater than that of Cd sorbed at pH 6.0 when all the reaction conditions were the same, which can be attributed to the sorption of Cd favored at lower pH. However, the analogy between sorption and release edges suggests that the mechanism of metal cation release is due to proton sorption at bonding sites of minerals and organic matter (Zan et al. 2013). In spite of being in the acidic range, sorption of Cd to hydroxylated sites may also cause mineral dissolution by weakening of bonds between metal surface cations and the bulk of the crystals. The preference of sorption for Cd over H^+ that was observed in the soil CG may be attributed to the smaller hydrated radius ($Cd^{2+} = 0.426$ nm) and the greater affinity of Cd for most functional groups of soil constituents. Further, a soft-soft interaction between O^{2-} ($r_O{}^{2-} = 1.4$ A°) and Cd^{2+} ($r_{Cd}{}^{2+} = 0.97$ A°) as well as its high electronegativity (1.69) make it a better candidate for electrostatic and inner sphere complexation reactions which follow the Soft Hard Acid Base (SHAB) principle (HSAB) principle (Huheey 1983). A similar trend of percent decreases of Cd with the increase of pH from soil solution to soil in CG soil was found when different initial concentrations of Cd were added (i.e., 75, 50, 25, and 15 mg L^{-1} Cd^{2+}) with the progress of reaction time (data not shown).

Figure 2a, b shows the percent of Cd sorption on soil LKPR at pH 6.00 within the reaction temperature range where the initial concentrations (C_0) were 100 and 5 mg L^{-1}, respectively. The percent of Cd sorbed on soil LKPR was significantly lower than that sorbed on soil CG. Cadmium(II) is a closed shell cation (valence orbital full-$4d^{10}$) that favors columbic-type reactions at soil surfaces as opposed to inner sphere surface reactions by electron sharing. Thus, Cd sorption should increase with increase in soil CEC (Appel and Ma

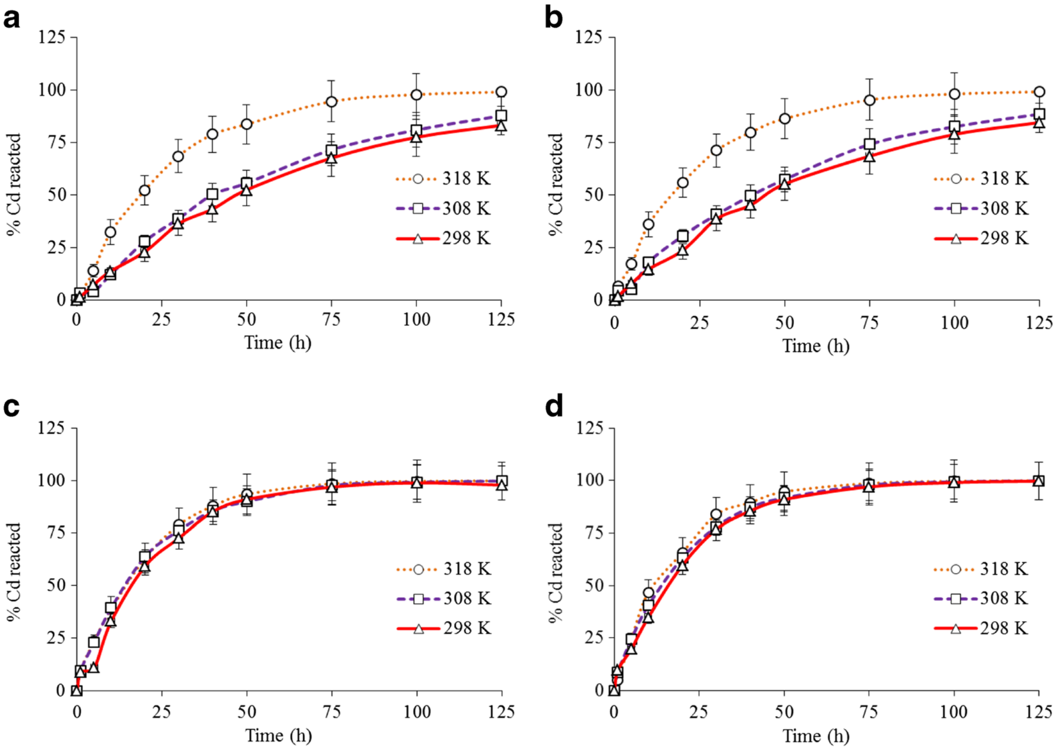

Fig. 2 Percent of Cd^{2+} sorbed on LKPR at different temperatures vs. time: **a** $C_0 = 100$ mg L^{-1} and pH = 6.0, **b** $C_0 = 5$ mg L^{-1} and pH = 6.0, **c** $C_0 = 100$ mg L^{-1} and pH = 8.18, and **d** $C_0 = 5$ mg L^{-1} and pH = 8.18

2002). In our study, the CEC of LKPR was 6.84 cmol kg^{-1} which is much lower than that of soil CG (16.51 cmol kg^{-1}). Holm et al. (2003) observed that CEC was positively correlated to the sorption of Cd in acid, humid temperate climate soil. Zachara et al. (1992) also reported that Cd on the edges of layer silicates was controlled by the CEC. In addition to CEC, based on soil properties (Table 1), influence of organic carbon on Cd sorption may be suspected for this phenomenon.

Figure 2c, d shows the percent of Cd sorbed on soil LKPR at pH 8.18 within the reaction temperature range where the initial concentrations (C_0) were 100 and 5 mg L^{-1}, respectively. The percent of sorbed Cd increases due to increase of pH which bears similarities with the findings of different researchers (Barrow and Whelan 1988; Brümmer et al. 1988; Naidu et al. 1994). The sharp increase of the percent of Cd sorbed with increase in pH has commonly been attributed to the preferential adsorption of $CdOH^+$ (Naidu and Harter 1998), the adsorption of Cd^{2+} (Anderson and Christensen, 1988), proton competition for adsorption sites (Boekhold et al. 1993), variations in the negative surface charge density of the soil (Naidu et al. 1994), and acid-catalyzed dissolution of reactive oxide sites (Elliot and Huang 1979) or precipitates (Collins et al. 2003). Unlike CG soils, the trend of percent of Cd sorbed was pH 9.0 > pH 8.18 > pH 6.0 > pH 4.0 within the range of reaction temperatures. This work also shows that at a low temperature (298 K), Cd sorbed is relatively slow, compared with Cd sorbed at 398 K. For example, Fig. 3a shows that about 55 % Cd was adsorbed at 398 K reaction temperature after 125 h of progress of the reaction at pH 6.0 on soil CG, whereas that was only 14.7 % at 298 K. A similar observation was also found in soil LKPR (Fig. 3b); however, the percent of sorption in this soil was much lower than that of sorption in soil CG. The results also revealed that sorption of Cd onto soil is relatively slow in the first 50 h of progress of the reaction and then becomes faster reaching 22.45 and 17.3 % at 308 K on soils CG and LKPR, respectively. In all systems, the percent sorption isotherms shifted to a higher pH as the temperature increased. On the other hand, Sapek (1975) reported that sorption of heavy metals like Cu on soils consisted of two distinct steps which were an initial fast adsorption followed by a much slower adsorption. In our

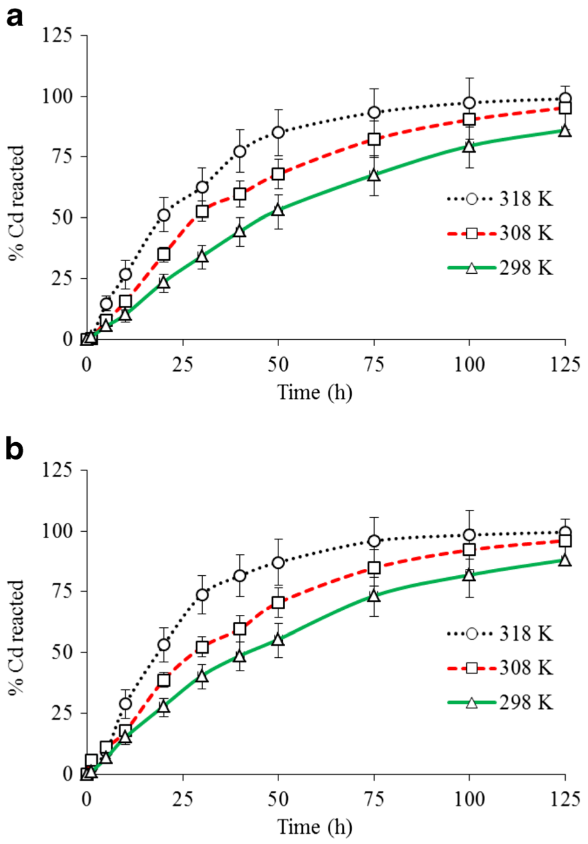

Fig. 3 Percent of Cd^{2+} sorbed (C_0 = 100 mg L^{-1}, pH = 8.18) at different temperatures vs. time: **a** CG and **b** LKPR

sorption studies, however, soils were finely subdivided and the sorption reaction was conducted on interim stirring. It is unlikely that the external diffusion could regulate the adsorption process or precipitation as hydroxide or carbonate of Cd^{2+}. At a given pH, hydrolysis of the cations present in soil proceeds to a greater extent as temperature increases. Thus, an increase in temperature will reduce the electrostatic repulsion between the soil surface and the adsorbing species, allowing sorption to occur more readily. Often, soil temperatures can fall below 298 K, indicating that sorption rates in the field can be even slower than reported here and thus allow transport of metals through the soil profile. Likewise, if the soil temperature is elevated, we have observed rapid sorption kinetics at higher temperatures that may lead to the prompt formation of stable metal precipitates at circumneutral pH. Higher surface loading levels at higher temperature at a particular time could enhance the formation of metal surface precipitates (Scheckel and Sparks 2001). Formation of metal precipitates may be an important mode of sequestering metals in the soil environment by significantly reducing the solubility of metals (Scheckel and Sparks 2000) and may be aided by increasing temperatures. In our study, the percent of Cd sorbed from soil solution increases with increase of temperature irrespective of treatment imposed. Therefore, the loss of Cd from soil solution to soil is an endothermic reaction. The previously reported results show that a trace metal reaction with soil particles indeed increases with temperature (Jayasiri et al. 2014) and such a reaction is therefore suggested to be endothermic (Hodgson et al. 1964).

Kinetics and thermodynamics of Cd sorption

Observed rate coefficient (k_{obs}), average observed rate coefficient (k_{avg}), and average half-life ($t_{1/2}$) of Cd sorption

Keeping in mind the importance of temperature in the study of sorption of Cd, the present work was initiated with the aim of using reaction kinetics and a thermodynamic approach of Cd sorption on soils. It was decided to conduct the experiment under different pH values to study how different temperatures affect the sorption of Cd metals on soils and the possible mechanistic pathways controlling the sorption of Cd in the soil-solution interface. As all the soil systems invariably reached a quasi-equilibrium with respect to Cd adsorption by the end of the 125-h reaction period (data not shown), therefore, it provides an indication that Cd sorption follows first-order kinetics with respect to the Cd concentration in soil solution. The plot of lnC_t vs. t (h) (Eq. 1) (figures not shown) revealed the good way to confirm that a reaction is of a particular order is to change only one parameter (e.g., initial concentration) and, in doing so, one should observe parallel kinetic plots resulting in similar apparent rate coefficients (Fendorf et al. 1993). The apparent observed first-order rate coefficients (k_{obs}) for soil CG are tabulated in Table 2. Sorption of Cd on the soil-solution interface was found to be a first order as the k_{obs} of each set of reaction is independent of initial concentration (C_0) where the pH of the soil suspension was kept constant. R^2 values (0.88–0.99) also favor a conclusive choice of a first-order reaction that best described our data because this is the index to judge their goodness of fit (Sparks and Jardine 1981). For a first-order kinetics, the k_{obs} is always independent of

Table 2 Observed rate coefficient (k_{obs}), average observed rate coefficient (k_{avg}), and average half-life ($t_{1/2}$) for Cd at different pH values and reaction temperatures on the CG soil-solution interface (data extracted from the plot of $\ln\left(\frac{C_0}{C_t}\right)$ vs. t (h) by using the equation $\ln\left(\frac{C_0}{C_t}\right) = k_{\mathrm{obs}}t$ and $t_{1/2}$ was calculated from $\frac{0.693}{k_{\mathrm{avg}}}$ (values represent the mean of three replications ± standard error of the mean)

pH	Temperature (K)	Initial concentrations (C_0, mg L^{-1})	Observed rate coefficient (k_{obs}, h^{-1}) × 10^3	R^2	Average observed rate coefficient (k_{avg}, h^{-1}) × 10^3	Average half-life ($t_{1/2}$, h)
4.00	318	100	8.31 ± 0.021	0.81	8.35 ± 1.22	82.99 ± 2.38
		75	8.33 ± 0.028	0.88		
		50	8.34 ± 0.023	0.98		
		25	8.41 ± 0.023	0.99		
		15	8.33 ± 0.011	0.93		
		5	8.52 ± 0.009	0.99		
	308	100	3.91 ± 0.001	0.91	3.97 ± 0.09	174.71 ± 13.29
		75	3.90 ± 0.001	0.89		
		50	3.92 ± 0.002	0.99		
		25	4.25 ± 0.003	0.96		
		15	4.03 ± 0.002	0.94		
		5	4.13 ± 0.004	0.99		
	298	100	2.23 ± 0.005	0.90	2.22 ± 0.01	312.63 ± 18.76
		75	2.24 ± 0.005	0.87		
		50	2.15 ± 0.002	0.92		
		25	2.26 ± 0.010	0.87		
		15	2.33 ± 0.007	0.88		
		5	2.32 ± 0.004	0.97		
6.00	318	100	6.14 ± 0.005	0.93	6.20 ± 0.07	111.77 ± 10.26
		75	6.15 ± 0.010	0.92		
		50	6.21 ± 0.013	0.89		
		25	6.30 ± 0.015	0.87		
		15	6.34 ± 0.004	0.88		
		5	6.27 ± 0.009	0.89		
	308	100	2.53 ± 0.081	0.93	2.47 ± 0.06	280.95 ± 21.99
		75	2.55 ± 0.002	0.96		
		50	2.53 ± 0.034	0.96		
		25	2.42 ± 0.006	0.99		
		15	2.51 ± 0.001	0.98		
		5	2.44 ± 0.003	0.89		
	298	100	1.16 ± 0.005	0.88	1.22 ± 0.01	569.59 ± 23.94
		75	1.27 ± 0.001	0.89		
		50	1.23 ± 0.001	0.87		
		25	1.26 ± 0.001	0.98		
		15	1.33 ± 0.002	0.95		
		5	1.35 ± 0.001	0.94		
8.18	318	100	9.23 ± 0.023	0.88	9.15 ± 0.82	75.74 ± 2.98
		75	9.06 ± 0.028	0.96		
		50	9.10 ± 0.032	0.93		
		25	9.23 ± 0.034	0.98		
		15	9.21 ± 0.054	0.95		
		5	5.00 ± 0.045	0.98		

Table 2 (continued)

pH	Temperature (K)	Initial concentrations (C_0, mg L^{-1})	Observed rate coefficient (k_{obs}, h^{-1}) × 10^3	R^2	Average observed rate coefficient (k_{avg}, h^{-1}) × 10^3	Average half-life ($t_{1/2}$, h)
	308	100	7.75 ± 0.034	0.99	7.62 ± 0.29	90.99 ± 10.01
		75	7.64 ± 0.041	0.92		
		50	7.66 ± 0.006	0.87		
		25	7.68 ± 0.011	0.90		
		15	7.62 ± 0.011	0.90		
		5	7.63 ± 0.028	0.95		
	298	100	6.35 ± 0.078	0.94	6.28 ± 0.88	110.29 ± 11.06
		75	6.22 ± 0.082	0.99		
		50	6.26 ± 0.096	0.94		
		25	6.33 ± 0.099	0.89		
		15	6.42 ± 0.029	0.87		
		5	6.34 ± 0.078	0.88		
9.00	318	100	15.52 ± 0.219	0.89	15.53 ± 1.02	44.61 ± 3.39
		75	15.55 ± 0.028	0.94		
		50	15.64 ± 0.501	0.86		
		25	15.68 ± 0.588	0.87		
		15	15.53 ± 0.889	0.90		
		5	15.55 ± 1.901	0.99		
	308	100	12.56 ± 0.678	0.94	12.45 ± 1.00	55.59 ± 4.59
		75	12.42 ± 0.778	0.98		
		50	12.61 ± 0.198	0.97		
		25	12.42 ± 1.201	0.99		
		15	12.54 ± 0.111	0.95		
		5	12.45 ± 0.283	0.89		
	298	100	9.46 ± 0.478	0.88	9.45 ± 1.27	73.33 ± 10.01
		75	9.48 ± 0.562	0.95		
		50	9.53 ± 1.092	0.93		
		25	9.55 ± 0.982	0.95		
		15	9.56 ± 0.883	0.92		
		5	9.41 ± 1.028	0.99		

the initial concentration of the reactant. One can observe in Table 2 that at a fixed temperature and a fixed pH, the k_{obs} values correspond well and are nearly equal, which further corroborates that Cd sorption on the soil-water interface is a first-order reaction with respect to Cd concentration. For example, at 308 K and pH 4.00 within 100 to 5 mg L^{-1} concentrations, Cd sorption on CG soil resulted in k_{obs} values of 3.91×10^{-3} to 4.25×10^{-3} h^{-1} (Table 2) and 1.14×10^{-3} to 1.15×10^{-3} h^{-1} on LKPR soil (Table 3); those are nearly equal to the same. However, k_{obs} values were always higher on soil CG than LKPR, which revealed that the rate of sorption of Cd on CG was much higher than that of sorption of Cd on LKPR irrespective of the reaction condition imposed. The variation of these k_{obs} values corresponds to different clay contents, carbonate, and PZC present in soils. Due to slight deviation of the k_{obs} of a particular set of sorption reactions, we calculate the average rate coefficient (k_{avg}). From k_{avg}, it was observed that elevated temperatures brought about the substantial increase in the rate coefficient of Cd sorption in all the systems. For example, in our experiment, the k_{avg} for Cd sorption on CG at pH 6.0 increases approximately twofold on every 10 °C increase of temperature. The same observation was also

Table 3 Observed rate coefficient (k_{obs}), average observed rate coefficient (k_{avg}), and average half-life ($t_{1/2}$) for Cd at different pH values and reaction temperatures on the LKPR soil-solution interface (data extracted from the plot of $\ln\left(\frac{C_0}{C_t}\right)$ vs. t (h) by using the equation $\ln\left(\frac{C_0}{C_t}\right) = k_{\text{obs}}t$ and $t_{1/2}$ was calculated from $\frac{0.693}{k_{\text{avg}}}$ (values represent the mean of three replications ± standard error of the mean)

pH	Temperature (K)	Initial concentrations (C_0, mg L^{-1})	Observed rate coefficient (k_{obs}, h^{-1}) × 10^3	R^2	Average observed rate coefficient (k_{avg}, h^{-1}) × 10^3	Average half-life ($t_{1/2}$, h)
4.00	318	100	2.10 ± 0.002	0.88	2.02 ± 0.09	343.64 ± 2.98
		75	2.00 ± 0.001	0.87		
		50	2.00 ± 0.001	0.82		
		25	2.11 ± 0.002	0.99		
		15	2.00 ± 0.003	0.89		
		5	1.90 ± 0.010	0.91		
	308	100	1.14 ± 0.005	0.99	1.15 ± 0.03	605.24 ± 4.52
		75	1.14 ± 0.001	0.95		
		50	1.15 ± 0.002	0.96		
		25	1.15 ± 0.004	0.88		
		15	1.15 ± 0.002	0.87		
		5	1.14 ± 0.001	0.92		
	298	100	0.71 ± 0.002	0.90	0.65 ± 0.01	1066.15 ± 11.89
		75	0.71 ± 0.001	0.99		
		50	0.71 ± 0.003	0.95		
		25	0.63 ± 0.001	0.93		
		15	0.62 ± 0.001	0.92		
		5	0.62 ± 0.002	0.90		
6.00	318	100	2.35 ± 0.023	0.89	2.18 ± 0.09	317.41 ± 7.73
		75	2.22 ± 0.018	0.84		
		50	2.21 ± 0.017	0.82		
		25	2.10 ± 0.011	0.89		
		15	2.20 ± 0.009	0.84		
		5	2.10 ± 0.006	0.88		
	308	100	1.50 ± 0.006	0.94	1.51 ± 0.06	462.0 ± 4.99
		75	1.50 ± 0.006	0.93		
		50	1.50 ± 0.001	0.96		
		25	1.50 ± 0.020	0.98		
		15	1.50 ± 0.010	0.93		
		5	1.50 ± 0.010	0.94		
	298	100	1.00 ± 0.003	0.99	1.02 ± 0.03	681.64 ± 14.67
		75	1.00 ± 0.001	0.93		
		50	1.10 ± 0.001	0.93		
		25	1.00 ± 0.003	0.87		
		15	1.00 ± 0.003	0.88		
		5	1.00 ± 0.003	0.89		
8.18	318	100	8.40 ± 0.028	0.94	8.32 ± 0.27	83.33 ± 8.91
		75	8.30 ± 0.024	0.96		
		50	8.30 ± 0.026	0.93		
		25	8.30 ± 0.021	0.95		
		15	8.30 ± 0.009	0.99		
		5	8.30 ± 0.004	0.92		

Table 3 (continued)

pH	Temperature (K)	Initial concentrations (C_0, mg L^{-1})	Observed rate coefficient (k_{obs}, h^{-1}) × 10^3	R^2	Average observed rate coefficient (k_{avg}, h^{-1}) × 10^3	Average half-life ($t_{1/2}$, h)
	308	100	7.30 ± 0.021	0.99	7.30 ± 0.33	94.93 ± 7.89
		75	7.30 ± 0.007	0.95		
		50	7.30 ± 0.018	0.94		
		25	7.30 ± 0.016	0.92		
		15	7.30 ± 0.009	0.91		
		5	7.30 ± 0.002	0.89		
	298	100	6.60 ± 0.005	0.90	6.48 ± 0.04	106.89 ± 10.25
		75	6.60 ± 0.007	0.99		
		50	6.40 ± 0.010	1.00		
		25	6.50 ± 0.010	1.00		
		15	6.40 ± 0.011	0.95		
		5	6.40 ± 0.005	0.94		
9.00	318	100	10.40 ± 0.010	0.93	10.37 ± 0.17	66.85 ± 6.68
		75	10.50 ± 0.041	0.88		
		50	10.30 ± 0.029	0.86		
		25	10.40 ± 0.022	0.89		
		15	10.30 ± 0.018	0.99		
		5	10.30 ± 0.011	0.93		
	308	100	8.71 ± 0.028	0.96	8.71 ± 0.21	79.56 ± 4.59
		75	8.71 ± 0.046	0.95		
		50	8.71 ± 0.023	0.92		
		25	8.71 ± 0.021	0.92		
		15	8.71 ± 0.020	0.93		
		5	8.71 ± 0.009	0.99		
	298	100	7.50 ± 0.011	0.94	7.33 ± 0.22	94.50 ± 3.87
		75	7.40 ± 0.012	0.98		
		50	7.30 ± 0.022	0.94		
		25	7.30 ± 0.030	0.88		
		15	7.20 ± 0.031	0.99		
		5	7.30 ± 0.045	0.99		

found in LKPR soils. This is attributable to the availability of more energy for bond breaking and bond formation brought about by the higher temperatures. Within the range of reaction temperatures in CG soil, each of the four pH values had a substantially different k_{avg} which followed the sequence pH 9.0 > pH 8.18 > pH 4.0 > pH 6.0, whereas that was pH 9.0 > pH 8.18 > pH 6.0 > pH 4.0 in LKPR soils. The average half-life ($t_{1/2}$) of Cd in soil solution also follows the reverse trend that was found in k_{avg}. Higher $t_{1/2}$ values for the acidic pH on CG and LKPR soils indicate longer life than those for the alkaline pH. Therefore, Cd contamination in an acidic pH soil suspension is a serious concern than that in an alkaline condition.

Arrhenius plots of Cd sorption

The effect of temperature on Cd sorption by the two soils was examined in greater detail by applying the Arrhenius equation on the average rate coefficient (k_{avg}) data using Eq. 6. Figure 4a, b shows the Arrhenius plots for the Cd sorption on the CG and LKPR, respectively. The yields of Arrhenius plots on Cd sorption show a decreasing trend with increasing temperature.

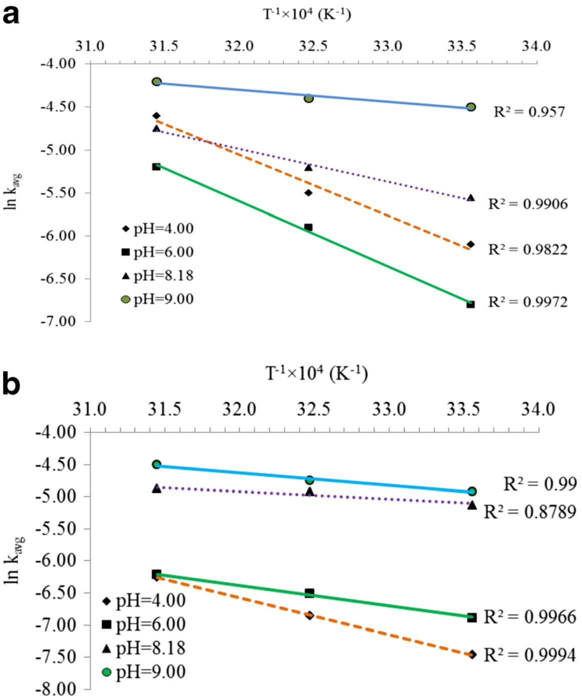

Fig. 4 Complied Arrhenius plots (**a** for CG soil and **b** for LKPR) of Cd sorption kinetics on the soil-solution interface at different pH values, where k_{avg} is the average apparent first-order rate coefficient and T is the temperature (K)

Activation energy and pre-exponential factor of Cd sorption

The estimated values of activation energy (E_a) and pre-exponential factor (A) are given in Table 4. The E_a values of Cd sorption ranged from 14.76 ± 0.29 to 64.45 ± 4.50 kJ mol^{-1} and 9.33 ± 0.09 to 44.60 ± 2.01 kJ mol^{-1} of Cd sorbed by the soils CG and LKPR, respectively. For both soils, the E_a values were higher in acidic pH than those in alkaline pH. The values of E_a in soil CG were always substantially higher than those in soil LKPR at a particular pH of the soil suspension. The activation energy of a diffusion-controlled process in solution is about 25 kJ mol^{-1} (Sparks 1999). However, in heterogeneous systems such as soil-solution interfaces, diffusion occurs not only in the bulk solution but also in micropores and macropores, in the films around solid particles, on the solid surface, and inside solid particles (Sparks 1989). Therefore, the activation energy for diffusion processes in heterogeneous systems is higher than that in solutions. Film diffusion typically has activation energy values of 17 to 21 kJ mol^{-1}, and intraparticle diffusion has E_a values of 21 to 42 kJ mol^{-1} (Sparks 1999). Thus, low E_a values (< or =42 kJ mol^{-1}) indicate diffusion-controlled processes whereas higher E_a values (>42 kJ mol^{-1}) indicate chemically controlled processes (Sparks 1989). Therefore, the rate-limiting step for most of the Cd sorption reactions in acidic pH onto the soil-solution interface is a chemically controlled process except LKPR at pH 6.0 (29.16 kJ mol^{-1}). At alkaline pH, sorption of Cd follows diffusion-controlled processes. The lower values of E_a at alkaline pH are due to the negative charge of clay particles which promotes lower activation energy for Cd sorption. The precipitation of Cd might also be a contributing factor to decrease E_a values on Cd sorption in both soils at higher pH because phase separation decreases E_a values. According to Doraiswamy and Sharma (1984), the small amount of soluble or insoluble foreign constituents may markedly alter the growth rate of crystals and their morphology. They further reported that the precipitation of Cd is influenced by primarily adsorbed Cd, which is present in the lattice structure in soil particles, and after that formation of insoluble Cd compounds such as hydroxide or carbonate or phosphate due to blockage of sorption sites in soil colloids. Walton (1967) also reported that the presence of small amounts of soluble impurities alters both the growth rate and habit of precipitates formed in the soil-solution interface.

The pre-exponential factor (A), an index of the frequency of collisions of Cd ions at the reactive sites on the soil surface, was substantially lower for the soil CG and LKPR at alkaline pH compared with acidic pH (Table 4). If the reaction is such that oppositely charged ions come together, there is less charge on the activated complex than on the reactant. There is then a decrease in electrostriction when the activated complex is formed, which creates a high A. But in our study, we observed that the A values on Cd sorption were higher in acidic pH where both Cd and soil particles carry a positive charge. We observed that sorption of Cd in all soils decreases with the decrease of pH contrary to the apparent fact, i.e., with the increase in the value of A. This might be because majority of collisions between the ions (i.e., Cd^{2+}) and soil particles are ineffective as at higher pH, soil particles bear positive charges and the collision between two positive reactive sites (Cd^{2+} and $Soil^{+}$) is ineffective and energy is insufficient to form sorbed Cd in soil from soil solution.

Table 4 Activation energy (E_a) and pre-exponential factor (A) of Cd sorption on CG and LKPR soils within the range of reaction temperatures and pH values (values represent the mean of three replications ± standard error of the mean)

Soil	pH	Activation energy (E_a, kJ mol^{-1})	Pre-exponential factor (A, h^{-1})
CG	4.00	52.47 ± 2.28	3.41×10^6
	6.00	64.45 ± 4.50	2.33×10^8
	8.18	14.76 ± 0.29	2.42
	9.00	19.88 ± 0.77	29.28
LKPR	4.00	44.60 ± 2.01	4.2×10^3
	6.00	29.16 ± 3.06	1.3×10^2
	8.18	9.33 ± 0.09	3.55
	9.00	13.53 ± 0.81	1.72

Enthalpy, entropy, and Gibbs free energy of activation of Cd sorption

Evaluations of thermodynamic parameters on the activation energy of Cd sorption from soil solution to soil provide an imminent mechanism of Cd sorption in the soils. The thermodynamic parameters, viz. enthalpy ($\Delta H^{\mp}$), entropy ($\Delta S^{\mp}$), and Gibbs free energy ($\Delta G^{\mp}$) of activation, on Cd sorption are also presented in Table 5. Enthalpy change of the activation state ($\Delta H^{\mp}$) is the measure of the energy barrier that must be overcome between reacting molecules (or ions) to progress product formation (Jencks 1969). The values of $\Delta H^{\mp}$ on Cd sorption were positive for all soils and ranging from 12.27 to 61.37 kJ mol^{-1} for CG soils and 7.28–42.10 kJ mol^{-1} for LKPR soils within the range of soil suspension pH values and reaction temperatures. The positive values of $\Delta H^{\mp}$ further suggested that sorption of Cd on the soil-solution interface is an endothermic one and they consume energy from the system. There is an enormous number of microscopic states that are consistent with any given macroscopic state. This concept leads at once to a molecular interpretation of entropy (S). It is a measure of how many different microscopic states are consistent with a given macroscopic state. When a system moves spontaneously from one sate to another, it goes to a state in which there are more microscopic states. One can express this differently by saying that when a spontaneous change takes place, there is increase in disorder. In other words, entropy is a measure of disorder; an increase in entropy means an increase in disorder (Laidler and Meiser 1985). The value of $\Delta S^{\mp}$ is also an indication of whether or not a reaction is an associative or dissociative mechanism. The entropy of activation ($\Delta S^{\mp}$) parameter is often regarded as a measure of the width of the saddle point of the potential energy surface over which reactant molecules must pass as activated complexes (Jencks 1969). S values >-10 J mol^{-1} generally imply a dissociative mechanism (Scheckel and Sparks 2001). However, in Table 5, one sees large negative values for $\Delta S^{\mp}$, suggesting that Cd sorption on these soils is an associative mechanism. Free energies of activation ($\Delta G^{\mp}$) are considered to be the difference in free energy between the activated complex and the reactants from which it was formed (Laidler 1965). The large, positive $\Delta G^{\mp}$ values suggest that the sorption of Cd from soil solution to soils necessitates energy to convert reactants

Table 5 Thermodynamic parameters of the activation state for Cd sorption on the soil-solution interface using the Eyring equation (values represent the mean of three replications ± standard error of the mean)

Soil	pH	$\Delta H^{\mp}$ (kJ mol^{-1})	$\Delta S^{\mp}$ (J mol^{-1})	Temperature (K)		
				298 $\Delta G^{\mp}$ (kJ mol^{-1})	308	318
CG	4.00	49.54 ± 2.56	−129.74 ± −2.38	88.21 ± 3.49	89.50 ± 3.49	90.80 ± 1.37
	6.00	61.37 ± 3.81	−95.11 ± −3.20	89.72 ± 4.05	90.67 ± 7.00	91.62 ± 2.34
	8.18	12.27 ± 2.01	−149.20 ± −4.59	56.73 ± 5.61	58.22 ± 4.59	59.71 ± 2.04
	9.00	17.03 ± 1.33	−168.62 ± −8.59	67.28 ± 3.40	68.96 ± 4.33	70.65 ± 3.49
LKPR	4.00	42.10 ± 2.39	−164.70 ± −2.99	91.18 ± 2.39	92.83 ± 2.09	94.47 ± 2.36
	6.00	27.36 ± 3.13	−184.70 ± −9.02	82.40 ± 3.49	84.25 ± 4.09	86.09 ± 7.17
	8.18	7.28 ± 1.10	−132.69 ± 9.92	46.82 ± 2.01	48.15 ± 1.29	49.48 ± 2.09
	9.00	11.10 ± 1.00	−146.56 ± 1.89	54.78 ± 2.00	56.24 ± 1.06	57.71 ± 2.16

into products. Typically, the $\Delta G^{\mp}$ value determines the rate of the reaction, and as rate increases, $\Delta G^{\mp}$ decreases (Scheckel and Sparks 2001). From Table 5, it is clear that the trend of $\Delta G^{\mp}$ on the particular reaction temperature follows the same trend of k_{avg} which is seen when comparing the data from Tables 2 and 3.

Conclusions

The results of this study indicate that the Cd sorption data can be described satisfactorily by an irreversible first-order kinetic equation at temperatures of 298, 308, and 318 K and different soil suspension pH values (4–9.0). The average rate coefficient (k_{avg}) of Cd sorption increases with increase in temperature, indicating that sorption of Cd on the soil-solution interface is an endothermic reaction. Using kinetics data, the Cd concentration in soil solution at any time can be calculated. Thus, the information provided by this research may contribute to the development of Cd reclamation strategies based on time phases and also toward the kinetics of individual Cd reaction processes in geological environments. Based on activation energy (E_a), the Cd sorption reactions in acidic pH onto the soil-solution interface are chemically controlled processes except LKPR at pH 6.0. However, at alkaline pH, the sorption of Cd follows diffusion-controlled processes. Cd sorption on the soil-solution interface examined in this study indicates the reaction is an associative mechanism based on $\Delta S^{\mp}$ values. The $\Delta H^{\mp}$ values as indicated by E_a values suggest that an energy barrier was present for the system to overcome in order for the reaction to occur.

The information in this study may be helpful to scientists seeking to develop inclusive models that describe all possible sorption conditions and reactions within the soil environment. Temperature and pH are crucial and often overlooked, and they play a critical role in the fate of contaminants in the environment. Temperature studies such as this are quite necessary to construct fully functioning models that will enable researchers to better predict mobility and bioavailability of metals in soils. Thus, the findings of the present study are of vital agro-environmental significance in understanding Cd transformation and transport in the soil and related environments. However, our study was performed in a laboratory condition where all the variables were completely controlled, but the result might change in a field condition. Therefore, further studies are also essential in a field condition related to the kinetics of Cd sorption on the soil-solution interface to better understand the sorption parameters on the soil-water interface.

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Conflict of interest The authors declare that they have no competing interests.

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