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Equilibrium and kinetic studies of Cd(II) ion adsorption from aqueous solution by activated red mud

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ABSTRACT

Red mud is an undesirable by-product of bauxite in Bayer process has been used as a low-cost adsorbent for the removal of Cd(II) from aqueous solution by batch mode of experiment. The red mud was activated by acid dilution followed by ammonia precipitation for better adsorption of Cd(II). To achieve optimum condition for adsorption, different variable parameters were studied. X-ray diffraction, SEM and EDX were used to characterize the adsorbent before and after cadmium adsorption. The maximum adsorption capacities of Cd(II) on activated red mud (ARM) were found to be 12.046 and 12.548 mg g^{-1} at temperature 293 and 303 K, respectively. Adsorption data of Cd(II) are best fitted to linearly transformed Langmuir isotherm with $R^2 > 0.99$. The pseudo-second-order model describes the kinetics of Cd(II) adsorption successfully to predict the rate constant of adsorption. Thermodynamic parameters reveal the endothermic, spontaneous and feasible nature of adsorption of Cd(II) onto ARM. The mass transfer study led to compute the external mass transfer coefficient (k_f) by the equation of McKay et al. and Weber–Mathews at temperature 293 and 303 K. The desorption efficiency of Cd(II) ions from ARM was 91.29% using 0.2-mol L^{-1} HCl.

Keywords: Activated red mud; Mass transfer; Adsorption; Adsorption isotherm; Thermodynamic parameters

1 Introduction

Water contamination by heavy metals is one of the most spartan environmental issues, and it is exceptionally hard to solve the problem. Cadmium occurs in air, water, soils and foodstuffs because of natural phenomenon such as erosion, abrasion of rocks and soils, forest fires and volcanic eruptions. Besides the natural process, cadmium enters to environment by various anthropogenic pathways such as, by-product from mining, smelting and refining of sulphide ores of zinc [1,2]. The electroplating, smelting, alloy manufacturing, pigments, plastic, cadmium–nickel batteries, fertilizers, pesticides, mining, pigments and dyes, textile operations and refining also generate cadmium

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containing waste [3–7]. Like other metals, cadmium is also non-degradable and can be accumulated effectively in living tissue and easily adsorbed into the human body. Cadmium and its compounds are extremely poisonous and long-term exposure can harm to human endocrine system, kidney and bones [8,9]. Therefore, several organizations such as World Health Organisation [10], American Water Work Association [11], Canadian drinking water quality guideline [12,13] and United States Environmental Protection Agency [14] have recommended 0.005 mg L^{-1} as the maximum permissible limit for Cd(II) in drinking water. According to Indian Standard Institution and Central Pollution Control Board [15], 0.01 mg L^{-1} is the desirable limit of cadmium in drinking water. In view of the above, the removal of cadmium ions from the water and wastewater is necessary in terms of safety of public health and environment.

There is a growing interest for the development of low-cost materials and methods for removal of Cd(II) ions from drinking water or industrial effluents. Although many different methods such as chemical precipitation [7,16], ion exchange [17], solvent extraction [18,19], reverse osmosis [20], dialysis/electrodialysis [21], supported liquid membrane [22] and adsorption [23–25] have been documented for the removal of heavy metal ions, the process based on adsorption methods is promising, due to its low cost and high removal efficiency [26]. Many low-cost materials [27–36] have been reported for Cd(II) removal from water and wastewater systems, but they are not very popular because of various limitation like cost, removal efficiency and maintenance.

In this work, attempts have been made to utilize red mud, an undesirable by-product produced after alkaline-leaching of bauxite in Bayer process. Red mud is highly alkaline waste material with $pH > 12$. Red mud is mostly composed of fine particles containing low cost aluminium, iron, silicon, titanium oxides and hydroxides, which are responsible for its high surface reactivity [37]. The storage and maintenance of highly caustic red mud are a challenging environmental problem in the alumina industry. The bulk utilization of red mud causes environmental benefit and it can also enhance the socio-ecological and economic value of alumina industries [38]. Only a limited number of studies have been investigated for the use of red mud as a low-cost adsorbent for the removal of Cd(II) ions from aqueous solution. Gupta and Sharma used red mud modified with hydrogen peroxide to increase the adsorption of Cd(II) ions from aqueous solution [39]. Zhu et al. and Shao-hua et al. reported that, after modification of red mud to granular red mud and red mud granulated with cement, the adsorption capacity of Cd(II) was increased [40,41]. Ma et al. stated that, the adsorption of water-borne Cd(II) ions increased on treatment with $CaCO_3$-dominated red mud [42].

However, reports about the adsorption of Cd(II) ions from aqueous solutions using acid activated red mud (ARM) are not clarified. The objective of this study is to find out the mass transfer of Cd(II) adsorption on acid ARM. Furthermore, this paper investigates the percentage removal of Cd(II) ions from the aqueous solutions by batch experiments. The effect of various parameters is examined on the adsorption of Cd(II) ions from aqueous solutions by ARM.

2. Experimental

2.1. Reagents and chemicals

All chemicals used for this study are of AR grade and are acquired from Merck. The glassware utilized is of borosil and tarson made. Stock solution (1,000 ppm) of Cd(II) is prepared by dissolving 2.736 g of $Cd(NO_3)_2{\cdot}4H_2O$ in 1 l of double distilled water. The stock solution was diluted further to obtain the test sample solutions as and when required.

2.2. Preparation and instrument used for characterization of the adsorbent

The waste red mud used in the present study was obtained from Vedanta Aluminium Industries, Lanjigarh, India. The ARM was prepared by acid dilution followed by ammonia precipitation method. In a 1,000 ml beaker, 10 g of the red mud was added to 190 g of distilled water and stirred to form slurry, to which 18 g of 31 wt.% HCl was added. The resulting solution was heated at 60°C for 20 min and diluted with water to make a total volume of ~800 cm^3 with constant stirring. After this process, the acidic solution was removed by decantation. Liquid ammonia solution (specific gravity 0.880) was added slowly with constant stirring, until a pH of ~8 was reached for complete precipitation. The solution and the resulting precipitate were heated at 50°C for ~10 min with constant stirring. The precipitate was separated by filtration, washed three times with distilled water, dried overnight in air oven at 110°C and finally, calcined in air oven at 500°C for 2 h which is referred as ARM and kept in an air-tight container until used [43].

Surface area of the sample was measured at liquid nitrogen temperature using BET surface area analyser (QUANTACHROME Autosorb I). Morphological analysis of the ARM was done by SEM and EDX (JEOL, JSM-6480LV). XRD (Philips X'Pert X-ray diffractometer) was used for the characterization of the material before and after adsorption. The pH of the solution was measured by a calibrated pH meter (Orion two star, USA). After adsorption, quantitative analysis of the Cd(II) in the filtrate was conducted using atomic absorption spectrophotometer (AAS, VARIAN, AA240).

2.3. Batch adsorption experiment

Adsorption experiments were conducted using the batch method. The experiments were carried in a 250-ml stopper conical flask containing a fixed amount of adsorbent with 100 ml of standard initial concentration of Cd(II). The initial pH of the solution was adjusted with 0.1-N HCl or 0.1-N NaOH solution. The flasks were shaken for the desired contact time in an electrically thermostatic reciprocating shaker at 120 rpm. The experiments were repeated at 283–363 K. The time required for reaching the equilibrium condition was estimated by drawing samples at regular intervals of time till equilibrium was reached. Adsorption experiments for the effect of pH were conducted using a solution having 10 mg L^{-1} of cadmium(II) concentration with an adsorbent dosage of 0.5 g L^{-1}. Throughout the study, the contact time is varied from 10 to 60 min, the pH from 2 to 12, initial metal concentration from 10 to 100 mg L^{-1} and the adsorbent dosage from 0.1 to 1 g L^{-1}. After stirring, the solutions are allowed to settle for 10 min and the samples are centrifuged at 3,000 rpm for 20 min and filtered through Whatman 42 filter paper. The filtrate is used for the analysis of residual Cd(II) concentration. For each experiment, the concentrations of the metals before and after adsorption were determined by atomic absorption spectrophotometer (AAS). The percentage amount of Cd(II) adsorbed was calculated by following equation:

$$\%\,\text{Removal} = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{1}$$

where C_0 and C_e are the concentration of cadmium at initial and equilibrium, respectively.

2.4. Adsorption kinetics models

In this study, three kinetic models (the pseudo-first-order, pseudo-second-order and intraparticle diffusion models) were used to understand the mechanism of adsorption of Cd(II) onto the ARM.

The pseudo-first order kinetic model for the removal of Cd(II) by ARM was carried out by Lagergren rate equation model [44]:

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1 t}{2.303}\right) \tag{2}$$

The equation about the pseudo-second-order kinetic model is as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amounts of the adsorbate adsorbed on the adsorbent at equilibrium and at time t (min), respectively. K_1 and K_2 are the pseudo-first-order rate constant and the pseudo-second-order adsorption rate constant, respectively.

The Weber–Morris rate constant for intraparticle diffusion model is represented as follows:

$$q_e = K_{ip} t^{1/2} + C \tag{4}$$

where K_{ip} is the intraparticle diffusion rate constant and "t" is the agitation time per minute. If the adsorption mechanism follows the intraparticle diffusion process, a plot of q_t vs. $t^{1/2}$ should be a straight line with a slope k_{ip} and intercept C.

2.5. Thermodynamic studies

The thermodynamics of the adsorption process was studied to know the thermodynamic behaviour of Cd(II) adsorption onto ARM. The thermodynamic parameters such as change in Gibb's free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) are calculated using van't Hoff equation [45].

$$\Delta G = -RT \ln K_c \tag{5}$$

$$K_c = \frac{C_1}{C_2} \tag{6}$$

$$\log K_c = \left[\left(\frac{\Delta S}{R}\right) - \left(\frac{\Delta H}{RT}\right)\right] \tag{7}$$

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

where ΔG is the standard free energy change, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is temperature in Kelvin, K_c is the equilibrium constant, and C_1 and C_2 are the equilibrium concentrations of metal ions on the adsorbent surface and in the solution, respectively.

2.6. Adsorption isotherm models

The adsorption isotherm is very important for defining adsorption behaviour to a solid–liquid system. In this study, Langmuir, Freundlich, Dubinin–Radushkevich and Temkin isotherm were applied to generate the data. The isotherm models were compared by the correlation coefficient (R^2) to identify which was batter fit for the experimental data.

The Langmuir isotherm is rested on the assumption that adsorption occurs at specific homogeneous sites within the adsorbent. The linearized form of this isotherm can be expressed as follows [46]:

$$\frac{C_e}{q_e} = \frac{1}{(q_m b)} + \frac{C_e}{q_m} \tag{9}$$

where C_e (mg L^{-1}) is the equilibrium concentration of the cadmium ions, q_e is the amount adsorbed at equilibrium (mg g^{-1}) and q_m (mg g^{-1}) and b (L mg^{-1}) are constants related to the adsorption capacity and energy of adsorption, respectively.

In order to predict the adsorption efficiency of the adsorption process, the dimensionless constant separation factor (r) is determined using the following equation [47]:

$$r = \frac{1}{(1 + bC_0)} \tag{10}$$

where C_0 is the initial Cd(II) concentration. The dimensionless constant separation factor "r" indicates the shape of the isotherm to be either unfavourable ($r > 1$), linear ($r = 1$), favourable ($0 < r < 1$) or irreversible ($r = 0$).

The Freundlich isotherm model is used to describe the heterogeneous adsorption process, i.e. adsorption which takes place on a heterogeneous surface through a multilayer adsorption mechanism and generally expressed as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{11}$$

where q_e refers to the amount of cadmium adsorbed (mg g^{-1}) at equilibrium, C_e is the equilibrium concentration of cadmium (mg L^{-1}), K_F is the Freundlich constant and gives the capacity of the adsorbent and $1/n$ is the heterogeneity factor and can be used as a measure of the deviation from linearity of the adsorption [48].

In order to understand the adsorption mechanism, equilibrium data were tested with Dubinin–Radushkevich isotherm. The linearized D–R equation can be written as:

$$\ln q_e = \ln q_m - K\varepsilon^2 \tag{12}$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{13}$$

where ε is the Polanyi potential, q_e is the amount of cadmium ion adsorbed per unit mass of adsorbent, q_m is the theoretical adsorption capacity, C_e is the equilibrium concentration of Cd(II) and K is the constant related to adsorption energy.

The Temkin isotherm can be used to study the effect of indirect adsorbent–adsorbate interactions on adsorption, and it suggests that the heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to these interactions [49]. This model also assumes that adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The linear form of Temkin isotherm equation is shown as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \tag{14}$$

where B_1 is the Temkin adsorption constant related to the heat of adsorption and K_T is the equilibrium binding constant (L mg^{-1}).

2.7. Mass transfer study

Mass transfer analysis was carried out for the determination of surface mass transfer coefficient, k_f and adsorption of cadmium on ARM using the mass transfer model given by McKay and co-workers [50] as:

$$\ln\left[\frac{C_t}{C_0} - \frac{1}{(1+mK)}\right] = \ln\left[\frac{mK}{(1+mK)}\right] - \left[\frac{(1+mK)}{mK}\right] \times k_f S_s t \tag{15}$$

where C_0 (mg L^{-1}) is the initial concentration of adsorbate, C_t (mg L^{-1}) is the concentration of the adsorbate at time t, m (g L^{-1}) is the mass of adsorbent per unit volume, K ($q_m b$) (L g^{-1}) is the Langmuir constant, k_f is the mass transfer coefficient (cm s^{-1}) and S_s (cm^{-1}) is specific particle surface area for mass transfer, given as:

$$S_s = \frac{6m}{d_p \rho_p (1 - \varepsilon_p)} \tag{16}$$

where d_p (cm) is the particle diameter, ρ_p (g L^{-1}) is the density of ARM particles and ε_p is the porosity of the adsorbent particles.

Further model developed by Waber–Mathews equation [51] to determine k_f as following equation:

$$\frac{\mathrm{d}\left(\frac{C_t}{C_0}\right)}{\mathrm{d}t} = -k_f S_s \tag{17}$$

where C_0 (mg L^{-1}) is the initial concentration of adsorbate, C_t (mg L^{-1}) is the concentration of the adsorbate at time t and S_s is the specific particle surface area of the adsorbent.

3. Result and discussion

3.1. Characterization of adsorbent

The BET surface area of the red mud is 33.5 $m^2\ g^{-1}$ which is increased to 67.10 $m^2\ g^{-1}$ on activation. Red mud contains the following mineral phases: hematite (Fe_2O_3), goethite ($FeO(OH)$), gibbsite ($Al(OH)_3$), calcite ($CaCO_3$), rutile/anatase (TiO_2) and quartz (SiO_2) which are identified by XRD analysis. These are in agreement with its chemical composition of red mud (Fe_2O_3—43.82%, Al_2O_3—46.89%, SiO_2—12.51%, TiO_2—3.90%, CaO—2.31%, Na_2O—9.87%, loss of the ignition—7.69%). XRD of ARM before and after cadmium adsorption is presented in Fig. 1. The results obtained from the analysis indicate that there are remarkable changes between the ARM and Cd-loaded ARM, which suggest that a phase transformation has taken place due to the formation of new mineral ilmenite ($FeTiO_3$). The appearance of this mineral (Ilmenite) influences the cadmium sorption mechanism. $FeTiO_3$ consisted of two simple oxides: TiO_2 and Fe_2O_3 which changes the surface properties of the adsorbent and helps for Cd(II) adsorption.

The EDX spectra and SEM images of ARM before and after adsorption are illustrated in Fig. 2(a) and (b), respectively. It is observed that it contains irregular shapes of black particle before adsorption which changes to shiny bulky particles spread all over the material before adsorption. It clearly indicates the presence of cadmium in the surface which is confirmed by the corresponding EDX.

3.2. Effect of adsorbent dose and pH

The effect of adsorbent dose on the removal of Cd (II) by ARM was investigated at pH 7, ambient temperature (298 K) and contact time of 60 min with initial Cd(II) concentration of 10 mg L^{-1}. The removal efficiency of Cd(II) increases gradually from 67.11 to 92.90% for 0.1–1.0 g/100 ml of ARM. As expected, removal capacity of cadmium ions increases with increase in the adsorbent dose and there is no significant change in percentage removal of cadmium

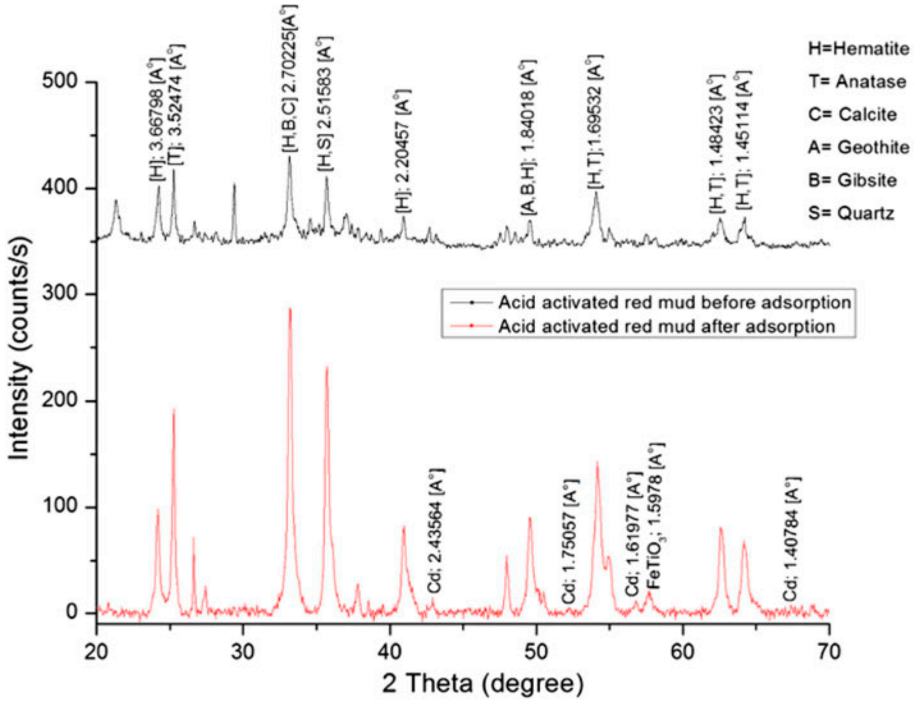

Fig. 1. XRD of acid ARM before and after adsorption.

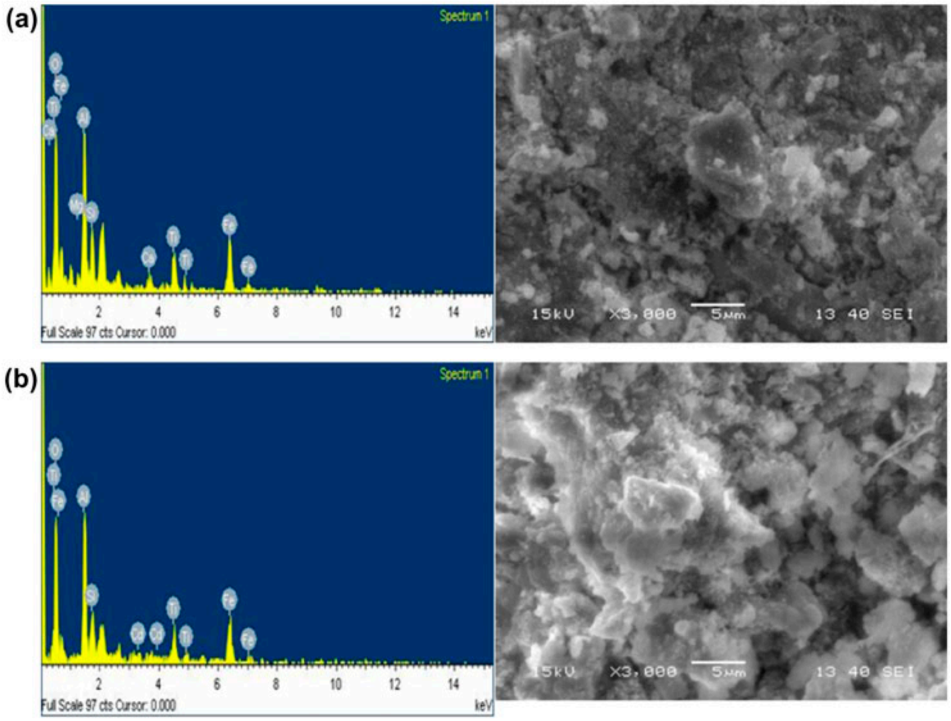

Fig. 2. EDX spectrum and SEM micrograph of ARM: before adsorption (a) and after adsorption (b).

after adsorbent dose of 0.5 g/100 ml. This may be attributed to overlapping or aggregation of adsorption site resulting in decrease in total adsorbent surface area available to metal ions and an increase in diffusion path length. Hence, 0.5 g/100 ml is considered the optimum dose and is used for further study.

Hydrogen ion concentration is one very significant parameter that controls the adsorption behaviour of metal ions in aqueous solution [52]. Fig. 3 depicts the effect of pH on Cd(II) removal with ARM. The red mud slurry obtained directly from the alumina refining plant (Vedanta Aluminium Industries) has a pH 12.2. The removal efficiency of Cd(II) increased gradually with increase in pH and was nearly constant above pH 6. It is evident that the adsorption of Cd(II) onto the ARM was highly pH-dependent, with maximum removal efficacies of 96.89% at pH 6. However, with increase in the pH values, adsorbent surfaces were more negatively charged due to protonation of adsorbent and becomes more accessible for the adsorption of metal ions (positive charged) through electrostatic force of attraction [53,54]. The pH_{zpc} (zero point charge) value of the adsorbent was determined by reported method [40]. The pH_{zpc} was found to be 4.8 where $\Delta pH = 0$. This may be explained by considering the pH_{zpc} for the ARM. At $pH < pH_{zpc}$, the surface charge is positive, at $pH = pH_{zpc}$, the surface charge is neutral, and at $pH > pH_{zpc}$, the surface charge is negative. The point of zero charge of ARM is 4.8 which was less than the pH value (pH 6). The

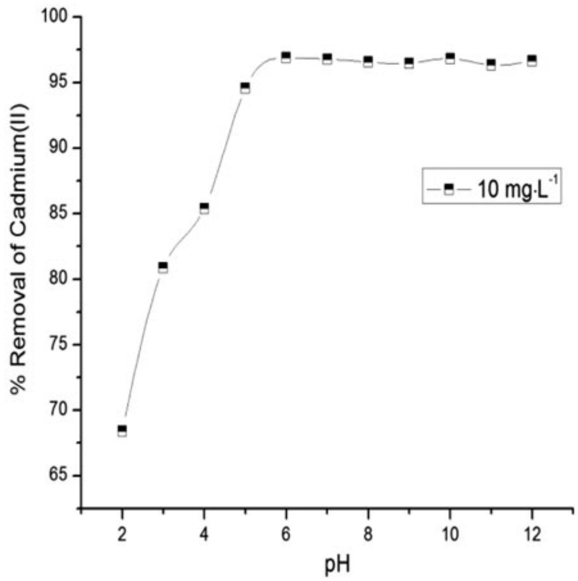

Fig. 3. Effect of pH on the adsorption of Cd(II) on ARM (initial concentration: 10 mg L^{-1}, adsorbent dose: 0.5 g/100 mL, contact time: 120 min, temperature: 298 K).

Table 1
A comparison of maximum adsorption capacities for cadmium ions by different adsorbents at different pH

Adsorbent	pH	Adsorption capacity (mg g^{-1})	Ref.
Bamboo charcoal	8.0	12.08	[55]
Coffee grounds	7.0	15.65	[56]
Rice straw	2.0–6.0	13.9	[57]
Chitosan/bentonite	6.5	120.5	[58]
Snail shell dust (PSD)	6	16.66	[59]
Acid activated red mud	6	12.54	Present study

maximum adsorption capacity obtained in this study is comparable with other adsorbent at different pH was shown in Table 1.

3.3. Effect of contact time and adsorption kinetics

The effect of contact time on the adsorption at different contact times from 10 to 60 min is depicted in Fig. 4(a). The equilibrium adsorption was established after 40 min of contact time and the maximum removal percentage was 94.38, 92.07 and 87.50% for initial cadmium concentration 10, 50 and 100 mg L^{-1}, respectively. After equilibrium was reached, the contact time no longer had an influence on the cadmium ion adsorption and the removal efficiencies remained constant over the time period of 60 min. The

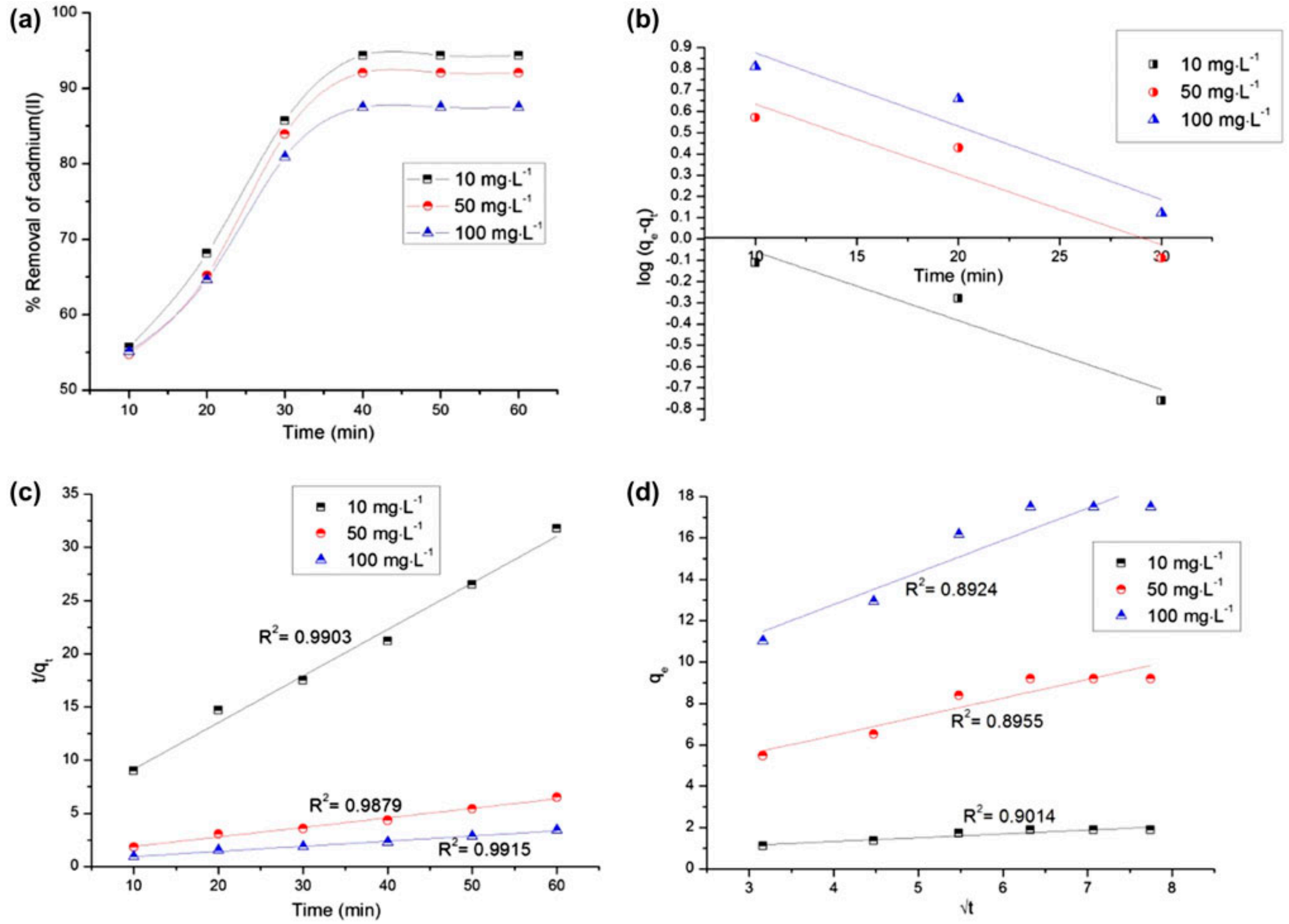

Fig. 4. Effect of contact time (a), kinetic study of pseudo-first-order (b), pseudo-second-order (c) and intraparticle diffusion models (d) for removal of Cd(II) onto ARM (adsorbent dose: 0.5 g/100 mL, pH 6 and temperature: 298 K).

Table 2
Kinetics and thermodynamic parameters (293 and 303 K) of cadmium adsorption onto the ARM at different initial cadmium concentration

		Initial Cd(II) concentration (mg L^{-1})		
Kinetics model/thermodynamics study	Parameters	10	50	100
Pseudo-first-order model	q_e (mg g^{-1})	0.9681	0.9672	0.9660
	K_1	0.0747	0.0761	0.0795
	R^2	0.9286	0.9029	0.9049
Pseudo-second-order model	q_e (mg g^{-1})	2.2853	11.1776	20.6232
	K_2	0.0400	0.0080	0.0052
	R^2	0.9903	0.9879	0.9915
Intraparticle diffusion Model	k_{ip}	0.1841	0.9003	1.5525
	C	0.5915	2.8622	6.5785
	R^2	0.9014	0.8955	0.8924
Thermodynamic study	ΔH (kJ mol^{-1})	1.1723	1.1545	1.0728
	ΔS (J K^{-1} mol^{-1})	11.7420	10.3922	9.4827
	ΔG (kJ mol^{-1})	293 K −233.669	293 K −206.690	293 K −188.582
		303 K −351.09	303 K −310.613	303 K −283.41
	R^2	0.711	0.699	0.674

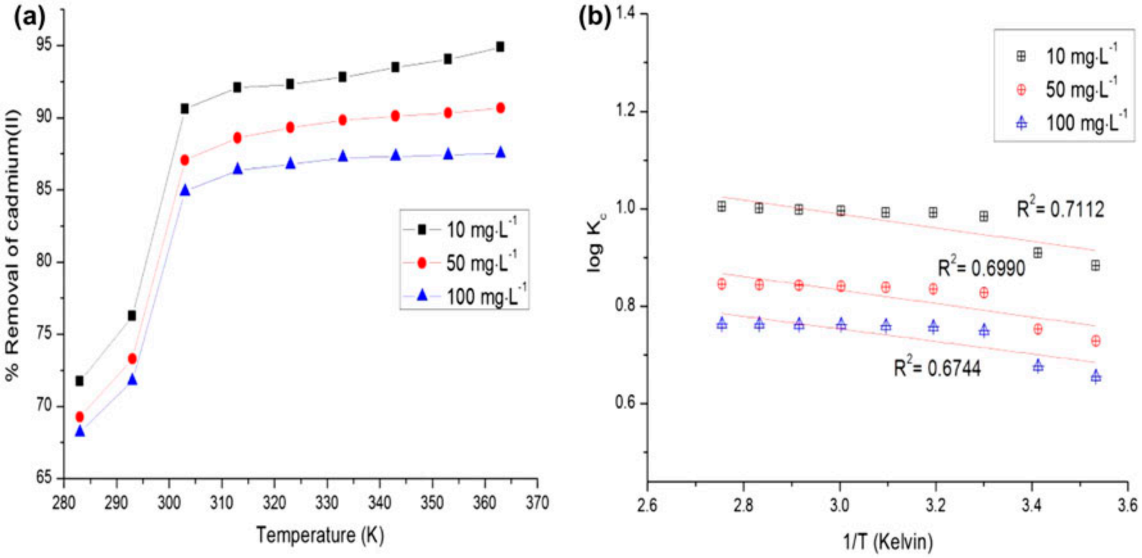

Fig. 5. Effect of temperature (a) and van't Hoff plots of log K_c vs. $1/T$ (b) for the adsorption of Cd(II) by ARM (adsorbent dose: 0.5 g/100 mL, pH 6 and contact time: 40 min).

adsorption rate increased rapidly in the first 10–30 min because the number of available adsorption sites on the surface is the highest at the beginning of the adsorption process, whereas a further increase in contact time decreases the number of available adsorption site. The result obtained implies that the sorption mainly took place at the surface of the sorbent during the initial stage. The adsorption time of 40 min was used for the rest of the study.

Different adsorption kinetics of Cd(II) onto ARM are shown in Fig. 4(b)–(d). The values of intraparticle diffusion rate constants (K_{ip}), pseudo first-order (K_1) and second-order (K_2) rate constants are tabulated in Table 2 for the different experimental parameters. The

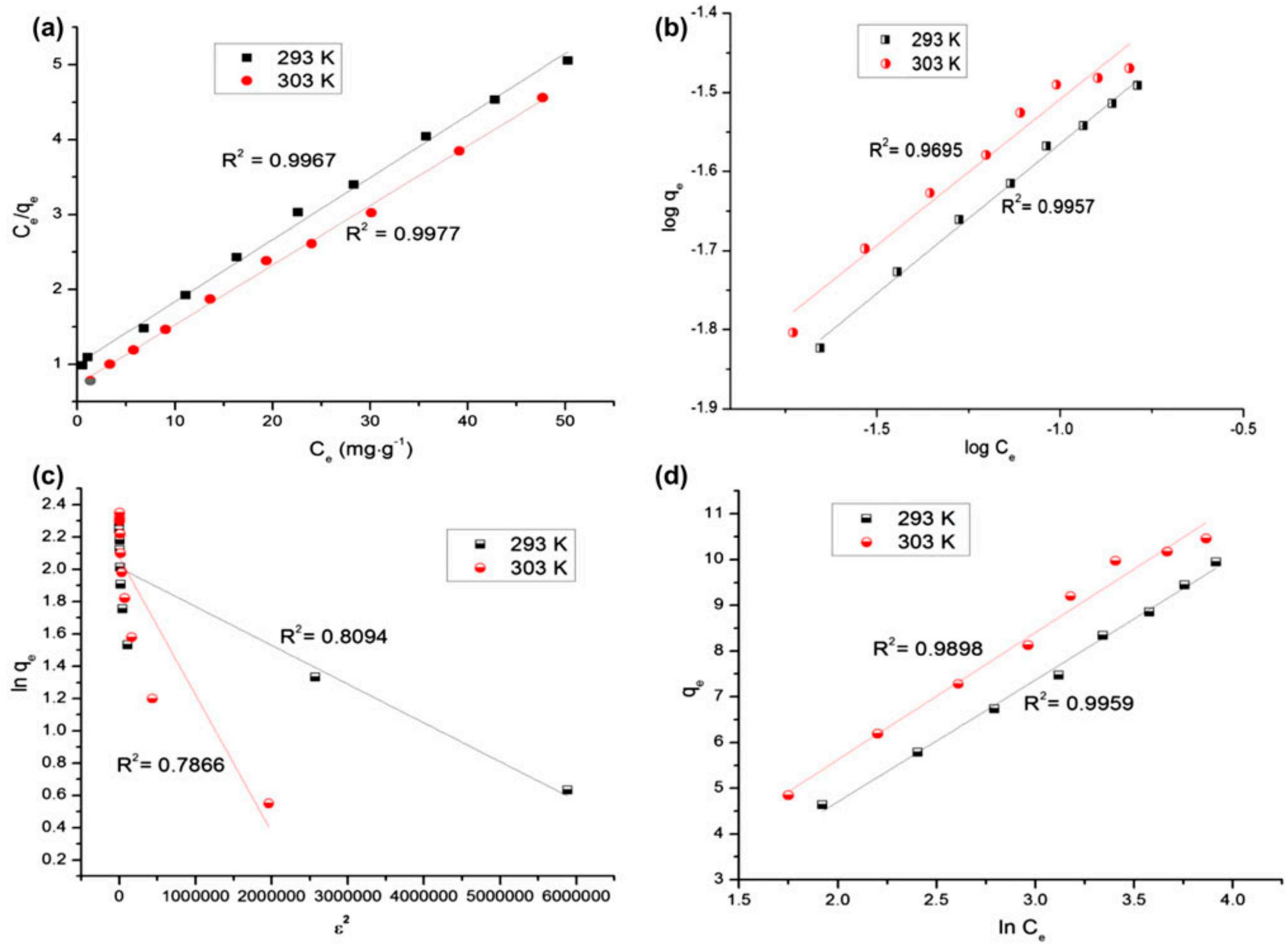

Fig. 6 Isotherm models of Langmuir (a), Freundlich (b), Dubinin–Radushkevich (c), and Temkin models (d) for the adsorption of Cd(II) onto ARM at temperature 293 and 303 K (adsorbent dose: 0.5 g/100 mL, pH 6 and contact time: 40 min, adsorbent dose: 0.5 g/100 mL, pH 6 and contact time: 40 min).

values of K_1 and q_e of pseudo-first-order kinetic model at different concentrations were calculated from the slope and intercept of the plots of $\log(q_e - q_t)$ vs. t, and the values of K_2 and q_e of pseudo-second-order kinetic model at different concentrations were calculated from intercept and slope of the t/q_t vs. t plot. From the data, it is concluded that the pseudo-second-order model shows excellent linearity with a high correlation coefficient ($R^2 > 0.99$) in comparison to other kinetic models. The calculated q_e values from the model were also in good agreement with the experimental values. The pseudo-second-order kinetic model is based on the assumption that the limiting rate step may be chemisorption, which involves valence forces by sharing or electron exchange between the adsorbate and the adsorbent [60]. The results are consistent with previous literatures in which adsorption kinetic of Cd(II) ion by different adsorbent were fitted with pseudo-second-order model [61,62].

3.4. Effect of temperature and thermodynamic studies

To determine the effect of temperature on Cd(II) adsorption from aqueous solutions, batch experiments were performed at different temperature (283–363 K) with initial concentration of 10, 50 and 100 mg L^{-1} with optimum adsorbent dose and the results are represented in Fig. 5(a) that shows the uptake capacity of metal ions increases with increase in temperature. Higher temperatures favour adsorption of metal ions, which reveal the endothermic nature of adsorption. An increase in percentage removal can be explained in terms of an increase in the number of active sites with increasing temperature due to some breakage of bonds near active sites.

Table 3
Isotherm parameters for cadmium adsorption onto ARM at temperature 293 and 303 K

		Temperature (K)	
Isotherm model	Parameters	293	303
Langmuir	q_m (mg g^{-1})	12.0464	12.5482
	b (L mg^{-1})	0.0826	0.1090
	R^2	0.9967	0.9977
Freundlich	K_F (mg g^{-1})	0.3055	0.3200
	$1/n$	0.3790	0.3692
	R^2	0.9956	0.9694
Dubinin–Radushkevich	K (mol k^{-1} J^{-1})	2.3999	8.4969
	q_m (mg g^{-1})	7.4574	7.9382
	R^2	0.8094	0.7865
Temkin	K_T (L mg^{-1})	0.7894	1.2140
	B_1	2.6666	2.6320
	R^2	0.9958	0.9898

The standard entropy change (ΔS) and the values of the standard enthalpy change (ΔH) were determined from the intercept and the slope of the van't Hoff's plot of log K_c vs. $1/T$ depicted in Fig. 5(b). The thermodynamic parameters for the adsorption of cadmium onto ARM at different temperature are summarized in Table 2. The negative values of Gibbs free energy change (ΔG) indicated the feasibility of the process and spontaneous nature of the adsorption. The ΔG values decreased with an increase in temperature, indicating an increased trend in the degree of spontaneity and feasibility of cadmium adsorption. Generally, 0 to −20 kJ/mol for free energy change was reported to be the physical range, and −80 to −400 kJ/mol was reported to be the range for chemical adsorption [63]. ΔG *value* was in the range of −188.582 to −233.669 kJ/mol and −283.41 to −351.09 for temperature 293 and 303 K, respectively, indicating chemical adsorption. The ΔH parameter was found to be 1.1723, 1.1545 and 1.0728 kJ mol^{-1} for initial concentration 10, 50 and 100 mg L^{-1}, respectively. The positive values of ΔH further confirmed the endothermic nature of the adsorption process. The ΔS values were found to be 11.7420, 10.3922, 9.4827 J K^{-1} mol^{-1} for initial concentration of 10, 50 and 100 mg L^{-1}, respectively. The positive value of ΔS suggested a higher randomness tendency at the solid/solution interface during the adsorption of Cd(II) on the adsorbent.

3.5. *Adsorption isotherm*

The values of Langmuir constant q_m and b were calculated from the slopes and intercepts of the plots of C_e/q_e vs. C_e respectively, and are represented in Fig. 6(a).

The result obtained from the different adsorption model is reported in Table 3. From the Langmuir plot, the values of q_m for the removal of Cd(II) at 293 and 303 K were found to be 12.05 and 12.55 mg g^{-1}, respectively. It was observed that the value of "*r*" in between the range of 0–1, for initial Cd(II) concentration of 10, 50 and 100 mg L^{-1}, confirmed the favourable uptake of the Cd(II) process [64].

The values of the Freundlich constants, K_F and $1/n$, were determined by intercepts and slopes of linear plot of log q_e vs. log C_e plot (Fig. 6(b)). From the Freundlich plot, the values of K_F for removal of Cd (II) from aqueous solution at 293 and 303 K were found to be 0.3055 and 0.3200 mg g^{-1}, respectively, and are shown in Table 3. If the slope, $1/n$ is less

Table 4
Comparison of adsorption capacities of Cd(II) ions with some low-cost adsorbents

Adsorbent	Adsorption capacity q_m (mg/g)	Refs.
Activated red mud	12.54	This work
Areca waste	1.32	[67]
Bentonite	9.30	[68]
Saw dust	5.37	[69]
Saw dust	0.29	[70]
Rice husk	0.89	[70]
Modified sewage sludge	14.7	[71]
Peanut hulls	5.96	[72]
Bagasse fly ash	2.00	[73]
Kaolinite clay	0.88	[74]
Pre-treated rice husk	8.58	[75]
Modified steel-making slag	10.16	[76]

than 1, then the adsorption process is favourable. The values $1/n$ obtained are 0.3790 and 0.3692 at temperature 293 and 303 K, respectively, which indicated that the cadmium adsorption onto ARM was favourable. The value of K and q_m was obtained from the slope and intercept from the Dubinin–Radushkevich plot of $\ln q_e$ vs. ε^2 and is shown in Fig. 6(c), and the values of K and q_m for the removal of Cd(II) at 293 and 303 K were found to be ($2.3999\ \mathrm{mol\ k^{-1}\ J^{-1}}$ and $7.4574\ \mathrm{mg\ g^{-1}}$) and ($8.4969\ \mathrm{mol\ k^{-1}\ J^{-1}}$ and $7.9382\ \mathrm{mg\ g^{-1}}$), respectively, given in Table 3. The constant K_T and B_1 can be determined by the linear plot of q_e vs. $\ln C_e$ shown in Fig. 6(d) and the Temkin parameters are presented in Table 3. The Temkin constant, B_1, showed that the heat of adsorption of cadmium ions onto ARM showed a slight increase in value at higher temperatures indicating an endothermic process [65].

Comparing the isotherm models results (Table 3), it could be deduced that the Langmuir isotherm fit the equilibrium data better ($R^2 > 0.99$) than the Freundlich, Dubinin–Radushkevich and Temkin models. It might be due to homogeneous distribution of active sites on adsorbent surface [66].

Table 4 lists a comparison of maximum monolayer adsorption capacity of Cd(II) on various adsorbents. The maximum adsorption capacity of ARM is higher than most adsorbents presented in Table 4. Therefore, the present ARM could be considered a promising material for the removal of Cd(II) from aqueous solutions.

3.6. Mass transfer study

The linear plot between $\ln[(C_t/C_0) - 1/(1 + mK)]$ and t shown in Fig. 7(a) proved the validity of the equation for the present study. The value of k_f was determined from the slope and intercept of the plot. The mass transfer coefficient values suggest that the velocity of adsorbate transport from the bulk to the solid phase is quite rapid which reveals the effectiveness of red mud for the treatment of cadmium bearing wastewater.

From the Weber model, k_f value was calculated from the slope of the straight line obtained from the plot of C_t/C_0 vs. t, given in Fig. 7(b).

The k_f values of McKay et al. equation and Waber–Mathews equation are given in Table 5, which shows that the mass transfer coefficient rate ranges from 0.084×10^{-3} to 0.012×10^{-3} for McKay et al. equation and 9.9×10^{-3}–11.5×10^{-3} for Waber–Mathews equation for temperature 293 and 303 K, respectively. It can be understood from the k_f value that ARM adsorbed cadmium ions faster at lower temperature (McKay et al. equation) and at higher temperature (Waber–Mathews equation).

3.7. Desorption

The applicability of ARM as a potential adsorbent depends on desorption property and reusability also. For regeneration, HCl solution was selected as the regeneration agent. Fig. 8(a) shows the effect of HCl

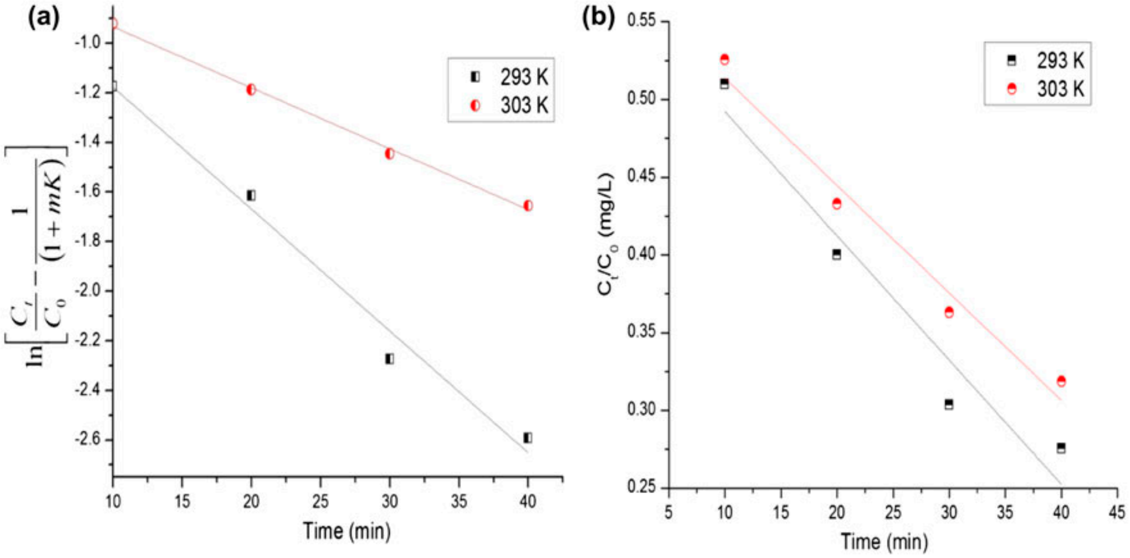

Fig. 7. Mass transfer plot MeKay et al. (a) and Waber–Mathews (b) for the adsorption of cadmium on ARM (adsorbent dose: 0.5 g/100 mL, initial concentration: 10 mg L^{-1}, pH 6.0, temperature: 293 and 303 K).

Table 5
External mass transfer coefficients (k_f) (cm min^{-1}) calculated from the equations of McKay et al. and Weber–Mathews related to the adsorption of cadmium on ARM from aqueous solution

Temperature (K)	McKay et al. equation k_f (cm min^{-1})	Weber–Mathews equation k_f (cm min^{-1})
293	0.084×10^{-3}	9.9×10^{-3}
303	0.012×10^{-3}	11.5×10^{-3}

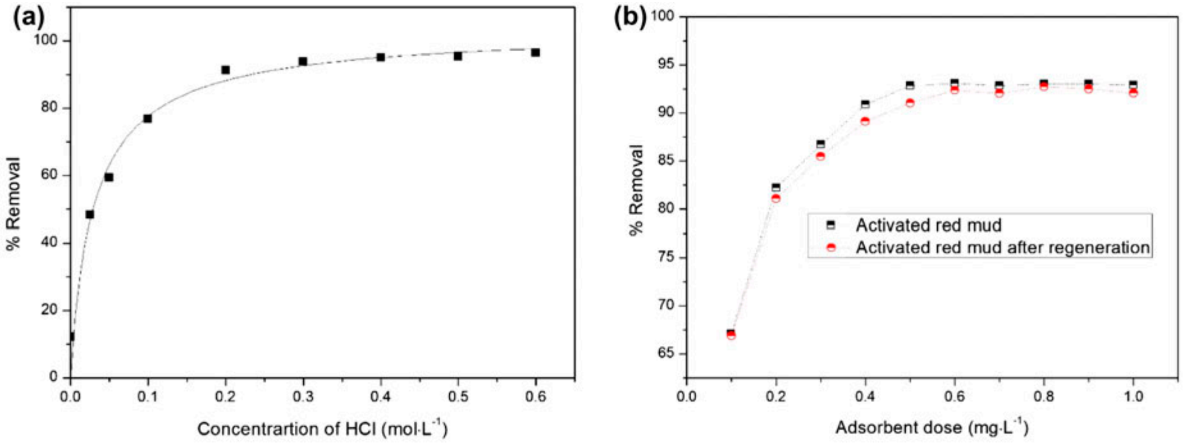

Fig. 8. Effect of HCl concentration on desorption of cadmium (a) and effect of the dosage on arsenate removal using ARM and ARM after regeneration (b) (room temperature, pH 6, initial concentration: 10 mg L^{-1}).

concentration on desorption efficiency. The regeneration efficiency reached 76.75–91.29% when the concentration of HCl reached 0.1–0.2 mol L^{-1}, respectively. A comparative experiment of ARM and ARM after regeneration was carried out as an effect of adsorbent doses to investigate the removal of Cd(II). As seen in Fig. 8(b), the adsorption capacity of adsorbent after regeneration was equal to the ARM unused.

3.8. Mechanism of Cd(II) adsorption

The mechanism of any adsorption process is an important component to understand the process as well as to know the characteristics of the material which help to design a new adsorbent for the future applications. Electrostatics interaction between the positively charged Cd(II) and the negative charge on ARM presented by ion exchange (Eq. (18)) or Si–O–Si structures (Eq. (19)).

$$2(\text{ARM-OH}) + \text{Cd}^{2+} \rightarrow (\text{ARM-O}^-)_2\text{Cd} + 2\text{H}^+ \quad (18)$$

$$2(\text{ARM-Si} - \text{O}^-) + \text{Cd}^{2+} \rightarrow (\text{ARM- Si} - \text{O}^-)_2\text{Cd}^{2+} \quad (19)$$

The adsorption of Cd(II) ions on ARM is maximum at pH 6, because when the pH value of the solution is greater than the pH_{zpc} value, the surface of the minerals is negatively charged while the number of H_3O^+ ions decreases. Therefore, the positively charged Cd(II) ions are adsorbed onto ARM surface via chemical ion exchange or electrostatics attraction [77] as suggested in Fig. 9.

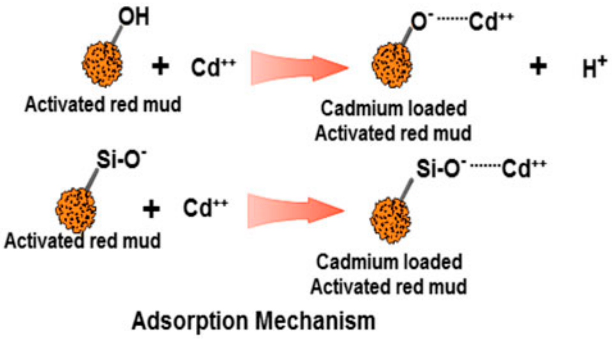

Fig. 9. Mechanism of adsorption of Cd(II) on ARM.

4. Conclusion

ARM is an excellent adsorbent for the treatment of wastewater containing Cd(II) ions. The adsorption kinetics was found to follow pseudo-second-order rate equation and equilibrates within 30 min. The adsorption data fit very well to the Langmuir model and the maximum removal of Cd(II) was found to be 12.046 and 12.548 mg g^{-1} at temperature 293 and 303 K, respectively, at pH 6. The thermodynamics of cadmium adsorption onto ARM confirmed the endothermic and spontaneous adsorption process. Cadmium can be desorbed from ARM with HCl and the removal efficiency reaches 91.29% when the concentration of HCl is 0.2 mol L^{-1}. The adsorption capacity of adsorbent after regeneration was equal to the ARM untapped. Thus, the ARM can be considered as a low-cost adsorbent for adsorption of Cd(II) from water. Also, ARM can be used for potential application for wastewater remediation since it has not been tested on samples from industry.

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