Kinetic and isotherm studies of cadmium adsorption on manganese nodule residue

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Abstract

The adsorption equilibrium and kinetics studies of cadmium (Cd) ions from aqueous solutions on manganese nodule residue were carried out by considering the influence of various parameters, such as contact time, solution pH and initial metal concentration in solution, temperature and adsorbent quantity. The adsorption of Cd increased with an increase in the concentrations of this metal in solution. Presence of manganese and iron content in manganese nodule residue (MNR) played a significant role in Cd(II) ions removal. The linear forms of the Langmuir and Freundlich equations were utilized for experiments with metal concentrations of 200 mg/L for Cd(II) as functions of solution pH (2.0–6.0). First-order rate equation and pseudo second-order rate equations were applied to study adsorption kinetics. Mass transfer study was also done to know the reaction rate. Thermodynamic parameters, such as standard Gibb's free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°), were also evaluated by Van't Hoff equation. Thus, adsorption of Cd on this adsorbent was found to be spontaneous and exothermic thermodynamically. The adsorption capacity for Cd was found to be 19.8 mg/g of MNR. Under the optimised conditions, cadmium level was brought down from 100 mg/L to Cd less than detection limits and from 200 to 2 mg/L. Thus, the wastewater after cadmium removal could be safely disposed off on to land or sewage. Finally, the metal loaded adsorbent was subjected to desorption using different mineral acids and leaching by using toxicity characteristic leaching procedure (TCLP), synthetic precipitation leaching procedure (SPLP) tests for its further treatment or its safe disposal.
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1. Introduction

Environmental pollution due to developments in technology is one of the most critical problems of this century. Heavy metals, such as cadmium, etc., having several industrial applications are the potential pollutants widely found in industrial wastewaters [1,2]. Its toxicity affects the ecosystem and presents human health risk. Cadmium as a pollutant is found in cadmium plating, alkaline batteries, copper alloys, paints, plastics and paper manufacturing industries [1,2]. In India, the tolerance limit for cadmium for discharge into inland surface waters is 2.0 mg/L [3] and for drinking water is 0.01 mg/L [4]. Safe and effective disposal of heavy metal-bearing wastewater is a difficult task partly owing to the fact that cost-effective treatment alternatives are seldom available. Conventional methods for removing toxic metal ions from wastewater include chemical reduction, ion exchange, reverse osmosis, co-precipitation, coagulation, complexation, electrodeposition, solvent extraction, electrochemical treatment and adsorption on activated charcoal. Such processes may be ineffective or extremely expensive for the treatment of effluents with low heavy metal concentrations ranging from 10 to 100 g/m³ [5]. Many of these methods also produce a sludge, which results in further disposal problem. Hence, industries are in search of low cost alternative ways of treating wastewater. To compete with conventional procedures, new methods must be economically viable as well as successful in contaminant removal. Of these methods, adsorption of metal ions present in low levels on to the solid can prove to be a cost-effective and better option for treating industrial effluents and wastewater streams. Numerous researchers have investigated the use of activated carbon to remove heavy metals from aqueous solutions [6–9]. Granular activated carbon (GAC) used in a column process can eliminate separation problems and minimize sludge production. Activated carbon, however, has a relatively small adsorption capacity and affinity for metals. Oxides have been widely discussed for metals removal from aqueous solutions

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[9–12]. Relative to GAC, oxides have higher metals affinities and adsorption capacities. Furthermore, oxides have the ability to remove metals to trace concentrations and the adsorbed metals can be recovered and reused. However, solid separation and sludge management after the adsorption process can be difficult, because the oxides are usually in colloidal forms. One possible solution to this problem is to prepare a granular adsorbent that can be used in a column process. Composite adsorbents of this type include Fe^{2+} treated activated carbon [13], Fe-coated sand [14–18], granular iron oxide [19] and Mn oxide-coated sand [20]. Results from the above studies suggest that composite adsorbents can be synthesized by forming an oxide surface coating on another solid and these composite adsorbents can be easily separated from aqueous solution after an adsorption process. Concerns about sludge management could be resolved by using the composite adsorbent in a column process. The adsorbent could be reused after regeneration and the metals could be concentrated for recovery. It was also found that Mn oxides have a higher affinity for many heavy metals [21–23]. In fact, several investigators have suggested applications for Mn oxides in water and wastewater treatment [9,23]. Adsorption on materials of waste category has also been proposed as an alternative to these conventional adsorbents for the economic removal of metal ion present at low concentration from wastewaters and effluents. Bailey et al. [24] reviewed a wide variety of low cost adsorbents for the removal of heavy metals as an alternative for the more costly processes, which involved the use of activated carbon and ion-exchangers. Many investigators have studied the feasibility of less expensive materials, such as goethite [25], clays [26], agricultural wastes [27], zeolites [28–29], fly ash [30,31], red mud [32], recycled iron [33], etc., for the removal of heavy metals from wastewater. Goethite is one of the most widespread iron oxide in natural environments [34,35] that can be used as low cost adsorbent.

The solid waste namely manganese nodule residue (MNR) used as an adsorbent in this study was generated during the processing of manganese nodules for the recovery of valuable metals by reduction roasting–ammoniacal leaching–solvent extraction–electrowinning route at NML. This waste was generated when the reduced and roasted manganese nodule was leached with a mixture of ammonia and ammonium carbonate as leachant. The metal ions go into the solution as ammoniacal complex leaving behind a black residue. This residue being rich in oxides of manganese, iron, silicon, aluminium, etc., was exploited for its use as an adsorbent for cadmium since the use of MNR for the adsorption of metals remains unexplored. Although this material is being tried for the preparation of value added products like silico-manganese, it was considered worthwhile to explore the use of this waste as an adsorbent to treat aqueous solutions containing cadmium. To understand the mechanism of metal adsorption different models were applied. Desorption using different acids and leaching studies by toxicity characteristic leaching procedure (TCLP) [36] and synthetic precipitation leaching procedure (SPLP) [37] were performed on cadmium adsorbed SNR to assess the desorption/leaching of the adsorbed metal, so that the loaded adsorbent can be further treatment if

required or can be finally disposed off. TCLP method is an agitated extraction test using leaching fluid that is a function of the alkalinity of the solid phase of the waste. Either a sodium acetate buffer solution having a slightly acidic pH or an acetic acid solution of known pH is used. The procedure requires particle size reduction to less than 9.5 mm whereas SPLP is an agitated extraction method developed in 1988 by the U.S. EPA for use in evaluating the impact that contaminated soils may have on groundwater. The procedure calls for use of simulated acid rain or reagent water as the extraction fluid, depending on the constituents of interest. The procedure requires particle size reduction to less than 9.5 mm, and as with the TCLP, extraction for volatile constituents is performed in a zero-headspace extractor.

2. Experimental

2.1. Materials

The residue generated during the processing of sea nodule for copper, cobalt and nickel recovery at NML, was washed with a very dilute HCl solution to neutralize the residual ammonia and thereafter washed with distilled water till the pH of the washing was 6.0. The washed product was dried in an oven at 80 °C overnight, ground and sieved to four different size fractions of >0.152, 0.104–0.152, 0.076–0.104 and 0.053–0.076 mm. The characteristics of the adsorbent were as follows—chemical composition: Fe, 9.03%; SiO_2, 19.04%; Mn, 18.23%; Al_2O_3, 1.58%; loss on ignition, 10.11%; pHzpc, 4.8; specific gravity, 2.99. Specific surface area of the residue measured by nitrogen adsorption technique at 78 K by BET apparatus 'Quantasorb' (Quantachrome, USA) was 125 m^2/g for the particle size of 0.104–0.152 mm.

The synthetic stock solution for the present study was prepared by dissolving $Cd(NO_3)_2$ in distilled water (1 L) to obtain 1000 mg/L Cd(II) concentrations. A few drops of HNO_3 were added to prevent hydrolysis of the solution. Solutions of 0.1 M HNO_3 and 0.1 M NaOH were used for pH adjustment. 0.1N KNO_3 was used to maintain the ionic strength in the adsorption experiments. All chemicals used were of analytical reagent grade and were obtained from Merck. The Borosil glassware was used for the experimental work.

2.2. Methods

2.2.1. Kinetic procedure

Batch studies were conducted in a temperature-controlled shaker using 100 mL of adsorbate solution and a fixed adsorbent dosage of 1.0 g. The concentration of Cd varied from 100 to 500 mg/L. The agitation speed of the shaker was fixed at 120 rpm for all batch experiments. The samples at different time intervals (5 min, 10 min, 15 min, 30 min, 1 h, 2 h, 4 h, 6 h and 8 h) were taken and filtered and the filtrate was analysed for the concentration of Cd(II) left unadsorbed using an atomic absorption spectrophotometer (Thermo Jarrel Ash Model) at wavelength of 228.8 nm.

2.2.2. Equilibrium experiments

Isotherm studies were conducted in a batch mode to determine the adsorption of Cd(II) on MNR, using stoppered conical flasks. In these experiments, 100 mL of Cd solution with a Cd concentration varying from 100 to 500 mg/L, were poured into each flask to which 1 g of MNR was added. The solution–MNR mixtures were stirred at 120 rpm in the pH range of 2.0–7.0 at temperatures varying from 303 to 323 K, using a temperature-controlled water bath shaker. Ionic strength was maintained with 0.1 M KNO_3. At the end of predetermined time intervals, samples were withdrawn, their contents were filtered and the filtrate was analysed for Cd(II) left unadsorbed. The difference between the initial and the final value gives the amount of Cd adsorbed per gram of the adsorbent. Effect of various parameters, such as contact time, pH of the aqueous feed, initial metal concentration in solution and adsorbent to solution volume ratio, were studied. Experiments were also conducted at three different temperatures keeping other variables constant in order to study Langmuir and Freundlich adsorption isotherms.

In order to find out the possibility of any adsorption on the walls of the glass conical flask, control experiments were carried out with Cd(II) solution in the absence of adsorbent. It was observed that there was no adsorption by the container wall. All the experiments were performed in duplicate and mean values were presented with a maximum deviation of 5%.

2.2.3. Desorption of Cd(II) from the loaded adsorbent

The adsorbent after the adsorption of metal ion was tested for the leaching of cadmium from the point of view of the safe disposal of the spent adsorbent. One gram of the metal loaded adsorbent was agitated with a solution of 0.01 M of different acids like HCl, H_2SO_4 and HNO_3 for 4 h, acetate buffer for TCLP test for 18 h and sulphuric acid solution for SPLP for 24 h. The slurry was then filtered and the filtrate was analysed for cadmium ion eluted/leached.

3. Results and discussion

3.1. Kinetic study

3.1.1. Effect of initial cadmium concentration and shaking time on adsorption

Several experiments were carried out to study the effect of varying initial cadmium concentration on cadmium removal by MNR. One hundred millilitres of Cd(II) solution of different concentrations ranging from 100 to 500 mg/L with 1 g of mixed fraction of MNR (as obtained) was stirred at ambient temperature (303 K) for a contact period of 24 h. The results obtained are shown in Fig. 1 and indicate that all the curves have the same shape. Percentage of cadmium adsorption increased with increase in agitation time and attained equilibrium at variable time according to the initial concentration of cadmium: about 0.5 h ($C_0 = 200$ mg/L), 2 h ($C_0 = 300$ and 400 mg/L) and 4 h ($C_0 = 500$ mg/L). It was also noticed that the capacity of cadmium removal by MNR at the equilibrium increases with the initial concentration of cadmium but the percent removal decreases with the increase in initial cadmium concentration
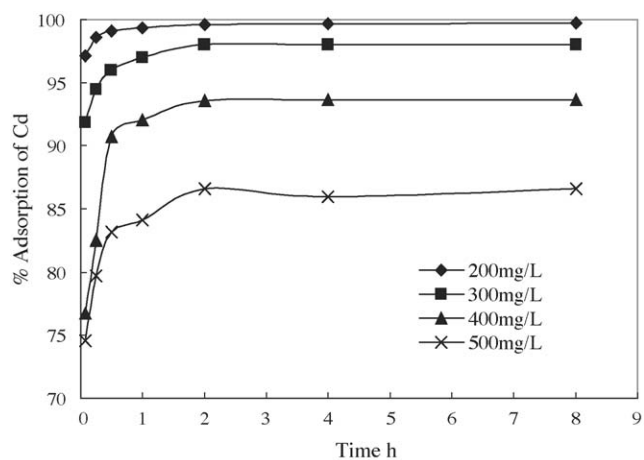

Fig. 1. Effect of initial concentration and shaking time on adsorption of Cd on MNR at 303 K: S/L, 1/100; pH 5.5; PS, 0.104 mm.

from 99.75% for 200 mg/L of Cd to 85% for 500 mg/L of Cd. In general, the percentage of metal removal increased rapidly up to approximately 30 min and thereafter, rose slowly before attaining a saturation value. Fig. 1 also shows that the metal removal in the first 30 min was approximately equal to 99, 96, 90 and 83% for 200, 300, 400 and 500 mg/L of Cd(II). All subsequent experiments were done with 200 mg/L of cadmium solution and equilibrium time was maintained at 4 h unless stated otherwise, which was considered as sufficient for the removal of Cd(II) ions by this adsorbent. The time curves in Fig. 1 are smooth and continuous, leading to saturation suggesting the possibility of monolayer coverage of Cd(II) on the adsorbent surface. Since the uptake of cadmium is highly dependent on the initial concentration of the metal ion in the solution, the higher uptake at low concentration can be explained as: at higher initial concentrations, the ratio of initial number of moles of Cd(II) to the available surface area is high, hence fractional adsorption becomes dependent on initial concentration. For fixed adsorbent dose, the total available adsorption sites are limited thereby adsorbing almost the same amount of adsorbate, thus resulting in a decrease in percentage removal of the adsorbate corresponding to an increase in initial adsorbate.

3.1.2. Effect of particle size

The surface of contact between any sorbent and the liquid phase plays an important role in the phenomena of sorption. The effect of particle size of MNR on the cadmium removal was studied using the size ranging 0.053–0.152 mm at 303 K. Fig. 2 shows a series of contact time curves at different MNR particle sizes. As can be seen, the curves of kinetics obtained have an identical shape, and that the capacity of cadmium sorption at the equilibrium increases with the decrease of the adsorbent particle sizes indicating that cadmium ion sorption occurs by a surface mechanism. Similar results have been reported for the sorption of metal ions by natural polymers and their derivatives [38]. It was also observed that the variation in particle size appears to have an influence on the time required to reach equilibrium. Thus, for particle size 0.053 mm, the time required to reach equilibrium is about 1 h and the cadmium adsorption was about 98.1%; while
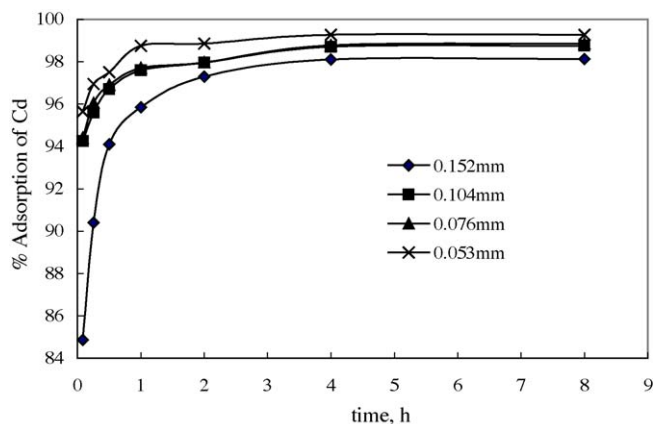
Fig. 2. Effect of particle size of MNR on Cd adsorption: [Cd], 200 mg/L; pH 5.5; *S*/*L*, 1/100; temperature, 303K.

for particle sizes 0.152 mm, the time necessary is about 4 h with cadmium adsorption of 99%. Consequently, increasing particle size increases the time needed to reach equilibrium. These observations suggest that the cadmium sorption kinetic by MNR is largely determined by the particle size.

3.2. Modeling adsorption kinetics

3.2.1. First-order kinetic model

Kinetics and the equilibrium of adsorption are the two important factors for the evaluation of the adsorption parameter. The adsorption of heavy metals from liquid phase to solid phase can be considered as a reversible reaction with equilibrium being established between the two phases [27]. A simple first-order kinetic model is represented by the Lagergren equation [39] as given below:

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}t}{2.303} \tag{1}$$

where k_{ad} is the rate constant of adsorption, q_t and q_e are the amounts of Cd(II) adsorbed (mg/g) at time t (min) and at equilibrium time, respectively. Linear plots of $\log(q_e - q_t)$ versus t at different temperatures on MNR (Fig. 3, figures for 300 and
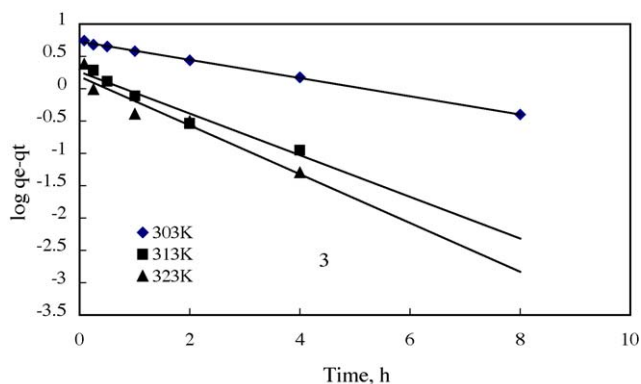

Fig. 3. Lagergren plot for Cd (200 mg/L) adsorption on MNR.

400 mg/L not given to save space) indicate the applicability of Lagergren equation. The k_{ad} values calculated from the slopes of these plots for different cadmium concentrations (Table 1) show that the adsorption is a first-order reaction.

3.2.2. Pseudo second-order model

A pseudo second-order model [40] was also applied to assess the kinetics of adsorption of cadmium on MNR. The differential equation for this reaction is given as:

$$\frac{dq}{dt} = k_2'(q_e - q)^2 \tag{2}$$

Integrating Eq. (8) for the boundary conditions $t = 0$ to >0 and $q = 0$ to >0 and rearranging it gives the linearized form of pseudo second-order rate kinetics, which is shown as follows:

$$\frac{t}{q_t} = \frac{1}{K_2'q_e^2} + \frac{1}{q_e}t \tag{3}$$

where q_t and q_0 are the amount of metal ion adsorbed (mg/g) at any time t and at equilibrium, K_2 the pseudo second-order rate constant and t is the time (min). The kinetic plots between t/q versus time were plotted for different initial cadmium concentration at three different temperatures gave a straight line (Fig. 4, figure for 313 and 323 K are not given to save space). Slope and intercept values were solved to give the value of pseudo

Table 1

Pseudo second-order rate constants and Lagergren constants for cadmium adsorption on MNR at different temperature and initial concentration

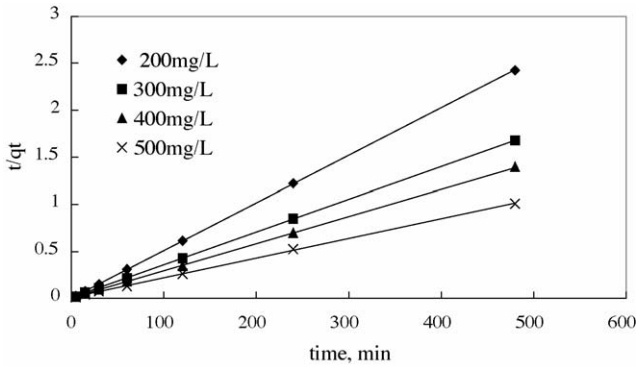| Pseudo second-order rate constants						Lagergren constants	
Temperature (K)	Cd (mg/L)	q_e	k	h_o	R^2	k	R^2
303	200	196.08	6.669×10^{-3}	256.41	1.0	0.32	0.9988
	300	285.71	1.531×10^{-3}	125.0	1.0	0.69	0.9935
	400	344.83	1.078×10^{-3}	128.21	0.9999	1.34	0.9873
	500	476.19	0.416×10^{-3}	94.34	0.9997	–	–
313	200	200	2.5×10^{-2}	1000.0	1.0	0.74	0.9573
	300	294.12	6.8×10^{-3}	588.24	1.0	1.57	0.9611
	400	370.37	2.35×10^{-3}	322.58	1.0	1.83	0.9661
	500	434.78	2.3×10^{-3}	434.78	1.0	–	–
323	200	200	4.17×10^{-3}	1666.66	1.0	0.90	0.9317
	300	303.03	2.14×10^{-3}	196.08	1.0	1.34	0.9627
	400	384.62	3.07×10^{-3}	454.55	1.0	1.77	0.9526
	500	476.19	0.85×10^{-3}	192.31	0.9998	–	–

Fig. 4. Pseudo second-order kinetics plots for different initial cadmium sorption by MNR at 303 K.

second-order rate constant (Table 1). It was observed that the R^2 values (Table 1), in case of pseudo second-order kinetics, were equal to 1. Thus, it could be inferred that cadmium adsorption on MNR obeys pseudo second-order rate kinetics more than the first-order rate kinetics.

3.2.3. Intraparticle diffusion

Since rate of adsorption is usually measured by determining the change in concentration of adsorbate with the adsorbent as a function of time, linearization of the data is obtained by plotting the amount adsorbed per unit weight of adsorbent q versus $t^{1/2}$ as given by ref. [41] and Eq. (4):

$$q_t = K_t'^{1/2} \qquad (4)$$

where q_t is the amount of metal adsorbed (mg/g) at time t (min) and K' is the rate constant for intraparticle diffusion. Plot q versus t is shown in Fig. 5 for two different initial concentrations show the same general feature, initial curved portion which can be attributed to the bulk diffusion followed by a linear portion within a certain extent attributed to the intraparticle diffusion. Thus, pore diffusion is not the only rate-controlling step [42] for the removal of cadmium. K' values obtained from the slope of the linear portion of the curves for each concentration of metal ions was found to be 0.0282 and 0.0681 for initial metal concentration of 200 and 300 mg/L, respectively, and was found to be higher for higher metal concentration. This possibility was
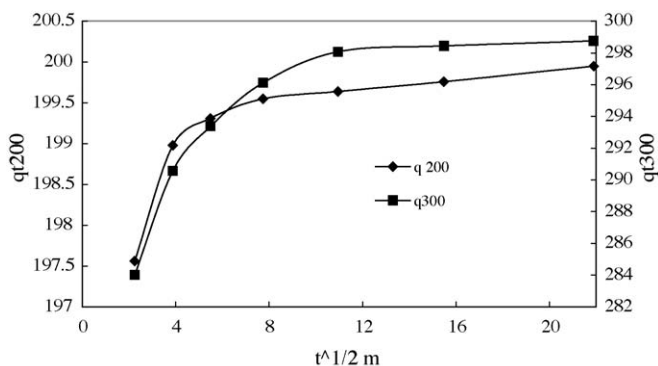

Fig. 5. Plot of q_t vs. $t^{1/2}$ for the intraparticle transport of Cd(II) on MNR: [Cd], 200, 300 mg/L; pH 5.5; temperature, 303 K; PS, 0.104 mm at 125 rpm.
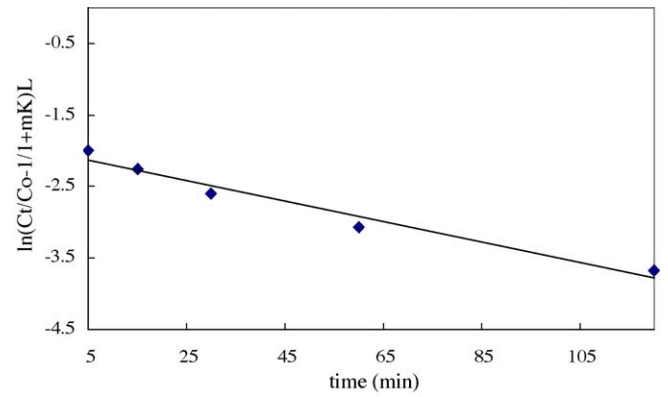

Fig. 6. Mass transfer plot for adsorption of Cd(II) on MNR: [Cd], 200 mg/L; pH 5.5; temperature, 303 K; PS, 0.104 mm.

further tested by determining the pore diffusion coefficient, D, from the following Eq. (5):

$$\bar{D} = \frac{0.03}{t_{1/2}} r_0^2 \qquad (5)$$

where $t_{1/2}$ is time for half adsorption and r_0 (cm) is the radius of the adsorbent particle. According to Michelsen et al. [43], a D value of the order of 10^{-11} cm^2/s is indicative of intraparticle diffusion as the rate-determining step. In this investigation, the value of D (3.85×10^{-8} cm^2/s) is more than three orders of magnitude higher which indicates that the intraparticle diffusion is not the only rate-controlling step. As a result, it may be concluded that both, film and pore diffusion are involved in the removal process.

3.2.4. Mass transfer study

Mass transfer study was carried out using the following Eq. (6):

$$\ln\left(\frac{C_t}{C_0} - \frac{1}{1 + mK_L}\right) = \ln\frac{mK_L}{1 + mK_L} - \frac{1 + mK_L}{mK_L}\beta_1 S_s t \qquad (6)$$

where C_t and C_0 both are expressed in terms of μmol/L are the cadmium concentrations at time t and 0, respectively, K_L the Langmuir constant, m the mass of the adsorbent per unit volume of particle-free adsorbate solution (g/L) which is given by $m = W/V$, S_s the outer surface of the adsorbate per unit volume of particle-free slurry (cm^{-1}) and β_1 (cm/s) is the external mass transfer coefficient. The slope and the intercept of the plot of $\ln(C_1/C_0 - 1/(1 + mK_L))$ versus t as shown in Fig. 6 gives the value of β_1 which was calculated to be 3.825×10^{-5} cm/s. This suggests that the velocity of mass transfer of Cd on MNR is rapid enough [44] to use this adsorbent for the treatment of wastewater rich in cadmium. The linear nature of the plots confirms the validity of the diffusion model for Cd–MNR system.

The activation energy for cadmium adsorption was calculated by the Arrhenius equation [45]:

$$k_{ad} = A \exp(-E_a/RT) \qquad (7)$$

where k_{ad} is the rate constant value obtained from Lagergren equation for the metal adsorption, E_a the activation energy in
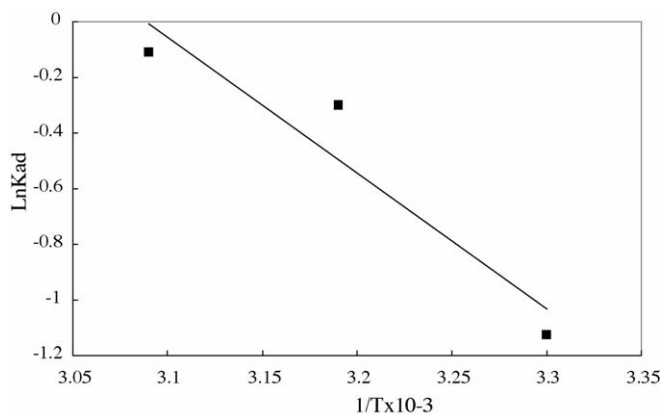
Fig. 7. Arrhenius plot Cd (200 mg/L) adsorption on MNR.

kJ/mol, T the temperature and R is the gas constant. The activation energy for cadmium adsorption was calculated from the slope of the plot of $\ln k_{ad}$ versus $1/T \times 10^{-3}$ (Fig. 7) and was found to be 12.29 kJ/mol, indicating the physical adsorption [46]. This shows the possibility of desorption of the adsorbed metal ion from the adsorbent.

3.2.5. Equilibrium study

3.2.5.1. Effect of amount of MNR on cadmium adsorption.
Adsorption was also studied by varying amount of the adsorbent to assess the optimum amount of adsorbent for maximum removal of metal. Weight of MNR was varied from 0.5 to 3 g per 100 mL of solution for 200 mg/L cadmium at 303 K (Fig. 8). The results show that the adsorption percentage of cadmium increases with increase in the weight of MNR. The percentage removal was found to be 56.25% for 0.5 g of MNR and about 99.9% for 3.0 g of MNR in 8 h. The presence of manganese phases as MnO_2/Mn_2O_3 and iron hydroxide in the MNR and its high surface area (125 m^2/g) was responsible for the uptake of 19.8 mg Cd/g of MNR. It may be noted that the higher surface area in MNR was due to the porosity available in the manganese oxides and iron hydroxide phases.

3.2.5.2. Effect of pH and mechanism of adsorption.
Adsorption of cadmium was studied at varying pH and the results are shown in Fig. 9. Earlier studies have indicated that solution pH
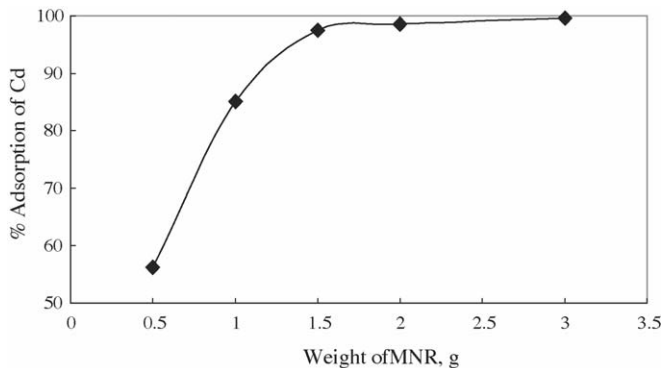

Fig. 8. Effect of weight of MNR on Cd adsorption: [Cd], 200 mg/L; temperature, 303 K; time, 8 h; pH 5.5; PS, 0.104 mm.
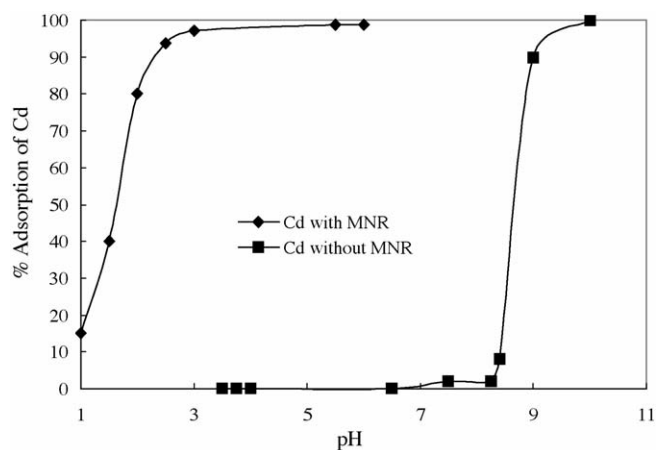

Fig. 9. Effect of pH on Cd adsorption on MNR: [Cd], 200 mg/L; temperature, 303 K; S/L, 1/100; PS, 0.104 mm.

is an important parameter, which affects adsorption of heavy metal ions [47–49]. It is apparent that the uptake is quite low at lower pH 2.0, however, with the increase in pH from 2.0 to 5.5, a significant enhancement in adsorption is recorded on this adsorbent. The optimum pH for metal adsorption was 5.5 with the removal of about 98.8% from the feed solution containing 200 mg/L Cd. At pH around 6, the Cd(II) adsorption capacity levelled off at a maximum value and beyond this pH cadmium ions precipitate out, hence the metal removal will be less due to adsorption, however experiments beyond pH 6.0 were not done. For comparison, precipitation curve at different pH values in the absence of MNR is also given in Fig. 9. It shows that precipitation of cadmium starts at pH 8.2. This figure clearly shows that at any pH, removal of cadmium is very much greater by adsorption than by hydroxide precipitation. Various reasons might be attributed to the metal adsorption behaviour of this adsorbent relative to solution pH. Since MNR contains a large number of surface active sites due to the presence of oxides of manganese, iron, aluminium and silicon, the pH dependence of metal uptake can largely be related to these active sites and also to the chemistry of the metal in solution [50,51]. The solution chemistry of transition metal elements is complicated due to the hydrolysis phenomenon: when pH increases from an acid value to a neutral value, various hydrolysed species exist and the affinities of these species to the adsorbent surface can vary. Cd(II) speciation diagram [52] shows that the dominant Cd(II) species at pH > 8.0 is $Cd(OH)_2$ and at pH < 8.0 is Cd^{2+} and $Cd(OH)^+$, therefore at lower pH there is a competition effect between the H_3O^+ ions and Cd(II) ions. Metal ions that could associate with the MNR surface would have to compete with the H_3O^+ ions for the active sites. At low pH values, the concentration of H_3O^+ far exceeds that of Cd(II) ions and hence, these ions occupy the surface binding sites, leaving Cd(II) ions free in solution. When the pH was increased, the competing effect of H_3O^+ ions decreased and the positively charged Cd^{2+} and $Cd(OH)^+$ ions hook up the free binding sites. Hence, the metal uptake was increased on the surface of the adsorbent with the increase in pH. Similar results were obtained by Namasivayam and Ranganathan [49] for the cadmium adsorption on waste hydroxide. According to
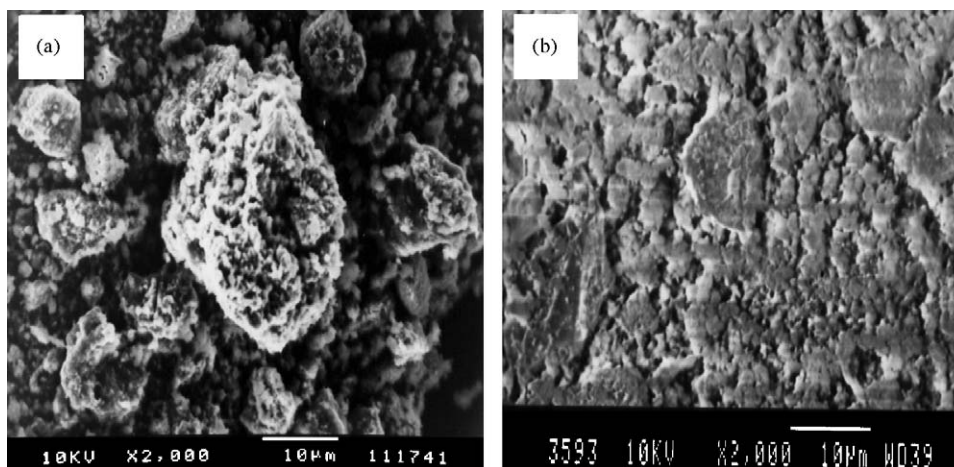
Fig. 10. SEM photograph of: (a) unadsorbed and (b) Cd adsorbed MNR.

the Pearson theory [53], during acid–base reaction, hard acids prefer to interact with hard bases and soft acids with soft bases. Positively charged Cd(II) species are soft acids and as a rule the interaction of Cd^{2+} and $Cd(OH)^+$ with surface bonding sites is likely favoured at the pH range of 5.0–8.0. The effect of pH can be explained in terms of pHzpc of the adsorbent and species of Cd(II) formed in the solution. The surface charge is a function of pH. The pH at which the charge of the solid surface is 0 is referred to as the zero point of charge (pHzpc). Above pHzpc, the surface charge of the adsorbent is negative. The zpc of MNR was determined by electrophoretic measurements [54] and was found to be 4.8. Thus, at pH values below 4.8, the surface of the adsorbent would have a high positive charge density due to the aqua complex formation of the oxides present in this adsorbent. Under these conditions, a positive charge developed on the surface of the oxides of the adsorbent in an acidic medium as follows [55]:

$$-MO + H-OH \xrightarrow{H^+} M-OH_2^+ + OH \tag{8}$$
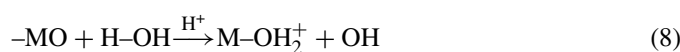
Thus, a lowering of cadmium adsorption at low pH is due to the fact that surface charge, thus, developed is not suitable for Cd^{2+} and $Cd(OH)^+$ species adsorption due to electrostatic repulsion. Schindler and Stumm [56] have developed and applied the surface complexation models to describe metal sorption reactions at the solid–water interface. As the pH increases the surface of MNR becomes negatively charged as shown in Eqs. (9) and (10), thereby favouring the adsorption of cadmium.

$$-MOH + OH^- \rightarrow -MO^- + H_2O \tag{9}$$

$$-MO^- + Cd \rightarrow -M-O-Cd \tag{10}$$
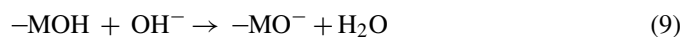
A similar theory was proposed by Yadava et al. [55] and Viraraghavan and Rao [31] for metal adsorption on fly ash, which is also made up of various oxides. The SEM examination of MNR before and after Cd adsorption (Fig. 10a and b) at pH 5.5 clearly shows the formation of precipitate covering the particles of the adsorbent. The surface coverage further confirms the adsorption of CdOH$^+$ species on MNR. Recent studies using advanced analytical methods have demonstrated

that the sorption of heavy metals on clay and oxide surfaces results in the formation of multinuclear or polynuclear surface phases much more frequently than previously thought. Polynuclear metal hydroxides of Pb, Co, Cu and Cr(III) on oxides and aluminosilicates have been discerned with XAFS [57,58]. Such polynuclear surface phases have been observed at metal surface loadings far below a theoretical monolayer coverage and in a pH-range well below the pH where the formation of metal hydroxide precipitates would be expected according to the thermodynamic solubility product [57,58]. Possible causes of this, such as enhanced surface concentration, reduction of the dielectric constant of water near the surface and solid solution formation, have been discussed by them.

3.2.6. Effect of temperature and adsorption isotherm studies

The removal rate of cadmium from the solution increases as the temperature increases from 303 to 323 K as shown in Fig. 11. As the temperature increases the active surface centres available for sorption also increases [59]. The increase in uptake of cadmium may also be caused by an enhanced rate of intraparticle (solid) diffusion of adsorbate. Thermodynamic parameters were
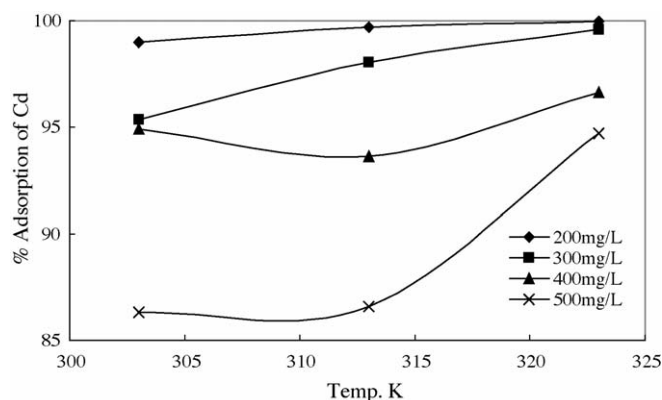

Fig. 11. Effect of temperature on adsorption of Cd for different metal concentration on MNR: *S/L*, 1/100; pH 5.5; time, 4 h; PS, 0.104 mm.
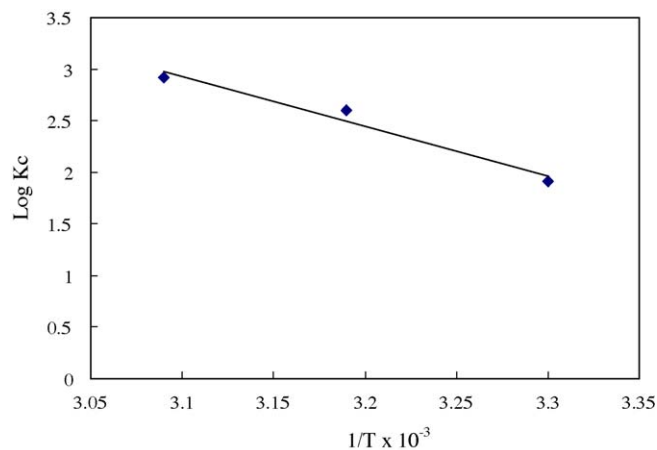
Fig. 12. Van't Hoff plot Cd (200 mg/L) adsorption on MNR.

also calculated using the following relations [60]:

$$K_c = \frac{C_A}{C_e} \quad (11)$$

where K_c is the equilibrium constant, C_e the equilibrium concentration in solution (mg/L) and C_A is the solid-phase concentration at equilibrium (mg/L). This K_c value was further used to calculate the thermodynamic parameters. Thus,

$$\Delta G^\circ = -RT \ln K_c \quad (12)$$

where R is the gas constant and T is the temperature (in Kelvin).

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

ΔG°, ΔH° and ΔS° are changes in free energy, enthalpy and entropy, respectively. ΔH° and ΔS° were obtained from the slope and intercept of the Van't Hoff plot (Fig. 12) and are presented in Table 2. The negative values of ΔG° (Fig. 12) indicate that the adsorption of cadmium on MNR is spontaneous in nature. The positive value of ΔH° confirms the endothermic adsorption of cadmium and the positive ΔS° suggests the increased randomness at the solid–solution interface during the adsorption of cadmium on MNR. This prevalence of randomness in the system is due to the displacement of the adsorbed water molecules, from the adsorbed species, thereby gaining more translational entropy than is lost by the adsorbate ions. Increase in the adsorption capacity of cadmium with the increase in temperature may be attributed to the enlargement of pore size and activation of the adsorbent surface [61]. The equilibrium data were correlated by both Langmuir and Freundlich equations for cadmium adsorption on MNR Langmuir treatment is based on the assumption that maximum adsorption corresponds
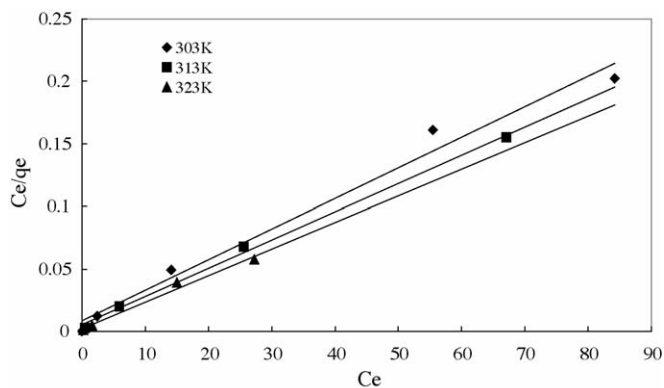

Fig. 13. Langmuir plot for Cd adsorption on MNR at different temperatures— 303 K: $Q_o = 416$, $b = 0.28$, $R^2 = 0.98$; 313 K: $Q_o = 434.8$, $b = 0.0.42$, $R^2 = 0.99$; 323 K: $Q_o = 476.2$, $b = 0.91$, $R^2 = 0.98$.

Table 3
Adsorption capacities of cadmium on various other low cost adsorbents

Low cost adsorbent	Adsorption capacity (mg/g)	Reference
Fly ash	198.2	[30]
Lignite	40.25	[62]
Red mud	12.01	[63]
Bone char	10.0	[64]
Peat	11.18	[46]
Slag	11.24	[65]

to a saturated monolayer of adsorbate molecule on the adsorbent surface, with a constant energy of adsorption and no transmigration of adsorbate in the plane of the surface. The isotherm plotted in Fig. 13 are well described by the linear form of the Langmuir equation [62]:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (14)$$

where C_e is the equilibrium concentration (mg/L) in solution, q_e the amount of metal adsorbed at equilibrium (mg/g) and Q_o and b are the Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The data fitted well in the Langmuir equation as shown by the regression coefficient values (Fig. 13). Q_o and b values determined from the slopes and intercepts of the straight-line plot are given in Fig. 13. The increase in the value of Q_o with the increase in temperature indicates an increase in the adsorption capacity of the adsorbent for cadmium and the endothermic nature of this process. Increasing values of b with temperature are accompanied by high-energy requirement for metal adsorption. A comparison of Q_o values with other adsorbents is given in Table 3. The essential characteristics of a Langmuir isotherm can also be expressed in terms

Table 2
Thermodynamic parameters for the adsorption of Cd

Metal ion	Temperature (K)	K_c	$-\Delta G^\circ$ (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
Cd/MNR [Cd]: 200 mg/L	303	82.3	11.11	66.34	786.18
	313	399.0	15.58		
	323	832.3	22.35		

Table 4
Equilibrium parameter R_L for the adsorption of Cd

Temperature (K)	Cd–MNR			
	200 mg/L	300 mg/L	400 mg/L	500 mg/L
303	0.0175	0.0117	0.0088	0.0071
313	0.0118	0.0079	0.0059	0.0049
323	0.0054	0.0036	0.0027	0.0021

of a dimensionless constant separation factor R_L, given by the following equation [63]:

$$R_L = \frac{1}{1 + bC_i} \quad (15)$$

where C_i is the initial metal concentration (mg/L) and b is the energy of interaction at the surface. For a favourable adsorption, the separation factor R_L lies between 0 and 1.

Thus, R_L values of 0.002–0.0175 calculated at different temperature and concentration lie between 0 and 1.0 indicating a highly favourable adsorption (Table 4). It is interesting to note that R_L values decreases with the increase in initial concentration of the metal ion in the solution at each temperature and also at any initial metal concentration, R_L value decreases with the increase in temperature from 303 to 323 K. Thus, it can be inferred that MNR is a very effective adsorbent for 200 mg/L of cadmium at 303 K.

The Freundlich adsorption was also applied for the adsorption of cadmium by MNR and is given as follows:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (16)$$

where q_e is the amount of Cd(II) adsorbed per unit weight of the adsorbent (mg/g), C_e the equilibrium concentration (mg/L), K_f and n the Freundlich constant, n gives an indication of favourability and K_f (mg/g) is the capacity of the adsorbent. Linear plots of $\log C_e$ and $\log q_e$ shows that the adsorption of cadmium on MNR follows Freundlich model (Fig. 14). The values of n and K_f calculated from the slope and intercept were found to be 0.1958, 0.1588 and 0.1686 and (K_f) 165.95, 218.77 and 260.6 mg/g at
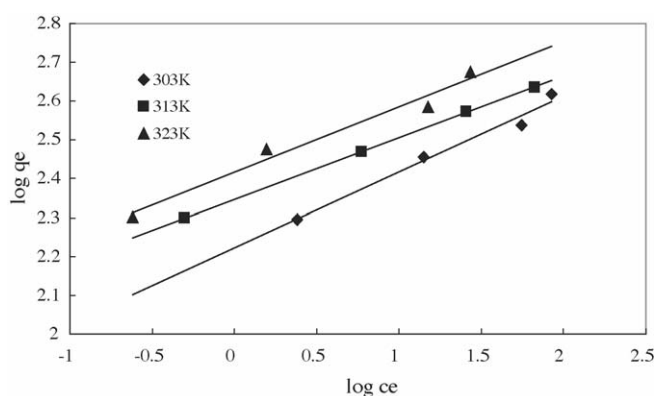

Fig. 14. Freundlich isotherm for Cd adsorption on MNR—303 K: $K_f = 165.9$, $1/n = 0.19$, $R^2 = 0.98$; 313 K: $K_f = 218.8$, $1/n = 0.16$, $R^2 = 0.99$; 323 K: $K_f = 260.6$, $1/n = 0.17$, $R^2 = 0.98$.

Table 5
Desorption of adsorbed metal ions from MNR with different acids and leaching by TCLP and SPLP test

System	Metal desorbed/leached (%)
0.01 M HCl	3.2
0.01 M HNO$_3$	10.65
0.01 M H$_2$SO$_4$	7.6
TCLP	58.9
SPLP	Nf[a]
TCLP limits (mg/L)	2.0

Metal laden adsorbents—Cd–MNR: 200 mg/L/100 mL/1g/199.85 ppm (adsorbed).
[a] Not found.

303, 313 and 323 K, respectively. The value if $1/n$ between 0.1 and 1 represents good adsorption of cadmium on MNR (Fig. 14).

4. Leaching/desorption of the cadmium loaded MNR

The Cd adsorbed MNR was subjected to leaching/desorption of cadmium from the point of view of the safe disposal of the spent adsorbent. Results of Cd leached or desorbed are shown in Table 4. The permissible limit for the discharge of Cd on to land is 2.0 mg/L [4] and as per Table 5 and concentration of cadmium exceeds this limit in all the eluents except for the SPLP test. Moreover, desorption of metal ion was also indicated by the E_a data for the adsorption of Cd on the sea nodule residues. The E_a values for Cd adsorption on MNR were 12.25 kJ/mol. Hence, the metal loaded adsorbent cannot be disposed off without any treatment.

5. Conclusion

- Manganese nodule residue was found to be a very effective adsorbent for the removal of Cd in a concentration range up to 200 mg/L from aqueous solution/wastewaters owing to a large surface area (125 m^2/g) and presence of various phases of manganese oxides and iron oxides.
- Metal adsorbed on this adsorbent in the pH range 5.0–6.0 is found to be 19.8 mg Cd/g MNR.
- The thermodynamic parameters (ΔG) reflect the feasibility of the metal removal from aqueous solution/wastewaters.
- The adsorption data show good fit to the Langmuir and Freundlich adsorption isotherm as depicted by the regression coefficient for these systems. R_L values between 0 and 1.0 further indicate a favourable adsorption of cadmium.
- Of the two rate kinetics equations, pseudo second-order rate kinetic equation was found to be more closely followed for cadmium adsorption on MNR due to regression coefficient values equal to 1. First-order kinetics equation was also solved for this system with R^2 values varying from 0.99 to 0.93 with the rise in temperature from 303 to 323 K.
- The mass transfer study suggests that the velocity of cadmium ion transfer on MNR is rapid enough as shown by the β_1 value (3.825×10^{-5} cm/s), hence this adsorbent can be effectively used as an adsorbent for the treatment of wastewater rich in cadmium.

- The desorption of metals from the loaded adsorbent (MNR) shows partial removal of the loaded cadmium with 0.01 M of mineral acids. TCLP and SPLP test indicates that the loaded adsorbent can be dumped only after desorption of the loaded cadmium or immobilization of the adsorbed cadmium on the adsorbent.

Acknowledgement

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