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Saw dust and neem bark as low-cost natural biosorbent for adsorptive removal of Zn(II) and Cd(II) ions from aqueous solutions

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ABSTRACT

The ability of saw dust and neem bark as low-cost natural adsorbents were investigated for adsorptive removal of Zn(II) and Cd(II) ions from aqueous solutions. Various physico-chemical parameters such as pH, initial metal ion concentration, and adsorbent dosage level and equilibrium contact time were studied. The optimum pH for adsorption was found to be 5 for Zn(II) and 6 for Cd(II). Kinetics data were best described by pseudo-second-order model. Mass transfer coefficients were also determined for individual adsorbents for removal of Zn(II) and Cd(II) ions from aqueous solutions. The equilibrium adsorption data were fitted to Langmuir and Freundlich isotherm models for Zn(II) and Cd(II) adsorption respectively. The adsorption capacities ($q_{\max}$) for individual metal ions in terms of monolayer adsorption were compared with the other reported values. The sorption energy calculated by using Dubinin–Radushkevich isotherm for different system indicated that the adsorption process is physical in nature. The thermodynamic equilibrium constant and the Gibbs free energy were determined for each system and results indicated the spontaneous nature of the adsorption process. FT-IR studies were carried out to understand the type of functional groups in saw dust and neem bark responsible for metal binding process.

1. Introduction

The discharge of heavy metals into the watercourse is a serious environmental problem, which affects significantly the demand of quality water supply. Increasing concentration of these metals in the water constitutes a severe health hazard due to their toxicity, persistent in nature and non-biodegradability particularly when it exceeds the permissible limits [1,2]. Heavy metals do not degrade into harmless end products in the metabolism and they are accumulated in the food chain water–plants–animals–humans [3] thereby posing the greatest threat to the living organisms.

Cadmium is introduced into the water from smelting, metal plating, cadmium–nickel batteries, phosphate fertilizers, mining, pigments, pigments, stabilizers, alloy industries and sewage sludge [4]. The harmful effects of Cd(II) include acute and chronic metabolic disorders, such as itai-itai disease, renal damage, emphysema, hypertension and testicular atrophy [5]. Symptoms of zinc toxicity include loss of appetite, nausea, irritability [6]. The routes of entries of zinc into the environment include mining, purifying zinc, lead and cadmium ores, steel production, coal burning and burning of wastes. Zinc is present in high concentration in wastewater of pharmaceuticals, galvanizing, paints and pigments, insecticides, cosmetics, etc., that causes severe problem to the environment. The permissible limit (mg/L) for Zn(II) and Cd(II) in wastewater, given by CPCB are 5 and 2 mg/L respectively [7]. The permissible level for Zn(II) and Cd(II) in drinking water, given by EPA and IS: 10500 are 5 and 0.01 mg/L respectively [8,9]. Therefore it seems to be utmost important to remove the aforesaid metals from water and wastewater before its transport and cycling into the natural environment.

Generally, the various techniques employed for the effective removal of heavy metals from aqueous solution are the reduction and precipitation, coagulation, flotation, adsorption, ion-exchange and reverse-osmosis or electrodialysis, etc. [10–13]. However in many instances, these methods do not work effectively. For instance, precipitation method for heavy meal removal produces voluminous sludge that must be treated and disposed off normally at higher cost. Ion-exchange and reverse-osmosis, even though effective and efficient, are expensive due to high operational and maintenance cost hence only, few industries can think of it. Adsorption onto activated carbon is considered as an effective technique that was extensively used in the last few years [14,15]. But considering the cost economics, recent research has focused on the development of low-cost readily available alternatives using

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Nomenclature

b	Langmuir constant (L/mg)
C	concentration of metal ion after certain period of time (mg/L)
C_a	concentration of metal ion on the adsorbent at equilibrium (mg/L)
C_e	concentration of metal ion in solution at equilibrium (mg/L)
C_{final}	final concentration of metal ion in solution (mg/L)
$C_{initial}$	initial concentration of metal ion in solution (mg/L)
C_0	initial concentration of metal ion in solution (mg/L)
C_t	concentration of metal ion after time t (mg/L)
E	mean sorption energy (kJ mol^{-1})
F	amount adsorbed per gram of adsorbent at time/amount adsorbed per gram of adsorbent at equilibrium
ΔG^0	Gibbs free energy (kJ mol^{-1})
K_2	pseudo-second-order rate constant of adsorption [(mg/g) min]
K_{ad}	Lagergren rate constant (min^{-1})
K_c	thermodynamic equilibrium constant
K_f	measure of adsorption capacity (mg/g)
K_{id}	intra-particle rate constant [(mg/g) min$^{1/2}$]
K_{bq}	the constant obtained by multiplying q_{max} and b
M	mass of the adsorbent per unit volume (g/L)
m	amount of adsorbent added in gram
n	Freundlich constants, intensity of adsorption
q	amount adsorb per gram of the adsorbent (mg/g)
q_e	amount adsorb per gram of the adsorbent at equilibrium
q_m	equilibrium adsorption capacity (mg/g) using model
q_t	experimental value of amount of metal ion adsorb (mg/g of adsorbent) at any time t (min) from experiment
q_{tm}	adsorption capacity (mg/g) at any time t (min), using model
q_{max}	maximum adsorption capacity (mg/g)
q_{exp}	experimental values of equilibrium adsorption capacity (mg/g)
q_t	amount (mg) adsorb per gram of adsorbent at time t (min)
r^2	correlation coefficient
R_L	separation factor
S_s	external surface area of the adsorbent per unit volume (m^{-1})
t	time (min)
V	volume of the solution in mL
X_m	maximum adsorption capacity (mmol/g)

Greek letters

β	mass transfer coefficient (m/s)
λ	constant related to energy (mol^2/kJ^2)
ε	Polanyi potential (kJ^2/mol^2)

various agricultural, industrial, natural/biological waste materials including synthetic, modified model adsorbents. Several contributions have made in this area utilizing number of materials like olive stone carbon [16], sunflower stalks [17], spent grain [18], carboxy methyl cellulose [19], almond-shell carbon [20], sugarcane baggase [21], oak saw dust [22], black locust [22], cassava waste [23], baggage fly ash [24], wheat bran [25], *Aspergillus niger* [26], bone char [27], olive pomace [28], carrot residues [29], red seaweed [30], tree fern [31], sugar beat pulp [32], grape stalk waste [33], maize bran [34] and different low cost adsorbents [35].

Present study deals with a series of batch adsorption experiments to assess the potentiality of saw dust and neem bark for removal of Zn(II) and Cd(II) from aqueous solutions. The effects of adsorbent concentration, pH, contact time and initial metal ion concentration on the adsorption capacity were investigated. The rate kinetics and equilibrium parameters were determined to understand the mechanism of adsorption. Adsorption isotherm models and thermodynamic parameters were also investigated to know the adsorption characteristics.

2. Materials and methods

2.1. Adsorbents

Saw dust and neem bark were used as low-cost natural biosorbent.

Neem bark was collected from a local neem tree near Kolkata, West Bengal, India.

Saw dust of teakwood origin was collected from a saw mill at Dum Dum near Kolkata, West Bengal, India.

2.2. Pretreatment of the adsorbents

Saw dust and neem bark after collection were thoroughly washed with distilled water to remove muddy materials. Then saw dust and neem bark were soaked in 0.1 N NaOH to remove lignin based color materials followed by 0.1 N H_2SO_4 [35]. Finally it again washed with distilled water several times and dried in an air oven at 105 ± 5 °C for 6 h and cooled to room temperature in desiccators.

The adsorbents after drying to constant weight were sieved to obtain particle size of 250–350 μm prior to use for adsorption studies. The analysis was carried using a Particle Size Distribution analyzer (Model 117.08, MALVERN instruments, USA). The results of particle size distribution are presented in Table 1.

2.3. Reagents and equipments

All the necessary chemicals used in the study were of analytical grade and obtained from E. Merck India Limited, Mumbai, India.

Characterization of the adsorbents was carried out by surface area analysis, Bulk density, Scanning Electron Microscope (SEM) and FT-IR studies. The surface area of the both the adsorbents was measured by BET (Brunauer–Emmett–Teller nitrogen adsorption technique). The density of the adsorbents was determined by specific gravity bottle. The moisture content determination in the sample of saw dust and neem bark were carried out with a digital microprocessor based moisture analyzer (Mettler LP16). Scanning electron microscopic (SEM; Model S415A, Hitachi, Japan) studies was also conducted to observe the surface texture and porosity of the adsorbent. FT-IR (FTIR RX-1, PerkinElmer, USA) spectrometer was employed to determine the type of functional groups in saw dust and neem bark responsible for metal adsorption.

HACH-DR-4000 UV–visible Spectrophotometer and Atomic adsorption spectrophotometer (VARIAN SPECTRA AA 55) were used for determination of Zn(II) and Cd(II) content respectively in standard and treated solution. The pH of the solution was measured with a 5500 EUTECH pH Meter using FET solid electrode calibrated with standard buffer solutions.

2.4. Preparation of Zn(II) and Cd(II) standards

The stock solution containing 1000 mg/L of standard Zn(II) and Cd(II) were prepared by dissolving 4.395 g of AR grade $ZnSO_4{\cdot}7H_2O$.

Table 1
Particle size distribution of saw dust and neem bark (250–350 μm)

Adsorbents	250–275 μm	275–285 μm	285–295 μm	295–305 μm	305–315 μm	315–325 μm	325–335 μm	335–350 μm
Saw dust	5.2%	29.7%	18.3%	17.1%	15.6%	3.2%	9.1%	1.8%
Neem bark	1.1%	25.7%	15.4%	23.5%	20.2%	10.5%	3.6%	–

For preparation of Cd(II) standard 2.77 g of $Cd(NO_3)_2{\cdot}4H_2O$ and two drops of concentrated nitric acid were added to 200 mL of distilled water. After dissolution both the solutions were diluted to 1000 mL with double distilled water in a 1000 mL volumetric flask. Batch adsorption experiments were performed after proper dilution of stock solution.

2.5. Batch adsorption studies

Using the necessary adsorbents in a 250 mL stopper conical flask containing 100 mL of test solution batch adsorption studies were carried out at the desired pH value, contact time and adsorbent dosage level, for both the adsorbents. Different initial concentration of metal solutions was prepared by proper dilution from stock 1000 mg/L metal solutions standard. pH of the solution monitored by adding 0.1 M HCl and 0.1 M NaOH solution as per required pH value. Necessary amount of adsorbent material was then added and contents in the flask were shaken for the desired contact time in an electrically thermostated reciprocating shaker at 110–125 strokes/min at 30 ± 2 °C. The time required for reaching the equilibrium condition estimated by drawing samples at regular intervals of time till equilibrium was reached. The contents of the flask were filtered through filter paper and the filtrate was analyzed for metal ion concentration.

The concentration of metal ions in standard and treated samples was determined by following Standard methods for examination of water and wastewater, APHA, AWWA [36]. The amount of metal ion adsorbed per unit mass of the adsorbent was evaluated by using the same following mass balance equation

$$q = \frac{(C_0 - C)V}{m} \tag{1}$$

The percent removal of metal ions was calculated as follows

$$\%\,\text{Removal} = \left(\frac{C_{\text{initial}} - C_{\text{final}}}{C_{\text{initial}}}\right) \times 100 \tag{2}$$

Throughout the study, the contact time was varied from 15 to 300 min, the pH of the solution from 2 to 11, the initial metal ion concentration from 3 to 100 mg/L and the amount of adsorbent from 2.5 to 30 g/L.

All the investigations were carried out in triplicate to avoid any discrepancy in experimental results with the reproducibility and the relative deviation of the order of ±0.5% and ±2.5% respectively.

3. Results and discussion

3.1. Characterization of the adsorbents

The different characteristics of the adsorbents are shown in Table 2. Fig. 1(a) and (b) shows the SEM micrographs of the saw dust and neem bark used for adsorption studies. These figures showed that the adsorbents had an irregular and porous surface. Saw dust and neem bark are cellulose-based material containing tannin and lignin based organic compounds. Characterizations of these two adsorbents were carried out with Fourier Transform Infrared Spectroscopic (FT-IR) studies to identify the functional groups in the 4000–400 nm range. The spectra obtained are shown in Fig. 2(a) and (b). The spectra indicated a number of absorption peaks showing the complex nature of saw dust and neem bark. The functional group is one of the keys to understand the mechanism of metal binding on saw dust and neem bark. There are several functional groups present in saw dust and neem bark such as carboxylic acid, amine, amino, amide and sulphonate groups.

Table 2
Characteristics of saw dust and neem bark

Adsorbents	Surface area (m^2/g)	Bulk density (g/cm^3)	Dry matter (%)	Moisture content (%)
Saw dust	3.85	0.53	96.7	3.3
Neem bark	3.47	0.56	97.8	2.2

3.2. Effect of pH

The pH of the aqueous solution is an important monitoring parameter in the process of adsorption and thus the effect of pH has been studied by varying the same in the range of 2–9 for Zn(II) and 2–8 for Cd(II) (Fig. 3). Such study helps in designing the appropriate pH of the effluent/wastewater for achieving maximum efficiency in the removal of metal ions by an adsorbent. The optimum pH value for adsorption of Zn(II) and Cd(II) by the selected adsorbents was found to be 5 and 6 respectively. For saw dust percentage removal efficiency was observed to be 85.8% and 94.25% for Zn(II) and Cd(II) adsorption respectively at optimum pH values. In case of neem bark, percent removal of 82.2% for Zn(II) adsorption and 84.5% for adsorption of Cd(II) was achieved at optimum pH values. Therefore, all the

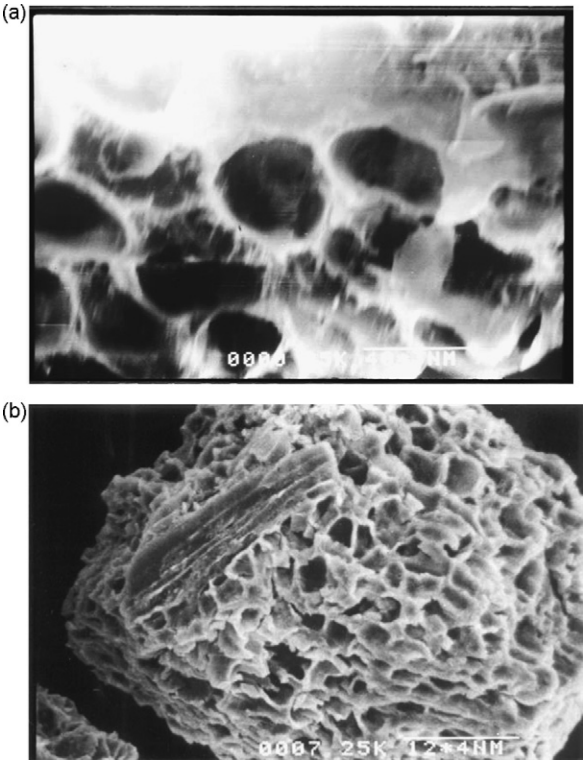

Fig. 1. (a and b) SEM micrographs of saw dust (250×) and neem bark (250×).

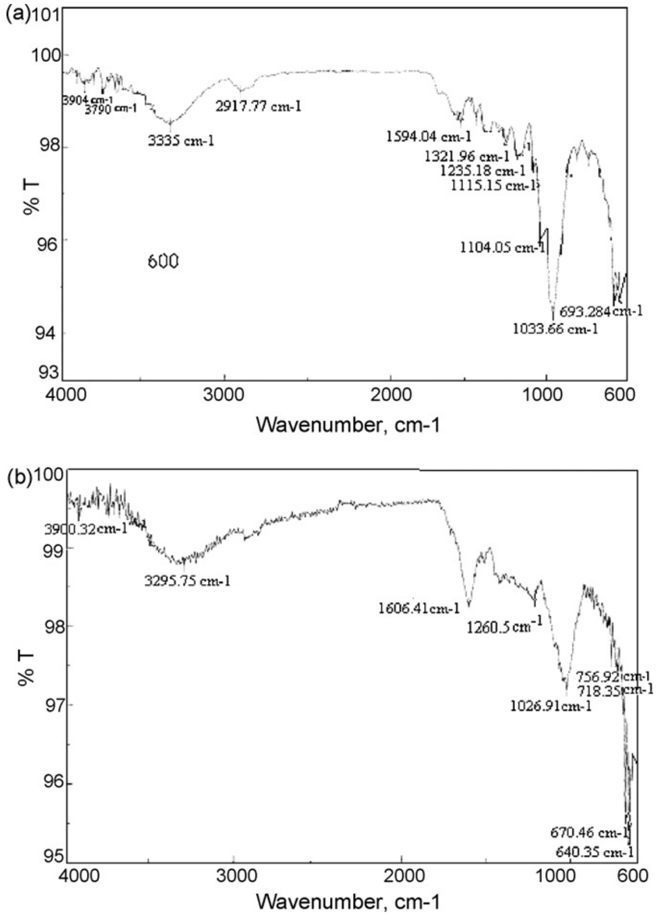

Fig. 2. (a and b) FT-IR spectra of saw dust and neem bark before adsorption.

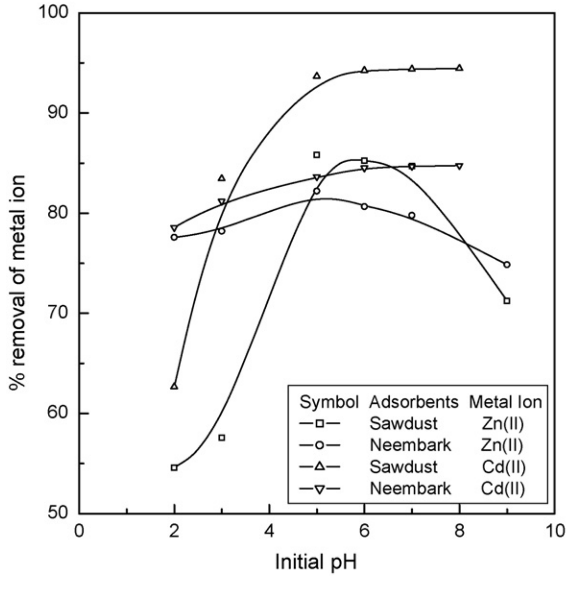

Fig. 3. Effect of pH on adsorption of Zn(II) and Cd(II). Experimental conditions: for Zn(II): adsorbent dosage 10 g/L, contact time 5 h, initial conc. 25 mg/L. For Cd(II): adsorbent dosage 10 g/L, contact time 5 h, initial conc. 10 mg/L.

following experiments on adsorption of Zn(II) and Cd(II) from aqueous solution were carried out by maintaining the solution at pH 5 for Zn(II) and pH 6 for Cd(II). Experiments on the effect of pH on the metal adsorption were carried out with the range of pH where metal precipitation does not takes place.

The effect of pH on Zn(II) removal can be explained considering the surface charge on the adsorbent material. At low pH, due to high positive charge density on the surface sites, electrostatic repulsion between metal ion and H^+ ion will be high during uptake of metal ions resulting in lower removal efficiency. With increasing pH, electrostatic repulsion decreases due to reduction of positive charge density of proton on the sorption sites thus resulting in an enhancement of metal adsorption. Similar observations were reported by earlier researchers [14,37].

The adsorption of Cd(II) ions on the surface of saw dust and neem bark can probably be explained by an ion-exchange mechanism based on surface complex formation model, which is facilitated by the dissociation of different functional groups present in wood tannin particles resulting in the formation of metal complex. This may be explained as follows [38]:

$$m[\mathrm{RO_7(OH)_{11}}] \leftrightharpoons m[\mathrm{RO_7(OH)_9(O^-)_2}] + m\mathrm{H}^+ \qquad (3)$$

$$\mathrm{Cd}^{n+} + m[\mathrm{RO_7(OH)_9(O^-)_2}] \leftrightharpoons \mathrm{Cd}[\mathrm{RO_7(OH)_9(O^-)_2}]_m{}^{n-m} \qquad (4)$$

The overall reaction can be represented as

$$\mathrm{Cd}^{n+} + m[\mathrm{RO_7(OH)_{11}}] \leftrightharpoons \mathrm{Cd}[\mathrm{RO_7(OH)_9(O^-)_2}]_m{}^{n-m} + m\mathrm{H}^+ \qquad (5)$$

Where

Cd^{n+} = Cadmium ion with n + charge; $-\mathrm{RO_7(OH)_{11}}$ = acidic part of wood surface, R represents the matrix part of the adsorbent; $m\mathrm{H}^+$ = number of protons released

The reaction is reversible in acid solution. The enhanced adsorption of metal ions with an increase in pH may possibly due to he condensation reaction between the hydrolysis product of sorbate ions and the sorbent carrying the –OH groups [38,39]. Therefore it may be concluded that the overall adsorption of Cd(II) ions on the surface of the saw dust and neem bark are mainly due to the ion-exchange mechanism involving combine effect of site binding adsorption and complexation phenomena.

3.3. *Effect of initial metal ion concentration variation*

Fig. 4 shows the effect of initial Zn(II) and Cd(II) concentrations on the removal efficiency by both the adsorbents. The efficiency of metal ions removal is also affected by the initial concentration of metal ions in aqueous solutions. Removal percentages of Zn(II) as well as Cd(II) from aqueous solution decreases as concentration increases from 3 to 100 mg/L at constant pH. As the metal ion/adsorbent ratio increases, the higher energy sites are saturated and adsorption begins on lower energy sites, resulting in decrease in the adsorption efficiency [40–42].

3.4. *Effect of adsorbent type and concentration*

The effect of adsorbent type and its concentration is depicted in Fig. 5. The selected adsorbents were used at concentration ranging from 2.5 to 30 g/L in a batch adsorption technique. In each case increase in adsorbent concentration resulted in an increase in percent removal of Zn(II) and Cd(II) from aqueous solutions. After certain adsorbent dosage the removal efficiency is not increased so significantly. At 10 g/L of saw dust the removal of Zn(II) was 85.76% and for neem bark it was 81.6% respectively. Maximum uptake of Cd(II) from aqueous solutions were found to be 94.5% and 84.5% respectively at an adsorbent dosage of 10 g/L for both saw dust

Table 3
Percentage removal of metal ions

Metal ion	Adsorbents	Initial metal ion concentration (ppm)	Percentage removal of metal ion (%)	Final metal ion concentration (ppm)	CPCB norms [7] (ppm)
Zn(II)	Saw dust	25	87.23	3.185	5
Zn(II)	Neem bark	25	84.75	3.810	5
Cd(II)	Saw dust	10	94.02	0.598	2
Cd(II)	Neem bark	10	86.24	1.376	2

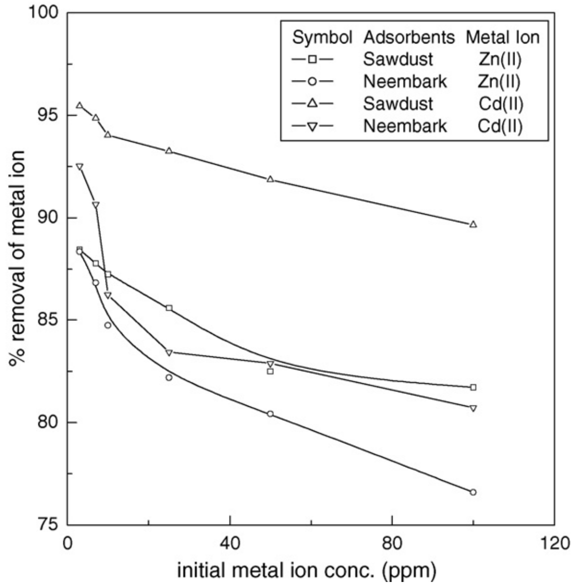

Fig. 4. Effect of initial metal ion concentration on adsorption of Zn(II)and Cd(II). Experimental conditions: for Zn(II): adsorbent dosage 10 g/L, contact time 5 h, pH 5. For Cd(II): adsorbent dosage 10 g/L, contact time 5 h, pH 6.

and neem bark. During the experimental investigations the initial Zn(II) concentration used was 25 mg/L and for Cd(II) it was 10 mg/L, contact time maintained at 4 h. It is evident that for all the adsorbents maximum removal efficiency was achieved at an adsorbent dosage level of 10 g/L for both Zn(II) and Cd(II) which may be considered as an optimum adsorbent dosage level. Therefore, the following experiments were carried out at adsorbent concentration of 10 g/L for adsorption of Zn(II) and Cd(II) from aqueous solutions. The adsorption was carried out at the optimum adsorbent dosage level and optimum pH using initial Zn(II) and Cd(II) concentration of 25 and 10 ppm respectively. The results of treated sample are depicted in Table 3. From the results we have seen that the final concentration in each case is well below the CPCB norms for discharge water [7]. The variation in sorption capacities between the various adsorbents could be related to the type and concentration of surface group responsible for adsorption of metal ions from solution [35,43]. With increasing adsorbent dosage more surface area is available for adsorption due to increase in active sites on the adsorbent. Saw dust and neem bark contain ligno-cellulose-based plant fibers with many nitrogenous, hydroxyl and carboxylic group that are responsible for binding metal ions from aqueous solution.

3.5. *Effect of contact time and adsorption rate kinetics*

The experimental runs measuring the effect of contact time on the batch adsorption of 25 mg/L Zn(II) at 30 ± 0.5 °C and at initial pH value 5 is shown in Fig. 6. For Cd(II), initial metal ion concentration of 10 mg/L was used for the experimental investigations on effect of contact time (Fig. 6). During the experiment contact time was varied from 0 to 5 h. It is obvious that increase in contact time from 0 to 2.0 h enhanced significantly the percent removal of metal ions. The initial rapid adsorption gives away a very slow approach to equilibrium. The nature of adsorbent and its available sorption

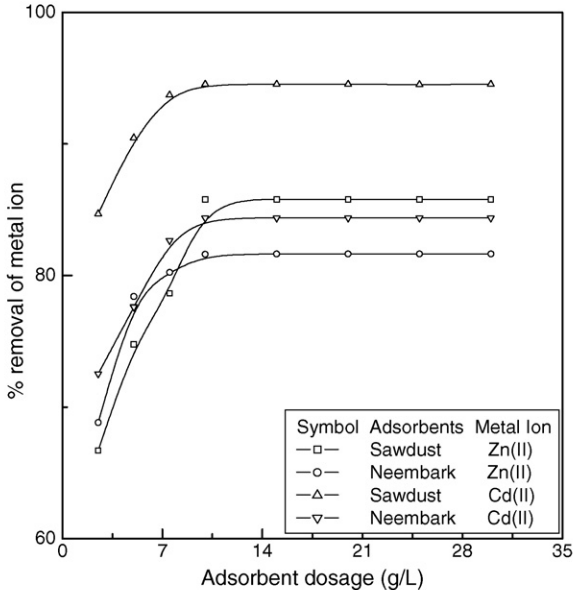

Fig. 5. Effect of adsorbent dosage level on adsorption of Zn(II) and Cd(II). Experimental conditions: for Zn(II): initial conc. 25 mg/L, contact time 5 h, pH 5. For Cd(II): initial conc. 10 mg/L, contact time 5 h, pH 6.

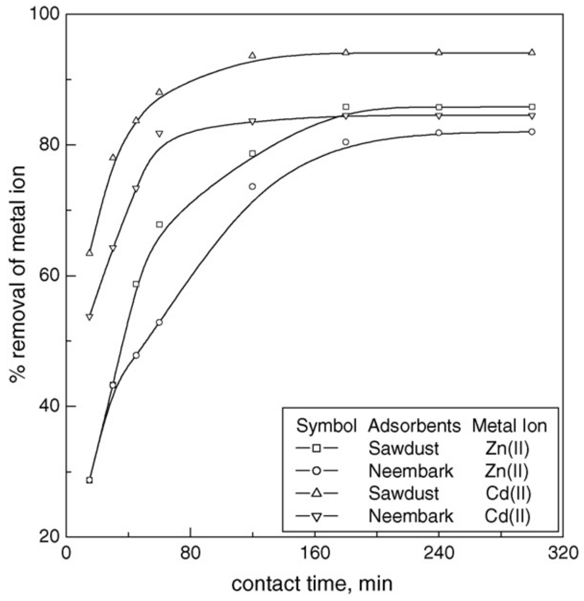

Fig. 6. Effect of contact time on adsorption of Zn(II) and Cd(II). Experimental conditions: for Zn(II): initial conc. 25 mg/L, adsorbent dosage 10 g/L, pH 5. For Cd(II): initial conc. 10 mg/L, adsorbent dosage 10 g/L, pH 6.

sites affected the time needed to reach the equilibrium. For saw dust equilibrium time was 3 h for both Zn(II) and Cd(II) adsorption. In case of neem bark, time needed to reach the equilibrium for adsorption of Zn(II) and Cd(II) from aqueous solutions were 3 and 4 h respectively. All the other experiments on the physical properties of adsorption are conducted after 4 h of contact time so that equilibrium is established.

3.6. *Adsorption kinetics study*

The study of adsorption kinetics describes the solute uptake rate and evidently these rate controls the residence time of adsorbate uptake at the solid–solution interface including the diffusion process. The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as on the mass transfer process [44].

The results obtained from the experiments were used to study the kinetics of metal ion adsorption. The rate kinetics of Zn(II) and Cd(II) adsorption on the saw dust as well as on the neem bark analyzed using pseudo-first-order [45], pseudo-second-order [46], and intra-particle diffusion [47] models. The conformity between experimental data and the model predicted values was expressed by correlation coefficients (r^2).

3.6.1. *Lagergren model*

The pseudo-first-order kinetic model was proposed by Lagergren [45]. The integral form of the model generally expressed as follows:

$$\log(q_e - q) = \log q_e - \frac{K_{ad}t}{2.303} \tag{6}$$

3.6.2. *Pseudo-second-order model*

The kinetics of adsorption process may also be described pseudo-second-order rate equation [46]. The lineralized form of equation is expressed as

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \tag{7}$$

3.6.3. *Intra-particle diffusion model*

The intra-particle diffusion model is based on the theory proposed by Weber and Moris [47]. According to this theory

$$q = K_{id}t^{0.5} \tag{8}$$

The intra-particle diffusion was involved in the adsorption process of metal ions by different adsorbents. When pore diffusion limits the adsorption process, the relationship between the initial solute concentration and the rate of adsorption will not be linear [48]. Besides for the adsorption on the outer surface of adsorbent, there is also possibility of transport of adsorbent ions from the solution to the pores of the adsorbent due to stirring on batch process. This possibility was tested in terms of intra-particle diffusion model. The linear portion of the plot (Fig. 9) for a wide range of contact time between the adsorbate and adsorbent does not pass through the origin. This deviation from the origin or near saturation may be perhaps due to difference in the rate of mass transfer in the initial and final stages of adsorption. Further such deviation from the origin indicated that the pore diffusion is not only the rate-limiting step. From Fig. 9 it may be seen that there are two distinct regions—the initial pore diffusion due to external mass transfer effects followed by the intra-particle diffusion. This indicates the mechanism of Zn(II) as well as Cd(II) adsorption by the selected adsorbents is complex and both, the surface adsorption as well as intra-particle diffusion contribute to the rate determining step [49].

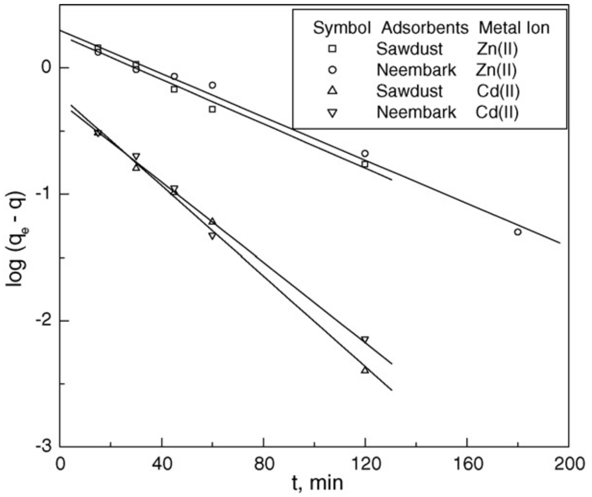

Fig. 7. Lagergren plot for adsorption of Zn(II) and Cd(II). Experimental conditions: for Zn(II): pH 5, adsorbent dosage 10 g/L, initial Zn(II) conc. 25 mg/L. For Cd(II): pH 6, adsorbent dosage 10 g/L, initial Cd(II) conc. 10 mg/L.

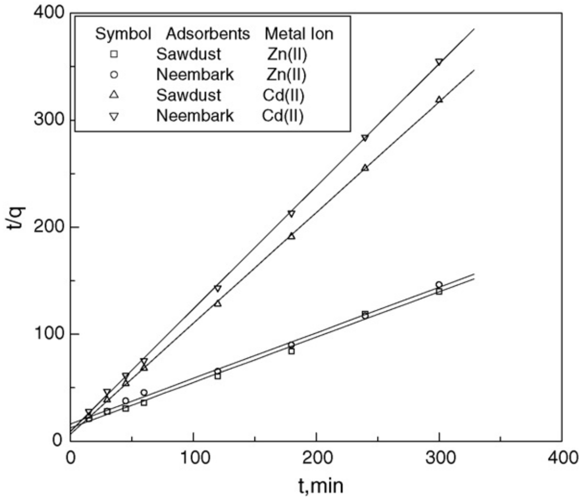

Fig. 8. Pseudo-second-order plot for adsorption of Zn(II) and Cd(II). Experimental conditions: for Zn(II); pH 5, adsorbent dosage 10 g/L, initial Zn(II) conc. 25 mg/L. For Cd(II): pH 6, adsorbent dosage 10 g/L, initial Cd(II) conc. 10 mg/L.

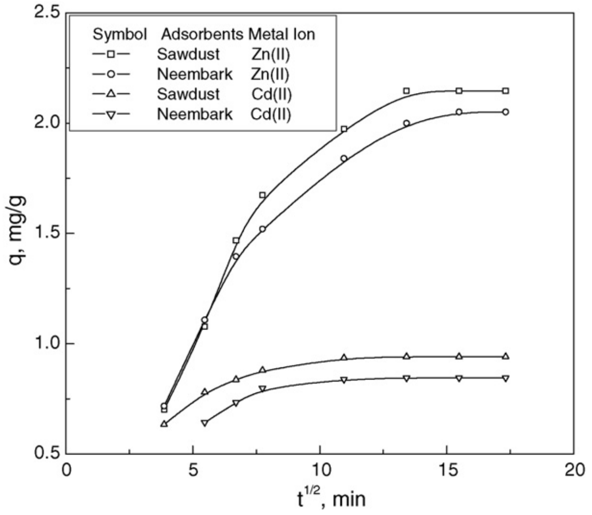

Fig. 9. Weber and Moris plot for adsorption of Zn(II) and Cd(II). Experimental conditions: for Zn(II): pH 5, adsorbent dosage 10 g/L, initial conc. 25 mg/L. For Cd(II): pH 6, adsorbent dosage 10 g/L, initial conc. 10 mg/L.

Table 4
Rate kinetics for adsorption of Zn(II) and Cd(II) by saw dust and neem bark

Adsorbents	Metal ion	Lagergren first order			Pseudo-second-order			Weber and Moris		
		K_{ad} (min^{-1})	r^2	χ^2	K_2 ((g/mg) min)	r^2	χ^2	K_{id} ((mg/g) min$^{1/2}$)	r^2	χ^2
Saw dust	Zn(II)	0.0203	0.985	7.956	0.0447	0.995	0.012	0.257	0.984	0.275
Saw dust	Cd(II)	0.0409	0.985	10.765	0.1499	0.999	0.007	0.0631	0.961	0.199
Neem bark	Zn(II)	0.0208	0.988	8.012	0.0584	0.997	0.018	0.243	0.994	0.452
Neem bark	Cd(II)	0.0363	0.991	8.976	0.1561	0.999	0.014	0.0677	0.991	0.335

The applicability of the above three models was examined by each linear plot of $\log(q_e - q)$ vs. t, (t/q) vs. t and q vs. $t^{0.5}$ respectively and are presented in Figs. 7–9 respectively. In order to quantify the applicability of each model, the correlation coefficients, r^2, was calculated from these plots. The linearity of these plots indicates the applicability of the three models. The values of rate constants and correlation coefficients for each model are shown in Table 4. The correlation coefficients, r^2, showed that the pseudo-second-order model, an indication of chemisorptions mechanism, fits better with the experimental data than the intra-particle diffusion and pseudo-first-order model. In addition, the Chi-square test was also carried out to support the best fit adsorption model. The equation for evaluating the best fit model is to be written as

$$\chi_t^2 = \sum \frac{(q_t - q_{tm})^2}{q_{tm}} \tag{9}$$

Thus based on the high co-relation coefficient and low χ_t^2 value (Table 4), it can be said that adsorption of Zn(II) and Cd(II) onto saw dust and neem bark follow pseudo-second-order model than that of intra-particle diffusion model and pseudo-first-order model.

3.6.4. Richenbeng model

The rate of sorption is determined by applying well-known equation for the diffusion and mass transfer phenomena. For the fast reaction, the sorption may be due to film diffusion [50] and occur within the microspores of the adsorbent. Reicherbeng equation is applied, i.e.,

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

Above equation may be written as,

$$\mathrm{Bt} = -0.4977 \ln(1 - F) \tag{11}$$

The plot of Bt vs. time depicted in Fig. 10 is linear with correlation factor as shown in Table 5, thereby indicating that sorption was controlled by film diffusion and also intraparticle diffusion.

3.6.5. Mass transfer analysis

Mass transfer analysis for the removal of Zn(II) and Cd(II) from aqueous solutions by the selected adsorbents were carried out using the following equation as proposed by McKay et al. [51]

$$\ln\left(\frac{C_t}{C_o} - \frac{1}{1+MK_{bq}}\right) = \ln\left(\frac{MK_{bq}}{1+MK_{bq}}\right) - \left(\frac{1+MK_{bq}}{MK_{bq}}\right)\beta S_s t \tag{12}$$

Table 5
Co-relation factor from Bt vs. shaking time plot for different systems

Metal ion	Adsorbents	Co-relation factors r^2
Zn(II)	Saw dust	0.9849
Zn(II)	Neem bark	0.9754
Cd(II)	Saw dust	0.9967
Cd(II)	Neem bark	0.9386

The plot of $\ln((C_t/C_o) - (1/1+MK_{bq}))$ vs. t resulted a straight line of slope $[(1+MK_{bq}/MK_{bq})\beta S_s]$ and the values of mass transfer coefficients (β) calculated from the slops of the plots were 4.64×10^{-5} and 8.98×10^{-5} cm^2 s^{-1} for Zn(II) and Cd(II) adsorption onto saw dust respectively. Similarly for neem bark–Zn(II) and neem bark–Cd(II) system the calculated values of mass transfer coefficient are 3.05×10^{-5} and 6.25×10^{-5} cm^2 s^{-1} respectively. The values of mass transfer coefficients (β) obtained from the study indicate that the velocity of the adsorbate transport from bulk to the solid phase was quite fast.

3.7. Adsorption isotherms

The adsorption isotherm for the Zn(II) removed were studied using initial concentration of Zn(II) between 10 and 100 mg/L at an adsorbent dosage level of 10 g/L at 30 + 2 °C. For Cd(II), initial concentration range of 10–300 mg/L were used for adsorption isotherm studies keeping the other conditions remain same. The adsorption equilibrium data are conveniently represented by adsorption isotherms, which correspond to the relationship between the mass of the solute adsorbed per unit mass of adsorbent q_e and the solute concentration for the solution at equilibrium C_e. The correlation coefficients, r^2 and the Chi-square (χ^2) test were also carried out to find the best fit adsorption isotherm model. The equation for evaluating the best fit model is to be written as

$$\chi^2 = \sum \frac{(q_{exp} - q_m)^2}{q_m} \tag{13}$$

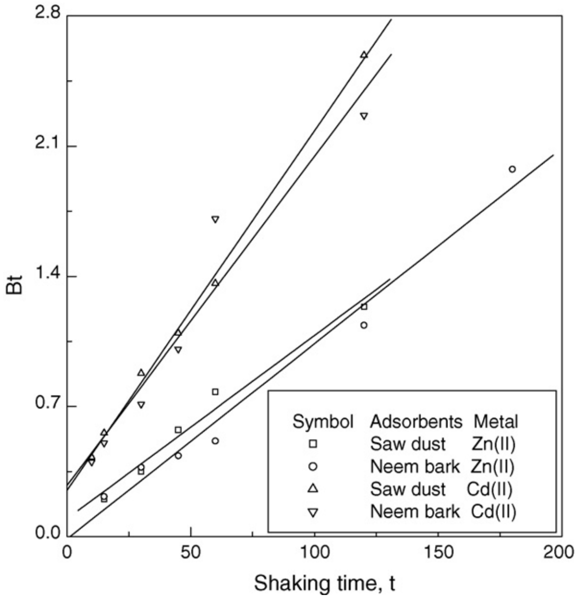

Fig. 10. Plot of Bt vs. shaking time in Reicherberg model for adsorption of Zn(II) and Cd(II). Experimental conditions: for Zn(II): pH 5, adsorbent dosage 10 g/L, initial conc. 25 mg/L. For Cd(II): pH 6, adsorbent dosage 10 g/L, initial conc. 10 mg/L.

Table 6
Langmuir and Freundlich adsorption isotherm constants for Zn(II) and Cd(II) on different adsorbents

Adsorbents	Metal ion	Langmuir				Freundlich			
		$q_{\max}$ (mg/g)	b (L/mg)	r^2	χ^2	K_f	n	r^2	χ^2
Saw dust	Zn(II)	14.10	0.05	0.992	0.123	0.78	1.33	0.973	0.106
Saw dust	Cd(II)	26.73	0.053	0.990	0.090	1.62	1.54	0.987	0.805
Neem bark	Zn(II)	13.29	0.047	0.982	0.233	0.68	1.32	0.991	0.163
Neem bark	Cd(II)	25.57	0.056	0.984	0.438	1.65	1.52	0.975	0.632

The data obtained were then fitted to the Langmuir adsorption isotherm [52] applied to equilibrium adsorption assuming monolayer adsorption onto a surface with a finite number of identical sites and is represented as follows,

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \tag{14}$$

Linear plots of C_e/q_e vs. C_e were employed to determine the value of $q_{\max}$ (mg/g) and b (L/mg). The data obtained with the correlation coefficients (r^2) and (χ^2) was listed in Table 6.

Weber and Chakraborti [53] expressed the essential characteristics and the feasibility of the Langmuir isotherm in terms of a dimensionless constant separation factor or equilibrium parameter R_L, which is defined as,

$$R_L = \frac{1}{1 + bC_o} \tag{15}$$

The R_L value indicates the shape of the isotherm as follows:

R_L value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

According to McKay et al. [54], R_L values between 0 and 1 indicate favorable adsorption. The R_L value for the adsorption of Zn(II) on saw dust and neem bark were 0.66 and 0.68 respectively at initial concentration of 10 mg/L whereas it were 0.16 and 0.18 respectively at initial concentration of 100 mg/L. Similarly the value of R_L calculated were 0.653 and 0.641 respectively for sawdust-Cd(II) and neem bark–Cd(II) adsorption at initial concentration of 10 mg/L whereas it were 0.158 and 0.151 respectively at initial concentration of 100 mg/L. The data obtained represent a favorable adsorption for all the adsorbents under study.

The adsorption data obtained were then fitted to the Freundlich adsorption isotherm [55], which is the earliest relationship known describing the adsorption equilibrium and is expressed by the following equation,

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{16}$$

The Freundlich isotherm constants K_f and n are constants incorporating all factors affecting the adsorption process such as of adsorption capacity and intensity of adsorption. The constants K_f and n were calculated from Eq. (12) and Freundlich plots (Fig. 11). The amount of absorbent required to reduce any initial concentration to predetermined final concentration can be calculated. The values for Freundlich constants and correlation coefficients (r^2) and (χ^2) for the different adsorbents used during the study are also resented in Table 6. The values of n between 1 and 10 (i.e., $1/n$ less than 1) represent a favorable adsorption [56]. The values of n, which reflects the intensity of adsorption. The n values obtained for all the four adsorbents considered for study represent a beneficial adsorption. From the value of co-relation coefficients (r^2) and Chi-square (χ^2) test we can conclude that adsorption of Zn(II) and Cd(II) adsorption onto saw dust and neem bark follow Freundlich and Langmuir adsorption respectively.

3.7.1. Dubinin–Radushkevich (D–R) isotherm

The D–R isotherm [57] was employed in the following linear form:

$$\ln C_{\mathrm{abs}} = \ln X_m - \lambda \varepsilon^2 \tag{17}$$

The Polanyi potential, ε, can be expressed as,

$$\varepsilon = RT \ \ln\left(1 - \frac{1}{C_e}\right) \tag{18}$$

A plot of C_{abs} vs. ε^2 in Fig. 12 gave a straight line from which values of λ and X_m of different system were evaluated. Using the calculated value of λ, it was possible to evaluate the mean sorption energy, E, from

$$E = \frac{1}{\sqrt{-2\lambda}} \tag{19}$$

The estimated value of E was which is the range expected for physisorption is shown in Table 7.

Although the Freundlich isotherm provides the information about the surface heterogeneity and the exponential distribution of the active sites and their energies, it does not predict any saturation of the surface of the adsorbent by the adsorbate. Hence, infinite surface coverage could be predicted mathematically. In contrast, D–R isotherm relates the heterogeneity of energies close to the adsorbent surface. If a very small sub-region of the sorption surface is chosen and assumed to be approximately by the Langmuir isotherm, the quantity $\sqrt{\lambda}$ can be related to the mean sorption energy, E, which is the free energy for the transfer of 1 mole of metal ions from the infinity to the surface of the adsorbent.

The difference in the free energy between the adsorbed phase and the saturated liquid adsorbate is referred to as the poten-

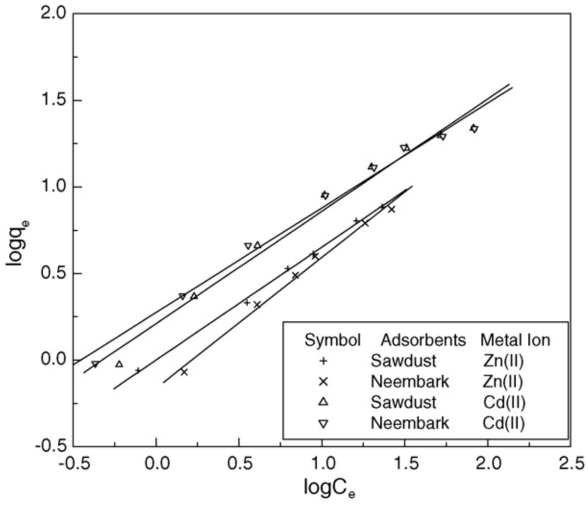

Fig. 11. Freundlich plot for adsorption of Zn(II) and Cd(II). Experimental conditions: for Zn(II): pH 5, adsorbent dosage 10 g/L, contact time 4 h. For Cd(II): pH 6, adsorbent dosage 10 g/L, contact time 4 h.

Table 7
Dubinin–Radushkevich (D–R) isotherm parameter and activation energy of different systems

Metal ion	Adsorbents	Dubinin–Radushkevich constant λ	Activation energy (kJ mol^{-1})	Correlation coefficient r^2
Zn(II)	Saw dust	−0.01209	6.431	0.98875
Zn(II)	Neem bark	−0.01158	6.571	0.9903
Cd(II)	Saw dust	−0.00533	9.415	0.9989
Cd(II)	Neem bark	−0.00488	9.911	0.9907

tial, a term first advanced by Polanyi [58] and later developed by Dubinin and his co-workers [59]. Thus the sorption space in the vicinity of the solid surface may be characterized by a series of equipotential surfaces with a given sorption potential. The sorption potential is independent of temperature but varies according to the nature of the adsorbent and adsorbate. As the calculated values of E are lesser than 8 kJ mol^{-1} in the adsorption of Zn(II) onto saw dust and neem bark, it follows that any bond formation between Zn(II) and the adsorbate may be physical in nature. The mean sorption energy was calculated as 9.415 and 9.911 kJ mol^{-1} for the adsorption of Cd(II) onto saw dust and neem bark respectively, which suggest that adsorption process onto the both adsorbents may be carried out by chemical ion-exchange mechanism [60].

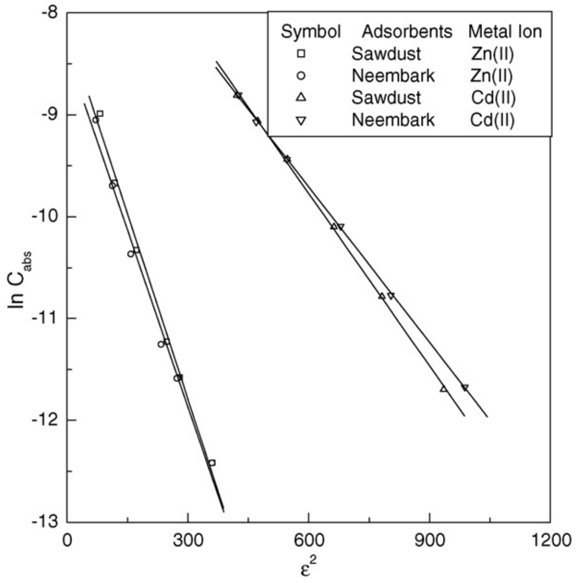

Fig. 12. Dubinin–Radushkevich isotherm plot for adsorption of Zn(II) and Cd(II). For Zn(II): pH 5, adsorbent dosage 10 g/L, contact time 4 h. For Cd(II): pH 6, adsorbent dosage 10 g/L, contact time 4 h.

3.8. *Thermodynamic parameters for adsorption*

The thermodynamic equilibrium constant (K_c^0) for each system was obtained by calculating the apparent equilibrium constant K_c^l at different initial concentration of metal ions, and by plotting C_a/C_e vs C_e and extra plotted to zero value of C_e.

$$K_c^l = \frac{C_a}{C_e} \tag{20}$$

The Gibbs free energy (ΔG^0) for the adsorption process was obtained at 30 ± 2 °C using the formula

$$\Delta G^o = -RT \ \ln \ K_c^o \tag{21}$$

The process of metal ion adsorption can be summarized by the following reversible process, which represents a heterogeneous equilibrium

$$\text{Metal ion in solution} \leftrightarrow \text{Metal ion in adsorbent} \tag{22}$$

The thermodynamic equilibrium constant (K_c^o) obtained from calculating the apparent equilibrium constant (K_c^l) at different initial metal ion concentrations of Zn(II) and Cd(II) and extrapolating to zero. The Gibbs free energy for the adsorption process was obtained at 30 ± 2 °C using Eq. (10). The thermodynamic equilibrium constant (K_c^o) for Zn(II) and Cd(II) adsorption onto saw dust were 7.24 and 19.73 whereas the values of Gibbs free energy estimated were −4.98 and −7.49 kJ mol^{-1} respectively. Similarly value of equilibrium constants for neem bark–Zn(II) and neem bark–Cd(II) system were 6.16 and 11.23 whereas the values of Gibbs free energy estimated were −4.76 and −6.09 kJ mol^{-1} respectively.

3.9. *Fourier transforms infrared spectroscopy (FT-IR) analysis*

In comparing between fresh adsorbents and metal loaded adsorbent, it was observed that there was a shift (more than 10 cm^{-1}) in wave number of dominant peaks associated with the loaded metal [61,62]. This shift in the wavelength [Figs. 13a, b and 14a, b] showed that there was a metal binding process taking place at the surface of bio adsorbent. The carboxylic groups contained following minor groups: O–H stretching and C–O stretching. C–O

Table 8
Wave number (cm^{-1}) for dominant peak from FT-IR

	Raw saw dust	Saw dust loaded with Zn(II)	Saw dust loaded with Cd(II)	Raw neem bark	Neem bark loaded with Zn(II)	Neem bark loaded with Cd(II)
Primary–OH	1033.66	1029.8	1031.73	1026.91	1027.87	1028.84
Carboxylic acid						
O–H stretching	2917.7	2920.66	2914.88	X	X	X
C–O stretching	1235.8	1224.5	1220.36	1026.91	1027.87	1028.84
Amine						
N–H stretching	3335.1	3324.5	3346.85	3297.75	3304.43	3259.11
C–N stretching	1321.9	1324.86	1323.09	X	X	X
Amide						
C–O stretching	1594.04	1593.88	1594.04	1606.4	1609.31	1610.27
Sulphonate						
S–O stretching	693.28	667.25	650.86	756.92	663.46	679.79

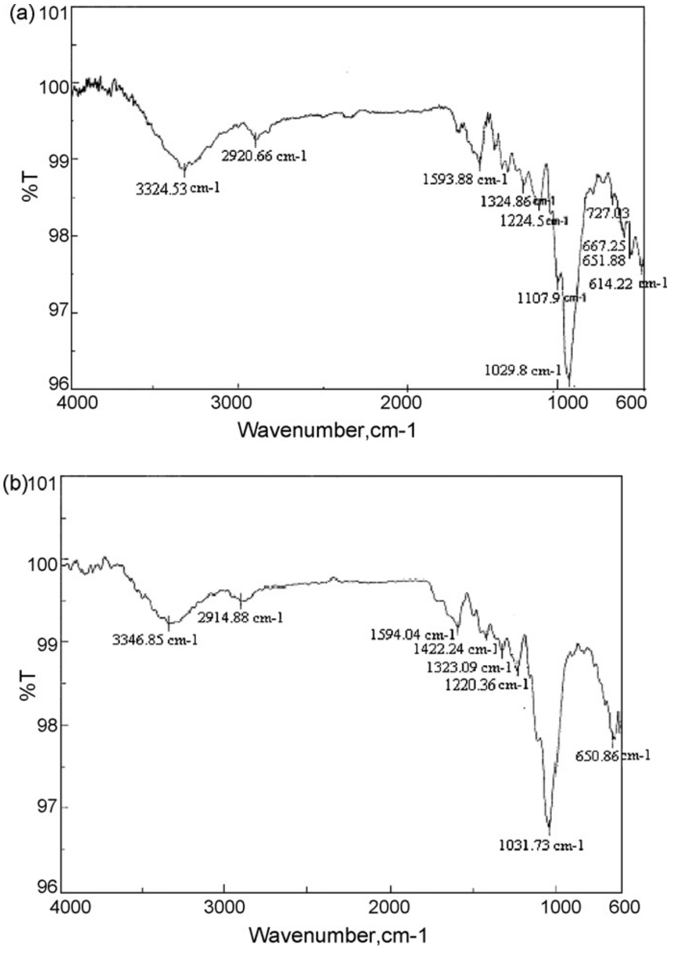

Fig. 13. (a) FT-IR spectra for Zn(II)–saw dust system. (b) FT-IR spectra for Cd(II)–saw dust system.

stretching was observed to shift clearly at a wave number of 1224.4 and 1220.36 cm^{-1} for saw dust–Zn(II) and saw dust–Cd(II) system from wave number of 1235.18 cm^{-1} for raw saw dust. Similarly the peak was observed to shift to 1249 and 1248.29 cm^{-1} for neem bark–Zn(II) and neem bark–Cd(II) system respectively from wave number of 1260 cm^{-1} for raw neem bark while the other groups did not seen to have shift the peak significantly. These major shift in band indicated there was a high potential that C–O stretching groups from the carboxylic acid involved with metal binding.

For amine group, there was a major shift in the wave number (from 3335.1 cm^{-1} for raw saw dust to 3324.5 and 3346.85 cm^{-1} for saw dust–Zn(II) and saw dust–Cd(II) loaded system respectively) for N–H stretching while the other groups like C–N stretching did not seem to have shifts the wave number of the peak significantly. In the process of adsorption there was also major change in the wave number (from 3295 cm^{-1} of raw neem bark to 3304 and 3259.11 cm^{-1} for neem bark–Zn(II) and neem bark–Cd(II) loaded system respectively) for N–H stretching while the other groups like C–N stretching did not seem to have shifts (minor shift) the wave number of the peak significantly. This should be interpreted that N–H stretching in the amine group was associated with metal adsorption.

The S–O stretching in the sulphonate group was found to have major shift a peak at 667.25 and 650.86 cm^{-1} for saw dust–Zn(II) and saw dust–Cd(II) loaded system respectively from 693.28 cm^{-1} for raw saw dust. Major shift in peak was also found for neem bark–Zn(II) (663.46 cm^{-1}) and neem bark–Cd(II) (679.79 cm^{-1}) loaded system from raw dust (756.92 cm^{-1}). These results indicated that sulphonate group has a strongly acidic characteristic which enabled the adsorbents for the adsorption of metal ion.

In briefs, possible functional groups that may be involved for metal binding by the said adsorbents are shown in Table 8. It should also be noted that FT-IR results did not provide any quantitative analysis, or the level of affinity to metal of the functional groups presented in the adsorbents [63]. They only presented the possibility of the coupling between the metal species and the functional group of the adsorbents.

Table 9
Comparison of adsorption capacities of the adsorbents for the removal of Zn(II) and Cd(II) with those other adsorbents

Serial no.	Adsorbents	Adsorption capacities (mg/g)		Reference
		Zn(II)	Cd(II)	
1	Olive stone carbon	–	5.91	[16]
2	Sunflower stalks	30.73	42.18	[17]
3	Spent grain	–	17.3	[18]
4	Carboxy methyl cellulose	–	28.7	[19]
5	Almond-shell carbon	–	2.7	[20]
6	Sugarcane bagasse	–	10.7	[21]
7	Oak saw dust	6.93	–	[22]
8	Black Locust	5.02	–	[22]
9	Cassava waste	–	14.3	[23]
10	Baggage fly ash	13.21	–	[24]
11	Wheat bran	–	21	[25]
12	*Aspergillus niger*	–	26.72	[26]
13	Bone char	31.79	61.72	[27]
14	Olive pomace		7.01	[28]
15	Carrot residues	29.61	–	[29]
16	Red seaweed, *Gracilaria salicornia*	–	17.98	[30]
17	Tree fern	–	16.3	[31]
18	Maize bran	–	7.43	[34]
19	Sugar beat pulp	17.78	–	[32]
20	Grape stalk waste	–	27.9	[33]
21	Saw dust	14.10	26.73	Present work
22	Neem bark	13.29	25.57	Present work

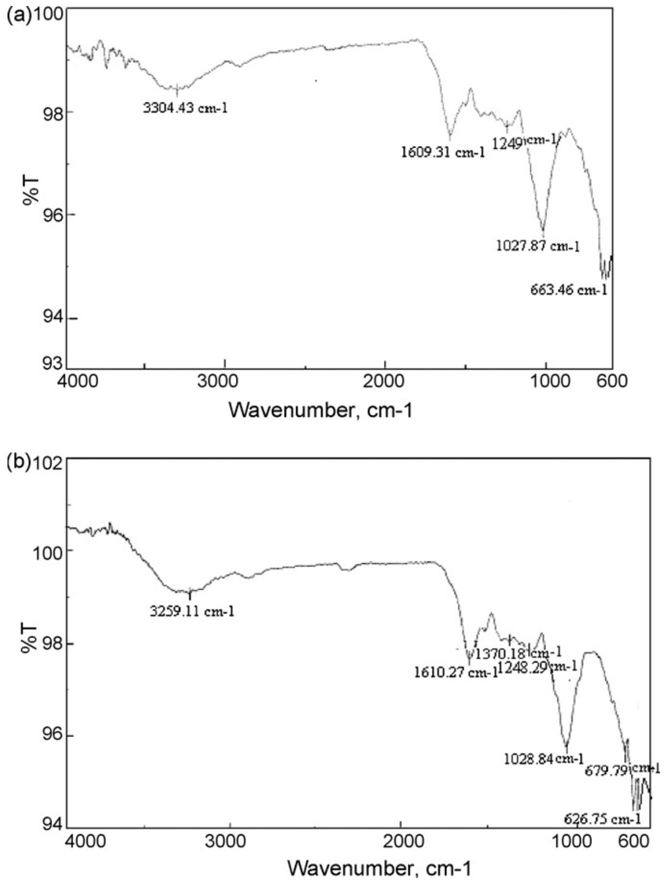

Fig. 14. (a) FT-IR spectra for Zn(II)–neem bark system. (b) FT-IR spectra for Cd(II)–neem bark system.

3.10. Comparison of adsorption capacity (q_{max})in mg/g for Zn(II) and Cd(II) removal with different adsorbents reported in literature

The adsorption capacities of the adsorbents for the removal of Zn(II) and Cd(II) have been compared with those of other adsorbents reported in literature and the values of adsorption capacities have been presented in Table 9. The values reported in the form of monolayer adsorption capacity. The experimental data of the present investigations are comparable with the reported values.

4. Conclusions

In this study, batch adsorption experiments for the removal of Zn(II) and Cd(II) from aqueous solutions have been carried out using saw dust and neem bark as low-cost, readily available natural adsorbents. The adsorption characteristics have been examined at different pH values, initial metal ion concentrations, contact time and different adsorbent dosage levels. The obtained results can be summarized as follows,

1. The pH experiments showed that the governing factors affecting the adsorption characteristics of all adsorbents are competition of the H^+ ions with metal ions at low pH values, maximum adsorption at pH 5–6 and at higher pH precipitation of hydroxyl species onto the adsorbents is more predominant (pH 6–11).
2. Increase in mass of adsorbent leads to increase in metal ion adsorption due to increase in number of adsorption sites. Maximum uptake was obtained at adsorbent dose of 10 g/L for Zn(II) and Cd(II) for both the adsorbents, which may be considered as optimum adsorbent dosage level at the specified conditions.
3. Experimental data were better described by pseudo-second-order model as evident from correlation coefficient values (r^2) and chi-square.
4. The adsorption of Zn(II) on saw dust and neem bark follows Freundlich adsorption isotherm and for Cd(II) adsorption on saw dust and neem bark follows Langmuir isotherm model.
5. Thermodynamic parameters studies showed that the both Zn(II) and Cd(II) adsorption were spontaneous in nature. The Gibbs free energy (ΔG^0) values for Zn(II) are -4.98 and $-4.76\,\text{kJ mol}^{-1}$ for saw dust and neem bark respectively. The Gibbs free energy (ΔG^0) values for Cd(II) are -7.49 and $-6.09\,\text{kJ mol}^{-1}$ for saw dust and neem bark respectively.
6. Fourier Transform Infrared Spectrophotometer (FT-IR) studies indicated the functional groups, like, C–O, C=O and C–N are responsible for metal binding.
7. The adsorption capacities of the adsorbents for the removal of Zn(II) and Cd(II) have been compared with other adsorbents reported in the literature. The values reported in the form of monolayer adsorption capacity.
8. Sorption energy calculated from Dubinin–Raduskevich (D–R) isotherm indicated that adsorption of Zn(II) and Cd(II) on the selected adsorbents are physical in nature and chemical in nature respectively.
9. Saw dust and neem bark can be used as an effective natural biosorbent for the economic treatment of wastewater containing Zn(II) and Cd(II).

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