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Adsorption capability of sawdust of *Populus alba* for Pb(II), Zn(II) and Cd(II) ions from aqueous solution

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ABSTRACT

Sawdust of *Populus alba* (poplar tree) has been investigated as an adsorbent for the removal of Pb(II), Zn(II) and Cd(II) ions. Since poplar tree is widely grown in almost all parts of Kashmir, it can be a common, most easily available, sustainable and low cost adsorbent for the treatment of wastewaters in this part of the world, where growing industrialization is affecting water quality like elsewhere in the world. Therefore, it is worthwhile to investigate the potential of sawdust of poplar tree as an adsorbent for the removal of Pb(II), Zn(II) and Cd(II) ions from aqueous solution as a first step. Batch experiments were conducted to study the effect of some parameters such as adsorbent dose, contact time, initial concentration of metal ions, solution pH and temperature. Langmuir and Freundlich models were employed for the mechanistic analysis of experimental data obtained. Results reveal that in our system, adsorption follows the Langmuir isotherm. The maximum adsorption capacity of Pb(II), Zn(II) and Cd(II) was found to be 10.1255, 8.477 and 8.877 mg/g, respectively, at optimum conditions. The pseudo-first-order and pseudo-second-order models were employed for kinetic analysis of adsorption process. The adsorption process follows pseudo-second-order kinetics. The efficacy of the adsorbent in the treatment of effluent from cement factory has been investigated, and the results have been found encouraging.

Keywords: Adsorption isotherm; Thermodynamics; Adsorption kinetics

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1. Introduction

Heavy metals are being excessively released into the environment due to rapid industrialization and have created a global concern. The pollution of surface water with heavy metals is a serious environmental problem due to the toxicity of heavy metals to various forms of life [1]. Unlike organic wastes, heavy metals are non-biodegradable and they tend to accumulate in living tissues, causing various diseases and disorders [2].

Lead is one of the most common toxic heavy metals widely discharged into the environment as liquid waste by metallurgical industry, electroplating and metal finishing industries, paint manufacture, storage battery manufacture, petroleum refining and drainage from ore mines in many developing countries [3]. Traffic emissions also contribute to lead pollution in the environment. Lead enters the body through inhalation, skin contact or with diet resulting in

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Table 1
Comparison of different technologies for removing heavy metals from wastewater

Technology	Disadvantages	Advantages
Membrane filtration	Valid at room temperature	Low solid waste generation
	High initial capital cost	Low chemical consumption
	High maintenance and operation costs	Small space requirement
	Membrane fouling and limited flowrates	Metal selective method
Chemical precipitation	Large volume sludge formation	Process simplicity
	High sludge disposal and maintenance cost	Applicable to different metals
		Low capital cost
Electrodialysis	High operational cost due to membrane fouling and energy consumption	High separation selectivity
Electrochemical Treatment	High initial capital, maintenance and operation cost	Applicable for the treatment of very toxic wastes.
	Needs continuous supply of electricity	Valid at room temperature and atmospheric pressure.
		Run by electricity and easy to operate
Ion exchange	High cost	Metal selective
	Less number of metal ions removed	Limited pH tolerance
		High regeneration capacity
Coagulation–Flocculation	Much chemical consumption	Bacterial inactivation capability
	Large volume sludge	Good sludge settling and dewatering characteristics
Adsorption	Performance depends on type of adsorbent	Low cost, high efficiency, minimization of chemical or biological sludge and regeneration of biosorbents and possibility of metal recovery.
	Needs chemical modification to improve its sorption capacity	High capacity and fast kinetics Possibly selective depending on adsorbent

adverse effects on every system in the body [4]. Excessive exposure to lead may cause anaemia, mental retardation, coma, seizures and bizarre behaviour [5]. Cadmium is another toxic heavy metal discharged into the environment as industrial waste from metallurgical industries, metalliferous mining, fertilizers, manures, sewage sludge, land fill leachate and batteries [6]. Long-term effects of Cd(II) poisoning include kidney damage and changes to the constitution of the bones, liver and blood. Short-term effects include nausea, vomiting, diarrhoea and cramps [7]. Zinc is another toxic metal released into the environment as industrial waste from galvanized coating on iron and steel, automotive parts, batteries, fungicides, zinc oxides-based skin cream (such as diaper rash cream and sunscreen), etc. Excessive exposure to zinc may cause abdominal pain, vomiting, diarrhoea, leukopenia, hypochromic microcytic anaemia, red urine, liver failure and kidney failure. WHO has recommended maximum permissible limit of Cd(II), Pb(II) and Zn(II) in drinking water as 0.003, 0.01 and 5 mg/L, respectively [8].

Numerous technologies have been developed for heavy metal removal as shown in Table 1. Traditional treatment processes include chemical coagulation, ion exchange, electroplating and membrane filtration [9]. However, most of these methods are either economically prohibitive or too complicated for the treatment of metals [10]. The removal of heavy metal pollutants, present in very low concentration, from aqueous solution can be readily accomplished by adsorption.

The major advantages of adsorption over other conventional treatment methods include low cost, high efficiency, minimization of chemical or biological sludge and regeneration of biosorbents and possibility of metal recovery [11]. In recent years, considerable attention has been focused on the removal of heavy metals using biosorbents derived from low-cost materials. In general, an adsorbent can be considered as cheap or low cost if it is abundant in nature, requires little processing and is a by-product or waste material from industry [12]. Several biosorbents such as microalgae [13], fungi [14], fungal biomass [15–17], walnut hull [18], *Helianthus annuus* stem waste [19], banana skin, green tea waste, oak leaf, walnut shell, peanut shell and rice husk [20], *Ocimum americanum* L. seed pods [21], chemically modified coir pith [22], groundnut shell [23], activated carbon from tamarind wood activated with zinc chloride [24], olive stone [25], grape waste [26], hazelnut [27], walnut, almond shell

[28], pistachio hull waste [29], agriculture wastes, carbons [30], rice husk-based carbon [31], fruit shell of gulmohar [32], coconut husk [33], husk of bengal gram [34], eucalyptus bark [35], agricultural waste biomass [36], pine needles [37], sugar cane bagasse [38], leaf mould [39] and waste pomace of olive factory [40] have been used as adsorbents for the removal of metal ions from aqueous solution. The adsorption of heavy metals by these materials might be attributed to their proteins, carbohydrates and phenolic compounds which have carboxyl, hydroxyl, sulphate, phosphate and amino groups that can bind metal ions.

The objective of this study was to investigate the adsorption potential of *Populus alba* for the removal of heavy metal ions from aqueous solution. *P. alba* used as timber belongs to the family *Salicaceae*. *P. alba* is widely distributed in Kashmir valley, and therefore, sawdust of *P. alba* can be most easily available, sustainable, low-cost adsorbent for the treatment of industrial wastewater in Kashmir valley. Therefore, it is worthwhile to investigate the potential of sawdust of poplar tree as an adsorbent for the removal of some toxic metal ions from aqueous solution as a first step. If sawdust could be used as adsorbent, both the environment protection and wooden industry could benefit. The effects of various factors such as adsorbent dose, contact time, pH, initial concentration and temperature were studied. Adsorption isotherm and kinetic studies were also investigated in order to understand the adsorption mechanism and efficiency of poplar sawdust. The effect of modification of adsorbent with HCl and NaOH on the adsorption capacity was also studied. The efficacy of the adsorbent in the treatment of effluent from cement factory has been investigated, and encouraging results were obtained.

2. Materials and methods

2.1. Adsorbent

The sawdust of poplar tree used as an adsorbent was collected from a local sawmill and was washed with double-distilled water several times to ensure that all fine particles were removed. The cleaned material was dried in an oven at 100°C for 24 h. The dried material was then crushed and sieved to 100–300 μm particle size and used as such.

2.2. Chemicals

All the compounds used to prepare reagent solutions were analytical grade reagents from E. Merck India Limited and were used as received. The stock solutions of Pb(II), Zn(II) and Cd(II) (1,000 mg L^{-1}) were prepared by dissolving weighed quantity of their respective nitrate salts in double-distilled water. The stock solutions were further diluted with double-distilled water to required concentrations.

3. Experimental

3.1. Modification of adsorbent

The adsorbent was treated separately with 0.1 N HCl and 0.1 N NaOH. One gram of sawdust was taken in 250-ml conical flasks containing 100 ml of modificant solution and was shaken at 120 rpm for 12 h at room temperature. The mixture was left overnight and was then filtered to remove the sorbent, which was washed several times with distilled water and dried in an oven, for further use as adsorbent in this study.

3.2. Adsorption experiments

The sorption of heavy metal ions on poplar sawdust was studied by the batch technique. One gram of sawdust was treated with 100 ml aliquot of the metal ion solution of desired concentration and shaken on a flask shaker for required time interval. After equilibration for the required time interval, the solution was filtered and the filtrate analysed for the metal ion concentration. The concentration of the adsorbed metal ion was calculated by subtracting the concentration of the metal ion in the filtrate from the initial metal ion concentration. Metal ion concentration was determined on atomic absorption spectrometer (Perkin Elmer Model Analyst-800). In order to obtain the adsorption capacity, the amount of ions adsorbed per mass unit of sawdust (mg/g) was evaluated using the following expression:

$$q_e = (C_0 - C_e)\frac{V}{m} \tag{1}$$

where q_e is the amount adsorbed at equilibrium (mg/g), C_0 is the initial metal ions concentration (mg/L), C_e is the equilibrium metal ions concentration (mg/L), V is the volume of the aqueous phase (L) and m is the amount of the sawdust used (g).

3.3. Statistical analysis

Least significant difference (LSD) was computed at P005 using SPSS 16 software.

3.4. Biosorbent characterization

FTIR analysis was carried out by recording IR spectra of sawdust (on FTIR interferometer IR Prestige-21, model 8400S) before and after metal adsorption by KBr pellet technique in the range of 400–4,000 cm (Fig. 1). The peaks obtained in the IR spectrum of the neat sawdust were assigned to functional groups, and the effect of adsorption of metal ions on these peaks has been deciphered.

The surface morphology of poplar sawdust was obtained using scanning electron microscope, Model Hitachi S3000H. SEM analysis was carried out by recording SEM images of sawdust before and after metal adsorption (Fig. 2).

3.5. Effect of adsorbent dose

A series of 250-ml conical flasks each containing 100 ml aliquots of metal ion solution (100 mg/L) were treated with varying amount of adsorbent (0.4–1.4 g) at room temperature. The flasks were shaken in temperature controlled flask shaker at 120 rpm, and after equilibrium, the solutions were filtered. The amount of metal ions in the filtrate was then determined by AAS.

3.6. Effect of contact time

The effect of contact time on the amount of metal ion adsorbed was analysed by taking 100 ml aliquots of metal ion solution (100 mg/L) in a number of stoppered conical flasks and shaking with 1 g of sawdust for different time intervals, e.g. 10, 20, 30, 40, 50, 60, 70 and 80 min at pH of 6 for Zn(II) and Pb(II) and pH 4 for Cd(II). After the given time interval, the mixture was filtered and the filtrate analysed for final metal ion concentration on AAS.

3.7. Effect of pH

The effect of pH on the amount of metal ion adsorbed was analysed over the pH range 1–7. The experiments were not conducted above pH 7 to avoid possible hydroxide precipitation. This is in agreement with the suggestions of many researchers [41–44]. In this study, 100 ml aliquots of metal ion solution of different pH values were shaken with 1 g of sawdust for 80 min. The pH of the solutions was adjusted to the required value by the addition of 0.1 N HNO_3 and 0.1 N NaOH solutions. After equilibration, the supernatant solutions were filtered and analysed for metal ion concentration.

3.8. Effect of metal ion concentration (adsorption equilibrium)

The effect of metal ion concentration on the adsorption was studied by shaking 1 g of sawdust with 100 ml aliquots of metal ion solutions of different initial concentrations (20–200 mg/L) for 80 min at pH 6 for Zn(II) and Pb(II) and pH 4 for Cd(II). After equilibration for 80 min, the supernatant solutions were filtered and the filtrates analysed for the final metal ion concentration.

3.9. Effect of temperature

The effect of temperature on the adsorption was studied at three different temperatures of 20, 30 and 40˚C by shaking 1 g of sawdust with 100 ml aliquots of metal ion solution of a particular concentration (100 mg/L) at pH 6 for Zn(II) and Pb(II) and pH 4 for Cd(II). The mixture was shaken and heated to the appropriate temperature using temperature controlled flask shaker. At a particular temperature, the supernatant solutions were filtered and filtrates analysed for the final metal ion concentration.

4. Results and discussion

4.1. Biosorbent characterization

4.1.1. FTIR and SEM analysis

In the spectra of the neat sawdust, the sharp peaks at 2,929.18 and 2,854.74 cm^{-1} were assigned to the C–H stretching vibrations and symmetric stretching vibrations of CH_2, respectively. The band at 2,854.74 cm^{-1} disappeared in the loaded sawdust while new peaks were observed at 2,362 cm^{-1} in Pb (II)- and Zn (II)-loaded sawdust which corresponds to P–H group. The peak around 1,739 cm^{-1} shows the carbonyl (C=O) stretching vibration of the carboxyl groups. The peaks between 1,750 and 1,850 cm^{-1} show anhydride C=O stretching vibrations. The peaks at 1,826 cm^{-1} shifted to 1,836, 1,834 and 1,828 cm^{-1} after loaded with Cd(II), Pb(II) and Zn(II), respectively, suggesting that the interaction occurs between the C=O and the metal ions. Similarly, the peak at 1,793 cm^{-1} shifted to 1,791 cm^{-1} in case of Cd(II), disappeared in case of Pb(II)-loaded sawdust but the peak at 1,739 cm^{-1} disappeared in Zn(II). The bands at 1,651 and 1,678 cm^{-1} may be attributed to C=C skeletal vibrations, and the peak at 1,651 cm^{-1} shifted to 1,653, 1,647 and 1,645 cm^{-1} after adsorption Cd(II), Pb(II) and Zn(II), respectively. While the peak at 1,678 cm^{-1} shifted to 1,691 cm^{-1} after Zn(II) adsorption. New peaks were observed at 1,560 cm^{-1} in Cd(II)-loaded

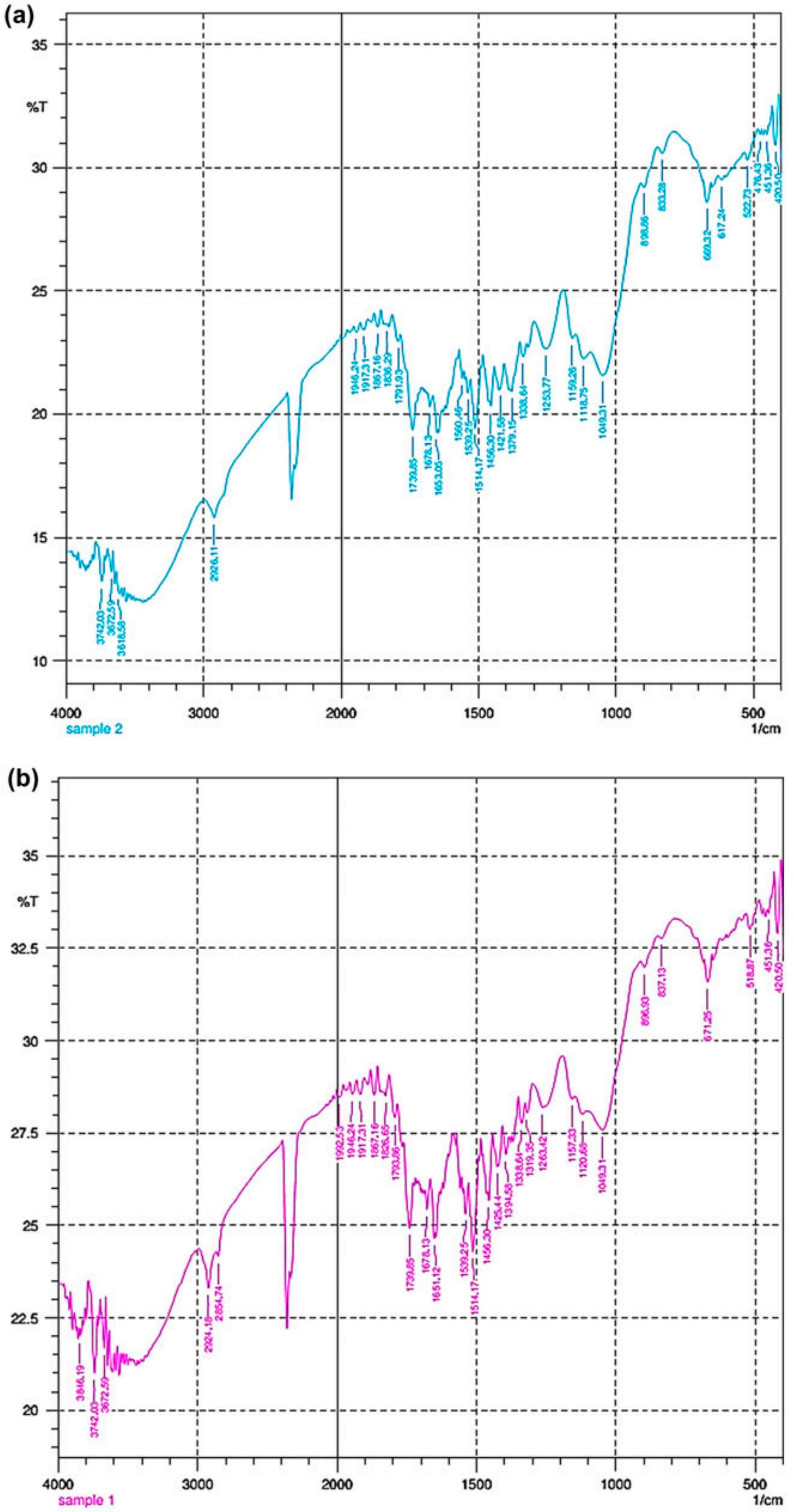


Fig. 1. FTIR Spectrum of (a) pure sawdust, (b) Cd(II)-loaded sawdust, (c) Pb(II)-loaded sawdust and (d) Zn(II)-loaded sawdust.

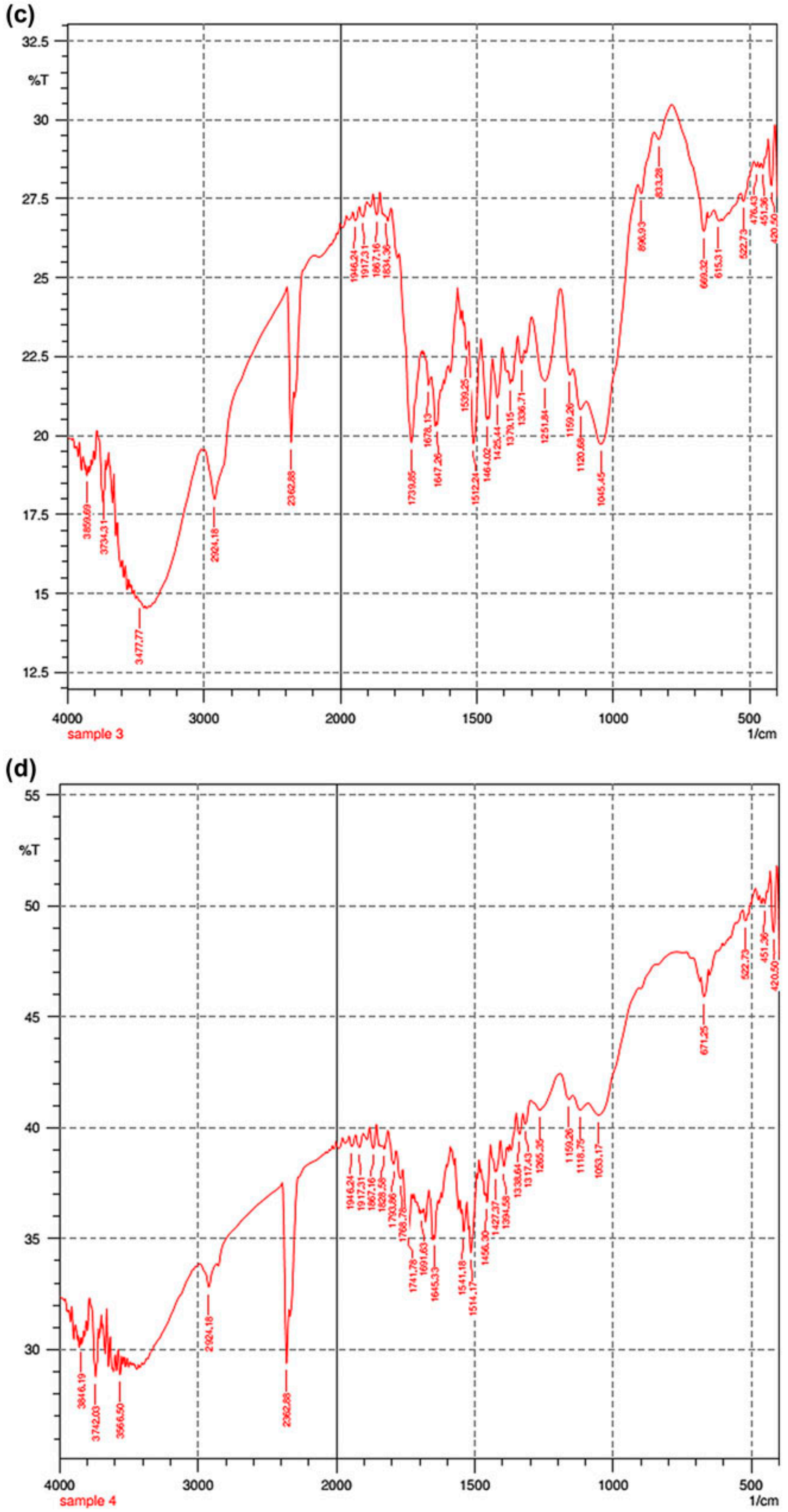
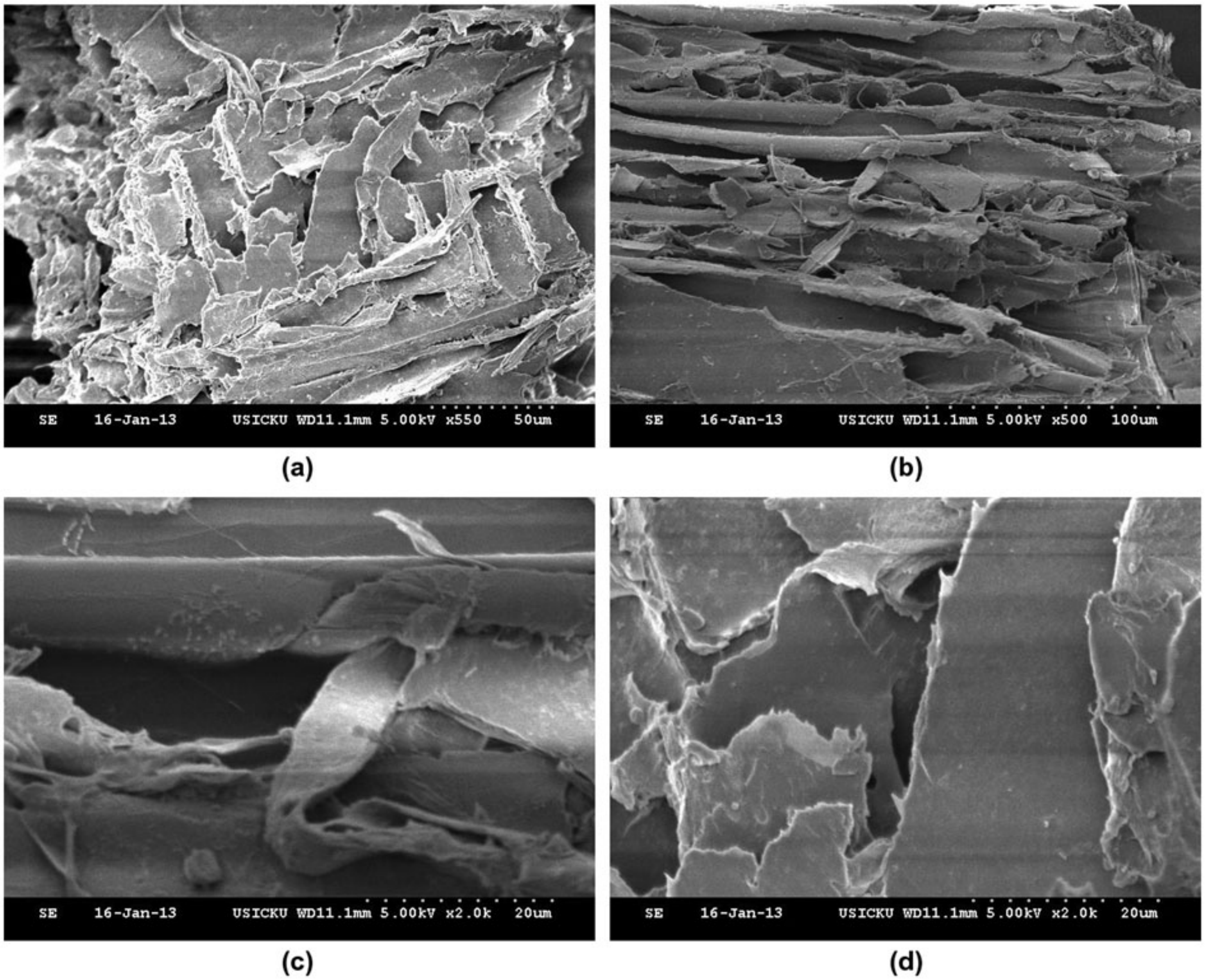


Fig. 1. (*Continued*).



(a) (b)

(c) (d)

Fig. 2. SEM images of (a) poplar sawdust, (b) Zn(II)-loaded sawdust, (c) Pb(II)-loaded sawdust and (d) Cd(II)-loaded sawdust.

sawdust and at 1,768, 1,741 cm^{-1} after Zn(II)-loaded sawdust. The peaks ranging from 1,400 to 1,600 cm^{-1} correspond to aromatic C=C skeletal vibrations. The bands at 1,456 and 1,049 cm^{-1} were assigned to a vibration of C–O–C and –OCH$_3$ (basis of lignin structure) and were shifted after adsorption. The peaks from 1,000 to 1,300 cm^{-1} correspond to the C–O stretching vibration in carboxylic acids and alcohols. The bands below 1,200 cm^{-1} represents fingerprint region for the adsorbents. The peak at 1,263 cm^{-1} indicates the presence of the C–N from amine, and this peak shifted to 1,253, 1,251 and 1,265 cm^{-1} after loaded with Cd(II), Pb(II) and Zn(II), respectively. The band at 1,157 cm^{-1} is attributed to the C–O stretching in ester and carboxylic groups, and this band gets shifted to 1,159 cm^{-1} in the loaded sawdust. Similarly, the bands at 1,120, 1,049, 896, 837, 671 and 518 cm^{-1} in the pure sawdust are shifted after loading with metal ions. New peaks appear in the Cd(II)-loaded sawdust at 617 and 476 cm^{-1} and at 615 and 476 cm^{-1} bands appear in case of Pb(II)-loaded sawdust.

SEM analysis was carried out by recording SEM images of sawdust before and after metal adsorption. The surface of sawdust before and after adsorption of metal ions exhibited irregularities with cavities of various sizes. Upon adsorption, the surface morphology seems to undergo changes due to interaction of the metal ions with donor functional groups on the sawdust.

4.2. *Effect of modification of adsorbent*

The effect of modification of adsorbent on the adsorption capacity is shown in Table 2. Maximum adsorption of metal ions was achieved by base treatment. The increase in adsorption capacities upon

Table 2
Effect of treatment of sawdust of poplar by HCl and NaOH

Metal ion	Modification	q (mg/g)
Pb	Unmodified	10.125
	NaOH treated	17.036
	HCl treated	11.932
Cd	Unmodified	8.87
	NaOH treated	12.479
	HCl treated	9.176
Zn	Unmodified	8.477
	NaOH treated	16.707
	HCl treated	8.94

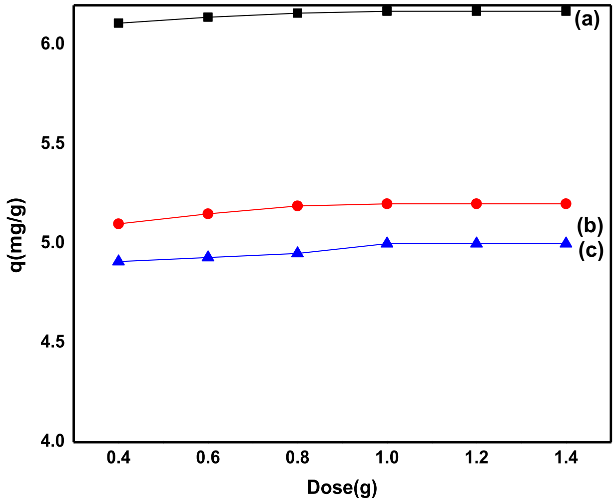


Fig. 3. Effect of adsorbent dose on the adsorption of (a) Pb (II), (b) Zn(II) and (c) Cd(II) on sawdust of poplar.

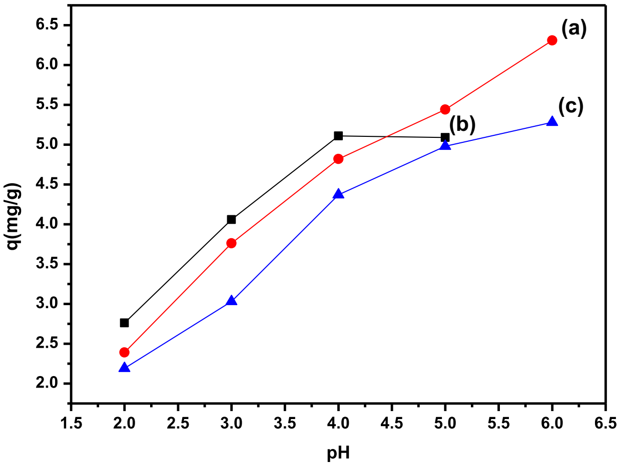


Fig. 4. Effect of pH on the adsorption of (a) Pb(II), (b) Cd(II) and (c) Zn(II) on sawdust of poplar.

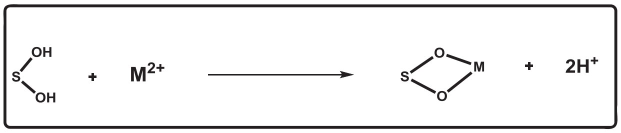


Fig. 5. Schematic representation of M^{2+} ion coordinating with adjacent hydroxyl groups on the surface of the adsorbent.

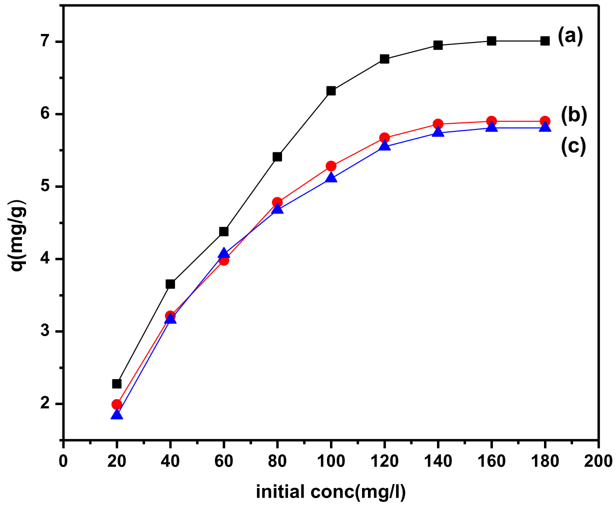


Fig. 6. Effect of initial concentration on the adsorption of (a) Pb(II), (b) Zn(II) and (c) Cd(II) on sawdust of poplar.

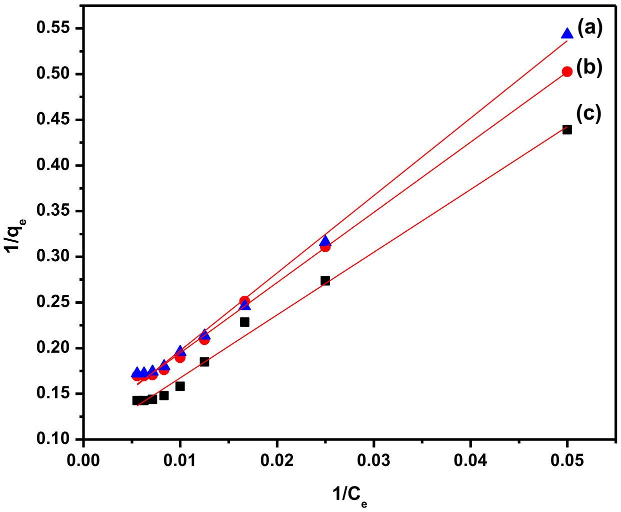


Fig. 7. Langmuir adsorption isotherm for the adsorption of (a) Cd(II), (b) Zn(II) and (c) Pb(II) on sawdust of poplar.

modification with 0.1 N NaOH can be attributed to the higher number of binding sites and better ion exchange ability that favour metal uptake. NaOH is a well-known fibre swelling agent and acts primarily on the hemicelluloses fraction and brings about the swelling of the cell wall [45]. Also pretreatment with NaOH leads to the transformation of methyl esters as inhibiting groups to carboxylate ligands, thus substantially increasing adsorption capability [46]. Hence, the alkali-modified sawdust was used as an adsorbent in subsequent experiments throughout this study.

4.3. Effect of adsorbent dose

The effect of adsorbent dose on the removal of metal ions is shown in Fig. 3. It may be observed that the adsorption of metal ions increases with increasing adsorbents dose from 0.4 to 1 g. The greater adsorption at high adsorbent dosage is due to availability of more active sites of the adsorbents for the adsorption [47]. As the adsorbent dose is increased beyond 1 g, the adsorption does not increase further, as the surface metal ion concentration and the solution metal ion concentration come to equilibrium with each other.

4.4. Effect of pH

The pH of an aqueous solution is an important controlling parameter affecting the adsorption of metal ions on sawdust because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate. For Zn(II) and Pb(II), maximum adsorption was attained at pH 6, while for Cd(II), maximum adsorption was attained at pH 4 (Fig. 4).

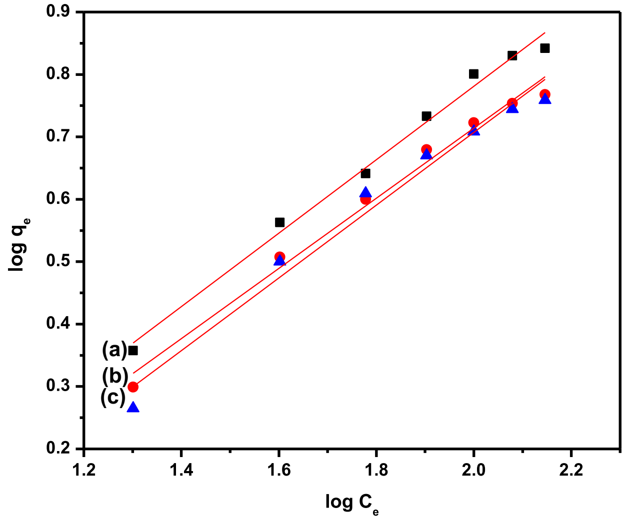


Fig. 8. Freundlich adsorption isotherm for the adsorption of (a) Pb(II), (b) Zn(II) and (c) Cd(II) on sawdust of poplar.

It is widely accepted that the adsorption of the metal ions on the sawdust is because of the functional groups of lignin, tannin, carbohydrates and proteins present in it. At low pH, the polar functional groups such as aldehyde, ketone, amine, alcohol, phenol and carboxyl functional groups are protonated and hence rendered unavailable for ion exchange and complexation with the metal ions. Therefore, at low pH, uptake of metal ions is low. At higher pH, these polar groups are deprotonated and hence are available for complexation with the metal ions. Therefore, at higher pH, more and more polar groups are free and uptake of the metal ions increases. The results conform to the ion exchange and complexation mechanism of the adsorption of the metal ions on the sawdust. At more basic pH, the metal ions start precipitating, which defeats the very purpose of employing adsorption and precludes further investigation.

The presence of ionizable hydroxyl groups (of lignin, tannins and other phenolic compounds) able to interact with metal ions was confirmed by FTIR analysis. A possible mechanism of ion exchange could be considered as a divalent heavy metal ion (M^{2+}) attaching itself to two adjacent hydroxyl groups which could donate two pairs of electrons to metal ion, releasing two hydrogen ions into solution [48] (Fig. 5).

4.5. Effect of metal ion concentration (adsorption equilibrium)

The effect of initial metal concentration (20–200 mg/L) of Pb(II), Zn(II) and Cd(II) on their adsorption on sawdust of poplar from aqueous solution was investigated. The results, presented in Fig. 6, show that adsorption starts from a low concentration, and with an increase in the metal ion concentration, the amount of metal ion adsorbed increases. The increase in the adsorption capacity is probably due to greater interaction between adsorbate and adsorbent [49]. At low concentrations, metal ions are adsorbed by specific active sites, while with increasing metal concentrations, the binding sites become more quickly saturated as the amount of biomass concentration remained constant.

An adsorption isotherm is characterized by certain constants, which express the surface properties and affinity of the adsorbent and can also be used to compare the adsorption capacities of the adsorbent for different metal ions. The Langmuir isotherm is valid

Table 3
Langmuir and Freundlich adsorption isotherm parameters of Pb(II), Zn(II) and Cd(II) heavy metals on sawdust of poplar

	Langmuir constant			Freundlich constant		
Metal	q_0 (mg g^{-1})	K_L (mg l^{-1})	r^2	K_F	$1/n$	r^2
Pb	10.1255	0.0143	0.993	0.4020	0.588	0.989
Zn	8.477	0.01536	0.997	0.388	0.562	0.984
Cd	8.87	0.0132	0.995	0.347	0.582	0.971

Table 4
Comparison of various adsorbents used in adsorption of Cd(II), Zn(II) and Pb(II) from wastewaters

Adsorbent	Heavy metal ion	q (mg/g)	Refs.
Pinus roxburghii	Cd	3.01	[55]
Neem oil cake	Cd	11.82	[56]
Bagasse fly ash	Cd	1.20	[57]
Lathyrus sativus husk	Cd	35	[58]
Rice husk	Cd	8.58	[59]
Banana peel	Zn	5.8	[60]
Barley straw	Zn	5.3	[61]
Coir fibres	Zn	1.83	[62]
Coir fibres	Zn	8.6	[63]
Cocoa shell	Zn	2.92	[64]
Peanut hulls	Zn	9	[65]
Sugar beet pulp	Zn	35.6	[66]
Orange peel	Zn	5.25	[67]
Palm kernel fibre	Pb	49.9	[68]
Watermelon seed hulls	Pb	24.15	[69]
Apple residue	Pb	17.76	[70]
Bagasse fly ash 2004	Pb	3.8	[71]
Pinus sylvestris cone	Pb	6.70	[72]
Cereal chaff	Pb	12.5	[73]
Okra waste	Pb	5	[74]
Sawdust	Pb	13.9	[75]
Barley straw	Pb	15.2	[61]
Coir fibres	Pb	18.9	[63]
Hazelnut shell	Pb	1.78	[76]
Rice husk	Pb	8.6	[59]

for monolayer adsorption onto a surface with homogeneous adsorption sites. The linear form of Langmuir equation is expressed as follows [50]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{2}$$

where q_m and K_L are Langmuir constants related to the saturated monolayer adsorption capacity and the sorption equilibrium constant, respectively. C_e is the equilibrium concentration in the aqueous solution, and q_e is the equilibrium adsorption capacity of adsorbent. Fig. 7 represents the Langmuir isotherms of the mentioned metal ions.

The Freundlich model is an empirical equation based on adsorption on heterogeneous surface. The linearized form of the Freundlich isotherm can be written as follows [51]:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{3}$$

where K_f and n are the Freundlich constants that indicate adsorption capacity and adsorption intensity,

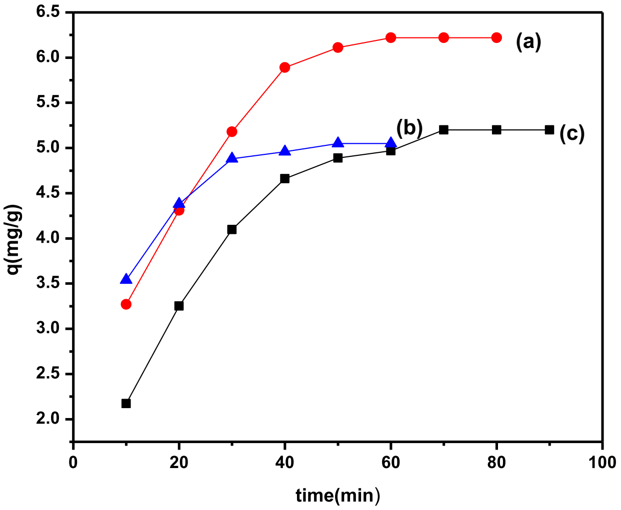


Fig. 9. Effect of time on the adsorption of (a) Pb(II), (b) Cd (II) and (c) Zn(II) on sawdust of poplar.

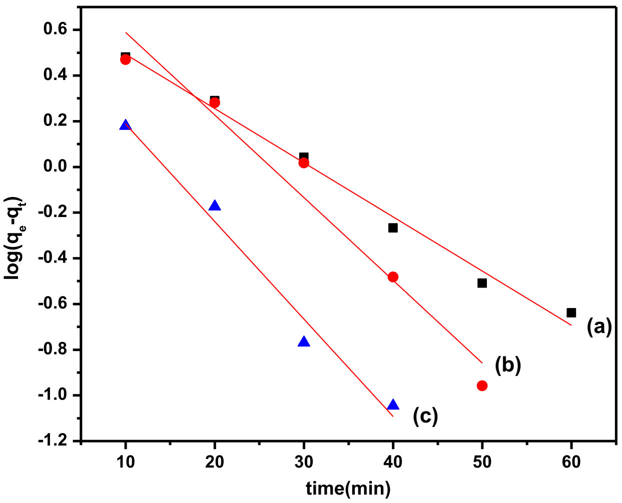


Fig. 10. Plot of log ($q_e - q_t$) vs. t (min) for (a) Zn(II), (b) Pb (II) and (c) Cd(II).

respectively. The Freundlich constants, K_f and $1/n$, can be determined from the intercept and slope of linear plot of ln q_e vs. ln C_e, respectively (Fig. 8).

The isotherm constants and correlation coefficients are given in Table 3. It is clear from the plots that the adsorption equilibrium data for Pb(II), Zn(II) and Cd (II) fitted well to the Langmuir equations with correlation coefficients close to 0.99 in all the cases. The Freundlich isotherm is an indication of surface inhomogeneity of the adsorbent while the Langmuir isotherm indicates an adsorption process onto a surface with homogeneous adsorption sites. The order of adsorption of metals on poplar sawdust under the same conditions is:

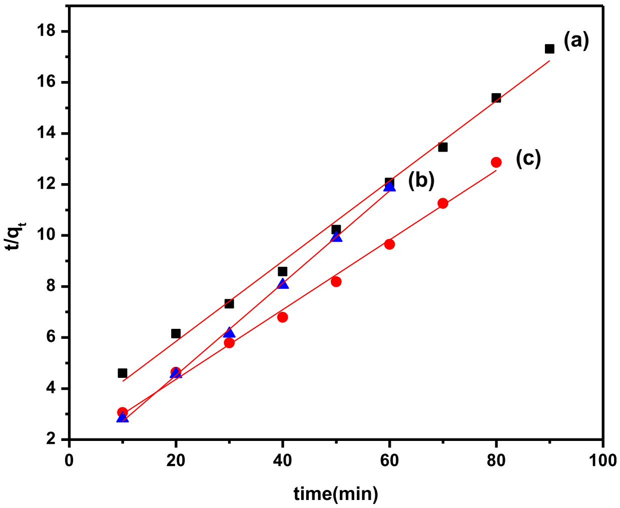


Fig. 11. Plot of t/q_t vs. t (min) for (a) Zn(II), (b) Cd(II) and (c) Pb(II).

Pb(II) > Cd(II) > Zn(II).

The difference in amount adsorbed of different heavy metal ions at the same initial metal ions concentration, adsorbent dose and contact time may be attributed to the difference in their chemical affinity and ion exchange capacity with respect to the chemical functional group on the surface of the adsorbent. Since the hydrated ionic radius increased in the order Pb(II) < Cd(II) < Zn(II), it leads us to the conclusion that adsorption of metals increased with their decreasing hydrated ionic radii.

The maximum adsorption capacities ($q_{\max}$) of the adsorbent calculated from Langmuir isotherm for Pb (II), Cd(II) and Zn(II) were found to be comparable with and sometimes better than the other adsorbents reported in the literature, especially for Cd(II) and Zn (II) (Table 4).

4.6. Effect of contact time (adsorption kinetics)

The results show that adsorption increases with increase in contact time and reaches equilibrium after 50, 60 and 70 min in case of Cd(II), Pb(II) and Zn(II), respectively (Fig. 9). The results indicate higher adsorption rate in the beginning and thereafter the sorption rate decreases. The study revealed that biosorption took place in two steps: a rapid surface adsorption and slow intercellular adsorption. That is probably due to larger surface area of the sawdust being available at the beginning for adsorption of metals. As the surface adsorption sites become exhausted,

Table 5
Kinetic parameters for the adsorption of Pb(II), Zn(II) and Cd(II) heavy metal ions on sawdust of poplar

		Pseudo-first-order kinetics			Pseudo-second-order kinetics		
Metal	q_{eexp} (mg g^{-1})	q_{ecal} (mg g^{-1})	K_1 (min^{-1})	r^2	q_{ecal} (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	r^2
Pb	6.22	8.940	0.0833	0.950	7.326	0.0113	0.994
Zn	5.2	5.367	0.05458	0.987	6.365	0.00911	0.994
Cd	5.05	4.119	0.0983	0.972	5.53	0.0359	0.998

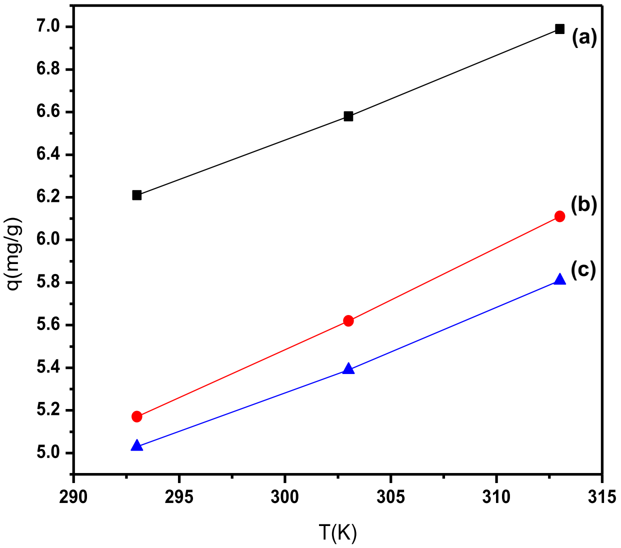


Fig. 12. Effect of temperature on the adsorption of (a) Pb (II), (b) Zn(II) and (c) Cd(II) on sawdust of poplar.

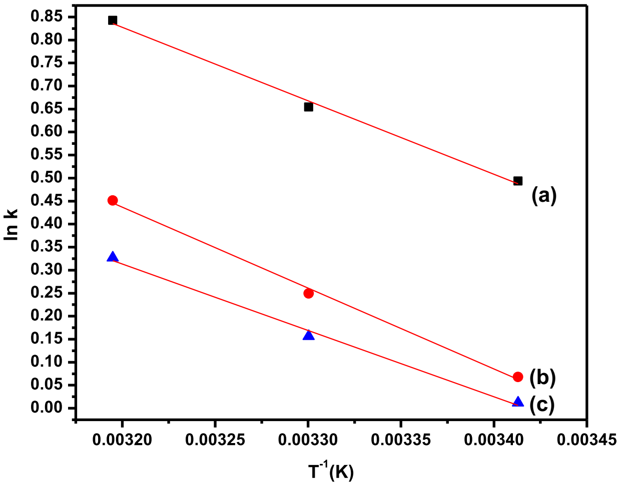


Fig. 13. Plot of ln k vs. T^{-1} (K) for (a) Pb(II), (b) Zn(II) and (c) Cd(II).

i.e. at equilibrium, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles.

Various adsorption kinetic models have been used to describe the adsorption of metal ions. The first-order kinetic process has been used for reversible reaction with an equilibrium being established between liquid and solid phases. The linear form of pseudo-first-order kinetic equation is expressed as follows [52]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{4}$$

where q_t and q_e are the amounts of ion adsorbed at time t and at equilibrium (mg g^{-1}), respectively, and k_1 is the rate constant of pseudo-first-order adsorption process (min^{-1}). The slope and intercept of plots of $\log(q_e - q_t)$ vs. t were used to determine the first-order rate constant k_1 and equilibrium adsorption capacity q_e (Fig. 10).

The pseudo-second-order model is based on the assumption that the rate limiting step may be a chemical adsorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate. The pseudo-second-order kinetic model is given as follows [53]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{5}$$

where k_2 is the equilibrium rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}). The plot of t/q_t vs. t gives a linear relationship, and k_2 and q_e can be calculated from the slope and intercept of the line (Fig. 11). The results are given in Table 5. The correlation coefficients (r^2) for the pseudo-second-order equation provide the best fit.

4.7. Adsorption thermodynamics

The variation of adsorption with temperature was studied. Fig. 12 shows the adsorption of metal ions on sawdust increases as temperature increases. The increase in adsorption capacity with temperature suggested that the active sites available for adsorption

Table 6
Values of thermodynamic parameters for the adsorption of Pb(II), Zn(II) and Cd(II) heavy metal ions on sawdust of poplar at various temperatures

Metal	T (K)	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1} k^{-1})
Pb	293	−1.2026	13.279	0.0493
	303	−1.648		
	313	−2.192		
Zn	293	−0.165	14.605	0.00048
	303	−0.6279		
	313	−1.1749		
Cd	293	−0.0293	11.988	0.04096
	303	−0.393		
	313	−0.850		

Table 7
Concentration of metal ions in cement wastewater

Heavy metals	Initial concentration (mg/l)
Pb(II)	171
Cd(II)	109
Zn(II)	92

have increased with temperature. This could also be attributed to the pore size variation and enhancing rate of intraparticle diffusion of solute since diffusion is an endothermic process.

In order to explain the effect of temperature on the adsorption of Pb(II), Zn(II) and Cd(II) on poplar sawdust, thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were obtained using the following equations:

$$\Delta G = -RT \ln K \tag{6}$$

where R is the ideal gas constant (kJ/mol/K), T is the temperature (K) and K is the equilibrium constant, which was calculated from the following relation:

$$K = C_A/C_E$$

where C_A and C_E are the equilibrium concentrations (mg/l) of metal ions on the adsorbent and in solution, respectively, at 100 mg/L initial concentration of the metal ions.

Table 8
Comparison between the metal uptake from synthetic metal solution and the cement factory effluent on sawdust of poplar

		Final concentration (mg/l)	
Heavy metals	Initial concentration (mg/l)	Synthetic solution	Industrial effluent
Pb(II)	20	2	2.53
	40	3.17	3.36
	60	15.92	16.71
	80	24.76	24.9
	100	35.6	36.7
Cd(II)	20	2.77	3.25
	40	8.18	8.98
	60	18.97	19.93
	80	32.89	33.18
	100	48.3	49.1
Zn(II)	20	3.45	3.57
	40	7.76	7.98
	60	19.7	21.3
	80	32.1	33.67
	90	40.51	41.03

Table 9
Removal of metal ions from cement effluent on sawdust using column

Heavy metal	Initial conc. (mg/l)	Final conc. (mg/l)
Pb(II)	100	35.6
	35.6	3.07
	3.07	0
Cd(II)	100	49
	49	14.23
	14.23	1.27
Zn(II)	80	32.98
	32.98	4.5
	4.5	0.13

The enthalpy and entropy of adsorption were determined from the Van't Hoff equation:

$$\ln K = \frac{\Delta S}{R} + \frac{\Delta H}{RT} \tag{7}$$

where ΔH and ΔS were obtained from the slope and intercept of the Van't Hoff's plot of $\ln K$ vs. $1/T$ as shown in Fig. 13.

The results of the thermodynamic calculations are shown in Table 6. A positive value of ΔH confirms the endothermic nature of the process. The negative value of ΔG indicated the spontaneous nature of the adsorption system. The more negative values obtained for ΔG with increasing temperature indicate that the adsorption process is more favourable at higher temperature. The positive value of ΔS shows the increased randomness at solid/solution interface during the adsorption process. The adsorbed water molecules, which are displaced by the adsorbate species, gain more translational energy than is lost by the adsorbate ions, thus allowing the prevalence of randomness in the system [54]. The enhancement of adsorption at higher temperature may be attributed to the enlargement of pore size and/or activation of adsorbent surface.

5. Treatment of cement industry effluent using glass column

Cement industry effluent was collected from the nearby cement industry. It was carefully bottled in a plastic container and was immediately taken to the laboratory for analysis. The effluent was digested, filtered through filter paper and the heavy metals present in the wastewater sample were analysed using atomic absorption spectrophotometer. The initial concentrations of the metal ions present in the wastewater are shown as in Table 7. Different concentrations of metal ions were prepared from the cement effluent solution by dilution with distilled water for comparison with synthetic metal ion solutions.

Column experiments were carried out using a glass column with internal diameter of 4 cm. The column was packed with 4 g of sawdust. Distilled water was run through the column and equilibrated for an hour. Different concentrations of the above metal ions were prepared from their corresponding nitrates. A volume of 100 ml of each of the synthetic heavy metal ion solution with different metal ion concentrations was passed through the column separately at an optimum pH (pH 6 for Pb(II), Zn(II) and pH 4 for Cd(II)) and at room temperature. The rate of flow of the metal ion solution was kept constant (1 ml/min) using a stopcock. The equilibrium concentration of each metal solution was established using AAS. The procedure was repeated for the cement wastewater. The difference between the metal uptake from the synthetic metal ion solution and the effluent may be attributed to the presence of other ions and impurities which compete with particular metal for the binding sites (Table 8).

In another experiment, 100 ml of the above metal ion solution of concentrations (as shown in table) was passed through the column at an optimum pH and at room temperature and the flow rate was kept constant. The amount of metal ion left in the solution was determined by AAS. This solution was again passed through another column and then analysed for final metal ion concentration. The procedure was repeated till complete removal of metal ions was achieved as shown in Table 9.

6. Conclusion

(1) Sawdust of *P. alba* was found to adsorb substantially Pb(II), Zn(II) and Cd(II) from aqueous solution.
(2) Various thermodynamic parameters such as ΔH, ΔS and ΔG were calculated. These thermodynamic parameters together with Langmuir and Freundlich isotherm constants indicated a favourable adsorption of Pb(II), Zn(II) and Cd (II)on the sawdust of *P. alba*.
(3) The adsorption of Pb(II), Zn(II) and Cd(II) on the sawdust of *P. alba* was found to be endothermic and spontaneous in nature.
(4) The adsorption of Pb(II), Zn(II) and Cd(II) on the sawdust of *P. alba* increased with increase in temperature.

(5) The equilibrium was attained after 50, 60 and 70 min for Cd(II), Pb(II) and Zn(II), respectively.

(6) The maximum adsorption capacity of sawdust of *P. alba* for Pb(II), Zn(II) and Cd(II) were found to be 10.1255, 8.477 and 8.877 mg/g, respectively, at optimum conditions.

(7) The efficacy of sawdust of *P. alba* in the treatment of effluent from cement industry has been investigated, and the results have been found satisfactory.

(8) On the basis of the above, it can be concluded that sawdust of *P. alba* can be effectively used as a low cost, sustainable and easily available adsorbent for the removal of toxic metals from aqueous solution.

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