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Adsorptive removal of heavy metals from aqueous solution by treated sawdust (*Acacia arabica*)

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Abstract

The removal of Cr(VI), Pb(II), Hg(II) and Cu(II), by treated sawdust has been found to be concentration, pH, contact time, adsorbent dose and temperature dependent. The adsorption parameters were determined using both Langmuir and Freundlich isotherm models. Adsorption capacity for treated sawdust, i.e. Cr(VI) (111.61 mg/g), Pb(II) (52.38 mg/g), Hg(II) (20.62 mg/g), and Cu(II) (5.64 mg/g), respectively. Surface complexation and ion exchange are the major removal mechanisms involved. The adsorption isotherm studies clearly indicated that the adsorptive behaviour of metal ions on treated sawdust satisfies not only the Langmuir assumptions but also the Freundlich assumptions. The applicability of Lagergren kinetic model has also been investigated. The adsorption follows first-order kinetics. Thermodynamic constant (k_{ad}), standard free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) were calculated for predicting the nature of adsorption. The percentage adsorption increases with pH to attain a maximum at pH 6 and thereafter it decreases with further increase in pH. The results indicate the potential application of this method for effluent treatment in industries and also provide strong evidence to support the adsorption mechanism proposed.
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1. Introduction

Industrial, agricultural and domestic wastes pollute water bodies with heavy metals, which reach tissues through the food chain. The toxicity of heavy metals to aquatic organisms has been a subject of interest to biologist for many years. Absorption of trace metals onto natural particulate matter can play a role in determining trace metal speciation in many aquatic systems. Among different types of pollution, the industrial waste constitutes the major source of various kinds of metal pollution in natural water. The important toxic metals, i.e. Cd, Hg, Pb, Cu, Cr, Ni, Mn, Zn, As, Co Ag, Au, Sn, V, Sb, Bi, Ce, Ga, Pt, Fe, etc., finds its way to the water bodies through waste water from such industries as metal plating industries of cadmium, nickel, batteries, pigment, stabilizers, alloys paint, metallurgical, tannery,

chemical manufacturing, mining, pulp and paper, oil refining, electrical, rubber processing and fertilizers [1].

The pollution of water resources due to the indiscriminate disposal of heavy metals has been causing worldwide concern for the last few decades. It is well known that some metals can have poisonous or harmful effects on many forms of life.

This problem has received considerable amount of attention in recent years. One primarily concern is that marine animals which can readily adsorb those heavy metals in wastewater and directly enter the human food chains present a high health risk to consumers.

In view of the toxicity and in order to meet regulatory safe discharge standards, it is essential to remove heavy metals from wastewaters/effluents before it is released into the environment. A number of technologies have been developed over the years to remove toxic metal ions from water. Conventional methods for the removal of heavy metals include precipitation, coagulation/flocculation, ion exchange, reverse osmosis [2,3],

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complexation/sequestration, electrochemical operation and biological treatment [4,5].

Application of above-mentioned methods becomes economically unviable for the removal of heavy metals at lower concentrations. Adsorption, as compared to other methods, appears to be a simple attractive process in view of its high efficiency, easy handling and cost-effectiveness as well as the availability of different adsorbents. In addition, the recoveries of pure metal for recycle as well as reuse of the adsorbent are the added advantages. Adsorptive treatment using non-conventional adsorbents, such as agricultural and industrial solids wastes, have been used for the removal of heavy metals [6–10].

Moreover, the removal of metal ions from their solutions in the presence of agricultural materials may be due to the adsorption on surface and pores, and also to complexation by these materials. In the present work, our search for a cheap, readily available and effective adsorbent material has identified sawdust as a potentially attractive adsorbent for the treatment of heavy metal contaminated aqueous solutions/wastewater after pretreatment with 2N sodium hydroxide and 0.2N sulphuric acid to remove lignin contents and to enhance the porosity. Since there is a huge deposit of sawdust around saw mills, there is a great potential for its utilization in water pollution control. The main objective of this study was to investigate the feasibility of using treated sawdust for the maximum removal of above metal ions from aqueous solutions at optimised process parameters such as initial concentration, adsorbent dose, contact time and pH.

2. Materials and experimental methods

2.1. Instrumentation

GBC 932 AA atomic adsorption spectrometer (AAS) operating with an air acetylene flame was used to analyze the concentration of heavy metals. The minimum detection limit was equal to or less than EPA requirement. Three standard solutions with concentrations of heavy metal ions in the linear range of the instrument were used to construct each calibration curve. During analysis of the samples for heavy metals concentration, those samples in which the concentration of heavy metals is observed beyond the linear range of the references were diluted to appropriate concentrations. All measurements were repeated three times and those results in which the standard deviations were found greater than 0.1 mg/L were not accepted.

The pH measurements were performed with a controlled pH analyser (LABINDIA). The pH meter was standardized using buffer solutions of pH values: 4.00, 7.00, 9.00 and 12.00. Micromeritics ASAP 2010 make surface area analyzer and a mechanical shaker of WIDSONS SCIENTIFIC make was used for all the adsorption experiments for agitating the sample for a desired contact time.

2.2. Chemicals

Analytical grade reagents were used for heavy metal solution; ACS reagent grade concentrated nitric acid, NaOH and pH buffer

Table 1
Characteristics of the treated sawdust

Parameters	Value
Color	Light-dark brown
Ash content (%)	2–4
Bulk density (g/mL)	0.07
Moisture (%)	6–7
BET surface area (m^2/g)	1.96
Langmuir surface area (m^2/g)	2.19
Micro pore volume (cm^2/g)	0.004
Average pore diameter (4 V/A)	7.85
Maximum pore volume (cm^3/g)	0.0007
Median pore diameter (A)	9.73
Carboxylic functional group (mequiv./g CA)	Present
Lactonic acid functional group (mequiv./g CA)	Present
Phenolic functional group (mequiv./g CA)	Present
Lignin	Present
Cellulose	Present

solutions (E. Merck) were used to adjusted pH values of samples. In all experimental work, distilled deionized water was used.

2.3. Adsorbate solution

Synthetic stock solution of heavy metals was prepared by dissolving required quantity of Analar grade salts $\{Cu(NO_3)_2$ for Cu(II), $K_2Cr_2O_7$ for Cr(VI), lead nitrate for Pb(II), $HgCl_2$ for Hg(II)$\}$ in the deionized water. The stock solution was further diluted with deionized water to desired concentration for obtaining the test solutions.

2.4. Adsorbent

The raw sawdust (particle size range 40–70 mesh) was obtained from Nonpura the nearby villages of Jaipur district, Rajasthan, India. Sawdust contained lignin, which resulted in poor adsorption and red colouration of the treated water; therefore, sawdust was first chemically treated to remove the lignin before using it for the adsorption study. Its characteristics are given in Table 1.

2.5. Treatment of sawdust with NaOH and H_2SO_4

The raw sawdust was completely immersed in 2N NaOH aqueous solution for a period of 8 h. Thereafter, it was washed several times with distilled water to remove the lignin content and excess of NaOH and then dried. It was observed that a dark red solution was generated during this treatment, which indicated the removal of lignin from the adsorbent material. The sawdust was repeatedly washed with double distilled water till no red coloration was observed. It was then immersed in 0.2N H_2SO_4 for a period of 8 h to remove traces of alkalinity and other impurities. The acid treated sawdust material was thoroughly washed with double distilled water to remove excess of sulphuric acid and other colouring materials till the wash water was colorless. After this, the treated sawdust adsorbent material was dried in the sunlight and stored in a dessicator for use as an adsorbent. The treated sawdust material was found to be

lighter in colour and weight. Ion exchange may be the principal mechanism for adsorptive removal of heavy metal ions by sawdust.

2.6. Batch mode adsorption studies

The adsorption of heavy metals on treated sawdust was studied by batch technique. The general method used for this study is described as below.

A known weight of adsorbent (e.g. 0.5–1.2 g adsorbent) was equilibrated with 100 mL of the heavy metals solution of known concentration in a stoppered borosil glass flask at a fixed temperature in a thermostatic mechanical shaker (WIDSONS Scientific) for a known period (24–72 h) of time. After equilibration, the suspension of the adsorbent was separated from solution by filtration using Whatman no. 1 filter paper. The concentration of heavy metal ions remaining in solution was measured by AAS (GBC 932 AA) using flame method. The effect of several parameters such as pH, concentrations, contact time and adsorbent dose on the adsorption was studied. The pH of the adsorptive solutions was adjusted using nitric acid, sodium hydroxide and buffer solutions when required. Adsorption of heavy metal ions on the walls of glass flasks determined by running the blank experiments was found negligible.

The results of these studies were used to obtain the optimum conditions for maximum heavy metals removal from aqueous solution.

The % heavy metal removal were calculated using the following equation:

$$\% \text{ metal ion removal} = \frac{(C_0 - C_e) \times 100}{C_0} \tag{1}$$

where C_0 is the initial concentration of test solution, mg/L, and C_e is the final equilibrium concentration of test solution, mg/L.

3. Results and discussion

The results of the experiments carried out for the removal of heavy metals from the synthetic samples using treated sawdust as an adsorbent are discussed below.

3.1. Effect of initial concentration of heavy metal

The effect of initial concentration on the percentage removal of heavy metals by treated sawdust is shown in Fig. 1. It can be seen from the figure that the percentage removal decreases with the increase in initial heavy metal concentration. For Hg(II) and Cr(VI) is seen the percentage removal is almost complete (nearly 100%) throughout the initial concentration range 1–5 mg/L for 1 g/100 mL adsorbent dose, at pH 6 and a contact time of 48 h. For Pb(II) at same adsorbent dose and contact time, there are slight drop in percentage removal at higher initial concentration, whereas for Cu(II), the percentage removal is highly effective upto 1 mg/L initial concentration after which percentage removal decreases gradually to below 85%. At lower initial concentrations, sufficient adsorption sites are available for adsorption of the heavy metals ions. Therefore,
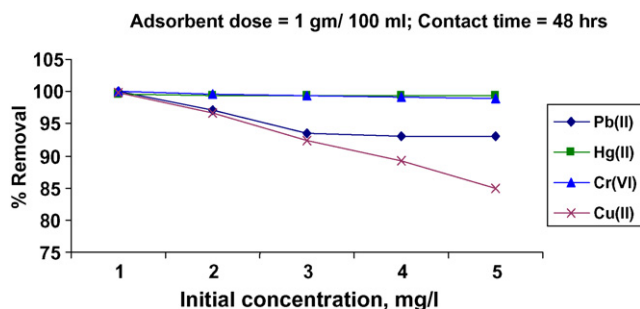

Fig. 1. Effect of initial concentration on % removal of heavy metal.

the fractional adsorption is independent of initial concentration. However, at higher concentrations the numbers of heavy metal ions are relatively higher compared to availability of adsorption sites. Hence the % removal of heavy metals depends on the initial concentration and decreases with increase in initial concentration. The difference in percentage removal of different heavy metal ions at the same initial 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.

3.2. Effect of adsorbent dose

The results for adsorptive removal of heavy metals with respect to adsorbent dose are shown in Fig. 2 over the range 0.6–1.2 g/100 mL, at pH 6 the percentage removal of heavy metals is seen to increase with adsorbent dose. From. Fig. 2, the percentage removal of Hg(II) and Pb(II) ions show nearly 100% removal. It is observed that there is a sharp increase in percentage removal with adsorbent dose for Cu(II) ions but in case of Cr(VI) ions, there is slight and gradual increase in percentage removal with increasing dose.

It is apparent that the percent removal of heavy metals increases rapidly with increase in the dose of the adsorbents due to the greater availability of the exchangeable sites or surface area. Moreover the percentage of metal ion adsorption on adsorbent is determined by the adsorption capacity of the adsorbent for various metal ions.
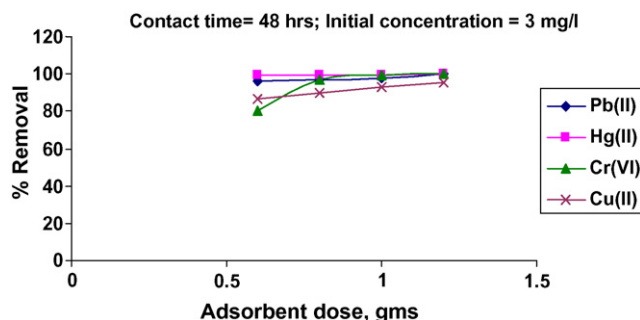

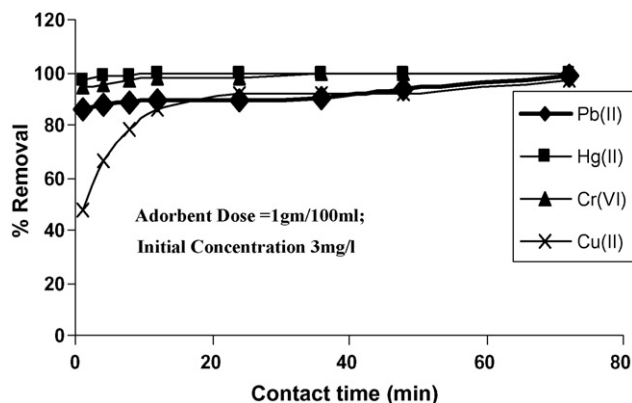Fig. 2. Effect of adsorbent dosage on % removal of heavy.

Fig. 3. Effect of contact time on % removal of heavy.

3.3. Effect of contact time

Fig. 3 shows the variation in the percentage removal of heavy metals with contact time using Ig/100 mL of treated sawdust at pH 6. It is observed that for Hg(II) and Cr(VI) ions, the percentage removal is nearly 100% even throughout the all-contact times.

It is observed that in all cases the percentage removal is comparatively lower for 24 h contact time, with increasing removal efficiencies at higher contact time. In case of Pb(II) and Cu(II) ions raise sharp rise in percentage removal with increasing contact time.

It is evident from the results that the contact time required to attain equilibrium is dependent on the initial concentration of heavy metals. For the same concentration, the % removal of heavy metal increases with increase of contact time till equilibrium is attained. The optimal contact time to attain equilibrium with treated sawdust was experimentally found to be about 48 h for Hg(II), Cr(VI), Pb(II) and 72 h for Cu(II), respectively.

3.4. Effect of pH

pH is one of the most important parameters controlling uptake of heavy metals from wastewater and aqueous solutions. Fig. 4 shows the effect of pH on heavy metals removal efficiencies of treated sawdust. These studies were conducted at a constant initial concentration of 3 mg/L, adsorbent dose 1 g/100 mL solution and agitation period of 48 h for all heavy metal ions at varying the pH on treated sawdust.
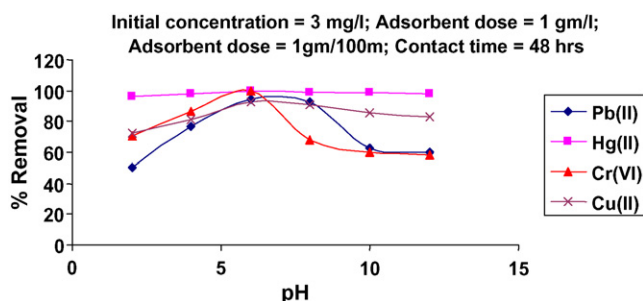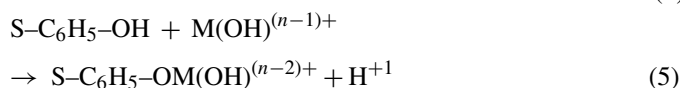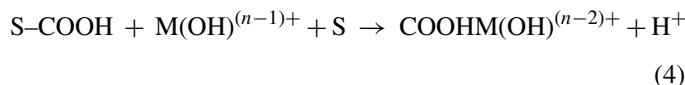
The percentage adsorption increases with pH to attain a maximum at pH 6 and thereafter it decreases with further increase in pH. The maximum removal of Hg(II), Cu(II), Pb(II) and Cr(VI) at pH 6 were found to be nearly 99.4, 92.2, 94.6 and 99.3%, respectively, The possible sites on sawdust for specific adsorption includes H^+ ions in $-OH$ and $-COOH$ functional groups in which H^+ ions can be exchanged for cations in solution

$$S–COOH + M^{n+} \rightarrow S–COOM^{(n-1)} + H^+ \tag{2}$$

$$S–C_6H_5–OH + M^{n+} \rightarrow S–C_6H_5–OM^{(n-1)} + H^+ \tag{3}$$

$$S–COOH + M(OH)^{(n-1)+} + S \rightarrow COOHM(OH)^{(n-2)+} + H^+ \tag{4}$$

$$S–C_6H_5–OH + M(OH)^{(n-1)+}$$
$$\rightarrow S–C_6H_5–OM(OH)^{(n-2)+} + H^{+1} \tag{5}$$

where S donates the modified surface.

However, the sites responsible for the adsorption process are not exclusively due to the $-COOH$ and $C_6H_5–OH$ groups. Other sites on the modified sawdust can also contribute to the adsorption process. In acidic medium, the electromeric effect of the amide group in sawdust leads to surface protonation and possesses not positive charge on the surface. These H^+ ions from the surface are also exchanged with positively charged sorbate species with subsequent coordination of a metal ion. An increase in pH a slight increase in adsorption in which the surface of the adsorbent is negatively charged and the sorbate species are still positively charged. The adsorbent surface is negatively charged as well as the increasing electrostatic attraction of metal ions. Decrease in removal of metal ions at lower pH is apparently due to the higher concentration of H^+ ions. Present in the reaction mixture, which compete, with the M^{2+} ions for the adsorption sites of sawdust. Decrease in adsorption at higher pH is due to the formation of soluble hydroxyl complexes.

3.5. Effect of temperature

Fig. 5 shows the experimental results obtained from a series of contact time studies for metal ion adsorption with an initial concentration of 3 mg/L at pH 6 in which temperature was varied from 20 to 60 °C. The adsorption of metal ions has been found to increase with an increase in temperature from 20 to 60 °C.
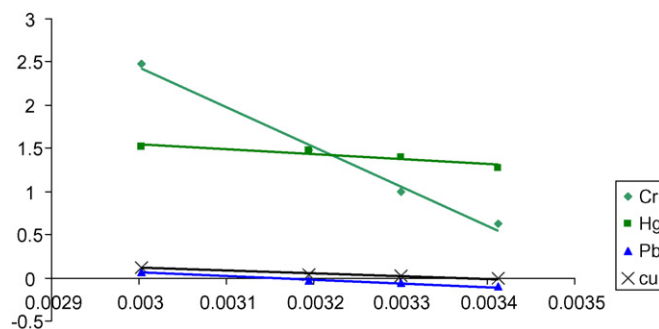

Fig. 4. Effect of pH on % removal of heavy metal ions.

Fig. 5. Plot of log K vs. 1/T for treated sawdust.

Table 2
Equilibrium constants and thermodynamic parameters for the adsorption of heavy metal ions on treated sawdust

Metal ions	Temperature (°C)	K_e	ΔG (KJ/mol)	ΔS (KJ/mol K)	ΔH (KJ/ mol)
Cr(VI)	20	4.185	−3.488	0.037	
	30	9.9	−5.776	0.043	7.461
	40	29.9	−8.843	0.052	
	60	299.9	−15.79	0.069	
Hg(II)	20	18.65	−7.128	0.113	
	30	24.9	−8.100	0.112	26.005
	40	29.9	−8.843	0.112	
	60	33.23	−9.701	0.107	
Pb(II)	20	0.782	0.598	0.071	
	30	0.867	0.357	0.070	21.62
	40	0.934	0.176	0.068	
	60	1.15	−0.387	0.066	
Cu(II)	20	0.971	0.071	0.1014	
	30	1.053	−0.132	0.098	29.79
	40	1.1	−0.248	0.096	
	60	1.328	−0.786	0.092	

Amount of adsorbent: 1 g/100 mL; contact time: 24 h; pH 6, initial concentration: 3 mg/L.

The increase in adsorption capacity of treated sawdust with temperature indicates an endothermic process. The increase in adsorption with temperature may be attributed to either change in pore size of the adsorbent causing intra particle diffusion within the pores or enhancement in the chemical affinity of the metal cations to the surface of adsorbent leading to some kind of chemical interaction to take place during adsorption process which results into increase in adsorption capacity. At higher temperatures, the possibility of diffusion of solute within the pores of the adsorbent may not be ruled out as reported by earlier workers for the adsorption of cations on activated carbon [11,12]. Since diffusion is an endothermic process, greater adsorption will be observed at higher temperature. Thus, the diffusion rate of ions in the external mass transport process increases with temperatures. The above results were further substantiated by the various thermodynamic parameters evaluated for adsorption.

The thermodynamic parameters namely free energy (ΔG), enthalpy changes (ΔH), and entropy change (ΔS) were determined using the following equations. The values obtained are presented in Table 2.

$$K_c = \frac{C_{Ac}}{C_e} \tag{6}$$

where K_c is the equilibrium constant, C_{Ac} and C_e are the equilibrium concentrations (mg/L) of the metal ion on adsorbent and in the solution respectively. The free energy change (ΔG) was calculated from the relation:

$$\Delta G = -RT \ln K_c \tag{7}$$

where T is temperature in kelvin (0 K) and R is gas constant (8.314×10^{-3} kJ/mol K). Enthalpy change (ΔH) was calculated from the following equation.

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

from Eqs. (6)–(8),

$$\log K_c = \frac{\Delta S}{2.303 R} - \frac{\Delta H}{2.303 RT} \tag{9}$$

ΔH and ΔS were obtained from the slope and intercept of Vant Hoff plots of $\log K_c$ versus $1/T$ (Fig. 5). Positive values of ΔH thermodynamically substantiates the assumption that the adsorption of metal ions on the treated sawdust is endothermic. The negative values of ΔG indicate feasibility and spontaneous nature of adsorption of metal ions on the adsorbent. ΔS has been estimated to be very small under these experimental conditions. Therefore, the entropic change occurring from adsorption is thought to be negligible.

3.6. Adsorption kinetics

Kinetics and equilibrium of adsorption are the two major parameters to evaluate adsorption dynamics. The kinetic constants of metal ion adsorption, which could be used to optimize the residence time of an industrial wastewater treated with treated sawdust, were computed using the above experimental data. Earlier workers proposed a surface complexation mechanism for metal ions removal onto treated sawdust. The mechanism involved in the metal ions removal is assumed to be, basically, complexation [13].

Adsorption occurs only on localized sites and involves no interaction between adsorbed ions, the energy of adsorption is independent of surface coverage, maximum adsorption corresponds to a saturated monolayer of adsorbates on the adsorbent surface, and the process of metal uptake on treated sawdust is governed by a first order and is chemical in nature, i.e. chemisorptions.

The adsorption kinetics of metal ions adsorption on treated sawdust follows first-order rate.

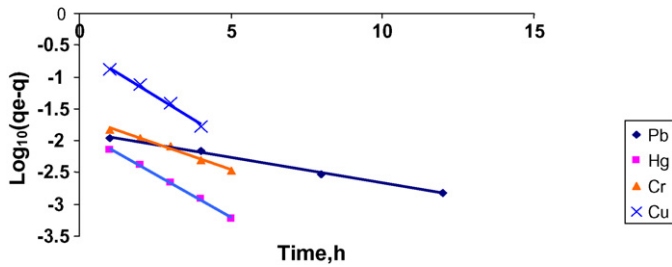$$\log_{10}(q_e - q) = \log_{10} q_e - K_{ad} \frac{t}{2.303} \tag{10}$$

Fig. 6. Plot of Largergren rate constant for treated.

Fig. 7. Freundlich isotherms of heavy metal ions for treated sawdust.

where $K_{ad}(1/h)$ is the rate constant of adsorbent, q and q_e are the amount of metal ions adsorbed (mg/g) at time t (h) and equilibrium time, respectively Linear plots of $\log_{10}(q_e - q)$ versus t (Fig. 6) show the applicability of above equation for treated sawdust. The K_{ad} values at metal ion concentrations of 3 mg/L and adsorbent dose of 1 g/100 mL were calculated from the slope of linear plots and presented in Table 3 the K_{ad} values were comparable with recently reported values for metal ions removal by treated sawdust.

The initial adsorption kinetic coefficients γ (1/mg h) are also computed as per [14] and are presented in Table 3.

$$\gamma = \left(\frac{dC}{dt}\right)_{t=0} \frac{V}{mC_0} \tag{11}$$

where t is the time (h), C the metal ion concentration at time (t), V the solution volume (lit), m the treated sawdust weight (mg) and C_0 is the initial concentration (mg/L).

3.7. Adsorption isotherms

The adsorption studies were conducted at fixed initial concentration of heavy metals by varying adsorbent dosage. The equilibrium data obtained were analyzed in the light of Langmuir and Freundlich isotherms. The Freundlich equation is given by [15].

$$\frac{X}{m} = KC_e^{1/n} \tag{12}$$

Taking the logarithmic form of the equation

$$\log \frac{x}{m} = \log K + \frac{1}{n}\log C_e \tag{13}$$

Langmuir equation is given by [16].

$$\frac{X}{m} = \frac{abC_e}{1 + bC_{e^-}} \tag{14}$$

Table 3
Kinetics constants for heavy metal ions adsorption

Metal ions	Adsorption rate constant (K_{ad}) ($\times 10^{-2}$ 1/h)	Initial adsorption coefficient (γ) (1/mg min)
Cr(VI)	38.22	1.37
Hg(II)	62.18	6.5
Pb(II)	18.49	0.012

Amount of adsorbent: 1 g/100 mL; temperature: 30 °C, pH 6, initial concentration of metal ions: 3 mg/L.
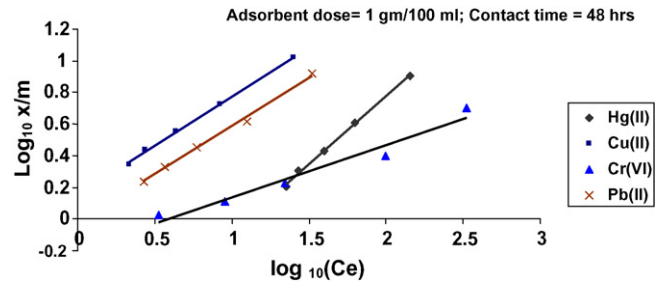
Table 4
Values of Langmuir and Freundlich isotherm constants for adsorption of heavy metal ions

Metal ions	a (mg/g)	b (l/mg)	R^2	R_L
Langmuir constants				
Pb(II)	52.38	0.35	0.99	0.15
Hg(II)	20.63	1.05	0.99	0.24
Cr(VI)	111.61	0.788	0.99	0.42
Cu(II)	5.64	0.50	0.97	0.50

Metal ions	K_e	n	R^2
Freundlich constants			
Pb(II)	2.4901	4.044	0.484
Hg(II)	0.39	1.17	0.99
Cr(VI)	1.302	3.443	0.99
Cu(II)	1	1	1

Amount of adsorbent: 1 g/100 mL; contact time: 48 h, pH 6.

or,

$$\frac{X}{m} = \left(\frac{1}{ab}\right)\left(\frac{1}{C_e}\right) + \frac{1}{a} \tag{15}$$

where x/m is the amount of heavy metal ions adsorbed per unit mass of adsorbent in mg/g, C_e the equilibrium concentration of heavy metal ions in mg/L, K_e and n are Freundlich constants, 'a' is a Langmuir constant which is a measure of adsorption capacity expressed in mg/g. 'b' is also Langmuir constant which is a measure of energy of adsorption expressed in L/mg. The parameters 'a' and 'b' have been calculated from the slope and the intercept of the plots.

Fig. 7 gives the Freundlich adsorption isotherm plot of $\log x/m$ versus $\log C_e$. The values of K_e and $1/n$ obtained from intercept and slope of the plot are given in Table 4.

The Langmuir adsorption isotherm plot for m/x versus $1/C_e$ is shown in Fig. 8 and the plots show two distinct regions, one for low $1/C_e$ values up to about 25 L/mg and another for higher
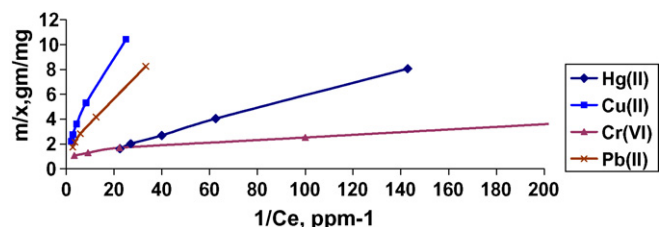

Fig. 8. Langmuir isotherms of heavy metal ions by treated.

$1/C_e$ values. The essential characteristics of Langmuir isotherm can be described by a separation factor or equilibrium constant R_L, which is defined as,

$$R_L = \frac{1}{1 + bC_i} \tag{16}$$

where C_i is the initial concentration of heavy metal ions (mg/L) and b is the Langmuir constant which indicates the nature of adsorption. The separation factor R_L indicates the isotherm shape and whether the adsorption is favourable or not, as per the criteria given below.

R_L values	Adsorption
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

The values of Langmuir constants 'a', 'b' and R_L are presented in Table 4. Since R_L values lie between 0 and 1 for treated sawdust, it is seen that the adsorption of heavy metal ions is favourable [17].

Adsorption capacity as indicated by value of 'a' is seen to be maximum for treated sawdust, i.e. Cr(VI) (111.61 mg/g), Pb(II) (52.38 mg/g), Hg(II) (20.62 mg/g), and Cu(II) (5.64 mg/g) with a much lower capacities. The energies of adsorption, as indicated by 'b' are seen to be highest for Hg(II) (1.05 l/mg), Cr(VI) (0.788 l/mg), Cu(II) (0.50 l/mg) and Pb(II) (0.35 l/mg) in that order. A comparison of the Freundlich adsorption isotherms for the metal ions show that n in that order Pb(II) > Cr(VI) > Hg(II) and Cu(II) .The values of n lie between 1 and 10 indicating favourable adsorption [18–24]. K_e seen to be Pb(II) > Cr(VI) > Cu(II) and Hg(II). This gives a similar inference as that obtained from Langmuir isotherms.

The shapes of isotherms suggest that there are high-energy adsorption sites to favour strong adsorption at low equilibrium concentrations for the treated sawdust. Ion exchange may be the principal mechanism for the removal of heavy metal ions as Cu(II), Pb(II), Cr(VI) and Hg(II). The major components of the polymeric material in sawdust are phenolic compounds; these kinds of material possess the capability of capturing heavy metal ions. It can be speculated that phenolic, tannins compounds are the active ions exchange compounds are that active sites are the phenolic groups of those compounds [22–24].

Physically adsorption can be another mechanism for the heavy metals removal. Sawdust is of cause a kind of organic material that contains two important parts in its adsorption site. One is the lipophilic part to which some lipophilic substances or neutral compounds can be adsorbed. The other part is hydrophilic part on which ion exchanges may take place. In this case the main mechanism may be the ion exchange. Allover pH, the existing of relatively large quantity of hydrogen ion may change the direction of reversible ion exchange equilibrium back to start materials, with increasing pH the metal ions will be associated with hydroxide and become neutral at a certain pH range. A neutral compound possesses hydrophobicity makes the metal precipitation or lipophilicty that makes the metal easily adsorbed

by sawdust. Therefore, at this stage the adsorption mechanism can be the adsorption of affinity [19–23].

In a higher pH range, existing of counter ions might result in lower efficiency of adsorption and ion exchange as well. The extent of adsorption will therefore, depend upon experimental parameters that could affect the surface charge.

4. Conclusion

(a) Treated sawdust showed nearly 100% adsorptive removal of heavy metal ions under optimized conditions of dosage 1 g/100 mL for aqueous solutions containing 3 mg/L metal ions in 48 h.

(b) The Langmuir model is found to be in good agreement with experimental data on adsorptive behaviour of metal ions on treated sawdust follows both Freundlich model & Langmuir models.

(c) The adsorption follows first-order kinetics. pH has been found to be a most effective variable, controlling the adsorption of metal ions on treated sawdust surface.

(d) These experimental studies on adsorbents would be quite useful in developing an appropriate technology for the removal of heavy metal ions from contaminated industrial effluents.

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