

Binary adsorption of [Pb(II) + Co(II)] from aqueous solution using thiolated saw dust

Neha Dhiman

Goswami Ganesh Dutta Sanatan Dharma College, Sector-32, Panjab University Chandigarh, Chandigarh, 160030, India
E-mail: neha.dhi5@gmail.com

ABSTRACT

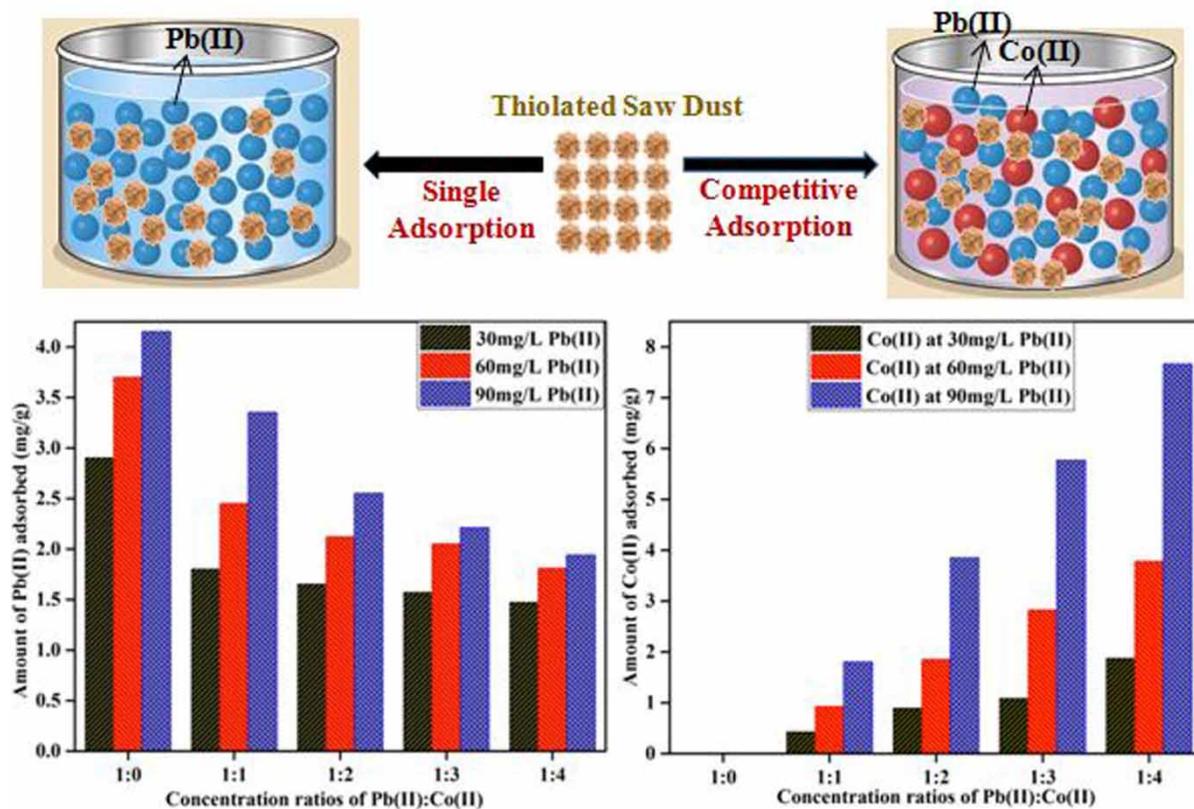
Technology advancement has contributed to an increase in industrial activities, resulting in the introduction of metal ions into water resources at concentrations well above the WHO limits. Heavy metals are highly toxic and carcinogenic; they usually occur as multicomponent mixtures in the aquatic environment. In the present study, batch experiments have been conducted to study the dependence of varying concentration, time, pH and temperature on the uptake of Pb(II) as a pure component under equilibrium conditions using thiolated saw dust. Saw dust has been chemically modified with thioglycolic acid and characterised using proximate and FTIR analyses, the degree of thiolation has also been determined. To determine the effect of the presence of Co(II) ions on the uptake of Pb(II) ions, batch experiments for [Pb(II) + Co(II)] mixture have been carried out for concentration ratios of 1:0, 1:1, 1:2, 1:3, 1:4 of Pb:Co at pH 5 and data has been interpreted using Langmuir competitive isotherm, which shows that adsorption of Pb(II) has been suppressed by the presence of Co(II) ions in the binary solution, hence the adsorption process is antagonistic in nature. The study also indicates the possibility of simultaneous removal of both metal ions using low cost bioadsorbent, which is economical especially for application in small-scale industries.

Key words: competitive adsorption, heavy metal ions, Langmuir competitive isotherm, thermodynamic study, thiolated saw dust

HIGHLIGHTS

- Thiolated saw dust shows excellent ability to adsorb Pb(II) and Co(II) ions.
- Binary adsorption is based on electrostatic interaction controlled by the solution pH.
- Thermodynamic adsorption behavior depends on adsorbent surface functional groups.
- Affinity of each metal ion is depressed by the presence of the other in the binary solution.
- Antagonistic effect on adsorption has been observed.

GRAPHICAL ABSTRACT



INTRODUCTION

In the last few decades, there has been a tremendous increase in the deterioration of the quality of freshwater due to rapid growth of human activities and the accelerated pace of industrialization (Czikkely *et al.* 2018). Lead and cobalt are highly toxic and are released into natural waters from various industrial activities including mining, refining ores, batteries and metal plating (Rashid & Yaqub 2017). The toxicity of these metals is due to their persistence and bioaccumulation in the body, which causes severe damage to the nervous system, reproductive system and kidneys, gastrointestinal irritation, lung cancer and so on (Ketsela *et al.* 2020; Okolo *et al.* 2020). A large number of methods have been used for the removal of these heavy metal ions from wastewater, these are chemical precipitation, ion exchangers, chemical oxidation/reduction, reverse osmosis, electro dialysis, and ultrafiltration. However, most of these methods have their limitations related to disposal problems, low efficiency, sensitive operation and production of secondary sludge (Rashid & Yaqub 2017; Czikkely *et al.* 2018), which increases its cost for application in small-scale industries. Consequently, there is a growing demand for efficient, novel and cost-effective techniques for the remediation of wastewater containing heavy metal ions present in the form of single or multicomponent mixtures (Jain *et al.* 2016; Cifci & Meric 2017). The adsorption of heavy metal ions using agricultural wastes or biosorption materials has attracted much attention over other conventional treatment methods, due to low cost, regeneration, high efficiency, lesser sludge production and the possibility of adsorbate recovery (Gupta *et al.* 2015; Alalwan *et al.* 2020). Agricultural waste materials have shown promising removal efficiency for metal ions from effluents either in unrestricted type or by further chemical treatment (Mahmood *et al.* 2017; Singh *et al.* 2017). Literature studies reveal that chemical modification of bioadsorbents enhances their surface capability, which is attributed to the presence of hemicellulose, lignin or other functional groups (Mahmood *et al.* 2017). The present study aims to check the surface assimilation behaviour of Pb(II) ions from aqueous solution in pure form as well as in the presence of Co(II) ions from a binary mixture of [Pb(II) + Co(II)] using thiolated saw dust (Robert & Girish 2018; Chikri *et al.* 2020) as adsorbent. Agricultural wastes as adsorbents are cost effective for wastewater treatment especially for simultaneous removal of contaminants in the form of

mixtures as compared to the use of conventional absorbents. Also there is no need for regeneration, which makes the sorption process of treating wastewaters cost effective and more economical for small-scale industries.

MATERIALS AND METHODS

Preparation of adsorbent

Saw dust of *Eucalyptus tereticornis*, obtained from a local mill in Pinjore, Panchkula district, Haryana. It was washed with distilled water then air dried and ground. Sieve analysis was performed using mechanical sieves and activation of adsorbent was done by soaking saw dust in excess of 0.3 M HNO₃ for 24 hr followed by washing and drying. For chemical modification, 100 g sample was treated with 0.1 M thioglycolic acid, continuously stirred for 24 hr at 25 °C–30 °C and then centrifuged, washed and dried at 80 °C and supernatants were discarded (Robert & Girish 2018; Chikri *et al.* 2020).

Preparation of adsorbate solution

For single component adsorption, stock solution of 300 mg/L concentration of Pb(II) ions was prepared from PbCl₂ (Merck A R grade) and working standard solutions (30–300 mg/L) were obtained by dilution. Binary solutions for [Pb(II) + Co(II)] mixture were obtained from PbCl₂ and CoCl₂ (Merck, AR grade), by varying the concentration ratios of [Pb(II):Co(II)] in the range 1:0, 1:1, 1:2, 1:3, 1:4 for fixed Pb(II) ion concentration of 60, 80 and 100 mg/L (Sharma *et al.* 2012; Singh *et al.* 2017).

Estimation of adsorbate concentration

Metal ion concentration was estimated titrimetrically (Singh *et al.* 2017) before and after adsorption using the standard methods with EDTA solution in single component and binary mixture. A 5 mL solution of PbCl₂/CoCl₂ solution was taken in a 250 mL titration flask and then 10 mL of distilled water was added. To this, 0.7 gm of hexamine was added as buffer and 2–3 drops of xylenol orange was added as the indicator. The titrations were carried out with 0.01M and 0.001M EDTA solutions for the estimation of Pb(II) and Co(II) ions respectively.

Batch adsorption studies

Single metal ion adsorption

250 mg of adsorbent was weighed and placed in contact with 10 mL of metal ion solutions for the concentration range of 30–300 mg/L at varying pH ranges 2–8 (adjusted using 0.1M HCl/NaOH). Test tubes were agitated for regular time intervals until equilibrium was attained. After agitation and centrifugation, supernatant was analysed titrimetrically (Singh *et al.* 2017) using the standard EDTA solution.

Binary metal ion adsorption

Binary adsorption was carried out for [Pb(II) + Co(II)] mixture for concentration ratios 1:0, 1:1, 1:2, 1:3, 1:4 for fixed Pb(II) ion concentrations of 60, 80 and 100 mg/L. The pH of the solution was adjusted at 5, where maximum adsorption was obtained for Pb(II) in the single adsorption study. After sample preparation, 250 mg of adsorbent was agitated with 10 mL of solution until equilibrium was attained. Samples were analysed after centrifugation, titrimetrically for Pb(II) and Co(II) ion concentration (Singh *et al.* 2017).

RESULTS AND DISCUSSION

Characterization of thiolated saw dust

Adsorbent has been characterised using sieve and proximate analyses, degree of thiolation, point of zero charge (pH_{pzc}) and FTIR spectroscopy (Perkin Elmer spectrophotometer) (Robert & Girish 2018).

Sieve analysis

Sieve analysis was performed using mechanical sieves to obtain adsorbent particles of size between 125 and 250 μm for adsorption experiments (Singh *et al.* 2017).

Proximate analysis

The loss on ignition was determined by heating 5 g of unmodified saw dust sample at 100 °C for 1 hr to obtain the moisture content and further heated up to 700 °C in a muffle furnace to get the ash content. The moisture content was found to be 8.9% and ash content at 700 °C was 40.3% (Singh *et al.* 2017).

Surface area analysis

Since surface area is an important parameter to characterise the adsorbent surface area, analysis has been carried out for untreated saw dust using the iodine adsorption method (Robert & Girish 2018). The amount of iodine absorbed was estimated by titrating a blank and against iodine containing saw dust with a standard thiosulphate solution using starch as the indicator and the surface area of unmodified saw dust was found to be 179.7 m²/g.

Degree of thiolation

0.5 g of thiolated saw dust was placed in contact with 20 mL of 0.5N iodine solution and agitated for 10 minutes, then allowed to settle. The unreacted iodine was back titrated with 0.1N sodium thiosulphate using starch as the indicator. The titre values were recorded and the degree of thiolation was calculated (Robert & Girish 2018) using Equation (1) and found to be 2.4 for thiolated saw dust.

$$T = \frac{(V - V')}{W} \times M \quad (1)$$

where T is degree of thiolation, V and V' are the volume (mL) of 0.1M Na₂S₂O₃ solution used in blank titration and 0.5 g thiolated saw dust respectively, W is the weight of the adsorbent sample and M is molarity of Na₂S₂O₃.

Point of zero charge

25 mL of 0.01M NaCl solutions were placed in different test tubes and the pH of each solution was adjusted in the range 2–12 using 0.1M HCl/0.1M NaOH solution, as the case may be. Then 0.25 g of chemically modified saw dust was added in each test tube and agitated mechanically for 1 hr and allowed to stand for 24 hr to attain equilibrium at 25 °C–30 °C. The zeta potential (mV) value of each solution was determined and plotted against initial pH to determine the point of zero charge (Singh *et al.* 2017; Robert & Girish 2018) and pH of point zero charge for thiolated saw dust was found to be 4.5.

Fourier transform infrared spectrum (FTIR)

FTIR of saw dust (Figure 1(a)) shows bands at 3,386 cm⁻¹ indicating the existence of free hydroxyl group (O-H), 2,924 cm⁻¹ may be assigned to symmetric or asymmetric C-H and symmetric stretching vibration of CH₂, 1,738 cm⁻¹ to stretching vibration of C-O bonds (-COOH, -COOCH₃) and 1,242 cm⁻¹, 1,054 cm⁻¹ to SO₃ stretching (Singh *et al.* 2017).

The FTIR spectrum of thiolated saw dust (Figure 1(a)) shows bands at 3,356.3, 2,918.6 and 1,722.2 cm⁻¹ are attributed to surface hydroxyl groups, stretching vibration of CH₂ and stretching vibration of C-O bonds (-COOH) respectively. The band at 1,624.7–1,510.0 cm⁻¹ is indicative of carboxylic acid and 1,350.0–1,000.0 cm⁻¹ of O-H of alcohol and aliphatic ethers. After thiolation, the band present below 800 cm⁻¹ is indicative of sulphur functional (-SH) groups (Sharma *et al.* 2009, 2012).

After adsorption of Pb(II) ions, most of the shifted peaks in the FTIR spectrum of thiolated saw dust (Figure 1(b)) were observed at 3,406.6–3,356.3 cm⁻¹ attributed to complexation of Pb(II) ions with ionised -OH groups and bonded -OH bands of carboxylic acids (Robert & Girish 2018). The changes in peaks observed between 1,067.7 and 1,057.9 cm⁻¹, caused by stretching vibration of SO₃, indicate the importance of SO₃ group in the adsorption of lead onto thiolated saw dust. The band present below 800 cm⁻¹ is the finger print zone of sulphur functional (-SH) groups (Sharma *et al.* 2009).

Effect of pH and point of zero charge (pHpzc)

Batch experiments for the removal of Pb(II) ions using thiolated saw dust have been conducted at varying pH in the range 2–8 (beyond which precipitation of Pb(II) ions occurs). It has been observed that adsorption of Pb(II) ions increases with increase in pH and maximum removal was obtained at pH 5; further increase in pH shows a decrease in the amount adsorbed, which is associated with pHpzc (Singh *et al.* 2017; Robert & Girish 2018). The pHpzc of thiolated saw dust is 4.5. At low pH, a higher concentration of H⁺ ions compete with positively charged Pb(II) ions. With an increase in pH, the competitive effect of H⁺ ions decreases and maximum adsorption of positively charged Pb(II) ions on the negatively charged adsorbent surface occurs at pH 5 (i.e pH > pHpzc). A further increase in pH shows a decrease in the amount of Pb(II) adsorbed due to the formation of soluble or insoluble Pb(OH)₂ (Singh *et al.* 2017). The relative ease of exchanging hydrogen atoms of the thiol groups of thiolated saw dust with Pb(II) ions also results in an improved level of adsorption.

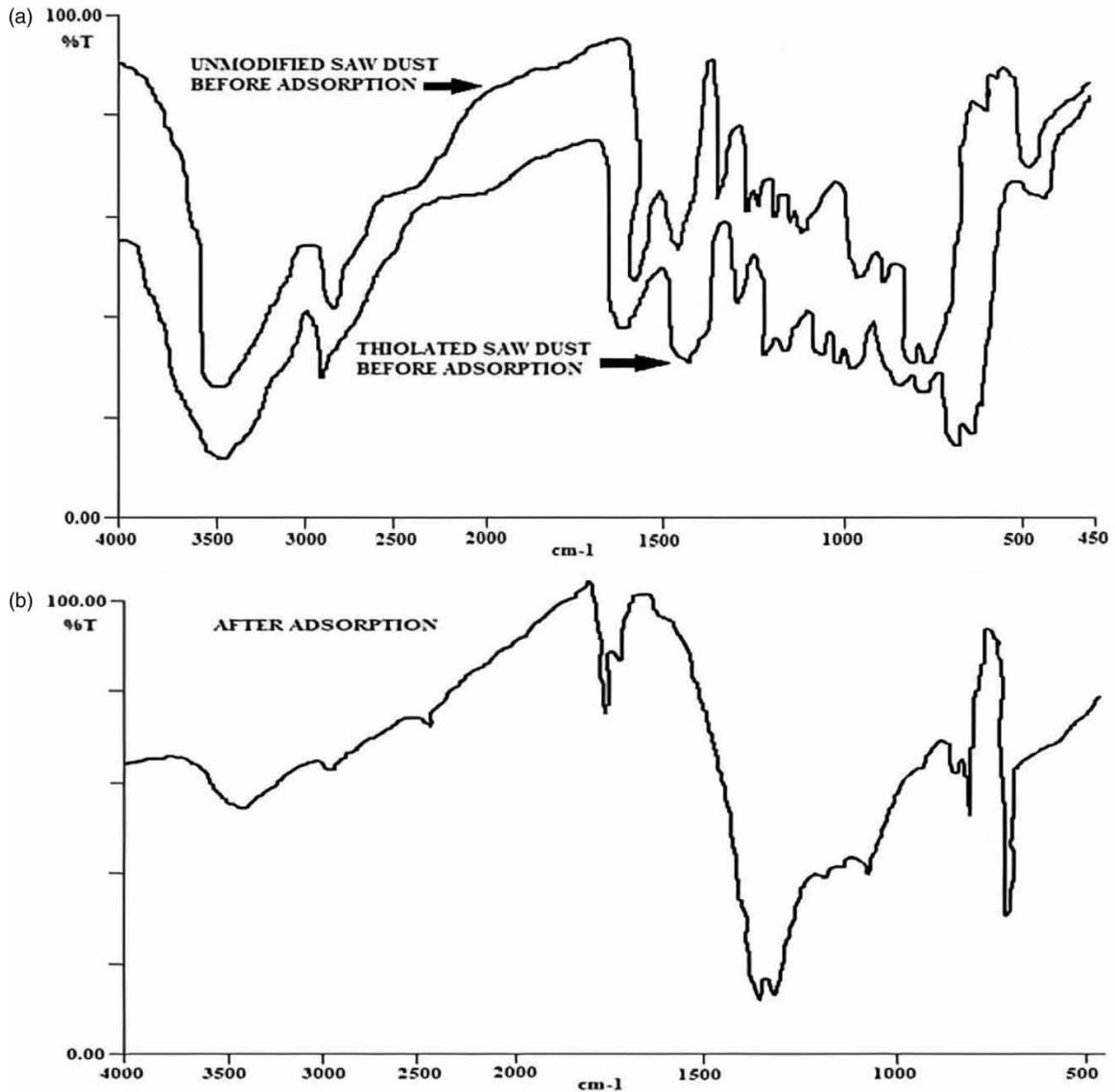


Figure 1 | FTIR spectrum of (a) unmodified and thiolated saw dust before adsorption (b) thiolated saw dust after adsorption of Pb(II) ions.

Effect of initial concentration and contact time

Maximum removal was obtained at lower concentration of Pb(II) ions, which decreases with increase in concentration from 30 to 300 mg/L. However, the adsorption capacity increases with increase in concentration. Adsorption takes place rapidly in the initial 15 minutes and equilibrium adsorption of 7.5 mg/g was attained within 150 minutes. This may be attributed to the availability of larger number of adsorption sites for a smaller number of metal ion species at higher dilution, which decreases with time (Dhiman & Sharma 2016; Singh *et al.* 2017).

Adsorption isotherm modelling

The equilibrium data obtained at pH 5 and contact time 150 min for adsorption of Pb(II) ions were analysed using Freundlich, Langmuir and Temkin adsorption isotherm models to determine the equilibrium metal ion concentrations and adsorption capacity of thiolated saw dust (Dhiman & Sharma 2016; Singh *et al.* 2017).

Freundlich isotherm

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (2)$$

Langmuir isotherm

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \quad (3)$$

where C_e is the equilibrium concentration (mgL^{-1}) and q_e is the equilibrium amount adsorbed (mgg^{-1}), n and K_f are Freundlich isotherm constants, K_L related to affinity of the binding sites (Lmg^{-1}), a_L the Langmuir isotherm constant. The values of the Freundlich and Langmuir constants are presented in Table 1. Results from Freundlich and Langmuir isotherm models suggest favourable and monolayer adsorption occurs with high correlation coefficient value, which indicates the effectiveness of thiolated saw dust.

The Langmuir model can be expressed in terms of separation factor or equilibrium parameter R_L (Dhiman & Sharma 2016),

$$R_L = \frac{1}{(1 + a_L C_0)} \quad (4)$$

The value of R_L is found to be 0.260 for Pb(II) ions, indicating favourable adsorption (Dhiman & Sharma 2016).

Temkin isotherm

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (5)$$

where A_T is the equilibrium binding constant (Lg^{-1}) corresponding to maximum binding energy, $B_T = (RT)/b_T$ is a constant related to heat of adsorption (Jmol^{-1}), b_T is the Temkin isotherm constant, T is absolute temperature (K) and R is the universal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. The values of isotherm constants have been calculated using the slope and intercept from the respective straight line plot of the linear isotherm model (Table 1), which indicates the applicability of the Temkin isotherm model (Dhiman & Sharma 2016, 2019a).

Error analysis for isotherm studies

Error functions of non-linear regression methods were used for the assessment of optimum adsorption isotherm model for the removal of Pb(II) ions using thiolated saw dust (Dhiman & Sharma 2019a).

Sum of squared errors (SSE)

$$SSE = \sum_{i=1}^n (q_{e,\text{cal}} - q_{e,\text{exp}})^2 \quad (6)$$

Table 1 | Isotherm and kinetic constants for adsorption of Pb(II) and Co(II) metal ions on thiolated saw dust for contact time of 150 min at 298 K and pH 5

Isotherm constants										
	Freundlich			Langmuir			Temkin			
	n	K_f (mg/g)	R^2	K_L (L/mg)	a_L	R^2	A_T (L/g)	B_T (J/mol)	b_T	R^2
Pb(II)	1.52	1.35	0.995	1.36	0.12	0.988	1.96	1.796	1.2×10^5	0.934
Kinetic constants										
	Pseudo-first order			Pseudo-second order			Intraparticle diffusion			
	K_{ad} (min^{-1})	q_e (mg/g)	R^2	q_e (mg/g)	K_2 (g/mg/min)	R^2	K_p ($\text{mgg}^{-1} \text{ min}^{-1}$)		R^2	
Pb(II)	0.013	7.04	0.968	6.94	5.14×10^{-4}	0.980	6.21		0.982	
Thermodynamic parameters										
	ΔG^0 (KJ/mol)			ΔH^0 (KJ/mol)			ΔS^0 (J/K/mol)			
	Pb(II)			15.2			61.5			
Pb(II)	- 5.2									

Sum of absolute errors (SAE)

$$SAE = \sum_{i=1}^n |q_{e,cal} - q_{e,exp}|_i \quad (7)$$

Average relative error (ARE)

$$ARE = \frac{100}{n} \sum_{i=1}^n \left| \frac{q_{e,cal} - q_{e,exp}}{q_{e,exp}} \right| \quad (8)$$

Hybrid fractional error function (HYBRID)

$$HYBRID = \sum_{i=1}^n \left[\frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,exp}} \right]_i \quad (9)$$

Marquardt's percent standard deviation (MPDS)

$$MPDS = \sum_{i=1}^n \left[\frac{q_{e,exp} - q_{e,cal}}{q_{e,exp}} \right]^2 \quad (10)$$

Analysis of the above five error functions suggests that applicability of the Freundlich and Langmuir isotherm models was better than the Temkin isotherm model (Singh *et al.* 2017; Dhiman & Sharma 2019a).

Kinetic studies

The equilibrium data obtained at pH 5 for Pb(II) ions have been analysed for kinetic studies using pseudo-first order (Equation (11)) and pseudo-second order (Equation (12)) rate equations:

$$\log(q_e - q) = \frac{\log q_e - k_{ad} X t}{2.303} \quad (11)$$

$$\frac{t}{q} = \frac{1}{K_2} \times \frac{1}{q_e^2} + \frac{t}{q_e} \quad (12)$$

where q_e and q (mg g^{-1}) are the amounts of metal ions adsorbed at equilibrium and at any time taken for study respectively, t (min) is the time of contact and k_{ad} is the adsorption rate constant (min^{-1}), K_2 is the equilibrium rate constant of pseudo-second order adsorption ($\text{gmg}^{-1} \text{min}^{-1}$). The values of kinetic constants are presented in Table 1. A straight-line plot obtained from plot of t/q_t vs. t indicates the applicability of pseudo-second order kinetics (Dhiman & Sharma 2019a).

The possibility of intraparticle diffusion was studied, using the Morris Weber model:

$$q = K_p \times t^{1/2} \quad (13)$$

where q is the amount of metal ions adsorbed at different time intervals (mg g^{-1}), K_p is the intraparticle diffusion constant ($\text{mg g}^{-1} \text{min}^{-1}$) and t is contact time (min.). K_p was calculated from the slope of the linear plot of q vs $t^{1/2}$ (Table 1). A straight-line plot has been obtained, which does not pass through the origin, indicating that intraparticle diffusion occurs but is not the rate determining step (Singh *et al.* 2017; Dhiman & Sharma 2019a).

Effect of temperature

In order to study the effect of temperature on the adsorption of Pb(II) ions using thiolated saw dust, adsorption capacity was determined at 25°, 30°, 35°, 40° and 45 °C. Results show that the adsorption capacity increases from 7.05 mg/g to 7.28 mg/g to 7.94 mg/g to 8.05 mg/g to 8.54 mg/g with increase in temperature from 298 to 303 K to 308 to 313 to 318 K, respectively. The increase in adsorption capacity with increase in temperature was observed due to the increase in the number of sorption sites

generated with breakage of some internal bonds near the active surface sites of adsorbent for each metal ion (Dhiman & Sharma 2016; Singh *et al.* 2017).

Thermodynamic studies

The thermodynamic parameters for the adsorption of Pb(II) ions have been determined using following equations:

$$\Delta G^{\circ} = -RT \ln K_c \quad (14)$$

$$\ln K_c = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \quad (15)$$

K_c is the equilibrium constant, T is the temperature (K) and R is the gas constant. The positive values of enthalpy change (ΔH°) and entropy change (ΔS°) (Table 1) suggest the endothermic nature of adsorption and increase in randomness at solid-solution interface during adsorption. The negative value of ΔG° indicates the feasible and spontaneous nature of adsorption (Singh *et al.* 2017; Dhiman & Sharma 2019a).

Effect of mutual interference in binary solutions

In order to study the effect of the presence of Co(II) ions on the amount of adsorbed Pb(II) ions using thiolated saw dust, batch studies have been undertaken for [Pb(II) + Co(II)] mixture by varying concentration ratios in the range 1:0, 1:1, 1:2, 1:3 and 1:4 for fixed Pb(II) ions concentrations of 30, 60 and 90 mg/L and the concentration of secondary metal ion was varied accordingly (Singh *et al.* 2017; Thakur *et al.* 2020). The pH of the solution was adjusted at 5, where maximum adsorption was obtained for both metal ions in single adsorption studies. A fixed amount of 250 mg of adsorbent was agitated with 10 mL each of the solution until equilibrium was attained at 120 minutes (Singh *et al.* 2017). Mahmood *et al.* (2017) also studied the removal of Cd(II) and Zn(II) using natural and modified biomass and maximum removal of approximately 90.1% was obtained using 0.5 g adsorbent at 5 mg/L concentration. Whereas in the present study a maximum removal of approximately 85–87% was obtained in single metal ions study using 0.25 g thiolated saw dust for 30 mg/L concentration of Pb(II) and Co(II) ions, which shows better efficiency of thiolated saw dust for very small adsorbent dosage.

For [Pb(II) + Co(II)] mixture, it has been observed that with increase in Co(II) ions concentration, the amount adsorbed of Pb(II) ions decreases from 2.90 to 1.47, 3.70 to 1.81 and 4.15 to 2.94 respectively for fixed Pb(II) ions concentration of 30, 60 and 90 mg/L for contact time of 120 minutes. The results suggest significant decrease in the uptake of Pb(II) ions in the presence of Co(II) ions. Similar results were obtained by Singh *et al.* (2017) for the competitive adsorption of manganese and iron using esterified saw dust as adsorbent.

The adsorption behaviour of the binary mixture of [Pb(II) + Co(II)] is shown in Figure 2. Maximum percentage removal of Pb(II) ions in mixture at pH 5 (i.e pH of maximum removal of Pb(II) ions in single component adsorption) for the fixed primary adsorbate concentration of 30 mg/L at 120 minutes. Equilibrium adsorption capacity for single component adsorption was found to be 2.90 mg/g for Pb(II) ions at fixed primary adsorbate concentration of 30 mg/L for the contact time of 120 minutes. With concentration ratios varying from 1:1, 1:2, 1:3 and 1:4 of [Pb(II):Co(II)], the amount of Pb(II) ions adsorbed decreases from 1.80 to 1.65 to 1.57 to 1.47 mg/g for fixed Pb(II) ions concentration of 30 mg/L, 2.45 to 2.12 to 2.05 to 1.81 mg/g for fixed Pb(II) ions concentration of 60 mg/L and 3.35 to 2.55 to 2.21 to 1.94 mg/g for fixed Pb(II) ions concentration of 90 mg/L at 120 minutes. Therefore, the binary adsorption data suggests that adsorption of primary adsorbate was strongly depressed in the presence of a secondary component when they are present together in the form of a binary set of metal ions (Singh *et al.* 2017; Dhiman & Sharma 2019b; Thakur *et al.* 2020).

For the analysis of adsorption equilibrium data obtained from the binary set of [Pb(II) + Co(II)], q'_e/q_e ratios have been determined, where q_e is the amount adsorbed for single component system at equilibrium and the prime denotes the equilibrium amount adsorbed in the presence of the other component (Singh *et al.* 2017; Dhiman & Sharma 2019b). The value of q'_e/q_e ratio was found to be 0.88, for [Pb(II) + Co(II)] mixture, for a fixed primary metal ion concentration of 30 mg/L for contact time of 120 minutes, where maximum removal was obtained. The $q'_e/q_e < 1$, which indicates the antagonistic behaviour of binary adsorption (i.e the effect of the mixture is less than that of the individual adsorbate in the mixture) (Dhiman & Sharma 2019b; Thakur *et al.* 2020).

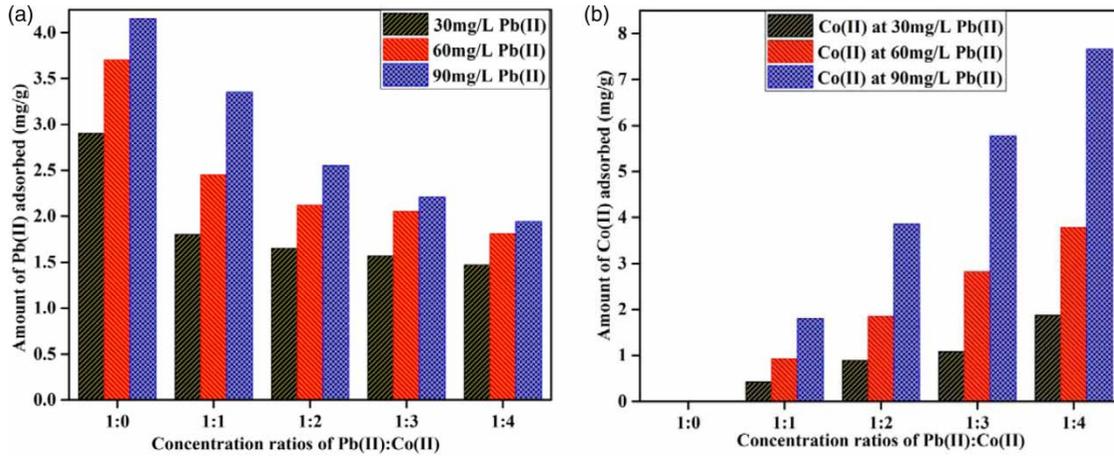


Figure 2 | Adsorption capacity of (a) Pb(II) ions in [Pb(II) + Co(II)] mixture (b) Co(II) ions in [Pb(II) + Co(II)] mixture at varying concentration ratios for contact time 120 min. at pH 5.

The Langmuir competitive model

Competitive adsorption of [Pb(II) + Co(II)] mixture, the Langmuir multicomponent isotherm (Singh *et al.* 2017; Dhiman & Sharma 2019b) has been applied to the binary sorption equilibrium data

$$\left(\frac{C_{e1}}{C_{e2}} \times q_{e1}\right) = \left(\frac{C_{e1}}{q_m} \times C_{e2}\right) + \left(\frac{K_{L2}}{K_{L1}} \times q_{e1}\right) \quad (16)$$

where K_{L1} and K_{L2} indicate the heat of adsorption, C_{e1} and C_{e2} are equilibrium concentrations and q_{e1} and q_{e2} are equilibrium adsorption capacity of Pb(II) and Co(II) ions in [Pb(II) + Co(II)] mixture (Singh *et al.* 2017), q_m is the maximum adsorption capacity corresponding to the primary adsorbate in the mixture (Figure 3). The values of Langmuir multicomponent isotherm parameters are $K_L = 0.040$ and $q_{m1} = 2.87$ mg/g.

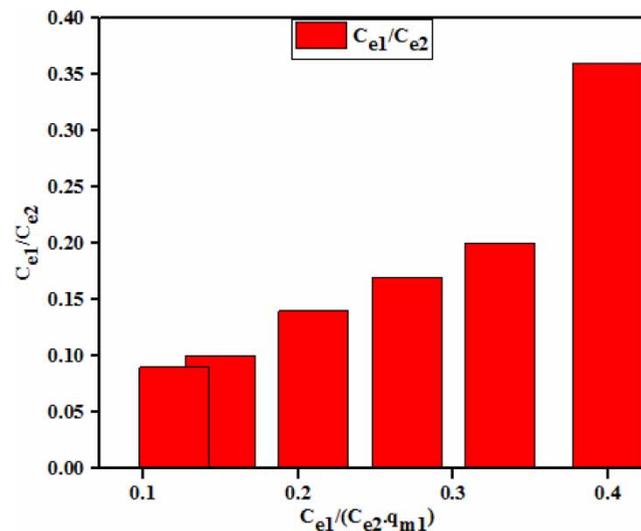


Figure 3 | Langmuir competitive model for [Pb(II) (C_{e1}) + Co(II) (C_{e2})], on thiolated saw dust for contact time 120 min. at pH 5, 298 K.

CONCLUSIONS

The data demonstrate the ability of thiolated sawdust as an effective, sustainable, and low-cost adsorbent for removal of lead ions due to high porosity and availability of functional sites. The equilibrium adsorption capacities evaluated for pure

component solution and binary mixtures show that chemical modification of the sawdust using thioglycolic acid enhances its adsorption capacity and were found to depend on the porous surface of the adsorbent and nature of the specific electrostatic interactions that are controlled by the solution pH. The application of the Langmuir multicomponent isotherm shows that the affinity of Pb(II) ions was depressed by the presence of Co(II) ions in the binary solution, hence the effect of the mixtures seemed to be antagonistic. The study also suggests that thiolated saw dust seems to be a good adsorbent for the simultaneous removal of both metal ions. Therefore, the present study highlights the future expectations of thiolated sawdust as a viable, cost effective and efficient bioadsorbent for the removal of heavy metal ion pollutants from wastewater in the pure form and multicomponent mixtures, specifically for small-scale industries.

ACKNOWLEDGEMENT

No funding has been provided for the research.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

- Alalwan, H. A., Kadhom, M. A. & Alminshid, A. H. 2020 Removal of heavy metals from wastewater using agricultural byproducts. *Journal of Water Supply: Research and Technology - AQUA* **69** (2), 79–112.
- Chikri, R., Elhadiri, N., Benchanaa, M. & El maguana, Y. 2020 Efficiency of sawdust as low-cost adsorbent for dyes removal. *Hindawi Journal of Chemistry* **2020**, 1–17.
- Cifci, D. I. & Meric, S. 2017 Single and binary adsorption of iron and manganese in synthetic water using activated pumice composites: effect of monovalent and divalent ions, desorption and reuse isotherms. *Desalination and Water Treatment* **71**, 52–61.
- Czikkely, M., Neubauer, E., Fekete, I., Ymeri, P. & Fogarassy, C. 2018 Review of heavy metal adsorption processes by several organic matters from wastewaters. *Water* **10** (1377), 1–15.
- Dhiman, N. & Sharma, N. 2016 Adsorption potential of ZnO nanoparticles for ofloxacin hydrochloride from aqueous solutions. *International Journal of Advanced Technology in Engineering and Science* **4**, 1–10.
- Dhiman, N. & Sharma, N. 2019a Removal of pharmaceutical drugs from binary mixtures by use of ZnO nanoparticles. *Environmental Technology & Innovation* **1**, 100392.
- Dhiman, N. & Sharma, N. 2019b Batch adsorption studies on the removal of ciprofloxacin hydrochloride from aqueous solution using ZnO nanoparticles and groundnut (*Arachis hypogaea*) shell powder: a comparison. *Indian Chemical Engineer* **61** (1), 67–76.
- Gupta, V. K., Nayak, A. & Agarwal, S. 2015 Bioadsorbents for remediation of heavy metals: current status and their future prospects. *Environmental Engineering Research* **20** (1), 1–18.
- Jain, M., Garg, V. K., Kadirvelu, K. & Sillanpaa, M. 2016 Adsorption of heavy metals from multi-metal aqueous solution by sunflower plant biomass-based carbons. *International Journal of Environmental Science and Technology* **13**, 493–500.
- Ketsela, G., Animen, Z. & Talema, A. 2020 Adsorption of lead (II), cobalt (II) and iron (II) from aqueous solution by activated carbon prepared from white lupine (GIBITO) HSUK. *Journal of Thermodynamics & Catalysis* **11**, 203. doi:10.4172/2157-7544.20.11.2.203.
- Mahmood, Z., Zahra, S., Iqbal, M., Raza, M. A. & Nasir, S. 2017 Comparative study of natural and modified biomass of *Sargassum* sp. for removal of Cd²⁺ and Zn²⁺ from wastewater. *Applied Water Science* **7**, 3469–3481.
- Okolo, B. I., Oke, E. O., Agu, C. M., Adeyi, O., Nwoso-Obieogu, K. & Akatobi, K. N. 2020 Adsorption of lead(II) from aqueous solution using Africa elemi seed, mucuna shell and oyster shell as adsorbents and optimization using Box–Behnken design. *Applied Water Science* **10**, 201. <https://doi.org/10.1007/s13201-020-01242-y>.
- Rashid, H. & Yaqub, G. 2017 Bioadsorbents and filters for removal of heavy metals in different environmental samples-a brief review. *National Environment and Pollution Technology* **16** (4), 1157–1164.
- Robert, R. J. & Girish, C. R. 2018 The removal of cobalt, nickel, cadmium and lead from wastewater using *Lantana camara* as adsorbent. *International Journal of Civil Engineering and Technology (IJCIET)* **9** (8), 292–303.
- Sharma, N., Kaur, K. & Kaur, S. 2009 Kinetic and equilibrium studies on the removal of Cd²⁺ ions from water using polyacrylamide grafted rice (*Oryza sativa*) husk and (*Tectona grandis*) saw dust. *Journal of Hazardous Materials* **163**, 1338–1344.
- Sharma, N., Singh, J. & Goyal, M. 2012 Studies on an economically viable treatment process for removal of Zn²⁺ ions from water using chemically modified rice (*Oryza sativa*) husk. In: *International Conference on Agricultural, Environment and Biological Sciences (ICAEB'S2012)*, pp. 34–38.
- Singh, J., Dhiman, N. & Sharma, N. K. 2017 Effect of Fe (II) on the adsorption of Mn (II) from aqueous solution using esterified saw dust: equilibrium and thermodynamic studies. *Indian Chemical Engineer* **60** (3), 255–268.
- Thakur, A., Sharma, N. & Mann, A. 2020 Removal of ofloxacin hydrochloride and paracetamol from aqueous solutions: binary mixtures and competitive adsorption. *Materials Today: Proceedings* **28**, 1514–1519.