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Sawdust: A green and economical sorbent for thallium removal

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Abstract

Removal/preconcentration of thallium(I) ions from aqueous solution by sawdust; a waste material derived from the commercial processing of Cedrus Deodar wood for furniture production was investigated. A simple and low-cost modification results in increasing the sorption capacity of raw sawdust from 2.71 to 13.18 mg g^{-1}. Sorption was found to be rapid (∼98% within 8 min). The binding of metal ions was found to be pH dependent, optimal sorption accruing at around pH 6–9. Potentiometeric titrations of sawdust revealed two distinct pK_a values, the first having the value similar to carboxylic groups (3.3–4.8) and second comparable with that of amines (8.53–10.2) with the surface site densities of 1.99×10^{-4} and 7.94×10^{-5} mol g^{-1}, respectively. Retained Tl(I) ions were eluted with 5 ml 0.1 mol l^{-1} HCl. Detection limit of 0.0125 μg ml^{-1} was achieved with an enrichment factor of 160. Recovery was quantitative using sample volume of 800 ml. The Langmuir, Freundlich and D–R isotherm equations were used to describe partitioning behavior for the system at different temperatures. Kinetic and thermodynamic behavior of sawdust for Tl(I) ions removal was also studied.
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Keywords: Sawdust; Thallium; Removal; Kinetics; Thermodynamics

1. Introduction

The presence of heavy metals in the environment poses a problem due to their harmful affects on human health. Thallium (Tl) is considered a non-essential and highly toxic element, which is produced as a by-product in the refining of iron, cadmium and zinc [1,2]. It is used as a catalyst in certain alloys, optical lenses, jewellery, low-temperature thermometers and semiconductors [2]. Industrial Tl poisoning is a special risk in the manufacture of fused halides for the production of lenses and windows. Thallium compounds, chiefly thallous sulfate, have also been employed as rat poison and insecticides [3]. These are the most common sources of human thallium poisoning.

The main toxicological effect of thallium includes GI irritation, acute ascending paralysis (Landry's paralysis), psychic disturbances, alopecia and acute cardiovascular effects [4]. The maximum contaminant levels of thallium in drinking water and wastewater (effluent) set by the United States Environmental Protection Agency (USEPA) are 2 and 140 μg l^{-1}, respectively. The environmental safe dose of thallium for human is 1.7 μg l^{-1} [5]. The acute cardiovascular effects of thallium ions probably result from competition in potassium for membrane transport systems, inhibition of mitochondrial oxidative phosphorylation and disruption of protein synthesis. It also alters heme metabolism [1].

Because of such toxic effects, the measurement of thallium in different types of samples for exposure monitoring and in order to determine the sources of contamination is very important. Therefore, it is important to develop an effective, fast, precise and accurate method for the determination/removal of the thallium in different materials. Flame atomic absorption spectrometry (FAAS) is largely utilized for the determination of metals, due to its inherent sensitivity [6], which may be improved by a preconcentration step.

During the past 15 years, extensive research has been conducted for the purpose of identifying new and economically priced sorbents for the removal and preconcentration of different metal ions. For example, material such as bone char [7], seaweed waste [8], algae [9], coal fly ash [10], yeast biomass [11], rice husk [12], spent grain [13], brown marine macroalgae [14], rice polish [15], peat biomass [16] and vegetable sponge [17] have been emerged as metal extractive sorbents. However, only a very few system such as silica gel [18] or Polyurethane Foam Modified with Molybdophosphate [19] have been emerged for

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sorption preconcentration of Tl. Among recently investigated sorbent materials, agriculture waste materials have attracted particular attention because such represents unused resources and in many cases, present their own disposal problems. Sawdust is one of the most appealing agricultural by-products that have been employed as a sorbent for removing heavy metals from water and wastewater [20].

The overall goal of this research was to characterize sawdust in order to establish an economical and environmental friendly method for the removal and preconcentration of thallium from aqueous matrices.

2. Materials and methods

2.1. Preparation of sorbent

Cedrus Deodar sawdust was obtained from local market (Hyderabad, Sindh, Pakistan) from furniture manufacturers and passed through a 25 mesh sieve. The sawdust was washed thoroughly with deionized water and was dried at 100 °C. The sorbent thus obtained was designated untreated sawdust. Caustic treated sawdust was prepared by mixing 5 g of sawdust with 50 ml of 1 mol l^{-1} NaOH for 2 h. Excess NaOH was removed with water and the material was dried at 100 °C for 8 h. The surface area of the fraction utilized, using BET method [21] was found to be ~400 cm^2 g^{-1}. Sawdust was analyzed for protein, crude fiber, acid detergent and ash content as per procedure [22].

2.2. Sawdust characterization

Surface site densities and acidity constants of the sawdust were determined using a batch acidimetric–alkalimetric titration method, similar to that described by Jianmin et al. [10] three S/L (Solid/Liquid) ratios 1/20, 1/10, and 1/5 were used. The sawdust mass was weighed individually for each 125-ml polyethylene bottle. For example, for the set of experiments with S/L ratio of 1:10, 10.00 g of sawdust and 100.0 ml of water solution containing 0.01 M $NaNO_3$ were added to each of the bottles. Next different amounts of 1 M (or 10 M) standard acid or base stock solution were added to different bottles to obtain a desired pH distribution over the pH range from 1 to 12. One bottle was used as a control unit, and its pH was not adjusted. After 24 h of shaking under closed conditions, the final pH values of the mixtures were measured and the data was analyzed by using protofit software.

2.3. Equilibrium metal adsorption

The metal adsorption behavior of treated and untreated sawdust was investigated using batch equilibrium experiments. A weighed amount of sorbent was equilibrated with the metal ion solution at constant pH (6), ionic strength (0.01 M) and temperature (20–40 °C) for 30 min. The sorbent was filtered and washed with deionized water. Metal ion desorption was achieved by subsequently mixing the solvent with HCl (0.1 M) solution and shaking. Concentrations of metal ions were determined by atomic absorption spectrometer both in equilibrated and desorbed solutions.

The following equations were used to calculate the percentage uptake (% sorption), the distribution ratio (R_d) and the separation factor (α):

$$\text{Sorption}\,(\%) = \frac{C_0 - C}{C_0} \times 100 \tag{1}$$

where C_0 and C are the initial and final metal ion concentrations in solution.

$$R_d = \frac{\text{amount of metal ions onto sawdust}}{\text{residual amount of metal ion in solution at equilibrium}} \times \frac{\text{volume of solution, } V\,(\text{ml})}{\text{mass of sawdust, } W\,(\text{g})} \tag{2}$$

$$\alpha = \frac{R_d(\text{thallium})}{R_d(\text{metal ion added})} \tag{3}$$

2.4. Adsorption kinetics

A 1 g mass of material was added to 22 flasks each containing 100 ml of thallium solution at a concentration of 10 mg/l and adjusted to optimum pH. The flasks were sealed and the mixtures agitated on an automatic thermostatic shaker (Gallenkamp BKS 305–010, UK) at a constant agitation speed of 100 rpm for the duration of the experiment. At designated times (0–30 min) a flask was taken off the shaker and the mixtures was filtered through a 0.45 mm filter paper and the filtrate was analyzed for thallium by AA.

2.5. Chemical analysis

A Varian Spectr AA-20 atomic absorption spectrometer was used to determine the thallium ion concentrations. All absorption measurements were performed under the following operating conditions: wavelength: 276.8 nm; slit setting: 0.5 nm; lamp current: 10 mA; flame: air/acetylene; acetylene flow rate: 3.2 l/min; air flow rate: 6.5 l/min. The pH measurements were made on calibrated digital (InoLab pH level I) pH meter equipped with a combination pH glass electrode. A Gallenkamp automatic shaker model BKS 305-010, UK was used for the batch experiments.

2.6. Data analysis

Protofit [23] software was employed to analyze the titration data and calculating pK_a values as well as surface site densities of the sawdust.

3. Results and discussions

3.1. Proton binding sites

Analysis of the sawdust indicated that it consists of 64.4% crude fiber, 30.4% acid detergent, 1.1% fiber (that contain cellulose and lignin) protein and 1.4% ash. All these components are

Table 1
Proton binding sites of sawdust

Site	Group	Portion of cell wall	pK_a range reported	pK_a values obtained for sawdust	Surface site densities (mol g^{-1})
01	Carboxylic	Peptidoglycan (peptide and muramic acid residue parts)	2–6	3.3–4.8	1.99×10^{-4}
02	Phospho-diesters; Phosphoric	Teichoic and linkage of teichuronic acids to peptidoglycan; Teichoic acid	3.2–3.5; 0.2–2.91; 5.65–7.20	6.6–7.0	2.5×10^{-5}
03–04	Amines; Hydroxyl	Peptidoglycan (peptide part); Peptidoglycan (muramic acid residue and possibly on peptide part)	9.0–11.0, 8–12, phenolic; 12–13, monosaccharide	8.53–10.20	7.94×10^{-5}

active ion exchanger due to the presence of amine, carboxylic moieties etc.

In order to identify possible metal binding sites, sawdust was treated with acid or alkali and the pK_a's determined (Table 1).

The most strongly acidic sites exhibited pK_a values of 3.3 and 4.8. These sites are in the range of values previously computed for model carboxylic compounds (pK_a 2–6, mean 4.5). Site 2 has pK_a values in the range of 6.6–7.0 and falls in the neutral range. The near neutral pK_a values are indicative of phosphoric group [24]. More basic pK_a values are observed for last two sites ranging from 8.53 to 10.20 that are suggestive of phenolic (pK_a 8–12, mean 10) or amine (pK_a 9–11) sites.

3.2. Sorption behavior of thallium ions on treated and untreated sawdust

The uptake of thallium ions onto pretreated and untreated sawdust as a function of pH is shown in Fig. 1. The general trend is similar for both types of sawdust. However, the amount adsorbed is significantly different ranging from 2.71 mg g^{-1} (untreated) to 13.18 mg g^{-1} (treated). This indicates that the pretreatment process can effectively stabilize the sawdust and enhances the sorption capacity. It was observed that the settling property of the pretreated sawdust was also much improved allowing for easier separation of the sorbent from the solution. This property is highly desirable in practical application. Fig. 1 shows the uptake of Tl(I) ions from a 4.9×10^{-5} M solution after 10 min as a function of pH. The amount of Tl(I) removed from solution increased with an increase in the pH range of 2–5 after which it leveled off and become constant (Fig. 1). This behavior can be explained by taking into account the pK_a values (Table 1). At pH values less than 3, the carboxylic groups become protonated and thus are no longer available to attract metal ions from solution. When the pH is greater than 4, the carboxyl groups are de-protonated and therefore negatively charged and able to bind the positively charged thallium ions. Thallium is present in the form of Tl^+ (≈100%) up to pH 8 [25].

3.3. Kinetics of sorption

The sorption of thallium ions on sawdust is very fast. A period of less than 10 min was sufficient to attain equilibrium. The kinetics of thallium sorption on sawdust was analyzed by the Lagergren [26,27] and Morris–Weber equation. The sorption of Tl(I) ions onto sawdust is evaluated by subjecting the data to the linear form of equation:

$$\ln(q_e - q_t) = \ln q_e - kt \quad (4)$$

where k is the first-order rate constant of sorption, q_e is the amount of metal ions sorbed at equilibrium and q_t is the amount of Tl(I) ions sorbed at time t. The linear fit of $\ln(q_e - q_t)$ versus t was obtained up to 7 min (see Fig. 2), indicates that the kinetics

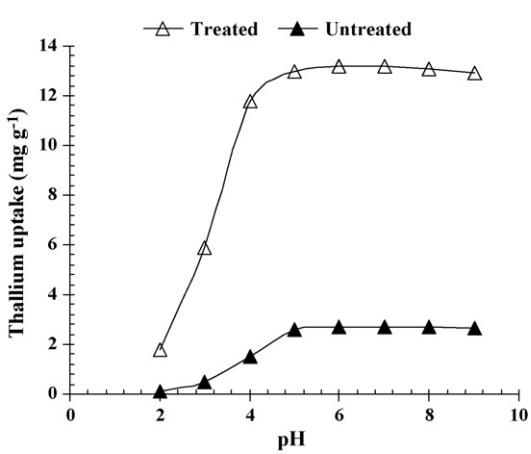

Fig. 1. Thallium ion uptake onto untreated and treated sawdust.

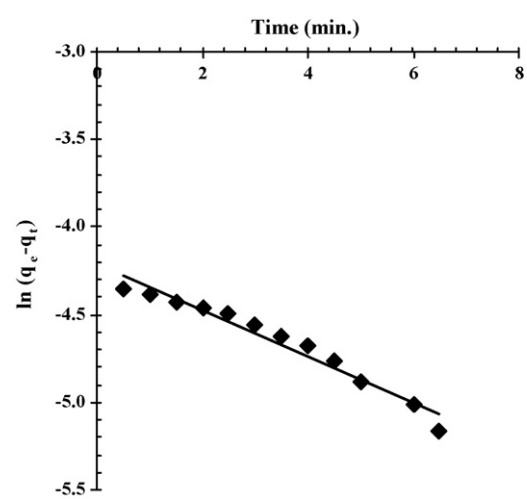

Fig. 2. Lagergren plot for the sorption of Tl(I) onto treated sawdust.

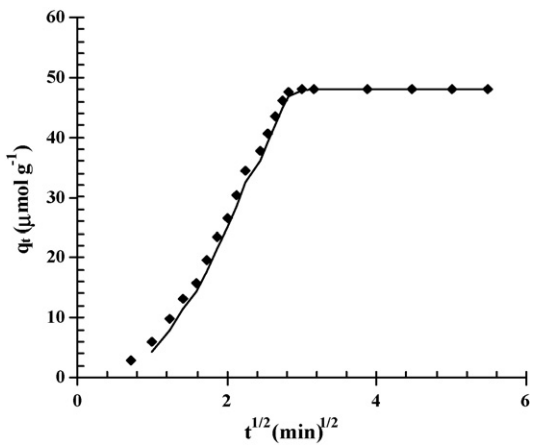

Fig. 3. Morris–Weber plot for the sorption of Tl(I) onto treated sawdust.

of sorption is first-order. The value of k calculated from slope and regression analysis is $0.14 \pm 0.09\ \text{min}^{-1}$. Beyond 7 min the sorption data does not follow the Lagergren equation and gives very steep slope. The data was also analyzed using the Morris–Weber equation [28]:

$$q_t = R_{\text{idr}}\sqrt{t} \tag{5}$$

where R_{idr} is the intra-particle diffusion rate constant and q_t is the amount of Tl(I) sorbed at time t. The equation fits the data only in the range of 1–8 min (see Fig. 3), which indicates the partial intra-particle diffusion. The value of R_{idr} was $22.59 \pm 0.745\ \mu\text{mol g}^{1}\ \text{min}^{-1/2}$.

3.4. Effect of metal ion concentration

Results of the equilibrium adsorption isotherms for Tl(I) at different temperatures in the range of 4.9×10^{-3} to $8.9 \times 10^{-9}\ \text{mol l}^{-1}$ using 200 mg sorbent with 8 min shaking (70 rpm) are shown in Fig. 4. The initial rapid sorption gives way to a slow approach to equilibrium at higher sorbate concentrations. The uptake of metal ion is 88–99% at low concentrations and 36–52% at higher concentrations. The uptake decreases

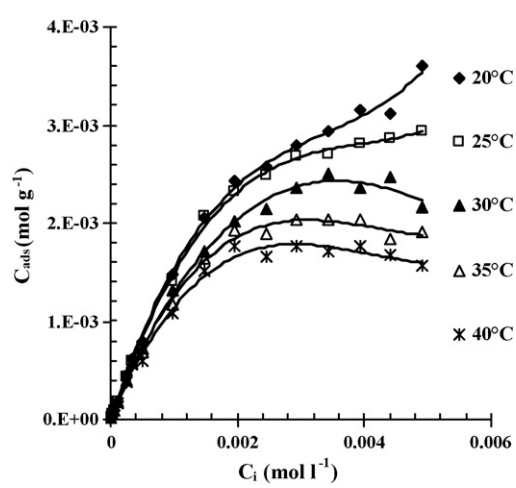

Fig. 4. Effect of concentration on the sorption of Tl(I) onto treated sawdust at different temperatures.

with an increase in temperature thereby indicating the process is exothermic. Thus sorption behavior of Tl^+ on sawdust were analyzed in terms of the Langmuir:

$$\frac{C_e}{C_{\text{ads}}} = \frac{1}{Qb} + \frac{C_e}{Q} \tag{6}$$

Freundlich:

$$\log C_{\text{ads}} = \log A + \frac{1}{n}\log C_e \tag{7}$$

and Dubinin–Radushkevich:

$$\ln C_{\text{ads}} = \ln X_m - \beta\varepsilon^2 \tag{8}$$

where

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{9}$$

equations, where C_{ads} is the amount of metal ions sorbed per unit mass of sawdust and C_e is the amount of metal ions in the liquid phase at equilibrium. Q ($\mu\text{mol g}^{-1}$), b (l g^{-1}), A ($\mu\text{mol g}^{-1}$), $1/n$, X_m ($\mu\text{mol g}^{-1}$), and β ($\text{mol}^2\ \text{g}^{-1}\ \text{kJ}^{-1}$) are the Langmuir, Freundlich and D–R constants, respectively [29]. The Freundlich, Langmuir, and D–R constant were evaluated from the slopes and intercepts of linear plots. The results are summarized in Table 2. One essential characteristic of the Langmuir treatment is the dimensionless constant separation factor (R_L), calculated from the equation $R_L = 1/(1 + bC_i)$ where C_i is the initial concentration of the metal ion. R_L describes the type of Langmuir isotherm [30,31], which can be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The values of R_L calculated in this work were between 0.2 and 0.99 (Table 3), indicating favorable sorption of Tl(I) ions onto sawdust at all temperatures. The free energy of transfer (E) of one mole of solute from infinity (in solution) to surface of sawdust was evaluated from the slope (β) of the D–R curve using the equation $E = 1/\sqrt{-2\beta}$ is (11.93–11.38) kJ mol^{-1} which falls in the range of 9–16 kJ mol^{-1} previously suggested for metal sorption due to ion exchange [32,33]. Hence, it is very likely that the thallium ions are sorbed on sawdust predominantly by an ion-exchange mechanism. The numerical value of Freundlich constant $1/n < 1$ shows that sorption capacity is only slightly suppressed at lower equilibrium concentrations.

3.5. Thermodynamics of sorption

The dependence on temperature of sorption of the thallium on sawdust was evaluated using the equations:

$$\ln K_c = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \tag{10}$$

and

$$\Delta G = -RT \ln K_c \tag{11}$$

where K_c is the equilibrium constant $= F_e/(1 - F_e)$, F_e the fraction sorbed ion at equilibrium, ΔH, ΔS, ΔG, and T the enthalpy, entropy, Gibbs free energy, and absolute temperature, respectively and R is the gas constant. A plot of $\log K_c$ against

Table 2
The Langmuir, Freundlich and D–R constant for sorption of Tl(I) ion onto sawdust at different temperatures

Temperature (°C)	Langmuir				Freundlich			D–R			
	Q (μmol g^{-1})	$b \times 10^3$ (l g^{-1})	R_L	r	A (μmol g^{-1})	$1/n$	r	X_m (μmol g^{-1})	E (kJ mol^{-1})	$\beta \times 10^{-3}$ (mol^2 g^{-1} kJ^{-1})	r
20	3.40 ± 0.128	5.41 ± 1.5	0.94–0.036	0.990	67.76 ± 9.7	0.481 ± 0.062	0.945	7.17 ± 0.27	11.38 ± 0.07	−3.86 ± 0.05	0.997
25	2.99 ± 0.068	6.06 ± 1.2	0.94–0.032	0.996	60.25 ± 8.9	0.481 ± 0.064	0.948	6.04 ± 0.35	11.53 ± 0.11	−3.76 ± 0.07	0.996
30	2.41 ± 0.071	7.13 ± 2.5	0.93–0.027	0.994	50.12 ± 8.1	0.484 ± 0.069	0.954	5.52 ± 0.34	11.56 ± 0.13	−3.74 ± 0.08	0.992
35	2.00 ± 0.046	8.66 ± 3.0	0.92–0.023	0.996	39.8 ± 7.4	0.473 ± 0.081	0.958	4.75 ± 0.29	11.77 ± 0.14	−3.61 ± 0.09	0.995
40	1.72 ± 0.045	9.11 ± 4.0	0.91–0.021	0.995	31.84 ± 6.6	0.466 ± 0.090	0.965	4.13 ± 0.29	11.93 ± 0.17	−3.51 ± 0.1	0.988

Table 3
Sorption of other metal ions on sawdust

Metal ion	Separation factor (α)
Ag(I)	5903
Al(III)	51721
Ca(II)	4244
Cd(II)	436
Co(II)	1455
Cr(III)	1809
Cr(VI)	1021
Cu(II)	744
Fe(II)	11067
Fe(III)	998.7
Li(I)	8082
Mg(II)	5035
Ni(II)	998
Pb(II)	1809
Zn(II)	1372

$1/T$ gives the numerical values of $\Delta H = -54.2 \pm 6.5$ kJ mol^{-1} and $\Delta S = -158 \pm 20$ J mol^{-1} K^{-1} from the slope and intercept, respectively. The negative values of ΔH and ΔG show the exothermic and spontaneous nature of reaction. The Gibbs free energy was determined to be -7.34 ± 1.1 kJ mol^{-1}.

3.6. Effect of concomitant ions

The selectivity of the technique for extraction of Tl(I) ions in aqueous solutions was determined under optimized conditions selected for the sorption. The effect was observed for ratios of 1:50 and 1:10 for anions and cations, respectively. The results are presented in Table 3, with the separation factors (α) for the metal ions, which is the ratio of the distribution ratios of two extractable solutes measured under the same conditions. The sorption of all metal ions examined was much less efficient than for Tl(I), especially Ag, Al, Ca, Cr(VI), Fe(II), Li and Mg. The difference in affinity of sawdust towards other metal ions can provide foundation for the effective separation of these ions from aqueous solutions. The value of separation factor 'α' for Ag, Al, Ca, Fe(II) and Li is >2000. Therefore, it is deduced from the results that these metal ions can be easily separated from Tl(I), using sawdust. In the case of anions the chloride reduces the sorption of Tl(I) to some extant. The reduction in % sorption in the presence of chloride may be due the formation of complexes of Tl(I) with chloride. The strong complexes of Tl(I) with chloride are reported in literature [25]. The anions acetate, bicarbonate,

Table 4
Cost analysis of thallium removal methods

Method	Estimated cost (USD)	References
Iron powder	137.638 for 1 dm^3 of water	[34]
Al_2O_3	81.321/kg	USEPA BAT http://www.epa.gov [a]
Calcium alginate beads	1705.51/kg	[35]
Present methods	24.5/kg	

[a] United States Environmental Protection Agency's best available technology.

carbonate, citrate, sulfate and sulfide did not interfere with Tl^+ sorption at the ratios investigated.

4. Cost comparison

Cost of some available thallium removal methods is given in Table 4. In comparison to available methods, present method is 3.3 to 71 times cheaper.

5. Conclusion

This study demonstrates the use of a waste material, sawdust for the extraction and preconcentration of toxic Tl(I) metal ions. The main advantages of procedure include: ease and simplicity of preparation of the sorbent, sensitivity, and rapid attainment of phase equilibration and good enrichment factor. The sorption kinetics follows a first-order rate equation. The negative value of ΔH and ΔG indicate the exothermic and spontaneous nature of sorption. Study shows that the sawdust has the ability to preconcentrate/remove Tl(I) from complex matrices.

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