

Sawdust—A green and economical sorbent for the removal of cadmium (II) ions

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Received 8 April 2006; received in revised form 2 June 2006; accepted 6 June 2006

Available online 10 June 2006

Abstract

The ability of sawdust (treated and untreated) waste, a waste material derived from the commercial processing of cedrus deodar wood for furniture production, to remove/preconcentrate Cd(II) ions from aqueous solution was determined. Sorption was found to be rapid (~97% within 8 min). The binding of metal ions was found to be pH dependent, optimal sorption accruing at around pH 4–8. Potentiometric 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 densities 1.99×10^{-4} and 7.94×10^{-5} , respectively. Retained Cd(II) ions were eluted with 5 ml of 0.1 mol l^{-1} HCl. Detection limit of $0.016 \mu\text{g ml}^{-1}$ was achieved with enrichment factors of 120. Recovery was quantitative using sample volume of 600 ml. The Langmuir and D–R isotherm equations were used to describe partitioning behavior for the system at different temperatures. Kinetic and thermodynamic behavior of sawdust for Cd(II) ions removal was also studied.

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Keywords: Sorption; Cadmium; Sawdust; Kinetics; Thermodynamics

1. Introduction

The presence of heavy metals in environment becomes a problem due to their harmful affects on human health.

Cadmium is considered as a non-essential and highly toxic element [1,2] possibly because it forms a strong bond with sulfur and hence can displace essential metals, i.e. Zn^{2+} and Ca^{2+} from the binding sites of certain enzymes [3]. A provisional maximum tolerable daily intake of cadmium from all sources is $1\text{--}1.2 \mu\text{g kg}^{-1}$ body mass [4] is recommended by FAO–WHO jointly. Cadmium may occur in substantial concentrations in hydrosphere due to discharge of wastewaters, especially of plating wastes [5]. Because of very toxic effects, its removal from hydrosphere and measurement in body fluids for exposure monitoring and in different kind of samples in order to know 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 cadmium in biological and environmental materials. Flame atomic absorption spectrometry (FAAS) is largely used for the determination of metals, showing good selectivity but low detectability, which may be improved by a preconcentration step. Several methods for the preconcentration have been developed, enhancing the detectability of the instrumental analytical techniques.

In the past 15 years, extensive research has been carried out to identify new and economically priced sorbents for cadmium ions removal/preconcentration such as bone char [6], seaweed waste [7], algae [8], coal fly ash [9], yeast biomass [10], rice husk [11], spent grain [12], brown marine macroalgae [13], rice polish [14] and sawdust [15,16]. Among these recently investigated adsorbent materials agriculture waste material have attracted particular attention because these waste represents unused resources and in many cases, present serious disposal problems. Sawdust is one of the most appealing agricultural waste materials for removing heavy metals from water and waste water [17].

The overall goal of this research was to characterize sawdust in order to establish an economical method for the removal and preconcentration of cadmium.

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2. Materials and methods

2.1. Materials

All chemicals used were of analytical or equivalent grade. Stock standard solution of Cd(II) has been prepared by dissolving the appropriate amount of its nitrate in deionized water (conductivity 0.5 mS cm^{-1} and pH 6), acidified with the small amount of nitric acid. Buffer solutions of pH 1–3, 4–6 and 7–9 were prepared by mixing appropriate ratios of 0.1 M HCl and KCl, 0.5 M acetic acid and sodium acetate and 0.5 M ammonia and NH_4Cl solutions, respectively.

2.2. Preparation of sorbent

Deodar Cedrus sawdust was obtained from local market (Hyderabad, Sindh) 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 of 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 [18] is found to be $\sim 400 \text{ cm}^2 \text{ g}^{-1}$. The analysis of sawdust for the determination of protein, fiber, dry matter and ash was carried out as per procedure reported in literature [19]. The results are cited in Table 1.

2.3. Batch titration

Surface site densities and acidity constants of the sawdust were determined through a batch acidimetric–alkalimetric titration method. Three S/L (solid sorbent/liquid) ratios 1/20, 1/10, and 1/5 were used. The procedure was similar to that described by Jianmin et al. [9]. 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. Different amounts of 1 M (or 10 M) standard acid or base stock solution were added to different bottles to obtain a desired pH values in the pH range from 2 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 software, ProtoFit.

Table 1
Proximate analysis of sawdust in percent

| | |
|----------------------|------|
| Dry matter | 97.5 |
| Crude fiber | 64.4 |
| Acid detergent fiber | 30.4 |
| Crude protein | 1.1 |
| Ash | 1.4 |

2.4. Equilibrium metal adsorption experiments

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 maintained at constant pH, ionic strength and temperature. The sorbent was filtered and washed with deionized water. The sorbed metal ions were desorbed by shaking with HCl. Concentration of metal ions were determined both in equilibrated and desorbed solution.

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

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

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

$$\alpha = \frac{R_d \text{ (cadmium)}}{R_d \text{ (metal ion added)}},$$

where C_0 and C are the initial and final concentrations, respectively, of metal ions in solution and R_d the distribution ratio.

2.5. Chemical analysis

A Varian Spectr AA-20 atomic absorption spectrometer was used to determine cadmium concentrations in the solution. The pH measurements were made on digital (InoLab pH level I) pH meter equipped with a combined pH glass electrode. Before measurements the pH meter was calibrated with the buffers of pH 4, 7 and 9. A Gallenkamp automatic shaker model BKS 305–010, UK is used for the batch experiments.

2.6. Data analysis

ProtoFit [20], software with the ability to calculate pK_a values from titration data were used to determine pK_a values and surface site densities of sawdust.

3. Results and discussions

3.1. Proton binding sites in sawdust

The cell wall of sawdust mainly consists of crude fiber, acid detergent fiber (containing cellulose and lignin), and many hydroxyl groups, such as tenins and other phenolic compounds (Table 1). All those components are active ion exchange compound [17]. Lignin, the third major component of the wood cell wall is a polymer material. Lignin molecule is built from the phenylpropane nucleus. The lignin content of hardwood is usually in the range of 18–25%, whereas that of soft wood varies between 25% and 35%. In order to identify possible dissociation

Table 2
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) |
|------|------------------------------|---|---|---|---|
| 1 | Carboxylic | Peptidoglycan (peptide and muramic acid residue parts) | 2–6 | 3.3–4.8 | 1.99 × 10 ⁻⁴ |
| 2 | 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 |
| 3–4 | 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 |

constants of groups responsible for metal binding a sample of sawdust was treated with acid or alkali.

The four site model results are shown in Table 2. The most strongly acidic sites determined here have pK_a values of 3.3 and 4.8. These sites are in the range of values determined for model carboxylic compounds (pK_a 2–6, mean 4.5). Site 2 has pK_a values between 6.6 and 7.0 falls in the neutral range. The near neutral pK_a values are generally ascribed to phosphoric site [21]. More basic pK_a values are observed for last two sites ranging from 8.53 to 10.20, which are similar to phenolic sites (pK_a 8–12, mean 10) or amines (pK_a 9–11).

3.2. Sorption of cadmium on treated and non-treated sawdust

The uptake of metal ions onto pretreated and non-treated sawdust as a function of pH is shown in Fig. 1. The general trend is similar for both treated and non-treated sawdust. However, the amount adsorbed is significantly different. This indicates that the pretreatment process can effectively stabilize the sawdust. It was also observed that the settling property of the pretreated sawdust was much improved making it easy to separate the adsorbent

from the solution. This property is desirable in practical application. Therefore, the sorption potential, thermodynamic and kinetic behavior of pretreated sawdust for the removal of cadmium was further evaluated.

Fig. 1 shows the removal of Cd(II) metal ions from 8.9 × 10⁻⁵ mol l⁻¹ solution after 10 min at solution pH values 2–9. The optimal removal accrued at pH 5. The least metal ions were removed when the solution pH was maintained at 2. This behavior can be explained by taking into account the pK_a value (Table 2) of 3.3–4.8. This means when the pH is higher than 4 the carboxyl groups are deprotonated and therefore negatively charged and able to bind positively charged metal ions. The main species of Cd(II) is Cd²⁺ (~100) up to pH 8 [22]. Therefore at pH 5 cadmium precipitation as hydroxide is not a possible retention mechanism. At pH values less than 3, the carboxylic groups become protonated and thus are no longer available to attract metal ions from solution. Percent sorption of cadmium decreases about 4% at pH value above 8 this slight decrease (~4%) in sorption after pH 8 may be due to the hydrolysis of metal ions as at pH 9 Cd(II) forms Cd(OH)⁺ (~3%) [22].

3.3. Limit of detection and preconcentration factor

To explore the possibility of enriching low concentrations of analyte from large volumes the maximum applicable sample volume must be determined. For this purpose different volume of sample solution, each containing 10 μg of Cd(II) ions were equilibrated with sawdust under the optimum conditions (2 g sawdust and shaking speed of 70 rpm) and recovery were calculated after desorbing the metal ion with 5 ml of 0.1 mol l⁻¹ HCl. Recovery was found quantitative using a 600 ml sample volume. As the adsorbed Cd(II) ions can be eluted with 5 ml of HCl, so the enrichment factors achieved was 120 (600/5) with the detection limit of 0.016 μg ml⁻¹.

3.4. Kinetics of sorption

The kinetic of sorption of cadmium ions on sawdust was determined under optimum (pH, shaking speed, etc.) experimental conditions and was found to be very fast (Fig. 2). The period of less than 10 min was sufficient to attain equilibrium. The kinetics of cadmium on sawdust was subjected to different equations namely, Lagergren and Morris–Weber. The order of the sorption of Cd(II) ions onto sawdust is evaluated by sub-

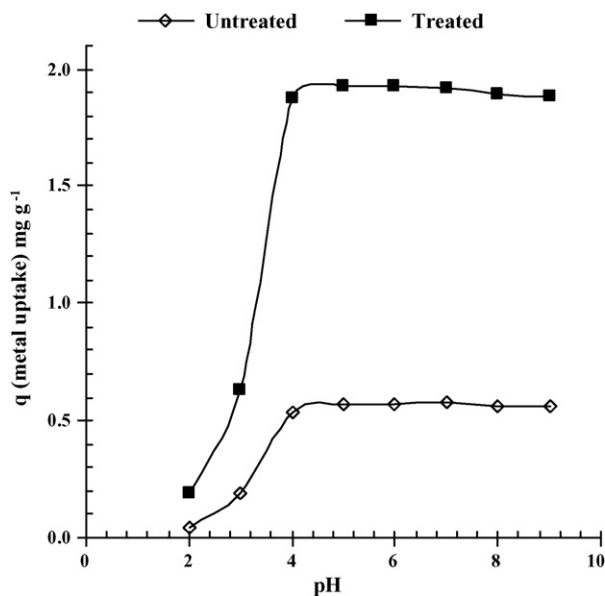


Fig. 1. Cd(II) ions uptake as a function of pH on treated and untreated sawdust.

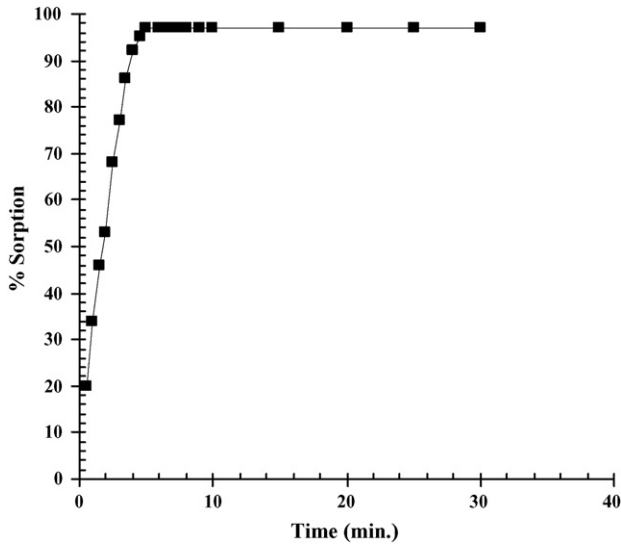


Fig. 2. Cd(II) ions sorption as function of time.

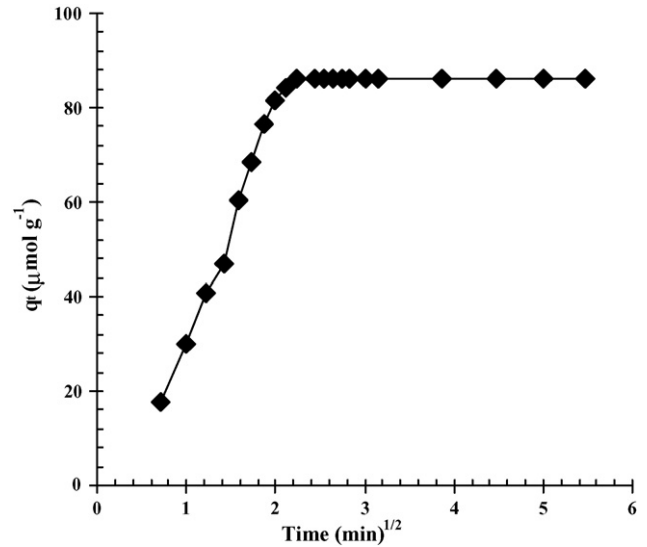


Fig. 4. Morris–Weber plot for the sorption of Cd(II) ions onto treated sawdust.

jecting the data to the linear form of Lagergren equation [23]:

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

where k is the first order rate constant of sorption and q_t the sorbed concentration of Cd(II) ions at time t ($\mu\text{mol g}^{-1}$). The linear fit of $\ln(q_e - q_t)$ versus t shown in Fig. 3 indicates the kinetic of sorption is of first order. The value of k , the first order rate constant was found to be $0.74 \pm 0.08 \text{ min}^{-1}$ from slope. The data is applied to the Morris–Weber equation [24]:

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

where R_{idr} is the intra-particle diffusion rate constant and q_t the amount of metal ions sorbed at time t . The linearity applies only in the range of 1–5 min as designated in Fig. 4, which indicates the partial intra-particle diffusion. The value of R_{idr} comes out to be $48.09 \pm 1.848 \mu\text{mol g}^{-1} \text{ min}^{-1/2}$.

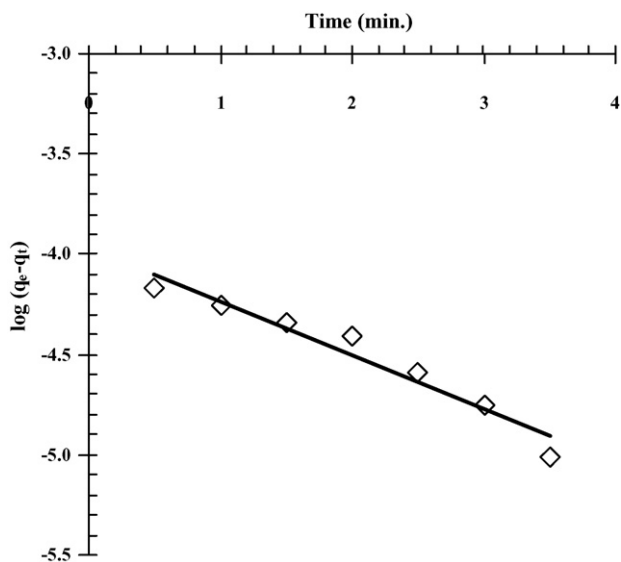


Fig. 3. Lagergren plot for the sorption of Cd(II) ions on treated sawdust.

3.5. Effect of metal ion concentration and temperature

Results of the equilibrium adsorption isotherms for Cd(II) at different temperatures in the range of concentration from 8.9×10^{-3} to $8.9 \times 10^{-9} \text{ mol l}^{-1}$ at pH 5 using 200 mg sorbent and 8 min shaking time at a shaking speed of 70 rpm are shown in Fig. 5. The sorption is rapid at lower sorbate concentrations and become slower at higher sorbate concentrations. The uptake of metal ion is 92–99% at low concentrations and 14–51% at higher concentrations. These results reflected the efficiency of sawdust for the removal of cadmium from aqueous solution in a wide range of concentration. The uptake decreases with an increase in temperature thereby indicating the process to be exothermic in nature. The effects of tested metal ion concentrations on sawdust were also analyzed in terms of Langmuir $[(C_e/C_{\text{ads}}) = (1/Qb) + (C_e/Q)]$ and Dubinin–Radushkevich $[\ln C_{\text{ads}} = \ln X_m - \beta \varepsilon^2, \text{ where } \varepsilon = RT \ln(1 + (1/C_e))]$ equa-

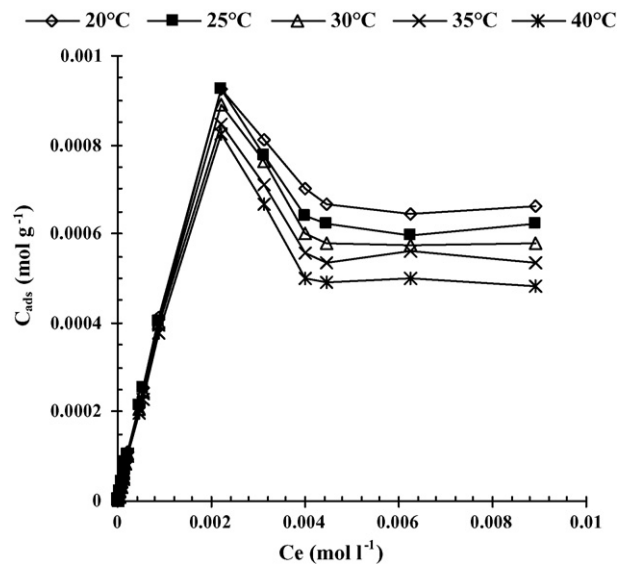


Fig. 5. Sorption as a function of concentration of Cd(II) ions and temperature.

Table 3
The Langmuir and D–R constant for sorption of Cd(II) ion onto sawdust at different temperatures

| Temperature (°C) | Langmuir | | | | D–R | | | |
|------------------|-----------------------------|---|------------|-------|-------------------------------|-----------------------------|--|-------|
| | Q (mmol g ⁻¹) | b ($\times 10^4$ l g ⁻¹) | R_L | r | X_m (mmol g ⁻¹) | E (kJ mol ⁻¹) | β ($\times 10^{-3}$ mol ² g ⁻¹ kJ ⁻¹) | r |
| 20 | 0.655 ± 0.0092 | 9.73 ± 3.0 | 0.92–0.001 | 0.998 | 2.196 ± 0.40 | 11.20 ± 0.28 | -3.98 ± 0.201 | 0.983 |
| 25 | 0.612 ± 0.0107 | 5.84 ± 1.4 | 0.95–0.019 | 0.997 | 2.03 ± 0.35 | 11.41 ± 0.27 | -3.84 ± 0.187 | 0.981 |
| 30 | 0.575 ± 0.0103 | 6.09 ± 1.5 | 0.94–0.001 | 0.997 | 1.84 ± 0.32 | 11.51 ± 0.27 | -3.77 ± 0.181 | 0.986 |
| 35 | 0.536 ± 0.0124 | 5.20 ± 0.52 | 0.95–0.002 | 0.995 | 1.66 ± 0.26 | 11.72 ± 0.26 | -3.64 ± 0.167 | 0.983 |
| 40 | 0.494 ± 0.0126 | 4.58 ± 1.33 | 0.96–0.002 | 0.994 | 1.43 ± 0.20 | 11.96 ± 0.25 | -3.5 ± 0.148 | 0.985 |

tions, where C_{ads} is the amount of metal ions sorbed per unit mass of sawdust and C_e the amount of metal ions in the liquid phase at equilibrium. Q , b , X_m , and β are the Langmuir, and D–R constants, respectively. The Langmuir, and D–R constant were evaluated from the slopes and intercepts of linear plots. The results are listed in Table 3. The essential characteristic of the Langmuir isotherm can be explained in terms of a dimensionless constant separation factor (R_L), calculated by use of the equation $R_L = 1/(1 + bC_i)$, where C_i is the initial concentration of metal ions. R_L describes the type of Langmuir isotherm [25] to 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 were between 0.2 and 0.99 (Table 3), indicating highly favorable sorption of Cd(II) ions on sawdust at all temperatures. The value of E 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 are in the range of 9–16 kJ mol⁻¹ which indicates the sorption to be ion exchange [26,27] in nature. Hence, it is very likely that the cadmium ions are sorbed on sawdust predominantly by ion-exchange mechanism.

3.6. Thermodynamics of sorption

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

$$\ln K_C = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad \text{and} \quad \Delta G = -RT \ln K_C$$

where ΔH , ΔS , ΔG , and T are the enthalpy, entropy, Gibbs free energy, and absolute temperature, respectively, R the gas constant and K_C the equilibrium constant. Plot of $\log K_C$ against $1/T$ (Fig. 6) gives the numerical values of $\Delta H = -42.19 \pm 4.5$ and $\Delta S = -158 \pm 20$ from the slope and intercept, respectively. The negative values of ΔH and ΔG show the exothermic and spontaneous nature of reaction. Gibbs free energy calculated was -7.34 ± 1.1 .

3.7. Effect of concomitant ions

The selectivity of the technique for extraction of Cd(II) ions in water was measured 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 for cations are presented in Table 4, with the separation factors for the metal ions. For all the metal ions sorption was less efficient than for

Cd(II), especially Al, Cr(VI), Fe(II), Ag, and Mg. It is deduced from the results that these metal ions can be easily separated from Cd(II), using sawdust. For Cd(II) ions there is no interference from common anions such as acetate, bicarbonate, biphosphate, bromide, carbonate, citrate, sulfate, and sulfide except fluoride investigated in this work. Fluoride reduces the sorption up to 15%, which can be tolerated using 1:25 concentration ratio.

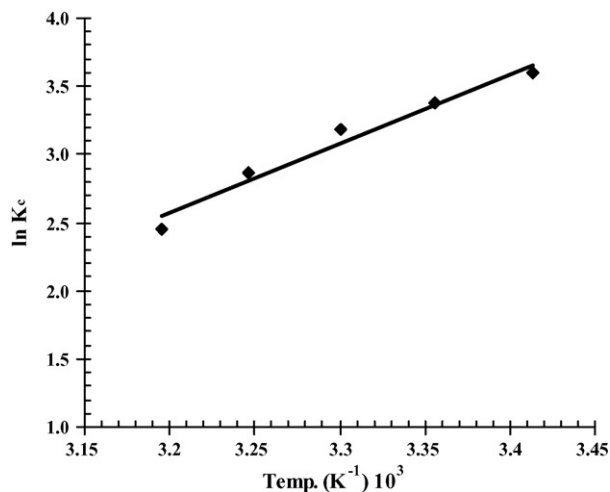


Fig. 6. Effect of temperature on sorption of Cd(II) ions.

Table 4
Sorption of other metal ions on sawdust

| Metal ion | α |
|-----------|----------|
| Ag(I) | 243 |
| Al(III) | 11110 |
| As(III) | 20.45 |
| Ca(II) | 182 |
| Co(II) | 69.0 |
| Cr(III) | 81.6 |
| Cr(VI) | 1090 |
| Cu(II) | 43.5 |
| Fe(II) | 1695 |
| Fe(III) | 52.8 |
| Hg(II) | 81.66 |
| Li(I) | 513.8 |
| Mg(II) | 225.7 |
| Ni(II) | 52.8 |
| Pb(II) | 81.6 |
| Zn(II) | 66.1 |

Table 5
Determination of cadmium in environmental water samples

| Water sample | Added amount (μg) | Found ($\mu\text{g g}^{-1}$) ^a | % Recovery |
|--------------|--------------------------------|---|------------|
| Surface | 0.0 | 0.123 | 100 |
| | 2.0 | 2.123 | |
| Surface | 0.0 | 0.06 | 100 |
| | 2.0 | 2.06 | |
| Surface | 0.0 | 0.088 | 99.9 |
| | 2.0 | 2.087 | |
| Ground | 0.0 | 0.063 | 99.9 |
| | 2.0 | 2.061 | |
| Ground | 0.0 | 0.047 | 99.8 |
| | 2.0 | 2.044 | |
| Ground | 0.0 | 0.028 | 99.7 |
| | 2.0 | 2.023 | |
| Ground | 0.0 | 0.038 | 100 |
| | 2.0 | 2.02 | |
| Ground | 0.0 | 0.034 | 99.1 |
| | 2.0 | 2.033 | |
| Ground | 0.0 | 0.029 | 96.6 |
| | 2.0 | 2.020 | |
| Ground | 0.0 | 0.051 | 100 |
| | 2.0 | 2.051 | |

^a Average of three determinations.

4. Removal of Cd(II) ions from water samples

The efficiency of sawdust for the removal of Cd(II) ions from environmental water samples was tested. The samples were obtained from Sindh, Pakistan. A 100 ml aliquot of water sample was adjusted at optimum pH and equilibrated with the sawdust (at optimum conditions). Another 100 ml aliquot of sample was spiked with 2.0 μg of Cd(II) and then treated with sawdust as per procedure discussed. The metal ions were eluted with 0.1 mol l⁻¹ HCl and determined by AAS. The results are given in Table 5, which shows the suitability of sawdust for preconcentration and removal of cadmium environmental water samples.

5. Conclusion

This study presents the use of waste material for the preconcentration of toxic Cd(II) metal ions. The main advantages of procedure are: ease and simplicity of preparation of the sorbent, sensitivity; and rapid attainment of phase equilibration and good enrichment. The kinetics of sorption follows a first-order rate equation. The negative value of ΔH and ΔG indicates the exothermic and spontaneous nature of sorption. Study of concomitant ions shows that the sawdust has the ability to preconcentrate Cd(II) from complex matrices.

References

[1] E.R. Plunket, Handbook of Industrial Toxicology, Edward Arnold, London, 1987.

- [2] H.G. Sieler, H. Sigel, A. Sigel, Handbook on Toxicity of Inorganic Compounds, Marcel and Dekker Inc., New York, 1988.
- [3] C.D. Klaassen, Toxicology the Basic Science of Poisons, McGraw-Hill, New York, 2001.
- [4] G. Bortoletto, G.T. Macarovsky, S. Cadore, Determination of cadmium by flame atomic absorption spectrometry after preconcentration on silica gel modified with cupferron, J. Braz. Chem. Soc. 15 (2004) 313–317.
- [5] S.D. Faust, O.M. Aly, Adsorption Processes for Water Treatment, Butterworth, USA, 1987.
- [6] W.C. Chun, K.C. Chak, F.P. John, G. McKey, Combined diffusion model for the sorption of cadmium copper and zinc ions onto bone char, Environ. Sci. Technol. 35 (2001) 1511–1520.
- [7] E.R. Maria, J.W. Ceri, H.E.G. Philip, Study of the mechanism of cadmium biosorption by dealginated seaweed waste, Environ. Sci. Technol. 35 (2001) 3025.
- [8] S. Klimmek, H.J. Stan, Comparative analysis of the biosorption of cadmium, lead, nickel, and zinc by algae, Environ. Sci. Technol. 35 (2001) 4283–4288.
- [9] W. Jianmin, T. Xinjun, W. Hao, B. Heng, Characterizing the metal adsorption capability of a class F coal fly ash, Environ. Sci. Technol. 38 (2004) 6710–6715.
- [10] G. Yekta, U. Sibel, G. Ulgar, Biosorption of cadmium and lead ions by ethanol treated bakers yeast biomass, Bioresour. Technol. 96 (2005) 103–109.
- [11] K. Upendra, B. Manas, Sorption of cadmium from aqueous solution using pretreated rice husk, Bioresour. Technol. 97 (2006) 104–109.
- [12] K.S. Low, C.K. Lee, S.C. Liew, Sorption of cadmium and lead from aqueous solutions by spent grain, Process Biochem. (2000) 59–64.
- [13] P. Lodeiro, B. Cordero, J.L. Barriada, R. Herrero, V.M.E. Sastre, Biosorption of cadmium by biomass of brown marine macroalgae, Bioresour. Technol. 96 (2005) 1796–1803.
- [14] K.K. Singh, R. Rastog, S.H. Hasan, Removal of cadmium from wastewater using agricultural waste 'rice polish', J. Hazard. Mater. 121 (2005) 51–58.
- [15] V.C. Taty-Costodes, H. Fauduet, C. Porte, A. Delacroix, Removal of Cd(II) and Pb(II) ions, from aqueous solutions, by adsorption onto sawdust of *Pinus sylvestris*, J. Hazard. Mater. 105 (2003) 121–142.
- [16] G.V. Cullen, N.G. Siviour, Removing metals from waste solutions with low rank coals and related materials, Water Res. 16 (1982) 1357–1366.
- [17] S. Alka, Z. Yu-Hui, P. Dubey, J.L. Margrave, S.S. Shyam, The role of sawdust in the removal of unwanted materials from water, J. Hazard. Mater. 95 (2002) 137–152.
- [18] P.C. Hiemans, R. Rajagopalan, Principles of Colloid and Surface Chemistry, Marcel Dekker Inc., New York, 1997.
- [19] C.B. Seng, Manual for Feed Analytical Laboratory, Directorate of Research Information, Pakistan Agricultural Research Council, Islamabad, Pakistan, 1982.
- [20] F.T. Benjamin, ProtoFit Version 2.0, A Program for Determining Surface Speciation Constants from Titration Data, 2005.
- [21] J.B. Fein, C.J. Daughney, N. Yee, T.A. Davis, A chemical equilibrium model for metal adsorption onto bacterial surfaces, Geochim. Cosmochim. Acta 61 (1997) 3319–3328.
- [22] C.F. Baes Jr., R.E. Mesmer, The Hydrolysis of Cations, Wiley-Interscience, New York, 1976.
- [23] S. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe, Handlingar 24 (1898) 1–39.
- [24] W.J. Morris, C. Weber, Kinetics of adsorption on carbon from solution, J. Saint. Eng. Div. ASCE 89 (1963) 31.
- [25] K. Kadirvelu, K. Thamaraiselvi, C. Namasivayam, Adsorption of Ni(II) from aqueous solutions onto activated carbon prepared from coirpith, Sep. Purif. Technol. 24 (2001) 497–505.
- [26] Helfferich, Ion-Exchange, McGraw Hill, New York, 1962.
- [27] M. Saeed, Adsorption profile and thermodynamic parameters of the preconcentration of Eu(III) on 2-thenoyltrifluoroacetone loaded polyurethane (PUR) foam, J. Radioanal. Nucl. Chem. 256 (2003) 73–76.