Removal of Copper (II) Ions from Aqueous Medium by Sawdust of Wood

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Summary: Removal of Cu (II) ions from aqueous solution by sawdust of wood was investigated as a function of time, pH, adsorbent concentration, adsorbate concentration and temperature. The amount of Cu (II) ions adsorbed onto sawdust increased with the increase in reaction time, concentration and temperature. Kinetic studies showed that adsorption process followed first order kinetic model. Langmuir and Freundlich equations were applied to the observed data, which showed that Cu (II) ions adsorption obeys both Langmuir and Freundlich isotherms. Thermodynamics parameters such as $\Delta H°$, $\Delta S°$ and $\Delta G°$ were also estimated which suggested that the adsorption of Cu (II) ions on sawdust of wood was an endothermic and spontaneous process.

Introduction

Natural water generally contains several heavy metals arising mostly from mining wastes and industrial discharges [1]. Copper, which is mined as a primary ore product from copper sulfide and oxide ores, is considered the major source of copper contamination in groundwater and surface water. Copper pipes are also the major source of copper contamination. In aerobic, sufficiently alkaline systems, $CuCO_3$ is the dominant soluble copper species. The cupric ion, Cu^{+2}, and hydroxide complexes such as $CuOH^+$, are also commonly present. Copper forms strong solution complexes with humic acids. In anaerobic environments, when sulfur is present, CuS will form. Copper mobility is decreased by sorption to mineral surfaces. Cu^{+2} sorbs strongly to mineral surfaces over a wide range of pH. The cupric ion (Cu^{+2}) is the most toxic species of copper. Because of the increasing environmental concern regarding heavy metal contamination, there has been an abundance of interest in the removal of heavy metal ions from contaminated soil and waste streams [2-4]. Although cleanup is necessary to prevent discharge of contaminated waste into the environment, a technology needs to be developed for the removal of metals from polluted water. Methods traditionally employed for removal of heavy metal ions from wastewater are filtration, precipitation, fractional crystallization and solvent extraction. One of the methods employed for removing contaminants like heavy metal ions from wastewater is adsorption.

Adsorption under certain condition has definite edge over other methods used for the removal of heavy metal ions from aqueous solution, because of its simplicity, low cost and its faster regeneration rate. Biosorption has emerged as an inexpensive solution. Many researchers have studied the use of live microbial systems for the purpose of remediating contaminated soils and water [5]. Since chemical functional groups are most likely responsible for metals binding, it is likely that higher plants cells might also be capable of metals binding. Various research groups have conducted studies on the metals binding properties of plant tissues [6,7]. Metal ions adsorption by agricultural by-products may involve metals interaction or coordination to functional groups present in natural proteins, lipids and carbohydrates positioned on cell wall [8]. Earlier researchers used different plant materials such as Mangifera Indica (mango) and Coconut fibers for metals removal from wastewater [9,10]. Coconut husk have also been used for removal of metal ions from polluted water [11]. Recently, researchers have extensively studied on the removal of the heavy metals by using biomass such as cellulose [12], banana and orange peels [13], waste tea leaves [14], peat and bark [15,16]. To add value to the tree waste in the present work attention has been focused on the utilization of sawdust of wood as an adsorbent for the removal of copper (II) ions from aqueous solution under different experimental condition of shaking time, concentration, and temperature.

Results and Discussion

pH Dependence study for metal ions binding

The effect of pH on the adsorption of Cu (II) ions were studied at different pH as shown in Fig. 1.

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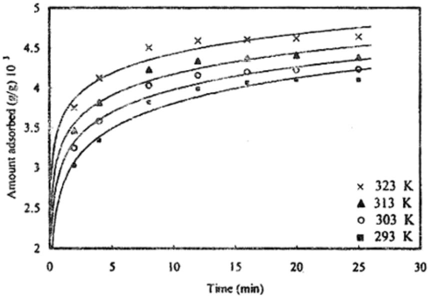

Fig. 1 Effect of pH on the adsorption of copper ions on sawdust particles at 25 °C.

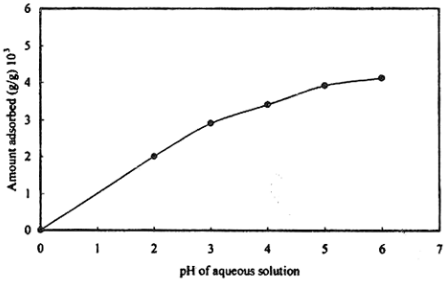

Fig. 2 Amount of copper ions adsorbed as a function of shaking time on sawdust particles at different temperatures.

Fifty cm^3 of 0.01 mol dm^{-3} solution of Cu (II) ions solution was stirred with one gram of sawdust at 25 °C at different pH. As the pH of the solution increases from 2.0 to 6.0, copper ions show an increase in binding to the adsorbent with optimum binding occurring at pH 6.0. This gives us an insight into the mechanism of the binding involved within the adsorbent. Previous studies have reported the binding of metals to some organic acids, which contain carboxyl ligands [17]. Our results also suggest that to some extent carboxyl groups (-COOH) are responsible for the binding of metal ions. Reportedly, the ionization constants for a number of carboxyl groups range between 4 and 5 [18]. At lower pH, the carboxyl groups retain their protons reducing the probability of their binding to any positively charged ions. Whereas at higher pH (above 4.0), the carboxyl groups are deprotonated and as such are negatively charged. These negatively charged carboxylate (-COO-) ligands attract the positively charged metal ions and binding occurs. Thus, metal ion binding to the biomass is in essence an ion-exchange mechanism, which involves electrostatic interaction between the negatively charged groups in the cell walls and metallic cations [19]. However, in Fig. 1 it is observed that the biomass binds copper ions even at pH below 4.0. This suggests that besides carboxyl groups, other groups may also be involved in metal ions binding.

Adsorption kinetics

Figure 2 shows data for Cu (II) ions adsorption on sawdust of Dalbergia sissoo as a function of time under the given experimental conditions. As can be seen, most of the adsorption occurred within first 10 minutes of the adsorption reaction irrespective of the reaction temperature. The same figure further reveals that the extent of adsorption increased with the increase in temperature. The latter observation pointed to the endothermic nature of the adsorption process.

Lagergren equation [20] (Eq. 2) was applied to the adsorption data, given in Fig. 2 for the determination of the rate constant for the adsorption reaction.

$$\log(q_e - q_t) \;=\; -\frac{kt}{2.303} + \log q_e \qquad (2)$$

Where q_e and q_t are the amount of copper (II) ions adsorbed at equilibrium and at time t respectively in (g g^{-1}) and k is the overall rate constant. Straight lines were obtained by plotting log (q_e-q_t) against t. This indicates that copper ions adsorption on sawdust follows the first order kinetics. The values of rate constant k were calculated from the slopes of straight lines and are given in Table-1. It is seen from this Table that the values of k increase with the increase in temperature.

Table-1: Values of reaction rate constant k (min^{-1}) for copper ions adsorption on sawdust of Dalbergia sisso (particles size 200 ± 10 μm) at different temperatures.

Temperature (K)	k (min^{-1})
293	0.239
303	0.251
313	0.262
323	0.283

To determine the activation energy, E_a, for copper ions adsorption, the following Arrhenius equation [21] was applied to the adsorption data.

$$\ln k \;=\; -\frac{E_a}{RT} + \text{Constant} \qquad (3)$$

Where E_a is the energy of activation, R is the gas constant and T is the absolute temperature. The value of activation energy was determined from the slope of the plot of lnk versus 1/T and is found to be 4.352 kJ mol^{-1}.

The Bangham equation as suggested by Aharoni *et al* [22] was applied to the adsorption data in the form:

$$\log \log \frac{\varphi_o}{\varphi_o - q_t w} = \log \frac{k_o w}{2.303 V} + \alpha \log t \qquad (4)$$

Where φ_o is the initial concentration (mol dm^3) of metal ions in solution, V is the volume (dm^3) of solution, w is the weight (g) of adsorbent, q_t is the amount of metal ions adsorbed (mol g^{-1}) at time t, while ∝ and K_o are constants.

Straight lines were obtained by plotting log log φ_o / φ_o -q_t w against log t, which indicated the validity of Bangham equation for describing the observed adsorption data. The values of ∝ and K_o at different temperatures were calculated from the slopes and intercepts of plots and are given in the Table-2. The trend in the numerical values of these constants points towards the diffusion controlled adsorption process [23].

Table-2: Kinetics parameters of Bangham equation for copper ions adsorption on sawdust of Dalbergia sisso (particles size 200 ± 10 μm) at different temperatures.

Temperature (K)	∝	$k_o 10^4$
293	0.0559	2.221
303	0.0475	2.429
313	0.0423	2.623
323	0.0370	2.862

Adsorption isotherm

Adsorption of Cu (II) ions was carried out on sawdust of Dalbergia sissoo from aqueous solutions of copper ions at various concentrations and temperatures. It was observed that the extent of adsorption increased with the increase in concentration of the copper ions and attained saturation values at high concentration, depending upon the temperature and content of the dispersion solids (sawdust of Dalbergia Sissoo) in the adsorption medium. Fig. 3 shows typical adsorption data obtained under the described conditions. It is clear from the plots that increase in temperature caused more adsorption. The data in Fig. 3 was fitted to Langmuir (Eq. 5) and Freundlich (Eq. 9) equations [24,25].

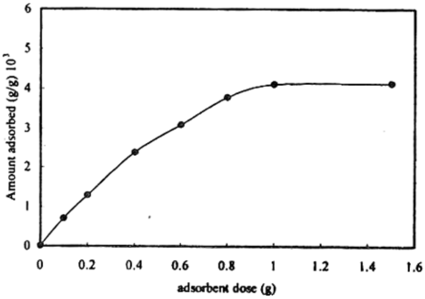

Fig. 3 Adsorption isotherms of copper ions adsorption on sawdust particles at different temperatures.

$$\frac{C_e}{q} = \frac{1}{K_1 X_m} + \frac{C_e}{X_m} \qquad (5)$$

Where C_e is the equilibrium concentration of metal ions (mol dm^{-3}), q is the amount of copper ions adsorbed (mol g^{-1}), X_m and K_1 are Langmuir constants, representing the adsorption capacity (mol g^{-1}) and energy of adsorption (dm^3 g^{-1}) respectively. Straight lines were obtained by plotting C_e/q_t against C_e, which indicates that the copper ions adsorption obeys Langmuir isotherm. Langmuir constants X_m and K_1 were calculated from the slopes and intercepts of plots of C_e/q against C_e respectively and are given in Table-3. It is observed from this Table that the X_m and K_1 values increases with increase in temperature.

In order to understand the effect of temperature, thermodynamic parameters such as free energy and enthalpy of copper ions adsorption were calculated from the binding constant K_1 obtained from Langmuir's equation by using the following relations [24].

$$\Delta G^o = - RT \ln K_1 \qquad (6)$$

$$\ln K_1 = - \frac{\Delta H^o}{RT} + \text{constant} \qquad (7)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (8)$$

The value of ΔH^o is calculated from the slope of linear variation of $\ln K_1$ versus 1/T. The values of ΔS^o were calculated using equation 8. The values of ΔS^o, ΔG^o and ΔH^o are given in Table-4. The negative values of ΔG^o obtained at various temperatures shows

Table-3: Values of monolayer capacity (X_m) and binding energy constant (K_1) for copper (II) ions adsorption on sawdust of Dalbergia sissoo (particles size 200 ± 10 μm) at different temperatures.

Temperature (K)	X_m (mol g^{-1}) 10^4	K_1 (dm^3 g^{-1})
293	1.1687	141.894
303	1.2142	169.622
313	1.2820	178.496
323	1.3300	196.602

Table-4: Various thermodynamics parameters for copper (II) ions adsorption on sawdust of Dalbergia sissoo (particles size 200 ± 10 μm) at different temperatures.

Temp. (K)	ΔH^o ($kJmol^{-1}$)	ΔS^o ($kJ.k^{-1}mol^{-1}$)	ΔG^o ($kJmol^{-1}$)
293	8.433	0.0699	-12.070
303	-----	0.0705	-12.932
313	-----	0.0700	-13.491
323	-----	0.0700	-14.182

the spontaneous nature of adsorption process. The positive value of ΔH^o shows that the process of copper adsorption on sawdust of Dalbergia sissoo is endothermic. Furthermore, the positive value of ΔS^o shows that some structural exchange may occur among the active sites of the adsorbent and the metal ions.

The linearized form of Freundlich isotherm is expressed by the following equation [26].

$$\ln \frac{x}{m} = \ln K + \frac{1}{n} \ln C_e \qquad (9)$$

Table-5: Values of Freundlich constants for copper (II) ions adsorption on sawdust of Dalbergia sissoo (particles size 200 ± 10 μm) at different temperatures.

Temperature (K)	1/n (g dm^{-3})	K (μmol g^{-1})
293	0.316	3.565
303	0.279	5.628
313	0.271	6.512
323	0.249	8.576

Where, K (mol g^{-1}) and n (g dm^{-3}) are Freundlich constants. Similarly, straight lines were obtained by plotting ln x/m against $\ln C_e$, which shows that adsorption of copper ions complies with the Freundlich isotherm. The values of 1/n and K were calculated from the slopes and intercepts of the plots of ln x/m versus $\ln C_e$ respectively and are given in Table-5. The mechanism and rate of adsorption are reported to be the functions of 1/n and K respectively. Since the values of 1/n are less than 1, it indicates favourable adsorption. Smaller values of 1/n indicate better adsorption mechanism and formation of relatively stronger bond between adsorbate and adsorbent [27].

Experimental

Materials

All the chemicals used were of analytical grade and were used without further purification. The Sawdust of Dalbergia sissoo was collected from a local sawmill at Peshawar, NWFP, Pakistan.

Treatment of sawdust

The adsorbent was characterized and various parameters such as moisture contents, particle size, ash contents, surface area and bulk density were determined. The various elements present in sawdust were also determined by Energy Dispersive X-rays Analyzer (INCA-200 of Oxford Instrument UK) attached with scanning electron microscope Fig.4. Various parameters are given in Table-6. Sawdust was treated with sodium hydroxide solution to increases the adsorption property of the adsorbent. Carboxylate ligands are believed to be responsible for metal binding by the biomasses. This means that metal binding can be enhanced by increasing the number of carboxylate ligands in the biomass. Cellulose, hemicellulose, and lignin, which are major constituents of most plant tissues, contain methyl esters, which do not bind metal ions significantly. However, these methyl esters can be modified to carboxylate ligands by treating the biomass with a base such as sodium hydroxide, thereby increasing the metal-binding ability of the biomass [28].

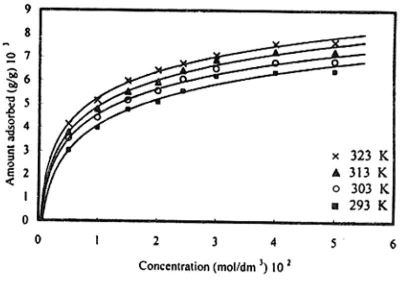

Fig. 4 EDX graphical representation of various elements present in sawdust of Dalbergia sissoo.

100 grams of the as-collected sawdust of Dalbergia sisso was transferred to 500 cm^3 of 0.5 mol dm^{-3} solution of NaOH in a 1dm^3 beaker provided with a lid. The resulting dispersion was stirred for one hour, using a magnetic stirrer. The solid was extensively washed with double distilled water, dried for 5 hours at 100 °C, and then cooled in a dessicator for 24 hours. By the sieving process, the sawdust particles of nearly 200 ± 10 μm in size were separated from the dried sample.

Table-6: Values of various parameters for the characterized adsorbent (sawdust of Dalbergia sisso)

Parameters	Values
pH (aqueous solution)	7.10
Particles size (μm)	200 ± 10
Surface area (m^2/g)	143.125
Bulk density (g/cm^3)	0.2587
% Ash content	0.10
% Moisture content	5.75
Calcium (w %)	0.24
Oxygen (w %)	8.08
Carbon (w %)	51.68

Adsorption studies

Adsorption of Cu (II) ions on sawdust of Dalbergia sissoo was carried out by batch technique [27]. In each batch a 50 cm^3 dispersion, containing one gram of the sawdust and 0.01 mol dm^{-3} of Cu (II) ions were equilibrated for various periods of time (2 – 25 minutes) and temperatures (20 - 50 °C) in a thermostatic water bath. At the end of the reaction time, the solid was separated from the liquid by filteration. The filtrate was collected and analyzed for Cu (II) ions by EDTA titration using Sulphon Black F indicator [29].

The amount of copper (II) ions adsorbed (g g^{-1}) was calculated from the volume of EDTA used in titration against metal ions solution using the following relation.

$$q = \frac{(Co - C_t)V \times \text{Atomic weight of metal}}{w.1000} \qquad (1)$$

Where q is the amount of metal ions adsorbed (g g^{-1}), C_o is the initial concentration (mol dm^{-3}), C_t is the concentration (mol dm^{-3}) of solution after adsorption at time t, V is the volume (cm^3) of metal ions solution used in adsorption and w is the weight of adsorbent in grams used for adsorption.

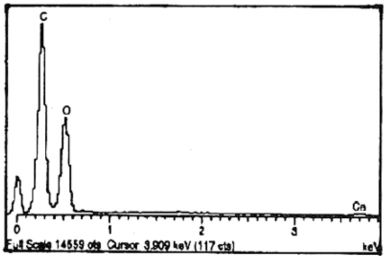

Fig. 5 Effect of adsorbent dose on the adsorption of copper ions on sawdust particles at 25 °C.

Optimization of experimental conditions

To optimize experimental conditions 50 cm^3 of 0.01 mol dm^{-3} solution of Cu (II) ions solution were stirred with different amount of sawdust at 25 °C for specific period of time, and it was found that maximum adsorption occur at adsorbent dose of one gram as shown in Fig. 5. Therefore one gram of adsorbent dose was selected for further study. Similarly it was also found that maximum adsorption occur at a pH 6 and above it precipitation was noted. Therefore pH 6 was selected for further study.

All the determinations were carried out in triplicate, the mean value were determined and plotted. The difference among the values obtained by different set of experiments were not more than ± 3 %. The level of the metal in aqueous solution was also determined by Atomic Absorption Spectrophotometer (equipped with graphite furnace). The results obtained were in good agreements with those determined by EDTA titration.

Conclusions

The present work demonstrated that the sawdust of Dalbergia Sissoo, which is abundantly available material, could be used with a reasonable success for the removal of copper ions from aqueous medium. It is mentioned that this study was the first exploratory attempt for this purpose. Further work is in progress in our laboratories for extending the reported methodology for the removal of other heavy metal ions of environmental concern.

References

1. E. Schalcsha, I.T. Ahumada. *Wat. Sci. Tech.* **37**, 251 (1998).

2. R. EL-Aziz, J.S. Angle, R.L. Change, *Soil Biol Biochem.,* **23,** 795 (1991).
3. M.J. Mench, *J. Environ. Qual.,* **23,** 58 (1994).
4. N.T. Basta, M.A. Tabatabi, *Soil Science,* **153,** 108 (1992).
5. R. P. Carvalho, K. H. Chong, B. Volesky, *Biotechnol. Prog,,* **11,** 39 (1995).
6. J. R. Lujan, *Solvent Extraction and Ion Exchange.* **12,** 803 (1994).
7. S. K. Jain, *Wat. Res.* ***24*,** 177 (1990).
8. L.R. Drake, S. Lin, G.D. Rayson, P.J. Jackson, *Environment Science and Technology,* **30,** 110 (1996).
9. M. Ali, M. Ajmal, Y. Rehana, A. Anees, *Indian Journal of Chemical Technology.* **4,** 223 (1997).
10. G.N. Manju, T.S. Anirudhan, *Indian Journal of Environmental Health.* **39,** 289 (1997).
11. G.W. Manju, C. Raji, T.S. Anirudhan, *Water Research.* **32,** 3062 (1998).
12. B. Acemioglu, M .H. Alma, *J. Colloid Interface. Sci.* **243,** 81 (2001).
13. G. Anadurai, R.S. Juang, D.J. Lee, *J. Haz. Mat.* **B92,** 263 (2002).
14. T.W. Tee, M. Khan, R.A. Environ. *Lett.* **9,** 1233 (1988).
15. G. Mckay, J.F. Portar, *J. Chem. Technol. Biotechnol.* **69,** 309 (1997).
16. M. Villaescusa, N. Miralles, *J. Chem. Technol. Biotechnol.* **75,** 812 (2000).
17. G. V. Korshin, A.I. Frenkel, E.A. Stern, *Environ. Sci. Technol.* **32,** 2699 (1998).
18. J. L. Gardea-Torresdey, K.J. Tiemann, J.H. Gonzalez, J.A. Henning, *Solvent Extraction and Ion Exchange.* **14,** 119 (1996).
19. D. A. J. Wase, C.F. Forster, *Wase, J, Forster, C., Eds. Taylor and Francis, UK.* 1 (1997).
20. S. Lagergen, Handlingar, Band. (1898).
21. J. H. Bikerman. Academic press lnc. N.Y. (1958).
22. C. Ahroni, S. Sidemen, E. Hoffer, *J. Chem. Tech. Biotechnol.* **27,** 404 (1979).
23. R. Qadeer, J. Hanif, M. Saleem, M. Afzal, *J. Chem. Soc. Pak.* **17,** 82 (1995).
24. B. Acemioglu, M.H. Alma, *J. Colloid Interface.* **243,** 81 (2001).
25. D.M. Ruthven, John Wiley, New York. (1984).
26. A.K. Saad, U. R. Riaz, M. A. Ali, *Waste Management,* **14,** 125 (1994).
27. P.B. Nagarnaik, A.G. Bhole, G.S. Natarajan, *The Int. Jour. Environ. Studies.* **5,** 1097 (2002).
28. T. H. Baig, A. E. Garcia, K. J. Tiemann, J. L. Gardea-Torresdey, *Proceedings of the 1999 Conference on Hazardous Waste Research,* 131 (1999).
29. A. I. Vogel,. 3rd Edition, McGraw Hill, New York. 1971.