Asian Journal of Chemistry Vol. 22, No. 5 (2010), 3936-3942

Removal of Cu(II) Ions from Aqueous Solutions by the Activated Carbon Obtained from Pine Cone

UNAL GECGEL*, KENAN SEZER and HAKAN KOLANCILAR
Chemistry Department, Faculty of Arts and Science, Trakya University, Edirne-22030, Turkey
Fax: (90)(284)2358754; Tel: (90)(284)2359592/1225; E-mail: unalgecgel@trakya.edu.tr

The activated carbon obtained from pine cone was investigated as a new adsorbent to remove copper(II) ion from aqueous solution. The adsorption process of copper(II) ion was carried out in a batch mode and the effects of adsorbent concentration (0.25-1.00 g/100 mL), initial pH's (2.0-6.0) and initial metal ion concentrations (25-100 mg/L) were investigated. Maximum removal capacity of the copper(II) ion from aqueous solutions was achieved at pH 5.0. Adsorption data was well fitted to the Langmuir and Freundlich isotherms. Langmuir monolayer capacity was a value of 15.05 mg/g. The results in this study indicate that the activated carbon obtained from pine cone can be an effective adsorbent for removal of copper(II) ions from aqueous solution.

Key Words: Adsorption, Adsorption isotherm, Activated carbon, Pine cone, Removal, Cu(II).

INTRODUCTION

Heavy metals are the most common toxic pollutants found both in industrial waters and soils. Increasing levels of these metals make them a public concern[1]. The major sources of heavy metal pollutants are usually from many industries and agricultural activities[2].

Copper, a widespread used heavy metal which finds many useful applications in our life is seriously harmful if present in aquatic environment[3]. Maximum acceptable copper concentration in drinking water is less[4] than 3000 mg/dm^3. Copper along with mercury and arsenic is recognized as one of the highest mammalian toxic ion[5].

The toxicity of copper on humans has been comprehensively reviewed by some researchers. Acute copper poisoning after ingestion may show systematic effects such as hemolysis, liver and kidney damage. The excessive intake of copper also results in its accumulation in the liver and produces gastrointestinal problems[6]. Hence, removal of copper from water and wastewater assumes importance.

There are many publications dealing with techniques for removal of heavy metal ions from aqueous effluents including precipitation, electroplating, evaporation, ion exchange, membrane separation and adsorption[7-10]. The adsorption with selection of suitable adsorbents can be an economic and effective technique for the removal of heavy metals from wastewater[11].

Though the use of commercial activated carbon is well known adsorbent for the removal of heavy metals from water and wastewater, high cost limits its usage. Hence, it is a growing need to derive the activated carbon from cheaper and locally available waste materials.

In recent years, agricultural by-products have been widely studied for metal removal from water. These include peat[12], wood[13], pine bark[14], banana pith[15], rice bran, soybean and cotton seed hulls[16], peanut shells[17], hazelnut shell[18], rice husk[19], sawdust[20], wool[21], orange peel and compost[22] and leaves[23].

Activated carbon was prepared from pine cone with zinc chloride. The obtained products are essentially microporous[24]. To our best knowledge, the adsorption of Cu(II) ions on activated pine cone has not been reported previously. The influence of several operating parameters, such as pH, adsorbent dosage and initial metal concentration on the adsorption capacity of the activated pine cone were investigated.

EXPERIMENTAL

The pine cones (*Pinus brutia*) were collected from Enez forest which is located in western Turkey during summer period and stored after drying in laboratory conditions until use. The stock solution of Cu(II) was prepared in 1000 mg/L concentration using $CuSO_4 \cdot 5H_2O$ and then diluted to desired concentrations. HCl and NaOH were used for pH adjustment. All chemicals used in this study were of analytical laboratory grade, being purchased from Merck.

Preparation of activated pine cone: Pine cones were ground using a laboratory mill to obtain the particle size of 0.5-1.2 mm. Chemical activation of the pine cone was done with $ZnCl_2$ solution. 10 g of dried pine cone was well mixed, by stirring, with 100 mL of an aqueous solution that contained 20 g of $ZnCl_2$. The chemical ratio was 200 % (20 g of $ZnCl_2$/10 g of pine cone in 100 mL H_2O) in this case. The chemical ratio is defined as the weight ratio of activating agent ($ZnCl_2$) to the precursor (pine cone). The mixture was heated at 80 °C for 1 h. After heating, the slurry was kept in an oven at 100 °C for 24 h. The resulting $ZnCl_2$ treated sample was then subjected to carbonization and activation process in a programmable electrical furnace (Severn Furnaces Ltd.) at 500 °C for 1 h. After activation, sample was allowed to cool and subsequently washed with 0.5 M HCl and then several times with deionized water. It was ground and sieved through a 65-mesh. The resulting product was kept in a desiccator for further use.

Adsorption studies: Batch adsorption experiments were carried out in 25 mL Cu(II) solutions of known concentration poured into flask containing certain amount of adsorbent. The adsorption studies were carried at 25 °C using temperature controlled shaker (Nüve ST-402). The flasks were shaken at 150 rpm for a prescribed length of time to attain equilibrium, then the reaction mixtures were filtered out and analyzed for its metal ion concentrations using Flame atomic absorption spectrometer (Unicam 929-FAAS).

The effect of pH of the initial solution on the equilibrium uptake of Cu(II) ions was evaluated over a pH ranges from 2-6. The pH values of the solutions were adjusted with 0.1 M NaOH and 0.1 M HCI using Orion 3 STAR pH meter. The adsorption studies were also conducted in batch experiments as a function of adsorbent dosage (0.25, 0.50, 0.75 and 1.00 g) and initial metal ion concentrations (25, 50, 75 and 100 mg/L). The amount of metal ion adsorbed was calculated as,

$$\text{Adsorption (\%)} = \frac{C_0 - C_{eq}}{C_0} \times 100 \qquad (1)$$

where C_0 and C_{eq} are the initial and equilibrium concentrations of the adsorbate, respectively. Adsorption capacity was calculated by using the mass balance equation for the adsorbent:

$$q_{eq} = \frac{(C_0 - C_{eq})V}{W} \qquad (2)$$

where q_{eq} is the adsorption capacity (mg/g) at the equilibrium; C_0, is the initial concentration of metal ion in solution (mg/L); C_{eq}, is the equilibrium concentration of metal ion in solution (mg/L); V, is the volume of metal ion solution (L) and W, is the weight of the adsorbent (g).

RESULTS AND DISCUSSION

Effect of pH: The pH of the solution is the most important parameter affecting the adsorption of metal ions. The effect of pH on the adsorption of Cu(II) ion on activated pine cone has been studied by varying it in the range of 2-6 as shown in Fig. 1. Results of the experiments show that the efficiency of Cu(II) ion adsorption was improved by increasing the pH from 2.0 (56.00 %) to 5.0 (87.70 %), however further increase of pH from 5.0-6.0 lead to decrease (85.34 %) of adsorption (Fig. 1). Low adsorption yield at pH 2.0 can be attributed to the fact that there are more protons at lower pH, available to protonate active binding sites of adsorbent. Thus generate electrostatic repulsion between metal ions and positive charged adsorbent surface. At pH values above 6.0, turbidity was observed. This can be explained by precipitation of copper ions in the solution. Similar results were obtained by some reserchers, who reported that pH has a significant role on Cu(II) ion removal found optimal at pH 5.0. They also reported that at pH values above 6.0, Cu(II) ions were precipitated as hydroxides[3, 25, 26].

Effect of adsorbent dosage: The adsorption study of Cu(II) ions on activated carbon from pine cone was done at 25 °C temperature by varying the quantity of adsorbent from 0.25-1.00 g. The influence of adsorbent dosage on adsorption yield of Cu(II) ions is illustrated in Fig. 2. The adsorption yield was increased from 65.00 -98.73 % with increasing the amount of adsorbent from 0.25-1.00 g/100 mL. The increase of the adsorption yield of Cu(II) ions is due to the increase of active sites on the adsorbent surface and thus making penetration of the metal ions to the active sites of the adsobent easier.

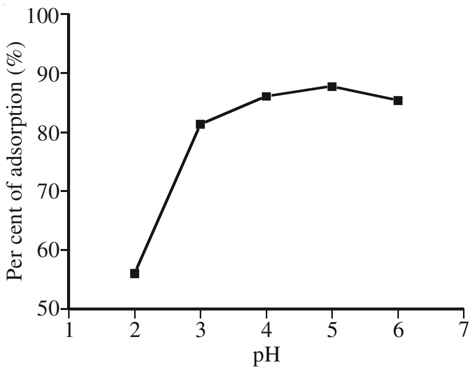

Fig. 1. Effect of initial pH on the adsorption of Cu(II) ions to the activated pine cone (initial concentration = 75 mg/L, adsorbent dose = 0.5 g/100 mL, temperature = 25 ± 0.1 °C, contact time = 30 min)

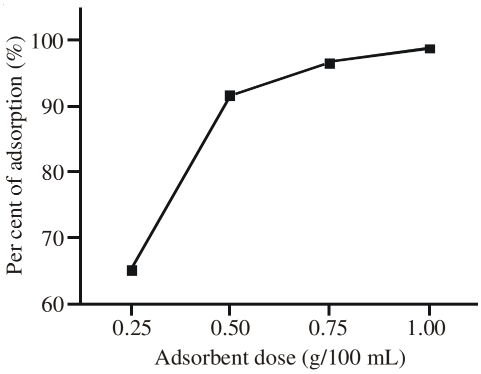

Fig. 2. Effect of adsorbent dose on the adsorption of Cu(II) ions to the activated pine cone (initial concentration = 75 mg/L, pH = 5, temperature = 25 ± 0.1 °C, contact time = 60 min)

Effect of initial metal ion concentration: The adsorption of metal ions by activated pine cone was studied at different Cu(II) ion concentrations at the range of 25-100 mg/L. The high adsorption yield (98.2 %) is obtained at initial concentration 25 mg/L and low adsorption yield (85.76 %) is obtained at initial concentration 100 mg/L. Similarly Ozer *et al.*[27] indicated that at low initial Cu(II) ion concentration all the Cu(II) ions present in solution could interact with the binding sites of adsorbent and thus the adsorption rate of ions are higher with respect to the adsorption values obtained from high initial Cu(II) ion concentration. At high initial Cu(II) concentration binding sites of adsorbent could became saturated which decrease the adsorption of metal ions (Fig. 3).

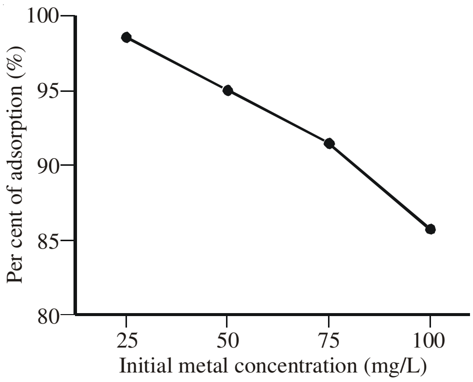

Fig. 3. Effect of initial metal concentration on the adsorption of Cu(II) ions to the activated pine cone (pH = 5.0, adsorbent dose = 0.5 g/100 mL, temperature = 25 ± 0.1 °C, contact time = 60 min)

Adsorption isotherms: The adsorption isotherms reveal the specific relation between the concentration of the adsorbate and its adsorption degree onto adsorbent surface at a constant temperature. The experimental data were fitted to Langmuir and Freundlich isotherm equations. The Langmuir equation was used to describe observed adsorption phenomena. The Langmiur isotherm applies to adsorption on completely homogenous surface with neglible interaction between adsorbed molecules[20,28]. The Langmuir equation is commonly expressed as in the linear form:

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{bq_{max}} + \frac{C_{eq}}{q_{max}} \tag{3}$$

where q_{eq}, is the amount of copper adsorbed on the adsorbent at equilibrium (mg/g); C_{eq}, is the equilibrium concentration of copper solution (mg/L); q_{max}, the monolayer capacity (mg/g) and b, (L/mg) is an equilibrium constant of Langmuir.

The Freundlich isotherm was also tested with our experimental data.The Freundlich adsorption isotherm can be expressed in the linear form[29] as:

$$\log q_{eq} = \log K_F + \left(\frac{1}{n}\right) \log C_{eq} \tag{4}$$

where K_F and n, are Freundlich adsorption isotherm constants, indicated the capacity and intensity of the adsorption, respectively.

The linear Langmuir and Freundlich plots for the adsorption of Cu(II) ions onto activated pine cone are obtained by plotting C_{eq}/q_{eq} *versus* C_{eq} (Fig. 4) and log q_{eq} *versus* log C_{eq} (Fig. 5), respectively. The Langmuir and Freundlich adsorption constants evaluated from the isotherms with the correlation coefficient are listed in Table-1.

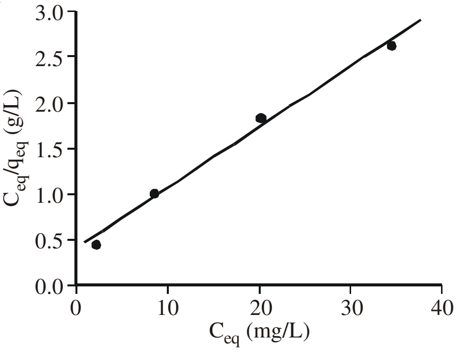

Fig. 4. Langmuir adsorption isotherm plots for the asorption of Cu(II) ions at 25±0.1 °C

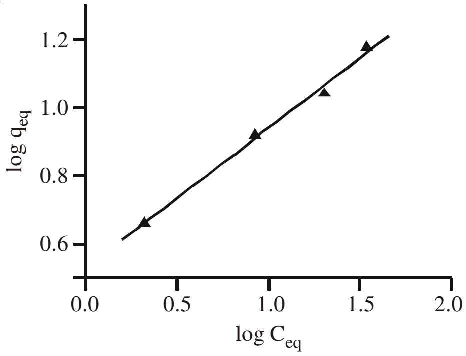

Fig. 5. Freundlich adsorption isotherm plots for the adsorption of Cu(II) ions at 25±0.1 °C

The high correlation coefficient shows that both models are suitable for describing the adsorption equilibrium of copper ions. As can be seen from the results in Table-1, equilibrium data agree well with the Langmuir model which illustrates that the adsorption on surface of the activated carbon from pine cone is a monolayer adsorption.

TABLE-1
LANGMUIR AND FREUNDLICH CONSTANTS FOR Cu(II)
ADSORPTION ON ACTIVATED PINE CONE AT 25 ± 0.1 °C

Adsorbent	Langmuir equation			Freundlich equation		
	q_{max} (mg g^{-1})	b (L mg^{-1})	R^2	K_F (L g^{-1})	n	R^2
Activated pine cone	15.05	0.165	0.9957	3.38	2.43	0.9964

The adsorption capacity (q_{max}) of activated carbon from pine cone for the uptakes of Cu(II) is 15.05 mg/g. The adsorption capacity of various adsorbents for Cu(II) ions taken from literature are presented in Table-2. It is clear from Table-1 that the value of the Freundlich constant 'n' obtained for this process indicates beneficial adsorption, as it lies between 1 and 10. The essential characteristics of the Langmuir isotherm can be expressed by means of 'R_L', a dimensionless constant referred to as separation factor or equilibrium parameter R_L is defined by Al-Degs *et al.*[39].

$$R_L = \frac{1}{1 + b(C_0)} \tag{5}$$

where b, is the Langmuir constant and C_0, is the initial metal concentration (mg/L). The R_L parameter indicates the type of isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). Dimensionless parameter R_L remained at 0.190, 0.110, 0.070 and 0.057 for following initial metal concentrations 25.0, 50.0, 75.0 and 100.0 mg/L, respectively. According to the values given above, it is concluded that the adsorption process is favourable.

TABLE-2
COMPARISON OF ADSORPTION CAPACITIES
OF VARIOUS ADSORBENTS FOR Cu(II) IONS

Adsorbents	Adsorption capacity (mg/g)	References
Activated pine cone	15.050	This study
Peanut husk	10.150	30
Corncobs	7.620	31
Blast furnace sludge	16.100	32
Hazelnut husk AC	6.645	33
Rubber wood sawdust AC	5.729	9
Bagasse fly ash	2.260	34
Ethylediamine grafted silica	16.580	35
Cotton boll	11.400	36
Activated carbon (filtrasorb 200)	24.100	37
Pine bark	9.470	38

Conclusion

The activated carbon from pine cone was selected as an adsorbent for the removal of copper ions from aqueous solutions. The adsorption experiments were carried out as a function of initial metal concentration, adsorbent dose and pH. The results indicated that more than 98 % of removal of copper ions was achieved by using 1.0 g/ 100 mL of activated carbon derived from pine cone (75 mg/L initial metal ion concentration, 60 min contact time). The removal efficiency was optimal at pH 5.0. The adsorption was highly dependent on initial metal concentration, adsorbent dosage and pH. Adsorption trends are founds to follow both Langmuir and Freundlich isotherms. As a result it can be said that the activated carbon derived from pine cone is an effective adsorbent for the removal of Cu(II) ions from aqueous solution.

REFERENCES

1. M. McCann, *Am. J. Ind. Med*., **30**, 125 (1996).
2 N. Li and R. Bai, *Sep. Purif. Technol*., **42**, 237 (2005).
3 A. Ozturk, T. Artan and A. Ayar, *Colloids Surf. B Biointerf.*, **34**, 105 (2004).
4 L. Murley, Pollution Hand Book, National Society for Clean Air and Environmental Protection, Brighton (1992).
5 H.J.M. Bowen, The Environmental Chemistry of the Elements, Academic Press, London (1979).
6 S. Rengaraj, Y. Kim, C.K. Joo and J. Yi, *J. Colloid. Interface Sci*., **273**, 14 (2004).
7 T.G. Chuah, A. Jumasiah, I. Azni, S. Katayon and S.Y.T. Choong, *Desalination*, **175**, 305 (2005).
8 M. Kobya, E. Demirbas, E. Senturk and M. Ince, *Biores. Technol*., **96**, 1518 (2005).
9 M.H. Kalavathy, T. Karthikeyan, S. Rajgopal and L.R.Miranda, *J. Colloid. Interface Sci*., **292**, 354 (2005).
10 M.M. Rao, A. Ramesh, G.P. C. Rao and K. Seshaiah, *J. Hazard. Matar*., **129**, 123 (2006).
11 A. Ozcan, A.S. Ozcan, S. Tunali, T. Akar and I. Kiran, *J. Hazard. Mater.,* **124B**, 200 (2005).
12 Y.S. Ho and G. McKay, *Water Res.*, **34**, 735 (2000).
13 V.J.P. Poots, G. McKay and J.J. Healy, *J. Water Pollut. Cont. Fed.*, **50**, 926 (1978).
14 S. Al-Asheh and Z. Duvnjak, *J. Hazard. Mater.*, **56**, 35 (1997).
15 K.S. Low, C.K. Lee and A.C. Leo, *Biores. Tech.*, **51**, 227 (1995).
16. W.E. Marshall and M.M. Johns, *J. Chem. Tech. Biotech.*, **66**, 192 (1996).
17 W. Wafwoyo, C.W. Seo and W.E. Marshall, *J. Chem. Tech. Biotech.*, **74**, 1117 (1999).
18 G. Cimino, A. Passerini and G. Toscano, *Water Res.*, **34**, 2955 (2000).
19 S.P. Mishra, D. Tiwari and R.S. Dubey, *Appl. Radiat. Isot.*, **48**, 877 (1997).
20 B. Yu, Y. Zhang, A. Shukla, S.S. Shukla and K.L. Dorris, *J. Hazard. Mater.*, **84**, 83 (2001).
21 D. Balkose and H. Baltacioglu, *J. Chem. Tech. Biotech*., **54**, 393 (1992).
22 M.S. Azab and P.J. Peterson, *Water Sci. Tech.*, **21**, 1705 (1989).
23 F.R. Zaggout, *Asian J. Chem.*, **13**, 639 (2001).
24 A. Bhatnagar, M. Ji, Y.-H. Choi, W. Jung, S.-H. Lee, S.-J. Kim, G. Lee, H. Suk, H.-S. Kim, B. Min, S.-H. Kim, B.-H. Jeon and J.-W. Kang, *Sep. Sci. Tech.*, **43**, 886 (2008).
25 W. Ma and J.M. Tobin, *Biochem. Eng. J.*, **18**, 33 (2004).
26 N. Basci, E. Kocadagistan and B. Kocadagistan, *Desalination*, **164**, 135 (2004).
27 D. Ozer and A. Ozer, *Process Biochem.*, **39**, 2183 (2004).
28 Y.S. Ho, *Adsorption*, **10**, 151 (2004).
29 H.M.F. Freundlich, *Z. Phys. Chem.*, **57**, 385 (1906).
30 Q. Li, J. Zhai, W. Zhang, M.Wang and J. Zhou, *J. Hazard. Mater.*, **141**, 163 (2007).
31 R. Zacaria, *Environ. Sci. Tech.*, **36**, 2067 (2002).
32 A. Lopez-Delgado, C. Perez and F.A. Lopez, *Water Res.*, **32**, 989 (1998).
33 M. Imamoglu and O. Tekir, *Desalination*, **228**, 108 (2008).
34 V.K. Gupta and I. Ali, *Sep. Purif. Tech*., **18**, 131 (2000).
35 N. Chiron, R. Guilet and E. Deydier, *Water Res*., **37**, 3079 (2003).
36 H.D. Ozsoy and H. Kumbur, *J. Hazard. Mater.*, **136B**, 911 (2006).
37 J.P. Chen and S. Wu, *J. Colloid. Interface Sci.*, **280**, 334 (2004).
38 S. Al-Asheh, F. Banat, R. Al-Omari and Z. Duvnjak, *Chemosphere*, **41**, 659 (2000).
39 Y. Al-Degs, M.A.M. Khraisheh, S.J. Allen and M.N. Ahmad, *Water Res.*, **34**, 927 (2000).

(*Received*: 27 August 2009; *Accepted*: 23 January 2010) AJC-8356