M. M. Al Subu, R. Salim, H. Braik, K. M. Swaileh

Removal of dissolved copper from polluted water using plant leaves. II. Effects of copper concentration, plant leaves, competing ions and other factors

Revista Internacional de Contaminación Ambiental, vol. 17, núm. 3, 2001, pp. 123-127,
Universidad Nacional Autónoma de México
México

Revista Internacional de Contaminación Ambiental

Revista Internacional de Contaminación Ambiental,
ISSN (Printed Version): 0188-4999
rvp@atmosfera.unam.mx
Universidad Nacional Autónoma de México
México

Rev. Int. Contam. Ambient. *17* (3) 123-127, 2001

REMOVAL OF DISSOLVED COPPER FROM POLLUTED WATER USING PLANT LEAVES. II. EFFECTS OF COPPER CONCENTRATION, PLANT LEAVES, COMPETING IONS AND OTHER FACTORS

M. M. AL-SUBU*[a], R. SALIM[a], H. BRAIK[a] and K. M. SWAILEH[b]

[a] Department of Chemistry, An Najah National University, P. O. Box 7, Nablus, Palestine
[b] Department of Biology & Biochemistry, Birzeit University, P. O. Box 14, Birzeit, Palestine

(Recibido mayo 2000, aceptado mayo 2001)

Key words: poplar leaves, *Populus euphratica,* copper uptake, polluted water, adsorption

ABSTRACT

Factors affecting copper removal from polluted water by poplar (*Populus euphratica*) leaves were investigated and a mechanism for copper removal was suggested. Increasing the amount of leaves from 5 to 25 g/L increased the rate and hence the amount of copper removed. Increasing the concentration of copper in solution from 2 to 20 mg/L caused a corresponding increase in copper uptake per unit weight of leaves at a constant leaf concentration of 20 g/L. The uptake of copper ions by poplar leaves was found to be noticeably affected by the presence of other metal ions. The effect of these ions could be dependent on the relative affinity of leaves to these ions and copper as well as to pH. Depending on the initial concentration, the presence of the chelating agent EDTA in the solution considerably reduced the rate and amount of copper uptake. Fresh leaves were found to uptake much less copper than dry leaves. Rough-crushing or fine-grinding of leaves slightly affected copper uptake. Agitation slightly increased the rate of copper uptake and cleaning leaves did not affect its ability to uptake copper. The main mechanism for copper removal by poplar leaves is most probably adsorption. Other mechanisms, such as complexation, may play a minor role as well. Intrapore diffusion is thought to be the rate-limiting step for the interaction between poplar leaves and copper ions.

Palabras clave: hojas de álamo, *Populus euphratica,* captación de cobre, agua contaminada, adsorción

RESUMEN

Se investigaron los factores que afectan la remoción de cobre por las hojas de álamo (*Populus euphratica*) de aguas contaminadas y se sugiere un mecanismo de esa remoción. Al incrementarse la concentración de hojas de 5 a 25 g/L aumentó la tasa y de aquí la cantidad de cobre removida. Cuando se incrementa la concentración de cobre en la solución de 2 a 20 mg/L provoca el correspondiente aumento en la captura de cobre por unidad de peso de las hojas a una concentración constante de hoja de 20 g/L. Se encontró que la captura de iones de cobre por las hojas de álamo fue afectada notablemente por la presencia de otros iones metálicos. El efecto de estos iones puede depender de la afinidad relativa de las hojas por estos iones, por el cobre así como del pH. Dependiendo de la concentración inicial, la presencia del agente quelante EDTA en la solución, redujo considerablemente la tasa y la cantidad de cobre capturado. Se encontró que las hojas frescas captaron menos cobre que las hojas secas. La trituración gruesa y fina de las hojas afectó ligeramente la captura del cobre. La agitación aumentó ligeramente la tasa de captura del cobre y la limpieza de la hojas no alteró su capacidad de captura. La adsorción es el mecanismo más probable de remoción

* Corresponding author: fax (+972) 92374439, e-mail: alsubu@najah.edu

de cobre por las hojas de álamo. Otro mecanismo, como la complejación tiene un papel menor. La difusión intraporo es una tasa limitante de la interacción de las hojas de álamo con los iones de cobre.

INTRODUCTION

Industrial effluents frequently contain a mixture of metal ions. Concentrations of these ions vary according to the type of industry. In addition, chelating agents, like EDTA, may be found in these effluents. This might affect metal removal processes by plant leaves.

Removal of metal ions from polluted water by plant leaves was reported to be efficient, direct, natural and low-cost (Salim and Robinson 1985ab, Salim 1988ab, Salim *et al.* 1992, 1994, Sayrafi *et al.* 1996).

In a recent work (Al-Subu *et al.* 2001), 15 leaves species were tested for their ability to remove copper from polluted water and the effect of pH on the removal process were investigated. In addition, a kinetics model of the interaction between copper ions and poplar leaves was presented. It was found that, using plant leaves to recover copper from solutions is a promising method and poplar leaves were found to be the best to recover copper from solution.

Therefore, the present work was conducted in order to investigate other factors that might affect the removal of copper from aqueous solutions. These factors include copper concentration and plant leaves amount, presence of chelating agents (EDTA) and competing ions, effects of agitation, washing leaves, drying leaves, leaf crushing and using leaf extract.

MATERIALS AND METHODS

All reagents used were of analytical grade (BDH) chemicals. Certified atomic absorption standards of copper solution containing 1000 mg/L were obtained from Perkin-Elmer, USA. Deionized water was used for the dilution of standards and samples.

Dry poplar (*Populus euphratica*) leaves were collected from El-badan, near Nablus in the West Bank. Leaves were cleaned with deionized water, soaked in 1M HNO_3 for 3 days, to remove their original content of copper and other heavy metals, and then were left to dry at room temperature before being used for the removal studies. Only negligible amounts of copper were found. Experiments were run at room temperature (about 20°C), the pH was adjusted to 4.40 using either 1M NaOH or 1M HCl, as required. The method of analysis was flame atomic absorption spectrometry.

The effect of varying leaves concentration (5, 10, 15, 20 and 25 g/L) was studied by following the decrease in copper concentration (from 20 mg/L) with time up to 100 hours.

The effect of changing copper concentration on its removal by leaves (20 g/L) was studied by employing 2, 6, 10, 14, 18, and 20 mg/L copper solutions.

The effect of other studied factors on copper removal was investigated by employing 20 g/L leaves suspended in 20 mg/L copper solutions. These factors include: competing ions (Na^+ Mg^{2+}, Ca^{2+}, Zn^{2+}, Ag^+, Cd^{2+} and Pb^{2+}) at 100 mg/L; complexing agent (EDTA) at 10, 20 and 100 mg/L; form of leaves employed (whole, crushed and ground leaves) at 20 g/L concentration; method of drying leaves (oven dried at 60 °C for 12 hours and naturally dried leaves); continuous agitation of leaf suspension (160 hours) and washing leaves with deionized water before being tested.

The leaf extract to be studied was made by soaking leaves in deionized water for 25 days or in 1 M HNO_3 for 24 hours or completely digested in 6 M HNO_3 and the resulted extract solutions were employed for copper removal.

The instruments used were Atomic Absorption Spectrometer, Pye Unicam, Model SP192 and a pH-meter from Hanna Instruments, model 8521.

Other details of the experimental procedure were described elsewhere (Al-Subu *et al.* 2001).

Statistical treatment of results

The standard deviation of five-fold readings was recorded directly from the *AAS* instrument and only those values with average standard deviation of less than 10% were reported.

RESULTS AND DISCUSSION

Effect of leaves concentration on copper removal

Various concentrations of poplar leaves ranging from 5 to 25 g/L were used to recover copper ions from 20 mg/L copper solutions. An obvious effect of leaf concentration was observed (**Fig. 1**). It was found that the uptake of copper per unit mass of the sorbent decreased with increasing sorbent mass. This may be due to the higher concentration of metal ions per binding site of the sorbent when the latter concentration was lower (AL-Asheh and Duvnjak 1997). This is supported by the fact that, increasing sorbent concentration from 5 to 25 g/L enhanced the rate and hence the total amount of copper removed from the solution. This is because

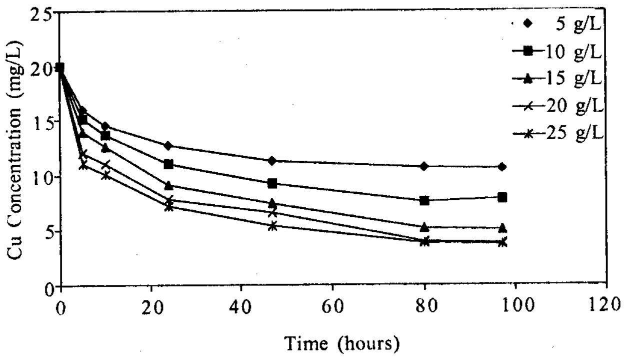

Fig.1. Effect of poplar leaves concentration on copper removal from 20 mg/L copper solution at pH 4.40

the number of binding sites increases with increasing sorbent concentration. These results are in good agreement with similar studies on plant adsorbents. For example, the removal of Pb^{2+}, Zn^{2+}, and Cd^{2+} by waste tea leaves (Tee and Khan 1988), removal of Cd^{2+} by beech leaves (Salim *et al.* 1992), removal of Cd^{2+}, Pb^{2+} and Hg^{2+} by hyacinth roots (Rosas *et al.* 1984, Wang 1995) and removal of copper by moss (AL-Asheh and Duvnjak 1997). Copper removal proceeded initially very fast but slowed down thereafter. Equilibrium was established between the amount of copper adsorbed to poplar leaves and copper remained in the solution after about 80 hours of contact. The high initial rate of copper uptake suggests that the adsorption occurs mainly at the surface of the leaf (Salim and Robinson 1985a, Salim *et al.* 1992, AL-Asheh and Duvnjak 1997).

Effect of copper concentration on its removal

Removal of copper from solutions containing different copper concentrations by 20 g/L poplar leaves was studied at pH 4.40 (**Fig. 2**). The results indicate that, increasing copper concentration in the solutions causes a corresponding increase in the rate and amount of copper lost from the solution. This can be explained by a progressive increase in the electrostatic interactions, relative to covalent interactions, of the sites with lower affinity for copper ions when the initial copper concentration is increased (Van Custem *et al.* 1984). The increase in metal uptake with increasing initial metal concentration is a well-known phenomenon. It was observed by Deshkar *et al.* (1990), Salim *et al.* (1992), Singh *et al.* (1993) and AL-Asheh and Duvnjak (1997) studying the uptake of metals by *Hardwickia binata* bark, beech leaves, tea leaves and moss, respectively.

Effect of competing ions on copper uptake

The effect of the presence of 100 mg/L competing metal ions on the removal of copper ions from the 20 mg/L copper solution was investigated using 20 g/L poplar leaves at pH 4.40. **Figure 3** indicates that these competing ions affect copper uptake by poplar leaves either positively or negatively. Pb^{2+}, Cd^{2+} Ag^{+} and Ca^{2+} slowed down the rate of copper uptake in the following order $Pb^{2+}>Cd^{2+}>Ca^{2+}>Ag^{+}$. On the other hand, the presence of Na^{+}, Zn^{2+} and Mg^{2+} enhanced copper uptake in the order $Zn^{2+}>Mg^{2+}>Na^{+}$. This means that poplar leaves have higher affinity for Pb^{2+}, Cd^{2+}, Ca^{2+} and Ag^{+}. The effect of competing ions seems to be dependent on the sorption affinity of the sorbent and the metal as well as to the effect of metal on the pH of solution. Wang (1995) concluded that the binding sites on the water hyacinth roots have higher affinity for Pb^{2+} compared to that for Cd^{2+} and Zn^{2+}. When the three metals were mixed in a solution, Pb^{2+} uptake was not affected by the presence of Cd^{2+} and Zn^{2+}. Whereas, the uptake of Cd^{2+} and Zn^{2+} was found to be noticeably less in the presence of Pb^{2+}. Similar results were observed by Low *et al.* (1994). The order of sorption affinity was $Pb^{2+}>Cu^{2+}>Cd^{2+}>Zn^{2+}>Ni^{2+}$ when hyacinth roots were used to remove metals at a

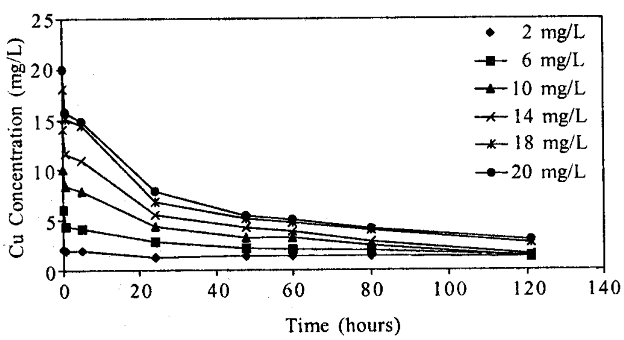

Fig.2. Effect of copper concentration on its removal by 20 g/L poplar leaves at pH 4.40

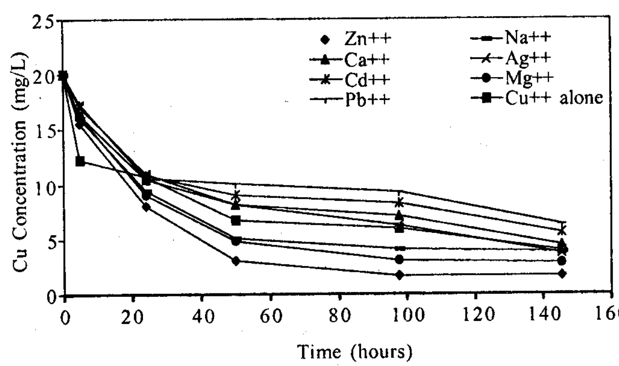

Fig.3. Effect of competing ions (100 mg/L) on the removal of copper by 20 g/L poplar leaves at pH 4.40

50 ppm metal levels. Salim *et al.* (1992), on the other hand, found that the presence of Pb^{2+} in solution increased the rate and amount of uptake of Cd^{2+} by beech leaves. While Cd^{2+} uptake was decreased by the presence of the other metal ions in the order $Cu^{2+}>Ag^{+}>Mg^{2+}>Ni^{2+}$.

Effect of EDTA as a chelating agent on copper removal

The effect of 10, 20 and 100 mg/L EDTA on copper removal by poplar leaves was investigated. Increasing the concentration of EDTA in the solution caused a noticeable decrease in copper removal (**Fig. 4**). After about 50 hours of contact, copper removal by 20 g/L poplar leaves decreased from 68% in the solution without EDTA to 42%, 33.5% and 26.5% in solutions containing 10, 20 and 100 mg/L EDTA, respectively. This is because EDTA rapidly forms a complex with copper ions thus, leaving smaller amount of copper available for binding on the biosorbent. Salim *et al.* (1994) treated lead-loaded cypress leaves with 100, 200 and 1000 mg/L EDTA and observed that lead ions were desorbed completely by EDTA. The rate and degree of this desorption process was dependent on EDTA concentration.

Effect of leaf crushing on copper removal

Whole, roughly crushed and finely ground poplar leaves were used to remove copper from solution. Copper removal was slightly increased by grinding and crushing. Metal removal by the three forms of leaves can be ordered as: ground leaves (*ca.*83%) > crushed leaves (*ca.*75%) > whole leaves (*ca.*70%).

Similar results were obtained by Salim *et al.* (1994) studying lead uptake by cypress leaves. The increase in copper uptake with could be due to an increase in the adsorption sites available for copper ions upon crushing or grinding leaves.

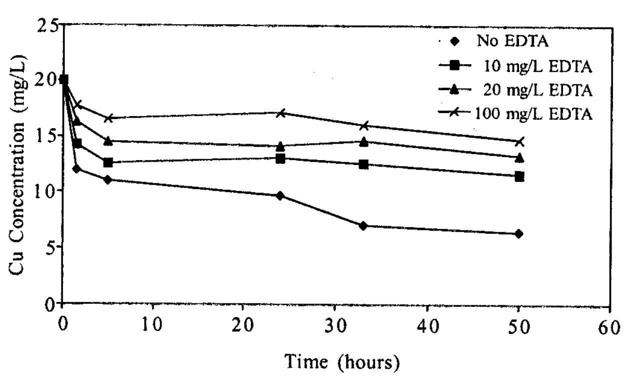

Fig.4. Effect of different concentrations of EDTA on copper removal from 20 mg/L copper solution using 20 g/L poplar leaves at pH 4.40

Effect of drying leaves on copper removal

Fresh, dried, and decaying leaves were used to uptake copper from solution. Dried leaves (oven and room temperature) were found to be more effective in removing copper than fresh leaves (**Fig. 5**). This could be due to the fact that fresh leaves are intact and their cuticle prevents adsorption of metals to cell wall material. Decaying leaves allow adsorption since the outer layer is no modified. Decaying poplar leaves were cleaned and dried either at room temperature or in an oven at 60 °C. Though, method of drying did not greatly influence copper removal efficiency, copper removal can be ordered as: naturally dried (decaying) > oven dried > fresh leaves.

Similar results were observed by Salim *et al.* (1994) for lead removal by cypress leaves. However, cadmium uptake by fresh beech leaves was found to be much greater than by dry leaves.

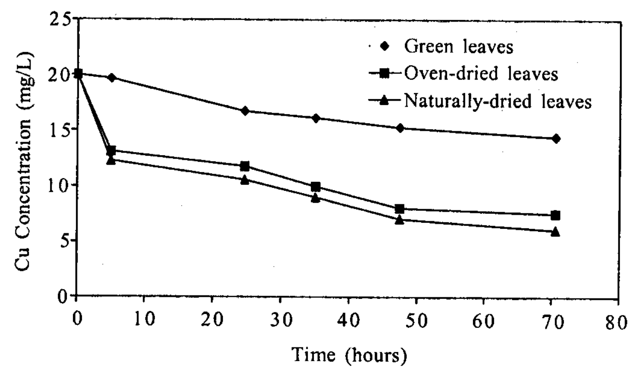

Fig. 5. Effect of leaf drying on copper uptake from mg/L copper solution by 20 g/L poplar leaves at pH 4.40

Effect of agitation on copper removal

Agitating the leaf suspension slightly increased the rate of copper uptake by poplar leaves only during the first 40 hours of contact. Thereafter, metal removal proceeded slowly and no effect of agitation was observed. Agitation might improve the opportunity of adsorption between copper ions and adsorption sites on the leaf surface.

Effect of leaf washing on copper removal

To investigate whether leaf washing has any effect on cooper uptake by poplar leaves, washed and unwashed leaves were used to remove copper from the metal solution. No effect of cleaning was observed neither on the rate nor on the amount of copper removed.

Mechanism of sorption of copper ions on poplar leaves

Recovery of copper ions by poplar leaves could occur throurgh adsorption on leaf surface, complexation with active components of the leaf or both. Based on the results of the present study, adsorption is thought to be the most probable mechanism The applicability of adsorption isotherm to the results (Al-Subu *et al.* 2001) for poplar leaves also support this assumption.

Rate-limiting step

Adsorption of copper on poplar leaves can be assumed to take place through three consecutive steps (Salim *et al.* 1992):

1. Film diffusion: diffusion of metal ions through a thin film of the solution to the external surface of the leaf. Cations are driven through this film by a concentration gradient.
2. Intrapore diffusion: diffusion of metal ions within the pores of the leaf.
3. Adsorption step: the actual adsorption of the metal onto the interior surface of the leaf bounding the capillary space of the leaf.

The straight-line relationships (Al-Subu *et. al.* 2001) between copper adsorbed (C_a) and the square root of time, and the negligible effect of agitation as well as the slight effect of crushing or grinding leaves on copper removal, all suggest that the rate-limiting step for adsorption is diffusion (Weber *et al.* 1963, Salim *et al.* 1992).

REFERENCES

Al-Subu M. M., Salim R., Abu-Shqair I. and Swaileh K. M. (2001). Removal of dissolved copper from polluted water using plant leaves: I. Effects of acidity and plant species. Rev. Int. Contam. Ambient. *17*, 91-96.

AL-Asheh S. and Duvnjak Z. (1997). Adsorption of metal ions by moss. Adv. Environ. Res. *2*, 194-212.

Clark C. (1989). *Marine pollution*. Oxford University Press, New York, 220 p.

Deshkar A. M., Bokade S. S. and Dara S. D. (1990). Modified *Hardwickia binata* bark for adsorption of mercury (II) from water. Wat. Res. *24*, 1011-1016.

Low K. S., Lee C. K. and Tai C. H. (1994). Biosorption of copper by water hyacinth roots. J. Environ. Sci. Health, A*29*, 171-188.

Rosas I., Carbajal M.E., Gómez-Arroyo S., Belmont R. and Villalobos-Pietrini R. (1984). Cytogenetic effects of cadmium accumulation on water hyacinth (*Eichhornia crassipes*). Environ. Res. *33*, 386-395.

Salim R. and Robinson J. W. (1985a). Removal of dissolved aluminum released by acid rain using decaying leaves. I. Effects of pH and species of leaves. J. Environ. Sci. Health, A*20*, 701-720.

Salim R. and Robinson J. W. (1985b). Removal of dissolved aluminum released by acid rain using decaying leaves. II. Effects of concentration of leaves, aluminum and other cations. J. Environ. Sci. Health, A*20*, 721-734.

Salim R. (1988a). Removal of nickel (II) from polluted water using decaying leaves – Effect of pH and type of leaves. J. Environ. Sci. Health, A*23*, 183-197.

Salim R. (1988b). Removal of nickel (II) from polluted water using decaying cypress leaves. J. Environ. Sci. Health, A*23*, 321-334.

Salim R., Al-Subu M. M. and Sahrhage E. (1992). Uptake of cadmium from water by beech leaves. J. Environ. Sci. Health, A*27*, 603-627.

Salim R., Al-Subu M. M. and Qashoa S. (1994). Removal of lead from polluted water using decaying plant leaves. J. Environ. Sci. Health, A*29*, 2087-2114.

Sayrafi O., Salim R. and Sayrafi S. A. (1996). Removal of cadmium from polluted water using decaying leaves – Effects of type of leaves and of concentration of cadmium. J. Environ. Sci. Health, A*31*, 2503-2513.

Singh D. K., Tiwari D. P. and Saksena D. N. (1993). Removal of lead from aqueous solutions by chemically treated tea leaves. Indian J. Environ. Health *35*, 169-177.

Tee T. W. and Khan R. M. (1988). Removal of lead, cadmium and zinc by waste tea leaves. Environ. Technol. Lett. *9*, 1223-1232.

Van Custem P., Metgdagh M. M., Rouxhet P. G. and Gillet C. (1984). Preliminary ESR study and relation with ion exchange thermodynamics of copper adsorbed on a biological ion exchanger- the *Nitella flexilis* cell wall. React. Polym. *2*, 31-35.

Wang G. (1995). Biosorption of heavy metal ions from aqueous solutions by nonliving water hyacinth roots. Ph.D. Dissertation, University of Nevada, Reno, UMI Company, 119 pp.

Weber W. J. Jr., Asce A. M. and Morris J. C. (1963). Kinetics of adsorption on carbon from solution. J. Sanit. Eng. Div. Am. Soc. Civ. Eng., *89* (SA2), 31-39.