Rev. Int. Contam. Ambient. 17 (2) 91-96, 2001

REMOVAL OF DISSOLVED COPPER FROM POLLUTED WATER USING PLANT LEAVES: I. EFFECTS OF ACIDITY AND PLANT SPECIES

M. M. AL-SUBU*[1], R. SALIM[1], I. ABU-SHQAIR[1] and K. M. SWAILEH[2]

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

(Recibido marzo 2000, aceptado enero 2001)

Keywords: plant leaves, copper, polluted water, adsorption, acidity

ABSTRACT

Removal of copper from polluted water by plant leaves was studied using 15 species. Copper was recovered in variable percentages depending on the species and pH value of the solution. Copper recovery from a 20 mg/L copper solution ranged between 88% (in poplar leaves) and 33% (in oak leaves). For all leaves studied, maximum copper recoveries were found to be between pH 4 and 6 depending on the plant species. At pH 2 the copper was not removed by the plant leaves studied. Adsorption was suggested as the main mechanism for the reaction between copper ions and plant leaves with a reaction order equal to one.

Palabras clave: hojas de plantas, cobre, agua contaminada, adsorción, acidez

RESUMEN

La remoción de cobre del agua contaminada por medio de hojas de plantas fue estudiada utilizando 15 especies. Se encontraron porcentajes variables de recuperación de cobre que dependieron de la especie y del valor del pH de la solución. De los 20 mg/L de la solución de cobre, el intervalo de recuperación de este metal estuvo entre 88 % (en las hojas de álamo) y 33 % (en las hojas de roble). El máximo de recuperación de todas las hojas estudiadas se encontró entre 4 y 6 de pH dependiendo de la especie de planta. A pH 2 el cobre no fue removido por las hojas de las plantas estudiadas. Se sugirió que la adsorción fue el mecanismo principal de reacción entre los iones de cobre y las hojas de las plantas con un orden de reacción igual a uno.

INTRODUCTION

Since metals have many useful industrial applications, removal of metals from municipal and industrial wastewaters is an important environmental issue. In addition, some trace metals are essential elements for the normal growth and development of living organisms. However, many heavy metals are highly toxic to a wide range of organisms when the metal accumulative concentration exceeds a certain limit. Copper is widely used in the industry of electrical equipment and wires, pipes, alloys, antifouling paints, algaecides and wood preservatives. It is considered the second toxic metal to aquatic organisms after mercury (Clark 1989). Absorption of excess

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

copper by man may cause "Wilson's Disease" which is characterized by the accumulation of copper in the brain, liver, pancreas, myocardium and skin (Bockris 1978).

Several methods are developed to recover metals from wastewaters. These include coagulation, chemical precipitation, ozonation, membrane filtration, biosorbents, adsorption to activated carbon and ion exchange. The last two are the most commonly used. However, these are expensive and the ion exchange resin and activated carbon must be regenerated. As a result, environmental scientists keep looking for other low-cost adsorbents such as cotton (Roberts and Rowland 1973), peat moss (Coupal and Lalancette 1976, Ho *et al.* 1995), peanut skins (Randall *et al.* 1978), waste tea leaves (Tee and Khan 1988), bark and other cellulose material (Deshkar and Dara 1988), green algae and rice hull (Roy *et al.* 1993), moss (AL-Asheh and Duvnjak 1997), and others. The efficiency of these methods depends on the adsorbent device and metal solution.

Plant leaves are natural wastes that are found to be efficient in removing considerable amounts of metals like lead, cadmium, nickel and aluminum, from aqueous metal solutions (Salim and Robinson 1985a,b, Salim 1988a,b, Salim *et al.* 1992, 1994 and Sayrafi *et al.* 1996). Using plant leaves offers the advantages of being simple, direct, and inexpensive. The efficiency of this method varies according to the type of plant species, metal, pH and other factors. In this paper, the ability of leaves from 15 different plant species to remove copper from polluted water and the effect of pH on copper removal process are investigated. In addition, a model for the kinetics of the interaction between copper ions and leaves is discussed.

MATERIALS AND METHODS

Naturally dried leaves of 15 different plant species common in Palestine were collected from Nablus and Jenin areas in the northern West Bank (**Table I**). To determine the leachable amount of copper, leaves were cleaned first with deionized water before being soaked in 1M HNO_3 for three days and the amount of copper leached to the solution was measured using atomic absorption spectrophotometer as described below.

Glass bottles (250 ml) were used as containers to run the experiment. These were carefully cleaned and soaked in 1M HNO_3 for three days. Thereafter, bottles were washed with deionized water.

Copper stock solution (1000 mg/L) was prepared using $CuSO_4 \cdot 5H_2O$ (Analar grade, BDH). Necessary dilutions were done to obtain the desired copper concentrations. Certain weight of the clean dry leaves was placed inside the glass bottles and 200 ml of the required copper solution concentration were added. The experiment was run at room temperature (about 20 °C) and the pH of the solutions was monitored and adjusted to the desired values using either 1M NaOH or 1M HCl as required. The pH values were determined using a pH-meter (Hanna Instruments, model 8521). The accuracy of the instrument was ± 0.01. Removal of copper from the solutions was monitored by tracing the decrease of copper concentration. Copper concentrations were measured using an acetylene-air flame atomic absorption spectrophotometer (Pye Unicam, SP 192). Each measurement of copper concentration was repeated five times and the average was taken. Readings with a standard deviation above 10% were rejected.

TABLE I. PLANT SPECIES STUDIED AND THEIR COLLECTION SITES

English name	Scientific name	Collection site
Carob	*Ceratonia siliqua*	Sieleh Harthieh/ Jenin
Cinchona	*Eucalyptus longifolia*	Sieleh Harthieh/ Jenin
Cypress	*Cupressus sempervirens*	Nablus
Ficus	*Ficus nitida*	Nablus
Guava	*Psidium guajava*	Sieleh Harthieh/ Jenin
Loquat	*Eriobotrya japonica*	Sieleh Harthieh/ Jenin
Olive	*Olea europea*	Sieleh Harthieh/ Jenin
Oak	*Quercus ithaburensis*	Sieleh Harthieh/ Jenin
Pine	*Pinus halepensis*	Sieleh Harthieh/ Jenin
Pistache	*Pistacia palaestina*	Sieleh Harthieh/ Jenin
Poplar	*Populus euphratica*	El-badan/ Nablus
Reed	*Phragmites australis*	Till/ Nablus
Sisso	*Dalbergia sisso*	Nablus
Walnut	*Juglans regia*	Nablus
Willow	*Salix alba*	El-badan/ Nablus

RESULTS AND DISCUSSION

All leaves employed were found copper-free, as indicated from the negligible concentration of leached copper ions in solutions of these leaves.

Ability of different plant leaves to remove copper

Leaves (20 g/L) of different plant species were found to have different abilities to remove copper from aqueous solutions containing 20 (mg/L) copper. Rate of copper removal was fast during the early stages of contact, then decreased to reach a steady state condition (**Fig. 1**). The fast recovery of copper at the beginning of the experiment could be due to the immediate adsorption of copper on the leaf surface (film diffusion). Then, the metal ions start to enter the pores of the leaf in a slower process called "intrapore diffusion" (Salim and Robinson 1985a,b, Salim *et al.* 1992).

Figure 1 shows the decrease in copper concentration, as a function of time, at the natural pH value of leaf suspension (pHn) with initial pH value been adjusted

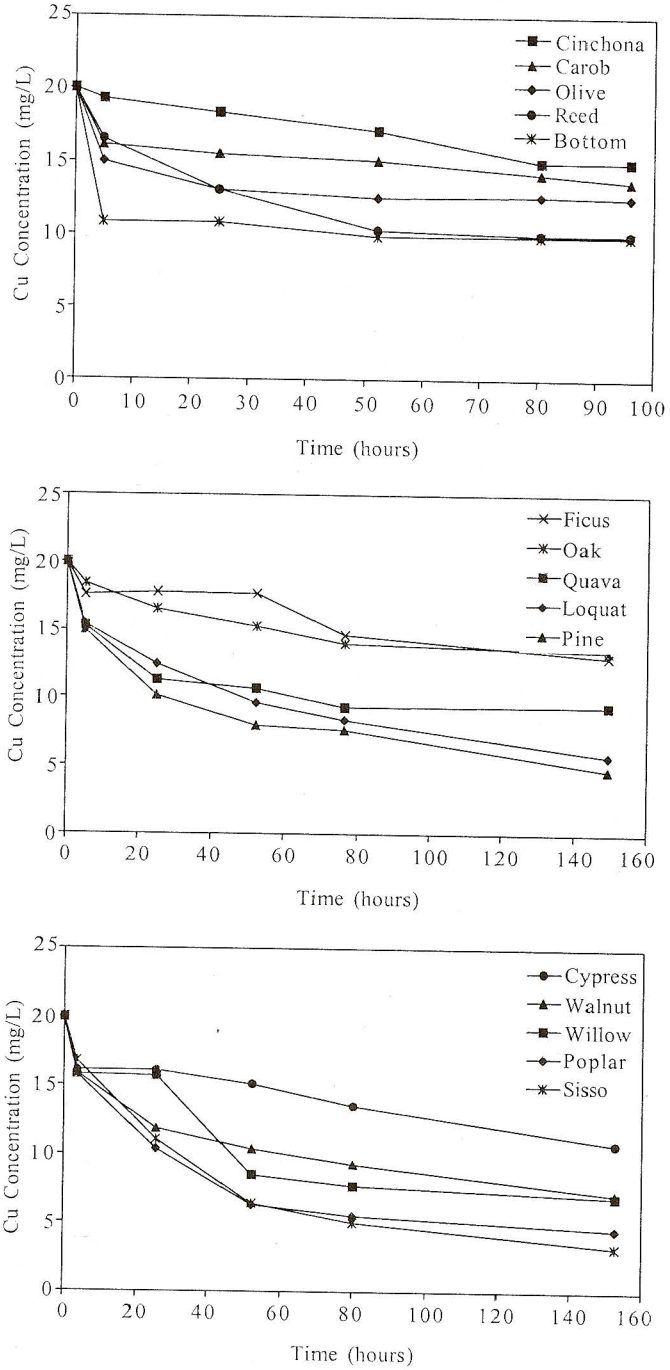

Fig. 1. Removal of copper from copper solution (20 mg/L) using 20 g/L dry leaves of different plant species. pH of the solution was not adjusted (pHn)

to pH 4 for all leaf suspensions. At equilibrium, pH values of different leaves were found between 3.98 and 7.06 with cinchona being the most acidic and ficus the least. Poplar and sisso leaves were found to be the most effective in removing copper from polluted water (> 80% removal) and cinchona, carob, oak and ficus were the least with percentage removal that did not exceed 35%.

Effect of pH on copper removal by plant leaves

Copper removal efficiency by leaves of different plants species was studied at different pH values (2, 4, 6 and pHn), and the maximum efficiency at each pH is reported in **table II**. For all plant leaves used, copper removal was minimal (if any) at pH 2 and maximum at pH between 4 and 6. Similar results were obtained for copper and cadmium removal by water hyacinth roots (Low *et al.* 1994, Wang 1995). According to Wang (1995), the isoelectric point for water hyacinth roots was around pH 2. At pH less than 2, most of the binding sites on the root surface would have positive charges making the binding and/or sorption of the metal ions unattractive. Another hypothesis is that higher H^+ concentrations do not allow precipitation of metal ions *in situ* within the roots, but keep metal ions available for free diffusion out of the roots and free space (Arvik and Zimdahl 1974). Our results indicate that metal binding raises with increasing pH to reach a maximum at about pH 5. Ke and Rayson (1992) observed similar results. It has been attributed to the change in the dominant functional groups responsible for binding on the cell wall, with carboxylate groups and diamine groups being the most important ones in pH $\leq$ 5 and pH 6, respectively. In addition, the binding sites of the leaf cell wall would have a net negative charge. This would lead to electrostatic attraction between metal ions and negatively charged binding sites of the cell wall (Wang 1995). At higher pH values, precipitation of metal occurs. The solubility product constant (Ksp) for copper hydroxide is 4.8×10^{-20}. This value predicts that copper begins to precipitate as hydroxide at pH 7.59. Maximal copper removal percentages of different plant leaves and the corresponding optimal pH values are presented in **table III**. Maximum removal of copper

TABLE II. PERCENTAGE REMOVAL OF COPPER (20 mg/L) BY PLANT LEAVES (20g/L) AT DIFFERENT pH VALUES AFTER 150 HOURS CONTACT

Plant species	% Cu removal at pH			
	2	4	6	pHn
Carob	2.5	20.0	37.5	25.0
Cinchone	0.0	82.5	90.0	20.0
Cypress	8.0	17.5	27.5	35.0
Ficus	12.5	20.0	20.0	27.5
Guava	0.0	47.5	40.0	47.5
Loquat	5.0	57.5	60.0	65.0
Olive	0.0	27.5	37.5	35.0
Oak	0.0	30.0	30.0	30.0
Pine	0.0	40.0	70.0	67.5
Pistachio	17.5	60.0	57.5	50.0
Poplar	20.0	80.0	65.0	70.0
Reed	7.5	60.0	52.5	45.0
Sisso	27.5	65.0	70.0	77.5
Walnut	5.0	70.0	55.0	60.0
Willow	35.0	70.0	55.0	57.5

was 88% (poplar leaves) and minimal was 33% (oak leaves).

TABLE III. MAXIMUM REMOVAL OF COPPER BY PLANT LEAVES FROM THE 20 mg/L COPPER SOLUTION AND THE pH VALUE OF THE MAXIMUM REMOVAL

Leaf type	Maximum % removal	pH
Poplar	88	4.00
Sisso	83	4.30
Willow	78	4.00
Pine	76	6.20
Loquat	71	6.19
Walnut	71	4.00
Reed	66	4.00
Pistachio	62	4.00
Guava	54	4.00
Carob	48	6.00
Cypress	42	6.08
Cinchona	37	6.00
Olive	37	6.00
Ficus	34	6.00
Oak	33	6.00

Kinetics of the interaction between copper ions and plant leaves

Application of adsorption isotherms

The present results agree with those reported by others authors (Salim and Robinson 1985a,b; Lee and Hardy 1987, Salim 1988a,b, Yadava *et al.* 1989, Salim *et al.* 1992, Wang 1995, AL-Asheh and Duvnjak 1997), i.e., that the loss of metal ions on biosorbents occurs mainly through adsorption of the metal ion on the adsorption sites of the biosorbent. The linearized form of the Freündlich isotherm model was applied to the results of this study. The model is

$$C_a = k\, C_s^{1/n}$$

where:

C_a = the equilibrium concentration of copper adsorbed on leaves (mg/g).

C_s = the equilibrium concentration of copper left in solution (mg/L).

k = the Freündlich constant related to sorption capacity of the sorbent (L/g).

1/n = the sorption intensity of the sorbent.

The values of k and 1/n were obtained from the intercepts and slopes, respectively, of the linear plots of $\log C_a$ *versus* $\log C_s$ of the experimental data (**Fig. 2**). Parameters of the Freündlich adsorption isotherm of copper on poplar leaves are:

$$\log k = 2.72 \text{ and } 1/n = 1.44$$

The linear plot in **Fig. 2** suggest the applicability of Freündlich adsorption isotherm on the uptake of copper ions by poplar leaves. Freündlich isotherm can be applied to substances with pores which are not too narrow (Ponec

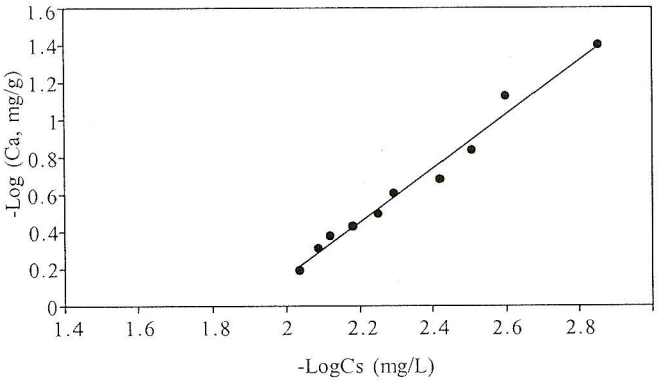

Fig. 2. Application of the Freündlich adsorption isotherm on the uptake of copper from various copper solutions by 20 g/L poplar leaves at pH 4.4. C_a is the amount of copper adsorbed on poplar leaves. C_s is the amount of copper left in the solution

et al. 1974). The value of k (the intercept) increases slightly with time, while 1/n values remained almost constant (average 1/n value = 1.42). The value of 1/n is usually dependent on the nature and strength of the sorption forces as well as on the distribution of active sites on the surface of the sorbent. If 1/n > 1, bond energies increase with surface density of the sorbent (Wang 1995).

Order of the adsorption reaction

Time-dependent loss of metal from solution with various metal concentrations can be used to study the effect of metal ion concentration on the rate of its adsorption by plant leaves and thus, gives the order of the reaction between metal ions and plant leaves (Salim *et al.* 1994). The concentrations of copper adsorbed on poplar leaves (C_a) was calculated (assuming C_a and C_s are additive). For each initial concentration of copper a plot of C_a against $\sqrt{t}$ was plotted (**Fig. 3**). The slopes of these straight lines

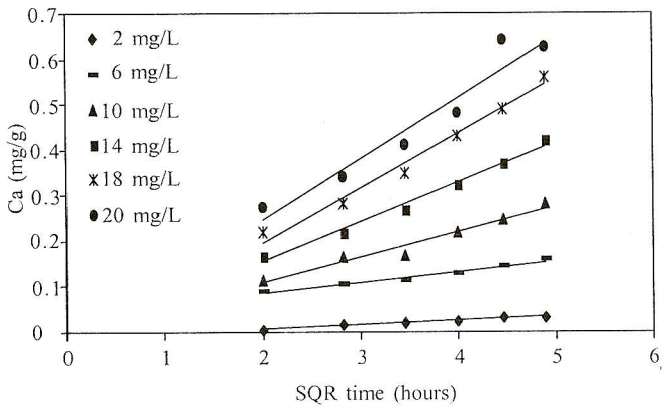

Fig. 3. Plots of copper uptake (C_a) by 20 g/ L poplar leaves versus square root of time (SQR) for various copper concentrations at pH 4.4

$(dC_a/d\sqrt{t})$ reflect the rate of copper adsorption (dC_a/dt) on poplar leaves, which can be expressed by the formula:

$$(dC_a / dt)_t = 1/2\sqrt{t}(dC_a / d\sqrt{t})_t$$

Plotting the rate of copper adsorption (dC_a/dt) against the concentration of copper left in the solution (C_s) results in a linear correlation as shown in **Fig. 4**. Each line corresponds to the rate of adsorption of copper as a function of concentration of copper left in the solution (C_s) after a certain exposure time and regardless of the initial concentration of copper in the solution. Therefore, it can be concluded that the loss of copper ions on poplar leaves is a first order reaction, or might be a pseudo first order reaction due to the high number of adsorption sites on leaves. In general, the first order reaction model is applicable to the sorption of heavy metals from liquid to solid phases, which is considered to be a reversible reaction with an equilibrium being established between two phases (Wang 1995).

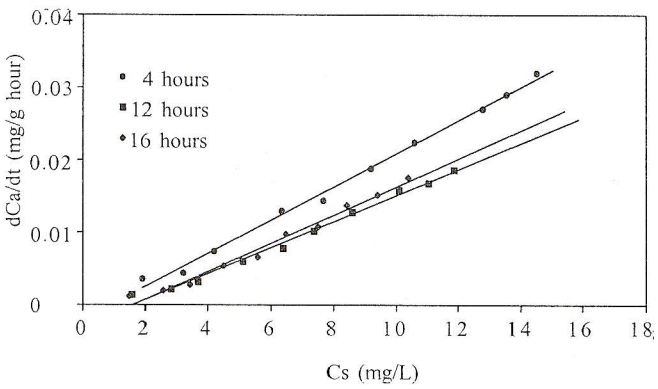

Fig. 4. Dependence of the rate of copper uptake (dC_a/dt) by 20 g/L poplar leaves on the concentration of copper remaining in the solution (C_s) at pH 4.4

CONCLUSIONS

Removal of copper ions from aqueous solutions was found to be dependent on the plant species used. Among the plant leaves studied, poplar and sisso leaves were the most effective in removing copper. Cinchona, olive, ficus and oak leaves were found to be weak removers of copper.

Metal removal by leaves of all 15 plants studied was found to be pH-dependent. Maximal metal removal was achieved between pH 4 and pH 6. Metal was not removed at pH 2 was almost negligible for all leaf types studied.

Freündlich adsorption isotherm was found to be applicable to the results of the present study. Therefore, adsorption can be suggested as the main way of interaction between plant leaves and copper ions. The reaction between copper ions and plant leaves was found to be a first order reaction.

REFERENCES

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

Arvik J.H. and Zimdahl R. L. (1974). The influence of temperature, pH and metabolic inhibitors on uptake of lead by plant roots. J. Environ. Qual. *4*, 374-376.

Bockris J. O. M. (1978). *Environmental chemistry*. Plenum Press, New York, pp. 465-466.

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

Coupal B. and Lalancette J. M. (1976). The treatment of wastewaters with peat moss. Water. Res. *10*, 1071-1076.

Deshkar A. M. and Dara S. D. (1988). Sorption of mercury by *Techtona grandis* bark. Asian Environ. *10*, 3-11.

Ho Y. S., Wase D. A. J. and Forster C. F. (1995). Batch nickel removal from aqueous solution by sphagnum moss peat. Water. Res. *29*, 1327-1332.

Ke H. D. and Rayson G. D. (1992). Characterization of cadmium binding sites on *Datura innoxia* using ^{113}Cd NMR Spectrometry. Environ. Sci. Technol. *26*, 1202-1205.

Lee T. A. and Hardy J. K. (1987). Copper uptake by water hyacinth. J. Environ. Sci. Health A*22*, 141-160.

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.

Ponec V., Knor Z. and Cerny S. (1974). *Adsorption on solids*. CRC Press, Cleveland, Ohio, 437 p.

Randall J., Hautala E. and Waiss A. C. (1978). Binding of heavy metal ions by formaldehyde polymerized peanut skins. J. Appl. Polym. Sci. *22*, 379-389.

Roberts E. J. and Rowland S. P. (1973). Removal of mercury from aqueous solutions by nitrogen containing chemically modified cotton. Environ. Sci. Technol. *7*, 552-556.

Roy D., Greenlaw P. N. and Shane B. S. (1993). Adsorption of heavy metals by green algae and ground rice hulls. J. Environ. Sci. Health A*28*, 37-50.

Salim R. and Cooksey B. J. (1980). Kinetics of adsorption of lead on river mud. Plant and Soil *54*, 399-417.

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.

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

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 p.

Yadava K. P., Tyagi B. S. and Singh V. N. (1989). Fly-ash for the treatment of water enriched with lead. J. Environ. Sci. Health A*24*, 783-808.