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Removal of Copper from Water by Decaying *Tamrix gallica* Leaves

FARID R. ZAGGOUT
Department of Chemistr,y Al-Azhar University, Gaza, P.O.Box 1277, Gaza, Gaza Strip, via Israel

Uptake of copper from aqueous solution by *Tamrix gallica* leaves has been studied. The effect of several factors on both rate and amount of this uptake has been investigated. These factors include concentration of copper, concentration of leaves, pH, competing ions, drying leaves and grinding leaves.

The pattern of curves showing the loss of copper from solution has been explained. Applicability of the Freundlich adsorption isotherm on the present results has been examined and the parameters of this isotherm have been calculated. The order of reaction between copper ion and *Tamrix gallica* leaves has been determined and a mechanism for this reaction has been suggested.

INTRODUCTION

In an increasingly industrialized world, the need to deal with the waste products generated by industrial processes cannot be ignored. Waste products enter the environment in various forms and threaten the quality of the air, land and water.

The presence of waste products in water is especially serious, as many of these products can enter the food chain, where the processes of bioconcentration can rapidly increase their concentration to toxic levels. For this reason, it is extremely important to find methods of treating these waste products and eliminating them from aqueous system. The United States Environmental Protection Agency has listed copper as a priority pollutant.[1]

Decaying leaves have shown their ability to remove heavy metals from aqueous solutions.[2, 3]

The use of decaying leaves as biological pollution control device offers an alternative method of pollution control that is economically attractive and environmentally feasible. This work investigates various solution factors that influence the removal of copper by decaying leaves with the goal of optimizing the process. Industrial sources of copper containing effluents are from mining, plating, fertilizers, fibre production and pipe corrosion.[4] Copper is easily maintained in aqueous solution and may be transported as inorganic complex.

From the water, copper ultimately finds its way into the body, resulting in damage to the nervous system and kidney[5]. In some instances exposure to copper has resulted in jaundice and enlarged liver. Copper is suspected to be responsible for one form of metal fume fever[6].

Several methods have been suggested in the literature to remove copper from water such as precipitation and ion exchange. The former method relies on the fact that copper forms an insoluble and relatively stable hydroxide under alkaline condition, and in the presence of complexing agent makes the precipitation of copper more difficult.[7] Ion exchange is technically feasible but considerably more expensive than precipitation. A number of other materials have also been used to remove heavy toxic metals from water such as peat, human hair,[8] wool and silk, water hyacinth[9, 10] and fly ash. In previous studies, decaying leaves were used for the removal of aluminum[2, 3] and nickel[11] from water.

The aim of this paper is to introduce leaves (represented by *Tamrix gallica* leaves) as a way for the removal of copper from polluted water and several solution factors will be studied in an attempt to optimize the copper uptake by *Tamrix gallica* leaves and study the kinetics of this uptake.

EXPERIMENTAL

Tamrix gallica leaves were collected and dry leaves were treated with 1 M HNO_3, then with distilled water and finally dried in an oven at 50°C. Green leaf samples were washed with 1 M nitric acid for few seconds and then with distilled water and finally left to dry in a hood at room temperature. Polyetheylene bottles (250 mL), cleaned and treated with 1 M nitric acid and finally washed with distilled water, were used as containers.

The metal solutions used for this study (Cu, Na, Pb, Cd and K) were prepared by dilution from standard solutions of $Cu(NO_3)_2$, $NaNO_3$, $Pb(NO_3)_2$, $Cd(NO_3)_2$ and KNO_3 respectively. High grade quality chemicals were used for the preparation of standards. Elements were analyzed using atomic absorption spectrometer (Shimadzu AA-6601 F).

RESULTS AND DISCUSSION

Pattern Curves Representing Loss of Copper from Solution

Curves showing the degree of loss of copper with time are shown in Figs. 1 to 7 under different conditions. These showed two stages of loss of copper. Stage 1 represents a very high rate of loss of copper on *Tamrix gallica* leaves up to ½ h. In Stage 2 copper started to be lost from solution with a very much lower rate than that of Stage 1; this stage is continued until the end of the time observed in the experiments of this work (*i.e.*, 48 h).

The two stages of the present curves might be explained on the assumption that leaves have ready sites for adsorption of copper; these sites are at or close to the surface of the leaf, and they are responsible for the high rate of loss of Cu during the first 30 min representing the first stage of curves. Saturation of these sites might result in decrease in the rate of loss of Cu which represent the second stage.

Effect of Copper Concentration: The uptake of copper from solution on similar amounts of *Tamrix gallica* leaves (20 g/L) was followed for various concentrations of copper ranging from 5 to 20 ppm in aqueous solutions at pH 6.7. The results, presented in Figs. 1-A and 1-B showed that increasing copper concentration increased the amount of copper lost from solution (Fig. 1-A) but the percentage of copper lost from solution was higher from low copper concentration than from solutions having higher concentration of copper.

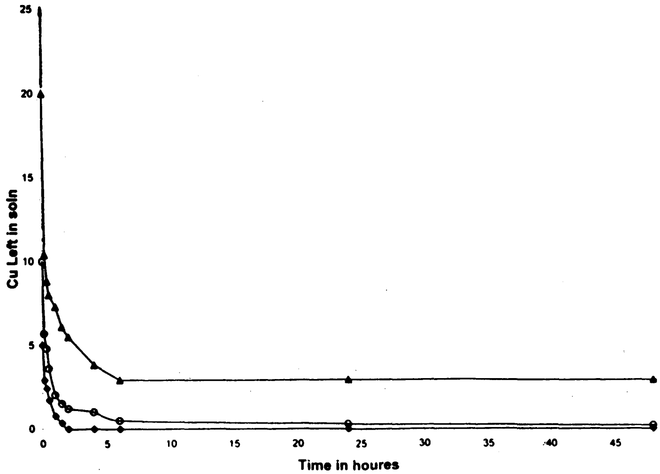

Fig. 1A. Effect of concentration of copper on its uptake by 20 g dry *Tamrix gallica* leaves/L copper aqueous solution at pH 6.7.

About 60–90% of copper was lost from each of the various copper solutions studied here in about 30 min to 1 h. This amount represents the amount of copper adsorbed during the first stage, then slowing down the rate of loss of copper afterwards becomes relatively constant.

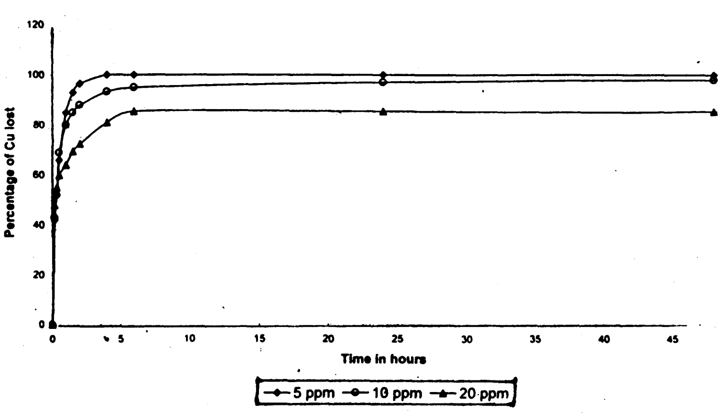

Fig. 1B. Percentage of copper lost from various copper concentrations on 20 g dry *Tamrix gallica* leaves/L copper solution at pH 6.7.

Effect of Concentration of Leaves on Copper Uptake from Solution: The effect of concentration on the removal of copper from solution was studied using dry *Tamrix gallica* leaves. From 4 to 40 g leaves/litre of solution were used to take copper from 20 ppm copper solution at pH 6.7. The results obtained showing the loss of copper and the percentage of this loss versus time shown are in Figs. 2-A and 2-B respectively. The effect of increasing concentration of leaves is to increase the rate of loss of copper. However, as might be seen in Fig. 2-B, this increase is high until a limit of approximately 12 g dry leaves/L after which the increase of concentration of leaves seems to have only a small effect on the rate of loss of copper from solution.

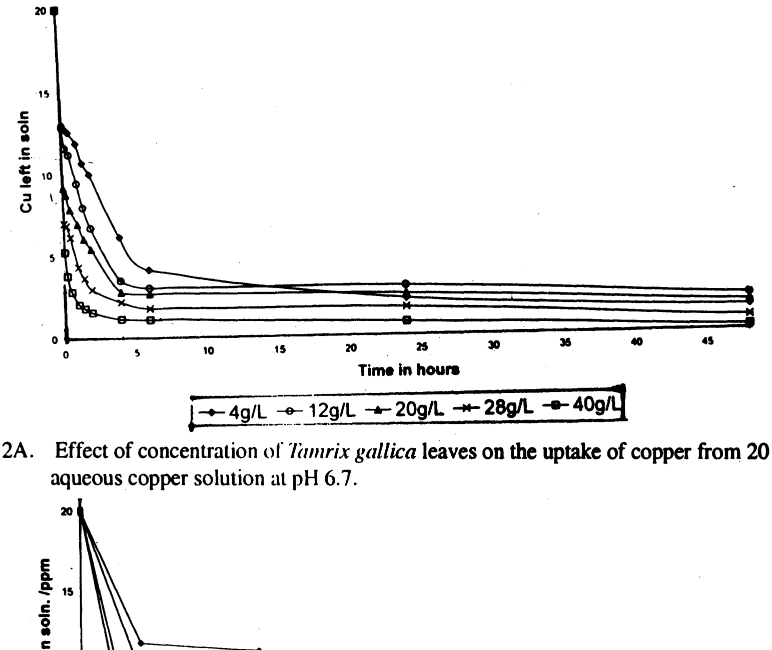

Fig. 2A. Effect of concentration of *Tamrix gallica* leaves on the uptake of copper from 20 ppm aqueous copper solution at pH 6.7.

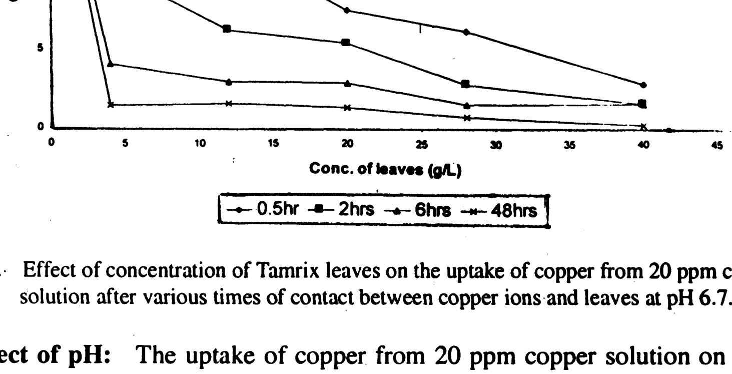

Fig. 2B. Effect of concentration of Tamrix leaves on the uptake of copper from 20 ppm copper solution after various times of contact between copper ions and leaves at pH 6.7.

Effect of pH: The uptake of copper from 20 ppm copper solution on 20 g dry *Tamrix gallica* leaves per litre was followed at various pH values ranging from pH 2.3 to 10.3. These results are shown in Fig. 3-A and 3-B.

In all cases, the curves presenting the loss of copper as a function of time

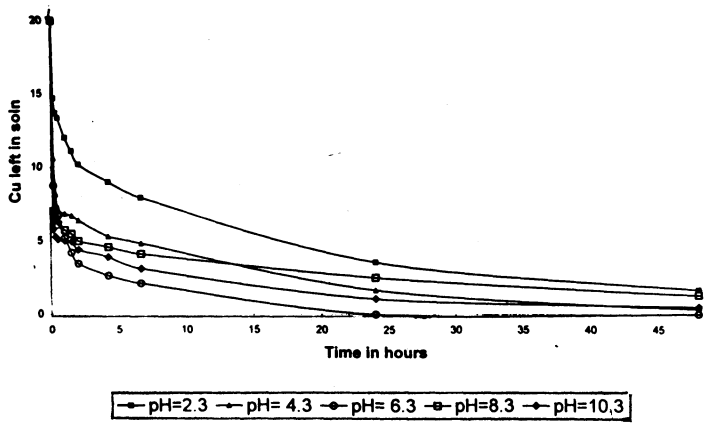

Fig. 3A. Effect of pH on the uptake of copper from aqueous solution (20 ppm) by 20 g *Tamrix gallica* leaves/L.

showed the same pattern as shown in curves of Figs. 1 and 2. Both rate of loss and amount of loss of copper were found to be much dependent on pH. An increasing pH increases both the amount and rate of copper uptake from solution until a maximum at pH 6.3; copper uptake again decreases with the increase of pH above 6.3. From Fig. 3B, the maximum amount of copper lost (90%) by *Tamrix gallica* leaves was found at pH 6.3.

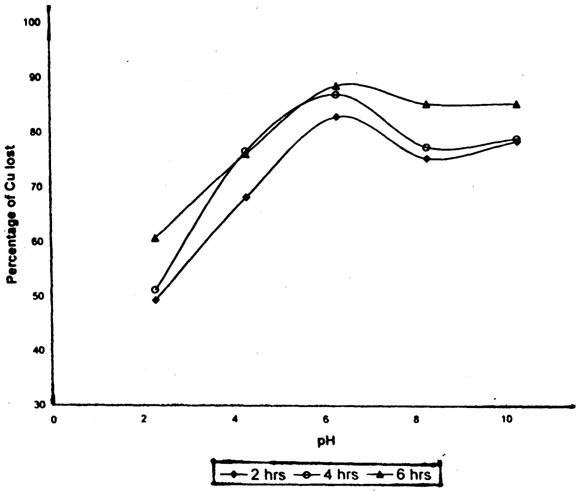

Fig. 3B. Effect of pH on the percentage of copper lost from 20 ppm aqueous solution in presence of 20 g/L dry *Tamrix gallica* leaves, after various times of contact between copper and

Effect of Competing Ions: The effect of presence of competing ions on the uptake of copper was studied by following the loss of copper from 20 ppm copper solution and 20 g dry leaves/L at pH 6.7 in the presence of 100 ppm of the competing ion. The results are shown in Fig. 4; these results indicate that the presence of competing ions in solution interferes with the adsorption of copper on leaves and thus affects its uptake from solution. Minimum rate of loss and minimum amount of loss of copper was found from solutions containing lead ions. The presence of sodium, cadmium and potassium ions in solution reduced the amount of uptake of copper. This reduction increased in the order K < Na < Cd < Pb.

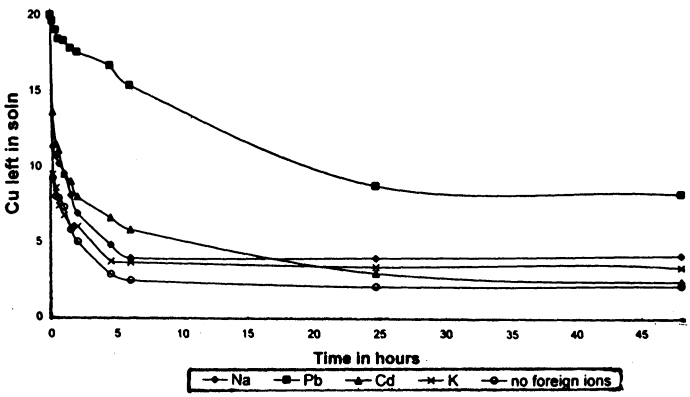

Fig. 4. Effect of presence of competing ions on the uptake of copper from 20 ppm aqueous solution in the presence of 20 g/L dry *Tamrix gallica* leaves at pH 6; concentration of each foreign ion is 100 ppm.

Effect of Drying Leaves: Loss of copper from solution was compared in the presence of green *Tamrix gallica* leaves and naturally dried *Tamrix gallica* leaves.

This was studied by following the loss of copper from 20 ppm copper solution on 20 g/L of *Tamrix gallica* leaves at pH 6.7. The results shown in Fig. 5 indicate that dry leaves are more effective than green leaves in removing copper from solution. From this curve, the loss of copper showed a general pattern in which

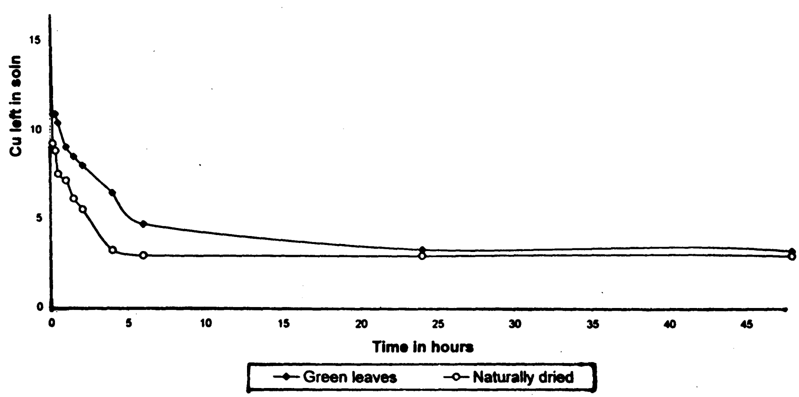

Fig. 5. Comparison between the uptake of copper by green *Tamrix gallica* leaves with naturally dried *Tamrix gallica* leaves at pH 6.3.

copper started to be lost at the beginning with a faster rate which slowed later to become less noticeable after 6 h of the experiment.

Effect of Grinding Leaves: Uptake of copper from 20 ppm copper solution was studied in the presence of ground leaves and normal leaves. The results shown in Fig. 6 indicate that in both cases, the curves presenting the loss of copper as a function of time showed the same pattern in which copper started to be lost at the beginning with a faster rate which slowed later to become negligible after several hours. Both rate and amount of loss of copper were found to be dependent on the form of leaves. The capacity of ground leaves to remove copper from solution was more than normal leaves due to the increased surface area of ground leaves.

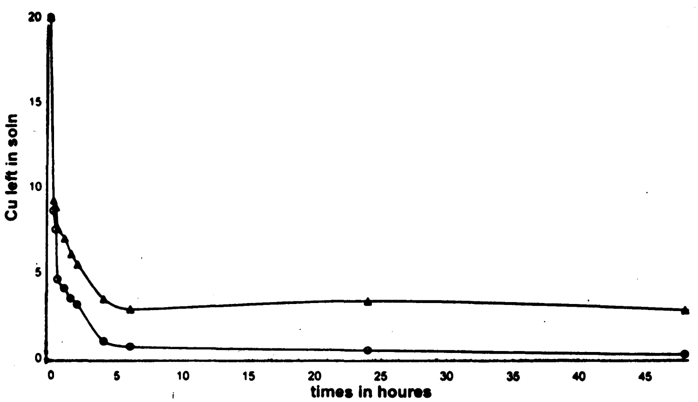

Fig. 6. Effect of grinding leaves on the removal of copper from 20 ppm aqueous copper solution using 20 g/L dry *Tamrix gallica* leaves at pH 6.3.

Effect of Agitation: The effect of agitation on the uptake of copper was studied by following the loss of copper from 20 ppm copper solution on 20 g/L *Tamrix gallica* leaves at pH 6.7. As shown in Fig. 7, the results indicate that agitation increased slightly the rate and amount of uptake of copper from solution.

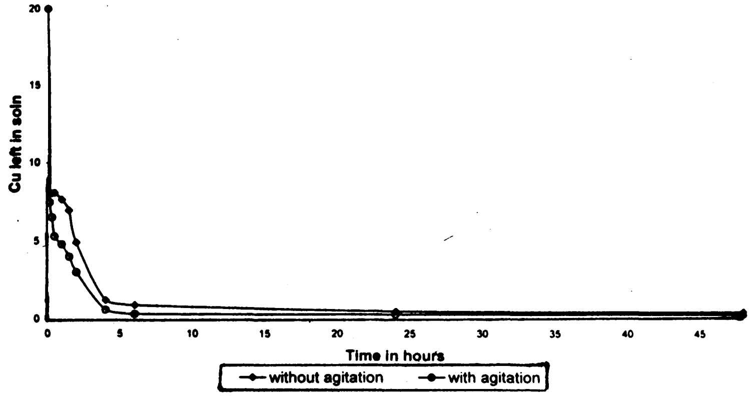

Fig. 7. Effect of agitation on the removal of copper from 20 ppm aqueous copper solution using 20 g/L dry *Tamrix gallica* leaves at pH 6.3.

Application to Adsorption Isotherm

Indications are arising from this study that adsorption is responsible for the copper lost from solution. This incites the application of adsorption isotherm on the present results.

The results of Fig. 8 show that the present results of loss of copper from various concentrations of copper (Fig. 1-A) agree well with the empirical Freundlich Adsorption Isotherm:

$$\log C_s = \log K + 1/n \log C_l$$

where

C_s = the concentration of copper adsorbed on leaves,
C_l = the concentration of copper left in solution,
K and n are constants.

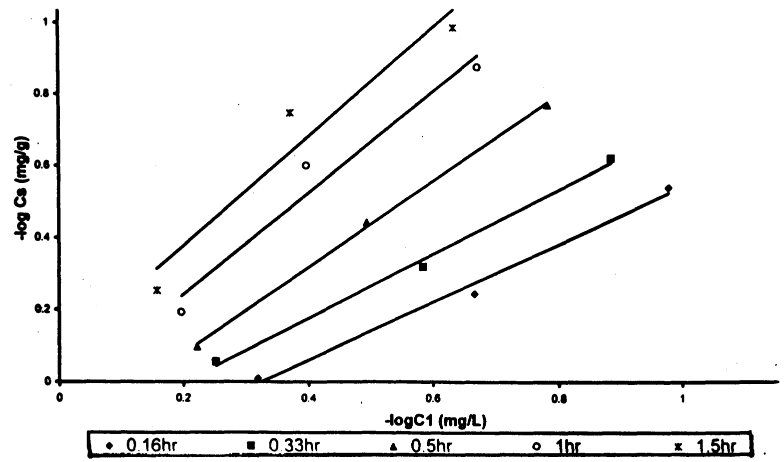

Fig. 8. Application of the Freundlich adsorption isotherm on the uptake of copper from various aqueous solutions by 20 g/L dry *Tamrix gallica* leaves at pH 6.3 after several times of contact between copper ions and *Tamrix gallica* leaves.

The parameters K and n for the present results shown are in Table-1. The parameters of the table show that n is almost constant at all times of exposure and around 1, however, the value of K increases slightly with time.

TABLE-1
THE PARAMETERS OF FREUNDLICH ADSORPTION ISOTHERM OF COPPER ON *Tamrix gallica* LEAVES

Parameters	Adsorption time				
	0.16 h	0.33 h	0.5 h	1 h	1.5 h
K	0.50	0.64	0.67	0.85	1.12
N	0.94	1.00	1.14	1.20	1.22

Kinetics of the Loss of Copper on *Tamrix gallica* Leaves

Order of Reaction: Amount of loss of copper, using various initial copper concentrations, can be used to study the relation between rate of reaction and concentration of copper left in solution in order to determine the order of the reaction between copper ions and leaf sites.

Results relating copper concentration on leaves C_s and their corresponding copper concentration in solution C_l are tabulated in Table-2.

TABLE-2
LOSS OF COPPER ON *Tamrix gallica* LEAVES (20 g/L) AT pH 6.7

Time of exposure (h)	Initial copper concentration					
	5 ppm		10 ppm		20 ppm	
	C_s (mg/g)	C_l (mg/L)	C_s	C_l	C_s	C_l
0.16	0.105	2.90	0.215	5.70	0.480	10.40
0.33	0.130	2.40	0.260	4.80	0.559	8.81
0.50	0.165	1.70	0.320	3.60	0.600	8.00
1.00	0.213	0.75	0.400	2.00	0.635	7.30
1.50	0.233	0.35	0.425	1.50	0.605	6.10

For each initial concentration of copper, shown in Table-2, a graph of C_s against $\sqrt{t}$ was plotted; the graphs were straight lines shown in Fig. 9. From the slopes of these lines (*i.e.*, $(dC_s/d\sqrt{t})$), the rate of loss dC_s/dt was calculated from the formula:

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

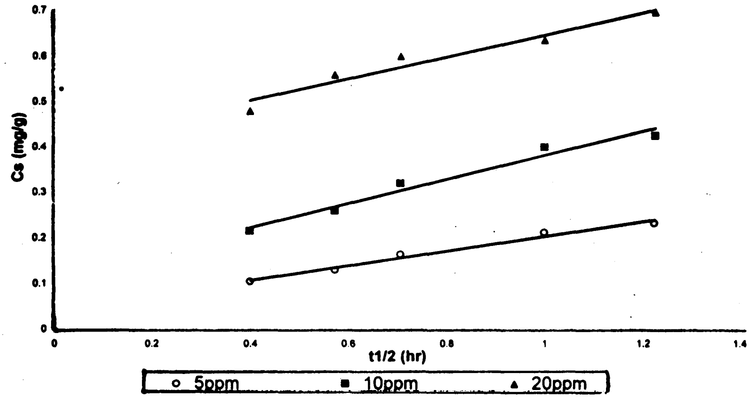

Fig. 9. Relation between the uptake of copper from various aqueous solutions by 20 g/L dry *Tamrix gallica* leaves at pH 6.3 and the square root of time.

Plotting the rate of loss of copper (dC_s/dt) against the concentraton of copper in solution C_l gave straight lines as shown in Fig. 10. Each line corresponds to the rate of loss of copper as a function of concentration C_l, after a certain time of exposure, irrespective of the initial concentration of copper in solution. Therefore, it can be concluded that the loss of copper on *Tamrix gallica* leaves is a first order reaction with respect to copper.

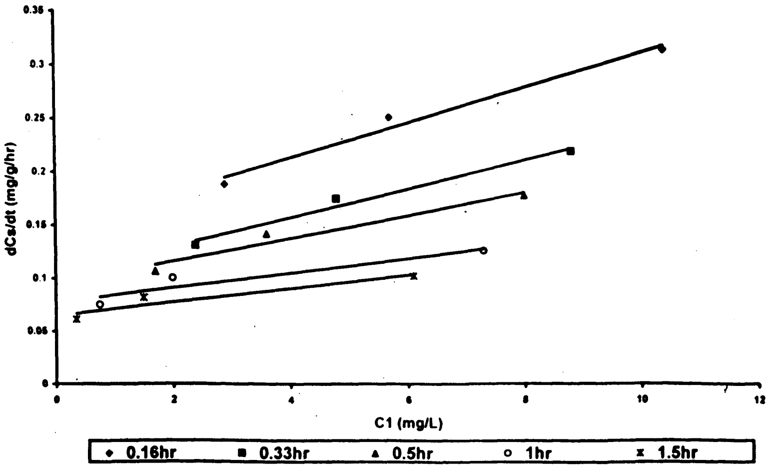

Fig. 10. The dependence of rate of copper uptake by 20 g/L dry *Tamrix gallica* leaves at pH 6.3 on the concentration of copper remaining in solution after several times of contact between ions and leaves.

Mechanism of the Reaction

Rate Limiting Step: Adsorption of copper on leaves occurs through three main steps:

1. The transport of copper by diffusion through a thin film of the exterior surface of the leaf. The cations are drive through this film by a concentration gradient. This step is called "film diffusion".
2. The second step, with the exception of the amount of adsorption, which occurs on the exterior surface of leaf, is the diffusion of copper ions within the pores of the leaf. This step is called "intrapore diffusion".
3. The last step is the actual adsorption of copper on the interior surface bounding the capillary space of the leaf. This is called "adsorption step".

The straight line relationship between C_s and $\sqrt{t}$ (*cf.* Fig. 9) of the present results suggests that the rate limiting step is mainly the intrapore diffusion.[12]

Only a slight effect of agitation on the rate and amount of adsorption of copper on leaves was observed (cf. Fig. 7). This might suggest that the rate limiting step is intrapore diffusion.[13] However, this might not be a conclusive evidence.

Adsorption *vs* Complexation

Loss of copper from solution in the presence of leaves may be due to adsorption or complexation by decaying components of the leaves. Based on the results of this work, adsorption is suggested as the most probable mechanism because:

1. If adsorption occurs on the leaves themselves, then adsorption is expected

to be effective as soon as contact between leaves and metal ions in solution occurs, whereas complexation is dependent on the time of interaction between metal ions and the active components of the leaves and is expected to be effective after a longer time. The present results indicate a decrease of the concentration of copper ions right after mixing copper ions and *Tamrix gallica* leaves, thus favour adsorption rather than complexation.

2. In case of complexation being responsible for the loss of ions, using leaf extract would be expected to have an effect similar to using leaves themselves. However, the present work shows only a slight effect of leaf extract on removing copper ions from solution, suggesting that complexations has only a small effect on the removal of copper by leaves.
3. The application of adsorption isotherm on the present results (cf. Fig. 8) suggests that adsorption might be the main factor controlling the inetraction between copper and leaves.
4. The high effect of surface area of leaves (cf. Fig. 6) suggests that increasing adsorption sites is a prime factor in increasing the capability of leaves for removing copper ions. This again is consistent with the assumption of having adsorption as the main process controlling the interaction between copper and leaves.

Conclusions

The following conclusions can be drawn from the results of the present work:

- Tamrix leaves are capable of removing large amount of copper from polluted water. Increasing the concentration of copper in solution increases the rate of its uptake by *Tamrix gallica* leaves up to a limit after which increasing the concentration of copper results only in small increase of copper uptake.
- Increasing the concentration of *Tamrix gallica* leaves in contact with copper increases the rate of loss of copper from solution, effective only up to a limit. After this limit the effect of additional leaves becomes very low on the rate of loss of copper.
- Maximum rate and amount of loss of copper on *Tamrix gallica* leaves occurs at pH 6.3. Increasing or decreasing pH around the value of 6.3 decreases both rate and amount of loss of copper.
- The presence of foreign ions with copper in contact with *Tamrix gallica* leaves has an effect on the uptake of copper by *Tamrix gallica* leaves; such ions studied in this work are Pb, Cd, Na, K; their efficiency in competing copper on leaves can be arranged in the order Pb < Cd < Na < K.
- Dry *Tamrix gallica* leaves have higher capability for removal of copper from water than green leaves. Agitation had only a slight effect on both rate and amount of copper uptake by *Tamrix gallica* leaves. Ground leaves had more capacity to remove copper ions from solution than whole leaves.
- There are indications that the loss of copper on leaves occurs mainly by adsorption of copper on the adsorption sites of leaves. The present results agree well with Freundlich adsorption isotherm.

Adsorption of copper on *Tamrix gallica* leaves is a first order reaction with respect to copper. The rate determining step seems to be the intrapore diffusion.

REFERENCES

1. L.H. Keith and W.A. Telliard, *Environmental Science and Technology*, **4**, 13 (1979).
2. R. Salim and J.W. Robinson, *J. Environ. Sci. Health*, **A20**, 701 (1985).
3. ———, *J. Environ. Sci. Health*, **A20**, 721 (1985).
4. D.C. Barrell, Atomic Spectrometers Analysis of Heavy Metals Pollutants in Water, Ann Arbor Science Publishers, Inc., Ann Arbor, MI, p. 25 (1975).
5. Chemistry Laboratory Safety Library, 491M, 5th Edn., National Fire Protection Association, Boston MA (1975).
6. U. Soffioti and J.K. Wagoner, Occupational Carcinogenesis, New York Academy of Science, p. 271 (1976).
7. R.F. Wernwer, *Plating*, **54**, 1345 (1967).
8. T.C. Tan, C.K. Chia and C.K. Teo, *Water Res.*, **19**, 157 (1985).
9. B.C. Wolverton, R.C. Mcdonald and J. Gordan, Bioconversion of Water Hyacinth into Methane Gas, NASA Technical Memorandom X-72721 (1975).
10. J.K. Hardy and D.H. O'Keeffe, *Chemosphere*, **14**, 417 (1985).
11. R. Salim, *J. Environ. Sci. Health*, **A23**, 183 (1988).
12. W.J. Weber, A.M. Asce and J.C. Morris, *J. Saint. Eng. Div. Proc. Am. Soc. Civil Eng.*, **89**, 31 (1963).
13. R. Salim and B.G. Cooksey, *Plant and Soil*, **54**, 399 (1980).

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