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Uptake of Zinc from Polluted Water by Decaying *Tamrix gallica* Leaves

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Uptake of zinc ions from aqueous solutions by *Tamrix gallica* leaves was studied. The effect of several factors on this removal was studied including metal ions concentration: tamrix leaves concentration, pH, presence of competing ions, agitation, crushing, drying, presence of complexing agent and leaf extract. Application of Freundlich adsorption isotherm on the present results has been examined and the parameters of this isotherm have been calculated. The interaction between metal ions and tamrix leaves has been determined and mechanism for this interaction suggested.

Key Words: Zinc, Uptake, Water, *Tamrix gallica* leaves, Adsorption isotherm.

INTRODUCTION

The main sources through which the pollutants reach human or animals are food, air and water, especially after the widespread of industrialization and technology where most of the industrial effluents are emitted to air or to water[1].

Zinc is ubiquitous and is considered an essential trace element[2]. The greatest sources of zinc pollution in water are smelters and galvanizing industry. Fungicides containing zinc are also a potential source of pollution[3].

Toxicity of zinc has been observed from the inhalation of fumes from galvanized baths. This toxicity causes zinc fever, which is characterized by chills, fever and nausea. Zinc is also toxic to plants. It accumulates in plant tissues with visible symptoms of toxicity[4, 5].

Several materials have been suggested in literature for the removal of zinc from water; examples of these materials are water hyacinth, human hair and peat[6]. The degree of uptake of metal from soil by growing plants is affected by several factors including concentration of metals, type of plant, plant age, pH, presence of foreign ions; growth rate and conditions have also been found to be important factors[7–9]. Dye treated oil palm fibres have been shown to be more effective in removing heavy metals than natural fibres[10]. Using plants and plant parts in removing of heavy metals from polluted water has gained general acceptance by the public and regulatory agencies[11]. Plant ability to remove heavy metals can be increased significantly through genetic engineering[12–14].

Using decaying leaves for removal of toxic heavy metals from polluted water is one of the recently suggested methods. This method has been found effective because it is simple, cheap, available and very acceptable[15]. By using this method, removal of several metals such as aluminum[16], nickel[17, 18] has been studied. Cyprus leaves have been found capable of removing nickel ions from water[19]. Tamrix leaves have been found to remove copper from water[20].

The aim of this paper is to introduce *Tamrix gallica* leaves as a method for the removal of zinc from water and to investigate several factors for the optimum removal of zinc including the kinetic study of this removal.

EXPERIMENTAL

High purity chemicals (Merck) were used for the preparation of standards. Solutions of metal ions (Zn, Cd, Pb, Ni, Cu, Na and K) were prepared by dilution from standard solutions.

The required amount of tamrix leaves were washed with distilled water and with 1 M HNO_3 and then rinsed with deionized water. The washed leaves were dried at room temperature. Polyethylene containers (250 mL) were used. The containers were washed with 1 M HNO_3 and then washed well with deionized water.

The concentration of metal is determined using flame atomic absorption spectrophotometer (Shimadzu AA-6601F) at wavelength 213.9 nm, slit width 0.5 mm, lamp current 10–300 mA. pH-meter (HM-40V pH) was used to measure the pH and to adjust the pH of solution.

RESULTS AND DISCUSSION

Effect of Metal Concentration

The zinc ions were removed from various concentrations of metal solution using the same amount of tamrix leaves (20 g/L). The results of this study are shown in Fig. 1. It is found that the removal rate of Zn ions from solution is high in the first 6 h, then slows down to reach almost constant rate after 8 h.

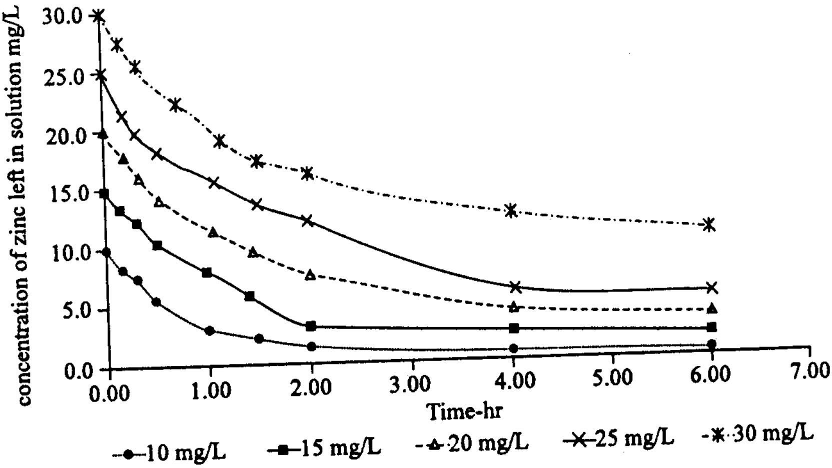

Fig. 1. Effect of zinc concentration on removal of its ions from zinc solution using 20 g/L tamrix leaves

The time after which the removal of metal becomes almost negligible is based on the concentration of metal in solution. Less time is required for the removal process to reach its limit from dilute solutions than that from the more concentrated solutions. It takes 4 h for 10 mg/L zinc solution and 24 h for 30 mg/L zinc solution. After 2 days of exposure, the tamrix leaves remove around 80–90% zinc.

Effect of leaves concentration

Different concentrations of tamrix leaves ranging from 4 to 40 dry leaves per L of solution were used to remove metal ions from 20 mg/L metal solutions as shown in Fig. 2. It is found that increasing/concentration of leaves from 4 to 40

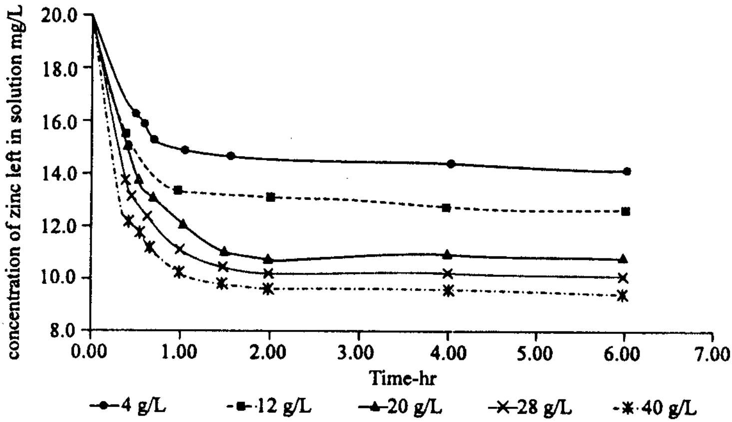

Fig. 2. Effect of tamrix leaves concentration on removal of Zn ions from 20 mg/L zinc solution

g/L increases both the rate and amount of loss of metal ions from solution. A relationship exists between the amount of metal removed from the solution after fixed time. As shown in Fig. 3, it is found that the amount of metal removed from

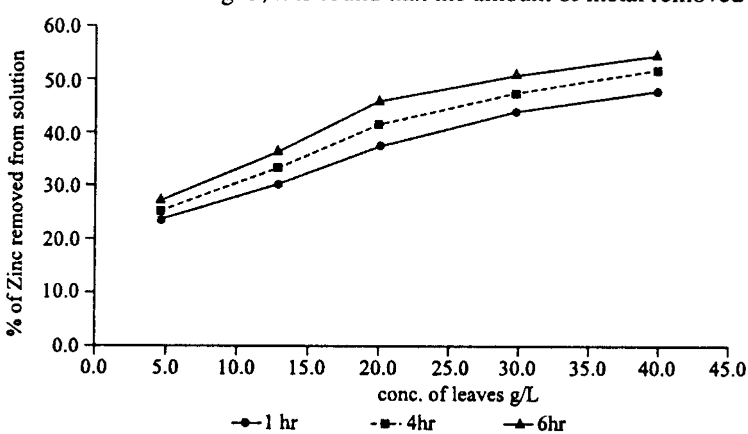

Fig. 3. Effect of leaves concentration on removal of Zn ions from 20 mg/L zinc solution at a certain time

solution is very much dependent on the concentration of leaves used. This is consistent with previous studies[20].

Effect of pH

Removal of zinc ions from 20 mg/L solution by 40 g dry tamrix leaves per L was followed at various pH values ranging from pH 1 to 10. As shown in Fig. 4, it is found that the maximum amount of Zn ions removed from solution was found to be at pH 5. Increasing or decreasing pH around this pH 5 decreases the amount of metal removed.

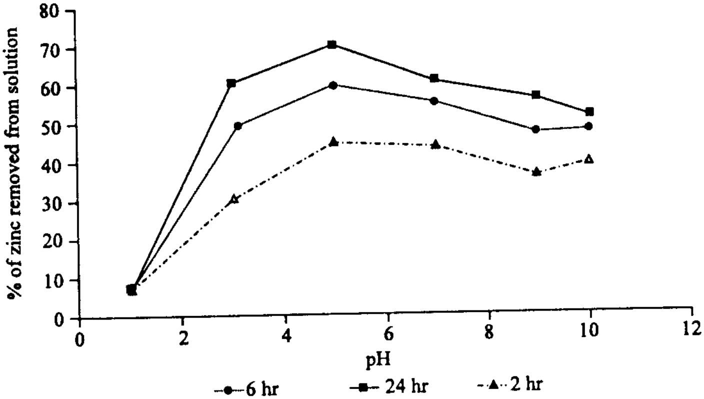

Fig. 4. Relation between removal of zinc ions from its solution and pH at fixed time using 20 mg/L Zn solution, 40 g/L tamrix leaves

Effect of competing ions

The effect of presence of 100 mg/L of the competing ion on the removal of zinc ions from 20 mg/L metal solutions was studied using 40 g/L dry tamrix leaves at pH 5. The study was carried out in the presence of Ni^{2+}, Cu^{2+}, K^+, Na^+ and Pb^{2+}.

The results are shown in Fig. 5. It is found that the presence of competing ions in solution interfered with interaction of Zn ions on leaves and thus affected its

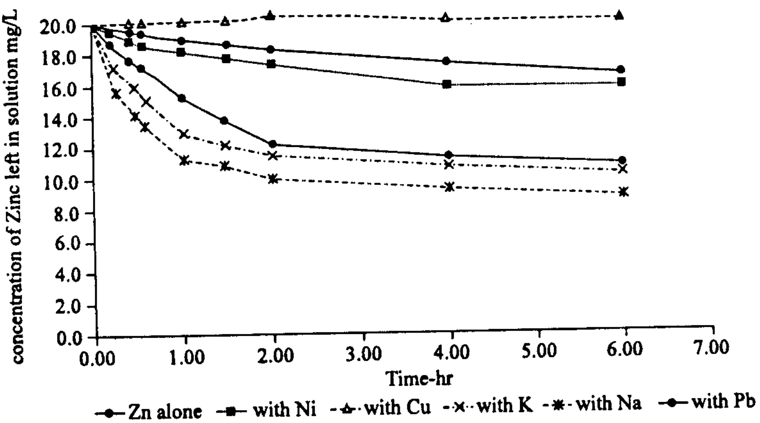

Fig. 5. Effect of competing ions on removal of zinc ions from 20 mg/L zinc solution using 40 g/L tamrix leaves at pH 5

uptake from solution. These competing ions may increase or decrease the uptake depending on the nature of competing ions. The presence of competing ions Ni, Pb, Cu in solution decreased the amount of uptake. This reduction increases in the order Cu > Pb > Ni. However, the presence of Na and K increases the amount of uptake.

Effect of Crushing

Removal of zinc ions from 15 mg/L aqueous metal solution was studied in the presence of two forms of tamrix leaves: normal leaves and crushed leaves, using 20 g tamrix leaves per L at pH 5. As shown in Fig. 6, it is found that crushed leaves have higher ability to remove metal ions from solution than the normal leaves. Also both rate of loss and amount of loss of Zn were found to be very

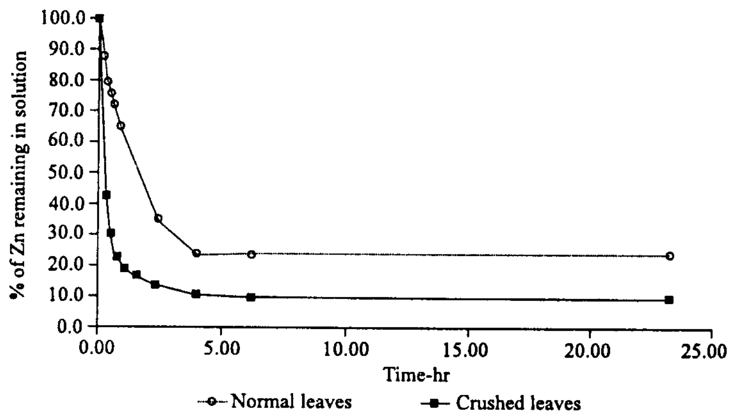

Fig. 6. Effect of crushing on removal of Zn ions from 15 mg/L zinc solution using 20 g/L tamrix leaves

much dependent on the form of leaves where the amount of loss increased by 20% in case of crushed leaves than normal leaves. This is due to the increase surface area where more Zn metal ions interact with the leaves.

Effect of Drying Leaves

Removal of zinc ions by leaves was compared in presence of green tamrix leaves and oven-dried leaves. The comparison was studied by following the decrease of metal concentration from 20 mg/L metal solution using 40 gm tamrix leaves per litre at optimum pH 5.

As shown in Fig. 7, it is found that the dried leaves are more effective in removal of metal ions from solution than the green leaves. The curve shows general pattern in which the loss of metal ions from solution is fast at the beginning and slows down at the end.

Effect of Agitation

The effect of agitation on the uptake of metal ions from the solution was studied by following the loss of metal ions from 20 mg/L metal solution by using 40 g/L tamrix leaves at pH 5. The results are shown in Fig. 8. These results indicate that the agitation increases the removal of metal ions. This is due to the increased diffusion from the bulk of solution to the surface of leaves.

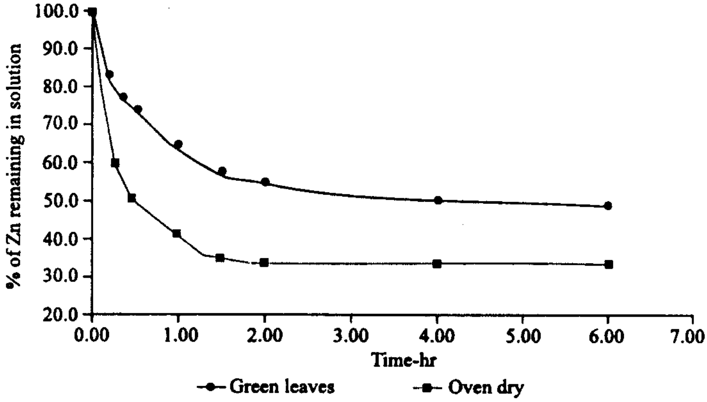

Fig. 7. Effect of drying on removal of Zn ions from 20 mg/L zinc solution using 40 g/L dry tamrix leaves at pH 5

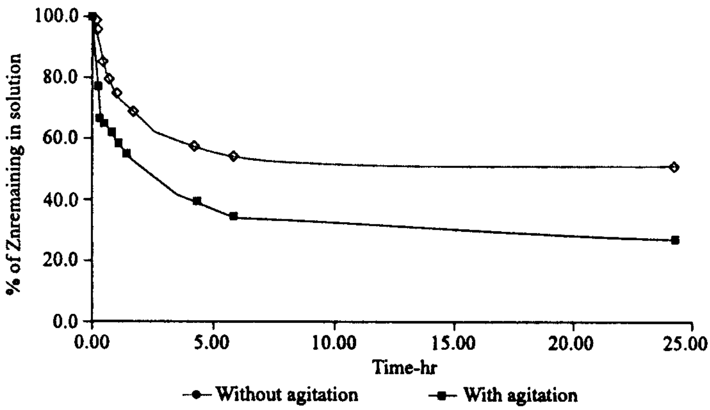

Fig. 8. Effect of agitation on removal of Zn ions from 20 mg/L zinc solution using 40 g/L dry tamrix leaves

Application of adsorption isotherms

Many studies on removal of metal ions by leaves showed that the loss of metal ions occurs by adsorption of metal ions on the adsorption sites of leaves[15]. This incites the application of adsorption isotherm in the present work.

From Fig. 9 it is found that the loss of metal ions from various concentrations of metal agrees well with the empirical Freundlich adsorption isotherm:

$$\log C_s = \log K + (1/n) \log C_i$$

where

C_s = concentration of metal adsorbed on leaves (mg/g),

C_i = concentration of metal ions left in solution (mg/L).

K = constant, indicative of the adsorption capacity of the adsorbent,

n = constant, indicative of the adsorption intensity of the adsorbent

The constants n and K were determined from the slopes and intercepts respectively of the straight lines of Fig. 9. These parameters are shown in Table-1. It indicates that n is almost constant for all times of interaction and around 5.3 while k increases with time.

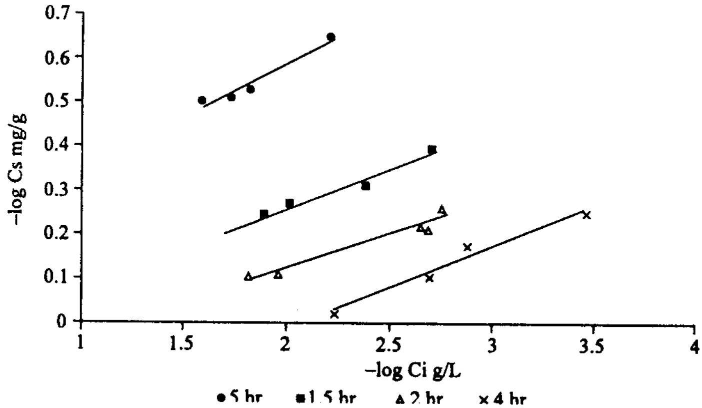

Fig. 9. Application of Freundlich adsorption isotherm on zinc ions uptake from 20 mg/L zinc solution using 20 g/L tamrix leaves

TABLE-1
THE PARAMETER OF FREUNDLICH ADSORBTION ISOTHERM OF ZINC

Parameter	Adsorption time h			
	0.5 h	1.5 h	2 h	4 h
1/n	0.21	0.18	0.17	0.19
n	5.00	5.50	5.80	5.20
k	1.34	1.38	1.62	2.39

Order of the adsorption process

Loss of zinc from various initial concentrations of metal ions can be used to determine the order of reaction. Results relating metal concentration adsorbed on leaves (C_s) and their corresponding metal concentration left in solution (C_i) are presented in Table-2. For each initial concentration of metal used, graph of C_s against $\sqrt{t}$ was plotted (Fig. 10). From the slopes of these lines ($dC_s/d\sqrt{t}$), the rate of loss (dC_s/dt) was calculated from the following formula:

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

Plotting the rate of adsorption of metal (dC_s/dt) against the concentration of metal left in solution (C_i) gave straight lines (Fig. 11). Each line corresponds to the rate of loss of metal as a function of concentration of metal remaining in solution after a certain time of exposure, irrespective of the initial concentration of metal in solution. Therefore, it can be concluded that adsorption process of metal on tamrix leaves is a first order reaction.

TABLE-2
RELATION BETWEEN Zn UPTAKE AND SQUARE ROOT OF TIME

Time (h)	$\sqrt{t}$	C_s (mg/g)				
		10 mg/L	15 mg/L	20 mg/L	25 mg/L	30 mg/L
0.50	0.707	0.35	0.45	0.54	0.59	0.61
1.50	1.225	0.40	0.53	0.59	0.65	0.75
4.00	2.000	0.42	0.58	0.72	0.84	0.90
6.00	2.449	0.45	0.60	0.78	0.89	1.00
24.00	4.899	0.48	0.68	0.92	1.20	1.28

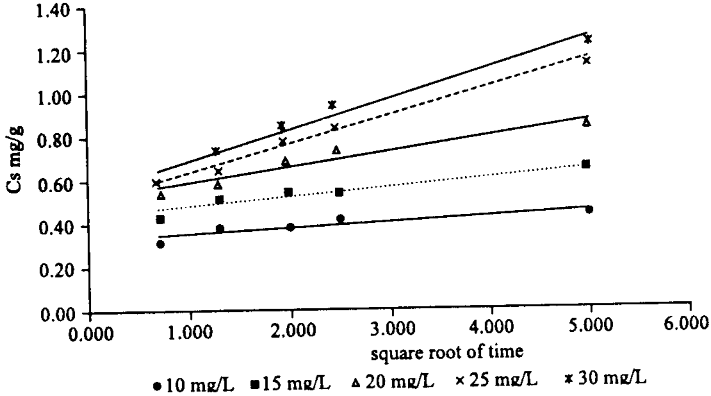

Fig. 10. Relation between uptake of Zn ions from different concentrations of zinc solution and the square root of time using 20 g/L tamrix leaves

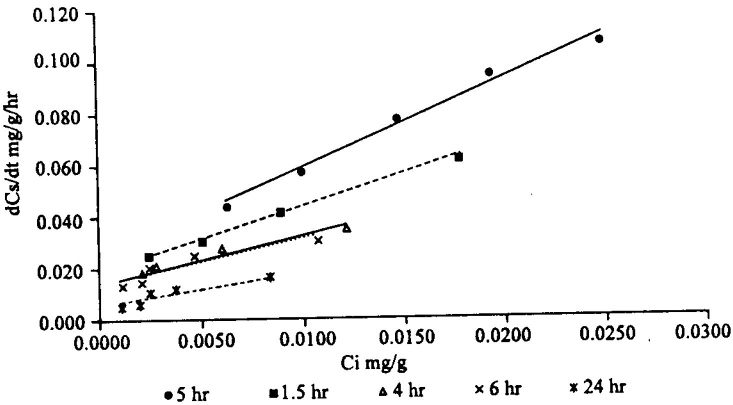

Fig. 11. The dependence of rate of zinc uptake by 20 g/L tamrix leaves on the concentration of Zn ions remaining in solution after several times of contact

Type of interaction between metal and leaves

Removal of zinc ions from their solutions in the presence of leaves may be due to adsorption of ions on the surface and pores or to complexation by the components of the leaves. This is because of the following:

(1) When adsorption occurs for zinc ions on leaves, it will be effective from the first time of contact between the leaves and zinc ions in solution. While in case of complexation, which is dependant on the decay components of leaves and ability to react with zinc ions, it will be effective after a certain time. This is consistent with the earlier studies[19].

(2) The applicability of adsorption isotherm on the results obtained (Fig. 9) suggests that adsorption might be the main factor controlling the interaction between zinc and tamrix leaves.

(3) The high effect of crushing of leaves on increasing leaves capacity to remove zinc ions, since crushing increases the surface area of leaves which is able to adsorb more ions.

(5) When different types of leaves were used to remove metal ions from solution, the same pattern of their curves was obtained. This suggests that adsorption is the main factor controlling metal ions removal.

Conclusion

From this study we concluded the following:

- *Tamrix gallica* leaves have good ability to remove zinc ions from polluted water.
- The rate and amount of zinc removal is increased as *Tamrix gallica* leaves concentration is increased.
- Maximum rate and amount of loss of zinc on tamrix leaves occurs at pH 5; increasing or decreasing pH around 5 decreases sharply both the rate and amount of loss of zinc.
- Some foreign ions decrease tamrix leaves ability to remove Zn ions from solution. Their efficiency of competing zinc on leaves can be arranged in the order Cu > Pb > Ni. Addition of sodium and potassium increases the uptake of zinc on tamrix leaves.
- Drying, crushing and agitation increase tamrix leaves ability to remove metal ions. Therefore, tamrix leaves can be used with high efficientcy in the removal zinc metal from water.
- Adsorption of zinc on tamrix leaves was suggested as the most probable mechanism of the interaction between zinc ions and tamrix leaves. The results obtained agree well with the Freundlich adsorption isotherm.

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