

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

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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 las hojas no alteró su capacidad de captura. La adsorción es el mecanismo más probable de remoción

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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 HNO₃ 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⁺ Mg²⁺, Ca²⁺, Zn²⁺, Ag⁺, Cd²⁺ and Pb²⁺) 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 HNO₃ for 24 hours or completely digested in 6 M HNO₃ 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

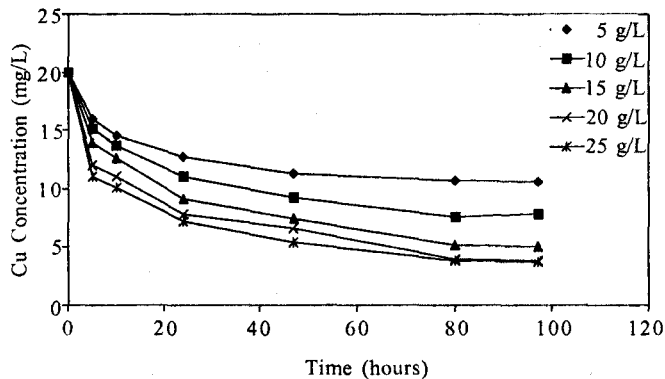


Fig. 1. Effect of poplar leaves concentration on copper removal from 20 mg/L copper solution at pH 4.40

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

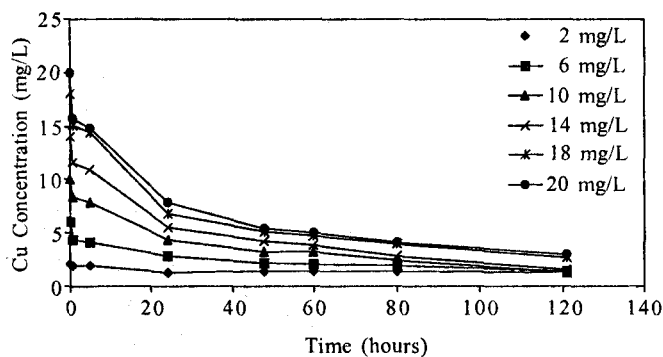


Fig. 2. Effect of copper concentration on its removal by 20 g/L poplar leaves at pH 4.40

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

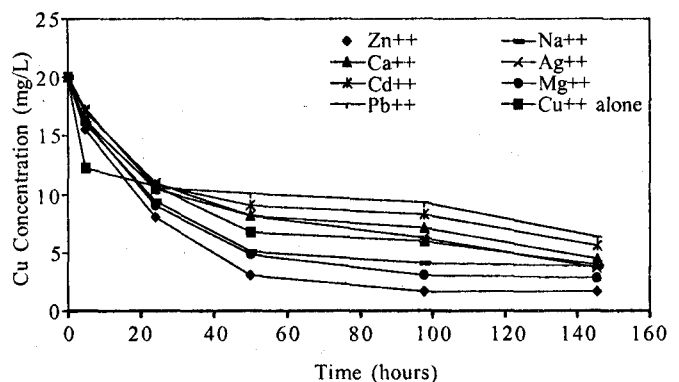


Fig. 3. Effect of competing ions (100 mg/L) on the removal of copper by 20 g/L poplar leaves at pH 4.40

