Phytoremediation of Cu(II) by *Calotropis Procera* Roots

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Abstract: The discharge of heavy metals into aquatic environment has become a matter of concern in Pakistan over the last few decades. These pollutants are introduced into the aquatic systems significantly as result of various industrial operations. Cu(II) is a priority pollutant and has been documented to be harmful to fauna, flora and human beings. The aim of the present study was to utilize the locally available wild plant material for Cu(II) removal from industrial waste water. The wastewater containing Cu(II) was treated with biomass prepared from roots of *Calotropis procera*, a wild abundant plant. These studies were carried out in order to determine some operational parameters of Cu(II) sorption such as the time required for the metal-biosorbent equilibrium, the effect of change in biomass quantity and effect of contact time on percentage removal of copper. It was found that a time of one hour was sufficient to attain equilibrium. It was concluded that adsorbent prepared from *Calotropis procera* roots can be used for treatment of heavy metals in waste waters. [New York Science Journal 2010;3(3):1-5]. (ISSN: 1554-0200).

Key words: Cu(II), *Calotropis Procera*, phytoremediation.

1. Introduction

Natural waters have been found to be contaminated with several heavy metals arising mostly from mining wastes and industrial discharges (Dönmez and. Aksu, 2001; Patterson, 1977). The presence of heavy metals in the environment is of major concern because of their toxicity, bio-accumulating capacity, threat to human life and the environment (Volesky, 1994; Volesky, 1995). Heavy metals are among the conservative pollutants that are not subject to bacterial attack or other break down or degradation process and are permanent addition to the marine environment (El-Nady and Atta, 1996). As a result of this, their concentrations often exceed the permissible levels normally foun they can profoundly disrupt biological processes. The discharge of heavy metals into surface waters has become a matter of concern in Pakistan over the last two decades. These contaminants are introduc d in soil, water ways and sediments. Hence ed into surface waters through various industrial operations (Kratochvil and Volesky, 1998).

According to World Health Organization (WHO) the metals of most immediate concern are chromium, copper, zinc, iron, cadmium and lead. (WHO 1984) Since copper is a widely used material, there are many actual and potential sources of copper pollution. Copper is used in jewelry, paints, pharmaceutical products, wood preservatives, pigments, metal works, petroleum refinery, motor vehicle and aircraft plating and finishing. Also copper may be found as a contaminant in food, especially shell fish, liver, mushroom, nuts and chocolates. (Antunes, 2003)

Copper is essential to human life and is required for various biological processes, but like all heavy metals, is potentially toxic as well. The presence of copper ions, cause serious toxicological concern, it is usually known to deposit in brain, skin, liver, pancreas and myocardium. . (Davis, 2003)]

In order to solve the problem of heavy metals pollution in the eco system it is important to bring pragmatic solutions to the issue. The techniques presently in existence for removal of heavy metals from wastewater are relatively expensive involving either elaborate and costly equipment or high costs of operation with ultimate disposal problems (Tsoumbaris and Tsoukali-Papadopoulou, 1994; Bossrez et al., 1997). In view of these reasons, development of a more cost effective remediation process using biological system for removal of heavy metal ions from wastewater is necessary. Biosorption or bioremediations consists of a group of applications which involve the detoxification of hazardous substances instead of transferring them from one medium to another by means of microbes and plants. This process is characterized as less disruptive and can be often carried out on site, eliminating the need to transport the toxic, materials to treatment sites (Bossrez et al., 1997).

The aim of this research is to use abundantly available wild plant *Calotropis procera* for treatment of copper wastes. Roots of *Calotropis procera* were used as biosorbent to remove copper from known concentration of copper solutions. The present work

deals with some operational parameters of process of adsorption of copper such as time required for the metal-biosorbent equilibrium, the effect of change in biomass quantity and effect of contact time on percentage removal of copper.

2. Materials and methods

All chemicals were of analytical grade. Copper(II) stock solution (1000 mgL^{-1}, Merck) was purchased from local suppliers. This was further diluted to get solutions of various known concentrations of copper. A temperature controlled variable speed shaker 20-500 rotations per minute (GFL 3033) was used for batch experiments. The pH for the experiments was taken as original pH of the solutions. A vacuum filter assembly having Pyrex filter funnel of porosity grade 4 was used for separating adsorbent from solution. The unknown quantities of Cu(II) were determined by Hitachi Z-5000 atomic absorption spectrophotometer using an air-acetylene flame. Adsorbent was analyzed by Midac 2000 FTIR spectrophotometer having spectral range from 7800-406cm^{-1}. All experiments were performed three times and average values were used in all calculations.

2.1 biomass prepration

Calotropis procera roots were collected from local environment of Old Kahna near Lahore in October, 2008. These roots were washed with distilled water to remove any soil or debris. The washed samples were oven dried at a temperature of 333K for two days. Dried roots were ground and sieved to 100 mesh sizes. This biomass was stored in air tight glass bottles to protect it from humidity.

2.2 Fourier transform infrared analysis

FTIR spectroscopy was used to identify the chemical groups present in roots. The samples were examined using Midac FTIR 2000 spectrometer within range 406-7800 cm^{-1}. KBr was used as background material in all the analysis. The roots powder (0.0035g) was mixed with 0.5 KBr and pressed to form a pellet. FTIR spectra of roots before and after adsorption were compared. http://www.scielo.cl/scielo.php?script=sci_pdf&pid=S0717-34582007000300008&lng=e...&nrm=iso&tlng=

2.3 Batch studies.

For the determination of rate of biosorption and the biosorption equilibrium time, the residual metal in the supernatant was determined by allowing metal sorbate–*Calotropis procera* roots sorbent contact for different periods between 2 and 300min. Experiments conditions were as follows: addition of *Calotropis procera* roots into each flask (dose varying from 5gL^{-1} to 25gL^{-1} of biomass), agitating mixtures using variable speed shaker (125rpm, GFL 3033) at temperatures 303K.

2.4 Data analysis

The metal sorption capacity (qt) of the Calotropis procera roots was calculated from the relationship (Horsfall, 2005) in eqn (1):

$$qt = \frac{ci - ct}{m} \times V$$

(1)

Also the percentage of Pb(II) ions removed (%RE) from the aqueous solution was calculated using formula in eqn. (2).

$$\%age RE = \frac{ci - ct}{ct} \times 100$$

(2)

Whereas the fraction of Pb(II) ions removed by *Calotropis procera* roots was determined from the relationship.

$$Yt = \frac{ci - ct}{ci - ce}$$

(3)

where qt is the metal sorption capacity of the adsorbent (mgg^{-1}), C_i is the initial metal ion concentration (mgL^{-1}), C_t is the metal ion concentration in solution at time t (mgL^{-1}), Y_t is the fraction of the metal adsorbed at time t, m is the weight of the adsorbent (g), V is the volume of the metal ion solution used for sorption (L) and Ce is the concentration of meta ion, hen sorption is completed, i.e. infinity sorption [$C\infty = Ce$].

3 Results and discussion
3.1 Fourier transform infrared spectroscopy investigations

The FT-IR spectra before and after adsorption of Cu(II) onto *Calotropis procera* roots was taken. The functional groups before and after adsorption on *Calotropis procera* roots with absorption bands are shown in Table I. The spectra display a number of absorption peaks, indicating the complex nature of chemical compounds of *Calotropis procera* roots. The band shifts in −OH, −NH and carboxyl groups indicates the involvement of these groups in biosorption of Cu(II) by *Calotropis procera* roots.

3.2 Determination of equilibrium time

Sorption equilibrium established when the concentration of metal in a bulk solution was in dynamic balance with that of the interface [Table 2]. The experimental results of determination of equilibrium time of sorption of Cu(II) on *Calotrpis*

procera roots using different amount of biomass ranging from 5.0 to $25gL^{-1}$ (5. 10, 15, 20, $25gL^{-1}$) showed that about 80% removal was attained in first 10 minutes as shown in Figure 1. The fast initial uptake was due to accumulation of metal ions on surface of adsorbent which was a rapid step, while more time was consumed on diffusion of ions to binding sites. It was concluded that one hour was sufficient for sorption to attain equilibrium.

Effect of Adsorbent Dose: Keeping all other parameters constant adsorbent dose was varied from 5.0 to $25gL^{-1}$ (5. 10, 15, 20, $25gL^{-1}$) and it was observed that increasing the dose of adsorbent increased the percentage of metal adsorbed as shown in Figure 2. The removal capacity was lowered at high dose and vice versa, due to metal concentration shortage in solution at high dose rates.

Copper Removing Capacity of Biomass: The copper removal capacity of Calotropis procera roots as a function of contact time was determined Figure.3. Biosorbent dose was $25gL^{-1}$. Initial concentration of Cu(II) was $20mgL^{-1}$ Figure 4 and the absolute amount of Cu(II) ions adsorbed onto the bark increased from 2 to about 40 min and then leveled off with further increase in time

Table 1**:** Difference between adsorption bands (cm^{-1}) of *Calotropis procera* roots before and after adsorption of Pb(II) on it.

IR peak	Absorption bands (cm^{-1})			Assignment
	Before adsorption	**After adsorption**	**Differences**	
1	3408	3415	+7	Bonded –OH groups, –NH stretching
2	2928	3154	+226	Carboxilic acids –OH stretching -CH STRECH
3	2358	2358	0	
4	1737	1739	+2	C=O streching
5	1631	1633	+2	C==C strech
6	1400	1397	-3	
7	1153	1153	0	C-O strechs
8	1031	1026	-5	R-O strech

Table2: Variation in the percentage of Cu(II) adsorbed on *Calotropis procera* roots at 300K with increasing agitation time

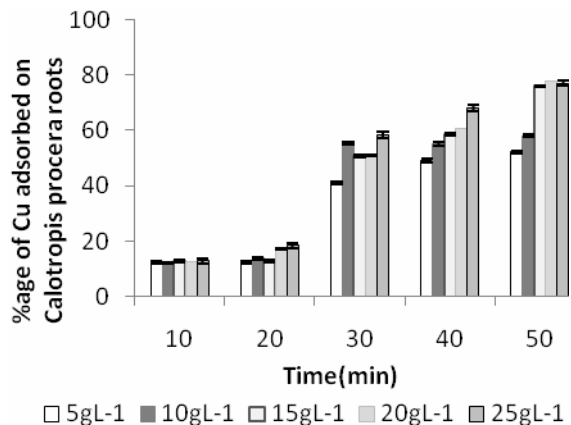| Sr.No	Agitation Time (min)	Amount of *Calotropis procera* roots				
		5g/L	10g/L	15g/L	20g/L	25g/L
1.	10	12.19	12.33	41.01	49.01	52.20
2.	20	12.15	13.70	55.23	55.13	58.00
3.	30	12.80	12.80	50.60	58.49	75.95
4.	40	12.33	17.23	50.93	60.59	77.95
5.	50	12.91	18.44	58.36	68.10	76.98

Fig1: Effect of time on %age removal of copper at 300K using at 300K using different amount of biomass.
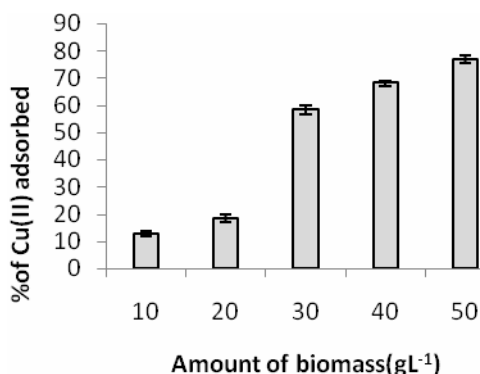

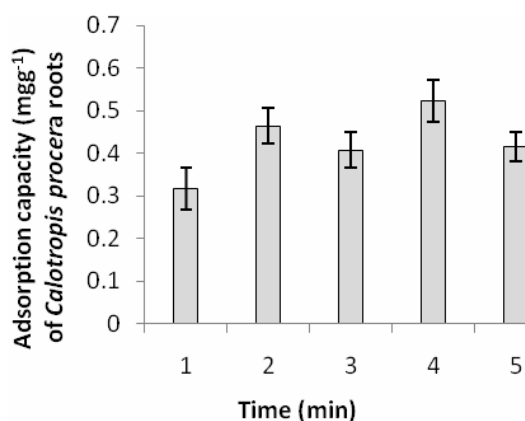Fig 2: Effect of adsorbent dose on %age adsorption of copper on *Calotropis procera* roots.

Fig 3: Effect of time on removal capacity of *Calotropis procera* roots.

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References:
1. Dönmez G, Aksu Z, Bioaccumulation of copper (II) and nickel (II) by the nonadapted and adapted growing Candida sp. Water Res. 2001;(35):1425-1434
2. Patterson JW, Wastewater Treatment Technol., Ann Arbor Science Publishers. Ann Arbor MI, USA (1977).
3. Volesky, B., Advances in biosorption of metals: selection of biomass types. FEMS Microbiology Reviews. 1994;(14): 291-302.
4. Volesky B, Holan ZR, Biosorption of Heavy Metals. Biotechnology Progress 1995;11 (3), 235-250.
5. El-Nady FE, Atta MM, Toxicity and bioaccumulation of heavy metals to some marine biota from the Egyptain coastal wasters. J. Environ. Sci. Health. A 1996;(31): 1529-1545.
6. Kratochvil D, Volesky B, Advances in the biosorption of heavy metals. Trends in Biotechnology. Trends Biotechnol. 1998;(16): 291-300.
7. WHO, World Health Organiztion, report, Guidelines for drinking water quality, Geneva (1984)
8. Antunes WM, Luna AS, Henriquies CA, daCosta ACA, Electr. J. Biotechno. 2003;(**6**):174-
9. Davis TA, Volesky B, Vieira R.H.S.F, Sargassum seaweed as biosorbent for heavy metals. Water Res. 2000;(34)**:** 4270-4278.
10. Tsoumbaris, P., Tsoukali-Papadopoulou, H., Heavy metals in common foodstuff: quantitative analysis Bull. Environ. Contam. Toxicol. 1994;(53): 61-.66.
11. Bossrez S, Remacle J, Goyette J. Adsorption of nickel by Enterococcus hirae cell walls. Journal of Chemical Technology and Biotechnology. 1997; (70): 45-50.
12. Horsfall M Jnr, Spiff AI, Effect of temperature on the sorption of Pb^{2+} and Cd^{+2} ions from aqueous solutions by caladium (wild cocoyam) biomass, Electronic j. Biotechnol. 2005;(8): Available

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