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Influence of operating conditions on the removal of Cu, Zn, Cd and Pb ions from wastewater by adsorption

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ABSTRACT: Nile Rose Plant was used to study adsorption of several cations (Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}) from wastewater within various experimental conditions. The dried leaves of Nile Rose Plant were used at different adsorbent/ metal ion ratios. The influence of pH, contact time, metal concentration, and adsorbent loading weight on the removal process was investigated. Batch adsorption studies were carried out at room temperature. The adsorption efficiencies were found to be pH dependent, increasing by increasing the pH in the range from 2.5 to 8.5 exept for Pb. The equilibrium time was attained within 60 to 90 min. and the maximum removal percentage was achieved at an adsorbent loading weight of 1.5 g/50 mL mixed ions solution. Isothermal studies showed that the data were best fitted to the Temkin isotherm model. The removal order was found to be $Pb^{2+} > Zn^{2+} > Cu^{2+} > Cd^{2+}$. The surface IR-characterization of Nile rose plant showed the presence of many functional groups capable of binding to the metal cations.

Key words: *Wastewater, adsorption, heavy metals, Nile rose plant, operating parameters*

INTRODUCTION

The awareness of increasing water pollution implies studies concerning water treatment. Removal of heavy metals from industrial wastewater is of primary importance. The use of natural materials for heavy metals removal is becoming a concern in all countries. Natural materials that are available in large quantities or certain waste from agricultural operations may have potential to be used as low cost adsorbents, as they represent unused resources, widely available and are environmentally friendly (Deans and Dixon, 1992). The application of low-cost natural adsorbents including carbonaceous materials, agricultural products and waste by-products has been investigated in many previous studies (Nguyen and Do ,2001; Singh, *et al.*, 2005; Abdel-Ghani, *et al.*, 2007) which have been recognized as potential alternative to the conventional technologies such as precipitation, ion exchange, solvent extraction and liquid membrane for removal of heavy metals from industrial wastewater because these processes have technical and/or economical constraints. Several studies have shown that non-living plant biomass materials are effective for the removal of trace metals from the environment (Mofa, 1995), (Lujan, *et al.*, 1994), (Gardea, *et al.*, 1996) and (Abia, *et al.*, 2002). Whereas many previous studies have reported the adsorption of metals by materials of diverse biological origin, these have remained limited to the removal of single metal ion and little information is available for multimetal adsorption systems (Al-Asheh, *et al.*, 2002) and (Sag, *et al.*, 2001). Nile rose plant (water hyacinth) is an aquatic plant, it grows on the surface of soft water in Nile River, and the scientific name of this plant is Echornia speciosa. This plant has been creating environmental nuisance in many regions in Egypt as it grows in the Nile water. Accordingly, this study aimed to investigate the adsorption potential of Nile rose plant for the removal of Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} from wastewater within various experimental conditions. In the same time, this can be considered a way of recycling such environmentally trouble maker materials.

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MATERIALS AND METHODS

Nile rose plant

This research was conducted in the agriculture research center, Egypt during 2005-2006. Plant samples were collected from clean area far from those which may be industrially polluted. Samples were washed with tap water and then cutted by using a small clean cutter and dried at 80 ºC for 72 h. The dried plants were grinded by using a clean electric mixer then stored in clean plastic bags so the samples become ready to use.

Infra red characterization of nile rose plant

The infra red spectrum of nile rose plant was performed using FTIR-8201PC (Shimadzu), with working range 200-4000/cm; the samples were introduced as KBr pellett.

Preparation of synthetic wastewater

Mixed metal ion solutions of Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} were prepared from Merck - analytical grade stock standards of concentration 1000 ppm. The synthetic wastewater solutions were then prepared by diluting the stock standard of each. The pH of the wastewater was adjusted using 1 M HCl and /or NaOH. The final concentrations of metal ions in the wastewater were analyzed by inductively coupled plasma (ICP-OES) Perkin Elmer Optima 2000.

Batch sorption experiments

The sorption studies were carried out at room temperature on a Lab-line reciprocating shaker using capped tubes, containing 50.0 mL of the test solution, with a known metal ion concentration. Before mixing with the adsorbent, the pH of the solution was adjusted with 1 M HCl and /or NaOH. A known amount of dried untreated plant was added and the tubes were thoroughly mixed, allowing sufficient time for adsorption equilibrium (also examined). The mixtures were filtered through filter paper Whatman # 42 and the metal ions were determined in the filtrate. The metals content in all the experiment was determined by inductively coupled plasma (ICP- OES) Perkin Elmer Optima 2000. Each experiment was repeated two times, and the results are given as averages.

Calculation of cations uptake by Nile rose plant

The amount of metal ion removal by the untreated Nile rose plant biomass during the series of batch investigations were determined using the following equation expressed as:

$$\text{Removal (\%)} = [(C_0 - C_f)/ C_0] \times 100$$

Where: C_o and C_f are the initial and equilibrium concentration (ppm) of metal ions in solution, respectively.

RESULTS

Nile rose plant surface characterization

The infrared spectrum of Nile rose plant given in Fig. 1 showed sharp peaks at 3471.6, 2923.9 and 2854.5 cm^{-1} which are assigned to Si-OH groups (Stuart, 1996), asymmetric alkyl group ($-CH_2-$) and aldehydic group (-CHO) respectively. Also, the spectrum showed a band at 1639 cm^{-1} and at 1037.6 cm^{-1} which were attributed to the presence of (C=C) and (C-O), respectively (Stuart, 1996). The bands in the range from 667.3 to 412.7/cm indicated the presence of metal-halogen bonds (Stuart, 1996). The surface IR-characterization of nile rose plant indicated the presence of many functional groups capable of binding to the metal cations.

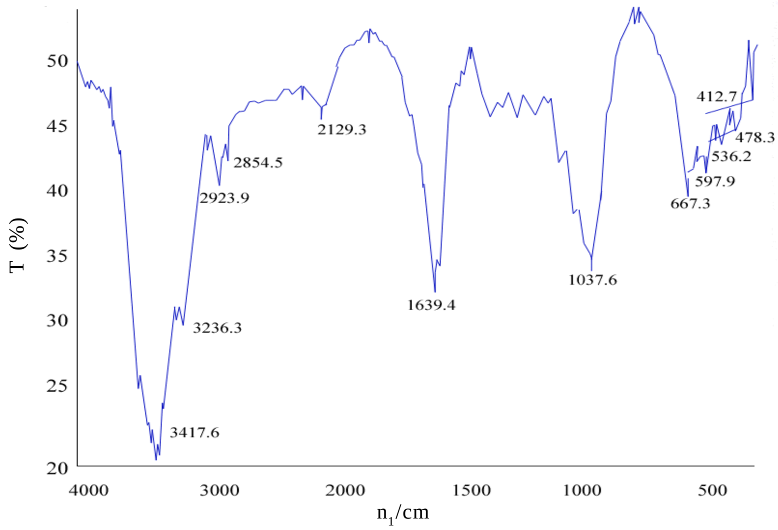

Fig. 1: I R spectrum of Nile rose plant

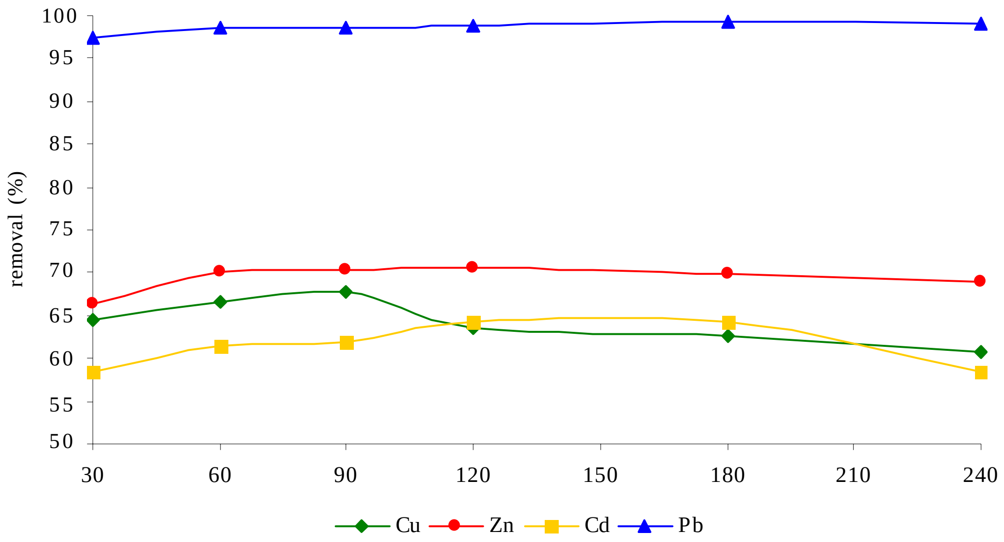

Fig. 2: effect of contact time on the removal of Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} by adsorption onto nile rose plant at an initial concentration 25 ppm, pH 4.5 and 1 g adsorbent weight

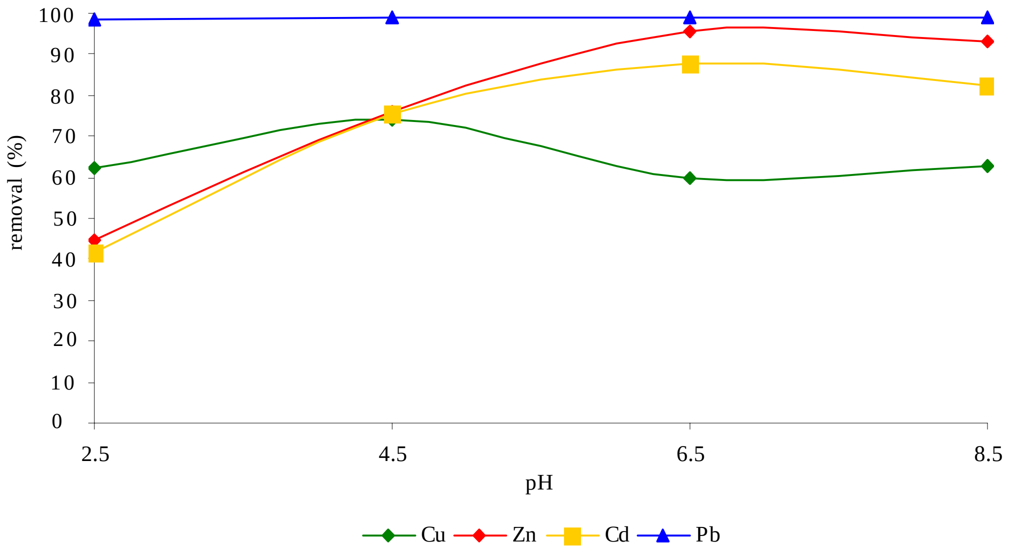

Fig. 3: Effect of pH on metal ions adsorption in their mixed solution by Nile rose plant

The effect of different operating conditions (contact time, pH, initial ions concentration and adsorbent loading weight) on the removal of Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} by adsorption onto nile rose plant was investigated. The metals removal studies were illustrated graphically in Figs. 2, 3, 4 and 5 which showed that their removals were strongly affected by these different operating conditions.

Effect of contact time

Fig. 2 shows the effect of contact time on the uptake of the studied cations onto Nile rose plant. This was achieved by varying the contact time from 30 to 240 min. in separate experiment runs. Equilibrium contact time was found to be 60 min. in case of Zn (II), Cd (II) and Pb (II) while the equilibrium in case of Cu (II) was attained after 90 min.

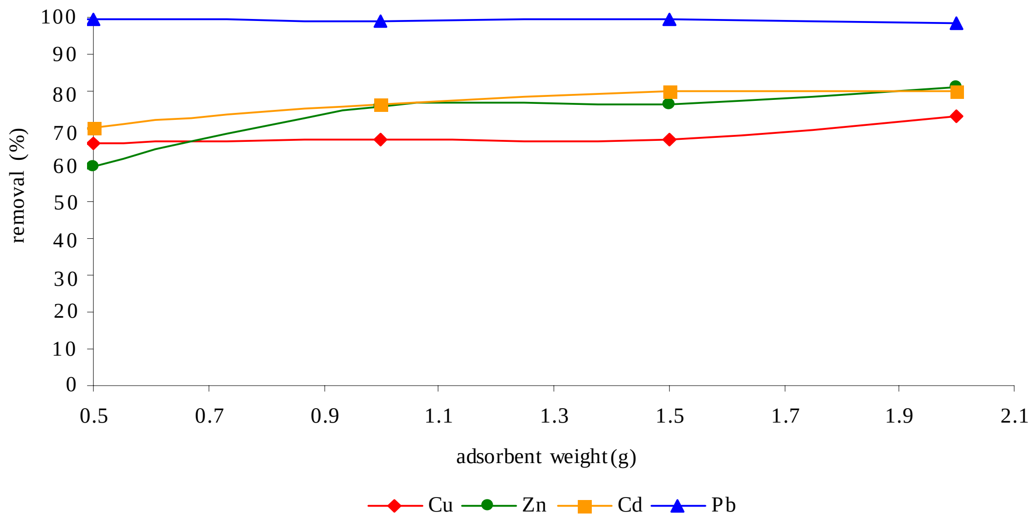

Fig. 4: The effect of variation in initial metal ions concentrations onto their adsorption using Nile rose plant

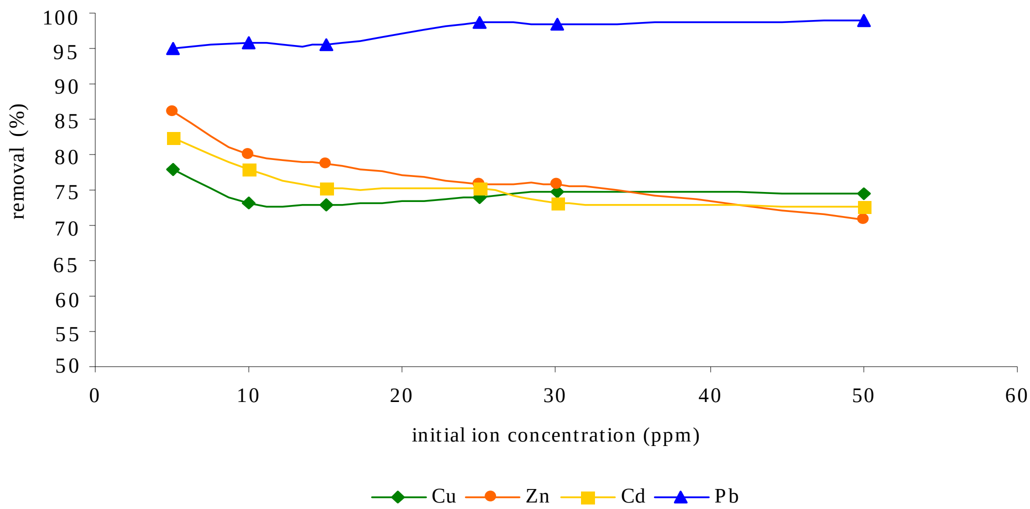

Fig. 5: Effect of Nile rose plant loading weight on metal ion adsorption in a mixed metal ion solution

The effect of pH

The effect of pH on adsorption of Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} onto Nile rose plant was investigated at pH range 2.5-8.5 (Fig. 3). The efficiency of metal ion removal by the adsorbent is affected by the initial pH of the reaction mixture (Horsfall and Abia, 2003). The uptake of Cu^{2+}, Zn^{2+} and Cd^{2+} was dependent on pH, where optimal metal removal efficiency occurred at pH 4. 5 for Cu (II) and at 6.5 for Zn (II) and Cd (II) and then declining at higher pH in case of copper. In case of PbThis may be explained by the fact that in a higher pH range, existance of counter ions might result in lower efficiency of adsorption (Bin Yu, 2001).

The effect of initial metal ions concentration

The effect of initial metal concentration on the adsorption efficiency of Nile rose plant is shown in Fig. 4. Adsorption experiments were carried out at different initial Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} concentrations ranging from 5 to 50 ppm in mixed metal ions solution. It was observed as a general trend that there is a decrease of the removal percentage with increase in initial concentration from 5 to 50 ppm. The maximum removal of Cu (II) was attained at an adsorbent dose of 1.5 g with no further increase in the removal percentage at 2 g of adsorbent.

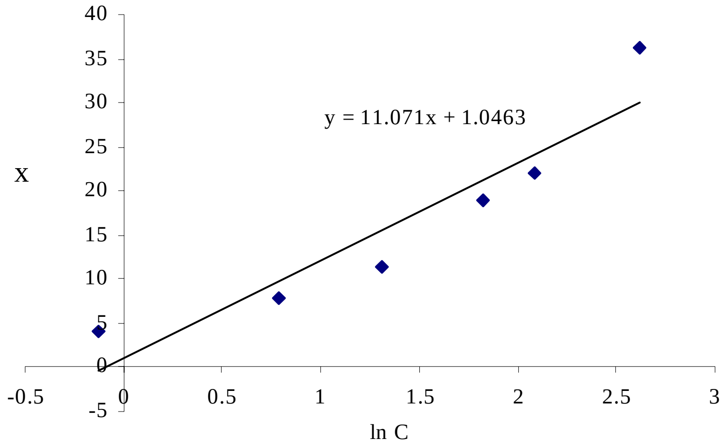

Fig. 6: Plot of X against ln C for Cd (II) sorption onto Nile rose plant

Whereas in case of Zn (II) and Cd (II) maximum removal was attained at 2 gm of adsorbent weight. In case of Pb (II) maximum removal was attained at an adsorbent loading weight (0.5 g) with non significant changes when increasing the adsorbent dose.

Isothermal studies

The experimental data for the uptake of metal ions by Nile rose plant were processed in accordance with the three of the most widely used adsorption isotherms: Langmuir, Freundlich and Temkin isotherms. The data were found to best fit the Temkin isotherm model assuming chemical adsorption between metal ions and Nile rose plant.

The Temkin isotherm model is given by the following equation:

$$X = a + b \ln C$$

Where C = Concentration of adsorbate in solution at equilibrium (mg/L). X = Amount of metal adsorbed per unit weight of adsorbent (mg/g)

a and b are constants related to adsorption capacity and intensity of adsorption.

Fig. 6 shows a plot of X against ln C for Cd (II) sorption onto Nile rose plant as a representative example for the application of Temkin model. The plot gives a straight line with slope representing the Temkin constant (b). The values of Temkin isotherm constant (b) were found to be 13.16, 9.98, 11.07 and 16.78 for the adsorption of Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} onto Nile rose plant, respectively.

DISCUSSION AND CONCLUSION

The batch adsorption results showed that the removal percentages order at equilibrium was Pb (98.66%) > Zn (70.00%) > Cu (67.84%) >Cd (61.42%). These results are important, as equilibrium time is one of the important parameters for selecting a wastewater treatment system. Where the time consumed for wastewater disposal should be considered. The susceptibility of the system to pH changes may be attributed to the nature of the ions in solution and the nature of the adsorbent used. The lower the pH, the more H^+ ions competing with copper, zinc, cadmium and lead ions for adsorption sites, thus reducing their adsorption. On the other hand, the higher the pH, the less the H^+ ions competing with metal ions for adsorption sites, thus increasing their adsorption, which explains the obtained results in Fig. 3. The adsorption efficiency decreased with the increasing of the initial concentration of the metal ions. These results may be explained on the basis that the increase in the number of ions competing for the available binding sites and also because of the lack of active sites on the adsorbent at higher concentrations. Therefore, more metal ions were left unadsorbed in solution at higher concentration levels (Krishnan and Anirudhan, 2003). From Fig. 5, it can easily be inferred that the percent removal of metal ions increases with increasing weight of Nile rose plant. This is due to the greater availability of the exchangeable sites or surface area at higher dose of the adsorbent. These results are in agreement with previous studies on many other adsorbents (Ajmal, *et al.*, 1998; Yu, *et al.*, 2001 and Dakiky, *et al.*, 2002). The results presented in this study, showed that dried leaves of Nile rose plant can efficiently remove Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} present in aqueous solutions. The removal percentages of the studied cations were dependent on the weight of the adsorbent, the initial ions concentration, contact time and pH of the solution. Metal sorption is pH dependent and maximum sorption for Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions was found to occur at a pH 4. 5 for Cu (II) and at 8.5 for Zn (II), Cd (II) and Pb (II) and the equilibrium conditions were attained after 60 min. in case of Zn (II), Cd (II) and Pb (II) and 90 min. for Cu (II). The Temkin isotherm was found to well represent the obtained sorption data. Nile rose plant is found to be a promising adsorbent for the removal of metal cations from mixed metal ions solution, representing an effective and environmentally clean utilization of waste matter. The Temkin isotherm fitted the present data because it takes into account the occupation of the more energetic adsorption sites at first. For natural unmodified materials such as Nile rose plant it is highly probable that their adsorption sites are energetically non-equivalent (Kolasniski, 2001).

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