

Biosorption of Cadmium from Aqueous Solution by ULMUS Leaves and their Ash

A. H. Mahvi

*Corresponding Author School of Public Health and Center for Environmental Research
Medical Sciences/ University of Tehran, Tehran, Iran
E-mail: ahmahvi@yahoo.com*

R. Nabizadeh

*School of Public Health and Center for Environmental Research
Medical Sciences/ University of Tehran, Tehran, Iran*

F. Gholami

*School of Public Health and Center for Environmental Research
Medical Sciences/ University of Tehran, Tehran, Iran*

J.Nuri

*School of Public Health and Center for Environmental Research
Medical Sciences/ University of Tehran, Tehran, Iran*

A.kaeiri

*School of Public Health and Center for Environmental Research
Medical Sciences/ University of Tehran, Tehran, Iran*

Abstract

The biosorption capability of Ulmus leaves and their ash for Cadmium ions removal from aqueous solutions has been investigated as a function of appropriate equilibrium time, concentration of adsorbate and pH using a batch system. The effect of metals such as Ca^{+2} , Mg^{+2} , Na^{+} and K^{+} on biosorption was studied. Studies showed that equilibrium time to biosorption of Cadmium was 60 minutes, optimum pH was 6 and initial concentration 2mg/L for both Ulmus Leaves and their ash respectively. Simultaneous adsorption of Cd (II) and Cr (VI) ions was studied using a medium that contained 2 mg/ L of each metal ion. The effect of these biosorbents on increasing COD in aqueous solution shows that 2g/L biosorbent cause increase 130 and 75 mg/L COD in deionized water at 60 minutes for Ulmus Leaves and their ash respectively. The Cadmium biosorption obeyed both Langmuir and freundlich isotherms but langmuir isotherm was better by $R^2=0.998$ for ash and $R^2=0.993$ for Ulmus Leaves. The studies showed that Ulmus Leaves ash was more favorable than Ulmus Leaves in removing Cadmium and thus was a better biosorbent.

Keywords: Biosorption, Cadmium, Ulmus Leaves, aqueous solution

Introduction

Cadmium(Cd), which is widely used and extremely toxic in relatively low dosages, is one of the principle heavy metals responsible for causing kidney damage, renal disorder, high blood pressure, bone fraction and destruction of red blood Cells(Drush,1993). Because of the toxicity and bioaccumulation Cd(II) is considered as a priority pollutant by the US Environmental Protection Agency.

The permissible limit for Cd(II) as described by WHO is 0.01 mg/dm^3 . The main anthropogenic pathway through which Cd(II) enters the water bodies is via wastes from industrial processes such as electroplating, plastic manufacturing, metallurgical processes and industries of pigments and Cd/Ni batteries (Charemisinoff, 1995). There are several methods to treat the metal contaminated effluent such as precipitation, Ion exchange and adsorption etc, but the selection of the treatment methods is based on the concentration of waste and the cost of treatment (Dozuane, 1990; Cheung et al, Peternele et al, 1999; 2001; Ajmallet et al, 2003). Adsorption of heavy metal ions on activated carbon has been applied widely as a unit operation in the treatment industrial Wastewater. The use of commercial activated carbon is not suitable for developing countries because of its high cost. Therefore, there is a need to produce activated carbon from cheaper and readily available materials, which can be used economically on a large scale. Activated carbons prepared from rice husk, ground nut husk, fertilizer waste slurry, Peanut hull, jute stick, moringa oleifera seed husk, coconut husk and sawdust (Manju and Anirudhun, 1997; Raji et al., 1997; Warhurst et al., 1997). Activated carbons have been used for Wastewater treatment and the potential of their ultimate usage may be determined by their adsorption capacity, regeneration characteristics and physical properties of the subsequent product. In recent years, biosorption has emerged as a cost-effective and efficient alternative for the removal of heavy metals from low strength Wastewaters.

Biosorption is the uptake of heavy metal ions and radionuclides from aqueous by biological materials.

Microorganisms, including algae's, bacteria, yeast, fungi, plant leaves and root tissues can be used as biosorbents for detoxification and recovery of toxic or valuable metals from industrial discharges (Veglio and Beolchini, 1997). Certain waste materials from industrial or agricultural operations may be potential alternative biosorbents (Baylor SE., et al 1999).

It has been reported that wood wastes such as saw dust, barks and tree leaves effectively adsorb Cadmium species from aqueous systems (Kumar P and Dara SS., 1982; Aoyama M et al., 1999).

Tree leaves that are in agricultural operations are generally little or no economic value.

Tehran plant leaves (such as ulmus) have been widely planted as street and park trees. Although the pruning of these trees produces waste foliage in large quantities, it has been discarded. Large piles of the waste foliage pose problems in its disposal. This study was performed to investigate the efficiency of Ulmus Leaves and their ash on removing Cadmium from dilute aqueous solutions. The parameters that effect on biosorption such as contact time, pH, initial Cadmium concentration, and the effect of metals such as (Ca^{+2} , Mg^{+2} , Na^{+} and K^{+}) were investigated and so in this study the effect of this biosorbent on increasing COD in aqueous solution were studied.

Material and Methods

Ulmus Leaves used were obtained from the various parks in Tehran. The ULMUS Leaves were then washed with deionized water to clean and then laid down to be flattened to be dried in sunlight for 14 days. Dry leaves were then ground with electrical grinder. After being grounded, the leaf particles were sieved with 60-70 mesh sieves (0.20-0.3mm). Then, leaf was dried at 100°C for 24 hours to be constant weight. The Ulmus Leaves ash obtained from burning of Ulmus Leaves in oven at 550°C for 15 minutes, dried leaf was stored in desiccator until used.

Adsorption of Cadmium in aqueous solution on Ulmus Leaves and their ash were examined by various physicochemical parameters such as: pH, contact time, concentration of Cd^{+2} and the effect of metals (Ca^{2+} , Mg^{2+} , Na^{+} and K^{+}) were studied.

Stock solution of Cadmium (1000 mg/L) was prepared by dissolving Cadmium nitrate in distilled water. The concentration range of Cadmium prepared from stock solution varied between 2 to 40 mg/L for both Ulmus Leaves and their ash. Before mixing the adsorbent, the pH of each last solution was adjusted to the required value with diluted and concentrated H_2SO_4 and $NaOH$ solution, respectively. The Ca^{2+} , Mg^{2+} , Na^{+} and K^{+} solution were prepared by its salt in concentration of 2 mol/L.

The experiments were carried out in the batch methods for the measurement of adsorption capacities. Each Cadmium solution was placed in 1000 ml beaker and known amount of adsorbents 1g were added to each beaker. The beakers were agitated on jar test equipment at a 300 rpm constant mixing rate for 30-300 minutes to ensure equilibrium was reached.

Finally the suitability of the Freundlich and Langmuir adsorption models to the equilibrium data were investigated for Cadmium-sorbent system. A duplicate analyzed for every sample to track experimental average of reproducing results. For quality control purpose, DI water digested and analyzed with every sample group to track and possible contamination source.

The residual Cadmium was analyzed through atomic spectrometry using an ALPH-4-flame atomic absorption spectrophotometer at wave lengths 228.8 using an acetylene air flame according to standard methods for the examination of water and wastewater (APHA, 2005).

Results and Discussion

Adsorption equilibrium was calculated according to the equation (1):

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

Where:

q_e = adsorbent (leaves) phase concentration after equilibrium, mg adsorbate/g adsorbent

C_o = initial concentration of adsorbate, mg/L

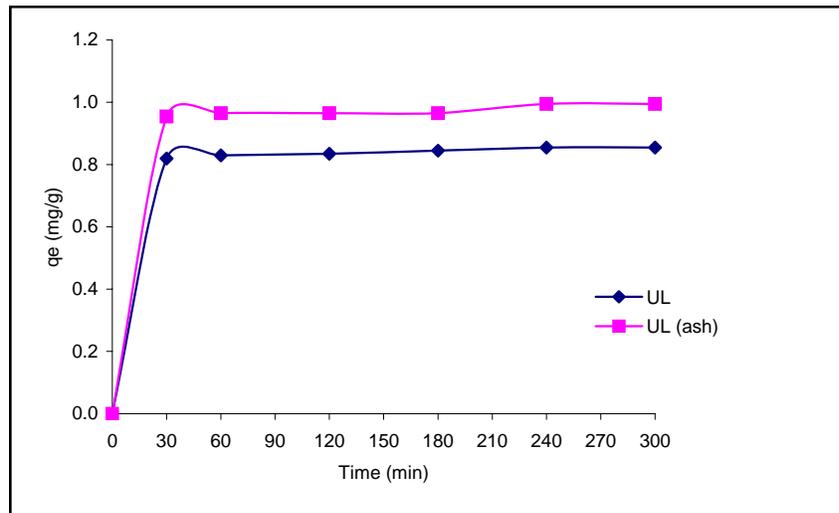
C_e = final equilibrium concentration of adsorbate after absorption has occurred, mg/L

V = Volume of liquid in the reactor, L

M = mass of adsorbent, g

At this experiment, the adsorption of Cadmium increased with increasing contact time and became almost constant after 60 min for ULMUS and 60 min for their ash [Fig.1]. These results also indicate that the sorption process can be considered very fast because of the largest amount of Cadmium attached to sorbent within the first 60 min. of adsorption. Similar results reported by Aj mol, *et al.* and, Alavi *et al.*

Figure.1: Effect of contact time on the removal of Cadmium by ULMUS Leaves and their ash (Adsorbent dosage = 2g/L, Cadmium concentration = 2 mg/L).



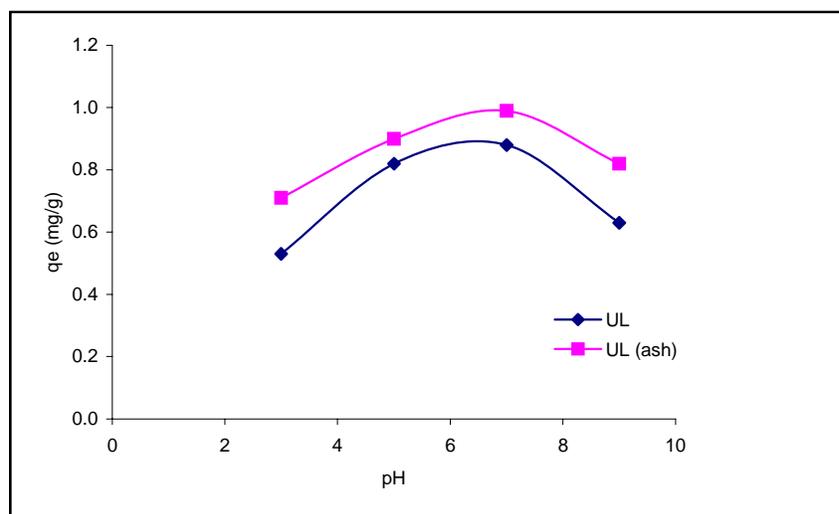
Experiments concerning the effect of pH on the sorption were carried out with the range of pH that was not influenced by the metal precipitation, as metal hydroxide. The suitable pH ranges for Cadmium was performed for the pH range variations of 3-9.

Fig.2 shows that in most cases, the removal increased steadily with pH. Adsorption of metal cation on adsorbent depends upon the nature of adsorbent surface and species distribution of the metal cation. Surface distribution mainly depends on the pH of the system (Namasi Vayam and Ranganathan, 1995).

The percent of adsorption for Cadmium ion decreased with the decrease in pH, because protons compete with metal ion for sorption sites on the adsorbent surface as well as the concomitant decrease of negative charge of the same surface (Namasivayam and Ranganathan, 1995).

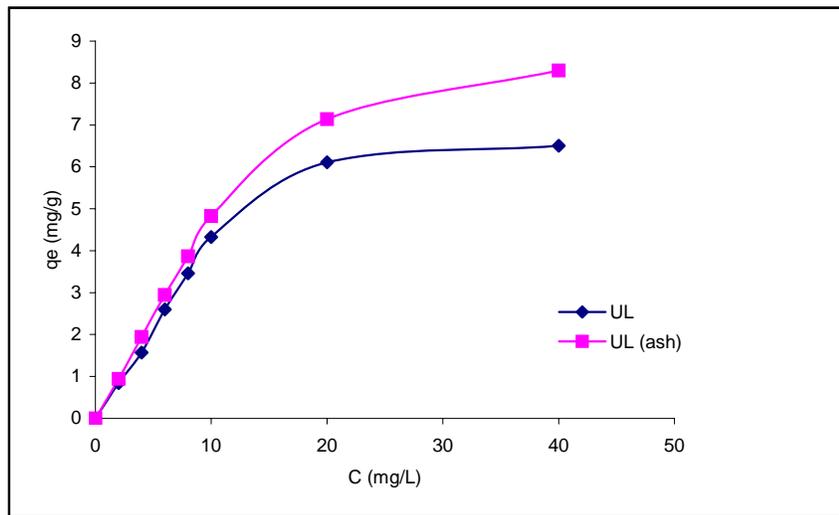
It has been reported that precipitation of Cadmium starts at pH 8.3 (Namasivayam and Ranganathan, 1995; Ajmalet et al., 2003).

Figure 2: Effect of pH on the removal of Cadmium by Ulmus Leaves and their ash (Adsorbent dosage = 2g/L, Cadmium concentration = 2 mg/L)



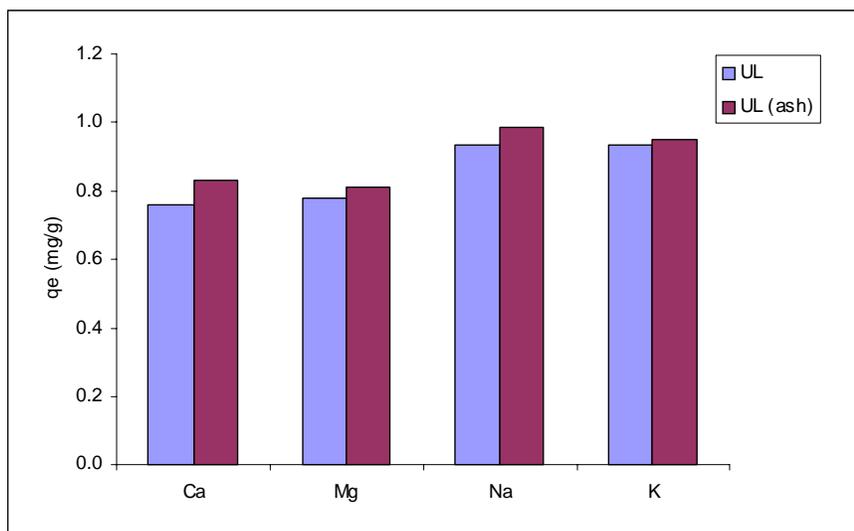
The effect of initial metal Ion concentration on the adsorption capacity of ULMUS Leaves and their ash was studied under optimum conditions. (pH = 6, Temp = 24-25⁰C). Adsorption of Cadmium on Ulmus Leaves and their ash increased with increasing initial concentration of Cd²⁺. These results may be explained by an increase in the number of metal Ions competing for the available binding sites in the adsorbent for complexation of Cd²⁺ Ion at higher concentration levels. These results were shown in Fig .3.

Figure 3: Effect of Cadmium concentration on the removal of Cadmium by Ulmus Leaves and their ash (Adsorbent dosage = 2g/L' pH=6, T=24⁰C, 300rpm, 60min).



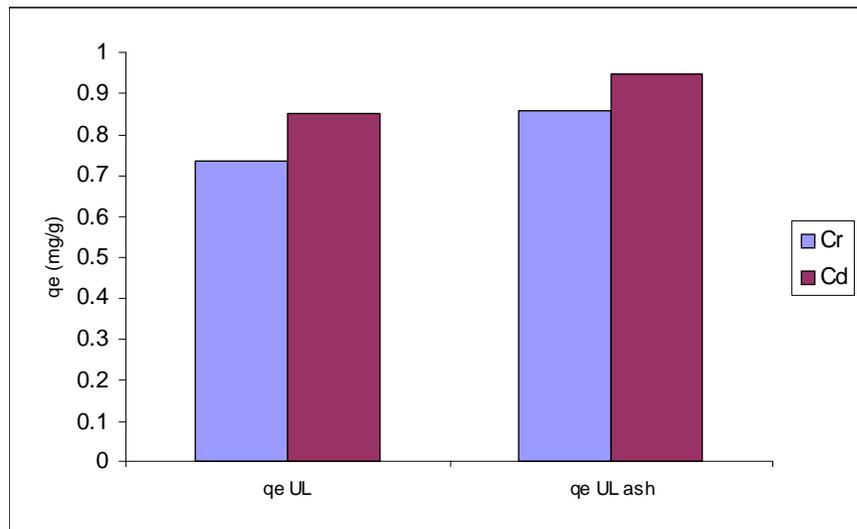
The effect of light metals such as Ca²⁺, Mg²⁺, Na⁺ and K⁺ on adsorption were studied and shown that these Ions can disturb to adsorption of heavy metals on any adsorbent. two valent metals such as Ca²⁺, Mg²⁺ have more effect than Na⁺ and K⁺. The effect of these metals on adsorption was shown in Fig.4.

Figure 4: The effect of light metals on adsorption capacity (Cd= 2mg/L and 2Mol/L Ca, Mg, Na, K).



Simultaneous adsorption of Cd (II) and Cr (VI) ions was studied using a medium that contained 2 mg/ L of each metal Ion. Fig .5, show that this adsorbent was more efficient for removed of Cd(II) Than Cr (VI).

Figure 5: Simultaneous adsorption of Cd (II) and Cr (VI) ions was studied using a medium that contained 2 mg/L of each metal Ion.



Two models, langmuir and freundlich equation, were used to determine adsorption of Cadmium on to Ulmus Leaves and their ash. Isotherm studies were than carried out as described in our earlier paper (Mahi et al. 2004).

The langmuir isotherm was also used to explain observed phenomena. K and n values were calculator from the intercept and slope of the Ulmus Leaves and found to be R² 0.993 for Ulmus Leaves and R² 0.998 for their ash.

The langmuir isotherm was fitted better than the freundlich isotherm as is evident from the values of regression coefficient in table 1.the results are given in Fig.6 and Fig.7. Similar results were reported by Alavi et al (Alavi et al: 2005).

Figure 6: The linearized Langmuir adsorption isotherm for Cadmium removal by Ulmus Leaves and their ash.

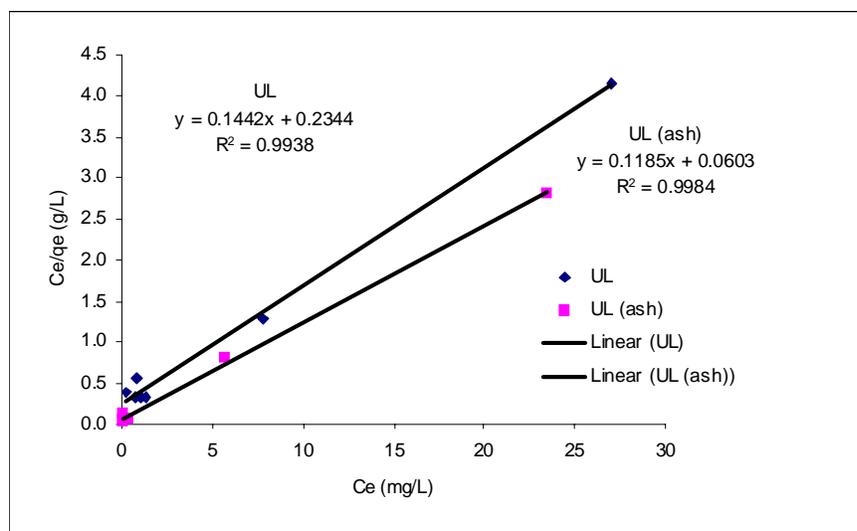
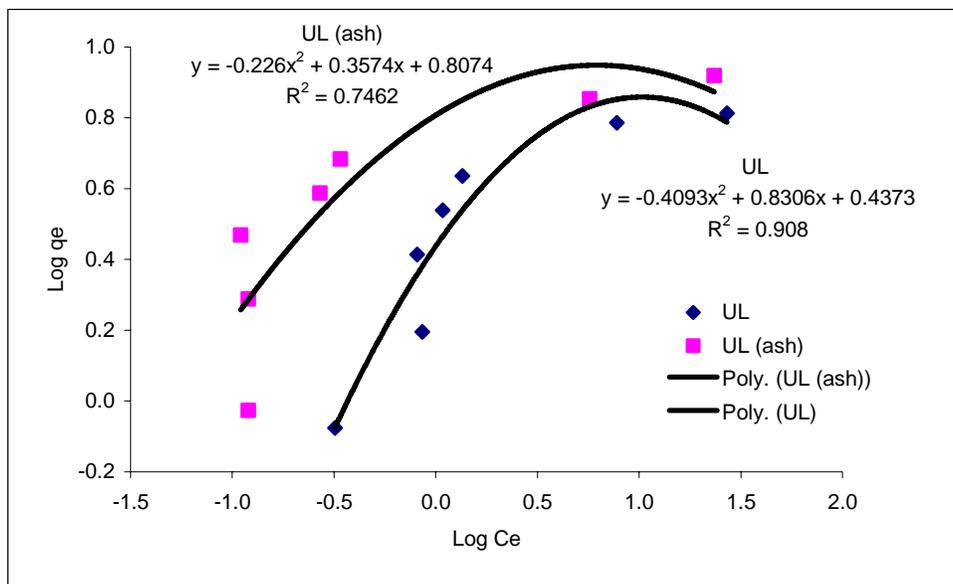
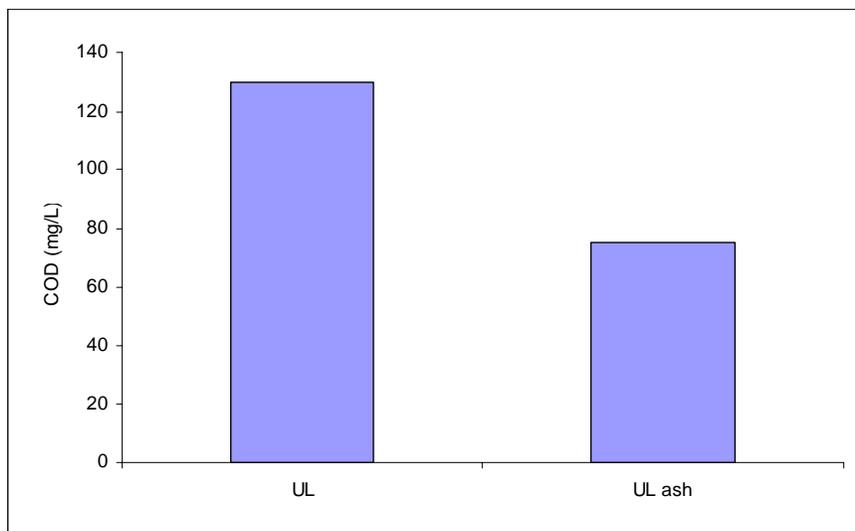


Figure 7: The Freundlich adsorption isotherm for Cadmium removal by Ulmus Leaves and their ash.

The effect of these adsorbents on COD in aqueous were studied. Fig.8, show that 2 g/Ladsorbent cause increase 120 and 95 mg /L COD in Deionizd water in 60 minutes for Ulmus Leaves and their ash. This can be favorable for biological treatment in industrial Wastewater treatment plant after chemical treatment.

Figure 8: The effect of 2g/L Ulmus Leaves and their ash on increase COD (mg/L) (60 min, pH=6, T= 24°C).

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