

## REMOVAL OF CHROMIUM (VI) FROM AQUEOUS SOLUTION BY *ULMUS* LEAVES

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### ABSTRACT

The Cr (VI) adsorption characteristics of *Ulmus* leaves (UL) and their ash were examined as a function of contact time, initial pH, and initial metal ion concentration. Batch adsorption experiments were performed. The effects of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^{+}$  and  $\text{K}^{+}$  on adsorption were studied. Maximum removal was achieved in the pH=7, contact time of 60 minutes and with initial Cr (VI) concentration of 2 mg/L. Because at pH  $\geq 6.5$ , precipitation of chromium may take place, optimum pH was selected at 6. Maximum adsorption rate values were found at the first 60 min at pH= 6. The effect of the adsorbent on COD removal from aqueous solution showed that 2g/L of adsorbent caused 130 and 75 mg /L increase in COD of deionized water in 60 min for UL and its ash, respectively. The chromium adsorption data obtained under the optimum condition were described by the Langmuir and Freundlich isotherms. Studies showed that the Langmuir adsorption model better fitted than Freundlich, with  $R^2 > 0.99$ . Also UL ash was more efficient than living leaves in removing chromium from aqueous solution.

**Key words:** Adsorption, chromium removal, *Ulmus* leaves, aqueous solution

### INTRODUCTION

The presence of heavy metals in drinking water sources and in edible agricultural crops can be harmful to human. It is well known that heavy metals can be toxic, e.g. they damage nerves, liver and bones and they block functional groups of vital enzymes (Ewan and Pamphlet, 1996). In the recent years, increasing awareness of water pollution and its far reaching effects has prompted efforts towards pollution abatement. Among the different heavy metals from toxic pollutants introduced into natural waters, chromium is of high concern (Donmez and Aksu, 2002). The two major sources chromium contamination are electroplating, metal finishing industries (hexavalent chromium) and tanneries (trivalent chromium). Chromium occurs most frequently as Cr (III) or Cr (VI) in aqueous solutions (Dakikiy *et al.*, 2002). Both valences of chromium are potentially harmful but hexavalent chromium poses a greater risk due to its carcinogenic properties (Dakikiy *et al.*, 2002). Hexavalent chromium,

which is primarily present in the form of chromate ( $\text{CrO}_4^{2-}$ ) and dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ), poses significantly higher levels of toxicity than the other valence states (Sharma and Forester, 1995). The toxicity of hexavalent chromium Cr (VI), even in small concentrations has been well documented. Since the discharge of chromium ions through industrial waste effluents into natural bodies of water causes serious environmental disruption, strict wastewater standards have been setup in many countries. In Japan the standard on wastewater quality states that the maximum level permitted in wastewater is 2mg/m<sup>3</sup>-d for total Cr and 0.05 mg/m<sup>3</sup>-d for Cr (VI) (Masakazu, 2003). Techniques to separate heavy metals from industrial wastewater include precipitation, ion exchange, adsorption, electrodialysis and filtration, but these methods have limitation on selective separation and high investment cost and operation of equipment (Dae, *et al.*, 2003). Adsorption of heavy metal ions on to activated carbon has been applied widely as a unit operation in the industrial wastewater treatments. The use of commercial

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activated carbon may not be 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, peanuts hull, jute stick, moringa oleifera seed husk, coconut husk and sawdust (Manju and Anirudhun, 1997; Raji *et al.*, 1997; Warhurst *et al.*, 1997) have been used for wastewater treatment and the potential of their ultimate usage are determined through by their adsorption capacity, regeneration characteristics and physical properties of the subsequent product. In recent years, adsorption 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 from aqueous system by biological materials. Microorganisms, including algae, 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 have potential alternative biosorbents (Baylor *et al.*, 1999). It has been reported that wood wastes such as saw dust, barks and tree leaves may effectively adsorb cadmium species from aqueous systems (Kumar and Dara, 1982; Aoyama *et al.*, 1999). The binding mechanisms of heavy metals by biosorption could be explained by the physical and chemical interactions between cell wall ligands and adsorbents by ion exchange, complexation, coordination and micro precipitation. The diffusion of the metal from the bulk solution to active sites of biosorbents occurs predominantly by passive transport mechanisms (Veglio and Beolchini, 1997) and various functional groups such as carboxyl, hydroxyl, amino and phosphate existing on the cell wall of biosorbents can bind the heavy metals (Avery and Tobin, 1993).

Tree leaves from agricultural operations have generally little or no economic value. In Tehran, plants (such as *Ulmus*) have been widely planted as street and park trees. Although the pruning of these trees produces waste foliage in large

quantities, 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 chromium from dilute aqueous solutions. The parameters that affect biosorption such as initial concentration, contact time, pH and the effect of light metals ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^{+}$  and  $\text{K}^{+}$ ) were investigated. The effect of this biosorbent on increasing COD in aqueous solution were also studied.

## MATERIALS AND METHODS

*Ulmus* leaves were obtained from various parks in Tehran. They were washed with deionized water and then left to be dried. The dried leaves were then ground with electronic grinder. After grinding, the leaf particles were sieved with 60-70 mesh sieves (0.2-0.3 mm). Then, the leaves were dried at 80 °C for 24 h. The *UL* ash was obtained from burning of in electrical oven at 550°C for 30 minutes. Dried leaves and their ash were stored in desiccators. Adsorption of chromium (VI) located in aqueous solution on *UL* and their ash were tested by optimizing various physicochemical parameters such as: pH, contact time, concentration of Cr (VI) and the effect of light metals ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^{+}$  and  $\text{K}^{+}$ ).

Stock solution of chromium (1000 mg/L) was prepared by dissolving titrizol chromium (VI) in distilled water. The concentration range of chromium prepared from stock solution varied between 2 to 40 mg /L for both *UL* and the ash. Before mixing the adsorbent, the pH of each solution was adjusted to the required value with diluted and concentrated  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  solutions, respectively.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^{+}$  and  $\text{K}^{+}$  solution were prepared in concentration of 2 mol/L. The experiments were carried out in batch method for the measurement of adsorption capacities. Each chromium solution was placed in 1000 mL beaker and known amount of adsorbents (1 g) were added to each beaker; the beakers were agitated on jar test equipment at a 300 rpm constant mixing rate for 0-300 minutes to ensure equilibrium was reached. pH range of 3-9 was selected to be studied in this work. Finally the suitability of the Freundlich and Langmuir adsorption models to the equilibrium data were investigated for

chromium sorbent system. A duplicate analysis of each sample was duplicated in order to track experimental error and show capability of reproducing results. For quality control purpose, deionized water was digested and analyzed with sample group to track and possible contamination source. The residual chromium was analyzed through atomic spectrometry using an ALPH-4-flame atomic absorption spectrophotometer at wave length 357.9nm using an acetylene air flame according to standard methods for examination of water and wastewater (APHA, 1995). The  $q_e$  was calculated according to equation (1):

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

Where:

$q_e$  = adsorbent phase concentration after equilibrium, mg adsorbate/g adsorbent

$C_o$  = initial concentration of chromium mg/L

$C_e$  = l equilibrium concentration of chromium after adsorption , mg/L

V = volume of liquid in the reactor, L

M = mass of adsorbent, g

## RESULTS

Fig. 1 shows the effect of contact time on the removal of chromium (VI) by UL and its ash. In

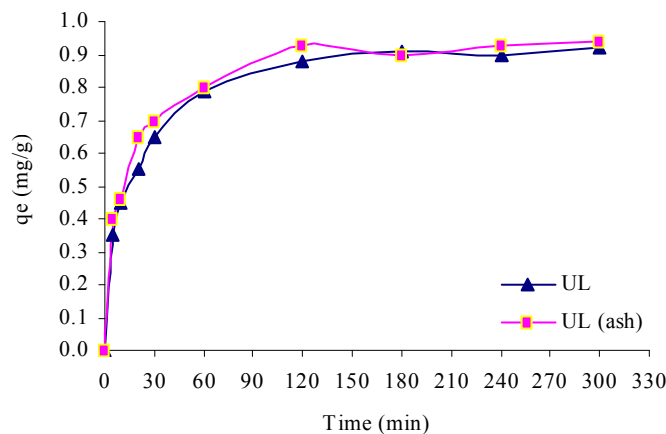


Fig.1: Effect of contact time on the chromium (VI) removal of (VI) by UL and its ash (adsorbent dosage = 2 g/L chromium concentration = 2 mg/L)

Fig. 2 the effect of pH on the removal of chromium (VI) is presented. The effects of chromium concentration on the removal efficiency from aqueous solution by UL and its ash are presented in Fig. 3. 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 effect of initial metal ion concentration on the adsorption capacity of UL and its ash was studied under optimum conditions. (pH = 6, Temp. = 24-25 °C). It has been reported that precipitation of chromium starts at pH= 6.5 (Namasi Vayam and Ranganathan, 1995; Ajmalet *et al.*, 2003). Fig. 5 shows that 2 g/L adsorbent causes 130 and 75 mg/L in COD increase in de-ionized water after 120 minutes for UL and its ash, respectively.

Two models, Langmuir and Freundlich equation, were used to determine adsorption of chromium on to UL and its ash. Isotherm studies were than carried out as described in our earlier paper (Mahvi *et al.* 2004).

The Langmuir isotherm was also used to explain observed phenomena. K and n values were calculat from the intercept and slopes were found to be  $R^2=0.994$  for UL and 0.998 for its ash, respectively.

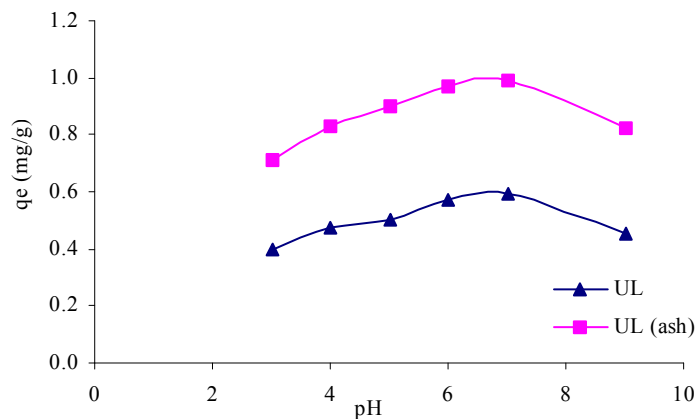


Fig.2: Effect of pH on the chromium (VI) removal by UL and its ash (adsorbent dosage = 2 g/L chromium concentration = 2 mg/L)

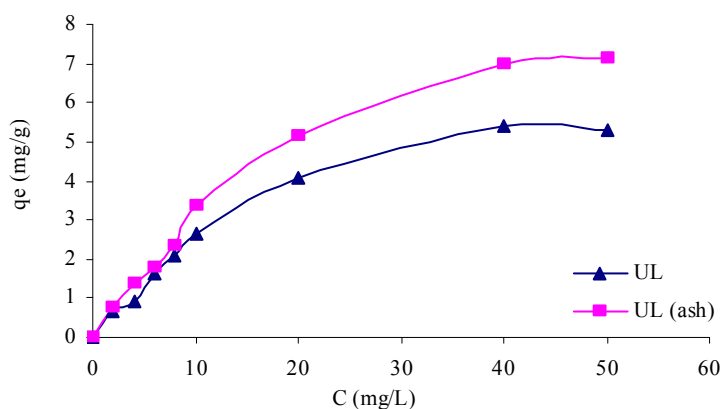


Fig. 3: Effect of Chromium concentration on the chromium (VI) removal by UL and its ash (adsorbent dosage = 2g/L pH=6, T=24 °C, 300rpm, 60 min).

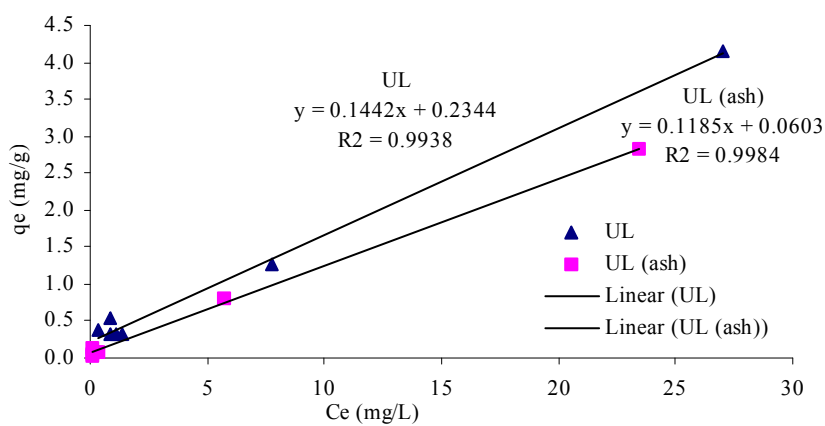


Fig.4: The linearized Langmuir adsorption isotherm for chromium (VI) by UL and its ash

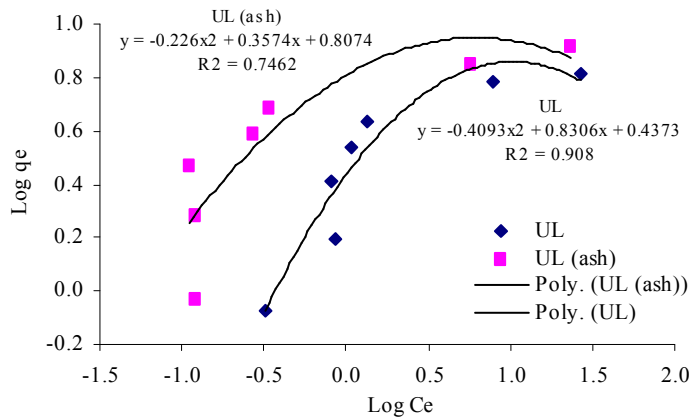


Fig. 5: Freundlich adsorption isotherm for chromium (VI) by UL and its ash

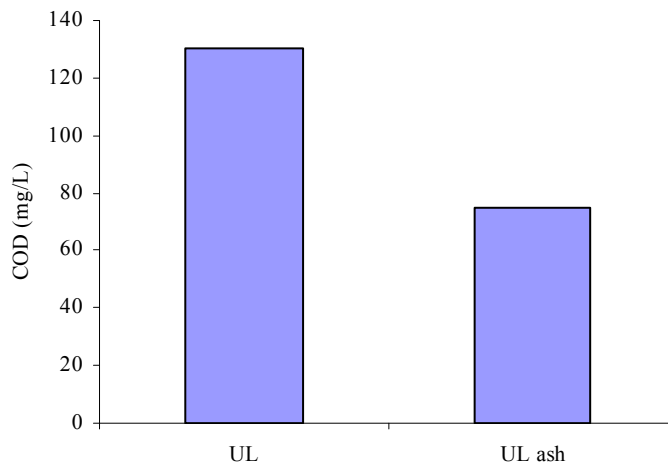


Fig. 6: Effect of 2 g/L UL and its ash on the increase COD (mg/L) (60 min, pH=6, T= 24°C)

## DISCUSSION

The results indicate that the sorption process can be considered very fast because of the largest amount of chromium attached to the adsorbent within the first 60 min. The results from Fig. 1 indicate that the adsorption of chromium increases with increasing contact time and becomes almost constant after 60 min for UL and its ash. Similar results have been reported by Ajmol, *et al.* and, Alavi *et al.*; (2005). The results indicate that the 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 results show that the percent of adsorption for chromium (VI)

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 (Namasi Vayam and Ranganathan, 1995). Adsorption of chromium on UL and its ash increased with increasing initial concentration of Cr (VI). These results may be explained by an increase in the number of metal ions competing for the available binding sites in the adsorbent for complexity of Cr (VI) ion at higher concentration levels, which are according to the results shown in Fig. 3. Based on the results of present study, it can be concluded that Ulmus leaves can be used in the wastewater treatment process for the removal of metal ions. Removal efficiency of

chromium (VI) has been found to be greater than 85%. The adsorption of metal ion on tree leaves (UL) reached equilibrium in 60 minutes; rapid adsorption of Cr ions was observed in first 60 minutes of reaction, pH=6 and initial concentration 20 mg/L. The Langmuir isotherm fitted better than the Freundlich isotherm as it is evident from the values of regression coefficient  $R^2=0.994$  for UL and 0.998 for UL (ash), as given in Fig.5 and Fig.6. Similar results were reported by Alavi *et al* (Alavi et al., 2005). Unfortunately the UL that was used as adsorbent in aqueous solution caused an increase in COD of the solution that is not suitable for treatment of very weak wastewaters or raw waters. Therefore it is suggested to use active ashes of UL.

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