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ADSORPTION OF CHROMIUM FROM WASTEWATER BY *PLATANUS ORIENTALIS* LEAVES

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ABSTRACT

The Cr (VI) adsorption characteristics of *platanus orientalis* leaves and their ash were examined as a function of contact time, initial pH and metal ion concentration. Batch adsorption experiments were performed. The effects of Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} on adsorption were studied. The effect of this adsorbent on COD in wastewater showed that 2g/L of adsorbent caused increase of 110mg/L and 76mg/L COD in deionized water in 120 minutes for *platanus orientalis* leaves and their ash , respectively. The maximum removal took place in the pH range of 6-7, contact time of 60 minutes and initial concentration of 2mg/L. Studies showed that the Freundlich adsorption model better fitted with the results than Langmuir with $R^2 > 0.85$. The study showed *platanus orientalis* leaves ash was more favorable than living ones as well as in removing chromium from the aqueous solution.

Key words: Cadmium removal, *Platanus orientalis* leaves, ash, aqueous solution

INTRODUCTION

The presence of heavy metals in drinking water can be toxic to consumers; these metals can damage nerves, liver and bones and 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 concerted efforts towards pollution abatement .Among the different heavy metals from toxic pollutant introduced into natural waters (Donmez and Aksu, 2002).

There are two major sources of heavy metals contamination, wastewater metal finishing industries (hexavalent chromium) and tanneries (trivalent chromium). Chromium occurs most frequently as Cr(VI) or Cr(III) in aqueous solutions (Dakikiy *et al*., 2002).

Both valences of chromium are potentially harmful but hexavalent chromium have a grater risk due to its carcinogenic properties (Dakikiy *et al*., 2002). Hexavalent chromium which is primarily present in the form of chromate(CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$), poses significantly higher levels of toxicity than the other valences states(Sharma and Forester, 1995).The toxicity of hexavalent Chromium, even in small concentrations has been well documented. Since the addition 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 are 2mg/dm^3 for total Cr and 0.05 mg/dm^3 for Cr (VI) (Masakazu, 2003).

Techniques for removal of heavy metals from industrial wastewater include precipitation, ion exchange, adsorption, electrodialysis and filtration; but these methods have limitations on selective separation and high cost of investment and operation of equipment (Dae *et al*., 2003).

Adsorption of heavy metal ions on to activated carbon has been widely applied 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.

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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 olefera 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 may be determined 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 and radionuclides from aqueous environments by biological materials such as: algae, bacteria , yeast, fungi , plant leaves and root tissues which 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, *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 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 cellwall ligands and adsorbates by ion exchange, complexation, coordination and microprecipitation. 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 that are in agricultural operations are generally little or no economic value. In Tehran, plants and trees such as *Plataneus Orientalis* have been widely planted as street and park trees. Although the pruning of these trees produces waste foliage in large quantities, they are discarded. Large piles of the waste foliage pose problems in its disposal.

This study was performed to investigate the efficiency of *Platanus orientalis* leaves (POL) and their ash on removing chromium from dilute aqueous solutions. The parameters that affect biosorbtion such as initial chromium concentration, contact time , pH and the presence of metals such as (Ca^{+2} ,Mg^{+2},Na^+ and K^+) were also investigated; the effect of this biosorbent on increasing COD in wastewater was studied.

MATERIALS AND METHODS

Platanus Orientalis leaves used were obtained from various parks in Tehran. They were washed with deionized water to clean and then laid down to be flatted dried. Dry leaves were then ground with mechanical grinder. After being ground grinded, the leaf particles were sieved with 60-70 mesh sieves (0.20-0.3mm). Then, leaf was dried at 100^{o}C to reach the constant weight. Adsorbents were stored in desiccators unitl use. The POL ash was obtained from burning of POL in oven at 550^{o}C for 30 minutes.

Adsorption of chromium (VI) in wastewater on POL and their ash were examined by optimizing various physicochemical parameters such as: pH, contact time and concentration of Cr(VI). The effect of metals such as (Ca^{2+}, Mg^{2+}, Na^+ and K^+) were also studied.

Stock solution of chromium (1000 mg/L) was prepared by dissolving titrazol chromium (VI) in distilled water. The concentration range of chromium prepared from stock solution varied between 2 to 40 mg/L for both POL and their ash. Before mixing the adsorbent, pH of each solution was adjusted to the required value with diluted and concentrated H_2SO_4 and NaOH solution, respectively. Ca^{2+}, Mg^{2+}, Na^+ and K^+ solutions were prepared by their salts in concentration of 2 mol/L. The experiments were carried out in batch for the measurement of adsorption capacities. Each chromium solution was placed in 1000 mL beaker and known amount of adsorbents (l g) were added to each beaker. The beakers were agitated on jar test equipment at a 300 rpm constant mixing rate for 30-240 minutes to ensure equilibrium was reached.

Finally the fitness of the Freundlich and Langmuir adsorption models to the equilibrium data were investigated for chromium-sorbent system. A duplicate analysis for each sample to track experimental error and show capability of reproducing results was done.
The residual chromium was analyzed through atomic spectrometry using an ALPH-4-flame atomic absorption spectrophotometer at wavelengths=357.9 nm and an acetylene air flame according to standard methods for analyzing water and wastewater (APHA, 2005).
q_e was calculated according to the equation (1):

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

Where:
q_e = adsorbent 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

RESULTS

The effect of contact time

In this experiment, the adsorption of chromium increased with increasing contact time and became almost constant after 120 min for *Platanus orientalis* leaves and their ash showed in Fig. 1. These results also indicate that the sorption process can be considered very fast because of the largest amount of chromium attached to sorbent within the first 60 min of adsorption.

Effect of pH

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 in the range of 3-7. The suitable pH ranges for chromium 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 (Namasivayam and Ranganathan, 1995).

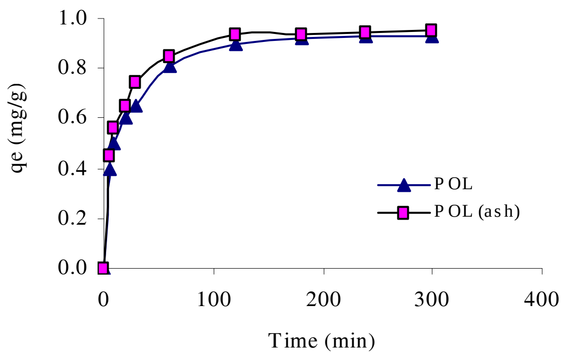

Fig. 1: Effect of contact time on the removal of chromium (VI) by POL and their ash (adsorbent dosage =2g/L; chromium concentration = 2 mg/L)

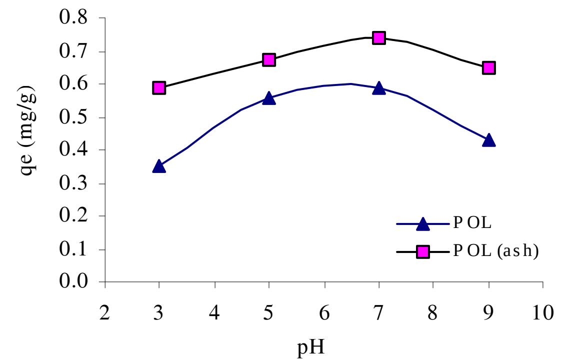

Fig. 2: Effect of pH on the removal of chromium (VI) by POL and their ash (adsorbent dosage = 2g/L; chromium concentration = 2 mg/L)

Effect of metal ion concentration

The effect of metal Ion concentration on the adsorption capacity of *Platanus orientalis* leaves and their ash were studied under optimum conditions. (pH=7, temperature=24-25°C). Adsorption of chromium on POL and its ash increased with increasing initial concentration of Cr(VI) to reach to 20mg/L. 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 Cr(VI) ion at higher concentration levels. These results are shown in Fig. 3.

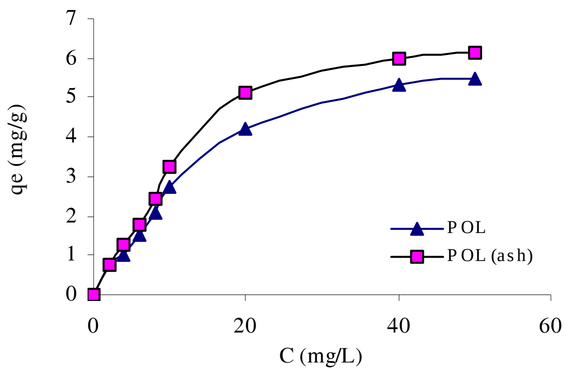

Fig. 3: Effect of chromium concentration on the removal of chromium (VI) by POL and their ash (adsorbent dosage=2g/L; pH =7; T=24°C; 300rpm; 120min)

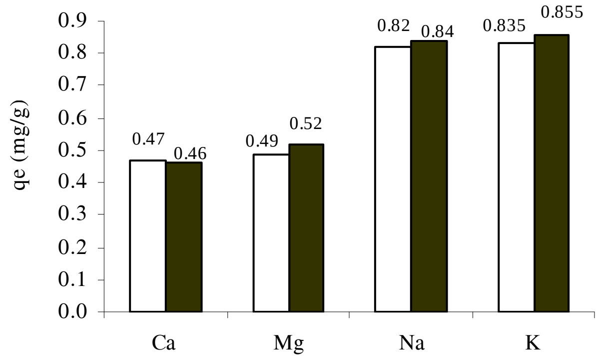

Fig. 4: The effect of other metals on chromium adsorption capacity (Cr= 2mg/L; 2mol/L of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+})

Effect of metals on adsorption

The effect of light metals on adsorption were studied in combination of two metal solutions and has shown that these ions can disturb the adsorption of heavy metals on any adsorbent. Ca^{+2} and Mg^{+2} had more effect than Na^{+} and K^{+} in decreasing of q_e for Cr(VI) adsorption. The effect of these metals on adsorption is shown in Fig. 4.

Adsorption isotherms

Two models, (Langmuir and Freundlich) were used to determine adsorption of chromium on to *Platanus orientalis* leaves and their ash.The Freundlich isotherm better fitted than the Langmuir isotherm as was evident from the values of regression coeffient with $R^2>0.9$. Results are given in Fig. 5 and Fig. 6.

Effect of adsorbents on COD

The effect of adsorbents on COD in aqueous solutions were studied. These studies show that 2g/L adsorbent causes 110 mg/L and 76mg/L COD increase in deionizd water after 120min for *Platanus orientalis* leaves and their ash, respectively. This is favorable for biological treatment in industrial wastewater treatment plant after chemical treatment.

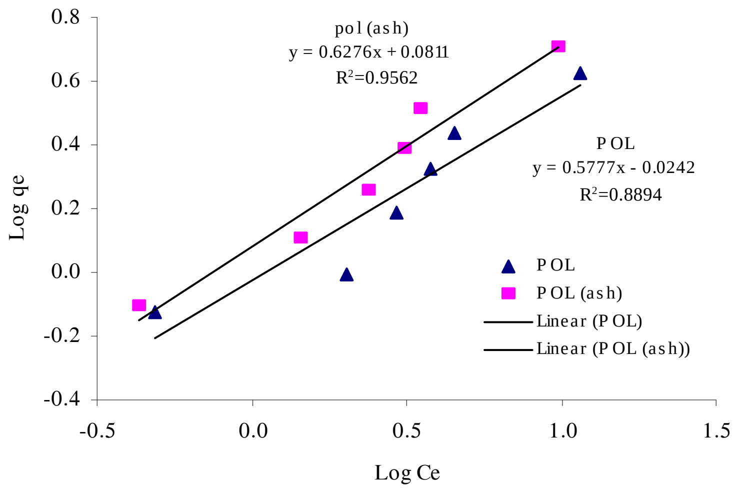

Fig. 5: Langmuir adsorption isotherm for chromium (VI) by POL and their ash

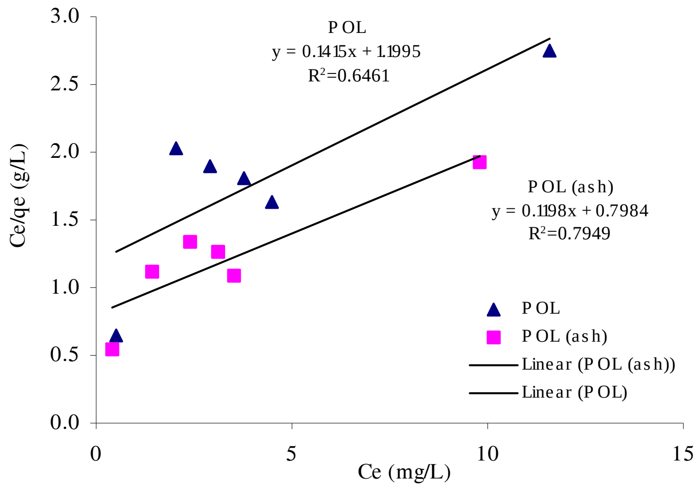

Fig. 6: Freundlich adsorption isotherm for chromium (VI) by POL and their ash

DISCUSSION

Tree leaves can be used in the wastewater treatment process for the removal of metal ions. 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 (Namasivayam and Ranganathan, 1995).The optimum pH in this study was 7. It has been reported that precipitation of chromium starts at pH=7.5 (Namasivayam and Ranganathan, 1995; Ajmalet *et al*., 2003).

Removal efficiency of chromium (VI) was greater than 85% and the adsorption of metal ion on tree leaves reached equilibrium in 120 min, pH=6-7 and initial concentration of 2mg/L. The Freundlich isotherm fitted better than the Langmuir isotherm with R^2>0.89 for POL and R^2>0.96 for POL ash, respectively. Similar results were reported by Alavi, 2005. *Platanus orientalis* leaves used as adsorbent in aqueous solutions may cause COD increase.

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