The Removal of Lead, Copper and Zinc from Industrial Wastewater Using Grape Fruit Peels

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ABSTRACT

The current study was designed for using grape fruit peels (*Citrus paradise*) to remove lead, copper and zinc from industrial wastewater. Three forms of these peels (fresh, dried small pieces and powder) were tested under some environmental factors such as pH, temperature and contact time. Current data show that grape fruit peels are capable of removing lead, copper and zinc ions with a significant capacity. Furthermore, the powder of grape fruit peels had a highest capability in removing all lead, copper and zinc ions followed by fresh peels whilst dried peels had the lowest bioremoving capacity again for all metals under test. The highest capacity was for lead then copper and finally zinc. All these data were significantly (LSD $_{peel\ forms}$ = 3.349 mg/l) varied. However, some examined factors were found to have significant impacts upon the bioremoval capacity of grape fruit peels such as pH, temperature, and contact time where best biosorption capacity was found at pH 4, at temperature 50 C° and contact time of 1 hour. It is true that grape fruit peels varied significantly in case of metal ions and increasing examined factor (pH, temperature, and contact time). The fourier transform infrared spectroscopy analysis (FTIR) illustrated that hydroxyl, carboxyl and carbonyl groups were the major binding sites for Pb, Cu and Zn ions by grape fruit peels.

Keywords: Grape fruit peels, biosorption, Lead, Copper, Zinc, FTIR.

(*Citrus paradise*)

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INTRODUCTION

The characteristics of industrial wastewater may differ considerably both within and among industries. The impact of industrial discharges would depend not only upon collective characteristics such as biochemical oxygen demand (BOD) and total suspended solids (TSS), but also on their content of specific inorganic and organic substances (Richman, 1997). Heavy metal water pollution represents an important environmental problem due to the possible toxic effects of the metal to both human and environment. The main sources of water contamination with various heavy metals are industrial wastewater (Volesky, 2001; Vijayaraaghavan *et al.*, 2005). Several techniques were applied to remove heavy metal ions from industrial wastewater such as activated carbon adsorption (Singh *et al.*, 2008), chemical precipitation (Ahalya *et al.*, 2005), reverse osmosis (Xia and Liyuan, 2002), electro-dialysis (Ahalya *et al.*, 2005) and ion exchange (Volesky, 2003). However, recently much attention has been focused on possible biological methods for the removal of heavy metals from industrial wastewater (Cho and Kim, 2003), such as microbial biomass (Volesky and Holan, 1995), and biological wastes (Reddad *et al.*, 2002; Saeed *et al.*, 2005; Chockalingam and Subramanian, 2006). These biosorbent materials are characterized as being less expensive, high bio-removal efficiency, metal selective, non sludge generation, possible ion recovery (Tunali and Akar, 2006), and environmentally sound methodology (Husoon, 2011). The technique of plant residues heavy metal ions adsorption was world widely used for wastewater treatment (Montanher *et al.*, 2005) such as peat and nut shells, coconut shells, rice husk, tea waste, peanut hulls, almond shells, peach stones, citrus peels, and many others (Khan *et al.*, 2004). These biosorbent materials consisting mainly of polysaccharides, proteins, and lipids, functional groups that can bind metal ions such as carboxyl, hydroxyl, sulphate, phosphate, and amino groups (Doyurum and Celik, 2006). The importance of any given group of biosorption of a certain metal by a certain biomass depends on several factors such as number of sites of biosorbent material, the accessibility of sites, the chemical state of the site (availability) and affinity between site and metal (binding strength) (Regine and Volesky, 2000).

MATERIALS AND METHODS

Examined industrial wastewater samples were collected from the wastewater of pasting unit before wastewater treatment unit, about 20 cm below the surface in Babylon 2 factory at Al-Waziriya area / Iraq-Baghdad. 500 ml wastewater samples replicated three times per week using pre-sterilized glass containers was collected in four random periods between 8th to 29th June 2011. Each sample was divided into two sub-samples, the first was examined for chemical and physical analysis and the second was employed for bioremoval of lead, copper and zinc ions.

Biosorption capacity of grape fruit peels
1. Chemical analysis of industrial wastewater

Samples of industrial wastewater were collected, 4 times at weekly rate, form pretreatment tank of pasting unit in Babylon 2 factory. Some factors such as pH and temperature were recorded *in situ* while the others such as heavy metal content were laboratory assessed.

2. Metal biosorption tests

Grape fruit peels were collected from local market and washed thoroughly by de-ionized distilled water (DDW) and used subsequently in the following examinations:

a. Various grape fruit peel forms

Three grape fruit peel forms have been used, where the first was as fresh pieces; the second was as dried pieces (using over night oven, 65 C° for three days) and finely powdered peels (using grinding agitator) that sieved through 2 mm stainless steel sieve. All peel forms were examined for bioremoval of lead, copper and zinc from aqueous synthetic solutions under various factors such as pH, temperature and contacting time. Synthetic aqueous metal solution was prepared by taking 20 ml of metal solution (100 mg/l) of lead, copper or zinc ions and placed into 50 ml volumetric flasks and pH was adjusted to 5. About 0.1g of grape fruit peels as fresh, dried and powder were added to each flask in three replicated experiments in addition to control (metal ion solution free from peels). All samples were left for almost one hour at 40 C°. Afterwards, each sample was passed through 0.45µm filter paper and metal concentration was determined by using flame atomic adsorption spectroscopy (FAAS) (Zafar *et al*., 2007), and the technique of Fourier transform infrared analysis was employed to determine the functional groups responsible for metal uptake. (Ahalya *et al*., 2005).

b. Factors affecting metal bioremoval

The test carried above was reassessed for the examination of possible effects of different levels of pH, temperature and contact time. For pH, the range of 1 − 6, and temperature range was from 10 C° to 60 C° was applied for all metals.

RESULTS AND DISCUSSION

All of the obtained data were subjected to various biometrical analysis such as the analysis of variance and least significant difference.

Chemical analysis of industrial wastewater

Table (1) shows mean values of temperature, pH, Pb, Cu, and Zn ions of industrial wastewater. The temperature values were ranged from 31.1±0.1 of 1st week sample (8/6/2011) to 31.7±0.05 C° of 4th week sample (29/6/2011). For pH data, the highest value (7.99±0.3) was found in water sample of 1st week (8/6/2011) while the lowest value

(7.15±0.04) was recorded in sample of 4th week. Regarding heavy metals content, the highest content was found in case of Pb ions that lied from 4.0±0.7 mg/l in sample of 2nd week to 5.1±0.2 mg/l in 4th week sample, followed by Zn ions content which was almost of similar levels ranging from 3.9±1.1 mg/l (1st week sample) to 4.1±0.6 mg/l (4th week sample). In case of Cu ions, again recorded values were almost similar to each other and varied from 1.1±0.2 mg/l (3rd week sample) to 1.5±0.9 mg/l (1st week sample).

Biosorption capacity of grape fruit peels
Various peel forms

Table (2) shows the mean biosorption capacity of grape fruit peels examined at different forms and presented in (Fig. 1). It is clear that grape fruit peel forms showed a significant ability for bio-removing heavy metals from industrial wastewater. However, powdered peels had higher values of bio-removed heavy metal concentrations than those fresh and dried peel pieces (LSD = 3.349). Furthermore, the highest metal concentration (57.9 ± 0.9 mg/l) was recorded in case of lead, followed by copper (34.3 ± 1.5 mg/l), while the lowest metal concentration (31.9 ± 0.8 mg/l) was found in case of zinc (Fig. 1). These values of biosorbed heavy metal concentrations were significantly differed from each other. The highest capacity of grape fruit powdered peels may be due to the surface area of peel particles (Lu *et al.*, 2008) and other environmental factors such as pH and temperature that may affect the biosorption mechanisms.

Factors affecting biosorption
pH

It is very clear that the increased pH (Fig. 2) had significant effects (P ≥ 0.001) upon biosorbed metal ions of all heavy metals under test. Also, these heavy metals had varied significantly (Table 3) from each other, but the highest biosorption concentrations were recorded for Pb ions, followed by Cu while the Zn ions showed the lowest bio-removed concentrations. However, it seems clearly that pH 4 was the best value for getting optimum bio-removal capacity for lead, copper and zinc ions. Various studies have examined the possible impact of pH upon heavy metal biosorption of different biosorbent materials and reported similar findings. A recent study (Hashem, 2007) showed that highest lead bioremoved by okra wastes was achieved at pH range of 4.5 – 5.5. Cd ions bioremoved by corn, durian, pummel and banana were found to be high at pH 5 (Eslamzadeh *et al.*, 2004). Optimum pH value for copper biosorption by marine algae was within a range of 4 – 6 (Yu and Kaewsarn, 2002). A study by (Scheiwer and Patil, 2008) had shown that highest lead bioremoved by maize leaf occurred at pH 3. The pH of aqueous solution plays a significant role in the biosorption process. This is partially due to the fact that H$^+$ ions are strongly competing adsorbents. The pH affects the specification of metal ions and the ionization of surface functional groups (Lu *et al.*, 2008).

Temperature

Fig. (3) shows the mean biosorbed metal concentration (mg/l) by grape fruit peels from solution of lead, copper and zinc at different temperatures. Apparently, increased temperature had significant impacts on bio-removed metal ions (LSD = 5.048 mg/l) of these heavy metals resulting in increased biosorption capacity but up to 50 C °. The highest capacities were found in case of Lead that ranged from 35.1 ± 0.1 mg/l to 86.0 ± 0.2 mg/l, and varied from 30.0 ± 0.2 mg/l to 80.9 ± 1.1 mg/l and from 26.1 ± 0.8 mg/l to 56.1 ± 1.2

mg/l for Cu and Zn respectively (Fig. 3). An analysis of variance (Table 4) shows significant differences (P ≥ 0.001) firstly between increased temperatures and secondly between heavy metal ions biosorbed by grape fruit peels.

The current results are similar to those of various studies that examined different biological materials (Reddad *et al.*, 2002; Ahalya *et al.*, 2005). A recent study (Saikaew and Kaewsarn, 2009) has reported that highest Cr bio-removed by tassel powder was at 45 C° while for Cd bio-removal, it was 25 C°. These contracting values may be related to several variables such as biosorbent species, quantity, and other environmental factors. However, the adsorbed species might have enough energy from temperature of the system and subsequently be desorbed at even a faster rate than adsorption rate, or may be due to a linkage of cells in both higher and lower temperature extremes which may reduce the availability surface area of contact (Zvinowwanda *et al.*, 2009).

Contact time

The impacts of various contact times upon all Pb, Cu, and Zn bio-removed by grape fruit peels (Fig. 4) are quite obvious but nevertheless, one hour contact time seems to be optimum in case of all heavy metals examined in this study. However, highest capacities (18.1 ± 1.1 mg/l to 93.5 ± 0.5 mg/l) were recorded for Pb biosorption, followed by those (23.8 ± 1.4 mg/l to 89.9 ± 0.6 mg/l) of Cu and (17.0 ± 0.75 mg/l to 76.1 ± 1.83 mg/l) Zn (Fig. 4). The analysis of variance of contact time effects shows significant differences (P ≥ 0.001) between firstly increased times and secondly between heavy metals biosorbed by grape fruit peels (Table 5).

The obtained results agreed with other studies (Cordo *et al.*, 2004; Al-Pachachi, 2006; Husoon, 2011). However another work (Habib *et al.*, 2007), has reported that the required contact time for the best copper bio-removed by orange peels was less than one hour (40 minutes).

Fig. (5) shows the spectra of the biosorbent of grape fruit peel after exposure to heavy metals solution for each metal. The FTIR spectra represent broad bands at 3365-3423 cm^{-1}, giving -OH and -NH groups. Bands observed at about 2850-2956 cm^{-1} assigned to the -CH groups, while the bands at 1660-1734 cm^{-1} represent -COO, the bands at 1640-1653 cm^{-1} are due to -COOH groups and the peaks at 1226-1400 cm^{-1} represent the -C=O groups. However, the peaks at 1049-1200 cm^{-1} are corresponding to the -C-O stretching, and peaks at 850-894 cm^{-1} are probably caused by -C-N bonding in amines. The previous results showed that the chemical groups that bind the metals are hydroxyl, carboxyl, amide and amine groups. This explains the reason behind the binding sites as they are nearly associated with the same sites. Also, this may indicate that bond stretching occurred to a less extent due to the exchange of hydrogen ions with lead, copper and zinc, and subsequently peak absorbance was attenuated (Kamsonlian *et al.*, 2011).

From the current work, it seems clear that the ability of grape fruit peels was significantly effective for the removal of Pb, Cu, and Zn ions from industrial wastewater due to the high affinity between the metal ions and the binding sites of the biosorbent. As it had been reported for various biosorbent plant materials (Khan *et al.*, 2004; Lu *et al.*, 2008; Husoon, 2011) and would successfully be applied for various heavy metals from industrial wastewater since it seems environmentally sound.

Table 1: Mean value ± standard deviation of several water variables

Variables	Mean value ± SD of some industrial wastewater components			
	1st week 8/6/2011	2nd week 15/6/2011	3rd week 22/6/2011	4th week 29/6/2011
Temp. C°	30.1±0.1	31.0±0.1	30.3±0.2	31.7±0.05
pH	7.99±0.3	7.4±0.4	7.37±0.09	7.15±0.04
Pb (mg/l)	4.1±0.74	4.0±0.7	4.6±0.7	5.1±0.2
Cu (mg/l)	1.5±0.9	1.2±0.2	1.1±0.2	1.4±0.22
Zn (mg/l)	3.9±1.1	4.0±0.4	4.1±0.4	4.1±0.6

Table 2: Mean Lead, Copper and Zinc concentrations percentage (mg/l) biosorbed by various grape fruit peel forms

Grape fruit peel forms	Mean metal biosorbed concentration (mg/l) ±SD		
	Lead %	Copper %	Zinc %
Dried pieces	36.7±0.6	22.9±0.9	20.8±0.8
Fresh pieces	47.8±1.6	30.1±1.1	28.1±1.2
Powdered	57.9±0.9	34.3±1.5	31.9±0.8
LSD	3.349		
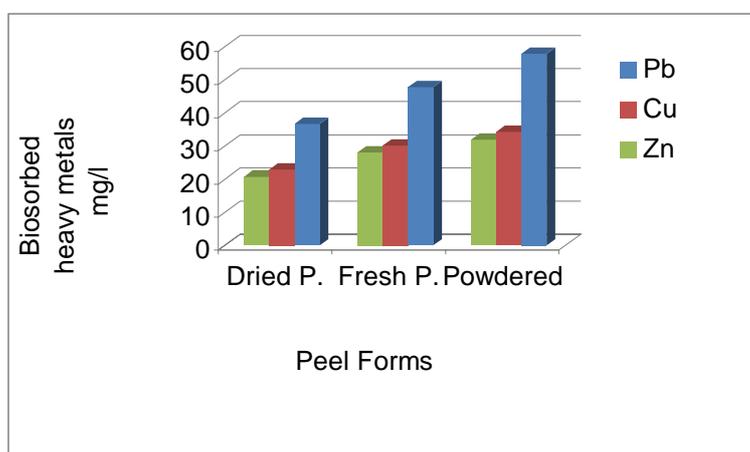
Fig. 1: Mean biosorbed metal concentration (mg/l) by grape fruit various peel forms
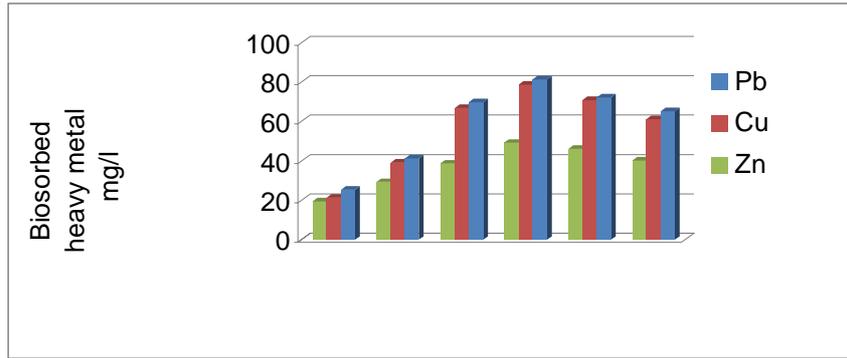
Fig. 2: Mean biosorbed metal concentration (mg/l) by grape fruit peels from solution of Pb, Cu and Zn at different pH values

Table 3: Analysis of variance of mean Pb, Cu, and Zn concentration biosorbed by grape fruit peels at six pH levels

Source of variance	df	SS	MS	Probability
Replications	2	0.827	0.484	N.S.
Treatment	17	5543.74	326.73	0.001
Metal (M)	2	838.94	419.55	0.001
pH (P)	5	3712.31	781.17	0.001
M × P	10	1099.5	109.95	0.001
Error	34	49.998	3.981	0.001
Total			53	

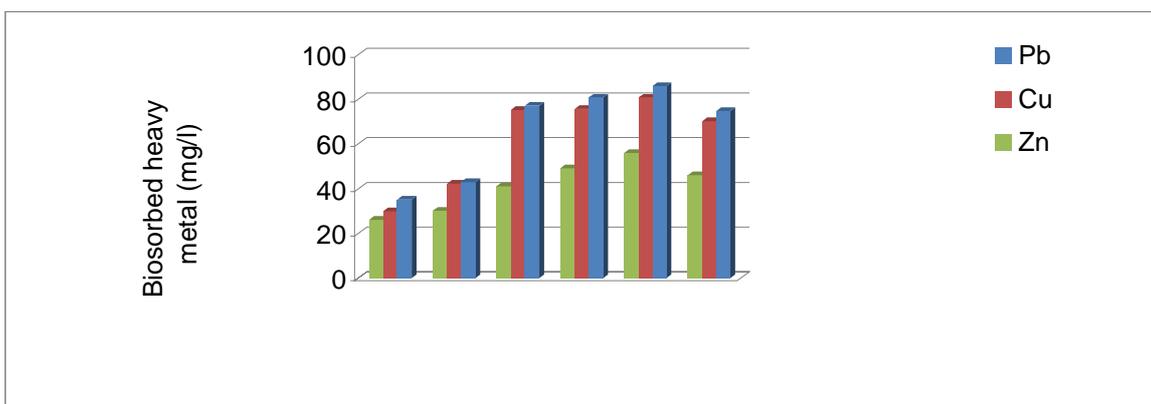df= degree of freedom, ss= sum square, ms= mean square

Fig. 3: Mean biosorbed metal concentration (mg/l) by grape fruit peels from solution of Pb, Cu and Zn at different temperatures

Table 4: Analysis of variance of mean Pb, Cu, and Zn concentrations biosorbed by grape fruit peels at six temperature values

Source of variance	df	SS	MS	Probability
Replications	2	8.9	4.7	N.S.
Treatment	17	9499.4	678.53	0.001
Metal (M)	2	682.4	344.7	0.001
Temp (T)	5	8209.3	1644.2	0.001
M × T	10	609.8	60.98	0.001
Error	34	73.7	2.978	0.001
Total			53	
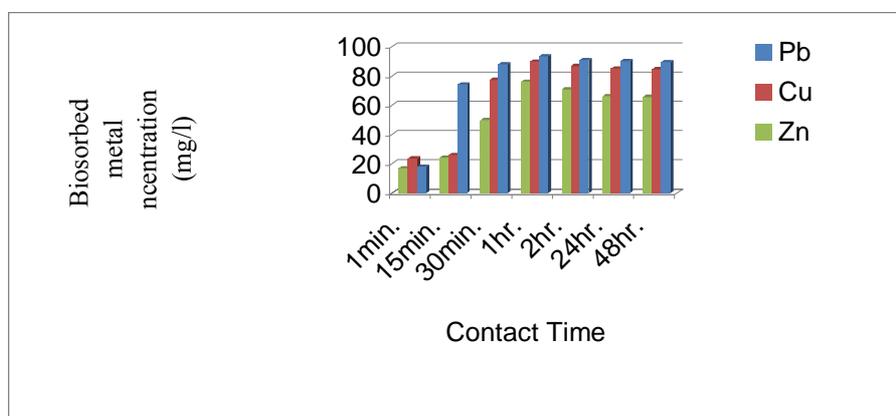
Fig. 4: Mean biosorbed metal concentration (mg/l) by grape fruit peels from solution of Pb, different contact time

Table 5: Analysis of variance of mean Pb, Cu, and Zn concentration biosorbed by grape fruit peels with different contact time

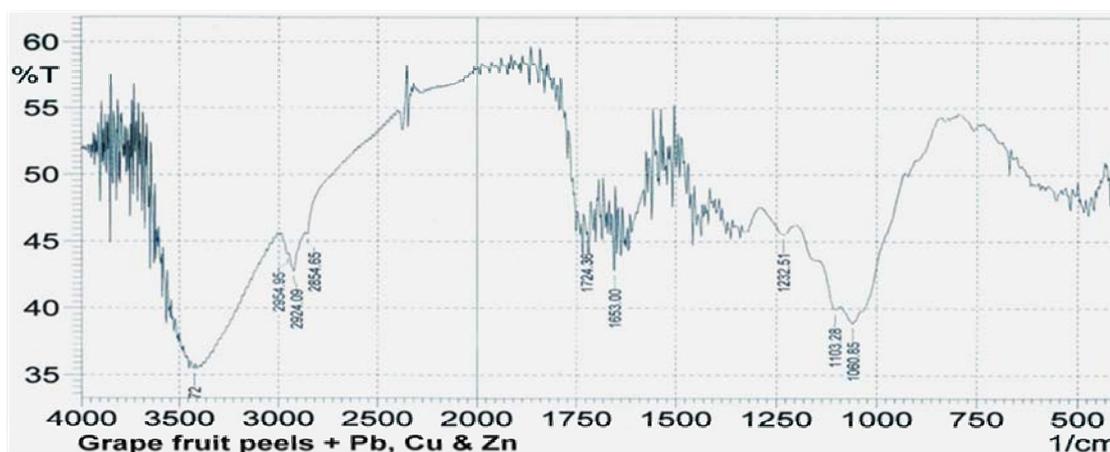| Source of variance	df	SS	MS	Probability
Replications	2	2.382	1.2	N.S.
Treatment	20	21315.63	1065.272	0.001
Metal (M)	2	1355.1	676.8	0.001
C*. time (T)	6	19528.44	3255.12	0.001
M × I	12	424.1	35.33	0.001
Error	40	119.62	3.01	0.001
Total			62	

*contact

Fig. 5: FTIR analysis of grape fruit peels in synthetic solution

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