Lettuce Leaves as Biosorbent Material to Remove Heavy Metal Ions from Industerial Wastewater

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Abstract:

The current study was designed to remove Lead, Copper and Zinc from industrial wastewater using Lettuce leaves (*Lactuca sativa*) within three forms (fresh, dried and powdered) under some environmental factors such as pH, temperature and contact time. Current data show that Lettuce leaves are capable of removing Lead, Copper and Zinc ions at significant capacity. Furthermore, the powder of Lettuce leaves had highest capability in removing all metal ions. The highest capacity was for Lead then Copper and finally Zinc. However, some examined factors were found to have significant impacts upon bioremoval capacity of studied ions, where best biosorption capacity was found at pH 4, at temperature 50º C and contact time of 1 hour.

Key words: Lettuce leaves, biosorption, Lead, Copper, Zinc, FTIR.

Introduction:

In the recent decades, heavy metals have been received considerable attention as a consequence of the increased environmental pollution from industrial, agricultural, energy and municipal sources [1]. Several techniques were applied to remove heavy metal ions from industrial wastewater such as activated carbon adsorption [2], chemical precipitation [3], reverse osmosis [4], electro-dialysis [3] and ion exchange [5].

However, recently more attention has been focused on possible biological methods for the removal of heavy metals from industrial waste water [6], such as microbial biomass [7], and biological wastes [8,9]. These biosorbent materials are characterized being less expensive, high bio-removal efficiency, metal selective, non sludge generation, possible ion recovery [10], and environmentally sound methodology [11]. The technique of plant residues heavy metal ions adsorption was world widely used for waste water treatment [12] such as peat and nut shells, coconut shells, rice husk, tea waste, peanut hulls, almond shells, peach stones, citrus peels, and many others [13]. 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 [14]. 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) [15].

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Materials and Methods:

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 8^{th} to 29^{th} June 2011. Each sample was divided into two sub-samples, the first was examined for chemical & physical analysis and the second was employed for bioremoval of Lead, Copper and Zinc ions. Samples of industrial wastewater were collected, 4 times at weekly rate, from 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. Lettuce leaves were collected from local market and washed thoroughly by de-ionized distilled water (DDW) and used subsequently in the various leaf forms examination; Three Lettuce leaf forms have been used, the first was as fresh pieces; the second was as dried pieces and finely powdered leaves that sieved through 1.18 mm stainless steel sieve. All leaf forms were examined for bioremoval of Lead, Copper and Zink from aqueous synthetic solutions (100 mg/l) 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 Lettuce leaves as fresh, dried and powder was added to each flask in three replicated experiment in addition of control (metal ion solution free from leaves). All samples were left for almost one hour at 40º C. Afterwards, each sample was passed through 0.45µm filter paper and metal concentration was determined by using Flame Atomic Absorption Spectroscopy (FAAS) [16], and the technique of Fourier Transform infrared analysis was employed to determine the functional groups responsible for metal uptake, using (FTIR) spectroscopy [3]. 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 was 1 – 6, and temperature range was from 10º C to 60º C applied for all metals.

Results and Discussion:

All obtained data were subjected to various biometrical analysis such as analysis of variance and least significant difference. Table 1 shows the mean values of temperature, pH, Pb, Cu, and Zn of industrial wastewater. The temperature values were ranged from 31.1±0.1 º C of 1^{st} week sample (8/6/2011) to 31.7±0.05 º C of 4^{th} week sample (29/6/2011). For pH data, the highest value (7.99±0.3) was found in water sample of 1^{st} week (8/6/2011) while the lowest value (7.15±0.04) was recorded in sample of 4^{th} week. Regarding heavy metals content, the highest content was found in case of Pb ions that ranged from 4.0±0.7 mg/l in sample of 2^{nd} week to 5.1±0.2 mg/l in 4^{th} week sample, followed by Zn ions content which was almost similar levels ranging from 3.9±1.1 mg/l (1^{st} week sample) to 4.1±0.4 mg/l (3^{rd} 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 (3^{rd} week sample) to 1.5±0.9 mg/l (1^{st} week sample).

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

Regarding to biosorption capacity of Lettuce leaves; Table 2 shows mean biosorption capacity of Lettuce leaves examined at different forms and presented in Figure 1. It is clear that Lettuce leaf forms shown significant ability for bio-removing heavy metals from industrial wastewater. However, powdered leaves had higher values of bio-removed heavy metal concentrations than those fresh and dried leaf pieces (LSD = 3.481). Furthermore, highest metal concentration (48.7 ± 1.1 mg/l) was recorded in case of Lead, followed by Copper (28.4 ± 1.7 mg/l), while the lowest metal concentration (26.8 ± 0.9 mg/l) was found in case of Zinc (Fig.1). These values of biosorbed heavy metal concentrations were significantly differed from each other. Highest capacity of Lettuce leaves may be due to the surface area of leaf particles [17, 18] and other environmental factors such as pH and temperature that may affect the biosorption mechanisms.

Table 2: The mean values of Lead, Copper and Zinc concentrations (mg/l) biosorbed by various Lettuce leaf forms.

Lettuce leaf forms	Mean metal biosorbed concentration (mg/l) ± SD		
	Lead	Copper	Zinc
Dried pieces	25.6±0.5	16.8±0.8	11.4±0.4
Fresh pieces	36.9±1.2	21.2±1.7	20.1±1.6
Leaf Powder	48.7±1.1	28.4±1.7	26.8±0.9
LSD	3.481		

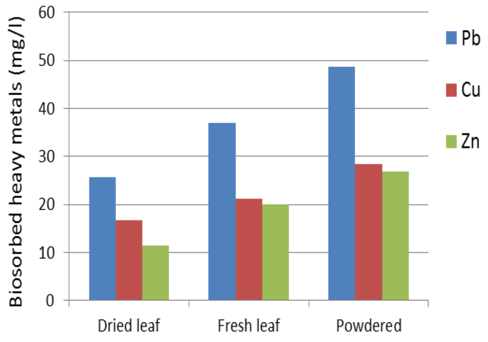

Fig. 1: The mean values of biosorbed metal concentrations (mg/l) by various Lettuce leaf forms

Factors affecting biosorption

1- pH

It is very clear that increased pH (Fig. 2) had significant effects ($P \geq 0.001$) upon biosorbed metal ions of all heavy metals under test. Also, these heavy metals varied significantly from each other, but the highest biosorption concentrations were recorded for Pb ions in all pH values, followed by Cu while the Zn ions shown 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 [19]. Recent study showed that highest lead bioremoved by okra wastes were achieved at pH range of 4.5 – 5.5. Cd ions bioremoved by corn, durian, pummel and banana was found to be high at pH 5 [20]. Optimum pH value for copper biosorption by marine algae was within a range of 4 – 6 [21]. A study by [22] 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 [18].

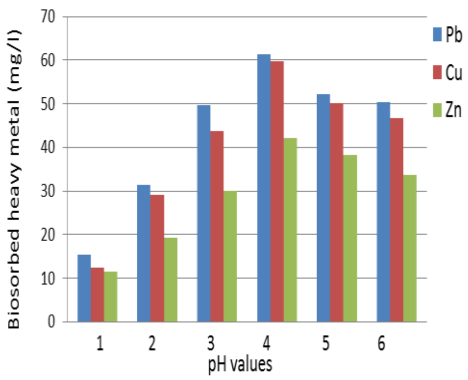

Fig. 2: The mean values of biosorbed metal concentrations (mg/l) by Lettuce leaves from solution of Pb, Cu & Zn at different pH values

2- Temperature

Figure 3 shows mean biosorbed metal concentration (mg/l) by Lettuce leaves from solution of Lead, Copper and Zinc at different temperatures. Apparently, increased temperature had significant impacts on bio-removed metal ions (LSD = 4.013 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 17.6 ± 0.4 mg/l to 66.1 ± 0.4 mg/l, and varied from 14.9 ± 0.8 mg/l to 62.3 ± 1.1 mg/l and from 11.9 ± 0.1 mg/l to 46.6 ± 1.2 mg/l for Cu and Zn respectively (Fig. 3). Analysis of variance (LSD = 4.013 mg/l) shows significant differences (P ≥ 0.001) firstly between increased temperatures and secondly between heavy metal ions biosorbed by Lettuce leaves. The current results are similar to those of various studies that examined different biological materials [3, 23]. Recent study [24] 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 [5]. 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 linkage of cells in both higher and lower temperature extremes which may reduce the availability surface area of contact [25, 26].

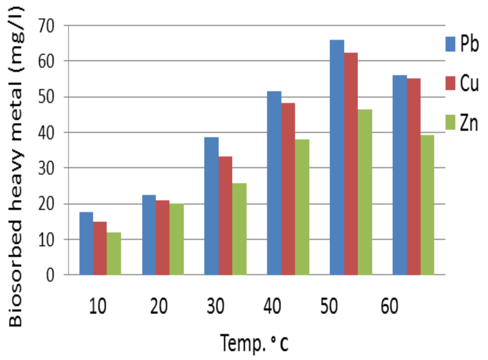

Fig. 3: The mean values of biosorbed metal concentrations (mg/l) by Lettuce leaves from solution of Pb, Cu & Zn at different temperatures

3- Contact time

The impacts of various contact times upon all Pb, Cu, and Zn bio-removed by Lettuce leaf (Fig. 4) are quite obvious but nevertheless, one hour contact time seems to be optimum in case of all heavy metal examined in this study. However, highest capacities (19.3 ± 0.5 mg/l to 68.2 ± 0.8 mg/l) were recorded for Pb biosorption, followed by those (16.2 ± 0.9 mg/l to 61.2 ± 0.7 mg/l) of Cu and (13.7 ± 0.3 mg/l to 44.7 ± 0.8 mg/l) Zn (Fig. 4). The analysis of variance (LSD = 2.041 mg/l) of contact time effects shows significant differences (P ≥ 0.001) between firstly increased times and secondly between heavy metals biosorbed by Lettuce leaves. The obtained results are agreed with other studies [27, 28, 29]. However other work [30], has reported that required contact time for best copper bio-removed by orange peels was less than one hour (40 minutes).

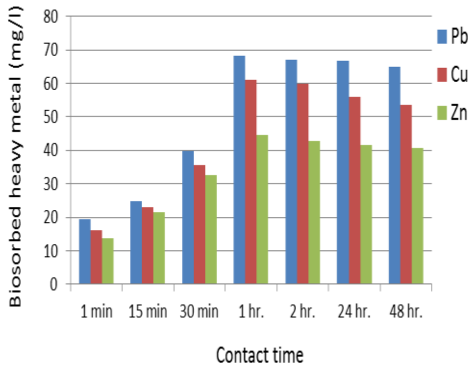

Fig. 4: The mean values of biosorbed metal concentrations (mg/l) by Lettuce leaves from solution of Pb, Cu & Zn at different contact time

Figure (5) shows the spectra of the biosorbent of Lettuce leaf 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} is 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 indicates 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 [31].

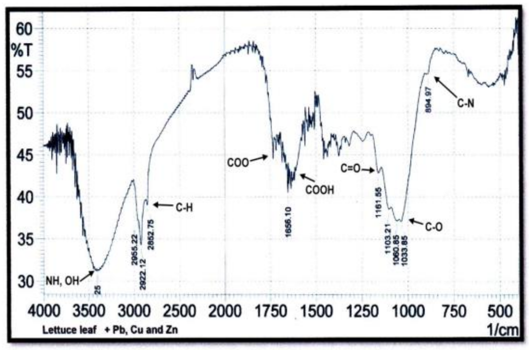

Fig. 5: FTIR analysis of Lettuce leaf in synthetic solution

From the current work, it seems clearly that the ability of Lettuce leaves were significantly effective for the removal of Pb, Cu, and Zn ions from industrial wastewater as it had been reported for various biosorbent plant materials [13, 18, 26, 29] and would successfully be applied for various heavy metals from industrial wastewater since it seems environmentally sound.

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إستخدام أوراق نبات الخس كمواد مازة لإزالة أيونات العناصر الثقيلة من مياه الفضلة الصناعية

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الخلاصة:

صممت الدراسة الحالية لإزالة أيونات الرصاص والنحاس والزنك من مياه الفضلة الصناعية باستخدام أوراق نبات الخس (*Lactuca sativa*) وبثلاثة أشكال (طري، مجفف، مطحون)، تحت بعض الظروف البيئية مثل الأس الهيدروجيني ودرجة الحرارة ووقت التماس. أظهرت نتائج الدراسة إمكانية استخدام أوراق نبات الخس في إزالة أيونات المعادن الثقيلة تحت الدراسة بشكل معنوي، إذ تفوقت معاملة أوراق الخس بالشكل المطحون على باقي الأشكال. كما أشارت النتائج إلى أن أعلى نسبة إزالة للعناصر المدروسة كانت للرصاص ثم النحاس والزنك على التوالي. كان للعوامل البيئية تأثيراً معنوياً على قابلية إزالة الأيونات أعلاه، إذ سجلت أفضل قابلية إمتزاز عند أس هيدروجيني 4 بدرجة حرارة 50 مئوي وبوقت تماس ساعة واحدة.