The Removal of Zinc, Chromium and Nickel from Industerial Waste-Water Using Banana Peels

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Abstract

The current study was designed for using banana peels to remove zinc, chromium and nickel from industrial waste-water. 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 banana peels are capable of removing zinc, chromium and nickel ions at significant capacity. Furthermore, the powder of banana peels had highest capability in removing all zinc, chromium and nickel ions followed by fresh peels whilst dried peels had the lowest bioremoving capacity again for all metals under test. The highest capacity was for chromium then nickel and finally zinc. All these data were significantly ($LSD_{peel\ forms}$ = 2.761 mg/l, $LSD_{metal\ ions}$ = 1.756 mg/l) varied. In case of chromium, these figures were 65.0 ± 1.0 mg/l, 54.0 ± 2.0 mg/l and 41.7 ± 1.5 mg/l for powder, fresh and dried peels respectively. Regarding nickel ions, these data were 56.7 ± 1.5 mg/l for peel powder, 47.7 ± 2.2 mg/l for fresh peel and 47.7 ± 2.2 mg/l for dry peel. While for zinc ions, the biosorption capacity was 51.7 ± 0.8 mg/l, 41.0 ± 1.0 mg/l and 34.7 ± 0.9 mg/l for powder, fresh and dry peels respectively. However, some examined factors were found to have significant impacts upon bioremoval capacity of banana peels such as pH, temperature, and contact time where best biosorption capacity was found at pH 4, at temperature 50 C^{o} and contact time of 1 hour. It is true that banana peels were varied significantly in case of metal ions and increasing examined factor (pH, temperature. And contact time). Regarding pH, the highest bioremoval ability was found at pH 5 for all heavy metals, but with the sequence of Cr, Ni, and Zn and the data were 59.4 ± 0.83 mg/l, 54.0 ± 0.0 mg/l and 39.1 ± 1.86 mg/l respectively. Similar pattern of bioremoval capacity was detected for temperature which was 50 C ^{o} where it was 66.7 ± 2.91 mg/l for chromium, 57.7 ± 1.12 mg/l for nickel and 52.0 ± 1.12 mg/l for zinc. However, in case of contact time, the capacity of biosorbing of these metals was again similar to those of pH and temperature factors where it was found to be 74.0 ± 1.76 mg/l , 66.0 ± 2.25 mg/l and 66.0 ± 1.95 mg/l for Cr, Ni, and Zn respectively but at 1 hour contact time.

Keywords: Banana peels, Biosorption, Zinc, Chromium, Nickel, Industrial waste-water

إزالة الزنك والكروم والنيكل من مياه الفضلة الصناعية باستخدام قشور الموز

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الخلاصة

صممت الدراسة الحالية لاستخدام قشور الموز في إزالة آيونات الزنك والكروم والنيكل من مياه الفضلة الصناعية، باستخدام ثلاث أشكال من القشور (طري ويابس ومسحوق) والتي اختبرت تحت بعض الظروف البيئية مثل الأس الهيدروجيني ودرجة الحرارة ووقت التماس.

بينت النتائج الحالية قابلية قشور الموز على إزالة آيونات المعادن الثقيلة مثل الزنك والكروم والنيكل بفروق معنوية. حيث كان لقشور الموز على شكل المسحوق أعلى قابلية على إزالة آيونات الزنك والكروم والنيكل ثم قشور الموز بالشكل الطري، في حين كان لقشور الموز بالشكل اليابس أقل قابلية على إزالة آيونات المعادن الثقيلة تحت الدراسة. كما بين البحث بأن أعلى قابلية للإزالة كانت للكروم ثم للنيكل وأخيراً للزنك. وكل هذه النتائج كانت تتباين معنوياً ($LSD_{peel\ forms}$ = 2.761 mg/l, $LSD_{metal\ ions}$ = 1.756 mg/l). في حالة الكروم كانت النتائج 65.0±1.0 ملغم/لتر، 54.0±2.0 ملغم/لتر و 41.7±1.5 ملغم/لتر لقشور الموز المسحوق والطري واليابس على التوالي. أما بالنسبة لآيونات النيكل فكانت النتائج 56.7±1.5 ملغم/لتر للمسحوق و47.7±2.2 ملغم/لتر لكل من الطري واليابس. في حين كانت نتائج إمتزاز آيونات الزنك 51.7±0.8 ملغم/لتر، 41.0±1.0 ملغم/لتر و34.7±0.9 ملغم/لتر لكل من قشور المسحوق والطري واليابس على التوالي.

كان لبعض العوامل البيئية المدروسة تأثيراً معنوياً على قابلية الإزالة الحيوية لقشور الموز مثل الأس الهيدروجيني ودرجة الحرارة ووقت التماس، فكانت أفضل قابلية للإمتزاز عند أس هيدروجيني 4 بدرجة حرارة 50 مئوي وبوقت تماس ساعة واحدة. وتباينت قشور الموز معنوياً بتغير العوامل البيئية قيد الدراسة. كانت أعلى قيمة أس هيدروجيني للإزالة الحيوية هو 5 لكل المعادن الثقيلة تحت الدراسة وبترتيب الكروم ثم النيكل ثم الزنك وكانت النتائج 59.4±0.83 ملغم/لتر ، 54.0±0.0 ملغم/لتر و 39.1±1.86 ملغم/لتر على التوالي. كما وجدت نتائج متقاربة لقابلية الإزالة الحيوية عند درجة حرارة 50 مئوي فكانت 66.7±2.91 ملغم/لتر للكروم و57.7±1.12 ملغم/لتر للنيكل و52.0±1.12 ملغم/لتر للزنك. أما في حالة وقت التماس فقد كانت النتائج متشابهة لنتائج الأس الهيدروجيني ودرجة الحرارة للعناصر المعدنية قيد الدراسة وكانت قابلية الإمتزاز 74.0±1.76 ملغم/لتر و66.0±2.25 ملغم/لتر و66.0±1.95 ملغم/لتر لكل من الكروم والنيكل والزنك على التوالي تحت وقت تماس ساعة واحدة.

Introduction

The characteristics of industrial waste-water may differ considerably both within and among industries. The impact of industrial discharges would depend not only upon collective characteristics such as BOD and total suspended solids (TSS), but also on their content of specific inorganic and organic substances [1].

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 waste water [2,3,4].

Several techniques were applied to remove heavy metal ions from industrial waste water such as activated carbon adsorption [5,6], chemical precipitation [7], reverse osmosis [8,9] , electro-dialysis [7,8] and ion exchange [10].

However, recently much attention have been focused on possible biological methods for the removal of heavy metals from industrial

waste water [11], such as microbial biomass [12, 13] and biological wastes [14,15,16,17]. These biosorbent materials are characterized being less expensive, high bio-removal efficiency, metal selective, non sludge generation, possible ion recovery [18] and environmentally sound methodology [19].

The technique of plant residues heavy metal ions adsorption was world widely used for waste water treatment [20,21] such as peat and nut shells, coconut shells, rice husk, tea waste, peanut hulls, almond shells, peach stones, citrus peels, and many others [22,23].

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 [24]. The importance of any given group of biosorption of a certain metal by a certain biomass depends on several factors such as a number of sites of biosorbent material, the accessibility of sites, the chemical state of thesite (availability) and affinity between site and metal (binding strength) [25].

Material and Methods

Industrial waste water samples were collected from pretreatment units of electroplating section in the State Electrical Manufacturing Company in Al-Waziriya area / Iraq-Baghdad. (500 ml wastewater samples were collected in three random periods between 8th to 29th 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 zinc, chromium and nickel ions.

Biosorption Capacity of Banana Peels

1. Chemical analysis of industrial wastewater.

Samples of industrial wastewater were collected, 4 times at weekly rate, form pretreatment tank from State Electrical Manufacturing Company. Some factors such as pH and temperature were recorded *in situ* while the others such as heavy metal content was laboratory assessed.

2. Metal biosorption tests.

Banana peels were collected and washed thoroughly by de-ionized distilled water (DDW) and used subsequently in the following examinations:

a. Various Banana Peel Forms.

Three banana peel forms have been used where the first was as fresh pieces, the second was as dried pieces and finely powdered peels that sieved through 4mm stainless steel sieve. All peel forms were examined for bioremoval of zinc, chromium and nickel 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 zinc, chromium or nickel ions and placed into 50 ml volumetric flasks and pH was adjusted to 5. About 0.05 g banana peels as fresh, dried and powder were added to each flask in three replicated experiment in addition of control (metal ion solution free from peels). All samples were left for almost one hour at 40 C^{o}. Afterwards, each sample was passed through 0.45µm filter paper and metal concentration was determined by using Flame Atomic Adsorption Spectroscopy (FAAS) [26].

b. Factors Affecting Metal Bioremoval.

The test carried above was reassessed for the examination of possible effects of different levels of pH, and temperature. For pH, the range of 1 – 5 and temperature range was from 10 C^{o} to 60 C^{o} was applied for both metals.

Results and Discussion

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

Chemical Analysis of Industrial Wastewater

Table 1 shows mean values of temperature, pH, Zn, Cr, and Ni of industrial wastewater. The temperature values were ranged from 31.0±0.0 of 1st week sample (8/6/2011) to 31.76±0.05 C° of 4th week sample (29/6/2011). For pH data, the highest value (7.67±0.094) was found in water sample of 3rd week (22/6/2011) while the lowest value (7.17±0.047) was recorded in sample of 4th week. Regarding heavy metals content, the highest content was found in case of zinc ion that lied from 418.7±0.942 mg/l in sample of 4th week to 612.0±2.16 mg/l in 1st week sample, followed by chromium ion content which was almost similar levels ranging from 44.0±0.0 mg/l (4th week sample) to 49.33±0.942 mg/l (2nd week sample). In case of nickel ions, again recorded values were almost similar to each other and varied from 8.06±0.055 mg/l (4th week sample) to 12.0±0.0 mg/l (1st 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.	31.0±0.0	31.13±0.05	31.33±0.12	31.76±0.05
pH	7.33±0.05	7.37±0.09	7.67±0.094	7.17±0.047
Zn (mg/l)	612.0±2.16	524.7±2.494	418.7±0.942	535.3±1.7
Cr (mg/l)	46.67±1.89	49.33±0.942	45.67±1.247	44.0±0.0
Ni (mg/l)	12.0±0.0	8.96±0.073	9.0±0.0	8.06±0.055

Biosorption Capacity of Banana Peels Various Peel Forms

Table 2 shows mean biosorption capacity of banana peels examined at different forms and presented in Figure 1.

It is clear that banana peel forms shown significant ability for bio-removing heavy metals from industrial wastewater. However, powdered peels had higher values of bioremoved heavy metal concentrations than those fresh and dried peel pieces (LSD = 2.761).Furthermore ,highest metal concentration (65.0 ± 1.0 mg/l) was recorded in case of chromium, followed by nickel (56.7 ± 1.5 mg/l), while the lowest metal concentration (51.7 ± 0.8 mg/l) was found in case of zinc Figure 1. These values of biosorbed heavy metal concentrations were significantly differed from each other (LSD = 1.756).

Table 2- Mean zinc, chromium and nickel concentrations (mg/l) biosorbed by various banana peel forms.

Banana peel form	Mean metal biosorbed concentration (mg/l) ±SD		
	Zinc	Chromium	Nickel
Peel dried pieces	34.7 ± 0.9	41.7 ± 1.5	47.7 ± 2.2
Peel fresh pieces	41.0 ± 1.0	54.0 ± 2.0	47.7 ± 2.2
Peel Powder	51.7 ± 0.8	65.0 ± 1.0	56.7 ± 1.5

Highest capacity of banana peels may be due to the surface area of peel particles [27] and other environmental factors such as pH and temperature that may affect the biosorption mechanisms.

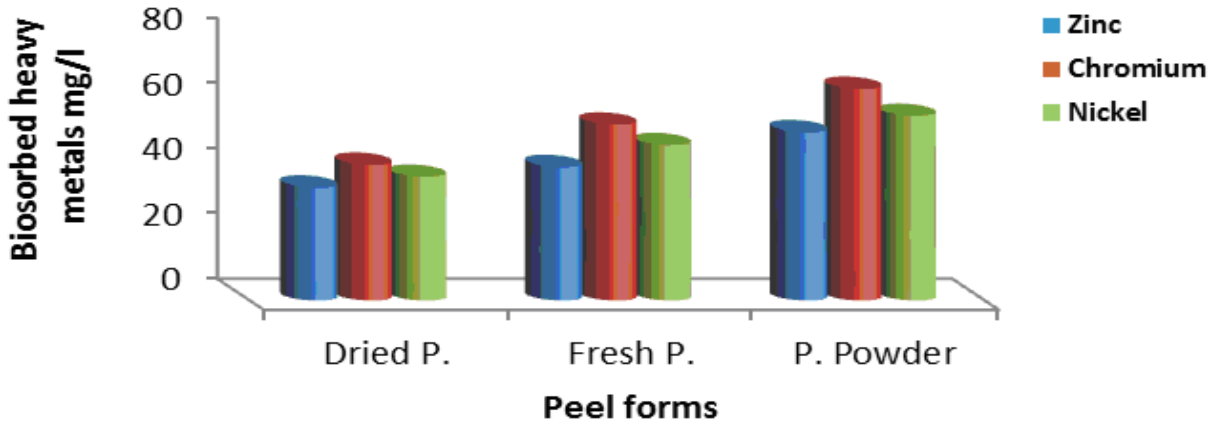

Figure 1- Mean biosorbed metal concentration(mg/l) by banana various peel forms.

Factors Affecting Biosorption.pH

It is very clear that increased pH Table 3 had significant effects ($P \geq 0.001$) upon biosorbed metal ions of all heavy metals under test. Also, these heavy metals had varied significantly Table 4 from each other, but highest biosorption concentrations were recorded for Cr ion, followed by Ni while the Zn ions shown the lowest bioremoved concentrations Figure 2. However, it seems clearly that pH 4 was the best value for getting optimum bioremoval capacity for chromium and nickel ions and pH 3 in case of zinc ions.

Table 3- Mean biosorbed metal concentration (mg/l) by banana peels from solution of zinc, chromium and nickel at different levels of solution pH.

pH level	Mean metal biosorbed concentration (mg/l) ±SD		
	Zinc	Chromium	Nickel
1	29.0 ± 1.75	33.34 ± 2.91	37.0 ± 1.95
2	32.7 ± 1.91	38.34 ± 1.01	37.0 ± 1.32
3	59.45 ± 2.88	48.0 ± 1.08	52.0 ± 1. 33
4	50.3 ± 2.66	64.4 ± 1.11	55.4 ± 1.47
5	39.1 ± 1.86	59.4 ± 0.83	54.0 ± 0.0
6	35.7 ± 1.02	54.0 ± 2.12	50.0 ±1.91
LSD	3.344 mg/l		

Various studies have examined the possible impact of pH upon heavy metal biosorption of different biosorbent materials and reported similar findings. Recent study [28] 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 [29]. Optimum pH value for copper biosorption by marine algae was within a range of 4 – 6 [30]. A study [31] had shown that highest lead bioremoved by maize leaf occurred at pH 3.

Table 4- Analysis of variance of mean Zn, Cr, and Ni concentration biosorbed by banana peels at six pH levels.

Source of variance	df	SS	MS	Probability
Replications	2	0.967	0.4835	N.S.
Treatment	17	5542.63	326.037	0.001
Metal (M)	2	838.91	419.455	
pH (P)	5	3605.3	721.06	
M X P	10	1098.42	109.842	
Error	34	135.703	3. 991	
Total	53			

The pH of aqueous solution plays a significant role in the biosorption process [32]. 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 [33].

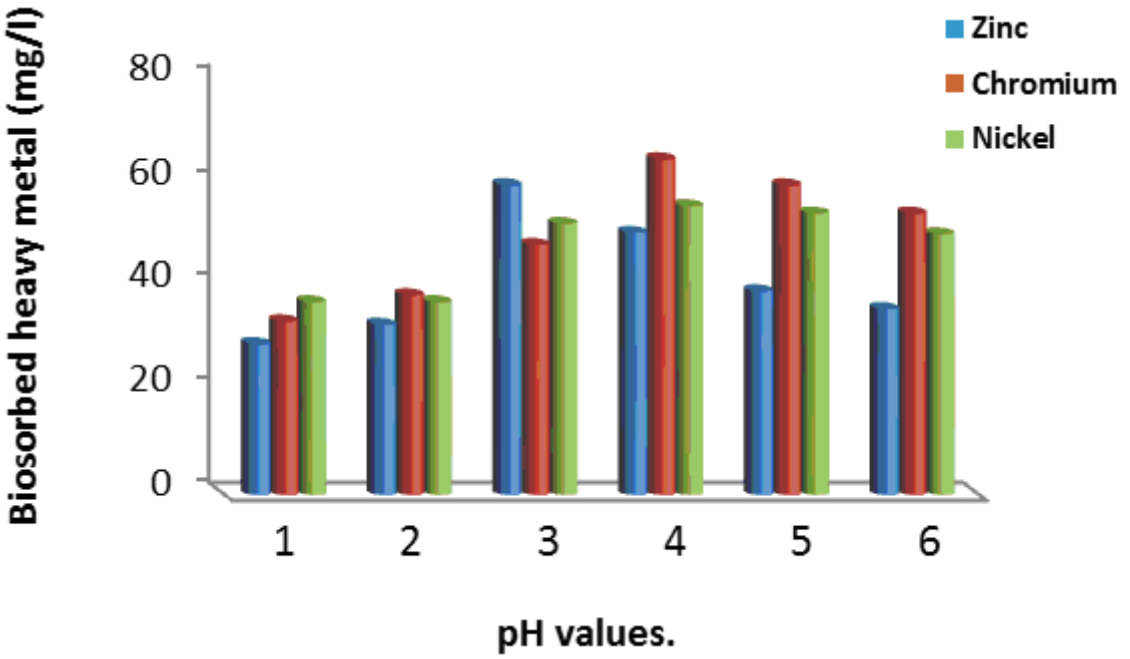

Figure 2- Mean biosorbed metal concentration(mg/l) by banana Mean peels from solution of zinc,chromium and nickel at different PH values

Temperature

Table 5 shows mean biosorbed metal concentration (mg/l) by banana peels from solution of zinc, chromium and nickel at different temperatures. Apparently, increased temperature had significant impacts on bioremoved metal ions (LSD = 3.003 mg/l) of these heavy metals resulting in increased biosorption capacity but up to 50 C º.

Table 5- Mean biosorbed metal concentration (mg/l) by banana peels from solution of zinc, chromium and nickel at different temperatures.

Temperature C°	Mean metal biosorbed concentration (mg/l) ±SD		
	Zinc	Chromium	Nickel
10	23.0 ± 0.83	21.0 ± 1.05	28.0 ± 0.0
20	32.0 ± 2.15	33.0 ± 1.21	33.7 ± 1.00
30	40.0 ± 2.0	50.0 ± 1.53	41.7 ± 2.03
40	48.0 ± 1.15	64.0 ± 2.00	49.4 ± 1.33
50	52.0 ± 1.12	66.7 ± 2.91	57.7 ± 1.12
60	47.0 ± 1.19	60.4 ± 1.06	54.0 ± 1.91

The highest capacities were found in case of chromium that ranged from 21.0 ± 1.05 mg/l to 66.7 ± 2.91 mg/l, and varied from 28.0 ± 0.0 mg/l to 57.7 ± 1.12 mg/l and from 23.0 ± 0.83 mg/l to 52.0 ± 1.12 mg/l for Ni and Zn respectively Figure 3.

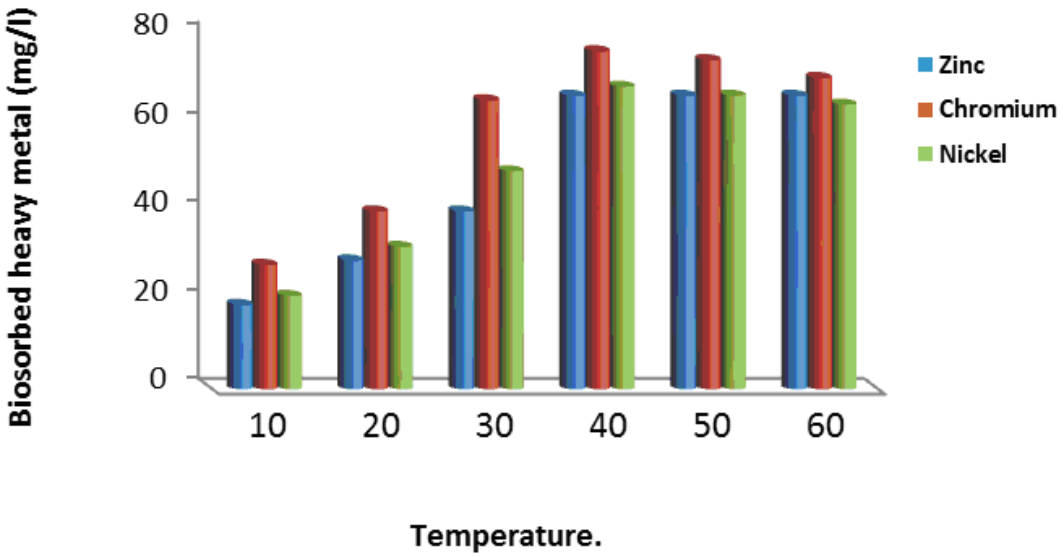

Figure 3- Mean biosorbed metal concentration(mg/l) by banana Mean peels from solution of zinc,chromium and nickel at different PH temperature

Analysis of variance Table 6 shows significant differences ($P \geq 0.001$) firstly between increased temperatures and secondly between heavy metal ions biosorbed by banana peels.

Table 6- Analysis of variance of mean Zn, Cr, and Ni concentration biosorbed by banana peels at six temperature values.

Source of variance	df	SS	MS	Probability
Replications	2	9.3	4.65	N.S.
Treatment	17	9499.3	678.521	0.001
Metal (M)	2	681.3	340.65	
Temp (T)	5	8209.3	1641.86	
M X T	10	608.7	60.87	
Error	34	74.7	2.197	
Total	53			

The current results are similar to those of various studies that examined different biological materials [7,14,15]. Recent study [34] has reported that highest Cr bioremoved by tassel powder was at 45 C° while for Cd bioremoval, 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 linkage of cells in both higher and lower temperature extremes which may reduce the availability surface area of contact [35].

Contact Time

The impacts of various contact times upon all Zn, Cr, and Ni bioremoved by banana peels Table 7 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 (28.0 ± 0.75 mg/l to 76.0 ± 0.93 mg/l) were recorded for Cr biosorption, followed by those (21.0 ± 2.13 mg/l to 68.0 ± 1.28 mg/l) of Ni and (19.0 ± 0. 75 mg/l to 66.0 ± 1.83 mg/l) Zn Figure 4.

Table 7- Mean biosorbed metal concentration (mg/l) by banana peels from solution of zinc, chromium and nickel at different contact time.

Contact Time	Mean metal biosorbed concentration (mg/l) ±SD		
	Zinc	Chromium	Nickel
1 min.	19.0 ± 0. 75	28.0 ± 0.75	21.0 ± 2.13
15 min.	29.0 ± 1.07	40.0 ± 1.22	32.0 ± 2.0
30 min.	40.0 ± 0.0	65.0 ± 1.06	49.0 ± 0.0
1 hour	66.0 ± 1.83	76.0 ± 0.93	68.0 ± 1.28
2 hour	66.0 ± 1.95	74.0 ± 1.76	66.0 ± 2.25
24 hour	66.0 ± 1.06	70.0 ± 2. 00	64.0 ± 1.55
48 hour	64.0 ± 1.79	71.0 ± 1.15	68.0 ± 1.40
LSD	2.854 mg/l		

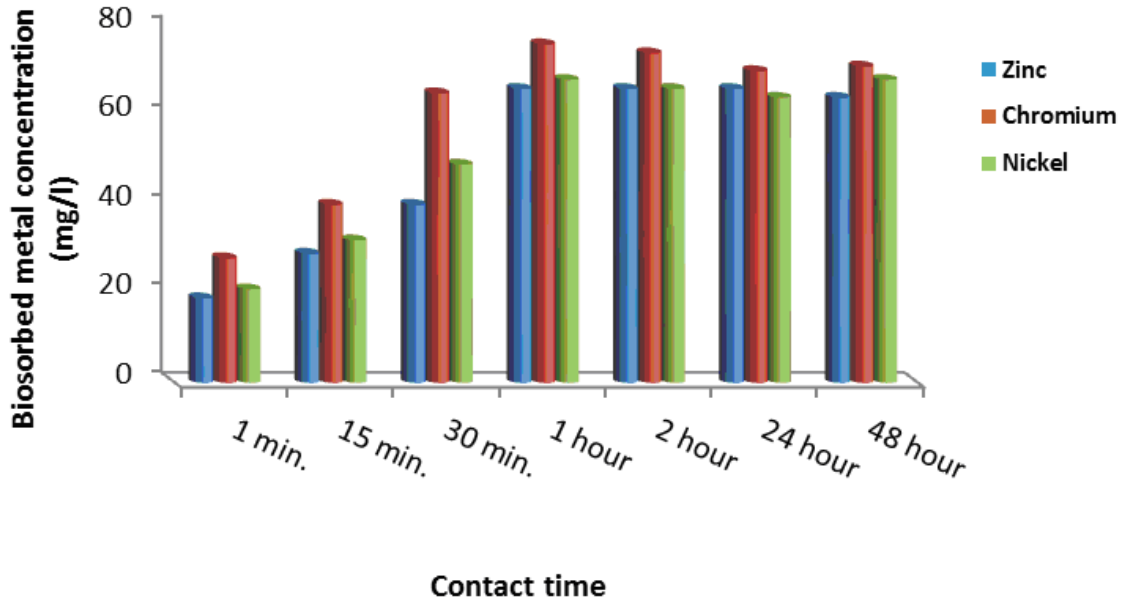

Figure 4- Mean biosorbed metal concentration(mg/l) by banana Mean peels from solution of zinc,chromium and nickel at different PH contact time

The analysis of variance of contact time effects shows significant differences ($P \geq 0.001$) between firstly increased times and secondly between heavy metals biosorbed by banana peels Table 8.

Table 8- Analysis of variance of mean Zn, Cr, and Ni concentration biosorbed by banana peels with different contact time.

Source of variance	df	SS	MS	Probability
Replications	2	2.382	1.191	N.S.
Treatment	20	21305.43	1065.272	0.001
Metal (M)	2	1352.0	676.0	
C. time (T)	6	19529.43	3254.905	
M X I	12	424.0	35.333	
Error	40	119.618	2.991	
Total	62			

The obtained results are agreed with other studies [19,36,37]. However other work [38], has reported that required contact time for best copper bioremoved by orange peels was less than one hour (40 minutes).

From the current work, it seems clearly that the ability of banana peels was significantly effective for the removal of Cr, Ni, and Zn ions from industrial wastewater as it had been reported for various biosorbent plant materials [19,22,,23,32,33] and would successfully be applied for various heavy metals from industrial wastewater since it seems environmentally sound.

References

1. Richman, M.I. **1997**. Water pollution. Wastewater, 5(2):24-29.
2. Volesky, B. **2001**. Detoxification of metal-bearing effluents: biosorption for the next century. Hydrometallurgy, **59**:203-216.
3. Vijayaraaghavan, K.J.; Jegan, K.P. and Velan, M**. 2005**. Batch and column removal of copper from aqueous solution using a brown marine alga. J. Chem. Eng. **106**:177-184.
4. Selatnia, A.; Bakhti, M.Z.; Madani, A.; Kertous, L. and Mansouri, D. **2004**. Biosorption Cd+2 from aqueous solution by a NaOH-treated bacterial dead streptomyces rimosus biomass. Hydrometallurgy, **75**:11-24.
5. Kobya, M.; Demirbas, E.; Senturk, F. and Ince, M. **2005**. Adsorption of heavy metal ions from aqueous solution by activated carbon prepared from apricot. Bio-resource. Technol., **96**: 1512-1518.
6. Singh, C.K.; Sahu, J.N.; Mahalik, K.K. Mohanty, C.R.; Mohan, B.R. and Meikap, B.C. **2008**. Studies on the removal of Pb (II) from wastewater by activated carbon developed from Tamarind wood activated with sulphuric acid. J. Hazard. Mater.**153**:221-228.
7. Ahalya, N.; Ramachandra, T.V. and Kanamadi, R.D. **2005**. Biosorption of chromium (VI) from aqueous solution by the husk of Bengal gram (Cicer arientinum). Elec. J. Bio technol. 18 (3), 44-48.
8. Xia, Y and Liyuan, C. **2002**. Study of gelatinous supports for immobilizing inactivated cells of Rhizopus oligosporus to prepare biosorbent for lead ions. Internat. J. Environ. Studies. **5(16):**33-38.
9. Rengaraj, S.; Kyeong-Ho, M. and Seung, H. **2001**. Removal of chromium from water and wastewater by ion-exchange resins. J. Hazard. Mater, **87**: 273-287.
10. Volesky, B. **2003**. Sorption and biosorption. Sorbex. Inc. St. Lambert (Montreal). Quebec, Canada.
11. Cho, D.H. and Kim, E.Y. **2003**. Characterization of Pb+2 biosorption from aqueous solution by Rhodotorula glutinis bioprocess. Bio syst. Eng. **25**: 271-277.
12. Gadd, G.M. and White, C. **1993**. Microbial treatment of metal pollution- a working biotechnology, Trends Bio technol. J. **11**: 353-359.
13. Volesky, B. and Holan, Z.R. **1995**. Biosorption of heavy metals. Bio technol. Prog. **11**: 235-250.
14. Laszlo, J.A. and Dintzis, F.R. **1994**. Crop resides as ion exchange material. Treatment of soybean hull and sugar beet fiber (pulp) with epichlorochydrin to improve cation-exchange capacity and physical stability. J. Appl. Polymer Sci. **52**(4):531-538.
15. Reddad, Z.; Gerente, C.; Andres, Y. and Pierre, L.C. **2002**. Adsorption of several metal ions onto a low cost biosorbent: Kinetic and Equilibrium studies. Environ. Sci. Technol., **36(9):**2067-2073.
16. Saeed, A.; Iqbal, M. and Akhtar, M.W. **2005**. Removal and recovery of lead (II) from single and multi-metal (Cd, Cu, Ni, Zn) solutions by crop milling waste (black gram husk). Hazardous Materials, **117**:65-73.
17. Chockalingam, E. and Subramanian, S. **2006**. Studies on removal of metal ions and sulphate reduction using rice husk and desulfotomaculum nigrificans with reference to remediation of acid mine drainage. Chemosphere, **62**: 699-708.
18. Tunali, S. and Akar, T. **2006**. Biosorption properties of Botrytis cinerea biomass. J. Hazard. Mater. **131**:137-145.
19. Husoon, Z. A **2011**. Biotreatment of some heavy metals in industrial wastewater. Ph.d. thesis, College of Science, University of Baghdad. Iraq.
20. Montanher, S.F.; Oliveira, E.A. and Rollengerg, M.C. **2005**. Removal of metal ions from aqueous solution by sorption onto rice bran. J. Hazard Mater.**117**:207-211.

21. Mohan, D. and Singh, K.P. **2002**. Single and multi-component adsorption of chromium and zinc using activated carbon derived from bagasse-an agricultural waste. Wat. Res.**36**:2304-2318.
22. Mohan, D. and Pittman, C.A.**2006**. Activated carbons and low cost adsorbents for remediation of tri-and hexavalent chromium from water. J. Hazard Mater.**137 (2):**762-811.
23. Khan, N.A., Ibrahim, S. and Subramanian, P (2004). Elimination of heavy metals from wastewater using agricultural wastes as adsorbents. Malaysian J. Sci., **23**:43-51.
24. Doyurum, S. and Celik, A. **2006**. Pb (II) and Cd (II) removal from aqueous solution by olive cake. J. Hazard. Mater, **138 (1):**22-28.
25. Regine, H. and Volesky, B. **2000**. Biosorption: a solution to pollution. Int. Micro. Bio. **3**:17-24.
26. Zafar, M.N.; Nadeem, R. and Hanif, M.A. (2007): Biosorption of nickel from protonated rice bran. J. Hazard Mater. **143**: 478-485.
27. Lu, D.; Cao, Q.; Li, X.; Cao, X.; Luo, F. and Shao, W. **2008**. Kinetics and equilibrium of cu (II) adsorption onto chemically modified orange peel cellulose biosorbents. Hydrometallurgy. **64**:1122-1127.
28. Hashem, M. **2007**: Adsorption of lead from aqueous solution by okra wastes. Int. J. Phys. Sci, **2**(7), 178-184.
29. Eslamzadeh, T.; Nasernejad, B. and Pour, B.B. **2004**. Removal of heavy metals from aqueous solution by carrot residues. Iranian J.Sci. & Technol. Transaction. **28(A):**16-19.
30. Yu, Q. and Kaewsarn, P. **2002**. Biosorption of copper (II) from aqueous solution by pre-treated biomass of marine alga Padina sp. Chemosp., **47**:1081-1085.
31. Scheiwer, S. and Patil, S.B. **2008**. Pectin-rich fruit wastes as biosorbents for heavy metal removal: Equilibrium and Kinetics. Bio. Res. Technol.**99**:1896-1903.
32. Vijayaraaghavan, K.J. and Yun, Y.S. **2008**. Bacterial biosorbents and biosorption. Biotechnol. Adv. **26**: 266-291.
33. Lu, D.; Cao, Q.; Li, X.; Cao, X.; Luo, F. and Shao, W. **2008**. Kinetics and equilibrium of cu (II) adsorption onto chemically modified orange peel cellulose biosorbents. Hydrometallurgy. **64**:1122-1127.
34. Saikaew, W. and Kaewsarn, P. **2009.** Cadmium ion removal using biosorbents derived from fruit peel wastes. Songklanakarin J. Sci. Technol. **31(5):**547-554.
35. Zvinowwanda, C.M.; Okonko, J.O.; Agyei, N.M. and Shabalala, P.N. **2009**. Physiochemical characterization of maize tassel adsorbent: Part I .Surface texture, microstructure and thermal stability. J. Applied Poly. Sci. **2**:1923-1930.
36. Cordo, B.; Loderio, P.; Herrero, R. and de Vicente, M.E.S. **2004**. Biosorption of cadmium by Fucus spiralis. Environ. Chem. **1**:180-187
37. Al-pachachi, U.S. **2006**. Bioremoval of Zinc by cell wall of bacteria Bacillus subtilis. M.Sc thesis, College of Science, University of Baghdad. Iraq.
38. Habib, A.; Nazrul, I.; Anarul, I. and Shafiqul Alam, A. M. **2007**. Removal of copper from aqueous solution using orange peel, sawdust and bagasse. Pak. J. Anal. Environ. Chem.**8 (1&2):** 21-25.