



Pomegranate Peels as Biosorbent Material to Remove Heavy Metal Ions from Industrial Wastewater

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Abstract

Pomegranate peels were used to remove zinc, chromium and nickel 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.

The obtained results showed that these peels are capable of removing zinc, chromium and nickel ions at significant capacities. The powder of the peels had the highest capability in bioremoving all zinc, chromium and nickel ions while dried peels had the lowest capacity again for all metals under test. However, the highest capacities were found in a sequence of chromium, nickel and zinc. Furthermore, all these data were significantly ($LSD_{\text{peel forms}} = 2.761 \text{ mg/l}$, $LSD_{\text{metal ions}} = 1.756 \text{ mg/l}$) varied.

In case of chromium, these figures were $69.7 \pm 0.9 \text{ mg/l}$, $58.0 \pm 2.4 \text{ mg/l}$ and $49.7 \pm 0.5 \text{ mg/l}$ for powder, fresh and dried peels respectively. Regarding nickel ions, the data were $58.7 \pm 1.1 \text{ mg/l}$ for peel powder, $50.7 \pm 2.0 \text{ mg/l}$ for fresh peel and $42.0 \pm 1.2 \text{ mg/l}$ for dry peel. While for zinc ions, the biosorption capacity was $48.4 \pm 2.2 \text{ mg/l}$, $39.4 \pm 0.8 \text{ mg/l}$ and $32.0 \pm 1.6 \text{ mg/l}$ for powder, fresh and dry peels respectively.

However, some examined factors were found to have significant impacts upon bioremoval capacity of pomegranate peels such as pH, temperature, and contact time where best biosorption capacities were found at pH 4, with temperature 50 C° and contact time of 1 hour.

Regarding pH, the highest bioremoval ability was found at pH 4 for all heavy metals, but with the sequence of Cr, Ni, and Zn and the data were $68.1 \pm 1.5 \text{ mg/l}$, $56.0 \pm 0.5 \text{ mg/l}$ and $47.88 \pm 1.21 \text{ mg/l}$ respectively. Similar pattern of bioremoval capacity was detected for temperature which was 50 C° giving capacities of $72.0 \pm 0.0 \text{ mg Cr/l}$, $60.0 \pm 1.84 \text{ mg Ni/l}$ and $54.0 \pm 1.72 \text{ mg Zn/l}$. In case of contact time, these capacities were again similar to those of pH and temperature and found to be $76.0 \pm 3.0 \text{ mg/l}$, $64.0 \pm 1.82 \text{ mg/l}$ and $60.0 \pm 2.0 \text{ mg/l}$ for Cr, Ni, and Zn respectively but at 1 hour contact time.

Keywords: pomegranate peels, biosorption, zinc, chromium, nickel, industrial wastewater

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استخدام قشور الرمان كمادة مازة لإزالة أيونات العناصر الثقيلة من مياه الفضلة الصناعية

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الخلاصة:

لقد استخدمت قشور الرمان في إزالة أيونات عناصر الخارصين ، الكروم و النيكل من مياه الفضلة الصناعية واختبرت ثلاث أشكال (القشور الطرية ، الجافة ، مسحوق القشور) تحت ظروف بعض العوامل مثل الدالة الحامضية ، درجة الحرارة و زمن التلامس.

تشير النتائج الى قدرة قشور الرمان على امتزاز ايونات هذه العناصر من مياه الفضلة الصناعية عند مستويات معنوية وان أفضل قدرة وجدت في حالة مسحوق القشور ثم القشور الطرية بينما كانت القشور الجافة اقل كفاءة. من جهة ثانية ، وجد أن أعلى التراكيز كانت لايون الكروم ثم النيكل و الخارصين. أن الفرق بين تراكيز العناصر الممتزة كانت واضحة ومعنوية بدلالة الفرق المعنوي الأصغر سواءً لأشكال القشور أو العناصر الممتزة (ف م أ للقشور = 2.761 ملغم/ لتر وللعناصر = 1.756 ملغم / لتر).

في حالة ايونات الكروم كانت قيم الامتزاز 69.7 ± 0.9 ملغم/ لتر ، 58.0 ± 2.4 ملغم / لتر لمسحوق القشور ، القشور الطرية و الجافة على التوالي. لايونات النيكل ، فان هذه القيم كانت 58.7 ± 1.1 ملغم / لتر لمسحوق القشور ، 50.7 ± 2.0 ملغم/ لتر للقشور الطرية و 42.0 ± 1.2 ملغم / لتر للجافة. في حالة عنصر الخارصين كانت قيم الامتزاز 48.4 ± 2.2 ، 39.4 ± 0.8 و 32.0 ± 1.6 ملغم / لتر للمسحوق والقشور الطرية و الجافة على التوالي.

بالمقابل ، فان بعض العوامل التي تم تقييم تأثيراتها وجدت ذات تأثيرات معنوية على قابلية هذه المازات على امتزاز ايونات العناصر الثقيلة تحت الدراسة وفي ذات الوقت وجدت أن أفضل قيمة دالة حامضية كانت 4 وأفضل درجة حرارة هي 50 م ° وزمن تلامس لمدة ساعة واحدة فقط حيث سجلت قدرة امتزاز بلغت 68.1 ± 1.5 ملغم/ لتر لايون الكروم و 56.0 ± 0.5 ملغم / لتر لايون النيكل عند درجة حامضية 4 وذات الترتيب من طاقة الامتزاز سجلت عند درجة حرارة 50 م ° حيث كانت 72.0 ± 0.0 ملغم كروم/ لتر ، 60.0 ± 1.84 ملغم نيكل / لتر و 54.0 ± 1.72 ملغم خارصين / لتر . كذلك الحال لزمن التلامس حيث وجدت طاقة امتزاز 76.0 ± 30 ، 64.0 ± 1.82 و 60.0 ± 2.0 ملغم / لتر للكروم ، النيكل و الخارصين على التوالي.

كلمات مفتاحية: قشور الرمان، الامتزاز، الزنك، الكروم، النيكل، مياه الفضلة الصناعية.

1. Introduction

Plant material wastes and peels have been used intensively in bioremoving various heavy metal ions from industrial wastewater [1-3]. However, industrial waste-water may vary significantly according to type of products and kind of processing and the environmental effects of such industrial discharges would not rely only on collective characteristics such as BOD and total suspended solids (TSS), but also on their content of specific inorganic and organic substances [4,5].

The contamination of water by various heavy metal ions would result in considerable

environmental problems as these ions being contain toxic impacts upon both public health and environment. The main sources of such water contamination with different heavy metals are industrial waste water [4].

However, decontamination of heavy metal ions of industrial waste water was received considerable attention by using various techniques such as activated carbon adsorption [1], chemical precipitation [6], reverse osmosis [7], electro-dialysis [8] and ion exchange [9]. Recently much attention has been spent on successfully using biological materials and wastes for the removal of heavy metals from

industrial waste water such as microbial biomass [10-13] and biological wastes [14-17]. These biosorbent materials are characterized being less expensive, high bio-removal capacity, metal selective, non sludge generation, possible ion recovery [2,18] and environmentally sound methodology [19].

The technique of plant residues heavy metal ions adsorption was world widely used for waste water treatment [20] such as peat and nut shells, coconut shells, rice husk, tea waste, peanut hulls, almond shells, peach stones, citrus peels, and many others [14-17,21].

It is well known that these biosorbent materials contain mainly polysaccharides, proteins, and lipids, functional groups that act to bind metal ions such as carboxyl, hydroxyl, sulphate, phosphate, and amino groups [22]. Any given group of biosorption of a specific ions would depend upon several variables such as the accessibility of sites, a number of sites of biosorbent material, the chemical state of the site (availability) and affinity between site and metal [18].

2. Material and Methods

Samples of industrial wastewater were collected, at a volume of 500 ml wastewater samples collected in plastic containers at three random periods between 8th to 29th June 2011, from both pretreatment units of electroplating section in the State Electrical Manufacturing Company in Al-Waziriya area / Iraq-Baghdad. Each sample was divided into two sub-samples, the first had been subjected to chemical & physical analysis while the second was used for bioremoval test of zinc, chromium and nickel ions.

3. Biosorption capacity of Pomegranate peels

3.1. Chemical analysis of industrial wastewater

Samples of industrial wastewater were collected, 4 times at weekly rate, from 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 were laboratory assessed.

3.2. Metal biosorption tests

Pomegranate peels were collected from different local markets, washed thoroughly by de-ionized distilled water (DDW) and used subsequently in the following examinations:

3.2.1. Various pomegranate peel forms

Three forms of pomegranate peels were used. The first form represents fresh pieces, the

second was as dried pieces and finely these dried peels were powdered and sieved through 2mm stainless steel sieve. These peel forms, however were tested for the bioremoval of zinc, chromium and nickel ions from aqueous synthetic solutions under various factors such as pH, temperature, and contacting time.

The examining 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. These heavy metal solutions were received about 0.05 g pomegranate peels as fresh, dried and powder. This experiment was carried out in three replicated test in addition of control (metal ion solution free from peels). All samples were left for almost one hour at 40 C°. Each sample after that, was passed through 0.45µm filter paper [23] and metal ion concentration was determined by using Flame Atomic Absorption Spectroscopy (FAAS) [24].

3.2.2. Factors controlling metal bioremoval

The experiment carried above, was retested for the examination of probable impacts of different levels of pH, and temperature. The ranges of 1 to 6 and from 10 to 60 were applied for pH and temperature (C°) respectively for all examined heavy metals.

4. Results and Discussion

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

Chemical analysis of industrial wastewater

The mean values of temperature, pH, Zn, Cr, and Ni of industrial wastewater are shown in (table 1). 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 \pm standard deviation of several water variables

| Variables | Mean value \pm SD of some industrial wastewater components | | | |
|-----------|--|-----------------------------------|-----------------------------------|-----------------------------------|
| | 1 st week 8/6/2011 | 2 nd week 15/6/2011 | 3 rd week 22/6/2011 | 4 th week 29/6/2011 |
| Temp. C° | 31.0 \pm 0.0 | 31.13 \pm 0.05 | 31.33 \pm 0.12 | 31.76 \pm 0.05 |
| pH | 7.33 \pm 0.05 | 7.37 \pm 0.09 | 7.67 \pm 0.094 | 7.17 \pm 0.047 |
| Zn (mg/l) | 612.0 \pm 2.16 | 524.7 \pm 2.494 | 418.7 \pm 0.942 | 535.3 \pm 1.7 |
| Cr (mg/l) | 46.67 \pm 1.89 | 49.33 \pm 0.942 | 45.67 \pm 1.247 | 44.0 \pm 0.0 |
| Ni (mg/l) | 12.0 \pm 0.0 | 8.96 \pm 0.073 | 9.0 \pm 0.0 | 8.06 \pm 0.055 |

Biosorption capacity of pomegranate peels Various peel forms

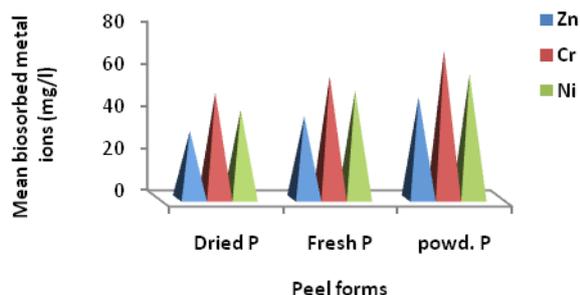
Mean bioremoval capacities of pomegranate peels examined at different forms is given in table 2 and presented in Fig. (1).

It seems clearly that pomegranate peel forms had significant ability for bio-removing heavy metals ions from aqueous heavy metal solutions. However, the form of powdered peels gave values of bioremoved heavy metal concentrations higher than those of both fresh

and dried peel pieces (LSD = 2.761) for all examined heavy metals. Furthermore, highest metal concentration (69.7 \pm 0.9 mg/l) was recorded in case of chromium, followed by nickel (58.7 \pm 1.1 mg/l), while the lowest metal concentration (48.4 \pm 2.2 mg/l) was found in case of zinc (Fig .1). In case of fresh and dried peels, similar sequences were shown. These values of biosorbed heavy metal ion concentrations were significantly differed from each other (LSD = 1.756 mg/l).

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

| Pomegranate peel form | Mean metal biosorbed concentration (mg/l) \pm SD | | |
|-----------------------|--|----------------|----------------|
| | Zinc | Chromium | Nickel |
| Peel dried pieces | 32.0 \pm 1.6 | 49.7 \pm 0.5 | 42.0 \pm 1.2 |
| Peel fresh pieces | 39.4 \pm 0.8 | 58.0 \pm 2.4 | 50.7 \pm 2.0 |
| Peel Powder | 48.4 \pm 2.2 | 69.7 \pm 0.9 | 58.7 \pm 1.1 |

**Figure 1-** Mean metal ions (mg/l) biosorbed by different pomegranate peel forms

Highest capacity of pomegranate peels may be due to the surface area of peel particles [18] and other environmental factors such as pH and temperature that may affect the biosorption mechanism.

Factors affecting biosorption

pH

It is well shown that increased pH values (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 ions while the Zn ions had the lowest bioremoved concentrations (Fig 2). However, it seems obviously that pH 4 was the best value for giving optimum bioremoval capacity for all heavy metals under test (Fig 2).

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

| pH level | Mean metal biosorbed concentration (mg/l) ±SD | | |
|----------|---|-------------|--------------|
| | Zinc | Chromium | Nickel |
| 1 | 28.0 ± 1.22 | 26.7 ± 2.29 | 41.0 ± 0.0 |
| 2 | 31.3 ± 1.25 | 33.0 ± 1.63 | 44.0 ± 1.04 |
| 3 | 46.04 ± 1.07 | 39.6 ± 1.01 | 53.55 ± 1.74 |
| 4 | 47.88 ± 1.21 | 68.1 ± 1.5 | 56.0 ± 0.5 |
| 5 | 43.0 ± 1.44 | 51.0 ± 0.79 | 51.8 ± 1.82 |
| 6 | 40.0 ± 0.0 | 49.0 ± 2.0 | 49.9 ± 1.35 |
| 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 [25] 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 [26]. Optimum pH value for copper biosorption by marine algae was within a range of 4 – 6 [27]. A study [28] 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 pomegranate peels at six pH levels

| Source of variance | df | SS | MS | Probability |
|--------------------|----|---------|---------|-------------|
| Replications | 2 | 0.744 | 0.372 | N.S. |
| Treatment | 17 | 5618.63 | 330.508 | 0.001 |
| Metal (M) | 2 | 930.97 | 465.485 | |
| pH (P) | 5 | 3734.86 | 813.074 | |
| M X P | 10 | 952.8 | 95.28 | |
| Error | 34 | 382.923 | 11.262 | |
| Total | | | 53 | |

The pH of aqueous solution plays a significant role in the biosorption process [29]. 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 [30].

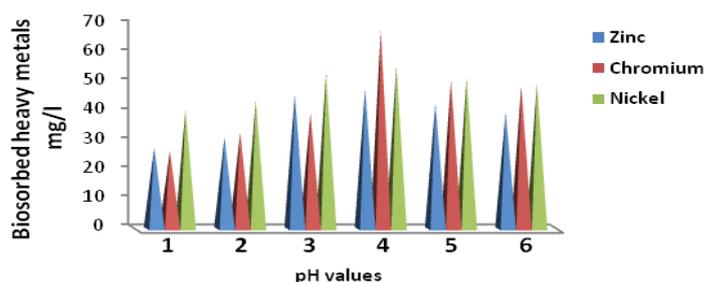


Figure 2- Mean absorbed metal concentration (mg/l) by pomegranate peels form solution of zinc, chromium and nickel different levels of solution pH.

Temperature

Table (5) shows mean biosorbed metal concentration (mg/l) by pomegranate 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

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

| Temperature C° | Mean metal biosorbed concentration (mg/l) ±SD | | |
|----------------|---|-------------|-------------|
| | Zinc | Chromium | Nickel |
| 10 | 26.0 ± 1.02 | 22.0 ± 1.6 | 19.0 ± 1.45 |
| 20 | 34.0 ± 1.33 | 34.0 ± 1.44 | 27.0 ± 1.05 |
| 30 | 43.0 ± 1.5 | 61.0 ± 2.0 | 40.0 ± 1.12 |
| 40 | 51.0 ± 0.98 | 71.0 ± 1.26 | 58.0 ± 1.52 |
| 50 | 54.0 ± 1.72 | 72.0 ± 0.0 | 60.0 ± 1.84 |
| 60 | 50.0 ± 0.0 | 68.0 ± 1.2 | 57.0 ± 1.31 |

The highest capacities were found in case of chromium that ranged from 22.0 ± 1.6 mg/l to 72.0 ± 0.0 mg/l, and varied from 19.0 ± 1.45 mg/l

to 60.0 ± 1.84mg/l and from 26.0 ± 1.02 mg/l to 54.0 ± 1.72 mg/l for Ni and Zn respectively (Fig 3).

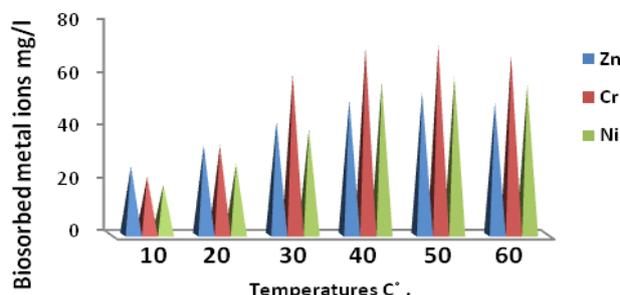


Figure 3- Mean metal ions (mg/l) biosorbed by pomegranate peels at different temperatures.

Analysis of variance (Table 6) shows significant differences (P ≥ 0.001) firstly between increased temperatures and secondly

between heavy metal ions biosorbed by pomegranate peels

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

| Source of variance | df | SS | MS | Probability |
|--------------------|----|-----------|---------|-------------|
| Replications | 2 | 9.13 | 4.565 | N.S. |
| Treatment | 17 | 1714724.0 | 866.118 | 0.001 |
| Metal (M) | 2 | 1521.0 | 760.5 | |
| Temp (T) | 5 | 12226.0 | 2445.2 | |
| M X T | 10 | 977.0 | 97.70 | |
| Error | 34 | 102.87 | 3.026 | |
| Total | | | 53 | |

The current results are similar to those of various studies that examined different biological materials [2,16, 31]. Recent study [24] 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 [31].

Contact time

The impacts of various contact times upon all Zn, Cr, and Ni bioremoved by pomegranate 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 (20.0 ± 1.3 mg/l to 76.0 ± 3.0 mg/l) were recorded for Cr biosorption, followed by those (10.0 ± 1.88 mg/l to 64.0 ± 1.82 mg/l) of Ni and (12.0 ± 1.34 mg/l to 60.0 ± 2.0 mg/l) Zn (Fig 4).

Table 7- Mean biosorbed metal concentration (mg/l) by pomegranate 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. | 12.0 ± 1.34 | 20.0 ± 1.3 | 10.0 ± 1.88 |
| 15 min. | 28.0 ± 3.0 | 31.0 ± 1.8 | 21.0 ± 1.68 |
| 30 min. | 40.0 ± 2.0 | 49.0 ± 1.71 | 31.0 ± 2.0 |
| 1 hour | 60.0 ± 2.0 | 76.0 ± 3.0 | 64.0 ± 1.82 |
| 2 hour | 60.0 ± 4.0 | 74.0 ± 1.44 | 64.0 ± 2.0 |
| 24 hour | 57.0 ± 1.5 | 71.0 ± 2.0 | 62.0 ± 3.0 |
| 48 hour | 56.0 ± 1.8 | 71.0 ± 1.64 | 60.0 ± 2.64 |
| LSD | 2.854 mg/l | | |

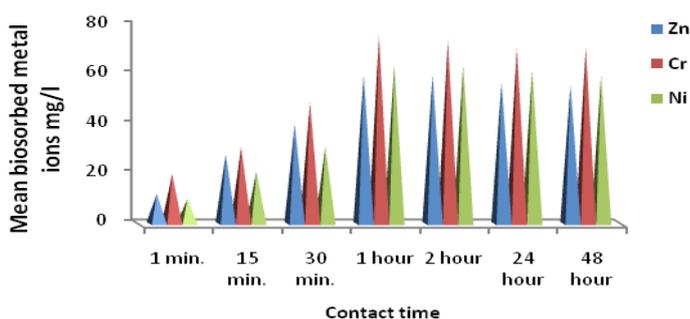


Figure 4- Mean metal ions biosorbed by pomegranate peels at different contact time.

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 pomegranate peels (Table 8).

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

| Source of variance | df | SS | MS | Probability |
|--------------------|----|----------|----------|-------------|
| Replications | 2 | 18.052 | 9.026 | N.S. |
| Treatment | 20 | 27381.71 | 1369.086 | 0.001 |
| Metal (M) | 2 | 1783.139 | 819.5695 | |
| C. time (T) | 6 | 25191.71 | 498.618 | |
| M X I | 12 | 406.861 | 33.905 | |
| Error | 40 | 131.948 | 3.299 | |
| Total | | | 62 | |

The obtained results are agreed with other studies [18,32,33,34]. However other work [35], 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 pomegranate 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 [3,18,30,36,37] and would successfully be applied for various heavy metals from industrial wastewater since it seems environmentally safe

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