The removal of Zinc, Chromium and Nickel from industrial waste water using Corn cobs

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Abstract
The aim of this study was to use low cost adsorbents, which consist of corn cobs as plant wastes adsorbents in treatment of Industrial waste water by fixed bed column technique and study the effect of two variables (pH value and contact time). The sample of plant waste (Corn cobs) was tested to determine its activity which gives the best performance in heavy metals removal and other pollutants (TSS, TDS and COD). Adsorption tests showed the corn cobs adsorbents had significant heavy metal removal efficiency. The best removal efficiency 95.05% of Cr was occurred at pH 5.4 and 4.18hr. Higher removal efficiency 99.90% of Ni was occurred at pH 6.5 and 2.38hr. While, lower removal efficiency 91.35% for Zn obtained at pH 6.5 and 0.15hr. Removal efficiency for TDS, TSS and COD were 56%, 65.7% and 83.3% respectively.
Keywords: Corn cobs, Adsorption, Zinc, Chromium, Nickel, Industrial waste water

أزالة ألزنك وألكروم وألنيكل من مياه ألفضلة ألصناعية بأستخدام كوالح ألذرة

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ألخلاصة
أن ألهدف من هذه ألدراسة هو أستخدام ألممتزات واطئة ألكلفة وألتي تشمل كوالح الذرة كمخلفات نباتية ممتزة في معالجة مياه ألفضلة ألصناعية بواسطة تقنية ألاعمدة ثابتة ألحشوة ودراسة تأثير متغيرين وهما قيمة ألاس ألهايدروجيني وزمن ألتلامس .أختبر نموذج ألمخلفات ألنباتية (كوالح الذرة) لتحديد فعاليتها وألتي تعطي أفضل أداء في أزالة ألمعادن ألثقيلة وألملوثات ألاخرى (المواد ألصلبة الذائبة الكلية والمواد الصلبة ألعالقة الكلية وطلب ألاوكسجين ألكيميائي).أظهرت اختبارات الامتزاز بان جميع الممتزات النباتية تملك كفاءة ازالة معنوية للمعادن الثقيلة، حصلت افضل ازالة وبكفاءة 95.05% للكروم عند pH 4.5 وزمن تلامس 4.18 ساعات، في حين أفضل أزالة وبكفاءة 99.90% كانت للنيكل عند pH 6.5 وبعد 2.38 ساعة، وأقل أزالة بلغت 91.35% كانت مع الزنك عند pH 6.5 وبعد 0.15 ساعة من ألتماس. بينما كانت كفاءة الازالة للمواد ألصلبة الذائبة الكلية والمواد الصلبة ألعالقة الكلية ومتطلب ألاوكسجين ألكيميائي هي 56% و 65.7% و 83.3% على التتالي.

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Introduction

Among all the pollutants, heavy metals are most dangerous one as these are non – biodegradable and persist in the environment. These pollutants enters the water resources through both natural and anthropogenic sources. More attention was being given to the potential health hazards posed by heavy metals. The term heavy metal refers to any metallic chemical element that has a relatively high density. The density of heavy metals is usually more than 5.0 g/cm^3. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), lead (Pb), Copper (Cu), Zinc (Zn), Cobalt (Co), Nickel (Ni), and Iron (Fe). These metals are classified into three categories: toxic metals (such as Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn, etc), precious metals (such as Pd, Pt, Ag, Au, Ru etc.) and radionuclides (such as U, Th, Ra, Am, etc.) [1, 2]. Toxic metals cause toxicity to organisms even at ppm (mg/L) level of concentration. Heavy metals are dangerous because these tend to bioaccumulations. Bioaccumulation means an increase in the concentration of a chemical in an organism over time, compared to its concentration in the environment. Heavy metals may enter a water supply through industrial or consumer wastes releasing heavy metals into streams, lakes, rivers, and ground water [3,4]. The waste water often comes from the dyes and pigment industries, film and photography, galvanometric, metal cleaning, electroplating, leather and mining industries. In this field, a lot of research has been conducted using some traditional techniques of waste water treatment such as precipitation and ion exchange. In general, these techniques used some expensive industrial materials such as activated carbon and some industrial ion exchange resins. Therefore, it was necessary to find a new strategy to remove these toxic heavy metals based on using cheap and abundant natural materials which is characterized by high efficiency. Some cheap biological wastes such as wood sawdust, rice husk, coir pith and charcoal were used to remove chrome ions from the waste water discharge from tanneries [5, 6]. The treatment activity of these biological plant wastes depend on adsorption technique, Adsorption is a separation process in which certain components of the fluid phase are transferred to the surface of the solid adsorbents, or Adsorption is selective binding of a substance by another solid substance [7]. Most adsorbents are highly porous materials, and adsorption takes place primarily on the walls of the pores or at the specific sites inside the particle. Separation occurs because differences in molecular weight, shape, or polarity cause some molecules to be held more strongly on the surface than others or because the pores are too small to admit the larger molecules. The overall rate of adsorption is controlled by the rate of diffusion of solutes within the capillary pores of the adsorbent and varies with the square root of the contact time with the adsorbent. The adsorption operation can be batch, semi-batch and continuous. Batch operations are generally conducted when small amounts are to be treated. The equilibrium distribution depends on the contact time in batch operation [8]. Moreover, these adsorbent materials consisting mainly of polysaccharides, proteins, and lipids, functional groups that can bind metal ions such as carboxyl, hydroxyl, sulphate, phosphate, and amino groups [9]. The importance of any given group of adsorption of a certain metal by a certain adsorbent depends on several factors such as a number of sites of adsorbent material, the accessibility of sites. [10]. Thus, this work is aimed to use low cost adsorbents, which consist of corn cobs as plant wastes in treatment of Industrial waste water by fixed bed column technique and study the effect of a two variables (pH value and contact time) on adsorption process.

Material and Methods

Industrial waste water samples were collected from pretreatment units of electroplating section in The State Company for Electrical Industries (SCEI), Al-Waziriya- Iraq-Baghdad. Waste water sample were collected in the period between 4th and 20th of March 2012. The sample was divided into two sub-samples, the first was examined for chemical & physical analysis and the second was employed for removal of zinc, chromium and nickel ions. On the other hand, the plant waste was Corn cobs which obtained from Local Markets (Grocery stores) in Baghdad.

Adsorption capacity of Corn cobs

1- Chemical analysis of industrial wastewater

Sample of industrial waste water was collected, from pre and post treatment tanks of (SCEI**)**. Some factors such as pH, COD, TSS, and TDS were determined according to standard methods [11] and heavy metals (Cr, Ni and Zn) content were estimated and recorded by atomic absorption spectroscopy in laboratory.

2- Preparation of Adsorbents

These adsorbents were selected for their cost effectiveness and ready availability. Corn cobs was crushed by grinder and washed with deionized water by mixing it in a shaker for 24 hrs. After that, the water was decanted, and the plant waste was then again shaken with fresh water for another 24 hrs. This process was repeated three times for all the apparent excess material and color were removed from the samples. The cleaned, wet Corn cobs were then placed in a large glass baking dish and dried in the room temperature. After that, the adsorbents (Corn cobs) were treated with 10% HCl for 6 hrs at 30°C for chemical modification. Then the modified adsorbents were washed with double distilled water and filtered. Modified Corn cobs and corn cobs were dried in oven at 125°C for 24 hrs. The sample sieved by using a 4 mm sieves and Adsorbents particles were stored in precleaned plastic bottles and kept for studies, [12].

3- Adsorption experimental studies

a- Laboratorial Column Design

The adsorption studies were carried out in transparent glass column that had 5.0 cm internal diameter and 50 cm in height. The adsorbents (Corn cobs) were confined in the column by fine Teflon (PTFE) filter (No.1) at the bottom and a glass beds layer packing at the top of the adsorbents to ensure a uniform distribution of influent through the adsorbent. The influent waste water was introduced to the column through a rubber stopper, fixed at the top of the column and controlled it by a valve at the lower end of the column. Two containers were used as wastewater containers, the first one is plastic container was used as waste water feed container (5 Liters) at the top of the column. Second one is a glass container (Beaker) was used as a waste water reservoir container (2 Liters) at the bottom of a column. A column was washed with de-ionized water before adsorption experiments. Column filled with prepared Corn cobs samples for industrial waste water samples. In order to determine and estimate the efficiency of adsorbent for treatment of industrial waste water. Efficiency of adsorbent was determined according to certain parameters such as: pH value and Contact time.

b- Factors Affecting Heavy metals removal and other pollutants

The adsorption tests were carried out for the examination of possible effects of different levels of pH and contact time. For pH, the range of 5-8 and contact time from 0.25 – 5 hrs. were used.

Results and Discussion

Chemical analysis of industrial waste water

Table 1 shows the values of pH, TDS, TSS, COD, zinc, chromium and nickel ions concentrations of all examined waste water samples from electroplating treatment unit of (SCEI) before and after treatment [chromic water and treated water]. The results observed for pH, TDS, TSS and COD were: 8.5, 15000, 1750, 2400 ppm, respectively.

Regarding heavy metal contents of these samples, the results found that the level of Cr, Ni and Zn were 145.66, 10.21, 20 ppm (mg/l) respectively. While samples collected after local treatment was rather higher from those of pre-treatment where; pH, TDS, TSS and COD were: 9, 17000, 3660, 9180 ppm, respectively. This could be related to the type of treatment which is often treated chemically. While the concentration of heavy metals collected after local treatment were decreased to 24, 0.58 and 2.8 ppm for Cr, Ni and Zn, respectively.

From these data, it seems obvious that some variables such as pH, TDS, TSS and COD increased in post treatment samples and this might be due to the additive chemicals used and type of treatment that used, whilst other variables such as heavy metals decreased due to such treatment.

Table 1- pH, TDS, TSS, COD, Cr, Ni, and Zn (ppm) in industrial waste water before and after company treatment system.

Examination	Unit	Sample	
		Chromic water	Treated water
pH value	-	8.5	9
TDS	ppm(mg/l)	15000	17000
TSS	ppm(mg/l)	1750	3660
COD	ppm(mg/l)	2400	9180
Cr	ppm(mg/l)	145.66	24
Ni	ppm(mg/l)	10.21	0. 58
Zn	ppm(mg/l)	20	2.8

Chemical and physical measurements of waste water sample after treatment by Corn cobs

For adsorption experimental studies, the best empirical conditions were selected in order to conduct this experiment. For industrial waste water samples treated with plant wastes adsorbents at pH: 6.5 and contact time: 5 hrs, the chemical and physical analyses were found in Table (2). The values of TDS, COD and TSS were decreased to 6600, 400 and 600 ppm with removal efficiency reached 56, 83.3 and 65.7% respectively after treatment by corn cobs. On the other hand, results of this experiment were compared with data of the electroplating treatment unit in table 1, it seems obvious that the results of measurements of wastewater samples after treating via Corn cobs was considered very good , as decreased the values of TDS , COD and TSS to almost half after treatment by adsorbents **.**

Table 2- Chemical and physical measurements of industrial waste water after treatment by Corn cobs.

Examination	Unit	Remaining concentration after treatment by C. cobs	ER (%) of Corn cobs at pH.=6.5 & time:5 hr.	ER of pollutants by treatment unit in (SCEI)
TDS	ppm	6600	56	-13.3
TSS	ppm	600	65.7	-282.5
COD	ppm	400	83.3	-16.6

Adsorption experimental studies

The results in Table 3 showed the adsorption experiment of heavy metals removal by corn cobs that carried out by laboratorial column (Figure 1). The results indicated ability of corn cobs to remove and reduce the level of heavy metals from the industrial waste water. Significant differences on removal efficiency of adsorbents for heavy metals removal is displayed in Table 4 as determined by one – way (Anova) test with the F and p value at probability level $P \leq 0.01$ and $P \leq 0.05$.

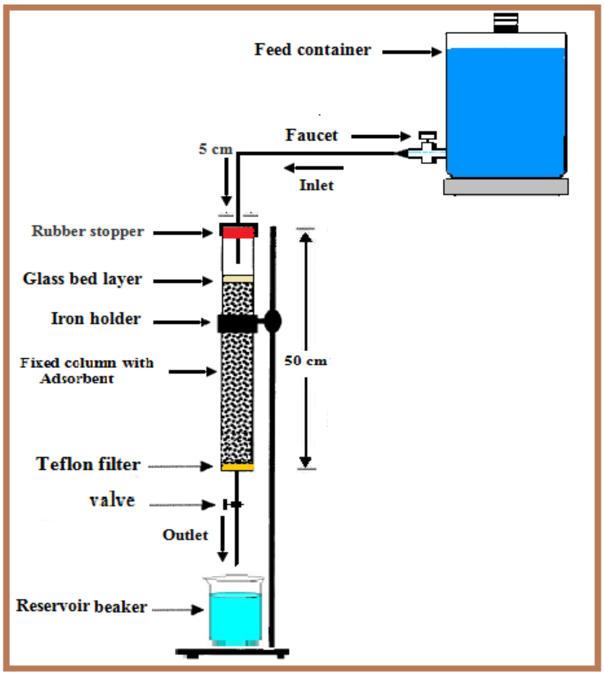

Figure 1- Schematic presentation of the experimental column.

Table 3- Removal and reduction of heavy metals by Corn cobs.

parameters		Remaining concentration of heavy metals removal (ppm)		
pH	Time(hr.)	Ni	Cr	Zn
5.439	1.0	0.002	26.22	1.83
5.439	4.18	0.097	7.2	2.31
7.651	4.18	0.021	18.40	2.53
7.651	1.0	0.042	36.80	2.16
5	2.38	0.043	32.21	2.55
8	2.38	0.040	18.40	1.97
6.5	0.15	0.040	26.22	1.73
6.5	5	0.034	7.36	2.50
6.5	2.38	0.021	18.40	2.64

Table 4- Efficiency of adsorbents removal for heavy metals.

Parameters		Efficiency of Removal (%)		
pH	Time(hr.)	Ni	Cr	Zn
5.439	1.0	99.90	82.00	90.84
5.439	4.18	99.02	95.05	88.45
7.651	4.18	99.70	87.36	87.35
7.651	1.0	99.51	74.73	87.20
5	2.38	99.51	77.88	87.25
8	2.38	99.60	87.36	90.15
6.5	0.15	99.60	82.00	91.35
6.5	5	99.60	94.94	87.50
6.5	2.38	99.90	87.36	86.80
Means of *ER* (%)		99.59	85.40	88.54
SD		0.26033	6.97475	1.75965

The results of corn cobs showed the higher adsorption higher adsorption capacities occurred at pH 5.4 for Ni and Cr removal but 6.5 for Zn removal, nickel ions had a better adsorption efficiency giving ion concentrations at 0.002ppm with removal efficiency 99.9%. At the same sequence, concentration of zinc ions after treatment was better at pH 6.5 that found to be 1.73 ppm with the removal efficiency 91.35%. On the other hand, lowest adsorption efficiency was recorded in case of chromium that was about 7.2ppm after treatment (Table 2), with removal efficiency 95.05% (Table 4 and Figure 2).

The pH of the adsorption process is an important controlling parameter in heavy metals adsorption process [13]. This parameter is directly related to the competition of hydrogen ions with metal ions at active sites on the adsorbent surface [14]. In a study carried out by Abdullah and Prasad [15], they found that the adsorption of nickel increased when the pH was increased from 1 to 6 by using tamarind bark. Dong *et al* [16] reported that the best pH for the chromium adsorption was 5.5 by amino starch preparation and its adsorption for Cr. Optimum pH for chromium and zinc adsorption was laid between 5 and 6 in case of using plant wastes [17].

Regarding contact time, Corn cobs exhibited high adsorption efficiency at a variable time 1.0, 2.38 and 4.18hrs for nickel ions, for zinc ions were 0.15, 1.0 and 2.38 hrs but 5hrs for chromium ions. Therefore, these adsorbents were found to be different in the adsorption of heavy metal ions that where zinc ions, nickel ions and chromium ions respectively (Tables 2). Highest efficiency of heavy metals removal (99.90%) was found in the case of nickel ions, but in case of chromium ions was 95.05%., and in the case of zinc was 91.35%, , highest efficiency (99.90%) was found with nickel ions Tables 4- ; Figure 3-.

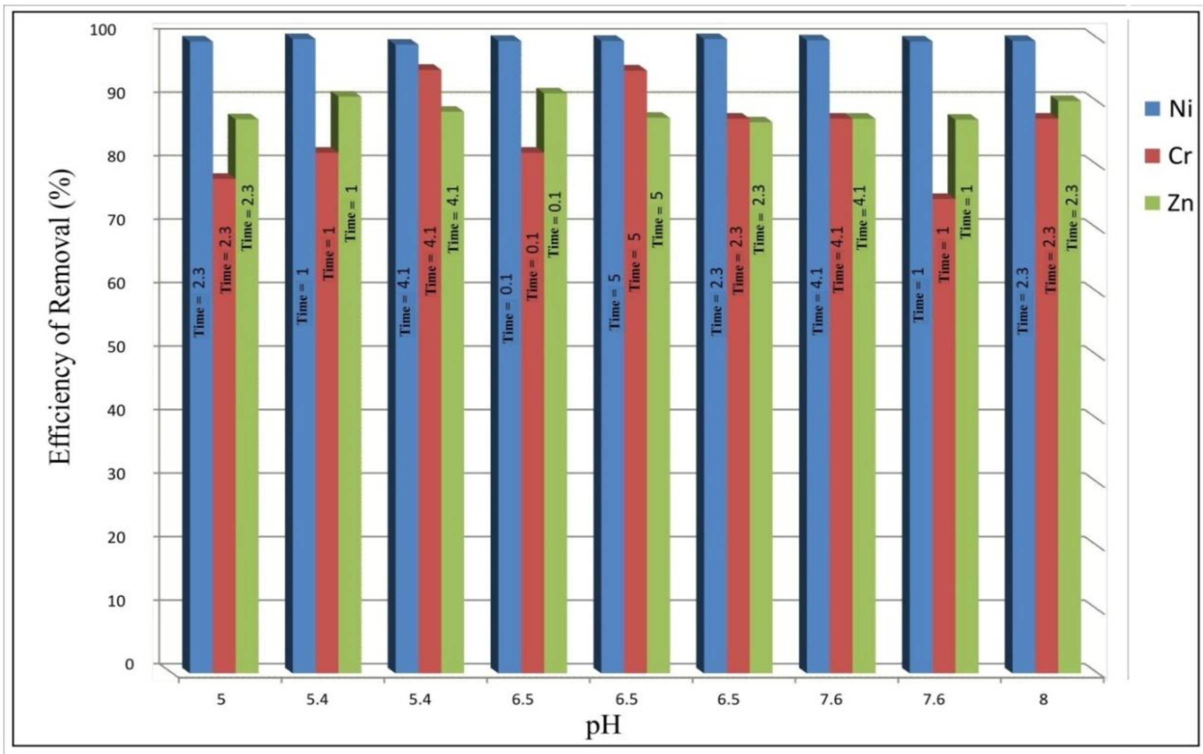

Figure 2- Effect of pH on three heavy metals removal efficiency by corn cobs.

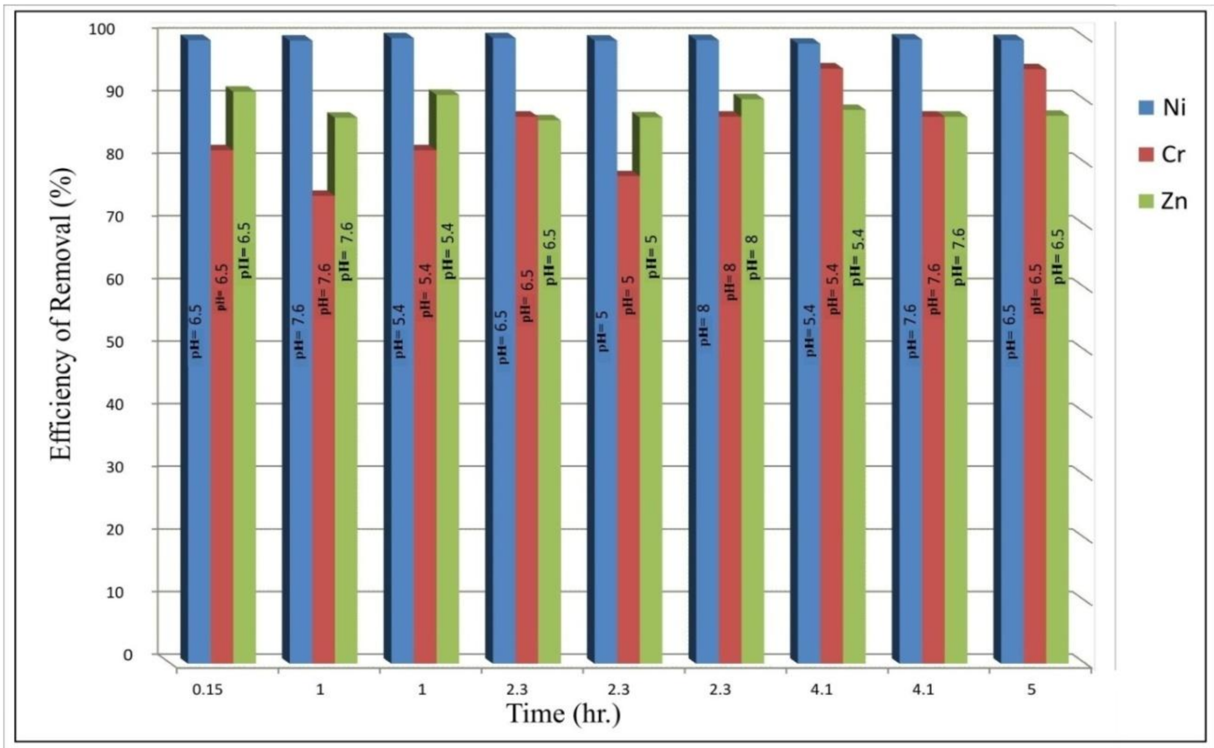

Figure 3- Effect of contact time on three heavy metals removal efficiency by corn cobs.

Contact time is inevitably a fundamental parameter in all transfer phenomena such as adsorption. Therefore, it is important to study its effect on the capacity of retention of chromium by plant wastes adsorbent [Srivastava VC, 2006]. Results obtained from current study considering the required time for adsorption was in accordance with the results of [18, 19 and 20]. But other studies have different results either less than one hour contact time [21, 22 and 23], and more than 1 h. contact time [24, 25].

From the results of present study it is possible to conclude the following subjects such as: Removal efficiency of corn cobs adsorbent have a significant ability in removal of zinc, chromium and nickel from industrial waste water and affected by various environmental factors such as pH and contact time according to Anova test. Additionally, corn cobs adsorbent showed a good and satisfactory reduction in values of TDS, TSS, TH, E.C and COD after treatment.

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