The removal of Zinc, Chromium and Nickel from industrial waste water using Rice husk

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Abstract

The aim of this study was to use low cost adsorbents, which consists of plant wastes in treatment of Industrial waste water by fixed bed column technique and study the effect of to two variables (pH value and contact time) on adsorption process. The sample of plant waste (Rice husk) 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 all tested plant adsorbents had significant heavy metal removal efficiency. The best removal efficiency 96.56% of Cr was occurred at pH 6.5 and 5hrs. Higher removal efficiency 99.02% of Ni was occurred at pH 6.5 and 0.15hr. While, lower removal efficiency 94% for Zn obtained at pH 5 and 2.83hrs. Removal efficiency for TDS, TSS and COD were 58.6%, 98.8% and 86.6% respectively.

Keywords: Rice husk, Adsorption, Zinc, Chromium, Nickel, Industrial waste water

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أزالة ألزنك وألكروم وألنيكل من مياه ألفضلة ألصناعية بأستخدام قشور ألرز[ألسبوس]

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ألخلاصة

أن ألهدف من هـ ذه ألدراسة هو أستخدام ألممتزات واطئة ألكلفة وألتي تشمل قشور ألرز 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 (قشور ألرز) لتحديد فعاليتها وألتي أعطت 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 96.56% للكروم عند pH 6.5 وزمن تلامس 5 ساعات، في حين أفضل أزالة وبكفاءة 99.09% كانت للنيكل عند pH 6.5 وبعد 0.15 ساعة، وأقل أزالة بلغت 94% كانت مع الزنك عند pH 5 وبعد 2.38 ساعة من ألتماس ، بينما كانت كفاءة الازالة للمواد ألصلبة الذائبة الكلية والمواد الصلبة ألعالقة الكلية ومتطلب ألاوكسجين ألكيميائي 58.6% و 98.8% و 86.6% على التوالي.

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Introduction

The term “waste water” properly means any water that is no longer wanted, as no further benefits can be derived out of it. About 99 % of waste water is liquid and only 1% are solid wastes. For the last three decades or so, the benefits of promoting waste water reuse as a means of supplementing water resources and avoidance of environmental degradation have been recognized by national governments. At low concentrations, some of the heavy metals stimulate some biological processes, but at a threshold concentration these become toxic. Being non biodegradable, these metals accumulate at various atrophic levels through the food chain and can cause human health problems [1]. In humans, non biodegradable these metals accumulate in living tissues and thus multiply the danger [2].

To prevent any health hazards caused by discharging waste water to water streams, the wastewater must be treated before discharge. Such treatment should comply with the terms of the legislation defining the characteristics of the effluent discharging into water streams. The concept of planning and development should be based on the criteria to protect land, water resources, aquatic life into streams and rivers and marine life from pollution and to safeguard public health as a high priority. The commonly used procedures for removing metal ions from aqueous streams include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction [3].

There are a lot of research work has been conducted using some traditional techniques of waste water treatment such as precipitation, ion exchange and adsorption. In general, these techniques use 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. The technique of plant residues for heavy metal ions adsorption was used worldwide for waste water treatment [4,5] such as peat and nut shells, coconut shells, tea waste, peanut hulls, almond shells, peach stones, citrus peels, and many others [6,7]. These adsorbent materials are consisted mainly of polysaccharides, proteins, and lipids, functional groups that can bind metal ions such as carboxyl, hydroxyl, sulphate, phosphate, and amino groups [8]. 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, the chemical state of the site(availability) and affinity between site and heavy metals (binding strength) [9]. Thus, this work is aimed to use low cost adsorbents, which consist of rice husk 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.

Materials and Methods

Industrial waste water samples were collected from pretreatment units of electroplating section in The State Company for Electrical Industries (SCEI**)**. Waste water sample were collected in the period lied between 4^{th} and 20^{th} of March 2012. The sample was divided into two sub-samples, the first was examined for chemical and physical analysis and the second was employed for removal of zinc, chromium and nickel ions. On the other hand, the rice husk was obtained from rice husking machine (rice peeling machine) located in As-suwayrah farms, south Baghdad.

Adsorption capacity of Rice husk

1- Chemical analysis of industrial waste water

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 [10] and heavy metals (Cr, Ni and Zn) content were estimated and recorded by atomic absorption spectroscopy in laboratory.

2- Preparation of Adsorbents

Adsorbents was selected for its cost effectiveness and ready availabile. Rice husk 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 rice husk was then placed in a large glass baking dish and dried at the room temperature. After that, the adsorbents (rice husk) 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 rice husk and corn cobs were dried in an oven at 125°C for 24 hrs. The sample was sieved by using 4 mm sieves and adsorbent particles were stored in precleaned plastic bottles and kept for future studies, [11].

3- Adsorption experimental studies

a- Laboratorial Column Design

The adsorption studies were carried out in transparent glass column with 5.0 cm internal diameter and 50 cm in height, figure-1. The adsorbents (Rice husk) 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 by a valve at the lower end of the column. Two containers were used as wastewater containers, the first one is a plastic container was used as waste water feed container (5 Liters) at the top of the column. The second one was a glass container (Beaker) used as a waste water reservoir (2 Liters) at the bottom of a column. The column was washed with de-ionized water before adsorption experiments. It filled with prepared Rice husk samples for industrial waste water samples for determine and estimate the efficiency of the adsorbent for treatment of industrial waste water according to certain parameters such as: pH value and Contact time.

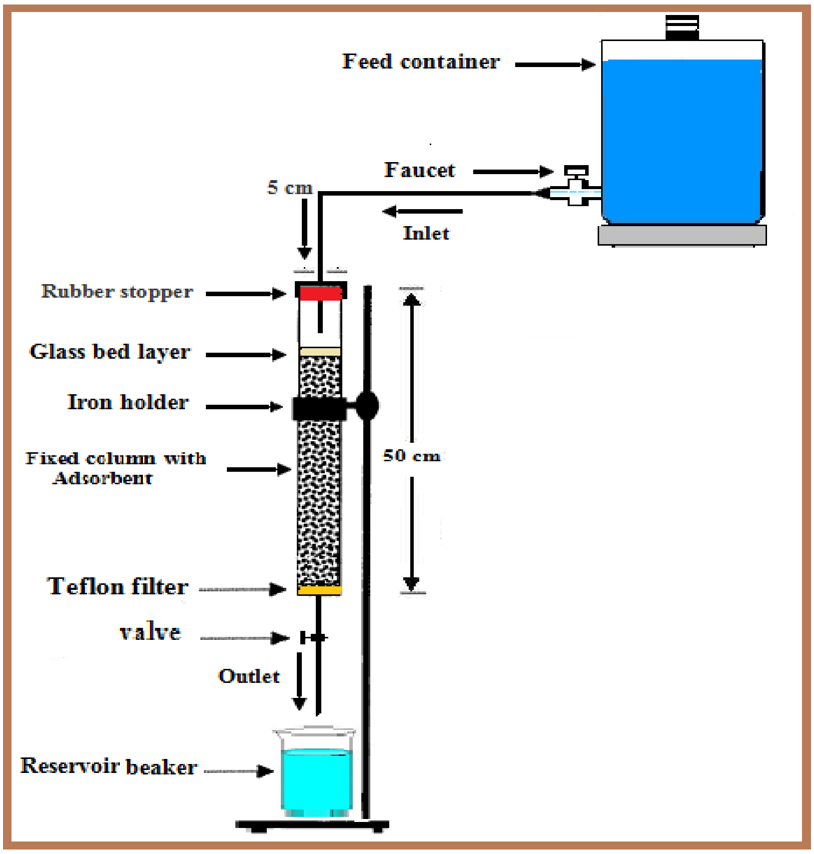

Figure 1- Schematic presentation of the experimental column.

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, results exhibited that the level of Cr, Ni and Zn were 145.66, 10.21, 20 ppm (mg/l) respectively. While samples collected after local treatment were 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) values 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 wastewater sample after treatment via Rice husk

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 6200, 320 and 200 ppm with removal efficiency reached 58.69, 86.6 and 98.8% respectively after treatment by rice husk. On the other hand, results of this experiment were compared with data of the electroplating treatment unit, table-1, it seems obvious that the results of measurements of waste water samples after treating via rice husk was considered fair, since values of TDS , COD and TSS were decreased to almost half after treatment by adsorbents **.**

Table 2- Chemical and physical measurements of industrial waste water after treatment by rice husk.

Examination	Unit	Remaining concentration after treatment by R. husk	ER (%) of Rice husk at pH.=6.5 & time:5 hr.	ER of pollutants by treatment unit in (SCEI)
TDS	ppm	6200	58.6	-13.3
TSS	ppm	200	98.8	-282.5
COD	ppm	320	86.6	-16.6

Adsorption experimental studies

The results in table-3, showed the adsorption experiment of heavy metals removal by rice husk that carried out by laboratorial column, figure-1. The results indicated ability of rice husk 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 $P \leq 0.05$.

Table 3- Removal and reduction the heavy metals by Rice husk.

parameters		Remaining concentration of heavy metals removal (ppm)		
pH	Time(hr.)	Ni	Cr	Zn
5.439	1.0	0.10	24.5	1.27
5.439	4.18	0.266	6.0	1.40
7.651	4.18	0.30	6.0	1.39
7.651	1.0	0.10	27.5	1.53
5	2.38	0.122	20.0	1.20
8	2.38	0.10	18.1	1.47
6.5	0.15	0.10	30.98	1.57
6.5	5	0.266	5.0	1.52
6.5	2.38	0.28	8.52	1.60

Table 4- Efficiency of heavy metals removal by adsorbents.

Parameters		Efficiency of Removal (%)		
pH	Time(hr.)	Ni	Cr	Zn
5.439	1.0	99.02	83.18	93.65
5.439	4.18	97.44	95.88	93.00
7.651	4.18	97.06	95.88	93.00
7.651	1.0	99.02	81.12	92.35
5	2.38	98.82	86.26	94.00
8	2.38	99.02	87.57	92.65
6.5	0.15	99.02	78.73	92.15
6.5	5	97.45	96.56	92.40
6.5	2.38	97.25	94.15	92.00
Means of *ER* (%)		**98.23**	**88.81**	**92.80**
SD		**0.84368**	**6.97340**	**0.67915**

It seems clearly that increasing pH values have significant effects upon the adsorption ability of rice husk on removal of Zn, Cr, and Ni from industrial waste water. Higher adsorption capacities occurred at pH 5.4 and 6.5 according to type of heavy metal in this study. A pH 6.5 showed highest adsorption efficiency for chromium and nickel at concentration of 5 and 0.1 ppm respectively, whilst pH 5 showed best adsorption capacity of zinc at concentration of 1.2 ppm. The removal efficiency at optimum pH of adsorbents reached 99.02, 96.56 and 94% for Ni, Cr and Zn respectively, table-3 and figure-2.

The current study is agreed with the study carried out by Abdullah and Prasad [12], they found that the adsorption of nickel increased when the pH was increased from 1 to 6 by using tamarind bark. Dong *et al* [13] reported that the best pH for the chromium adsorption was 5.5 by amino starch preparation and its adsorption for Cr (VI). Optimum pH for chromium and zinc adsorption was laid between 5 and 6 in case of using plant wastes [14].

Regarding contact time, rice husk exhibited high adsorption efficiency at a variable time from 0.15 to 2.38h. for nickel and zinc ions and 5h. for chromium ions. Therefore, these adsorbents were found to be different in the adsorption capacity of heavy metal ions namely; nickel, chromium and zinc ions respectively, table-2. Highest efficiency of heavy metals removal reached to 99.02 and 96.56% with Ni and Cr respectively, while the removal efficiency decreased to 94% with Zn at contact time ranged from 0.15 to 2.38 h, table-3 and figure-3.

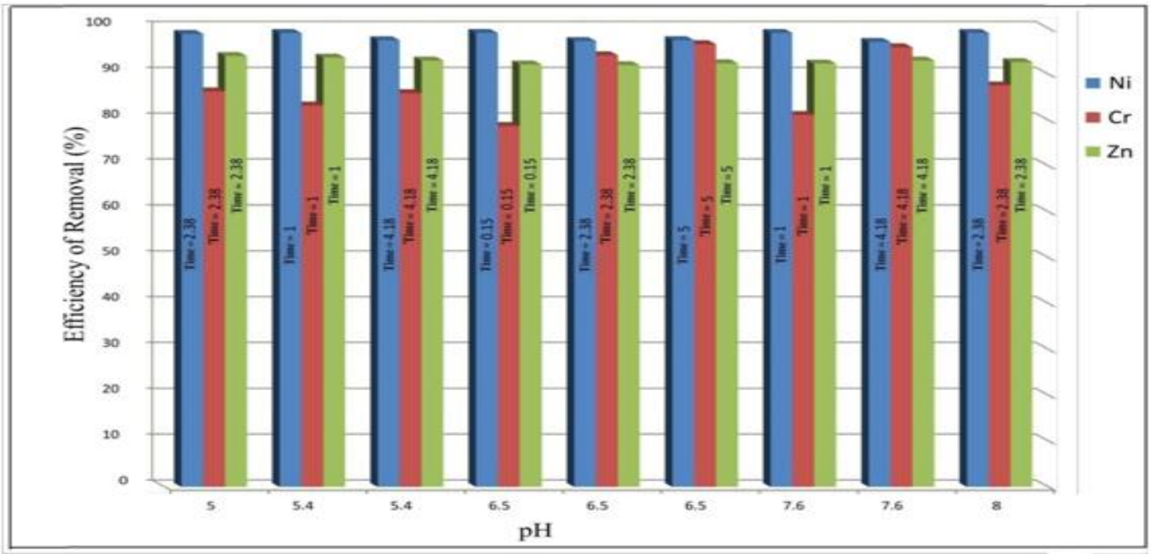

Figure 2- Effect of pH on three heavy metals removal efficiency by rice husk.

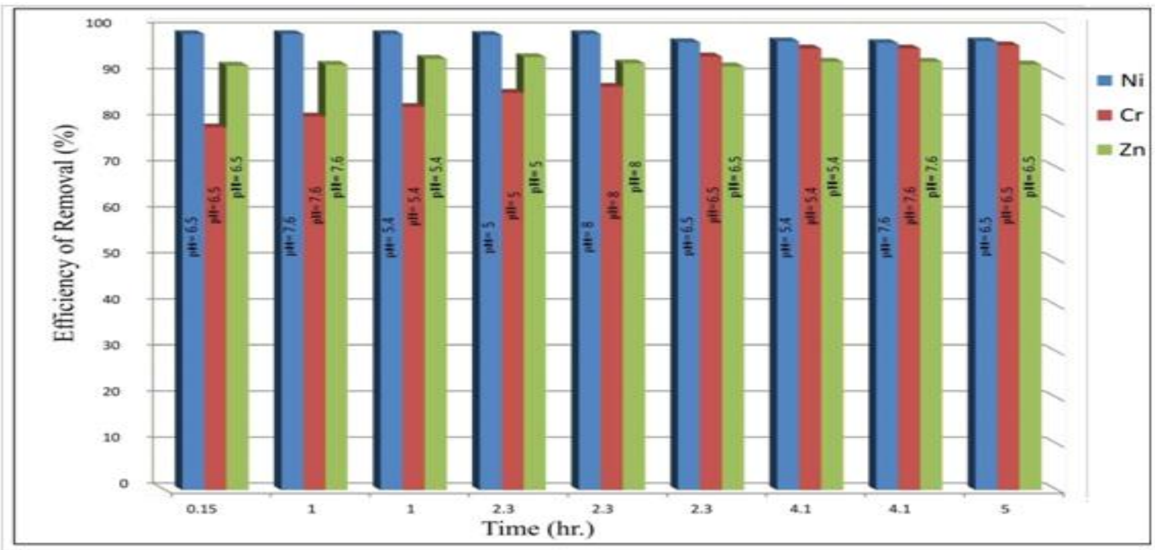

Figure 3- Effect of contact time on three heavy metals removal efficiency by rice husk.

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 [15-17]. But other studies showed different results either less than one hour contact time [18-20], and more than 1h. contact time [21, 22].

From the results of present study it is possible to conclude the following subjects such as: Removal efficiency of rice husk 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, rice husk adsorbent showed a good and satisfactory reduction in values of TDS, TSS, TH, E.C and COD after treatment.

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