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Research Article

Utilization of Iraqi Rice Husk in the Removal of Heavy Metals from Wastewater

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Abstract: This study deals with the potential of Iraqi Rice Husk (IRH) for the removal of nine heavy metal pollutants which are Al, As, Cd, Cr, Cu, Fe, Ni, Pb and Zn ions from industrial wastewater using different design parameters by the adsorption process. Samples were taken of the IRH remaining after being used for the removal of the nine metal ions above from aqueous solutions using different methods. One of these methods was the preparation of a promoted type Y-zeolite catalyst which was compared with normally type Y-zeolite catalyst prepared from IRH alone and tested in the process of n-heptane isomerization under different temperatures. Another method involved the study of IRH as a rodenticide directly without any pre-treatment. The results show that the promoted type Y-zeolite catalyst by Cd^{+2}, Cr^{+6}, Cu^{+2}, Fe^{+3}, Ni^{+2} and Zn^{+2} ions gives a higher conversion and better selectivity of n-heptane isomerization than the normal type Y-zeolite catalyst and the IRH which had previously adsorbed Al^{+3}, As^{+5}, Zn^{+2} and Pb^{+2} from an aqueous solution and also showed good behavior as a rodenticide.

Keywords: Adsorption, catalyst, heavy metal, residue, rice husk, wastewater, zeolite

INTRODUCTION

The greater environmental awareness in both the public and regulatory sphere in recent years has necessitated greater treatment of industrial effluent (Townsed, 2001). This interest has increased in recent years over the discharge of pollutants from industrial wastewater which have to be cleaned sufficiently to reach the standard values allowed of these pollutants before their discharge into the aquatic system (such as rivers) or into the sewer network. In the field of environmental pollution, there are few subjects that, during the latest years, have developed as rapidly as the study of toxic metals (Bhattacharya and Venkobachar, 1984). According to the World Health Organization (WHO), the metals of most immediate concern are Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg and Pb (3). It is apparent that the presence of a toxic metal may not represent a hazard if a threshold exists below which there are no observable effects. It should be noted that certain heavy metals, including Al, Cu, Cd, Fe, Pb, Mn and Ni are essential or beneficial or harmful in trace quantities (Kirk and Laster, 1984). The toxicity of a given heavy metal depends on the total amount ingested, the pH of the treated water as well as a number of other factors (Kasim, 1990). Heavy metal ions can arise from many sources such as industrial and municipal wastewater in the absence of effective treatment, urban runoff, rain water and agricultural fertilizer may be the most important sources of heavy metals in the aquatic environment. A large number of different industries produce effluents contaminated with heavy metal ions. Industries such as minerals and metallurgical processing, leather, textile, chemical manufacture, metal finishing and many other industries produce heavy metals in aqueous solutions as waste (Townsed, 2001). In this study the adsorption of heavy metals which are Al, As, Cd, Cr, Cu, Fe, Ni, Pb and Zn using Iraqi Rice Husk (IRH) was tested to endeavour to utilize the residue in a convenient, economical and eco-friendly way.

METHODOLOGY

Iraqi rice husk (adsorbent media): Iraqi rice husk was collected from the Al-Shanafia rice fields in Southern Iraq. The rice husk was washed three times with doubled distilled water. Excess distilled water was used to remove the soluble materials present in the rice husk brought in from the field and boiled to remove the color and other fine impurities that may be found in the rice husk and then dried at 105°C for 24 h. The adsorbent thus processed was used in its original size pieces. The surface area of Iraqi Rice Husk was measured by BET (Brunauer-Emmett-Teller nitrogen adsorption technique). The characteristics of the Iraqi Rice Husk are presented in Table 1. When the Iraqi Rice Husk was heated at 105°C in an oven, most of the water was removed while the second major mass loss of about 45-65% was attributed to the breakdown of cellulose constituent char, which is a carbonaceous residue.

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Table 1: Characterization properties of Iraqi rice husk

Chemical composition	
Compound	Composition wt %
SiO_2	90.700
Al_2O_3	0.130
Fe_2O_3	0.060
TiO_2	0.015
CaO	0.610
MgO	0.250
Na_2O	0.090
K_2O	2.640
P_2O_5	0.730
LOI	4.710
S.A (m^2/g)	57.500

Table 2: Heavy metals and their salts

Heavy metal	Salt of heavy metal used
Al	AlK (SO_4) $2.12H_2O$
As	$Na_2HAsO_4.7H_2O$
Cd	$CdSO_4.8H_2O$
Cr	$K_2Cr_2O_7$
Cu	$CuSO_4.5H_2O$
Fe	$FeSO_4.7H_2O$
Ni	$NiSO_4.6H_2O$
Pb	Pb $(NO_3)^2$
Zn	$ZnSO_4.7H_2O$

Table 3: Experimental results of final percentage removal of heavy metals after reusing the Iraqi rice husk

Heavy metal	Final percentage removal reached after reuse %	Times of repeated use
Al	7.50	10
As	11.25	8
Cd	3.50	11
Cr	5.00	13
Cu	9.00	11
Fe	10.00	9
Ni	13.00	8
Pb	6.50	5
Zn	8.00	9

Stock solutions: In order to avoid interference from other elements that may be present in the wastewater, the experiments in this study were carried out using a simulated synthesized aqueous solution of different heavy metals. An amount of 1000 mg/L stock solution of each heavy metal ion was prepared by dissolving a known weight of each heavy metal salt in 1 L of double distilled water as shown in Table 2. All solutions used in the experiments were prepared by diluting the stock solution with double distilled water to the desired concentration for the experimental work of this investigation. The heavy metal ion concentrations were measured using a spectrophotometer thermo-Genesys 10 UV, USA.

Sorption unit: A fixed bed column of continuous mode experiments were conducted in order to test the removal of heavy metal (Al, As, Cd, Cr, Cu, Fe, Ni, Pb and Zn) ions by a treated simulated synthesized aqueous solution of the above heavy metals. Each one of the heavy metals was set at the desired concentration with various bed heights of the adsorbent media (Iraqi Rice Husk) using different flow rates of the simulated synthesized aqueous solution at various pH.

The pH value was adjusted using 0.1 N NaOH and 0.1 N HCl solutions. The sorption unit consisted of two glass containers of simulated synthesized aqueous solution of a selected heavy metal ion, one for the inlet and another for the outlet with each having a capacity of 1 L. The glass column had a 2.54 cm internal diameter and 100 cm height. The sorption column was packed with adsorbent media to a height of (10, 20, 30, 40, 50, 60 and 70 cm, respectively) supported from the top and the bottom by a glass hollow cylinder layer, each cylinder having a 0.5 cm internal diameter and was 1 cm long with a thickness of 0.1 cm. Before starting the runs, the packed bed sorption column was rinsed by a double distilled water flow down through the column.

The Iraqi rice husk as the media was packed in the column to the desired depth and fed as slurry by mixing the media with distilled water in order to avoid the formation of air bubbles. After the packed bed sorption column was filled by the required amount of adsorbent media, the adsorption process started by allowing the heavy metal simulated synthesized aqueous solution at the required concentration and pH to flow down by gravity through the sorption column from the inlet container at a precise flow rate in experiment which is adjusted by a valve.

To determine the best operational conditions, the experiments were carried out at temperatures between 20 and 45°C and various pH values between 1 and 8. Also the initial feed concentrations were applied of the simulated synthesized aqueous solution of each selected heavy metal ion of between 5 and 50 mg/L and at different flow rates between 5 and 50 mL/min for each heavy metal initial feed concentration. Outlet samples after treatment in each experiment were collected every 10 min from the bottom of the packed column and the un-adsorbed concentration of heavy metal ions in the aqueous solution was analyzed by using a spectrophotometer.

Reusability of Iraqi rice husk: In order to check the reusability of the sorbent media, the treated Iraqi rice husk containing different heavy metals was firstly dried at 105°C and then tested again in the sorption unit under the conditions of the experiment that gave the best percentage removal of heavy metal ions from the aforementioned aqueous solution. The capacity of the sorbent for reuse was found to decrease until it became constant at a particular percentage of removal after a different number of times of repeated use as shown in Table 3. The particular percentage removal and the number of repeated uses were found to be dependent on the heavy metal. Thus multiple uses of the sorbent was seen to be feasible.

Tests with real wastewater solution: The ability of Iraqi rice husk to adsorb heavy metal ions from real wastewater solution was tested in the sorption unit under the experimental conditions that gave the best

Table 4: Experimental results of heavy metal removal using heavy metal aqueous solution and using real wastewater containing all the heavy metals together

Heavy metal	% removal using aqueous solution of individual heavy metal	% removal using real wastewater solution with all heavy metals
Al	96.24	48.77
As	95.78	44.36
Cd	96.21	39.09
Cr	98.73	46.36
Cu	95.75	50.17
Fe	97.61	45.78
Ni	95.82	47.98
Pb	97.05	34.87
Zn	96.33	49.76

removal of heavy metal ions from the aforementioned simulated aqueous solution. The results show that the removal efficiency for the real wastewater solution which contained all the heavy metals is different from the removal efficiency obtained when using the simulated synthesized aqueous solution for each selected heavy metals when tested individually. The experimental results obtained using the real wastewater solution containing all the heavy metals together and using the simulated synthesized aqueous solution of each selected heavy metal is summarized in Table 4.

Mathematical model: Fixed bed dynamics are described by a set of convection-diffusion equations, coupled with source terms due to adsorption and diffusion inside adsorbent particles. Inside the particle, molecules of adsorbate diffuse into the inner portions of the particle via surface diffusion, pore diffusion, or both. The solution of these equations will give rise to a prediction of the required concentration distribution. The focus of this investigation is to gain an understanding of the mechanism of both surface diffusion and pore diffusion. To formulate a generalized model corresponding to the dispersion flow as well as the surface diffusion and pore diffusion mechanism, the following assumptions are made:

- The system operates under isothermal conditions.
- The equilibrium of adsorption is described by the Langmuir isotherm.
- Intra-particle mass transport is due to Fickian diffusion and it is characterized by the pore diffusion coefficient, Dp and the surface diffusion, Ds.
- Mass transfer across the boundary layer surrounding the solid particles is characterized by the external-film mass transfer coefficient, kf.
- Film transfer resistance exists for mass transport from the mobile to the stationary phase.
- Local adsorption equilibrium exists between the adsorbate adsorbed onto the adsorbent surface and the adsorb ate in the intra-particle stagnation fluid.
- Both surface and pore diffusion are included in the mass transport mechanism.
- There is axial dispersion.

Simulation technique: The equations used in the simulation technique represent a set of simultaneous, nonlinear, Partial Differential Equations (PDEs) that can be solved numerically. The discretatization was applied to the space coordinates (Z and r) to convert the Proper Orthogonal Decomposition (PODs) to a set of Ordinary Differential Equations (ODEs). The resulting ODEs can be solved using an existing ODE solver provided by MATLAB (Rahman *et al.*, 2009).

RESULTS AND DISCUSSION

The ability of Iraqi Rice Husk to remove heavy metal ions from the simulated synthesized aqueous solution in a continuous mode fixed bed column with various parameters, namely the pH of the simulated synthesized aqueous solution of the selected heavy metal ion (pH), the height of the bed of adsorbent media (Iraqi Rice Husk) (h), the flow rate of the simulated synthesized aqueous solution (F), the temperature of the simulated synthesized aqueous solution (T_{feed}) and the time of treatment (t) was investigated. The experiments were undertaken by varying all the above parameters for different initial concentrations (C_o) of selected simulated synthesized aqueous solutions of heavy metals tested individually. The results thus obtained are explained below.

Effect of initial concentration: The results show that using IRH adsorbent material, the percentage removal of individual heavy metal ions decreased when the initial Concentration (Co) of the simulated synthesized aqueous solution of the individual heavy metal ions was increased with the other variables held constant as shown in Fig. 1 and 2. This can be explained by the fact that the initial concentration of the heavy metal ions had a restricting effect on the removal capacity whilst simultaneously the adsorbent media had a limited number of active sites, which would have become saturated at a certain concentration. This led to an increase in the number of heavy metal ion molecules competing for the available function groups on the surface of the adsorbent material. Since a solution with a lower concentration has a smaller amount of heavy metal ions than a solution with a higher concentration, so the percentage removal decreased with increasing initial concentration of the individual heavy metal ions. For the IRH adsorbent media, the highest percentage

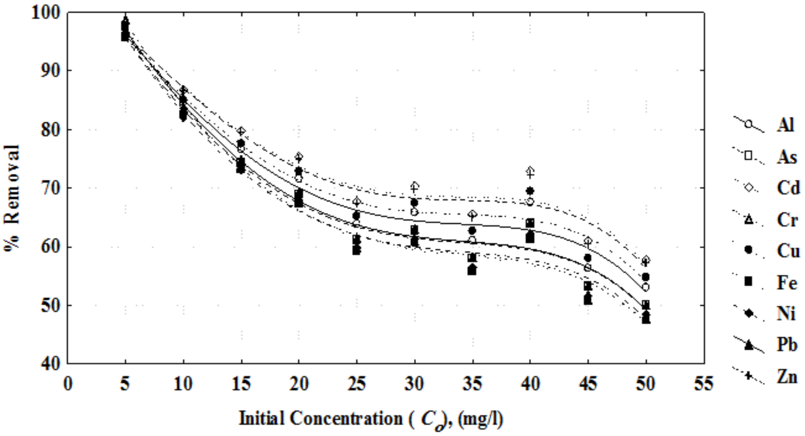

Fig. 1: Effect of initial concentration (C_o) on the percentage removal of different heavy metal ions @ Tf = 45°C, hb = 0.7 m, t = 60 min and F = 5 mL/min

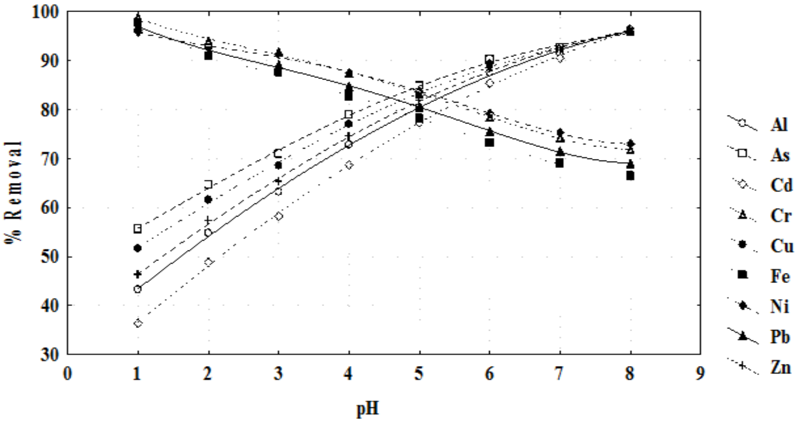

Fig. 2: Effect of pH on the percentage removal of different heavy metal ions @ C_o= 5 mg/L, Tf = 45°C, hb = 0.7 m, t = 60 min and F = 5 mL/min

removal were 96.24, 95.78, 96.21, 98.73, 95.75, 97.61, 95.82, 95.05 and 96.33% for heavy metals Al, As, Cd, Cr, Cu, Fe, Ni, Pb and Zn respectively, at an initial heavy metal ion concentration of 5 mg/L. Thus the IRH adsorbent material was found to be efficient for removal of heavy metal ions from the simulated synthesized aqueous solution and from the wastewater.

Effect of pH: The results show that using IRH adsorbent material, the percentage removal of the heavy metals Cr, Fe, Ni and Pb ions when tested individually decreased when the pH of the simulated synthesized aqueous solution of the heavy metal ions increased when all the other variables were held constant. However, the percentage removal of the heavy metals Al, As, Cd, Cu and Zn ions when tested individually tended to increase when the pH of the simulated synthesized aqueous solution of the heavy metal ions increased when all the other variables were held constant as shown in Fig. 2. It is well recognized that the pH of the aqueous solution is an important parameter that affects the adsorption of heavy metal ions (Cayllahua and Torem, 2010). The high adsorption of the heavy metals Cr, Fe, Ni and Pb ions when tested individually at a low pH can be explained both in terms of the species of the metal and the adsorbent surface. In this case, at a low pH, i.e., acidic conditions, the surface of the IRH adsorbent becomes highly protonated and favors the adsorption of the above group of heavy metals in their anionic form. With increasing pH of the aqueous solution, the degree of protonation of the surface reduces gradually and hence the adsorption decreases (Selvi *et al*., 2001).

Furthermore, as the pH increases there is competition between the hydroxide ions (OH^-) and the metal ions, the former being the dominant species at higher pH values. The net positive surface potential of the sorbent media decreases, resulting in a reduction in the electrostatic attraction between the (sorbent) metal ion species and the (sorbate) IRH adsorbent material surface, with a consequent reduced sorption capacity which ultimately leads to a decrease in the percentage

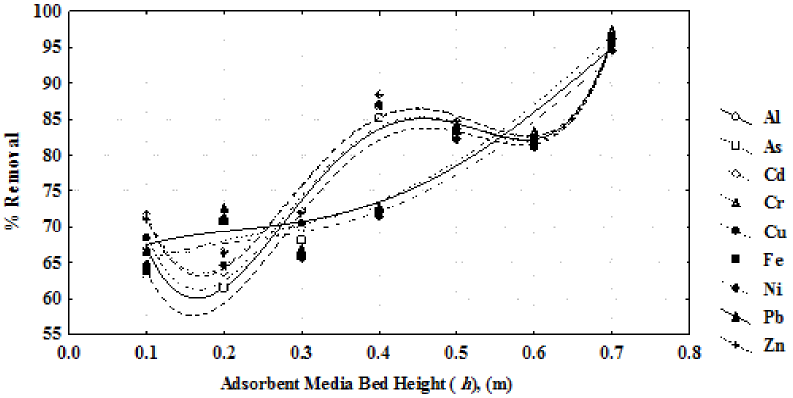

Fig. 3: Effect of adsorbent media bed height (h_b) on the percentage removal of different heavy metal ions @ C_o= 5 mg/L, T_f = 45°C, t = 60 min and F = 5 mL/min

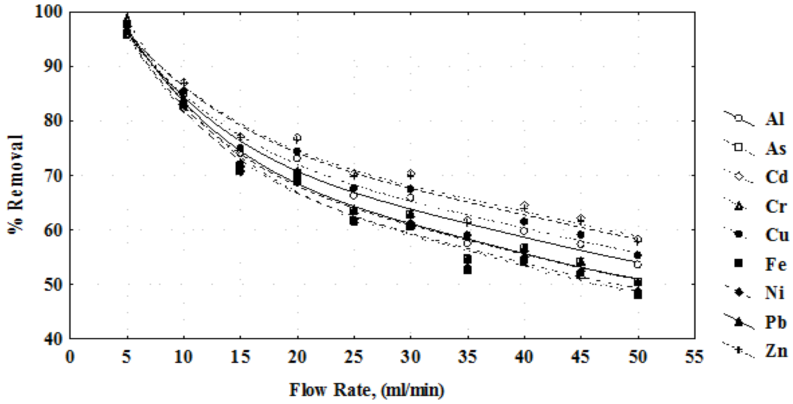

Fig. 4: Effect of aqueous solution flow rate (F) on the percentage removal of different heavy metal ions @ C_o= 5 mg/L, T_f = 45°C, h_b = 0.7 m and t = 60 min

adsorption of metal ions (Hamadi *et al*., 2001). On the other hand, the adsorption of the separate heavy metals Al, As, Cd, Cu and Zn ions when tested individually can be explained by the ion-exchange mechanism of sorption in which an important role is played by the functional groups that have cation exchange properties. In this case at lower pH values, the metal ion removal was inhibited, possibly as a result of the competition between hydrogen and the metal ions for the sorption sites, with an apparent preponderance of hydrogen ions, which restricts the approach of metal cations as a consequence of the repulsive force. As the pH increases, the ligand functional groups in the IRH adsorbent media are exposed, thus increasing the negative charge density on the adsorbent material surface, which increases the attraction of the metallic ions with a positive charge and allowing the sorption onto adsorbent material surface.

Effect of adsorbent media bed height: The results indicated that when the IRH adsorbent media bed height was increased, the percentage removal of all heavy metal ions when tested individually also increased while all the other variables were held constant as shown in Fig. 3. The increase in the bed height (h) meant an increase in the amount of adsorbent media, thus increasing the surface area of adsorbent material available. This in turn increased the number of active sites in the adsorbent material surface i.e., an increase in the availability of binding sites for adsorption and consequently increasing the heavy metal ion removal capacity of the Iraqi rice husk. This leads to an increase in the ability of the IRH adsorbent media to adsorb a greater amount of heavy metal ions from the simulated synthesized aqueous solution at different initial concentrations and ultimately the percentage removal of all the heavy metal ions also increased when tested individually.

Effect of flow rate: The results illustrate that when the flow rate of the simulated synthesized aqueous solution of heavy metal ions was increased, the percentage removal of the heavy metal ions tended to decrease when tested individually with all the other variables held constant as shown in Fig. 4. This may be due to the fact that when the flow of the simulated

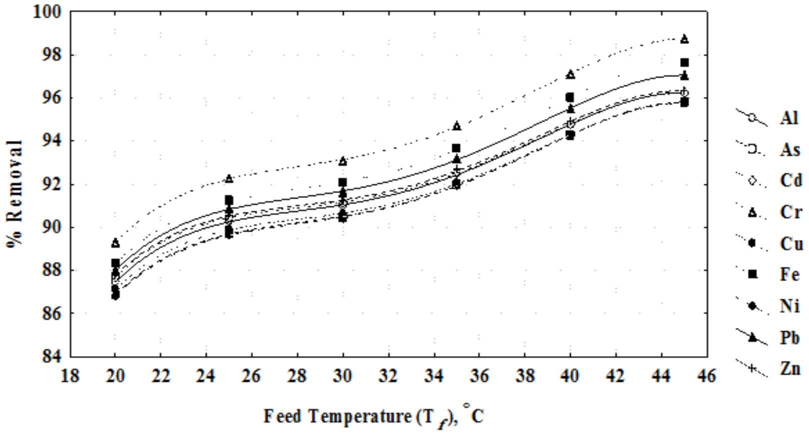

Fig. 5: Effect of feed temperature (T_f) on the percentage removal of different heavy metal ions @ C_o= 5 mg/L, h_b = 0.7 m, t = 60 min and F = 5 mL/min

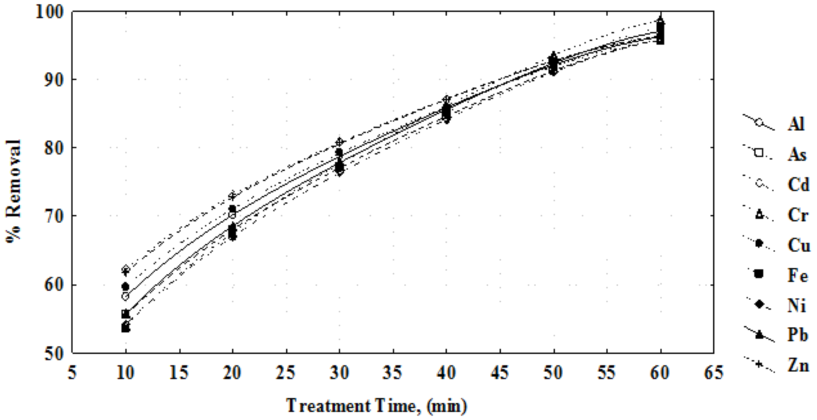

Fig. 6: Effect of treatment time (t) on the percentage removal of different heavy metal ions @ C_o= 5 mg/L, T_f = 45°C, h_b = 0.7 m, and F = 5 mL/min

synthesized aqueous solution of the heavy metal ions increased, the velocity of the solution in the column packed with the IRH adsorbent media increased as well. Hence the solution spent a shorter time in the column than the time spent at a low flow rate. When a low flow rate is applied, the simulated synthesized aqueous solution of heavy metal ions resides in the column for a longer time and therefore undergoes more contact time with the adsorbent media. So for a high flow rate the adsorbent media uptake will be a low amount of heavy metal ions from simulated synthesized aqueous solution and therefore the percentage removal of heavy metal ions decreases when the flow rate increases.

Effect of feed temperature: The results demonstrate that when the temperature of the feed consisting of simulated synthesized aqueous solution of heavy metal ions increased, the percentage removal of heavy metal ions also increased when tested individually with the other variables held constant as shown in Fig. 5. The effect of temperature is fairly common which causes an increase in the mobility of the metal cations. Furthermore, increasing the temperature may produce a swelling effect within the internal structure of the IRH adsorbent media thus enabling the heavy metal ions to penetrate further. It is indicated that the heavy metal ion adsorption capacity increases with increasing feed temperature from 5 to 45°C. This effect may be due to the fact that at higher temperatures an increase in active sites occurs due to bond rupture.

Effect of treatment time: The results indicate that when the treatment time of the simulated synthesized aqueous solution of heavy metal ions increases the percentage removal of heavy metal ions also increases when tested individually with all other variables held constant as shown in Fig. 6. This may be due to the fact that when the time of treatment of the simulated synthesized aqueous solution of heavy metal ion increases and the velocity of the solution in the column packed with the IRH adsorbent material remains

Table 5: Statistical equations of heavy metal ion removal using Iraqi rice husk

Heavy metal	Equation	(R^2)
Al	$\%R = 1.5925 \times 10^{-4} \left(\frac{T_f . P . h_b . Cp_{sol} . t}{F . d . C_o . g}\right)^{0.164} (pH)^{0.280}$	0.942
As	$\%R = 6.2333 \times 10^{-5} \left(\frac{T_f . P . h_b . Cp_{sol} . t}{F . d . C_o . g}\right)^{0.188} (pH)^{0.157}$	0.943
Cd	$\%R = 8.3758 \times 10^{-4} \left(\frac{T_f . P . h_b . Cp_{sol} . t}{F . d . C_o . g}\right)^{0.127} (pH)^{0.363}$	0.958
Cr	$\%R = 1.7366 \times 10^{-5} \left(\frac{T_f . P . h_b . Cp_{sol} . t}{F . d . C_o . g}\right)^{0.221} (\frac{1}{pH})^{0.053}$	0.965
Cu	$\%R = 4.2030 \times 10^{-4} \left(\frac{T_f . P . h_b . Cp_{sol} . t}{F . d . C_o . g}\right)^{0.148} (pH)^{0.192}$	0.968
Fe	$\%R = 1.9919 \times 10^{-5} \left(\frac{T_f . P . h_b . Cp_{sol} . t}{F . d . C_o . g}\right)^{0.218} (\frac{1}{pH})^{0.085}$	0.954
Ni	$\%R = 4.3199 \times 10^{-5} \left(\frac{T_f . P . h_b . Cp_{sol} . t}{F . d . C_o . g}\right)^{0.202} (\frac{1}{pH})^{0.031}$	0.968
Pb	$\%R = 6.8336 \times 10^{-5} \left(\frac{T_f . P . h_b . Cp_{sol} . t}{F . d . C_o . g}\right)^{0.193} (pH)^{0.064}$	0.947
Zn	$\%R = 8.3147 \times 10^{-4} \left(\frac{T_f . P . h_b . Cp_{sol} . t}{F . d . C_o . g}\right)^{0.132} (pH)^{0.248}$	0.955

%R: Percentage removal of heavy metal ions form aqueous solution; T_f: Feed temperature, (K); P: Pressure, (Pa); h_b: Adsorbent material bad height, (m); C_{Psol}: Heat capacity of aqueous solution, (J/g. K); F: Aqueous solution flow rate, (m^3/s); d: Internal diameter of sorption column, (m); C_o: Initial concentration of heavy metal ion, (g/m^3); t: Treatment time, (s); g: Acceleration of gravity, (m/s^2)

constant, the solution spends a longer time in the column than when the time of treatment is decreased.

So the IRH adsorbent material can uptake a greater amount of heavy metal ions from the simulated synthesized aqueous solution, therefore, the percentage removal of heavy metal ions from the aqueous solution increases.

Statistical model: A statistical model was developed for the experimental results obtained in this study. Regression Analysis and the π Theorem were adopted to determine a relation between the percentage removal of different heavy metal ions and the feed temperature, flow rate, pressure, pH of the feed solution, initial concentration of heavy metal ions, IRH adsorbent media bed height, treatment time and column diameter. These relations are shown in Table 5, which has a correlation coefficient (R^2) as explained.

UTILIZATION OF IRAQI RICE HUSK AFTER USE

A large amount of Iraqi rice husk remained over after using it for the removal of heavy metal ions from the simulated synthesized aqueous solution as explained above. Utilization of the used Iraqi rice husk can be achieved in different ways:

Employment of used Iraqi rice husk as a raw material to prepare promoted zeolite type Y catalyst: Iraqi rice husk waste which had previously adsorbed Cd^{+2}, Cr^{+6}, Cu^{+2}, Fe^{+3}, Ni^{+2} and Zn^{+2} ions from aqueous solutions under different operating conditions were segregated and classified separately according to the content of the above heavy metal ions. These samples were utilized as raw material in the synthesis of promoted catalyst used in n-heptane isomerization which is zeolite type Y. The samples gave different ratios of heavy metal ions to Iraqi rice husk. The ratios were between 0.05 to 5.5 wt % for Cd, Cr, Cu, Fe, Ni and Zn ions when tested individually. The used Iraqi rice husk with different heavy metal ion ratios was firstly treated with 10% phosphoric acid (H_3PO_4) for 24 h for preliminary removal of all impurities.

Then the samples were washed with double distilled water, filtered, dried in air and calcined at 750°C for 6 h. An amount of 12 g of calcined Iraqi rice husk was then subjected to dissolution in sodium hydroxide NaOH (4 M) followed by refluxing at 90°C for 12 h. After that concentrated hydrochloric acid (HCl 37%) was added to the aforementioned base dissolved Iraqi rice husk for complete precipitation. The Iraqi rice husk samples were filtered, washed with excess distilled water to be free from chloride ions and finally dried in an oven at 120°C for 6 h. Zeolite type Y was synthesized using prepared Iraqi rice husk as described above as a silica source in the following method. A 500 mL Teflon beaker containing a magnetic stirrer was washed with deionized water. Sodium hydroxide of 1.6616 g was added slowly to deionized water and stirred until clear and a homogenous solution appeared after about 5 min. The aqueous solution of sodium hydroxide was ready for the preparation of seed gel. The gel was prepared according to the following molar chemical composition: 10.67 Na_2O: Al_2O_3: 10 SiO_2: 180 H_2O.

Two millilitres aqueous solution of sodium hydroxide was added to 0.7515 g sodium aluminate oxide until a homogenous mixture was formed; 1.5361 g of Iraqi rice husk prepared as above was added separately to 5.5 mL aqueous sodium hydroxide until homogenously mixed. Both of the preparations were heated under vigorous stirring to obtain a homogenous mixture. The sample was aged for 24 h at room temperature in the Teflon bottle. The aluminate and silicate solutions were mixed together in the

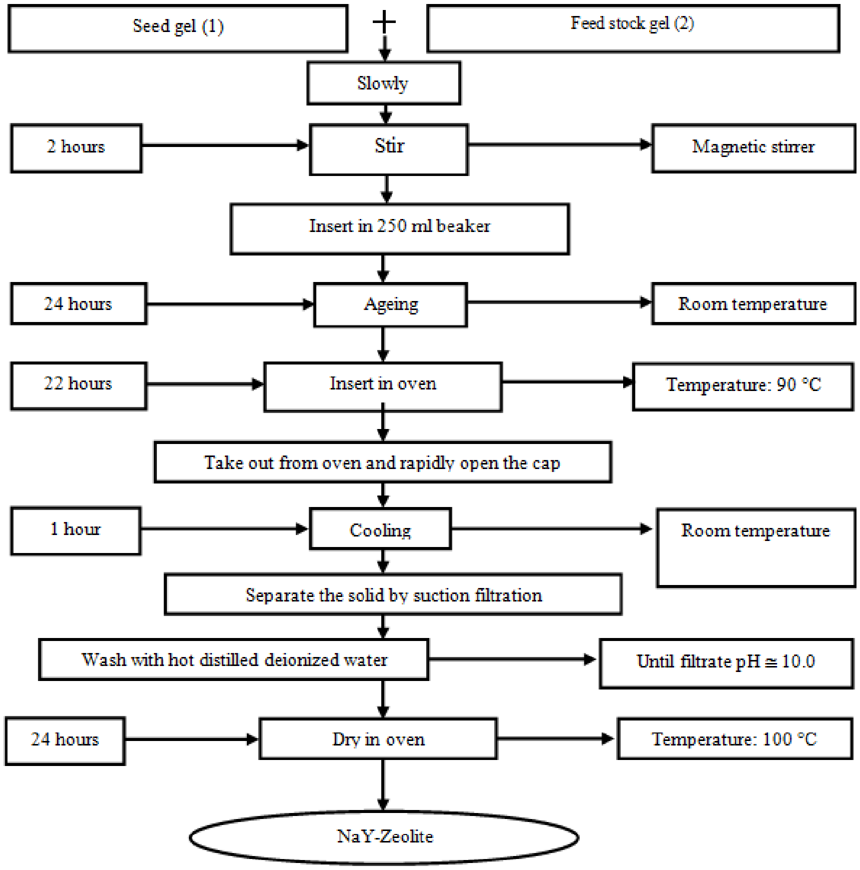

Fig. 7: Flow chart of the synthesis of type Y-Zeolite catalyst using Iraqi rice husk (Rahman *et al*., 2009)

polypropylene beaker, subsequently stirred for 2 h with the purpose of making it completely homogenized.

This combined solution was used as the feed stock gel (Rahman *et al*., 2009; Mohammed *et al*., 2008). The flow chart of the process is shown in Fig. 7. The synthesized zeolite type Y which was in sodium (Na$^+$) powder form, mixed with 15% montmorillonite clay as a binder then mixed with water to form a paste. A spherical shape (0.5 cm) was formed and dried overnight at 110°C. In order to make a promoted catalyst ready for testing in any process, a hydrogen zeolite (H-zeolite) form must be prepared. The M-HY-zeolite (where M is one of heavy metal ions used) was prepared by exchanging Na$^+$ ions in the sodium form zeolite type Y with ammonium chloride solution NH$_4$Cl. In order to obtain the ideal degree of ion exchange the technique of multi-steps (repeating three times) was used. Thus, in the first step, 2N of ammonium chloride solution (26.75 g of NH$_4$Cl in 250 mL of distilled water) contacted with 90 g of prepared M-NaY-zeolite and stirred for 2 h. In the second step, the procedure from the first step was repeated under the same conditions but using about 60 g of zeolite taken from the total zeolite amount produced in the first step.

Finally, in the third step, the procedure was repeated again using the same conditions but with about 30 g of zeolite taken from the total zeolite amount produced in the second step. The exchanged ammonia zeolite was filtered off, washed with deionized water to be free of chloride ions and dried overnight at 120°C and then calcined initially at 150°C for 2 h. The temperature was increased by 75°C/h until it reached 550°C at which point it was held constant for 5 h at this temperature. During calcinations, ammonia and water were liberated and promoted zeolites which are Cd^{+2}HY-zeolite, Cr^{+6}HY-zeolite, Cu^{+2}HY-zeolite, Fe^{+3}HY-zeolite, Ni^{+2}HY-zeolite and Zn^{+2}HY-zeolite were formed (Sherman *et al*., 1978).

Catalytic activity of synthesized catalysts: The catalytic activity of the synthesized promoted zeolite type Y catalysts was studied by applying the n-heptane isomerization reaction which was carried out in a laboratory isomerization unit shown in Fig. 8 and 9. This is achieved in a packed bed catalytic reactor of a laboratory isomerisation unit. The n-heptane was supplied by Sigma Aldrich Co. and used as a raw material for the isomerization process. The isomerization of n-heptane experiments were carried

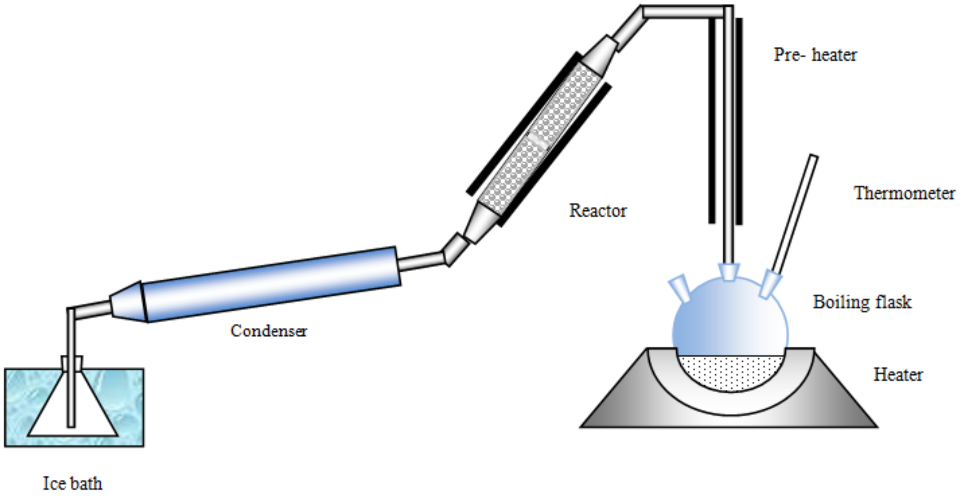

Fig. 8: Isomerization unit (Jawad, 2009)

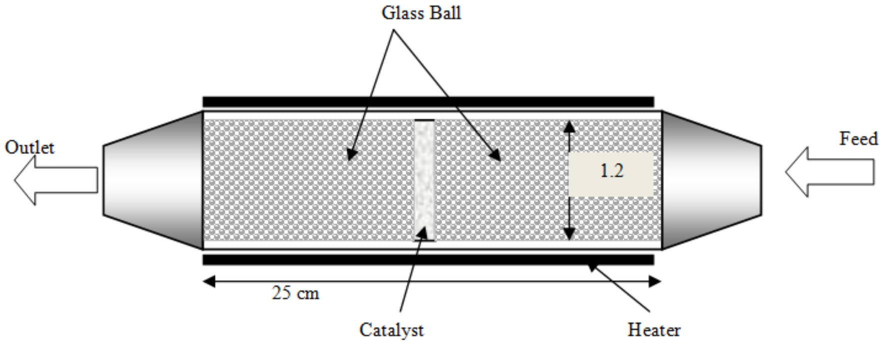

Fig. 9: Isomerization unit reactor (Jawad, 2009)

out in a laboratory isomerization unit at a temperature range of 300 to 400°C and atmospheric pressure for different quantities of prepared zeolite type Y catalysts. The n-heptane is evaporated at its normal boiling point which is 98.5°C and by pre-heating the vapour before passing into the reactor which contains a known quantity of prepared zeolite type Y catalyst sample between two layers of glass wool and glass balls. The product vapour is cooled in the condenser and condensed in an ice bath. After that samples of the product are collected to be tested by a Gas Chromatography device (GC) (Dani, Model GC 1000 DPC).

The isomerization results of n-heptane over six prepared zeolite type Y catalysts are given in Table 6. The results listed in Table 6 were calculated using Eq. (1) based on the concentration of n-heptane in the output of the reactor measured by gas chromatography GC investigation with corresponding input of 99% n-heptane purity:

$$Conversion\ (wt\%) = \frac{(Initial\ weight\ of\ n-heptane)-(final\ weight\ of\ n-heptane)}{(Initial\ weight\ of\ n-heptane)} \quad (1)$$

Employment of used Iraqi rice husk as a rodenticide: Iraqi rice husk waste which had previously adsorbed Al^{+3}, As^{+5}, Zn^{+2} and Pb^{+2} ions from aqueous solutions under different operating conditions were segregated and classified according to their content of the above heavy metal ions tested individually and utilized as a rodenticide without any further treatment. The samples contained different ratios of heavy metal ions to Iraqi rice husk. The ratios were between 0.05 to 5.5 wt % for Al^{+3}, As^{+5}, Zn^{+2} and Pb^{+2} ions with each one tested separately.

Before the treated Iraqi rice husk waste containing the above heavy metals were given to the rats, the rats were kept as normal for one week and fed with normal feed to make sure that the rats were not suffering from anything that could lead to death. After that the rats were fed with treated Iraqi rice husk waste containing Al^{+3}, As^{+5}, Zn^{+2} and Pb^{+2} ions with each one tested individually. The results indicate the fate of the rats over different periods as shown in Table 7. Inorganic pesticide is one of the most important types of pesticide used in rodent control and perhaps the most important components used in this field are zinc, arsenic, lead, phosphorus, fluorine and aluminium inorganic

Table 6: n-heptane isomerization using prepared zeolite catalysts @ 350°C

Catalyst of heavy metal ions to Iraqi rice husk ratio (0.5%)	Substances (wt %)								
	Propane	Butane	Isobutane	2, 4-dimethyl pentane	2, 3-dimethyl pentane	2-methyl hexane	3-methyl hexane	n-heptane (isomerizes)	n-heptane (un-reacted)
HY-zeolite	3.11	1.65	2.03	-	-	-	0.66	7.45	92.55
Cd^{+2}HY-zeolite	1.17	2.29	2.41	3.10	7.14	3.13	3.71	22.95	77.05
Cr^{+6}HY-zeolite	1.58	1.16	2.42	4.17	22.79	6.98	4.36	43.46	56.54
Cu^{+2}HY-zeolite	2.70	1.71	2.70	3.20	7.56	3.42	3.62	24.91	75.09
Fe^{+3}HY-zeolite	1.43	1.51	0.96	3.29	22.01	6.15	4.02	39.37	60.63
Ni^{+2}HY-zeolite	2.33	0.49	0.93	1.20	7.72	1.55	1.49	15.71	84.29
Zn^{+2}HY-zeolite	2.78	0.13	0.20	2.51	7.89	1.57	1.24	16.32	83.68

Table 7: Hours taken to kill a rat when fed with treated Iraqi rice husk

	Heavy metal ions (Al^{+3}, As^{+5}, Zn^{+2} and Pb^{+2}) to Iraqi rice husk ratio (wt %)								
Heavy metal ion adsorbed on Iraqi rice husk	0.05	0.5	1	2	3	4	4.5	5	5.5
Aluminium, (Al^{+3})	-	-	122	72	36	24	16	14	10
Arsenic, (As^{+5})	144	96	72	36	24	18	8	6	3
Zinc, (Zn^{+2})	-	192	122	72	40	20	13	10	6
Lead, (Pb^{+2})	168	96	80	48	26	18	9	7	3

compounds. There are several ways to use these pesticides, which can be applied by spraying vegetative plants in places where rodents pass whereby the pesticide enters the mouth of the rodent when it cleans itself, or through mixing with materials that are attractive to rodents such as rice husk or bread or vegetables pieces. Characterized compounds of this rodenticide have been used successfully to combat the rodent menace. These compounds are used as infectious toxins for their secured effectiveness and severity of toxic, in addition to being non-degradable and remaining in place for a long time without changing their composition. There is more than one way to interpret the mechanical toxic effect of these compounds on rodents, which are:

- The compounds of these elements operate to prevent the phosphorylation process of Adenosine Diphosphate (ADP) material in the process of oxidative phosphorylation and thus preventing the formation of Adenosine triphosphate ATP material necessary in the storage of energy required for the rodent.
- These compounds are linked with many important enzymes required by the rodent body, the lack of which discourages work. These enzymes are dehydrogease, cytochrome oxidese, phosphatase where the inhibition process leads to an imbalance in the processes of chemical or biological factors which eventually leads to the death of the rodent.
- The high concentration of element compounds leads to a holistic deposition which works quickly against the protein in a living cell because it attacks the sulphur bonds, which play an important role in keeping the distinctive shape of the protein. It is observed that the effect of these element compounds is concentrated in the epithelium in the central gut of the rodents.
- A low concentration of these element compounds leads to excessive drowsiness and lack of movement and the collapse of the immune system. In addition, the rodent loses the ability to reproduce (infertility).

Employment of used Iraqi rice husk in electric generation as a low value material: In many agricultural countries that are producers of rice, such as Thailand, Malaysia, Sri Lanka and others (Jittima, 2011; Asanka and Shantha, 2011), residual rice husk is used for the generation of electrical energy. Thus, it is possible to use rice husk to remove heavy metals from wastewater and subsequently use it in the production of electrical power and thus we have achieved two benefits from the use of rice husks and contributed to reducing the use of fossil fuels and thus preserve the environment in a more convenient and economical way by getting rid of two pollutants by using one material.

CONCLUSION

The following conclusions can be drawn:

- Iraqi Rice Husk shows a good ability to remove heavy metals from simulated synthesized aqueous solution using a fixed bed adsorption unit. So, it can be recommended for the removal of heavy metal ions from treatment plant wastewater in Iraq instead of other materials such as activated carbon because it is valid, cheaper, economical, easier and simpler to use and has a high ability to adsorb heavy metal ions, can be used several times without the need for a costly regeneration method and finally can be further used for other beneficial uses.
- The maximum removal of heavy metal ions were 96.24, 95.78, 96.21, 98.73, 95.75, 97.61, 95.82, 95.05 and 96.33% for heavy metals Al, As, Cd, Cr, Cu, Fe, Ni, Pb and Zn, respectively, at an initial heavy metal ion concentration of 5 mg/L.
- The percentage removal of heavy metal ions was increased with a decreasing flow rate of the simulated synthesized aqueous solution and the initial concentration of heavy metal ions while the

percentage removal increased with increasing treatment time and the height of the IRH adsorbent material. For the pH, the percentage removal decreased with increasing pH for Cr, Fe, Ni and Pb and increased with increasing pH for the other heavy metal ions.

- A promoted catalyst can be prepared (which is zeolite type Y) for the isomerization process from the residual samples of Iraqi rice husk that have previously adsorbed the heavy metal ions Cd^{+2}, Cr^{+6}, Cu^{+2}, Fe^{+3}, Ni^{+2} and Zn^{+2} from the aqueous solution to produce a fuel with a higher octane number and at the same time remove the hazardous carcinogenic waste in an economic and eco-friendly way.
- IRH can be prepared as a rodenticide for rodent control from the residual samples of Iraqi rice husk that have previously adsorbed heavy metal ions Al^{+3}, As^{+5}, Zn^{+2} and Pb^{+2} from the aqueous solution.
- The Iraqi rice husk can be used to generate electric power after using it to remove the heavy metal ions from wastewater, thus two pollutants can be removed by one material using an economical and eco-friendly method.

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