Synthesis of Promoted Catalyst from Iraqi Rice Husk Used as a Raw Material for Treating Tannery Wastewater

Mohammed Nsaif Abbas, Firas Saeed Abbas, Hala Husham Nussrat, Safaa Neamat Hussein

Abstract: In this investigation, the removal of Cr$^{+6}$ ions in a semi continuous packed bed column by adsorption using a low cost adsorbent material which is Iraqi Rice Husk (IRH) at different operating conditions of pH, flow rates of polluted solution through the bed, weight of IRH and time of treatment was studied for two different initial concentration of Cr$^{+6}$ ions. The results show that all factors have a significant effect on the percentage removal of Cr$^{+6}$ ions from aqueous solutions and the optimum pH, flow rate, weight of IRH and time of treatment are 2, 10 ml/min, 50 g and 120 min respectively for two initial concentrations of Cr$^{+6}$ ions. Freundlich and Langmuir adsorption isotherms were also applied and they showed good fits to the experimental data. A comparison of kinetic models applied to the adsorption of Cr$^{+6}$ ions on the IRH was evaluated for the first order, pseudo first-order and pseudo second-order kinetic models, respectively. The results show that the pseudo first-order kinetic model was found to correlate with the experimental data well. A mathematical model is proposed for a packed bed isothermal adsorption column with a porous adsorbent. The mathematical model takes account of both external and internal mass-transfer resistances as well as of non-ideal plug flow along the column. A statistical model is also devised to find an expression that relates the overall operating parameters used in this investigation in a general equation. Samples of the Iraqi rice husk remaining after use in the removal of Cr$^{+6}$ ions from the aforementioned aqueous solutions were taken to study the utilization of IRH as a raw material in the synthesis of promoted type Y-zeolite catalyst and compared with normal type Y-zeolite catalyst prepared from IRH alone in the process of n-heptane isomerization. The results show that the promoted type Y-zeolite catalyst gives a higher conversion of n-heptane to isomer substances than the normal type Y-zeolite catalyst.

Key words: Cr$^{+6}$ Removal, Tannery Wastewater, Freundlich and Langmuir and Zeolite Type Y

INTRODUCTION

Chromium (Cr) is found naturally in rocks, soil, plants, animals, volcanic dust and gases. It is present in aqueous solutions mainly in Cr$^{+3}$ and Cr$^{+6}$ oxidation states. The Cr$^{+6}$ salts show higher mobility than Cr$^{+3}$ and hence are considered more toxic to humans. Chromium enters water bodies from industries such as electroplating, leather tanning, cement, steel, paint, ink, dyes, metal-finishing plants and textiles. It can also percolate into the soil by leaching and has the potential to contaminate groundwater, which can be an important source of drinking water (1-3). The physiological effects of chromium on the biological system depend upon its oxidation state i.e. Cr$^{+3}$ and Cr$^{+6}$. The Cr$^{+3}$ ions may be considered as an essential trace element for the proper functioning of living organisms (mammals) e.g. for the maintenance of the “glucose tolerance factor”; it is thought to be a cofactor for the insulin action and to have a role in the peripheral activity of this hormone. The toxicity of metal ions comes to play when their concentration values exceed the threshold value. Cr is toxic, corrosive and an irritant, and the maximum allowable limit for total chromium in drinking water as recommended by the World Health Organization (WHO) is 0.05 mg/l (4). The conventional chromium treatment method consists of following three steps: (i) the precipitation of Cr$^{+3}$ as Cr(OH)$_3$ at a high pH, (ii) the settling out of the insoluble metal hydroxide and (iii) the disposal of the dewatered sludge. The major shortcoming of the conventional treatment includes the high cost of safely disposing of the sludge. Wastewater containing Cr$^{+3}$ is usually treated with ion-exchange resins, which offer the advantage of the recovery of chromic acid but at a high cost brought about mainly by the use of expensive resins.

During the past two decades, extensive research has been carried out to identify new sorbents for the removal of chromium, which are both effective and economical. The following materials have been assessed for chromium uptake including coconut husk (Hasany, S.M. and R. Ahmad, 2006), sawdust (Memon, S.Q., 2005), sunflower stem (Malik, U.R., 2005), activated carbon fibres (Park, S. and Y. Kim, 2004) and banana peel (9). IRH, which is often considered as a solid waste from rice milling, contains approximately 70 % of organic compounds and 30 % of hydrate silica (SiO$_2$). In general, the rice husk can be used as a cheap energy source through combustion to generate heat or electric power or for other purposes as a low value material such as the...
adsorption of heavy metals, the synthesis of different types of zeolites and also to produce metallurgical silicon. In a research field related to catalysis, rice husk silica (RHS) is used as a silica source for the synthesis of microporous materials such as zeolites and mesoporous silica such as MCM-41 and zeolite type Y in a sodium form (NaY) (Jatuporn Wittayakun, 2008; Hasliza Bahruji, 2005). For a catalyst where the metal function and the acid function are well balanced such as zeolites, isomerization and hydrocracking are consecutive reactions and the rate limiting step is the skeletal rearrangement of the alkenes obtained via dehydrogenation over the metal sites, which takes place on the Bronsted acid sites (Akhmedov, V.M., 1999).

The alkane n-Heptane has been widely used in catalytic isomerization of alkanes as a probe molecule, due to the variety of reaction paths that it can take on different catalysts. However the skeletal isomerization of n-heptane, for which the octane number is 0, could be enhanced to 42–112 through a good synthesis catalyst (Biju, M. Devassy, 2004). In this study, the use of a low cost agricultural waste, namely IRH in the removal of Cr\(^{6+}\) ions from tannery wastewater in a semi continuous packed bed was undertaken. The investigation continued by using the remaining samples of IRH after treating with aqueous solutions containing Cr\(^{6+}\) ions as a raw material in the synthesis of a promoted type Y-zeolite catalyst and this catalyst was compared with a normal type Y-zeolite catalyst prepared from IRH alone in an n-heptane isomerization process.

**MATERIALS AND METHODS**

**Iraqi Rice Husk (Adsorbent Material):**

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

**Effluent Samples:**

Industrial tanning effluent samples were supplied from the wastewater of the Adnan Judie tannery in the Al-Nahrawan district, southeast of Baghdad. Two sample groups were taken from this tannery, the first group (Group 1) was taken in winter and spring (November, December, January, February, March and April) and the second group (Group 2) was taken in summer and autumn (May, June, July, August, September and October). The samples were stored in brown bottles at 5\(^\circ\)C throughout transportation from the tannery to the laboratory in the middle of Baghdad. These effluent samples were immediately analysed to determine the concentration of Cr\(^{6+}\) ions in the samples. The gross characteristics of these effluent samples are presented in Table 2.

**Stock Solution:**

In order to avoid interference with other elements in the wastewater, the experiments in this study were carried out using simulated synthesis aqueous solutions of Cr\(^{6+}\). A 1000 mg/l stock solution of Cr\(^{6+}\) was prepared by dissolving 2.282 g of potassium dichromate (K\(_2\)Cr\(_2\)O\(_7\)) in one litre of double distilled water. All solutions used in the experiments were prepared by diluting the stock solution with double distilled water to the desired concentrations for the experimental work. The Cr\(^{6+}\) concentrations were measured using a Thermo Scientific spectrophotometer– Genesys 10 UV, USA.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Composition</th>
<th>XRD of Iraqi Rice Husk</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>90.70</td>
<td></td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>0.015</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>0.61</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>Na(_2)O</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>K(_2)O</td>
<td>2.64</td>
<td></td>
</tr>
<tr>
<td>P(_2)O(_5)</td>
<td>0.73</td>
<td></td>
</tr>
<tr>
<td>LOI</td>
<td>4.71</td>
<td></td>
</tr>
<tr>
<td>S.A (m(^2)/g)</td>
<td>57.5</td>
<td></td>
</tr>
</tbody>
</table>
Table 2: Effluent Samples Characterization

<table>
<thead>
<tr>
<th>Parameter</th>
<th>(Group 1) winter and spring samples</th>
<th>(Group 2) summer and autumn samples</th>
<th>Value of Parameter Taken in this Investigation (Group 1)</th>
<th>(Group 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>1.95–4.02</td>
<td>3.95–6.17</td>
<td>2–4</td>
<td>4–6</td>
</tr>
<tr>
<td>Cr⁶⁺ Concentration, (mg/l)</td>
<td>144.526–151.472</td>
<td>118.019–122.841</td>
<td>150</td>
<td>120</td>
</tr>
</tbody>
</table>

**Sorption Unit:**

Semi continuous mode experiments were conducted in this research by using treated 250 ml of simulated synthesis aqueous solution of Cr⁶⁺ at desired concentrations with the various amounts of the adsorbent material IRH using different flow rates of simulated synthesis aqueous solution of Cr⁶⁺ at various pH. The pH value was adjusted using 0.1 N NaOH and 0.1 N HCl. The sorption unit used to conduct the experiments of this investigation is shown in Figure 1. The sorption unit consists of a packed bed sorption column, feeding burette and sample flask collector. The packed bed sorption column consisted of a clear glass tube of 5 cm ID, 5.3 cm OD and 55 cm height with a perforated disk in the bottom. The sorption column was packed with Iraqi rice husk with a mass of 6, 7, 8, 9, 10, 11, 12, 13, 14 and 15 gm supported from the top and the bottom by a glass hollow cylinder layer, each cylinder being 0.5 cm diameter, 0.1 cm thickness and 1 cm long. Before starting the runs, the packed bed sorption column was rinsed by using double deionized water as a down flow through the column. Subsequently the column was filled by placing the required amount of adsorbent IRH material within the cylinder. The adsorption process was started by allowing the desired simulated synthesis aqueous solution of Cr⁶⁺ of the required concentration and pH to flow down through the sorption column from a 250 ml feeding burette at a precise flow rate in each experiment. For the evaluation of the best operational conditions, the experiments were carried out at a constant environment temperature of 30 °C corresponding to the working temperature in the tannery. Various pH values were applied of 2, 4 and 6 to emulate the pH values of the tannery wastewater. Two initial feed concentrations of the simulated synthesis aqueous solution of Cr⁶⁺ which were 120 and 150 mg/l were selected from the analysis data for the wastewater samples of the tannery over a year and at different flow rates which were 10, 20 and 30 ml/min for each initial feed concentration. The outlet samples after treatment in each experiment were collected from the bottom of the packed bed sorption column at a regulated running treatment time period of 30, 60, 90 and 120 minutes from first entering the initial feed concentrations of the simulated synthesis aqueous solution of Cr⁶⁺ through the column.

![Sorption Unit](image)

**Fig. 1:** Sorption Unit.

**Determination of Cr+6 Ions in the Samples After Treatment:**

Measurement of the unadsorbed Cr⁶⁺ ions in the collected samples after treatment with IRH in the sorption unit was carried out spectrophotometrically (Reza Ansari, 2006). The collected samples were filtered using Whatman No.1 filter paper (0.45 μm). A specific volume from the filtrate was taken and 5 drops (0.25 ml) of concentrated sulphuric acid (H₂SO₄) were added. Sufficient 0.23 N H₂SO₄ and a pH meter were used to adjust the solution to be pH=1.0±0.3. Recent work identifies the optimum pH range for colour development to be 1.6 to 2.2; the matter of the optimum pH range is currently being considered by use of the standard method. The
solution was transferred to a 100 ml volumetric flask, diluted to 100 ml, and mixed. Subsequently 2.0 ml of 1,5-
diphenylcarbazide solution was added, mixed, and allowed to stand for 5 to 10 minutes for full colour
development. A single beam spectrophotometer (Perkin-Elmer, model 35) was employed for the Cr\(^{6+}\) analysis.
An appropriate portion was transferred to a 1 cm absorption cell to measure the absorbance at \(\lambda = 540\) nm using reagent water as a reference. The correct absorbance reading of the sample was obtained by subtracting the absorbance of a blank carried through the method. From the correct absorbance, the amount of Cr\(^{6+}\) ions present was determined by reference to a calibration curve, prepared previously. The sorption percentage of Cr\(^{6+}\) was calculated from the following equation:

\[
\frac{([Cr^{6+}]_o - [Cr^{6+}])}{[Cr^{6+}]_o} \times 100
\]

where: \([Cr^{6+}]_o\) and \([Cr^{6+}]_o\), are the unadsorbed and initial concentration of unadsorbed Cr\(^{6+}\) ions respectively. The percentage of desorption was calculated from the following equation:

\[
\frac{[Cr^{6+}]}{[Cr^{6+}]_o} \times 100
\]

Fig. 2: Calibration Curve of the Hexavalent chromium ion.

Fig. 3: Comparison between percentage removal of Hexavalent Chromium Ions from Real Tannery astewater and Synthetic Aqueous Solution using Iraqi Rice Husk SAS; Synthetic Aqueous Solution, RTW: Real Tannery Wastewater.

**Reusability of Iraqi Rice Husk:**

In order to check the reusability of the sorbent, the IRH was firstly dried at 105 °C for 24 hours and after that tested in the sorption unit using the same two concentrations of 120 and 150 mg/l using the conditions of
the experiment that gave the best percentage removal of Cr\(^{6+}\) ions from the aforementioned aqueous solution which was as follows: pH = 2, flow of simulated synthesis aqueous solution \(F = 10\) ml/min, treatment time of simulated synthesis aqueous solution \(t = 120\) min, and weight of adsorbent material \(w = 50\) g. The capacity of the sorbent was found to decrease until becoming constant at 5% for an initial concentration \(C_0 = 120\) mg/l after 10 times repeated use and constant at 3% for an initial concentration \(C_0 = 150\) mg/l after 13 times repeated use; thus multiple use of the sorbent was seen to be feasible.

**Tests with Real Tannery Wastewater Solution:**

The ability of IRH to adsorb Cr\(^{6+}\) ions from the real solution (tannery wastewater) was tested in the sorption unit using the conditions of the experiment that gave the best percentage removal of Cr\(^{6+}\) ions from the aforementioned aqueous solution which was as follows: pH = 2, flow of simulated synthesis aqueous solution \(F = 10\) ml/min, treatment time of simulated synthesis aqueous solution \(t = 120\) min, and using different weights of adsorbent material \((w = 5, 10, 15, 20, 25, 30, 35, 40, 45\) and \(50\) g). The results show that the removal efficiency for real tannery wastewater is comparable to the removal efficiency obtained for the simulated synthesis aqueous solution. The experimental results obtained when using real tannery wastewater are summarized in Figure 3.

**Synthesis of Zeolite Type Y Catalyst from Iraqi Rice Husk:**

**Synthesis of Promoted Zeolite Type Y Catalyst from Iraqi Rice Husk Adsorbed Cr\(^{6+}\) Ions:**

Iraqi rice husk samples which had previously adsorbed Cr\(^{6+}\) ions from aqueous solutions under different operating conditions as explained in Section 2.1.2 above were segregated and classified according to their content of Cr\(^{6+}\) ions and utilization, and these samples were used as raw material in the synthesis of a promoted catalyst used in n-heptane isomerization which is zeolite type Y. The samples gave different ratios of Cr\(^{6+}\) ions to IRH. The ratios were between 0.05 to 5.5 wt%. IRH samples with different ratios were firstly treated with 10% phosphoric acid (H\(_3\)PO\(_4\)) for 24 hours for preliminary removal of all impurities. Then the samples were well washed with double distilled water, filtered, dried in air, and calcined at 750 °C for 6 hours. An amount of 12 g of calcined IRH was then subjected to dissolution in sodium hydroxide NaOH (4 M) followed by refluxing at 90°C for 12 hours. Subsequently, concentrated hydrochloric acid (HCl (37%)) was added to the aforementioned base dissolved IRH for complete precipitation.

The IRH was filtered, washed with excess distilled water to be free of chloride ions and finally dried in an oven at 120 °C for 6 hours. Zeolite type Y was synthesized using the prepared IRH 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 a clear and homogenous solution appeared after about 5 minutes. 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: \(\text{10.67 Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 10 \text{ SiO}_2 \cdot 180 \text{ H}_2\text{O}\). Two millilitres of aqueous solution of sodium hydroxide were added to 0.7515g sodium aluminate oxide until a homogenous mixture was formed; 1.5361 g of prepared IRH was added separately to 5.5 ml sodium oxide aqueous until homogenously mixed. Both of the preparations were heated under vigorous stirring to obtain a homogenous mixture. The sample was aged for 24 hours at room temperature in the Teflon bottle.

The aluminate and silicate solutions were mixed together in a polypropylene beaker, and subsequently stirred for 2 hours with the purpose of making it completely homogenized. This combined solution was used as the feed stock gel (Rahman, M.M., 2009; Mohammed Mokhtar Mohammed, 2008). The flow chart of the process is shown in Figure 4. The synthesized zeolite type Y which was in sodium (Na\(^+\)) powder form i.e. Cr\(^{6+}\)Na\(_2\)Y-zeolite, was mixed with 15% montmorillonite clay as a binder and 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 test in any process, the hydrogen zeolite (H-zeolite) form must be prepared. The Cr\(^{6+}\)HY-zeolite was prepared by exchanging Na\(^+\) ions in the sodium form of zeolite type Y (Cr\(^{6+}\)Na\(_2\)Y-zeolite) with an ammonium chloride solution NH\(_4\)Cl. In order to obtain the ideal degree of ion exchange the technique of multi-steps (repeated three times) was used. Thus, in the first step, 2 N of ammonium chloride solution (26.75 g of NH\(_4\)Cl in 250 ml of distilled water) contacted with 90 g of prepared Cr\(^{6+}\)Na\(_2\)Y-zeolite and stirred for 2 hours. In the second step, the procedure in the first step was repeated under the same conditions but using about 60 g of zeolite which was taken from the total zeolite amount produced in the first step. Finally, in the third step, the procedure was repeated again under the same conditions but using about 30 g of zeolite which was 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 two hours. The temperature was increased by 75 °C per hour until it reached 550 °C and it was held constant for 5 hours at this temperature. During calcination, ammonia and water were liberated and the promoted zeolite which is Cr\(^{6+}\)HY-zeolite was formed (Sherman, J.D., 1978).
**Synthesis of Normal Zeolite Type Y Catalyst From Iraqi Rice Husk Only:**

In the same way as described in Section 2.2.1 above exactly, normal zeolite type Y catalyst was prepared except that the raw material was normal IRH, i.e. IRH without first being treated with aqueous solutions containing Cr\(^{6+}\) ions.

**Catalytic Activity of Synthesized Catalysts:**

The promoted and normal zeolite type Y catalyst activity was studied by applying an n-heptane isomerization reaction. The n-heptane isomerization reaction was carried out in an isomerization unit as shown in **Figure 5** and **Figure 6**. This unit is operated under atmospheric pressure and the n-heptane evaporated at its boiling point of 98.5°C and heated to around 250°C in the preheater to enter the reactor to pass through the catalyst layer where the isomerization reaction takes place. The product is then cooled in the condenser and condensed out in the ice bath. After that samples of the product were collected to be tested by gas chromatography (GC) (Dani, Model GC 1000 DPC).

![Flow Chart of the Synthesis of Type Y-Zeolite Catalyst Using Iraqi Rice Husk (Weckhuysen, B.M., 1996).](image-url)
Mathematical Model:

Fixed bed dynamics are described by a set of convection-diffusion equations, coupled with source terms due to adsorption and diffusion inside the 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 the prediction of the concentration distribution needed. This investigation focuses on understanding the mechanism of both surface diffusion and pore diffusion. To formulate a generalized model corresponding to the dispersion flow, surface diffusion and pore diffusion mechanism, the following assumptions are made:

1. The system operates under isothermal conditions.
2. The equilibrium of adsorption is described by the Langmuir isotherm.
3. Intraparticle mass transport is due to Fickian diffusion, and it is characterized by the pore diffusion coefficient, \( D_p \), and the surface diffusion, \( D_s \).
4. Mass transfer across the boundary layer surrounding the solid particles is characterized by the external-film mass transfer coefficient, \( k_f \).
5. Film transfer resistance for mass transport from the mobile to the stationary phase.
6. Local adsorption equilibrium between the adsorbate adsorbed onto the adsorbent surface and the adsorbate in the intraparticle stagnation fluid.
7. Both surface and pore diffusion are included in the mass transport mechanism.

Simulation Technique:

Equations used in the simulation technique represent a set of simultaneous, nonlinear, partial differential equations (PDEs) that can be solved numerically. Discretization was applied to space coordinates (Z and r) to convert the proper orthogonal decomposition (POD)s to a set of ordinary differential equations (ODEs). The resulting ODEs can be solved using an existing ODE solver provided by MATLAB. (Lazo Cesar, 1999).

RESULTS AND DISCUSSION

The ability of IRH to remove Cr\(^{6+}\) ions from the simulated synthesis aqueous solution of Cr\(^{6+}\) ions in a semi continuous packed bed column with various parameters such as the pH of the simulated synthesis aqueous solution of Cr\(^{6+}\) ions solution (pH), the weight of adsorbent material IRH \((w)\), the flow rates of the simulated synthesis aqueous solution \((F)\), and the duration time of treatment \((t)\) was investigated. In all, 720 experiments were undertaken by varying all the above parameters for two initial concentrations \((C_0)\) of simulated synthesis aqueous solution of Cr\(^{6+}\) ions. The results obtained are discussed below.
Effect of Initial Concentration:
The results indicated that using IRH as an absorbent material, the percentage removal of hexavalent chromium ion Cr$^{6+}$ decreased from 99.99% to 98.9%, from 88.62 to 83.65 and from 82.08 to 77.19 at a pH of 2, 4 and 6 respectively when the initial concentration (C$_i$) of simulated synthesis solution of Cr$^{6+}$ ions was increased from 120 to 150 mg/l as shown in Figure 7. This can be explained by the fact that the initial concentration of the Cr$^{6+}$ ions solution had a restricting effect on the Cr$^{6+}$ adsorption capacity, and simultaneously the adsorbent material had a limited number of active sites, which would have become saturated at certain concentrations.

This led to an increase in the number of metal ions (Cr$^{6+}$ ions) competing for the available functional groups on the surface of the adsorbent material IRH. Since the lower concentration solution had a smaller amount of Cr$^{6+}$ ions than the solution with a higher concentration of metal ions, so the percentage removal of metal ion (Cr$^{6+}$ ions) decreased with increasing initial concentration of metal ion (Cr$^{6+}$ ions). For the adsorbent material IRH, a higher percentage removal was 99.99% at an initial concentration of Cr$^{6+}$ ions of 120 mg/l and the highest percentage removal was 98.90% at an initial concentration of Cr$^{6+}$ ions of 150 mg/l. Thus IRH was found to be very efficient at removing Cr$^{6+}$ ions.

Effect of pH:
The results show that the removal of Cr$^{6+}$ ions using IRH as an absorbent material decreased from 98.90% to 30.65% for an initial concentration of 150 mg/l and decreased from 99.99% to 53.21% for an initial concentration of 120 mg/l when the pH increased from 2 to 6 respectively for both the two initial concentrations above as shown in Figure 8. The variation in adsorption capacity in this pH range (2, 4 and 6) is largely due to the influence of pH on the adsorption material characteristics of the Iraqi Rice Husk, which indicates that the adsorption capacity of the adsorbent is clearly pH dependent. The pH of the solution is an important factor that controls the uptake of Cr$^{6+}$.

The pH dependence of metal adsorption can largely be related to the type and ionic state of the functional group present in the adsorbent and also to the metal chemistry in the solution. High adsorption of Cr$^{6+}$ ions at a low pH can be explained by the species of the Cr and the adsorbent surface. For an acidic pH, the predominant species of Cr are Cr$_2$O$_7^{2-}$, HCrO$_4^-$, Cr$_3$O$_10^{2-}$ and Cr$_4$O$_13^{3-}$ ions and above pH 6, only the CrO$_4^{2-}$ ion is stable and as the pH decreases into the region of 2 - 6, the equilibrium shifts to dichromate according to the overall equilibrium: 2CrO$_4^{2-}$ + 2H$^+$ ⇌ Cr$_2$O$_7^{2-}$ + H$_2$O. At still lower pH values, Cr$_3$O$_10^{2-}$ and Cr$_4$O$_13^{3-}$ species are formed. Thus, decreasing pH results in the formation of more polymerized Cr oxide species. On the other hand, under acidic conditions, the surface of the adsorbent becomes highly protonated and favours adsorption of Cr$^{6+}$ in its anionic form. With an increase in pH, the degree of protonation of the surface reduces gradually and hence adsorption is decreased. Furthermore, as the pH increases there is competition between (OH$^-$) and (CrO$_4^{2-}$), the former being the dominant species at higher pH values. The net positive surface potential of the sorbent decreases, resulting in a reduction in the electrostatic attraction between the (sorbent) Cr$^{6+}$ ions species and the (sorbate) adsorbent material surface IRH, with a consequent reduced sorption capacity which ultimately leads to a decrease in percentage adsorption of the Cr$^{6+}$ ions.

Effect of Adsorbent Material Weight:
The results revealed that when the adsorbent material weight IRH was increased from 5 to 50 gm the percentage removal of Cr$^{6+}$ ions increased from 33.71% to 98.90%, 35.52% to 83.65% and 30.65% to 77.19% when the pH was varied from 2, to 4 to 6 respectively for an initial concentration of Cr$^{6+}$ ions of 150 mg/l. Similarly the percentage removal of Cr$^{6+}$ ions increased from 50.76% to 99.99%, 50.65% to 88.62% and 51.62% to 82.08% when the pH was varied from 2, to 4 to 6 for an initial concentration of Cr$^{6+}$ ions of 120 mg/l. Both of these results are shown in Figure 9. The increase in the weight (w) of IRH meant an increase in the surface area of adsorbent material. As a result this increased the number of active sites in the adsorbent material i.e. increased the availability of binding sites for adsorption and consequently increased the adsorption capacity of the IRH weight. This led to an increase in the ability of IRH to absorb a greater amount of Cr$^{6+}$ ions from the simulated synthesis aqueous solution of Cr$^{6+}$ ions at the different initial concentrations and ultimately the percentage removal of Cr$^{6+}$ ions increased.

Effect of Flow Rate:
The results illustrated that when the flow rate of the simulated synthesis aqueous solution of metal ion Cr$^{6+}$ increased from 10 to 30 ml/min the percentage removal of Cr$^{6+}$ ions decreased from 98.90 to 97.75, 83.65 to 73.57 and 77.19 to 70.43 for pH values of 2, 4 and 6 respectively, for an initial concentration of 150 mg/l and from 99.99 to 99.96, 88.62 to 87.23 and 82.08 to 80.88 for pH values of 2, 4 and 6 respectively, for an initial concentration of 120 mg/l as shown in Figure 10. This may be due to the fact that when the flow of the simulated aqueous solution increased, the velocity of the solution in the column packed with the IRH increased as well, so the solution spent a shorter time working through the IRH than when the flow rate was less, thus the
IRH uptake reduced to a low amount of Cr\textsuperscript{6+} ions from the simulated aqueous solution, therefore the removal of Cr\textsuperscript{6+} ions from the simulated aqueous solution decreased.

**Effect of Treatment Time:**

The results demonstrated that when the treatment time of the simulated synthesis aqueous solution of metal ion Cr\textsuperscript{6+} was increased from 30 to 120 minutes the percentage removal of Cr\textsuperscript{6+} ions increased from 90.71 to 98.90, 69.57 to 83.65 and 67.28 to 77.19 for pH 2, 4 and 6 respectively for an initial concentration of 150 mg/l, and from 81.25 to 99.99, 80.37 to 88.62 and 74.40 to 82.08 for pH 2, 4 and 6 respectively for an initial concentration of 120 mg/l as shown in Figure 11. This may be due to the fact that when the time of treatment of the simulated aqueous solution increased and the velocity of the solution in the column packed with the IRH remained constant, the solution spent a longer time in the IRH than when the treatment time was reduced, the IRH could uptake a greater amount of Cr\textsuperscript{6+} ions from the simulated aqueous solution, therefore the percentage removal of Cr\textsuperscript{6+} ions increased.

![Figure 7: Effect of Initial Concentration on % Removal of Hexavalent Chromium Ions Cr\textsuperscript{6+} @ F = 10 ml/min, t = 120 min and w = 50 g.](image)

![Figure 8: Effect of pH on the % Removal of Hexavalent Chromium Ions Cr\textsuperscript{6+} @ F = 10 ml/min, t = 120 min and w = 50 g.](image)

![Figure 9: Effect of Adsorbent Weight on the % Removal of Hexavalent Chromium Ions Cr\textsuperscript{6+} @ pH = 2, F = 10 ml/min and t = 120 min.](image)
Fig. 10: Effect of Flow Rate on the % Removal of Hexavalent Chromium Ions Cr^{6+} @ pH = 2, \( t = 120 \) min and \( w = 50 \) g.

Fig. 11: Effect of Treatment Time on the % Removal of Hexavalent Chromium Ions Cr^{6+} @ pH = 2, \( F = 10 \) ml/min and \( t = 120 \) min.

**Sorption Isotherms:**

The isotherm constants were calculated from the slopes and intercepts of Figures (12–17) for the Langmuir isotherm (Eman Abd Al-Gumailiy, 2005) and Figures (18–23) for the Freundlich isotherm (Eman Abd Al-Gumailiy, 2005) and these are presented in Table 3. The value of \( R^2 \) was higher for the Langmuir isotherm than the Freundlich isotherm. This indicates that the Langmuir equation represents the adsorption process very well. The value of \( Q_e \), which is defined as the maximum capacity of sorbent, was calculated from the Langmuir plots. The maximum capacity of Iraqi Rice Husk for Cr^{6+} ions removal was calculated in the range of 3.347 mg/g for initial an concentration of 150 mg/l and 2.349 mg/g for an initial concentration of 120 mg/l at constant temperature that indicated the best sorbing capacity of Iraqi Rice Husk for hexavalent chromium removal Cr^{6+}. The equilibrium parameter \( R_L \), which is defined as \( R_L = 1/(1 + bC_0) \) in the range \( 0 < R_L < 1 \) reflects a favourable adsorption process (Bhattacharya, A.K., 2006). In the present investigation the equilibrium parameter was found to be in the range \( 0 < R_L < 1 \) which is shown in Table 3. This points to the fact that the sorption process was very favourable and the adsorbent employed exhibited a good potential (Selvi, K., 2001).

Fig. 12: Langmuir isotherm plot for removal of hexavalent chromium Cr^{6+} using Iraqi Rice Husk @ pH: 2.0; \( C_0 = 150 \) mg/l; \( w = 50 \) g; \( F = 10 \) ml/min and \( t = 30, 60, 90 \) and 120 min.
Fig. 13: Langmuir isotherm plot for removal of hexavalent chromium Cr\(^{6+}\) using Iraqi Rice Husk @ pH: 4.0; \(C_0 = 150\) mg/l; \(w = 50\) g; \(F = 10\) ml/min and \(t = 30, 60, 90\) and 120 min.

\[
\frac{C_e}{q_e} = 58.12 + 0.270 C_e
\]

Fig. 14: Langmuir isotherm plot for removal of hexavalent chromium Cr\(^{6+}\) using Iraqi Rice Husk @ pH: 6.0; \(C_0 = 150\) mg/l; \(w = 50\) g; \(F = 10\) ml/min and \(t = 30, 60, 90\) and 120 min.

\[
\frac{C_e}{q_e} = 42.962 + 0.205 C_e
\]

Fig. 15: Langmuir isotherm plot for removal of hexavalent chromium Cr\(^{6+}\) using Iraqi Rice Husk @ pH: 2.0; \(C_0 = 120\) mg/l; \(w = 50\) g; \(F = 10\) ml/min and \(t = 30, 60, 90\) and 120 min.

\[
\frac{C_e}{q_e} = 62.14 + 0.393 C_e
\]

Fig. 16: Langmuir isotherm plot for removal of hexavalent chromium Cr\(^{6+}\) using Iraqi Rice Husk @ pH: 4.0; \(C_0 = 120\) mg/l; \(w = 50\) g; \(F = 10\) ml/min and \(t = 30, 60, 90\) and 120 min.

\[
\frac{C_e}{q_e} = 71.27 + 0.417 C_e
\]

Fig. 17: Langmuir isotherm plot for removal of hexavalent chromium Cr\(^{6+}\) using Iraqi Rice Husk @ pH: 6.0; \(C_0 = 120\) mg/l; \(w = 50\) g; \(F = 10\) ml/min and \(t = 30, 60, 90\) and 120 min.

\[
\frac{C_e}{q_e} = 63.86 + 0.410 C_e
\]
Fig. 18: Freundlich isotherm plot for removal of hexavalent chromium Cr$^{6+}$ using Iraqi Rice Husk @ pH: 2.0; $C_0 = 150$ mg/l; $w = 50$ g; $F = 10$ ml/min and $t = 30, 60, 90$ and 120 min.

$$\log q_e = 0.234 + 0.462 \log C_0$$

$$K_F = 1.714, n = 2.165$$

Fig. 19: Freundlich isotherm plot for removal of hexavalent chromium Cr$^{6+}$ using Iraqi Rice Husk @ pH: 4.0; $C_0 = 150$ mg/l; $w = 50$ g; $F = 10$ ml/min and $t = 30, 60, 90$ and 120 min.

$$\log q_e = 0.691 + 0.484 \log C_0$$

$$K_F = 4.901, n = 2.066$$

Fig. 20: Freundlich isotherm plot for removal of hexavalent chromium Cr$^{6+}$ using Iraqi Rice Husk @ pH: 6.0; $C_0 = 150$ mg/l; $w = 50$ g; $F = 10$ ml/min and $t = 30, 60, 90$ and 120 min.

$$\log q_e = 0.583 + 0.395 \log C_0$$

$$K_F = 3.828, n = 2.532$$

Fig. 21: Freundlich isotherm plot for removal of hexavalent chromium Cr$^{6+}$ using Iraqi Rice Husk @ pH: 2.0; $C_0 = 120$ mg/l; $w = 50$ g; $F = 10$ ml/min and $t = 30, 60, 90$ and 120 min.

$$\log q_e = -1.023 + 0.395 \log C_0$$

$$K_F = 0.095, n = 2.532$$

Fig. 22: Freundlich isotherm plot for removal of hexavalent chromium Cr$^{6+}$ using Iraqi Rice Husk @ pH: 4.0; $C_0 = 120$ mg/l; $w = 50$ g; $F = 10$ ml/min and $t = 30, 60, 90$ and 120 min.

$$\log q_e = 0.824 + 0.632 \log C_0$$

$$K_F = 6.668, n = 1.582$$
Fig. 23: Freundlich isotherm plot for removal of hexavalent chromium Cr\(^{6+}\) using Iraqi Rice Husk @ pH: 6.0; \(C_0 = 120\) mg/l; \(w = 50\) g; \(F = 10\) ml/min and \(t = 30, 60, 90\) and 120 min.

Table 3: Values of Langmuir and Freundlich Sorption Constants and \(R_L\) Values for Sorption of Cr\(^{6+}\) Ions on IRH at Different pH’s

<table>
<thead>
<tr>
<th>No.</th>
<th>pH</th>
<th>(C_o) (mg/l)</th>
<th>Langmuir Isotherm</th>
<th>Freundlich Isotherm</th>
<th>(R_L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Q_o) (mg/g)</td>
<td>(b) (l/mg)</td>
<td>(K_L)</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>150</td>
<td>3.374</td>
<td>0.00452</td>
<td>0.979</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>150</td>
<td>3.706</td>
<td>0.00465</td>
<td>0.996</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>150</td>
<td>4.899</td>
<td>0.00477</td>
<td>0.997</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>120</td>
<td>2.542</td>
<td>0.00632</td>
<td>0.998</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>120</td>
<td>2.398</td>
<td>0.00585</td>
<td>0.995</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>120</td>
<td>2.439</td>
<td>0.00642</td>
<td>0.988</td>
</tr>
</tbody>
</table>

Sorption Kinetics:

In order to determine the sorption kinetic models of Cr\(^{6+}\) ions from an aqueous solution, first order reversible, pseudo first order and pseudo second order kinetic models were applied to the data obtained from the experimental work. The effect of the initial Cr\(^{6+}\) ion concentrations and pH were investigated to find the best kinetic model. The straight line plots of \(-\ln(1-U(t))\) versus \(t\) (min) were tested to obtain the first order rate constant under the different experimental conditions. Approximate linear fits were generally observed for all initial concentrations and pH values as shown in Figure 24 and Figure 25, indicating that the sorption reaction can be approximated to be of the first order reversible kinetics. The correlation coefficients \(R^2\) were found to be between 0.81 and 0.91 as shown in Table 4, which means that there is a good agreement but not a perfect one. The equilibrium rate constants of the pseudo first order were determined by plotting \(\ln (q_e - q_t)\) against \(t\) (min) for all initial concentrations and pH values as illustrated in Figure 26 and Figure 27. The kinetic constant and correlation coefficients of these models were calculated and these are given in Table 5. Good correlation coefficients \(R^2\) were observed for all the initial concentrations and pH values indicating that the chromium uptake process can be approximated by the pseudo first order kinetics model. The smallest correlation coefficient in this case was 0.93, which is even better than the first-order reaction model. For the pseudo second order adsorption rate constant, the straight line plots of \(t/q_t\) against \(t\) (min) were analyzed. Approximately, linear fits were observed for all initial concentrations and pH values as shown in Figure 28 and Figure 29 indicating that the sorption reaction can be approximated by the pseudo second order kinetics. The smallest correlation coefficient \(R^2\) in this case was 0.88, which is still better than the first order reversible reaction model. Constant \(k'_2\) values for all situations tested have been calculated and summarized in Table 6. Thus, the pseudo first order kinetics was considered to be the pathway to reach equilibrium.

Fig. 24: First Order Reversible Reaction Kinetics Plot for Adsorption of Hexavalent Chromium ions Cr\(^{6+}\) for different pH [Conditions: weight 50g \(C_o = 150\) mg/l and Flowrate=10 ml/min].
Fig. 25: First Order Reversible Reaction Kinetics Plot for Adsorption of Hexavalent Chromium ions Cr$^{6+}$ for different pH [Conditions: weight 50g $C_o$ = 120 mg/l and Flowrate=10 ml/min].

Table 4: First Order Reversible Reaction Kinetic Model.

<table>
<thead>
<tr>
<th>pH</th>
<th>$C_o$=150 mg/l</th>
<th>$C_o$=120 mg/l</th>
<th>$k_1$(min$^{-1}$)</th>
<th>$k_2$(min$^{-1}$)</th>
<th>$K_c$</th>
<th>$R^2$</th>
<th>$k_1$(min$^{-1}$)</th>
<th>$k_2$(min$^{-1}$)</th>
<th>$K_c$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.068</td>
<td>0.016</td>
<td>0.235</td>
<td>0.89</td>
<td>0.0859</td>
<td>0.0244</td>
<td>0.284</td>
<td>0.91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.0498</td>
<td>0.0138</td>
<td>0.277</td>
<td>0.86</td>
<td>0.0763</td>
<td>0.0162</td>
<td>0.212</td>
<td>0.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.0468</td>
<td>0.0121</td>
<td>0.258</td>
<td>0.81</td>
<td>0.0675</td>
<td>0.0137</td>
<td>0.203</td>
<td>0.86</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 26: Pseudo First Order Reaction Kinetics Plot for Adsorption of Hexavalent Chromium ions Cr$^{6+}$ for different pH [Conditions: weight 50g $C_o$ = 150 mg/l and Flowrate=10 ml/min].

Fig. 27: Pseudo First Order Reaction Kinetics Plot for Adsorption of Hexavalent Chromium ions Cr$^{6+}$ for different pH [Conditions: weight 50g $C_o$ = 120 mg/l and Flowrate=10 ml/min].

Table 5: Pseudo First Order Reaction Kinetic Model.

<table>
<thead>
<tr>
<th>pH</th>
<th>$C_o$=150 mg/l</th>
<th>$C_o$=120 mg/l</th>
<th>$K_s$(min$^{-1}$)</th>
<th>$R^2$</th>
<th>$K_s$(min$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.550</td>
<td>0.550</td>
<td>0.95</td>
<td>0.95</td>
<td>0.570</td>
<td>0.95</td>
</tr>
<tr>
<td>4</td>
<td>0.431</td>
<td>0.431</td>
<td>0.96</td>
<td>0.96</td>
<td>0.453</td>
<td>0.96</td>
</tr>
<tr>
<td>6</td>
<td>0.308</td>
<td>0.308</td>
<td>0.93</td>
<td>0.93</td>
<td>0.337</td>
<td>0.93</td>
</tr>
</tbody>
</table>

Fig. 28: Pseudo Second Order Reaction Kinetics Plot for Adsorption of Hexavalent Chromium ions Cr$^{6+}$ for different pH [Conditions: weight 50g $C_o$ = 150 mg/l and Flowrate=10 ml/min].
Fig. 29: Pseudo Second Order Reaction Kinetics Plot for Adsorption of Hexavalent Chromium ions Cr\textsuperscript{+6} for different pH [Conditions: weight 50g \( C_0 = 120 \) mg/l and Flowrate=10 ml/min].

<table>
<thead>
<tr>
<th>pH</th>
<th>( k_1 )</th>
<th>( q_e )</th>
<th>( R^2 )</th>
<th>( k_1 )</th>
<th>( q_e )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.173</td>
<td>58.417</td>
<td>0.93</td>
<td>0.298</td>
<td>65.314</td>
<td>0.95</td>
</tr>
<tr>
<td>4</td>
<td>0.158</td>
<td>50.799</td>
<td>0.91</td>
<td>0.232</td>
<td>61.672</td>
<td>0.90</td>
</tr>
<tr>
<td>6</td>
<td>0.103</td>
<td>44.138</td>
<td>0.88</td>
<td>0.199</td>
<td>59.927</td>
<td>0.90</td>
</tr>
</tbody>
</table>

Catalytic Activity of Prepared Catalysts:

The activity of normal and promoted zeolite type Y catalysts prepared from non-treated and treated IRH with Cr\textsuperscript{+6} ion solution was tested by using the n-heptane isomerization reaction. This was achieved in a packed bed catalytic reactor of a laboratory isomerization unit as described in Section 2.3. 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 out in a laboratory isomerization unit at a temperature range of 300°C to 400°C and at atmospheric pressure for different quantities of prepared zeolite type Y catalysts. The n-Heptane was evaporated at its normal boiling point of 98.5°C and the vapour was pre-heated 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 then condensed and collected. The isomerization results of n-heptane over two prepared zeolite type Y catalysts are given in Figure 30 and Figure 31. The results were calculated based on the concentration of n-heptane in the output of the reactor measured by gas chromatography GC investigation with a corresponding input of 99% n-heptane purity by using equation (3):

\[
\text{Conversion(wt%)} = \left( \frac{\text{initial wt% of n-heptane} - \text{final wt% of n-heptane}}{\text{initial wt% of n-heptane}} \right) \times 100
\]
It can be seen from Figure 30 and Figure 31 that the conversion of n-heptane isomerization increased for both prepared zeolite type Y catalysts as the temperature increased. This may be due to the considerable enhancing effect of acid sites in both type of Zeolite catalysts normal and promoted, which emerged when the HY-zeolite adsorbed the n-heptane at a higher temperature and may be due to the fact that an increase in the reaction temperature lead to an increase in the reaction rate (for all reactions) with respect to n-heptane isomerization to produce a material with a high octane number. It can also be seen from the tables and figures referred to above that the conversion of n-heptane isomerization increased when promoted zeolite type Y was used compared to the conversion when using normal zeolite type Y for the same temperature. This result may be due to the metal hydrogenation/dehydrogenation activity which increases for the catalyst which contains a metal promoter which is Cr$^{6+}$, because the mechanism of an n-paraffin (n-heptane is as example) isomerization has three steps. In the first step n-paraffin is dehydrogenated to n-olefins which preferably occur on the metal sites (Cr$^{6+}$ ions in this investigation), secondly n-olefins isomerize to isoolefins which occurs on the acid sites in zeolite and the third step is the isoolefins hydrogenated to an isoparaffin which occurs on the metal sites again. Therefore, the increase in the conversion of n-heptane isomerization may be due to the existence of Cr$^{6+}$ ions in the raw material (IRH treated with Cr$^{6+}$ ions solutions) before the preparation of the isomerization catalyst which activates the hydrogenation/dehydrogenation activity rather than the other zeolite type Y catalyst which is prepared from normal IRH only (IRH without being treated with Cr$^{6+}$ ions solutions).

Comparison Between the Theoretical and Experimental Results:

The model used, as described above, determines the percentage removal of Cr$^{6+}$ ions at different times based on different operating conditions. The simulated results using the model were compared with the experimental data obtained from the sorption unit. The comparison between the experimental results and the results obtained from the theoretical model were carried out in order to obtain the most acceptable values for the model parameters as illustrated in Table 7, and to determine the effect of each parameter on the prediction of the results. The results predicted by the proposed model show good agreement with the experimental data as seen in Figure 32 and Figure 33 with 94.6 % accuracy. Based on the good agreement of the model results, an exhaustive parametric study was carried out to understand the influence of various important parameters such as flow rate, weight of IRH and initial concentration.
Table 7: Model and Required Parameters.

<table>
<thead>
<tr>
<th>Model Designation</th>
<th>Solution Method</th>
<th>Required Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersed flow, pore and surface model</td>
<td>Numerical solution</td>
<td>Pe, D, Ds, k, K, n</td>
</tr>
</tbody>
</table>

Statistical Model:

A statistical model was developed for the results obtained from this study. Regression Analysis and the π Theorem were adopted to maintain a relation between the percentage removal of Cr^{6+} ions after treatment and the flow rate, time of treatment, initial concentration of Cr^{6+} ions and the weight of IRH. This relation is shown in Equation (4), which has a correlation coefficient (r) equal to 86.3%.

\[
\text{%R} = \frac{263.03 w^{0.12}}{p^{0.14} F^{0.12} t^{0.12} C_s^{0.12}} \quad \ldots \text{Equation (4)}
\]

where:
- %R: Percentage Removal of Hexavalent Chromium Ions Cr^{6+}
- F: Flow rate of Samples, (ml/min)
- t: Time of Treatment, (min)
- C_s: Initial Concentration of Hexavalent Chromium Ion Cr^{6+}, (mg/l)
- w: Weight of Adsorbent Material IRH, (g)

Conclusions:

The following conclusions can be drawn:

1. IRH indicates a good ability to remove Cr^{6+} ions from an aqueous solution using a semi continuous adsorption unit. So, it can be recommended for removal of Cr^{6+} ions from tannery wastewater in Iraq instead of other materials such as activated carbon because it is valid, cheap, economical, easy and simple to use, has a high ability to adsorb metal ions, can be used several times by a costly regeneration method and can be employed finally for another beneficial uses.

2. Maximum removal of Cr^{6+} ions was 99.99 % performed at an initial Cr^{6+} ions concentration of 120 mg/l, flow rate = 10 ml/min treatment time = 120 min and pH = 2.

3. The percentage removal of Cr^{6+} ions increases with decreasing pH, flow rate of simulated synthesis aqueous solution and initial concentration of Cr^{6+} ions while the percentage removal increases with increasing treatment time and the weight of adsorbent material (Iraqi Rice Husk).

4. IRH can be prepared as a good catalyst (zeolite type Y) for the isomerization process from the left over samples of Iraqi rice husk that have adsorbed the Cr^{6+} ions from the aqueous solution to produce a fuel with a higher octane number and thus it is able to remove the carcinogenic elements in the tannery wastewater using an economic and eco-friendly method.

5.

REFERENCES


