Removal of reactive yellow dye 145 from wastewaters over activated carbon that is derived from Iraqi kehdrawy date palm seeds

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ABSTRACT

This work involves synthesis of activated carbon from Iraqi date palm seeds as agricultural wastes using kehdrawy palm seeds. The preparation was conducted by chemical activation method using ZnCl₂ as an activator. The synthesized activated carbon (AC) was characterized by different analytical and spectroscopic methods. This involves using scanning electron microscopy (SEM), flourier transformation infrared (FTIR), ash content, adsorption capacity, the percentage of humidity and the point zero charge (PZC). The activity of the prepared activated carbon was investigated by following the removal of reactive yellow 145 dye (RY 145) from the aqueous solutions. For a comparison a sample of non-activated carbon (NAC) was used in the same process. From the obtained results it was found that AC was more efficient in dye removal in comparison with NAC under the same conditions.

Keywords: Activated carbon, Activated charcoal, Adsorption over activated carbon, Textile dyes, activated carbon, date palm seeds, linear Freundlich, linear Langmuir
1. INTRODUCTION

Recently, industrial processes have been widely contributed in pollution of our environment including air, water, and soil. Among different types of wide range of pollutants, synthetic dyes are the main source for pollution of the environment. These polluted dyes are produced daily from different artificial and human activities as well as form industrial processes such as textile plants, papers, cement factories, and food processing\(^\text{(1)}\). These processes can produce high levels of industrial wastewaters that containing high concentrations of these synthetic dyes.

Due to the chemical structure of these dyes which containing different chromophoric, and oxochromic groups, these dyes show high degree of colors and hence produce colored industrial wastewaters. Accordingly, most of the dyes can exhibit a deep visual color even for low contaminate of dyes\(^\text{(2,3)}\).

Currently, treating of industrial wastewaters that are produced from different human activities still a big environmental challenge especially for the industrial countries\(^\text{(4,5)}\). Nowadays, different types of synthetic dyes are used in different industries and among different types of these dyes, reactive dyes are of much importance due to their wide applications in many processes such as dying of cellulose, textile, cosmetics and food processing\(^\text{(6)}\). Presence of these dyes with the colored water can reduce the amount of sunlight that is gained by the living organisms\(^\text{(7,8)}\).

So that, the aim goal is how to deal with this industrial wastewaters and reduce the level of pollution before effluent into the stream water and of drinking water sources. To achieve this aim, different treatment methods and techniques can be applied including chemical, physical and biological treatment. More efficient methods for dyes removal can be conducted by chemical and physical methods.

Generally, removal of dyes from colored wastewater can be performed by electrochemical techniques and by using different adsorbents\(^\text{(9,10)}\). Generally, adsorption processes seem to be the best method in comparison with other treatment methods.

This probably arises from the simplicity of this process, less toxicity, ability to treat dye at high levels of dye contamination. In addition, this technique can produce sludge free cleaning processes as well as the used adsorbent can be activated and recycled easily\(^\text{(9)}\). Recently, activated carbon is considered as an important type of adsorbents due to its high microporosity with a high surface area, not expensive, and non-toxicity. So that, it can be used as a good adsorbent for wide range of polluted synthetic dyes\(^\text{(12,13)}\).

Although AC widely uses as an adsorbent for dyes especially for textile wastewater, it still has relatively high cost\(^\text{(14)}\). In order to overcome this drawback in synthesis of AC, many researchers have been focused in the development of low cost adsorbent materials. These adsorbents involve sugarcane, bagasse, plant wood, plant roots, orange peel, saw dust, palm ash, rice husk, rice straw, and flay ash\(^\text{(15,16)}\). All these agricultural wastes can be used in synthesis of relatively low cost AC.

The current study describes the synthesis of AC from locally available Iraqi kehdrawy date palm seeds. This would be synthesis by physiochemical activation method using ZnCl\(_2\) as an activator.

The activity of AC would be investigated by removal of RYD145 from simulated industrial wastewater by adsorption process.
2. EXPERIMENTAL PART

2.1. Used dye

Reactive yellow - 145 dye (C_{18}H_{14}Cl_{2}N_{8}Na_{2}O_{9}S_{2}) was used in this study as this dye uses widely in dying processes in textile industries and thus it can be found in industrial wastewater. Simulated industrial wastewater was prepared using 10 ppm of this dye in all experiment during this work.

2.2. Synthesis of the activated carbon

Iraqi kehdrawy dates palm seeds (IKDPS) were used as starting materials to prepare activated carbon (AC). For all samples, kehdrawy seeds were collected from local markets and washed with hot distilled water to remove dust and others wastes. These seeds were dried at 110 °C for two hours and mixed with a suitable portion of used activator (ZnCl₂). Date palm seeds were immersed with the activator for overnight. Activation processes was performed by heating these treated seeds at 700 °C in a graphite furnace for one hour under nitrogen atmosphere. The resultant AC washed again with distilled water until pH of the washing solution reached around 7. The product was dried again at 110 °C for two hours.

2.3. Uptake adsorption capacity of the synthesized activated carbon

Uptake adsorption capacity of the synthesized activated carbon was estimated using a suspension of 0.1 g of AC in 100 mL of aqueous solution of methylene blue (MB) 20 ppm. This mixture was shacked for under air for 24 hrs at room temperature. Then this mixture was centrifuged and the absorbance of the resultant supernatant solutions was recorded at 665 nm using UV-visible spectrophotometer. A suitable calibration curve of standard solutions of MB was used to calculate the amount of the adsorbed dye on the AC. The uptake adsorption capacity were calculated by comparing these concentrations with the initial concentration of MB (20 ppm)\textsuperscript{(17)}.

2.4. Ash contents of the synthesized activated carbon

Ash content for the prepared AC samples was calculated via weighting a quantity of the used AC and NAC in a crucible. This then was burned in a furnace under normal air conditions at 1000 °C for one hour. Then it was cooled to room temperature in dry desiccator, and the remaining material was reweighed to find weight of the ash. From this weight and the original weight of activated carbon the ash percentage can be calculated\textsuperscript{(18)}.

2.5. Humidity of the synthesized activated carbon

Humidity percentage for the AC and NAC samples was calculated via subjecting a weighted quantity of dried materials (0.10 g) to ambient air conditions in the Lab for 24 hour. This sample then re- weighted accurately, and the humidity percentage was calculated from the difference in the weights for these two cases\textsuperscript{(19)}.

2.6. Fourier transformation infrared spectroscopy (FTIR)

The functional groups in surface of AC and NAC samples were studied using FTIR spectroscopy. FTIR spectra were recorded with Perkin Elminer Spectrophotometer. Samples
of these materials were grounded with KBr crystal at a ratio roughly 1/50 of all samples and then mixed samples were made as pellets by using a suitable pressing with Perkin Elmer hydrolytic pump.

2.7. The point zero charge of AC (PZC)

The point zero charges of the prepared AC samples were investigated according to the potentiometric titration method\(^{(20)}\). According to this method, 100 mL of 0.03 M KNO\(_3\) was used as a blank solution and to this solution NaOH (1 mL of 1 M) was added. The resultant mixture was titrated with HNO\(_3\) (0.01 M). Another mixture of 100 mL of KNO\(_3\) with 0.10 g of AC sample was stirred for 24 hour, then; 1.0 mL of NaOH was added. The resultant mixture was titrated with HNO\(_3\) by the same above manner. For the above two case, the results of titration are plotted as a volumes of the added acid against pHs of the mixtures and the intersection point for the formed two curves was taken to be equal to the PZC of the AC. These results are shown in Table 4.

2.8. Scanning electron microscopy (SEM)

Surface morphology of the synthesized AC was studied using SEM (Scanning Electron Microscope Inspect 550, Netherland), this machine was operated at 25 kV. AC samples were dried prior to adhesive on carbon tape attached to aluminum – stubbed sputter coated with platinum.

2.9. Adsorption studies

In order to investigate the activity of the synthesized AC as an adsorbent, it was used to remove RYD145 from simulated wastewater. All adsorption batches were carried out in a magnetic stirrer at temperatures ranged from 15-30 °C under normal atmospheric conditions. Adsorption processes were performed using 100 mL of 10 ppm of dye concentration. To study the effect of AC concentration on the activity of dye removal, used AC was loaded in different masses in 100 mL of aqueous solution of the dye. The used masses of AC were ranged gradually as follows: 0.01, 0.05, 0.10, and 0.15 g. After stirring reaction mixture, periodically 2 mL of the solution were withdrawn from the reaction mixture. This mixture was centrifuged many times and the absorbance was recorded at a wavelength of 416 nm. Absorbance was measured using 1650 PC-UV-visible Spectrometer Shimadzu. The efficiency for dye removal from the suspension (R%) can be calculated according to the following relation\(^{(21,22)}\):

\[
R\% = \frac{C_i - C_f}{C_i} \times 100
\]

where: \(C_i\) is the initial concentration of the dye, \(C_f\) is the final concentration at the end of adsorption process. A specific amount of dye that adsorbed on the adsorbent (q), this amount of dye is referred to as (mg/g). Adsorption capacity at a given time (qt) can be obtained as follows\(^{(23)}\):

\[
q_t = \frac{(C_i - C_f) \times v}{m}
\]
Herein, $C_t$ represents concentration of the dye as a function of time, $(v)$ refers to the volume of solution and $(m)$ is mass of the AC.

3. RESULTS AND DISCUSSION

3.1. Uptake adsorption capacity of the synthesized activated carbon

The uptake adsorption capacity of the activated and non-activated samples were performed via investigating the adsorption of methylene blue from the aqueous solution. The results of uptake MB by AC samples are summarized in Table 1 as (mg/g). From the obtained results it was found that, these materials have a high external surface areas as they showed high adsorption capacities. This indicates that these materials have a high porosity in their structures$^{(24)}$. The ability of the AC to adsorb materials with high efficiency is mainly dependent on the pore volumes and porous structure.

<table>
<thead>
<tr>
<th>Type of AC</th>
<th>Adsorption capacity (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>non-activated carbon</td>
<td>190.2</td>
</tr>
<tr>
<td>activated carbon with ZnCl$_2$</td>
<td>199.4</td>
</tr>
</tbody>
</table>

3.2. Ash contents of the synthesized activated carbon

Ash content that may present in AC normally can be related to some residual non-carbon materials (inorganic materials) that have high thermal stability and thus these materials remain even when the carbonaceous material is subjected to high temperatures around 1000 °C under normal atmospheric conditions. Generally, presence of these non-carbons materials within the composition of AC can reduce adsorption capacity of AC. Accordingly, this can lead to reduce its total activity as adsorbent with increase content of these materials. However, in the current study, the percentage of ash content for AC samples was very low this can make this type of AC to be as a good candidate adsorbent material which can be used in wide spectrum of applications$^{(25)}$. The percentages of ash content for activated and inactivated AC are shown in Table 2.

<table>
<thead>
<tr>
<th>Type of AC</th>
<th>ash%</th>
</tr>
</thead>
<tbody>
<tr>
<td>non-activated carbon</td>
<td>0.22</td>
</tr>
<tr>
<td>activated carbon with ZnCl$_2$</td>
<td>0.11</td>
</tr>
</tbody>
</table>
3.3. Humidity of the synthesized activated carbon

Humidity that is present in the AC samples results from the ability of AC to absorb moister that is available in the ambient atmospheric conditions. When AC is subjected into humid conditions, AC can absorb moisture into the porous structure. From obtained results in this work it was found that there is an increase in moisture content of the activated AC samples in comparison with that of inactivated AC samples. This property makes these materials as good adsorbents due to high ability of adsorption\(^{(26)}\). The percentages of content of moisture for AC samples are summarized in Table 3.

**Table 3.** The percentage of moisture content for AC samples.

<table>
<thead>
<tr>
<th>Type of AC</th>
<th>humidity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>non-activated carbon</td>
<td>14</td>
</tr>
<tr>
<td>activated carbon with ZnCl(_2)</td>
<td>50</td>
</tr>
</tbody>
</table>

3.4. FTIR spectroscopies of AC samples

![Figure 1. FTIR spectra for activated and non-activated carbon samples.](image-url)
Functional groups of the surface of AC were investigated using FTIR spectroscopy. FTIR spectra for all the samples of AC both activated and non-activated carbon showed almost similar functional.

The band appears around 1600 cm\(^{-1}\) can be assigned to the stretching vibrations modes of aromatic rings on the surface\(^{(27)}\). The band that appears around 1100-1200 cm\(^{-1}\) can be assigned to the stretching modes of C=O bonds.

A weak bands that appear around 3000 cm\(^{-1}\) can be assigned to the presence of unsaturated alkynes C=C stretching modes. In all samples of AC there were weak peaks around 600 to 850 cm\(^{-1}\) which indicating the presence of the, the peaks around 600 to 850 cm\(^{-1}\) is assigned to C-H bending mode\(^{(28)}\).

Other Bands around 3500-3600 cm\(^{-1}\) can be assigned to the stretching modes which are related to OH groups. From the general similarity for the FTIR spectra for activated and non-activated carbon it can be concluded that the nature of the activator that used in activation of samples doesn’t have a significant effect in type of the oxygenated surface functional groups that are present on the surface of the synthesized AC. FTIR spectra for both AC and NAC are shown in Figure 1.

3. 5. The point zero charges of the activated carbon (PZC)

The PZC of the AC samples were calculated according to potentiometric method and the results are presented in Table 4. From the results that are obtained in this study it can be concluded that all the samples showed an alkaline pH values ranged from 8.35 to 9.50. Untreated samples showed a higher pH value (9.50), followed by samples that activated with ZnCl\(_2\) (8.35).

These results are shown in Table 4.

<table>
<thead>
<tr>
<th>Activator</th>
<th>pH of AC</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated</td>
<td>9.50 ±0.15</td>
</tr>
<tr>
<td>ZnCl(_2)</td>
<td>8.35 ±0.10</td>
</tr>
</tbody>
</table>

3. 6. Scanning electron microscopy (SEM)

Surface morphology of the synthesized activated carbon samples was studied using SEM and these images are shown in Figure 2. These images show irregular structure of these materials with heterogeneous morphology of the surface. Also these images show pores and cavities for activated carbon samples.

The increase in porosity and cavities can lead to enhance the ability of these materials to adsorb dyes and others adsorbents with high efficiency. SEM images of both AC and NAC are shown in Figure 2.
Figure 2(A,B). SEM images for the activated and non-activated carbon samples.
3. 7. Effect of duration of contact time

**Figure 3.** Effect of loading of AC on the removal of RYD145 from the simulated wastewater.

**Figure 4.** Effect of contact time on the removal of the RY-145 dye by using 0.15 g of the AC.
The effect of mass and contact time for activated and non-activated carbon are shown in Figures 3 and 4. From Figure 3, it can be seen that the efficiency of dye removal was increased with the increase of AC loading from 0.01 to 0.15 g. This can be attributed to increase of adsorption capacity with the increase of concentration of the used adsorbent (AC) for a fixed dye concentration.

From Figure 4, there is a progressive enhancement in the removal of RYD145 over the used AC with the development of adsorption time. In this study, all batches were shacked for a time of one hour at 25 ºC in order to achieve a full equilibration for all doses of the AC(30). From the obtained results for these two types of AC, it can be concluded that activated carbon showed a better activity in dye removal in comparison with NAC. This may result from the effect of the activator in the removal of humidity within the structure of AC with increase the porosity of the AC.

This can enhance the activity of the AC towards adsorption in comparison with NAC under the same adsorption conditions. These results are shown in Figures 3 and 4.

3.8 Adsorption isotherms

The adsorption isotherms for removal of RYD145 over AC that is synthesized from IKDPS were investigated using Langmuir and Freundlich adsorption isotherms model. Langmuir model is based on the formation of homogeneous monolayer coverage on the adsorbent surface (AC).

According to this model, all adsorption positions on the surface of the adsorbent are considered to be energetically equivalent. For natural adsorption that is described by Freundlich equation and it can be used for multilayers adsorption. Langmuir and Freundlich adsorption isotherms can be explained mathematically in the following relations(30-32):

\[
\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{K_L Q_m C_e} \quad \text{(Langmuir)}
\]

\[
\log Q_e = \log K_F + \frac{1}{n} \log C_e \quad \text{(Freundlich)}
\]

From the above equations, \(Q_e\) refers to as (mg/g), it represents concentration of the adsorbed dye (RY), \(Q_m\) refers to as (mg/g), it represents capacity of the monolayer adsorption of the adsorbed dye, \(K_L\) refers to as (L/mg), it represents Langmuir adsorption constant, this relates to energy that requires for the adsorption, \(C_e\) refers to as (mg/L), it represents concentration of dye in the equilibrium, and both of \(K_F\) and \(1/n\) are represented the constants of Freundlich adsorption isotherm.

Maximum adsorption capacity for the AC can be calculated by applying Langmuir equation as mentioned above. Reaction conditions were as follows: temp. 25 ºC, pH 5.5, and the initial concentration of dispersed dye was 10 ppm.

The doses of the used AC were ranged from 0.05 to 0.20 g with increasing of 0.05 g for each dose. Generally, results of the isotherms constants and \(R^2\) are represented in Table 1 and then these results are plotted in Figures 5 and 6 as \(1/Q_e\) against \(1/C_e\). These results are more fitted with Freundlich isotherm.

This arises from a high value of correlation coefficient for these results. Adsorption isotherms are shown in Figures 5 and 6.
**Figure 5.** The linear Freundlich adsorption isotherms for the adsorption of RY145 on AC.

\[
y = 0.1321x + 0.1026 \\
R^2 = 0.9787
\]

**Figure 6.** The linear Langmuir adsorption isotherms for adsorption of RYD n AC.

\[
y = 0.3543x + 0.6481 \\
R^2 = 0.9792
\]

**Table 5.** Langmuir and Freundlich isotherm constants.

<table>
<thead>
<tr>
<th>Isotherms</th>
<th>Constants/Correlation coefficients</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>( R^2 )</td>
<td>0.9780</td>
</tr>
<tr>
<td></td>
<td>( q_m )</td>
<td>9.748</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_L$</td>
<td>0.135</td>
</tr>
<tr>
<td>------------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9794</td>
</tr>
<tr>
<td></td>
<td>$K_F$</td>
<td>4.441</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td>2.822</td>
</tr>
</tbody>
</table>

4. CONCLUSION

In this study an activated carbon was synthesized from IKDPS and this material can be used effectively in the removal of the reactive yellow-145 dye. Activated carbon with $\text{ZnCl}_2$ exhibited a better activity in dye removal in comparison with non-activated samples. In addition to that, synthesized AC showed high uptake adsorption capacity with low ash content and high moisture content.

References


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