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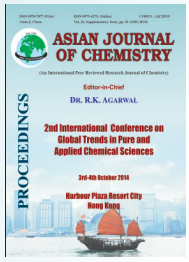

Effects of Activators on Adsorption Ability of Reactive Yellow-145 Dye on Activated Carbon from Iraqi Zahdi Date Palm Seeds

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In the present study, activated carbon from Iraqi zahdi date palm seeds was synthesized. Different activators were used in the synthesis process (*e.g.*, KOH, H_3PO_4 and $ZnCl_2$). Preparation of the activated carbon was done using a chemical activation method. The kinetics of adsorption and the removal of reactive yellow-145 (RY-145) as a model of the polluted dyes was investigated from batch tests. Different reaction conditions were investigated, such as the mass loading of activated carbon and contact time. The Langmuir and Freundlich adsorption isotherms were both performed in each case. In terms of physical properties, the external of surface area, the ash content and the humidity of the activated carbon were investigated. The point zero charges of the prepared samples were also evaluated. The FTIR spectra of these materials showed almost the same characteristic vibration modes. The morphology of the activated carbon was screened by scanning electron microscopy and the results showed irregular and heterogeneous morphology for these samples of the activated carbon. The activity of these materials in terms of their ability to adsorb reactive yellow-145 dye was as follows:
AC-KOH > AC-H_3PO_4 > AC-$ZnCl_2$ > AC untreated.

Keywords: Activated carbons, Dye removal, Date palm seeds, Reactive yellow-145.

INTRODUCTION

At the beginning of 20th century, mass applications of industry in all aspects of life emerged and these industrial processes widely contributed to the pollution of the air, water and soil of our planet. Out of a wide range of pollutants, dyes are important to the environment; these dyes are produced as a result of many daily activities, as well as from industrial processes such as textile plants, paper and pulp mills and food processing. All these, among other sources, produce high levels of dyes, which can produce colored wastewater. Most of these dyes can exhibit a strong visual color even for low contamination levels, which in turn causes concern for the environment[1-3].

Generally, polluted wastewater can be recognized primarily *via* changing of the color, which can be detected in case of the presence of traces of the dyes in the water. However, the treatment of colored wastewater produced from different sources is still a major environmental challenge for industrial countries[4,5]. Out of the different types of dyes, reactive dyes are of great importance due to their wide range of applications in many processes such as the dying of cellulose, textiles, cosmetics and food processing[6]. Major environmental problems arise when colored wastewater is discharged into rivers and streams. This can have a serious effect both esthetically and in affecting the transmission of sunlight into the water. This can reduce the amount of sunlight received by living organisms, which reduces their ability to synthesize carbohydrates and energy *via* photosynthesis[7,8].

The biological treatment of colored wastewater is not sufficient as these dyes are not particularly biodegradable. More efficient methods for the removal of dyes can be conducted by chemical and physical methods. Generally, the removal of dyes from colored wastewater can be performed by electrochemical techniques and by using different adsorbents[9,10]. Out of these methods, adsorption seems to be the best method. This is probably due to the simplicity of this process and the ability to treat dyes at high levels of dye contamination. In addition, this technique can produce sludge-free cleaning processes[11,12].

Out of the different adsorbents, activated carbon is one of the most promising. However, activated carbon is widely used as a standard adsorbent for the removal of a wide range of polluted dyes from colored wastewater. Recently, activated carbon has been considered an important type of adsorbent

due to its high microporosity, large surface area and non-toxicity[13]. It can therefore be used as a good adsorbent for a wide range of adsorbates. Many attempts have been made by researchers to synthesize low-cost activated carbon or adsorbents from widely available agricultural wastes such as coconut shells[14]. Although activated carbon is widely used as an adsorbent for dyes and especially for textile waste, it has a relatively high cost[15]. For this reason, many researchers have been focusing on the development of low-cost adsorbent materials. These adsorbents include sugarcane, bagasse, soy meal hulls, orange peel, sawdust, palm ash, rice husks, rice straws and flay ash[16-20].

In this study, activated carbon has been synthesized by a physio-chemical activation method from Iraqi zahdi date palm seeds and by using different activators such as potassium hydroxide, phosphoric acid and zinc chloride. The activity of activated carbon was tested by the adsorption of reactive yellow-145 dye as a model of a polluted dye from their aqueous solutions.

EXPERIMENTAL

Adsorbate: The reactive yellow-145 dye ($C_{18}H_{14}Cl_2N_8Na_2O_9S_2$), was used as an adsorbate model in this study as it was provided without any further purification being necessary. Distilled water was used to prepare all the solutions and reagents in this work.

Synthesis of the activated carbon: Iraqi zahdi dates palm seeds were used as starting materials to prepare the activated carbon. For all samples the seeds were washed with hot distilled water to remove dust and other waste and then dried at 110 ºC for 2 h. The dry seeds were mixed with the desired activator in an appropriate ratio in a chemical activation process. The activation process was done by heating at 700 ºC in a graphite furnace for 1 h under a nitrogen atmosphere. After heating, all the samples were cooled to room temperature and the resultant activated carbon was washed again with distilled water until the pH of the solution reached around 7. The product was dried again at 110 ºC for 2 h.

Adsorption studies: Many adsorption studies were carried out during this study in order to determine the effects of different parameters influencing adsorption processes. In this context, all adsorption tests were performed in a magnetic stirrer at temperatures ranging from 15 to 30 ºC. The adsorption processes were undertaken using a concentration of reactive yellow-145 equal to 10 ppm. The adsorbent was loaded in different masses into 100 mL of aqueous solution of the dye. These masses were: 0.01, 0.05, 0.10, 0.15 and 0.20 g. Periodically, 2 mL of the solution was taken from the reaction mixture and centrifuged; then the absorbance was recorded at a wavelength of 416 nm. The absorbance was measured using a 1650 PC-UV-visible Spectrometer Shimadzu. The efficiency for the dye removal from the suspension (R %) was calculated using the following equation[21-23]:

$$R\ (\%) = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

where C_i is the initial concentration of the dye and C_f is the final concentration at the end of adsorption process. A specific amount of dye that was adsorbed by adsorbent (q) is referred to as mg/g. The adsorption capacity at a given time (q_t) can be obtained as follows:

$$q_t = \frac{(C_i - C_t) \times v}{m}$$

where C_i is the initial concentration; C_t represents the concentration of the dye as a function of time and (ν) refers to the volume of the solution and (m) is the mass of the activated carbon.

External surface areas of the synthesized activated carbon: The external surface areas of the synthesized activated carbon were measured by a suspension of 0.1 g of activated carbon in 100 mL of aqueous solution of methylene blue 20 ppm in a 250 mL conical flask. The mixture was shaken for 24 h at room temperature. Then it was separated by centrifuge and the absorbance of the supernatant solutions was measured using a UV-visible spectrophotometer at 665 nm. A suitable calibration curve of standard solutions of methylene blue was used to estimate the amount of the adsorbed dye on the activated carbon. The external surface areas were calculated by comparing these concentrations with the initial concentration of methylene blue (20 ppm)[24].

Ash content of the synthesized activated carbon: The ash content of the prepared samples was estimated as follows: a required amount of activated carbon was weighed accurately in a crucible. This was then burned in a furnace under an air atmosphere for 1 h. Then it was cooled to room temperature in a dry desiccator, after which the remaining material was reweighed to determine the weight of the ash. From this weight and the original weight of the activated carbon the percentage of ash was calculated[25].

Humidity of the synthesized activated carbon: The humidity was calculated by subjecting a weighed quantity of dried activated carbon (0.10 g) to an ambient atmosphere in the laboratory for 24 h. This sample was then weighed accurately, after which it was dried in an oven at 110 °C for 1 h. Then the sample was reweighed and the humidity percentage was calculated from the difference in weight[26].

FT-IR analysis: The surface chemistryof all the samples of activated carbon was investigated using FTIR spectroscopy. The FTIR spectra were recorded using a Perkin Elminer Spectrophotometer. Measurements were taken as wave numbers ranging from 4000 to 450 cm^{-1}. The activated carbon samples were ground with KBr at a ratio of roughly 1/50 for all the samples. Then the mixed samples were made into pellets under a suitable pressure using a Perkin Elmer hydrolytic pump.

Point zero charge (PZC): The point zero charges of the synthesized activated carbon were carried out by potentiometric titration[27]. 100 mL of 0.03 M KNO_3 was used as a blank solution and 1 mL of 1 M NaOH was added. The resulting solution was titrated with HNO_3 (0.10 M). A mixture of 100 mL of KNO_3 with 0.10 g of synthesized activated carbon was stirred for 24 h. Then 1 mL of NaOH was added and titrated with HNO_3 by following the same process that applied for the blank solution. The results of the titration were plotted as a volume of the added acid (VS) and pH of the mixture and the intersection point was taken to be equal to the point zero charge of the activated carbon. These results are shown in Table-5.

Scanning electron microscopy (SEM): The morphological patterns of activated carbon the samples were investigated by using SEM (Scanning Electron Microscope Inspect 550, Netherlands). The SEM was operated at 25 kV and the derided samples of activated carbon were affixed with carbon tape to aluminum stub and sputter coated with platinum.

RESULTS AND DISCUSSION

Effects of contact time: The effects of contact time for activated and non-activated carbon synthesized from Iraqi zahdi date palm seeds are shown in Fig. 1. From this Figure it is clear that there is a progressive increase in the adsorption of the used dye on activated carbon. In all the batches, a shaking time of 1 h at 25 ºC was used in order to achieve a full equilibration for all the doses of activated carbon in this study[28]. From these results for both the activated and non-activated types of activated carbon, it can be derived that the activated carbon was better. Also, in terms of different activators it was found that activated carbon activated with KOH was more efficient in the removal of dye in comparison with the other activators. This is probably due to the role of the activator in the dehydration of activated carbon and then providing more active sites which contributed to the adsorption of dye molecules from an aqueous solution. These results are shown in Fig. 1.

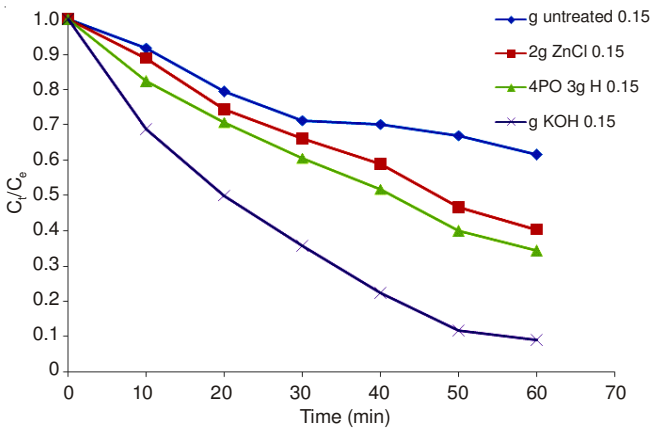

Fig. 1. Effects of contact time on the removal of the RY-145 dye by using activated carbon synthesized from Iraqi zahdi date palm seeds using different activators

Adsorption isotherms: The adsorption isotherms were carried out by applying Langmuir and Freundlich isotherms for the adsorption of reactive yellow-145 dye on the activated and non-activated carbon. However, the Langmuir model is based on the formation of homogeneous monolayer coverage on the adsorbate. In this case, all the adsorption positions on the surface of the adsorbent are considered to be energetically equivalent. In case of physical adsorption, the Freundlich equation is used to investigate adsorption isotherms. The Langmuir and Freundlich isotherms can be represented mathematically as shown in the following equations[29-32]:

$$1/q_e = 1/q_m + 1/K_L q_m C_e \text{ (Langmuir)} \quad (3)$$

$$\log q_e = \log K_F + 1/n \log C_e \text{ (Freundlich)} \quad (4)$$

In the above equations, q_e is referred to in (mg/g) and it represents the concentration of the adsorbed dye (reactive yellow-145); q_m is referred to in (mg/g) and it represents the capacity of the monolayer adsorption of the adsorbed dye; K_L is referred to in (L/mg) and it represents the Langmuir adsorption constant, which relates to the energy required for adsorption; C_e is referred to in (mg/L) and it represents the concentration of dye in the equilibrium; both K_f and 1/n represent the constants of the Freundlich adsorption isotherm.

The maximum adsorption capacity for the activated carbon can be calculated by applying the Langmuir equation as mentioned above. The reaction conditions were as follows: temp. 25 ºC, pH 5.5 and the initial concentration of dispersed dye 10 ppm. The doses of the used activated carbon ranged from 0.05 to 0.20 g with an increase of 0.05 g for each dose. The overall results of the isotherm constants and R^2 are shown in Table-1 and these results are plotted in Fig. 2 and 3 as $1/q_e$ against $1/C_e$. These results fitted more with the Freundlich isotherm, which arises from high value correlation coefficients for these results.

Uptake adsorption capacity of the synthesized activated carbon: The adsorption ability of the activated and non-activated samples of the activated carbon was investigated by following the adsorption of methylene blue from the aqueous solution. The results of the methylene blue uptake by the activated carbon samples are summarized in Table-2 in (mg/g).

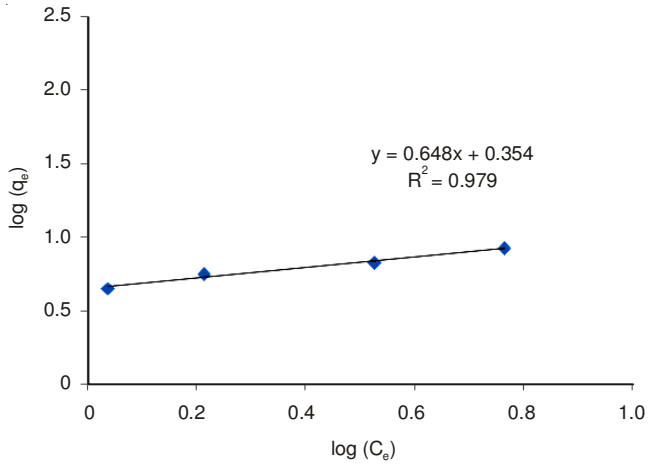

Fig. 2. Linear Freundlich adsorption isotherms for reactive yellow-145 adsorption by activated carbon

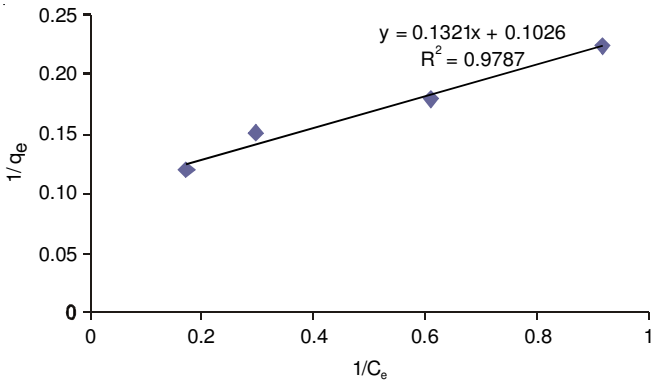

Fig. 3. Linear Langmuir adsorption isotherms for reactive yellow-145 adsorption by activated carbon

TABLE-1
LANGMUIR AND FREUNDLICH ISOTHERM CONSTANTS

Langmuir	R^2 q_m 0.9787	K_L 9.746	0.133
Freundlich	R^2 K_F n 0.9792	4.447	2.822

TABLE-2
ADSORPTION CAPACITY FOR THE SYNTHESIZED ACTIVATED CARBON (AC) BY METHYLENE BLUE ADSORPTION

AC type	Non-activated	AC/KOH	$AC/ZnCl_2$	AC/H_3PO_4
Uptake capacity (mg/g)	197.2	199.4	197.8	198.0

These results indicate that these materials have large external surface areas, which confirms that they have a high porosity in their structures[33]. The ability of the activated carbon to adsorb materials with high efficiency is mainly dependent on the pore volumes.

Ash content of the synthesized activated carbon: In the activated carbon, the ash content is related to non-carbon materials that remain when the carbonaceous material is subjected to high temperatures. These residual materials after the activated carbon has been burned at 1000 ºC in ambient air conditions may be related to the inorganic materials. However, these materials may be found as constituent materials in the composition of activated carbon. The presence of these materials within the composition of activated carbon may reduce the adsorption capacity of activated carbon. This can lead to a reduction in its total activity as an adsorbent with an increase in content of these materials. However, in the present study, the percentage of ash content for all the activated carbon samples was very low. This property makes the activated carbon synthesized in this study a good adsorbent material[34]. The percentages of ash content for activated and non-activated activated carbon are shown in Table-3.

TABLE-3
PERCENTAGES OF ASH CONTENT FOR THE ACTIVATED AND NON-ACTIVATED CARBON SAMPLES

AC type	Non-activated	AC/KOH	$AC/ZnCl_2$	AC/H_3PO_4
Ash (%)	0.19	0.11	0.16	0.15

Humidity of the synthesized activated carbon: The humidity of the activated carbon results from the ability of activated carbon to absorb moisture when it is subjected to humid conditions. Under humid conditions activated carbon can absorb moisture into its porous structure. However, from the results obtained in the present work it was found that there was an increase in the moisture content of the activated activated carbon samples compared to that of the non-activated activated carbon samples. This property would make these materials good adsorbents for a wide spectrum of adsorbates[35]. The percentages of moisture content for the activated carbon samples are summarized in Table-4.

TABLE-4
PERCENTAGES OF MOISTURE CONTENT FOR THE ACTIVATED CARBON SAMPLES

AC type	Non-activated	AC/KOH	$AC/ZnCl_2$	AC/H_3PO_4
Humidity (%)	16	48	45	46

Scanning electron microscopy (SEM): The morphology of the synthesized activated carbon samples are shown in Fig. 4. The SEM images show the irregular, heterogeneous morphology of their surfaces. Also, these images show pores and cavities in the carbon samples. High porosity and irregularities can be seen in the samples treated with KOH and H_3PO_4. The increase in porosity and cavities can lead an improvement in the ability of these materials to adsorb dyes and other adsorbents with a high efficiency. The images of the activated carbons samples are shown in Fig. 4.

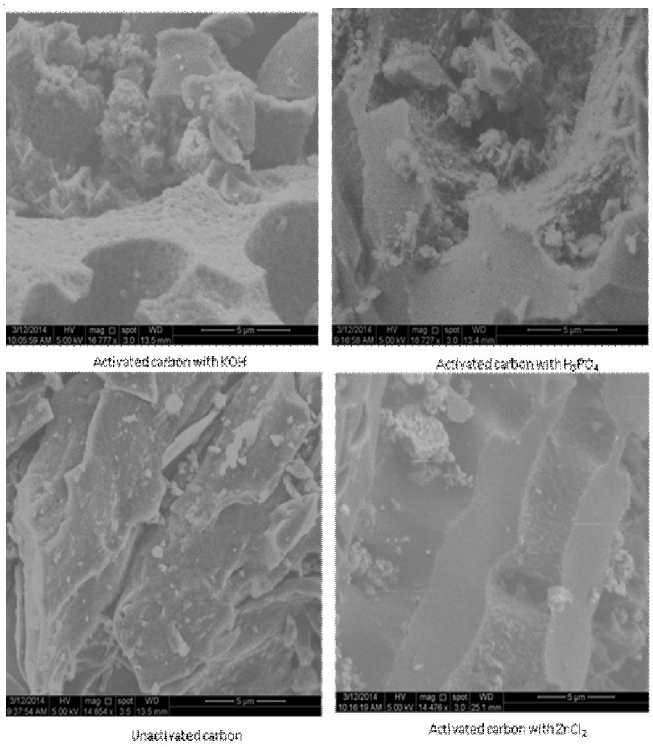

Fig. 4. SEM images for the activated and non-activated activated carbon samples synthesized from Iraqi zahdi date palm seeds

FTIR spectroscopies of activated carbon samples: In general there is a similarity in the FTIR spectra for all the samples of both activated and non-activated activated carbon. The FTIR spectra of the activated carbon showed three main absorption bands in the region from 1700 to 1400 cm^{-1}. The strong band that appears around 1700 cm^{-1} relates to the stretching modes of the C=O bonds[36]. The band that appears around 1425 cm^{-1} can be assigned to the stretching vibrations of the C-C bonds[37]. The strong band around 1600 cm^{-1} is related to the stretching vibrations of the bonds of the aromatic rings coupled with the conjugated carbonyl groups on the surface[38]. The stretching modes of the C=O bonds can be seen from around 1200 to 1100 cm^{-1}. In all the activated carbon samples there were weak peaks at around 3000 cm^{-1}, which indicates the presence of unsaturated alkynes C=C stretching modes; the peaks from around 850 to 600 cm^{-1} confirm the vibration of the C-H bending mode. The bands from around 3600 to 3500 cm^{-1} are assigned to the stretching modes which are related to the OH groups. From these spectra, it can be concluded that the nature of the activator that was used in the activation of the samples in this study does not have a significant effect

on the type of the oxygenated surface functional groups that are present on the surface of the synthesized activated carbon.

Point zero charges of the activated carbon (PZC): The results of the point zero charges of the activated carbon samples were investigated according to a potentiometric method. The results are shown in Table-5. From these results it is clear that all the samples showed alkaline pH values ranging from 8.40 to 10.20. The untreated samples showed the highest pH value (10.20), followed by the samples activated with KOH (9.40) and the lowest pH value was for the sample that was treated with H_3PO_4 (8.20).

TABLE-5
POINT ZERO CHARGES FOR THE ACTIVATED AND NON-ACTIVATED ACTIVATED CARBON (AC) SAMPLES SYNTHESIZED FROM IRAQI ZAHDI DATE PALM SEEDS

AC type	Non-activated	AC/KOH	AC/$ZnCl_2$	AC/H_3PO_4
PH of AC	10.20±0.10	9.10±0.1	28.20±0.15	8.40±0.10

Conclusion

The activated carbon synthesized in this study can be used as an efficient adsorbent for many applications. The efficiency of the removal of the reactive yellow-145 dye for activated carbon with KOH was much better than for the non-activated samples. The synthesized materials showed large external surface areas, which makes them good adsorbent materials. Besides that they show low ash content with relatively high moisture content. These properties are considered as encouraging physical properties for materials to be used as adsorbents. The adsorption isotherm studies showed that they fitted with the Langmuir model.

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