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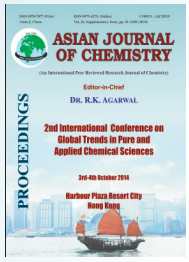

Adsorption of Reactive Yellow Dye 145 from Wastewater onto Iraqi Zahdy and Khestawy Date Palm Seeds Activated Carbons

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This study involves synthesis of two types of the activated carbon from Iraqi zahdy date palm seeds and Iraqi khestawy date palm seeds. These two types of activated carbon were synthesized using H_3PO_4 as an activator. Synthesis processes of activated carbon were performed by chemical activation method. The activity of these materials as adsorbents was investigated by following removal of reactive yellow dye 145 (RYD-145). Kinetics of adsorption and removal of reactive yellow as a model of the polluted dyes were investigated from batch tests. Different reaction parameters and conditions were investigated, such as amount of loading of activated carbon and duration of the adsorption process. The point zero charges of the synthesized samples were also calculated. It was found that Iraqi zahdy date palm seeds based activated carbon was more efficient than Iraqi khestawy date palm seeds in dye removal under the same reaction conditions.

Keywords: Activated carbons, Reactive yellow dye removal, Iraqi date palm seeds.

INTRODUCTION

Wastewaters that are discharged from wide variety of industrial and domestic activities and a particularly from textile industries are highly coloured. In this type of industries both of dyeing and finishing processes produce wastes with high content of coloured materials as well as many of hazard organic compounds. Textile industries use different types of synthetic dyes and these dyes have a complex structure with different functional groups. These types of dyes use widely with other types of common industries such as leather, plastic, paper and food industry. Generally, most of these dyes are polluted for the environment and can generate carcinogenic and toxic by-products under environmental conditions[1,2]. In general, the vast majority of these synthetic dyes have structures that have a high resistance for decomposition and/or fragmentation when they are exposed to the air, sunlight and/or oxidizing agents[3,4]. Due to these observations, these dyes can not be easily treated *via* applying normal physical, chemical and biological treatment methods. However, these methods are not promising in the removal of these pollutants from the environment. These methods have low efficiency with relatively high cost additionally, they may lead to generate sludge and/ or hazard by-products[5,6]. Among above different dye removal treatments from wastewaters, adsorption processes seem to be the most suitable method that shows a high removal efficiency, relatively low cost and easily processing[7]. In this type of dye removal from the waste, the important factor in this process is the used adsorbent. Different types of adsorbents can be used to conduct this process and among of these adsorbents, activated carbons seems to be as a good candidate to perform this job[8]. Currently, the used commercially available activated carbon (AC) is relatively expensive, this makes mass applications of activated carbon in dye removal is not applicable. So that, the big challenge in this field of researches is the looking for low cost synthetic activated carbon that is suitable for mass applications. The key point here is the synthesis of activated carbon from widely available raw materials which can reduce the final cost of the synthetic activated carbon. In this context, synthesis of activated carbon from agricultural raw materials and/or by products can offer alternative routes towards production of low cost and widely available activated carbon that can be used for mass applications[9]. So that high abundance and availability of local agricultural raw materials makes them too promising in the synthesis of commercial quantities of activated carbon that can be used for wide ranges of applications[10-15].

The present study, describes the synthesis of the activated carbon from Iraqi zahdy and khestawy date palm seeds. These materials were synthesized by physio-chemical activation method with using phosphoric acid as an activator. The activity of activated carbon was investigated by adsorption of reactive yellow dye145 from their aqueous solutions.

EXPERIMENTAL

Adsorbate: The dye that was used in this study was reactive yellow 145 dye (RYD-145), its molecular formula ($C_{28}H_{20}ClN_9Na_4O_{16}S_5$). This dye was used as model of polluted dye that is normally used in textile factories. It was provided by Fluka Company 98 % and it used as it was provided without any further purification. During preparation processes in this study, distilled water was used to prepare all the solutions and reagents in this work.

Synthesis of the activated carbon: In this study, Iraqi zahdy and khstawy dates palm seeds were used as raw materials to prepare the activated carbon. For both samples, seeds were collected from local markets and washed with hot distilled water to remove dust and others wastes. Then these samples were dried at 110 ºC for 2 h and mixed with the desired activator in appropriate ratio in a chemical activation process (H_3PO_4). According to this process samples were heated at 700 ºC in a graphite furnace for 1 h in inert atmosphere by nitrogen flush. After heating, all the samples were left to cool to room temperature and the samples were washed again with distilled water. This process was continued until pHs of the washed solutions reach around 7. After that, final products were dried at 110 ºC for 2 h to give final activated carbon. In this study Iraqi khestawy date palm seeds will be termed as AC1 and Iraqi zahdy date palm seeds as AC2.

Adsorption studies: In this study, all adsorption experiments were carried out using a magnetic stirrer at temperatures ranged from 15-30 ºC in air atmosphere. Adsorption processes were conducting using an initial concentration of the RY145 dye equal to 10 ppm. The used activated carbon was loaded in different masses in 100 mL, 10 ppm of aqueous solutions of the dye and these masses were: 0.01, 0.05, 0.10, 0.15, 0.20 g. For each run, 2 mL of the reaction mixture was withdrawn from the reaction system for each 10 min and for duration of 1 h of reaction time. Then these samples were centrifuged for several times and the absorbance was followed at a wavelength of 416 nm. The optical density was recorded using spectrophotometer Shimadzu 1650 PC-UV-visible. The efficiency for dye removal from the aqueous suspension (R %) was calculated using the following equation[16-18]:

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

From this equation, C_i refers to the initial concentration of the dye and C_f is the final concentration after 1 h of adsorption and the term q refers to the concentration of the dye that adsorbed on the used activated carbon in (mg/g). The capacity of adsorption at a given time (q_t) can be obtained as follows:

$$q_t = \frac{(C_i - C_t) \times v}{m} \quad (2)$$

According to this relation, C_t is the concentration of the dye as a function of time, the term (v) refers to the volume of solution and (m) is the mass of the used activated carbon.

Effect of contact time and adsorbent dosage: To study the effects of contact time and adsorbent dosages on dye removal, a series of experiment were undertaken using RYD145 (10 ppm, 100 mL). These experiments were performed using different contact times ranged from 0 to 60 min. Also to investigate the effect of mass of the used adsorbent, different dosages of activated carbon were used to study their effects on dye removal.

Effect of pH of mixture on dye removal: The effect of the pHs of the reaction mixture on RY145 removal from aqueous solution was conducted by following dye removal under three different values of pH of the AC/RY145 mixture, these are 3, 7 and 9. The pH of mixture was adjusted to a desired values by properly adding of small droplets from 0.1 N HCl and NaOH to the initial mixture with using pH meter measurement.

Effect of mesh size of the activated carbon: To study the effect of particle size of the used activated carbon, a series of experiments were performed using three different sized of both of AC1 and AC2. These experiments were performed using 0.15 g of activated carbon at a pH of 7.

Adsorption capacity of the synthesized activated carbon: Adsorption capacity of the synthesized activated carbon was investigated by suspension of 0.1 g of activated carbon in aqueous solution of methylene blue, (100 mL, 20 ppm). The resultant mixture was shaked in air atmosphere for 24 h at room temperature. Then this mixture was centrifuged several times to ensure fully removal of fine particles of the activated carbon. Then the optical density of the supernatant liquid was measured at 665 nm using UV-visible spectrophotometer. The adsorption capacity of activated carbon, a suitable calibration curve of standard solutions of methylene blue was used to find the amount of the methylene blue dye on the activated carbon. Then the adsorption uptake capacity of the synthesized activated carbon were calculated by comparison these concentrations with the initial concentration of methylene blue (20 ppm)[19].

Ash contents of the synthesized activated carbon: The percentage of ash content for both AC1 and AC2 samples was estimated by precise weighing of a required amount of carefully dried activated carbon accurately in a finely dried crucible. This then was burned in a furnace under air atmosphere for 1 h. Then it was cooled to room temperature in dry desiccator. The weight percentage of the ash was calculated by comparing the remaining amount of material in the crucible was the initial weight of the activated carbon. By comparison this weight and the initial weight of the taken activated carbon the ash percentage can be estimated[20].

Humidity of the synthesized activated carbon: Humidity percentage of both of the AC1 and AC2 samples was estimated by subjecting (0.10 g) of dried activated carbon to the ambient atmospheric conditions in the laboratory for 24 h. These samples then were weighed accurately and then dried in an oven at 110 ºC for 1 h. Then the sample reweighed accurately and the humidity percentage was calculated from difference in the weights for these two cases[21].

Fourier transform infrared spectroscopy (FTIR): The surface of AC1 and AC2 sample was studied using FTIR spectroscopy using Perkin Elminer Spectrophotometer. FTIR analysis was measured in the range of 4000 to 450 cm^{-1}. The samples were prepared for run by making them as pellets by grounding with KBr salt at a ratio roughly 1/50.

Point zero charge (PZC): Point zero charges of AC1 and AC2 samples were calculated using potentiometric titration[22]. In 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. Then this mixture was titrated with HNO_3 (0.10 M). Another mixture of 100 mL of KNO_3 with 0.10 g of the activated carbon was stirred in air atmosphere for 24 h. Then 1 mL of NaOH was added and it was titrated with HNO_3 by following the same process that was applied for the blank solution. Then the results of the titration were plotted as a volume of the acid against pH of the mixture and the obtained intersection point was taken to be equal to the point zero charges of the activated carbon. These results are shown in Table-4.

Scanning electron microscopy (SEM): The morphology of surface of both AC1 and AC2 samples were studied using SEM (Scanning Electron Microscope Inspect 550, Netherland). This machine was operated at 25 kV. The activated carbon samples were derided before they were adhesive on carbon tape attached to aluminum-stubbed sputter coated with platinum.

RESULTS AND DISCUSSION

Effect of activated carbon loading and contact time on removal of dye: Effect of contact time for both AC1 and AC2 samples in aqueous solution of RYD145 is shown in Fig. 1. From this Figure it is a clear that there is a progressive increase in adsorption of the used dye on both of AC1 and AC2. In all batches, a shaking time of 1 h at 25 ºC was applied in order to achieve a full equilibration for all doses of the activated carbon in this study[23]. From these results for both types of activated carbons, there was a progress development in dye removal on activated carbon with time. This probably arises from the increase of uptake adsorption capacities of AC1 and AC2 with the development of time of adsorption. By comparison the ability of each type of activated carbon in dye removal under the same conditions, we found that AC2 was more efficient in dye removal as shown in Fig. 1. This is probably due to the porous structure of AC2 which makes it has a high humidity percentage and low ash contents in comparison with that for AC1. Beside that it has a higher uptake adsorption capacity in comparison with that for AC1. These observations can make AC2 more efficient than AC1 in dye removal under applying the same adsorption parameters. The results of dye removal using AC1 and AC2 are shown in Figs. 1-3.

Effect of particle size of activated carbon on dye removal: In order to investigate to the effect of particle mesh size of both AC1 and AC2 samples on RY145 removal, series of experiment were performed using the same adsorption conditions that were applied in the previous investigation. Three mesh sizes were used for each AC1 and AC2. The results of dye removal using 100, 200 and 300 mesh size of these materials are shown in Figs. 4 and 5.

From the above results, it is found that the mesh size 200 was more efficient in dye removal for both AC1 and AC2 and AC2 was relatively more efficient than AC1. It is clear that the efficiency of RYD-145 removal was increased with decrease of the mesh size from 300 to 200. The surface area of the

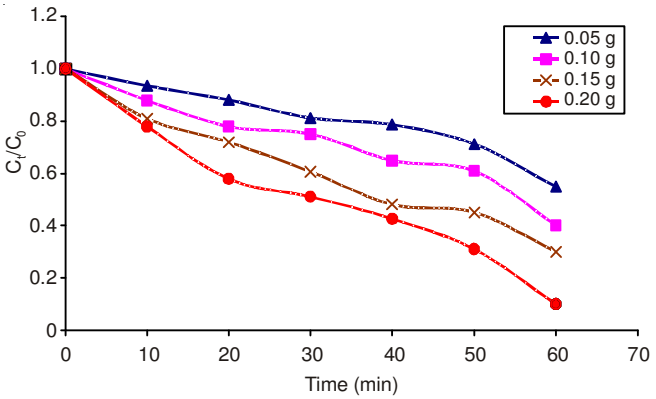

Fig. 1. Effect of contact time of AC1 on the adsorption of RYD-145 dye

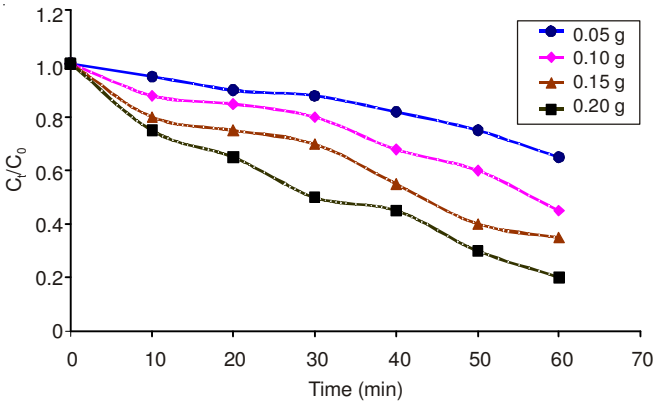

Fig. 2. Effect of contact time of AC2 on the adsorption of RYD-145 dye

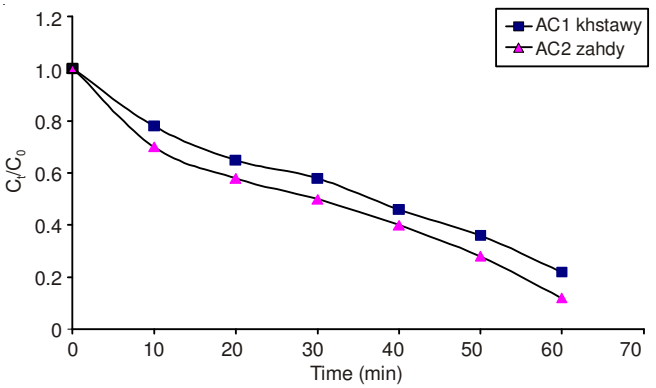

Fig. 3. Removal of RYD-145 onto AC1 and AC2 samples

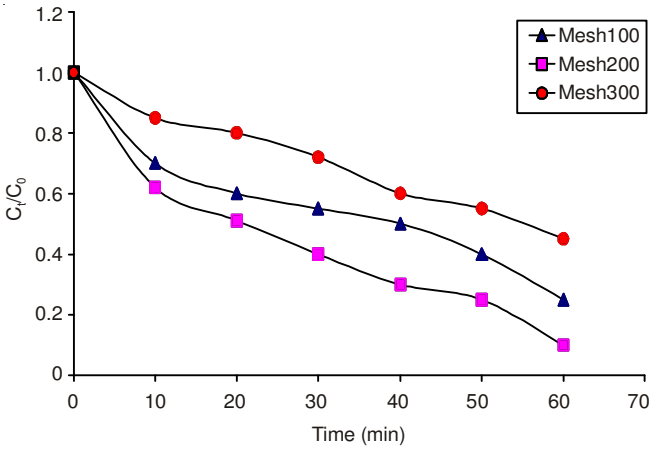

Fig. 4. Effect of mesh particle size of AC1 on the adsorption of RYD-145 dye

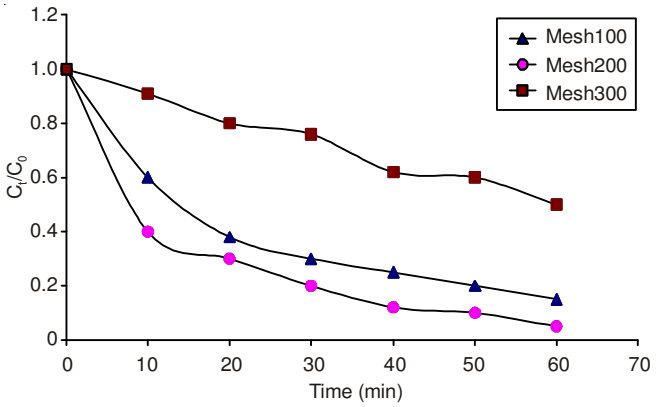

Fig. 5. Effect of mesh particle size of AC2 on the adsorption of RYD-145 dye

catalyst increases with decreasing of particle size, this can provide more sites that are contributed in the adsorption of the dye. Low efficiency in dye removal at size 100 is probably due to the aggregation of these small particles to form agglomerate in the reaction mixture. This can lead probably to reduce the activity of dye removal using this small particle size[24].

Effect of pH of solution on dye removal: The value of pH of the reaction mixture can affect significantly on the adsorption processes. Figs. 6 and 7 show the percentage of RYD-145 dye on both AC1 and AC2 at three pHs values (3, 7 and 9) for a reaction mixture.

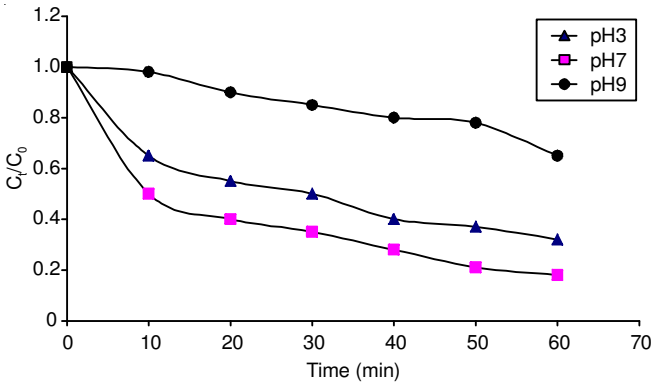

Fig. 6. Effect of pH of the AC1 on the adsorption of RYD-145 dye

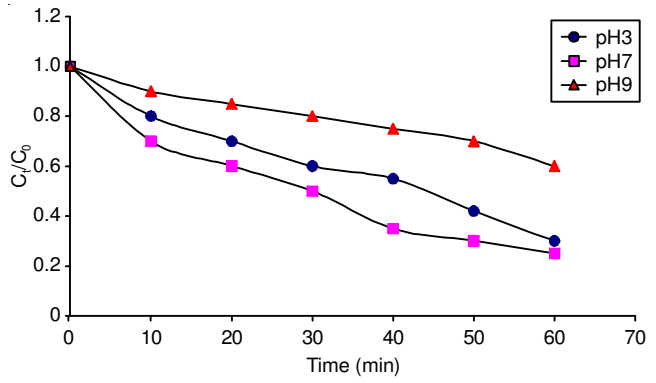

Fig. 7. Effect of pH of AC2 on the removal of RYD-145 dye

From these figures its clear that, the activity of dye removal are changed significantly with change of pH values for both AC1 and AC2. The best removal percentage of dye for two cases of activated carbon were obtained at pH = 7 (around 80 %), while higher pH (pH=9) gave less activity in dye removal around (40 %). It seems that neutral pH value (pH = 7) gave a higher activity for dye removal. From these results, the best results were obtained at neutral pH value, this probably due to less adsorption capacities of this dye at acidic and basic pH values[25].

Uptake adsorption capacity of the synthesized activated carbon: The adsorption capacity of both AC1 and AC2 samples were estimated by following the adsorption of RYD-145 from the aqueous solution. These results are shown in Table-1 as (mg/g). From the obtained results it can be concluded that, these synthesized activated carbons materials are exhibited high external surface areas. This means that these materials have a high porosity in their structures[26,27] and consequently these materials can be used as efficient adsorbent materials for wide range of applications. The uptake adsorption capacities for AC1 and AC2 are shown in Table-1.

TABLE-1
ADSORPTION UPTAKE CAPACITY FOR
THE SYNTHESIZED ACTIVATED CARBON

Sample	AC1	AC2
Uptake capacity (mg/g)	197.2	199.4

Ash contents of the synthesized activated carbon: Ash content of activated carbons is due to of non-carbon materials (inorganic materials), these materials are still within the structure of activated carbon after heating at high temperature during activation processes under inert atmospheric conditions. However, these materials may be found as constituents' materials in the composition of activated carbon. In case of presence of these residual materials in the structure of activated carbon, this can affect negatively on the adsorption capacity of activated carbon. This can lead to reduce its total activity as adsorbents with increase content of these materials. In present current study, the percentage of ash content for both AC1 and AC2 was very low. According to this result, the synthesized activated carbon in this work can be considered as good candidate adsorbent material[28]. The results of ash contents for both AC1 and AC2 are shown in Table-2.

TABLE-2
ASH CONTENT PERCENTAGES FOR
THE SYNTHESIZED ACTIVATED CARBON

Sample	AC1	AC2
Ash (%)	0.18	0.11

Humidity of the synthesized activated carbon: The presence of humidity in activated carbon results from the ability of activated carbon to absorb the available ambient moister when it is subjected to normal atmospheric conditions. activated carbon has ability to adsorb humidity into the porous structure. Generally, the obtained results in this work there is a considerable levels of the moisture content for both AC1 and AC2 and AC2 has relatively higher value in comparison with AC1 under the same humid conditions. This probably arises due to the porous structure of these materials[29,30]. The percentages of moisture content for activated carbon samples are summarized in Table-3.

TABLE-3
PERCENTAGE OF MOISTURE CONTENT FOR THE SYNTHESIZED ACTIVATED CARBON

Sample	AC1	AC2
Humidity (%)	44	48

Scanning electron microscopy: SEM images of surface morphology of both AC1 and AC2 are shown in Fig. 8. These images exhibit relatively irregular with heterogeneous morphology of the surface. Beside that, these images show pores and cavities for carbon samples. Both porosity and cavities are important features that can improve the efficiency of the adsorbent to uptake dyes and others adsorbents with high efficiency from their solutions. Scanning electron microscopy images for AC1 and AC2 are shown in Fig. 8.

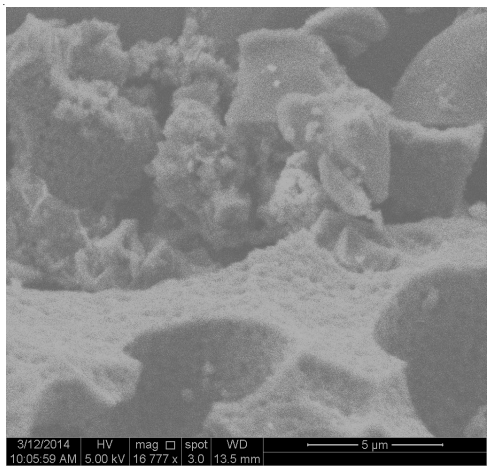

Fig. 8. SEM images for the AC1 and AC2 samples that synthesized from Iraqi zahdy date palm seeds and Iraqi khestawy date palm seeds

FTIR spectroscopies of activated carbon samples: FTIR spectra of both AC1 and AC2 are almost similar. These spectra exhibit three main peaks ranged from 1700 to 1400 cm^{-1}. The peak that appears around 1700 cm^{-1} can be assigned to the stretching vibration modes for C=O bonds. The other band that occurs around 1425 cm^{-1} is assigned to the stretching vibrations of C-C bonds[31]. Additionally, the broad peak that appears around 1600 cm^{-1} is assigned to vibrations modes of aromatic rings[32]. Both AC1 and AC2 show absorption band around 3000 cm^{-1}, this peak confirms the presence of the unsaturated alkynes C=C stretching modes. Broad bands in the range of 3600-3500 cm^{-1} are related to the vibration modes of OH groups.

Point zero charges of the activated carbon: The point zero charges of the AC1 and AC2 of the synthesized activated carbon in this study were conducted using potentiometric method. These results are summarized in Table-4. The point zero charges values of both AC1 and AC2 show in almost basic value (8.10-8.20). From these results we conclude that both AC1 and AC2 are exhibited an alkaline pH values. These results are shown in Table-4.

TABLE-4
POINT ZERO CHARGES FOR THE SYNTHESIZED AC1 AND AC2

Sample	AC1	AC2
pH of activated carbon	8.20 ± 0.1	8.10 ± 0.08

Conclusion

In this study activated carbon was synthesized from Iraqi zahdy and khestawy date palm seeds. These materials used for the removal of RYD145 dye from its aqueous solution. Physical properties of AC1 and AC2 were studied such as ash content, humidity, adsorption capacity. Additionally, FTIR spectra for these materials were undertaken. AC2 was more active in dye removal in comparison of AC1 under the same adsorption conditions. The synthesized materials showed high external surface areas which make them as good adsorbent materials. Beside that they showed low ash content with relatively high moisture content. These properties are considered as encouraging physical properties for these materials to be used as adsorbent material. Adsorption isotherm studies showed that they are fitted with Langmuir model. This study can play important role in the environmental and industrial applications as we have synthesized efficient adsorbent materials from raw agricultural waste, especially from palms seeds of Iraq is state that is too famous with different types of dates.

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