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Removal of Reactive Yellow 145 Dye from Simulated Industrial Wastewaters on Iraqi Khestawy Date Palm Seeds Based Activated Carbons.

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ABSTRACT

This study involves synthesis of activated carbon (AC) from Iraqi khestawy date palm seeds (IKDPS) using KOH and H_3PO_4 as a chemical activator. These two types of activators yielding two types of activated carbons, the first one is that activated with KOH and termed as AC1 while that activated with H_3PO_4 is termed as AC2. Synthesis processes for both AC1 and AC2 were performed using chemical activation method. Different physical and chemical properties of the synthesized AC were investigated such as adsorption uptake capacity, humidity percentage, ash content, and the point zero charges of the synthesized samples were also calculated. Surface functional groups of the synthesized ACs were investigated with Fourier transform infrared spectroscopy (FTIR) and the surface morphology was studied using scanning electron microscopy (SEM). Adsorption activity of both AC1 and AC2 was investigated by following removal of reactive yellow dye 145 (RYD145) from simulated industrial wastewaters. Different reaction parameters and conditions were undertaken including the amount of loading of AC, duration of the adsorption process, and the effect of pH of the used samples. It was found that AC1 was more efficient than AC2 in dye removal under the same adsorption conditions.
Keywords: Activated carbons, Textile dyes removal, wastewaters treatment, Iraqi date palm seeds.

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INTRODUCTION

In the last few decades there was high levels of pollution as a result of mass applications of industrial products in our modern life including food, medicines, clothes, dying processes and many other applications. Using these materials can result in high levels of pollution in water, air and soil. Among these different sources of pollutants, textile industries are an important source for water pollution. This type of industry use different types of synthetic dyes in different processes especially in dying processes. Most of these dyes normally have a complex structure that is can't be fragmented easily under ambient circumstances. Normally these dyes are charged with industrial waters from textile factories. Vast majority of these dyes are polluted and toxic for all living organisms. Besides that, some of these dyes can participate in other reactions and generate carcinogenic and toxic by-products. Massive effect can occur if these polluted industrial wastewaters are effluent to the stream river and / or to sources of drinking water [1,2]. Most of these synthetic dyes are highly resistance for decomposition and/or fragmentation when they are exposed to normal treatment conditions such as using normal air conditions, industrial light, sunlight and/ or chemical oxidizing agents [3,4]. Using normal treatment methods such as physical, chemical and biological treatment seems to be not efficient with these dyes due to the above mentioned reasons [5,6]. Recently adsorption processes was a promising alternative route that can be used more efficiently in dye removal in comparison with the above methods. It can give a high removal efficiency, relatively low cost and easily processing with the reproducibility of the used adsorbent under simple recycling processes [7] . In this type of treatment, the adsorbent is the key factor so that its physical and chemical properties play crucial role in this process.

Among different types of the used adsorbents is the activated carbons (ACs) which can be used to remove wide spectrum of the polluted materials including synthetic dyes [8]. The commercially available AC is expensive which makes the use of this materials in mass applications is not efficient and not applicable economically . So that the current researches are aimed to synthesis different types of AC from ambient natural agricultural wastes with low cost and a high porosity and surface area. So that the synthesis of AC from available agricultural raw materials and /or by products can offer alternative routes towards production of low cost and widely available of this type of adsorbent [9] . In this context, high abundance of cheap local agricultural raw materials makes them too promising in the synthesis of commercial types of AC that can be used for many applications [10 -15].

The current work, involves the synthesis of the ACs from Iraqi khestawy date palm seeds. These types of ACs would be synthesized by physiochemical activation method using KOH and H_3PO_4 as activators. The activity of each type of AC would be studied by following adsorption of reactive yellow dye145 from the simulated industrial wastewaters.

EXPERIMENTAL

Adsorbate

Reactive yellow 145 dye (RY145) was used in this study as a model of polluted dye, its molecular formula is ($C_{28}H_{20}ClN_9Na_4O_{16}S_5$). This dye was provided by Fluka Company (98%) and it was used as provided without any further purification.

Synthesis of the activated carbon

Iraqi khestawy dates palm seeds was used as raw agricultural materials in the preparation of the AC. In this process, date palm seeds were collected from local markets and washed with hot distilled water to remove any wastes that are stacked or adsorbed on the date palm seeds. After that these samples were decanted and dried at 110 ºC for two hours and then mixed with the used activator in appropriate ratio in a chemical activation process. The used activators in this study were H_3PO_4 and KOH. After treating these samples with the activator, they were filtered of and then dried. Then they were heated at 700 ºC in a graphite furnace for one hour under nitrogen flush. Then the resultant samples were cooled to room temperature and washed with distilled water until pHs of the washed solutions reach around 7. After that, final products were dried at 110 ºC for two hours to give final activated carbon. In this study the obtained AC that was activated with KOH will be termed as AC1 and that activated with H_3PO_4 as AC2.

Adsorption studies

The adsorption processes were performed under normal atmospheric conditions using a magnetic stirrer. Initial RY145 dye concentration in this study was equal to 10 ppm. In each run a simulated industrial wastewater containing a dye concentration of 10 ppm in 100 mL. To this solution the used AC was loaded in different masses : (0.01, 0.05, 0.10, 0.15, 0.20 g). In all experiments, periodically 2 mL of the reaction mixture was withdrawn for each ten minutes and for duration of one hour of reaction time. These samples then were centrifuged for several times and the absorbance was systematically recorded at a wavelength of 416 nm. The absorbance of the supernatant liquid was recorded using Spectrophotometer Shimadzu 1650 PC-UV-visible. The efficiency for dye removal from the simulated industrial wastewaters (R%) was calculated using the following equation [16,17]:

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

Where, C_i is the initial dye concentration and C_f is the final dye concentration that is remaining after one hour of adsorption, and q is the dye concentration that is adsorbed on the used AC in (mg/g). Adsorption capacity at a given time (q_t) can be calculated from the following relation as follows:

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

From the above equation, C_t is the dye concentration as a function of time, the term (v) is the volume of solution and (m) is the amount of the used adsorbent (AC).

Effect of contact time and adsorbent dosage

The effect of adsorbent dosages and contact time on dye removal were conducted by performing a series of experiment, in each one an aqueous solution of RY145 (10 ppm, 100 mL) was used. These experiments were undertaken at different contact times that are ranged from (0- 60) minutes. To investigate the effect of mass of AC on the dye removal, different dosages of AC were used with aqueous solution of RYD145 10 ppm, 100 mL.

Effect of pH of mixture on dye removal

In order to investigate the effect of the pHs of the reaction mixture on the removal of RY145 from the used aqueous solution. A series of experiments were performed under three different values of pH, these are 3, 7, and 9. The pH of mixture was adjusted to a desired values by adding small droplets from 0.1N HCl and NaOH to the initial aqueous solutions with using pH meter measurement to adjust the pHs to precise values .

Adsorption capacity of the synthesized activated carbon

Adsorption ability of the AC was estimated by methylene blue method[18], according to this method 0.1 g of AC was suspended in an aqueous solution of methylene blue (MB), (100 mL, 20 ppm). This mixture was stirred in atmospheric conditions at room temperature for 24 hours. After that, this mixture was separated by centrifuge and the absorbance of the supernatant liquid was measured at 665 nm using UV-visible spectrophotometer. Adsorption capacity of both AC1 and AC2 was calculated using a suitable calibration curve of standard solutions of MB. Then the adsorption uptake capacity of the synthesized AC were calculated by comparing these concentrations with the initial concentration of MB (20 ppm) [18] .

Ash contents of the synthesized activated carbon

Ash content for the synthesized AC1 and AC2 samples was evaluated using a desired accurate weight of a sample that is dried carefully in a suitable crucible. This sample then was burned at ^{o}C in a furnace under normal atmosphere for one hour. Then the burned samples were cooled to room temperature. The

weight percentage of the ash was calculated by considering the remaining amount of material in the used crucible was relative to the initial weight of the AC. So that the ash percentage can be estimated by comparing this weigh and the initial weight of the taken AC[19].

Humidity of the synthesized activated carbon

The percentage of humidity of both AC1 and AC2 samples was investigated using (0.10 g) of the dried AC. This was   subjecting to the normal atmospheric conditions in the Lab for 24 hour. Then these samples were weighted accurately, and then dried in an oven at 110 ºC for one hour. Then the sample weighed again accurately and the humidity percentage can be calculated by comparison of the final weight with initial weight of the used materials [20].

Fourier transform infrared spectroscopy (FTIR)

Functional groups of the synthesized AC1 and AC2 sample was investigated with FTIR spectroscopy using Perkin Elminer Spectrophotometer. FTIR analysis was recorded in the range of 450 to 4000 cm^{-1}. Prior to run, samples were prepared by KBr disc method making them as pellets by grounding with KBr salt at a ratio roughly 1/50. FTIR spectra were recorded with a resolution power of 1 cm^{-1} for each run.

The point zero charge (PZC)

Surface charging of both AC1 and AC2   were calculated according to the   potentiometric titration method [21]. According to this procedure, 100 mL of 0.03 M of KNO_3 was used as a blank solution. This solution, then was mixed with NaOH (1mL of 1M) and this mixture was titrated with HNO_3 (0.10M). Another prepared mixture (100 mL of KNO_3) with 0.10 g of the synthesized AC was stirred under normal atmospheric air conditions at room temperature   for 24 hour. To this mixture,   1.0 mL of NaOH was added and then titrated with HNO_3 as it mentioned above. The results of the titration processes were plotted as a volume of the added acid against pHs values for each   mixture and the obtained intersection point was considered   as a PZC for each AC and these results are shown in Table 4.

Scanning electron microscopy (SEM)

The morphological study the of surface for both AC1 and AC2 samples were performed using SEM (Scanning Electron Microscope Inspect 550, Netherland). SEM machine was operated at 25 kV. All the samples of synthesized AC were dried prior to e adhesive on carbon tape attached to aluminum – stubbed sputter coated with platinum.

RESULTS AND DISCUSSION

Uptake adsorption capacity of the synthesized activated carbon

The uptake adsorption capacity of the synthesized activated carbon samples were measured by considering   the adsorption of methylene blue dye from its aqueous solution. Adsorption capacity for both AC1 and AC2 were measured as (mg/g) and   are shown in Table 1. This means that these materials have a high porosity in their structures and are exhibiting high external surface areas [22,23]. So that these materials can be used as efficient adsorbent materials for wide range of applications. Uptake adsorption capacity of the synthesized activated carbon.

Table 1: Adsorption uptake capacity for the synthesized AC

Sample	AC1	AC2
Uptake capacity (mg/g)	198.1	195.3

Ash contents of the synthesized activated carbon

For the activated carbon, the presence of ash is attributed to the presence of inorganic materials that are found in the composition of this type of materials. These materials are resistant towards high temperatures and therefore still within the structure of AC 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 AC. In case of presence of these residual materials in the structure of AC. The presence of these residual materials in the structure of AC can affect negatively on the adsorption capacity of the used. However, in this current work, the percentage of ash content for the synthesized AC was very low. So that, these materials can be considered as efficient adsorbent materials [24]. The results of ash contents for both AC1 and AC2 are shown in Table 2.

Table 2: Percentage of ash content for the synthesized AC

Sample	AC1	AC2
Ash%	0.12	0.16

umidity of the synthesized activated carbon

Humidity in the AC results from the ability of AC to absorb the available ambient moisture when it is subjected to normal atmospheric conditions. This arises from the ability of AC to adsorb available humidity into its porous structure. Generally, the obtained results in this study showed that these materials can absorb the ambient humidity with considerable efficiency. Also it was found that AC1 has relatively higher value in comparison with AC2 under the same humid conditions. This probably can be attributed to the porous structure of these materials [25,26]. The percentages of moisture content for the synthesized AC samples are summarized in Table 3.

Table 3:The percentage of moister content for the synthesized AC1 and AC2

Sample	AC1	AC2
Humidity%	46	42

Scanning electron microscopy (SEM)

The surface morphology of the synthesized AC1 and AC2 are shown in Figure 1. These images are relatively irregular in their texture with heterogeneous morphology of the surface. In addition to that, these images show pores and cavities for both AC samples. These porosity and cavities are important features that can improve the efficiency of the adsorbent to have high adsorption capacity and hence can adsorb dye molecules with high efficiency from their solutions.
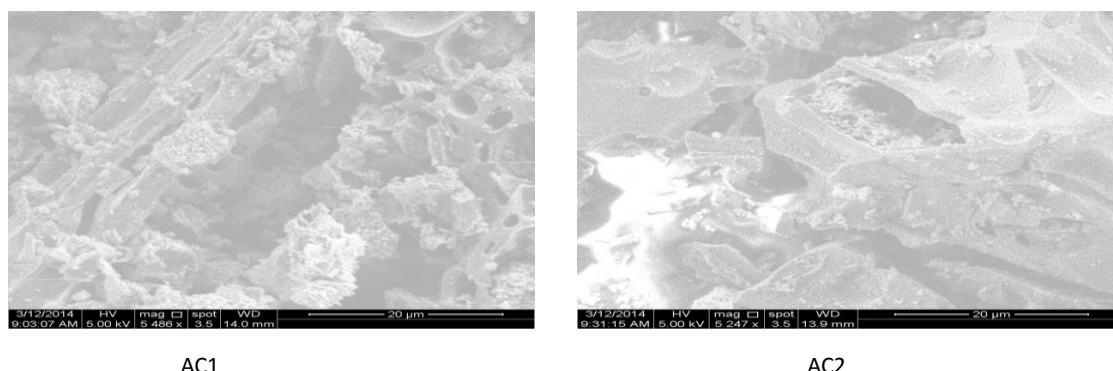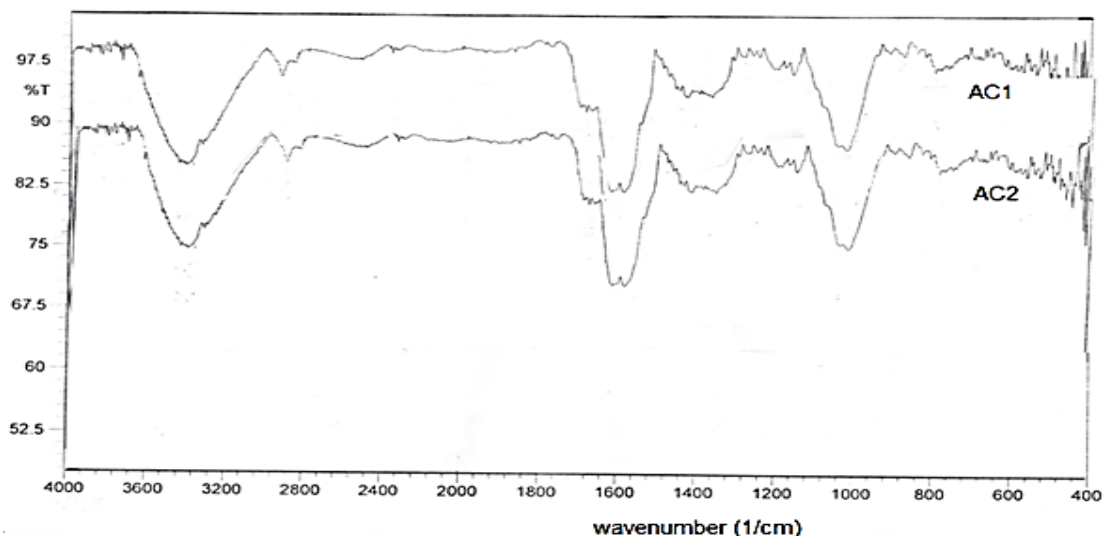

AC1   AC2

Figure 1: SEM images for the AC1 and AC2 samples that synthesized from IKDPS

FTIR spectroscopies of AC samples

Surface functional groups of both AC1 and AC2 were investigated using FTIR spectroscopy and these spectra were almost similar for the both samples. Generally, FTIR spectra for these samples show three main peaks around 1400 to 1700 cm^{-1}. The peak that appears around 1700 cm^{-1} can be attributed to the stretching vibration modes for C=O bonds. The other band that appears around 1425 cm^{-1} is related to the vibration mode of C-C bond [27]. The broad peak that appears around 1600 cm^{-1} is assigned to vibrations modes of aromatic rings [28]. Both AC1 and AC2 show absorption band around 3000 cm^{-1}, this peak confirms the presence of the unsaturated alkynes C=C stretching modes. The bands that are appeared around 3500-3600 cm^{-1} can be assigned to the vibration modes of OH groups of the surface of the synthesized AC. FTIR spectra for the synthesized AC1 and AC2 samples are shown in Figure 2.

The point zero charges of the activated carbon (PZC)

The points zero charge of the synthesized activated carbon in this study was calculated according to potentiometric method[21], PZC results are summarized in Table 4. These values of PZC for both AC1 and AC2 show in almost basic value (8.15- 8.25). From these results we conclude that both AC1 and AC2 are exhibited an alkaline pH values.

Table 4:The point zero charges for the synthesized AC1 and AC2

Sample	AC1	AC2
pH of AC	8.25± 0.1	8.15±0.08

Effect of AC loading and contact time on dye removal

The effect of contact time on removal of e RY145 dye from the aqueous solution is shown in Figures 3 and 4 . From these figures it can see that there is a an improvement in dye removal over both AC1 and AC2 with the development of adsorption time. In this process all samples were shacked for one hour at room temperature under normal atmospheric conditions in in order to achieve a full equilibration for all doses of the AC in this study [29]. By comparison of the ability of each type of AC in dye removal under the same conditions, it was found that AC1 was more efficient in dye removal as it shown in Figures 5 and 6. This is probably due to the porous structure of AC1 which makes it has a high humidity percentage and low ash contents in comparison with that for AC2 [30]. Beside that it has a higher uptake adsorption capacity in comparison with that for AC1. These observations can make AC1 more efficient than AC2 in dye removal under applying the same adsorption parameters.
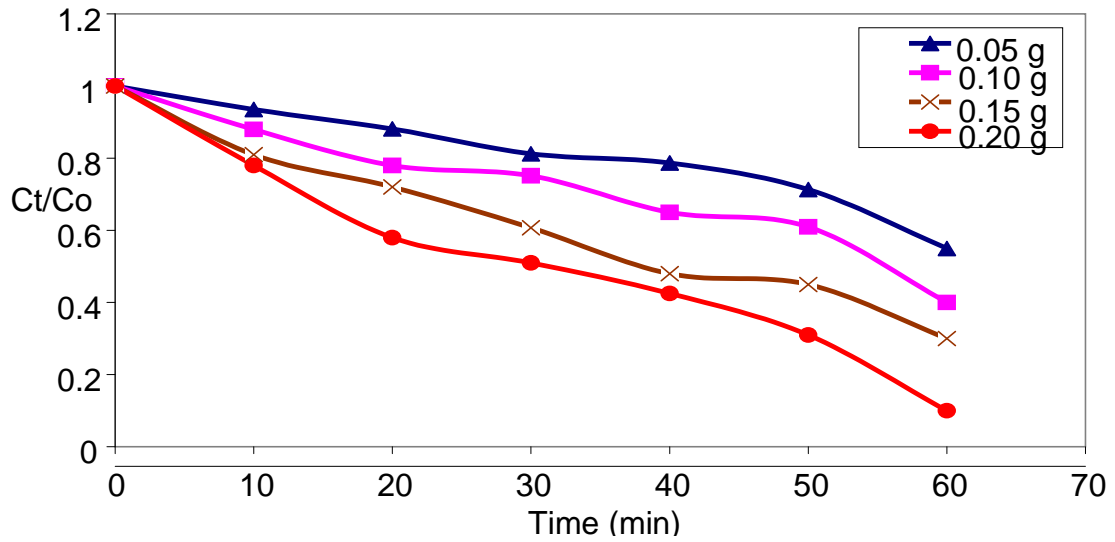
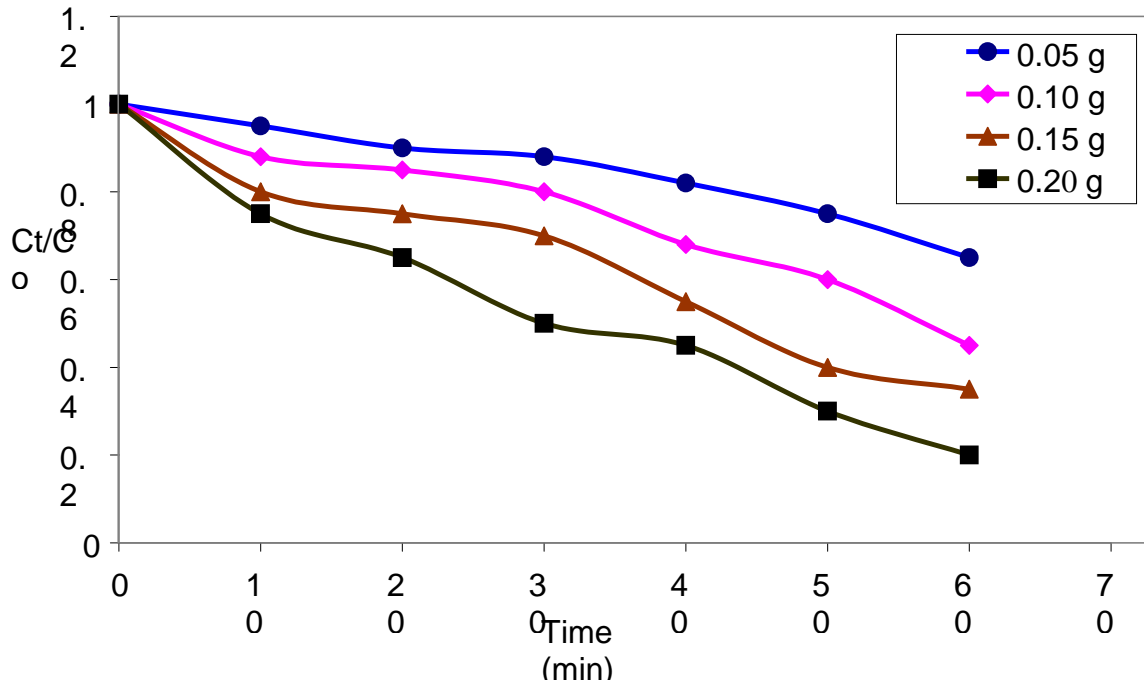**Figure 3: Effect of contact time of AC1 on adsorption of RY145 dye.**

Figure 4: Effect of contact time of AC2 on adsorption of RY145

Effect of pH of solution on dye removal

The percentage of dye removal over AC is affected by the value of pH of the reaction mixture. This arises from the change on the surface charge which can affect significantly on the adsorption of dye molecules on surface of the used AC. The results of dye removal of each of AC1 and AC2 under different pH values are shown in Figures 5 and 6.
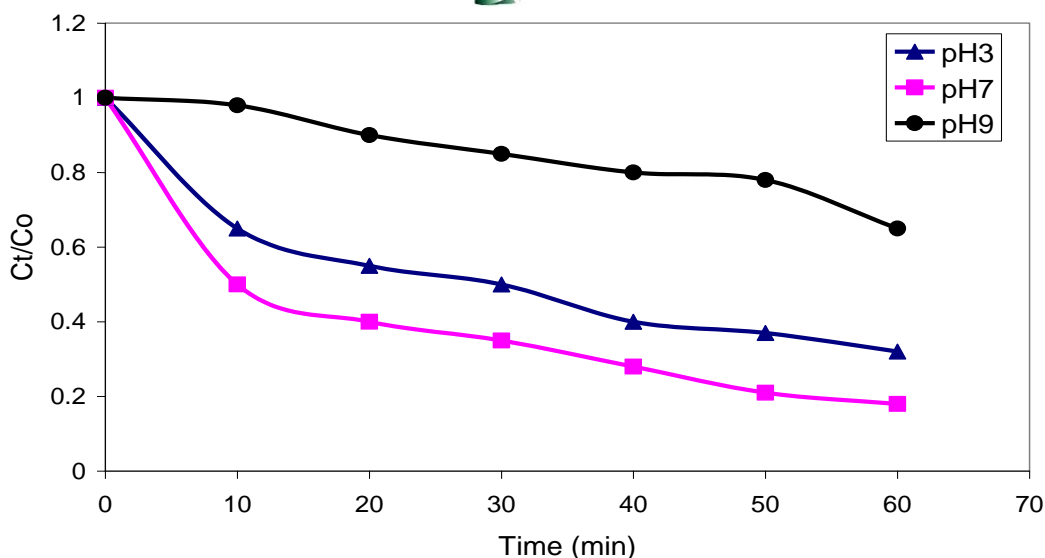.

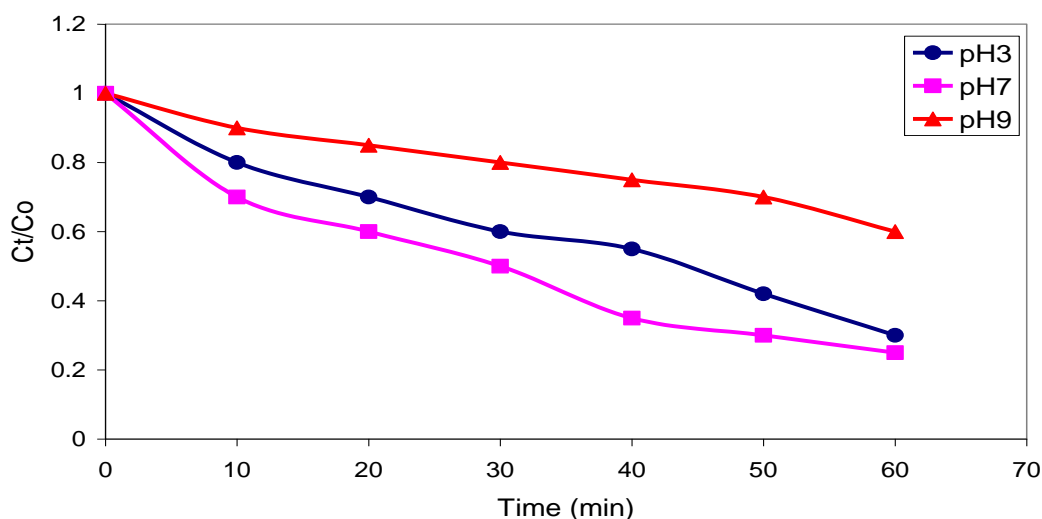**Figure 5: Effect of pH of AC1 on adsorption of RY145 dye**

Figure 6: Effect of pH of AC2 on removal of RY145 dye.

From these results it can be seen that, the activity of dye removal was influenced with the changes of pH values for each of the synthesized AC1 and AC2. The best obtained removal percentage of dye for two cases of AC were obtained at neutral media (pH=7). When the pH of the simulated industrial water was around pH=7,   around 80% of the dye were removed from the bulk solution for both of AC1 and AC2. The efficiency of dye removal was reduced under basic mixture (pH=9). In addition to that the efficiency was also reduced under acidic reaction mixture (pH=3). From these obtained results, neutral pH value showed a higher activity for dye removal in comparison with high basic and acidic mixture [31]. This probably arises from the repulsion forces that are established between the adsorbed species of dye molecules and the surface of the adsorbent. This can lead   to less adsorption capacities of this dye at high acidic and basic pH values [32].

CONCLUSIONS

In this study activated carbon was synthesized from Iraqi khestawy date palm seeds using KOH and H3PO4 as activators to yield AC1 and AC2 respectively. These materials were used as adsorbents in the removal of RY145 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. AC1 was more active in dye removal in comparison with of AC2 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.

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