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Removing Crude Oil from Water by Activated Carbon Prepared From Dried Papyrus Plant

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Abstract

Crude oil pollution is a serious problem that causes severe damage to the environment. The adsorption process by using one of the adsorbents is considered one of the most important and successful methods for getting rid and removing crude oil from the water. In this study, activated carbon was used as a sorbent to clean the water from crude oil. This use of activated carbon is new. Adsorption parameters tested included the contact time on adsorption, sorbent dosage, the impact of pH, and temperature. The removal of crude oil from water by activated carbon was investigated by batch adsorption after varying contact time (5–30 min), adsorbent dosage (5–50 g), pH (2–11), and temperature (10–50 ^{0}C). hydrophobicity of carbon has increased very significantly due to the modification that was made on carbon, and this, in turn, led to the creation of a sorbent with a very high ability to remove crude oil from the water and thus increase the adsorption capacity. As the results of the study show that the highest value of adsorption capacity was 96% at contact time 20 min, sorbent dosage (25 g), pH (7), and temperature (30 ^{0}C). The prepared adsorbent showed the potential to use as a low-cost adsorbent in oil-spill clean-up.

Keywords: Adsorption**,** Papyrus plant, Activated carbon, Crude oil

1. Introduction

Oil spills are among the huge problems that happen repeatedly due to human mistakes and neglect, once they are intended and the other unintended. There are many examples, including wars and sabotage, as well as natural disasters such as hurricanes, earthquakes, and explosions. [1]. All these events caused a lot of serious health damage to humans, animals, and the environment, as well as great losses in energy and precious oil products[2,3]. Therefore, appropriate methods must always be found to quickly remove oil stains after every spill. The process of treating oil slicks and removing them continuously and with the latest methods using materials with great ability to adsorption has a very great importance in various environmental, economic and health fields. Therefore, work has been done to search for different materials used in this field [4,5].
Activated carbon is one of the important ways widely used in pollutant removal from water. Several studies about the preparation of activated carbon from plants and agricultural residues seeds of have been conducted including coconut shells, groundnut shell, bamboo dust [6-8], palm kernel shell [9,10], coir pith [10], wheat husk [11]and rice husk [13-15].In this study, it was obtained active carbon from papyrus plant by chemical and physical activation methods. In this study, well-known and common aquatic plants, papyrus plant, were used for the purpose of getting rid of one of the dangerous pollutants, which is crude oil. Activated carbon was prepared from the papyrus plant. This plant is found in stagnant water swamps. In the form of evergreen plant clusters, this plant reproduces by division in the form of fibers in the depths of the water. The adsorption process is a well-known method used to remove organic and inorganic pollutants, where these pollutants are present in aqueous solutions, and when a suitable solid material is available, it has certain properties that make it have the ability to attract these unwanted particles because the forces of attraction between the solid and dissolved materials are large and thus work on Precipitation of these pollutants on the surface of the adsorbent material.The solute which is retaining (on the solid surface) during the adsorption processes is called adsorbate, while, the solid where it is reserved is known as an adsorbent. Adsorption is the accumulation of atoms or molecules of the adsorbing

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material on the surface of the adsorbent material, whenever the adsorbent material has a surface that possesses certain properties, the adsorption process is good. The atoms on the surface of the adsorbent material are not all surrounded by other atoms, so it can attract a lot of atoms and molecules[15].

2. Experimental

2.1. Procedure for oil removal tests

Crude oil was obtained from the Dhi Qar refinery of the Dhi Qar Oil Company in southern Iraq. Experiment samples were obtained by forming a mixture of crude oil and water by using an appropriate amount of crude oil with a certain volume of water. The tests were initially performed by taking 5 g of the adsorbent and placing them in 500 ml of the pre-prepared test solution at a temperature of 10 ° C for a limited period of time of 5 min of contact time. After that, the experiment was repeated by increasing the sorbent doseg, increasing the temperature, and increasing the contact time periodically, all at different pH value s. Then determine the optimal conditions to achieve the highest possible value for the adsorption capacity [16,17]. In a (1 liter) baker's capacity, 500 mL of test solution was prepared at (10 °C), 100 ml of crude oil was added to 400 ml of water for the purpose of forming the first test solution with a volume of 500 ml, then 5 g of sorbent was added and the solution was stirred for 5 min after which solution was filtered, the sorbent isolated, left to dry and then weighed. The remaining oil is extracted with hexane after repeated washing of the adsorbent. The oil concentrations were estimated using spectroscopy devices (Perkin Elmer Lambda2 UV/Vis/ NIR).As it is known, determination of the concentrations depends on the principle of the linear relationship between absorbance and concentration, or by relying on the well-known Lambertian law. Where different concentrations of crude oil were used in hexane, and for estimating the concentration of crude oil, wavelengths were 223 , 224 and 294 nm.

2.2. Instrumental

1-Water-distillation mega pure 6 liter automatic water still is a compact unit, which designed to provide 6 liter per hour of ultra-high purity distilled water . 2-pH meter "JENWAY- LTD Instrument, digital model 3310". 3-Perkin Elmer Lambda2 UV/Vis/ NIR Spectroscopy. 4-Shaker used is: "Germany. RPM=20 - 400 - Heidolph Prom ax 2020".

2.3. Preparation of Stationary Phases

Papyrus plants were collected from a lake in southern Iraq in the city of Nasiriyah, and then they were cleaned well to prepare them in order to prepare the adsorbent material through many stages.

2.3.1. Dried of Papyrus Plant

The first step is to remove the roots of the plant and then wash the remaining part with plain water and then with distilled water, after that it is treated with EDTA at a concentration of 0.056 M with a pH number 10. Then the product is dried in an oven where the temperature in all its parts is 110 for a period of 24 hours, and thus the material becomes ready for the following modification or activation processes.

2.3.2. Activated Carbon (Carbonization)

In this study, two samples of activated carbon were prepared, each sample was prepared in a way that differs from the other in the use of different acids in the oxidation process. The first sample (SAC) was prepared by drenching 200 g of the dried plant in sulfuric acid at a ratio of 1: 3 (wt:wt). While the second sample (PAC) is prepared in the same way, except that it uses phosphoric acid instead of sulfuric acid, where 750 g of the plant is soaked in phosphoric acid in a ratio of 1: 3 (wt:wt)) in both cases the plant remains for two days in contact with the acid at room temperature After that, the excess acid in each of the samples is removed by washing with distilled water, and then the two washed samples are dried at a temperature of 110 ° C and kept in the oven for 48 hours. For a period of 4 hours after that the product is cooled down and carbon dioxide is passed to it and an appropriate amount of distilled water is added until reaching a pH = 6. Finally the two samples are dried at 110 ° C for 24 hours.

2.3.3. Modified of Activated Carbon

The two carbon samples were modified from the carbonization process in two ways. As for the first sample (SAC), where the amendment was made by taking 20 g of this sample and adding 200 ml of nitric acid at a ratio of 1:10 (w:v), while the second sample (PAC) was taken 25 g of it and adding 250 ml of nitric acid in a ratio of 1:5 (w:v) For the purpose of improving the formation of the functional groups, the composition of the two samples was boiled for a period of time of 4 hours, after which the product was washed with distilled water until the pH reached a value of 6 and finally the activated carbon was dried at a temperature of about 120 C. After performing the appropriate analysis, it was found that the prepared

materials of the activated carbon contains active acid groups that are responsible for the effectiveness of the prepared materials. And there were other researchers who suggested the formation of other new functional groups such as hydroxylases, anhydrides and aldehydes that provide a great potential for ion exchange that helps in the adsorption process. It is important to know that when the concentration of nitric acid used increases, the carboxylate group increases [17-20].

3. Result and Discussion

3.1. Characterization of activated carbon

3.1.1. FTIR spectroscopy

A Mattson four thousand FTIR spectrometer was used for the purpose of recording FTIR between four thousand and 100 cm^{-1} in which a mixture of 1 mg of activated carbon was placed in the tablets with 500 mg of KBr (Merck pertaining to spectroscopy) in a mortar made of agate and then applied high pressure up to about 5 tons /cm^2 for a period of 5 minutes, and then applying 10 tons /cm^2 for another 5 minutes in a vacuum.

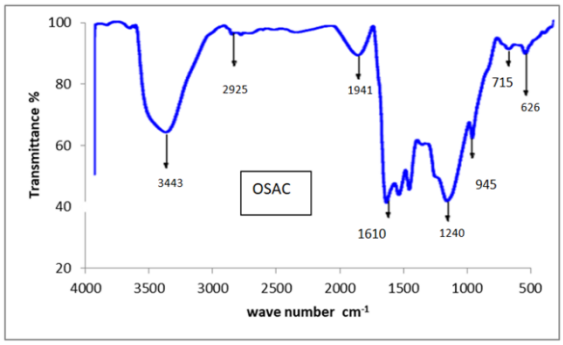

Fig. 1. FTIR spectrum of oxidized activated carbon (OSAC)

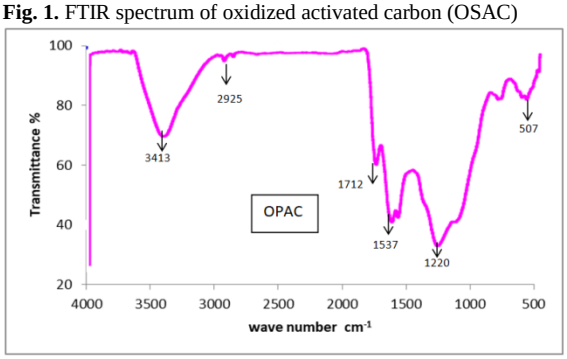

Fig. 2. FTIR spectrum of oxidized activated carbon (OPAC)

Table 1: Function group of OSAC and OPAC

Function group	Wave Number (Cm^{-1})
stretching (O-H) mode of hexagonal group	(3413 - 3443)
Aliphatic (C-H)	(2922 - 2925)
stretching (C=C) in aromatic ring	Bonds near (1633 - 1500)
bonds (C-O) such as in phenols, esters and ethers	(1300 - 1000)
Highly stretching of (C=O), stretching of C-O in carboxylic moieties and carboxylic groups	Bonds near (1220 - 1240)
(C=O) stretching vibrations of carboxyl groups saturated about OSAC and OPAC.	Band at (1712 and 1713)

3.1.2. Scanning Electron Microscopy (SEM)

Before the scanning process with the electron microscope, the samples were ground and heated at 110 ^{0}C for 4 hours for the purpose of drying. For the purpose of obtaining the scanning electron microscope of the two samples (OSAC and OPAC).A scanning electron microscope was used (SEM; JSM, model 6510. Urgently, the secondary electronic imaging position was relied upon, and the voltage difference used was approximately 30 KV.The images obtained from scanning with an electron microscope showed a true and rare porous structure of this material used as an adsorbent, where the magnification was (x1500) for OSAC and (x500) for OPAC.

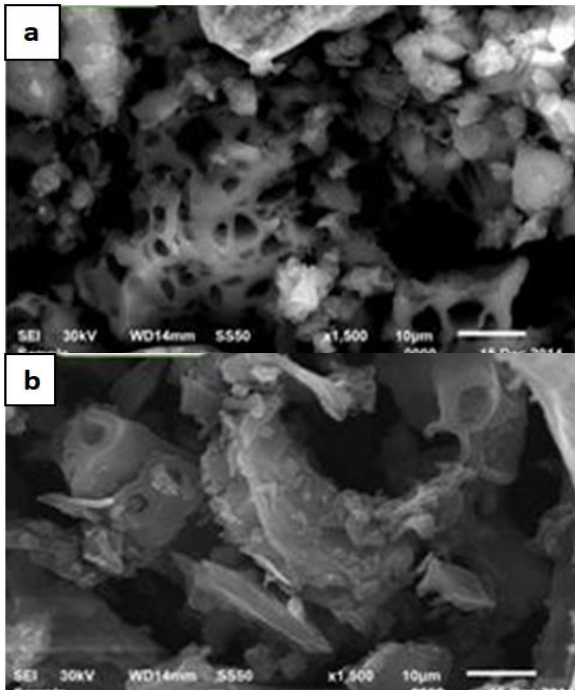

Fig.3. a: SEM photographs of OSAC **b**: SEM photographs of OPAC

3.1.3 Nitrogen adsorption measurements

The surface area and porosity of the carbons are prominent factors in determining their adsorption capacities [21] the textural proprieties of solids are conventionally determined from the adsorption of nitrogen at 77.350 K and the adsorption data are usually analyzed by the application of the BET (Brauner Emmet Teller) Eqs [22].

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Oxidized activated carbon	S_{BET} ($m^2.g^{-1}$)
OSAC	195.6
OPAC	79.89

3.2. Studying the effects on adsorption

3.2.1. Effect of contact time

Tests were conducted at different times for the purpose of knowing the effect of the contact time on the removal of crude oil. The change in contact time with adsorption capacity was plotted and the obtained output was shown in figure 4. The greater the contact time between the crude oil and the adsorbent, the greater adsorption capacity. However, when the contact time was increased, it was found that the rate of adsorption of crude oil remained stable. This is clear by the rule that huge vacant sites of surface are present at the beginning of the first stage of the adsorption process, and after a few seconds, the remaining surface sites become scarce and their subscription process is very weak because of the repulsion forces between the molecules of crude oil on the sorbent surface. This explains why the highest amount of crude oil can be removed is at a contact time 20 min.

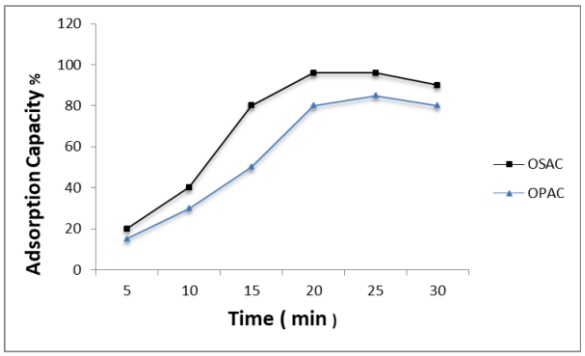

Fig. 4. Effect of contact time on adsorption capacity by OSAC and OPAC

3.2.2. Effect of sorbent dosage

The adsorption of crude oil by activated carbon is expected to be affected by the dosage amount of the adsorbent.The results in figure.5 reveal the effect of sorbent dosage on the crude oil removal. This figure shows that the crude oil removal ratio grows thru the growth in dosage of activated carbon. The percentage of removal crude oil by sorbent increases (5 -50 g) correspondingly. There is not a noteworthy rise in the removal of crude oil when the dosage of sorbent rises more than (25 g) which proposes that the highest sorption is reached after a definite dosage of sorbent, and henceforth the crude oil amount stays unchanged even with the extra increase in the area surface of the sorbent, that in sequence makes the binding sites number higher. Nevertheless, at high dosages of sorbent, the molecules of crude oil available are not adequate to all the exchange sites on the sorbent, which causes crude oil adsorption to decrease [23]. Thus, the best dosage for activated carbon improved is (25 g) dosage is utilized for all experiments.

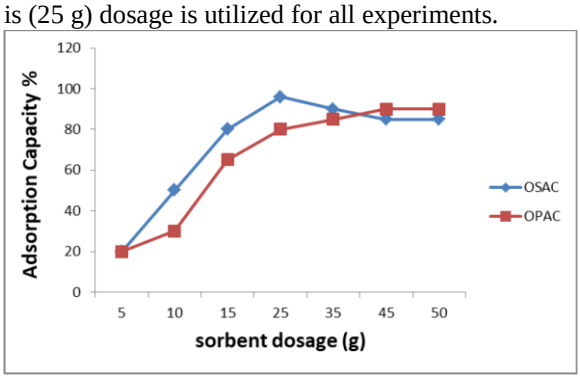

Fig. 5. Effect of sorbent dosage on adsorption capacity of OSAC and OPAC

3.2.3. . Effect of PH

The available active sites on the surface of the adsorbent material depend greatly on the pH, so the pH is an important factor affecting the adsorption process[24]. In this study the test was performed at different pH values ranging from (2-11) as shown in the figure (6). Since the optimum pH is 7 for which the adsorption capacity is highest possible, the reason for this may be the large difference in concentration of both the hydroxide ion and the hydrogen ion formed in solution.

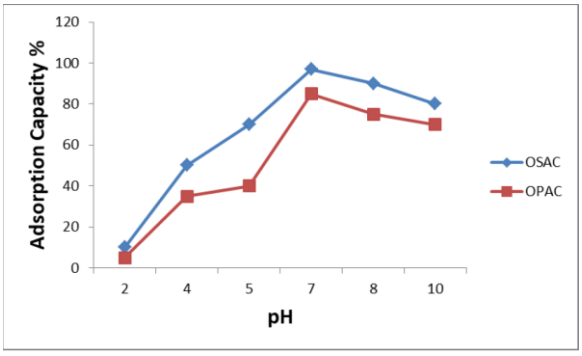

Fig. 6. Effect of PH on adsorption capacity by OSAC and OPAC

3.2.4. Effect of temperature

The effect of temperature on the removal of crude oil by OSAC can be seen clearly through the results presented in figure 7. Show that the temperatures effect is changing depending on the amount of the area exposed to the air from the crude oil, so the more the area exposed to the air, the greater the temperature effect. As it is known when the

temperature rises, the viscosity decreases and when the temperature decreases, the viscosity increases. The effect of temperature on the removal of crude oil by OPAC can be seen clearly through the results presented in figure 8. As temperatures rise, the rate of removal of crude oil increases due to the increase in chemical reactions between the crude oil molecules and the active groups found on the surface of sorbent.

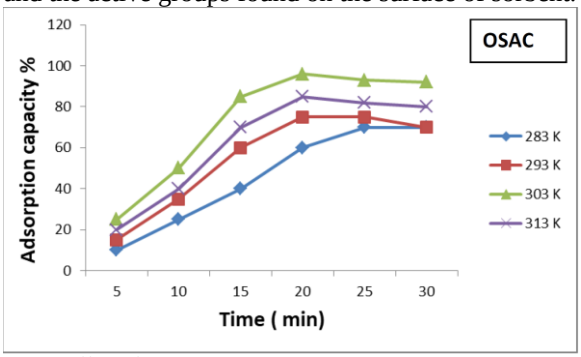

Fig. 7. Effect of temperature on adsorption capacity by OSAC

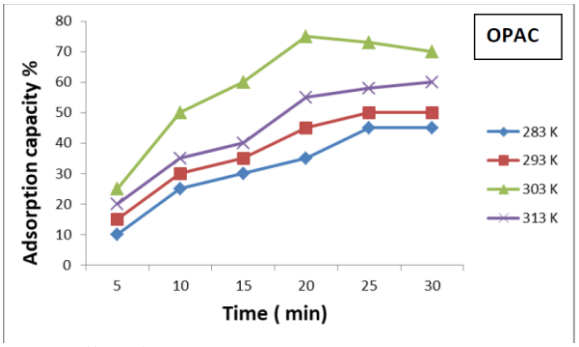

Fig. 8 . Effect of temperature on adsorption capacity by OPAC

4. Conclusions

This study showed the high potential of activated carbon to remove crude oil from water. There are many advantages and characteristics that make the use of activated carbon as an adsorbent is that it is widely available, especially in southern Iraq, in addition to being economical and easy to process and does not require high technology. All the analyzes that were studied confirm the success of the modified activated carbon process. The study showed that modified raw carbon by sulfuric acid thus increased the adsorption capacity compared with the carbon treated by phosphoric acid. By observing the analyzes of FTIR and FE-SEM micrographs, it was found that there is a great ability to adsorb crude oil using activated carbon. The study showed the ideal conditions for the occurrence of the process of adsorption of crude oil in water, by studying the most important factors that have a clear effect on the removal of crude oil, the most important of which are contact time, adsorbent dosage, pH, and temperature. Through the experimental results, it was found that (OSAC) achieved the largest value of adsorption capacity compared to (OPAC) due to the different functional groups available on activated carbon. The optimal conditions for adsorption were contact time 20 min, sorbent dosage (25 g), pH (7), and temperature (30 ^{0}C).

5. Conflicts of interest

There are no conflicts to declare.

6. Formatting of funding sources

There are no formatting sources.

7. Acknowledgments

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