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## Converting Iraqi Hazardous Crude Oily Sludge into Value-Added Activated Carbon using KOH Activation Technique

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### Abstract

Annually, a high amount of hazardous oily sludge (OS) is produced by North Refineries Company (NRC) Baiji. This work aims to study the specifications of oily sludge in crude oil storage tanks and to convert it into activated carbon (AC) by pyrolysis using KOH activated agent. The physical properties of OS have been measured and analyzed. The AC is produced by carbonizing oily sludge to char under N<sub>2</sub> flow using KOH at an impregnation ratio of 2:1 KOH/char. The pore structure, morphology of the surface, and surface chemistry of the AC produced were characterized using Brunauer-Emmet-Teller (BET), Fourier Electron Scanning Electron Microscopy (FESEM), and Fourier-Transform Infrared Spectroscopy (FTIR). The result shows the surface area of the produced AC was 350 m<sup>2</sup>/g with a mesoporous structure. Based on the findings, the obtained surface area of the AC indicates the oily sludge was a light precursor, which is helpful in producing gas and liquid fuels rather than solid fuel.

**Keywords:** Oily Sludge (OS), Activated Carbon (AC), Pyrolysis, KOH activation.

تحويل الحمأة الزيتية الخام العراقية الخطرة إلى كربون منشط ذو قيمة مضافة باستخدام تقنية تنشيط بهيدروكسيد البوتاسيوم

### الخلاصة:

يتم إنتاج كمية كبيرة من الحمأة الزيتية الخطرة سنويًا من قبل شركة مصافي الشمال. يهدف هذا العمل إلى دراسة مواصفات الحمأة الزيتية في صهاريج تخزين النفط الخام وتحويلها إلى كربون منشط عن طريق التحلل الحراري باستخدام هيدروكسيد البوتاسيوم. تم قياس وتحليل الخصائص الفيزيائية للكربون المنشط المنتج. يتم إنتاج الكربون المنشط عن طريق تفحيم الحمأة الزيتية إلى الفحم تحت جو من النتروجين بنسبة تشريب تبلغ 2:1 KOH/char. تم تشخيص تركيبة المسامات في الكربون

المنتج وبنائية سطحه وكيمياء السطح باستخدام عدة اجهزة تشخيصية مثل (BET)، ومجهر المسح الإلكتروني (FESEM)، ومطياف فورييه لتحويل الأشعة تحت الحمراء (FTIR). تظهر النتائج أن المساحة السطحية للكربون المنشط المنتج كانت 350 م<sup>2</sup>/غم مع بنية مسامية. بناءً على النتائج، تشير المساحة السطحية التي تم الحصول عليها إلى أن الحمأة الزيتية كانت بمثابة مصدر لوقود خفيفة، وهو ما يساعد في إنتاج الغاز والوقود السائل بدلاً من الوقود الصلب.

## 1. Introduction

The rapid economic growth and energy demand in recent years call for exploiting and utilizing global crude oil. From petroleum refineries, a substantial amount of oily sludge (OS) is produced[1]. OS is a heavy oily residue made up of water, oily chemicals, and particles [2]. Generally, oily sludge consists of 30–50% water, 30–80% heavy oil, and 10–20% solid particles [3-5]. OS is produced in large quantities (i.e., over 60 million tons) per year from oil-water mixtures all over the world. China produces more than 1,000,000 tonnes of OS, which comprises mostly of the OS from the cleaning of oil storage tank processes[3, 6]. It is thus essential to utilize this OS for economic and environmental benefits. However, the recovery of the OS is not straightforward as the viscosity of the OS is exceptionally high containing a complicated combination structure of wastes, which varies based on the grade of crude oil and the water-oil separation procedures utilized. Thus, dealing with the OS has become a major issue for the oil industry given its rapid development and the ever-rising need for fuel. Not to mention, the increase in wastewater treatment facilities has also produced a large amount of sludge.

OS is a carbonaceous substance that can be transformed into porous carbons by a wide range of methods such as deoiling treatment[7-9], pyrolysis[10-12], and chlorinating[13]. In addition, OS is a great material for the manufacturing of char because it contains high carbon content and high heavy fractions[8, 14]. Commercial activated carbon (AC), which is industrially used as an absorbent, catalyst support, and electrode material (to name a few), is generally expensive due to the relative cost of raw materials [14, 15]. Therefore, to reduce the cost of AC, alternative materials with a low cost and available materials like different solid wastes should be explored. [16-19]. Previous studies showed that AC can be prepared from agro wastes such as date stones [15, 18, 20-22], coconut shell [15], scrape tires[18], chitin [23], sawdust [24], seaweed [25]. In terms of OS, previous researchers mostly focused on its carbonization and a composite of sewage sludge along with the production of porous carbon using it with physical or chemical activation [26]. Traditional approaches utilized to minimize sludge amounts such as incineration, biodegradation, and landfilling are becoming less desirable due to their environmental issues, low performance, and high cost [27, 28]. For instance, the incineration approach consumes a lot

of energy and might result in secondary pollutants[29]. Centrifugation is another approach but is limited by the viscosity of the OS; it's frequently paired with solvent extraction to enhance the activity of the process. However, solvent extraction is impracticable for practical usage due to its associated large cost [30, 31]. On the other hand, pyrolysis suggested a promising and efficient method to convert tar and heavy oil because of the cost and the thermal stability of the process[32]. However, few studies exist on the production of AC from oily sludge *via* thermochemical treatment to produce adsorbent carbon material from various sewage feedstocks [33, 34].

Simple pyrolysis (or potassium hydroxide (KOH) activation) was used to study the possibility of converting OS to porous carbons. Shohreh Mohammadi & Mirghaffari[11] prepared carbonaceous adsorbents from oily sludge for wastewater treatments using thermal treatment (i.e., simple pyrolysis) and thermochemical treatment (KOH activation) at a pyrolysis temperature of 600°C, 10°C/min heating rate under N<sub>2</sub> atmosphere. The results obtained revealed that the AC produced by KOH activation has a higher surface area (328 m<sup>2</sup>/g) at 2:1 (mass ratio of KOH to char) than that produced by thermal treatment (3.6 m<sup>2</sup>/g). Shohreh and Nourollah[35] produced two carbonaceous adsorbents from crude oil storage tanks using thermal pyrolysis with steam (at 600°C, with a residence time of 60 minutes r) and thermochemical treatment with KOH (99.5% purity) at 600°C under 200 ml/min N<sub>2</sub> flow, and 2:1 g/g (KOH/Char), with a residence time of 60 minutes. The obtained results proved that the AC prepared by KOH activation is very efficient in Cd removal from the aqueous solution with a large surface area of 327.97 m<sup>2</sup>/g. In contrast, the study showed low adsorption capacity of AC produced via the thermal pyrolysis method. Mohammadi S.,[11] also prepared ACs from the OS using KOH activation. In addition to the feasibility of converting OS produced in a storage tank of fuel oil to porous carbons, the viability of using them to purify drinking water and adsorption was also examined. The surface area, total pore volume, and micropore surface area of porous carbon produced by KOH activation were 328.0 m<sup>2</sup>/g, 0.21 cm<sup>3</sup> /g, and 289.10 m<sup>2</sup> /g, respectively. The findings indicate that AC produced from OS adsorbs Cd<sup>2+</sup> is better than commercial AC [11].

Mojoudi et al. [36] prepared high microporous ACs from oil refinery sludge collected from crude oil storage tanks through chemical activation by KOH at various activation temperatures (600, 700, 800, 900 °C) and different impregnation ratios of 1:1, 2:1, and 3:1 (mass ratio of activating

agent to produced char). The AC prepared showed a microporous structure with a high surface area of 2263 m<sup>2</sup>/g, a total pore volume of 1.37 cm<sup>3</sup>/g, and a micropore volume of 1.004 cm<sup>3</sup>/g at optimum preparation conditions, i.e., 800 °C activation temperature and 2:1 impregnation ratio. It can be concluded from this study that the synthesized AC could be an efficient adsorbent for the removal of phenol from polluted water[36]. Almahbashi et al. [37] studied the optimum preparation conditions of AC from sewage sludge by applying the Box-Behnken Design (BBD) in response surface methodology (RSM). The variables studied and optimized in RSM are activation temperatures (500 to 800 °C), contact time (60 to 180 min), and chemical activation ratios (KOH/Char) (1, 1.5, 2 g/g). Based on the findings obtained, the AC is produced with a maximum area of about 377.7 m<sup>2</sup>/g, obtained in optimum conditions of 500 °C activation temperature, 3 hr contact time, and 1 g/g chemical activation ratio.

The primary objective of this study is the conversion of hazardous and complex NRC oily sludge of Iraqi origin, which poses even greater environmental and human health risks compared to other regions, into valuable activated carbon (solid char) through the pyrolysis process (chemical activation with KOH). Owing to the unique nature of Iraqi-origin oily sludge and its potential to contain higher concentrations of toxic heavy metals and other contaminants, the urgency to address this issue is more significant in this context.

The Iraqi OS differs from the other sludge used worldwide for preparation of activated carbon, it is much lighter and contains heavy metals. The methods published previously[11, 38] were followed to prepare AC from Iraqi OS but it gave approximately nil surface area. The present work provides a methodology of preparation using specific ratios of solvents and heat treatment to prepare AC. The Iraqi environment has already been severely contaminated due to years of conflict, insufficient infrastructure, and a lack of proper management and remediation efforts for crude oil sludge. These factors exacerbate the detrimental effects of this hazardous waste on the environment, ecosystems, and human health. Moreover, the local population is often left vulnerable to the health hazards posed by the contamination, with limited resources and options available for remediation. This innovative and efficient approach aims to degrade these previously unexplored wastes and cost-effectively produce valuable products, demonstrating the potential for sustainable utilization of Iraqi-origin oil sludge. By tackling this critical issue head-on, the project highlights the importance of prioritizing environmentally friendly remediation and management of oily sludge in Iraq to preserve both environment and human well-being. Furthermore, this study has the potential to contribute to the development of localized solutions that can be tailored to the specific challenges

presented by Iraqi-origin oily sludge. By addressing this issue, it is aimed that this work can promote further research and innovation, ultimately leading to improved environmental conditions and public health outcomes in Iraq and other regions facing similar challenges.

## 2. Experimental work

### 2.1 Preparation of Oily Sludge

In the present study, a sample of oil sludge (OS) was obtained from the North Refinery Company (NRC) in Baiji-Salahaldin, Iraq, to serve as the precursor material for the synthesis of activated carbon (AC). The OS, a semi-solid substance, was collected from various locations at the base of crude oil storage tanks during the tank cleaning process. To ensure a more representative analysis, the collected samples were thoroughly mixed before the examination. Potassium hydroxide (KOH) with 99% purity was employed as the chemical activation agent in the process of producing activated carbon.

### 2.2 Experimental Methodology

The preparation process of activated carbon AC from OS is depicted in Figure (1). Initially, the OS was dried at 105°C for 24 hours in an oven. A 20 g sample of the dried OS was weighed and placed in an alumina crucible, then subjected to pyrolysis in a tubular horizontal furnace (Safe Thermal, heating length 300 mm, maximum temperature 1200°C, China). The pyrolysis process consisted of two main steps. First, carbonization of the OS occurred in the presence of air, resulting in the formation of OS char. This step took place in a tubular horizontal furnace at a carbonization temperature of 420°C, a heating rate of 2°C/min, and a residence time of 120 minutes. The OS char was then cooled to room temperature. In the second step, the OS char was ground to a particle size of less than 2 mm and physically mixed with potassium hydroxide (KOH) at an impregnation ratio of 2:1 (KOH/Char) in an alumina crucible. The mixture was subsequently activated in a tubular horizontal furnace at an activation temperature of 400°C for 30 minutes, before being heated to 850°C at a rate of 4°C/min (under a nitrogen atmosphere at 150 cm<sup>3</sup> STP/min) and held for 80 minutes to produce AC. The resulting AC product was cooled to room temperature under the same flow of nitrogen atmosphere. Finally, the AC product was washed with hot deionized water to remove alkali impurities until a neutral pH was achieved. The AC was then dried at 105°C in an oven for 24 hours to obtain the final AC product.



**Fig. (1): Graphical description of the AC preparation.**

### 2.3 OS Analysis

The oil sludge (OS) sample was subjected to various analyses and tests to ascertain its primary constituents and the characteristics of its structure. The physical and chemical properties of OS are very important and must be calculated to investigate the appropriate undergoes of the production of solid, liquid, and gas fuel. Five main physical properties of the oily sludge, including specific gravity (Sp.gr.), American Petroleum Institute (API) gravity, color, water content, and asphalt content, were measured at the laboratories of the Ministry of Oil, Oil Products Distribution Company, Salahuldeen Branch, Tikrit, Iraq. Additionally, proximate analyses for both OS and activated carbon (AC) were conducted, providing information on moisture, ash, fixed carbon, and volatile matter content. Each test adhered to standardized methods.

For example, the API gravity of oily sludge was calculated by equation 1 based on the standard method (ASTM D 1298) [39]. The moisture content was estimated gravimetrically by equation 2 using the oven-drying method (ASTM D3173-11) by the reduced weight of the sample due to drying in an oven at 100°C for 24 h. The volatile matter was measured by taking a

1 g sample and heating in a muffle furnace (absence of air) at  $950 \pm 10$  °C for 7 minutes, then estimating the reduced weight from evaporation matter content, based on the standard method of an experiment for volatile matter content in the analysis of particulate matter as shown in equation 3. The ash content was measured also by taking 1 g of sample and heating using a muffle furnace (in the absence of air) at  $950 \pm 10$  °C for 180 minutes, then estimating the reduced weight from evaporation matter content, based on Standard Test Method for Ash in fuel[40] as illustrated in equation 4. The fixed carbon contents were estimated using equation 5 by summation of volatile matter, moisture, and ash and subtracted from 100 percent. Furthermore, the heavy metals such as (Fe, Cu, Pb, Cd, and Zn) were determined using an Atomic Absorption Spectrophotometer (ASS) (Shimadzu AA-6200, Japan), Department of Chemical Engineering/ Tikrit University-Iraq. Before, analysis of 0.5 g of AC was digested in  $\text{HNO}_3$  solution and diluted with 20 ml deionized water to make a solution for analysis.

$$\text{API} = \frac{141.5}{\text{Sp.gr}} - 131.5 \quad (1)$$

$$\text{M}\% = \frac{\text{initial weight} - \text{final weight}}{\text{initial weight}} * 100 \quad (2)$$

$$\text{VM}\% = 1 - \frac{\text{final weight}}{\text{initial weight}} * 100 \quad (3)$$

$$\text{Ash}\% = \frac{\text{final weight}}{\text{initial weight}} * 100 \quad (4)$$

$$\text{FC}\% = 100 - (\text{M} + \text{VM} + \text{Ash}) \quad (5)$$

### 3. Results and Discussions

#### 3.1 Physical Properties of Oily Sludge

Table (1) shows the properties of the OS used in the present study. The composition of oily sludge is highly dependent on the crude oil source, processing method, and the machinery and reagents used in the refining process. For example, total petroleum hydrocarbon (TPH) concentrations typically range from 15% to 50% w/w in oily sludge, while water and solid contents vary between 30-85% and 5-46%, respectively[41, 42].

**Table (1): Physical properties of the oily sludge**

Oil	Water	Ash	Solid particles	SARA Analysis, %			
				Saturates	Aromatics	Resin	Asphaltenes
52.7%	45.2%	0.75%	1.35	38.7	32.4	18.6	10.3

In this study, the physical properties of NRC oily sludge were thoroughly tested and analysed, as

depicted in Figure (2). The preliminary screening of the raw material OS was also conducted to assess its suitability for pyrolysis, as shown in Figure (2). The tests included specific gravity, API gravity, colour, water content, and asphalt content. As illustrated in Figure (1), the results revealed that the specific gravity, API, water content, and asphaltic content were 0.9510, 20.48, 50%, and 10%, respectively. The colour of both wet and dry oily sludge was found to be black. These results fall within the range of specification properties, consistent with previous research [37]. The color of the activated carbon (AC), which is not influenced by its chemical composition, remained black throughout the pyrolysis process. Physical properties such as density, viscosity, and heating value can vary significantly in oily sludge due to differences in chemical content. The density result in this study is in line with prior literature[43, 44]. Furthermore, the characteristics of oily sludge from one source cannot be directly applied to another source or to samples from the same source collected at different times or locations[45]. The laboratory certificate results also indicated a low asphalt content of 10%, suggesting that the OS is not carbon-rich since asphalt content serves as a source of carbon materials.

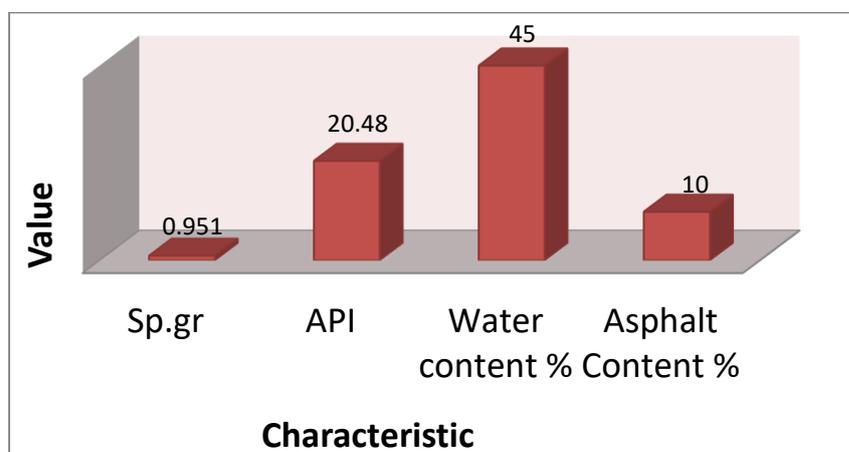


Fig. (2): Physical Characteristics of OS.

### 3.2 Proximate analysis of OS and AC

Table (2) Shows the bold proximate analysis of the OS and AC.

Materail	Oily sludge	Activated carbon
Ash	0.75	0.12%
Volatiles	98.84	1%

In this study, the proximate analysis assessed the relative quantities of volatile matter (VM), fixed carbon (FC), moisture (M), and ash for both the raw material (OS) and activated carbon

(AC) within the pyrolysis process, as depicted in Figure (3).

Figure (3) compares the proximate analyses of OS and AC to further examine and understand their compositions. The fixed carbon percentage for the OS is 18.2%, which is lower than the 23.88% found in AC. This difference can be attributed to fixed carbon representing the residual carbon resulting from the carbonization process, where some carbon is lost due to the release of volatile matter. Consequently, the total carbon percentage serves as an indicator of carbon content[46]. The KOH/Char ratio has a significant impact on carbon yield, as increasing this ratio raises the amount of KOH, which inhibits tar formation and reduces carbon yield [47]. The volatile matter content of OS (66%) decreased to 38.08% for AC during the pyrolysis process at elevated temperatures. This reduction is due to the thermo-chemical pyrolysis of the OS, which causes a decrease in volatile matter content and, in turn, carbon content[39, 48]. A similar trend can be observed for ash content, with OS (22.3) being lower than AC (33.2). A high ash content in the raw material is undesirable, as it negatively impacts the adsorption capacity of the produced AC. The increased ash content in AC may result from residual chemicals after the activation process and higher carbonization and activation temperatures[49]. Moisture content for both samples, which arises from the evaporation of water and gases at high temperatures during the pyrolysis process, is an important parameter in AC production. In this study, the higher moisture content of OS (41.07) compared to AC (18.76) suggests that OS is a lighter precursor, favoring gas and liquid fuels over solid fuels. Increased moisture content leads to lower calorific value, higher transportation costs, and significant heat loss through evaporation. The results show that the pyrolysis process caused a decrease in VM and an increase in the percentage of ash content.

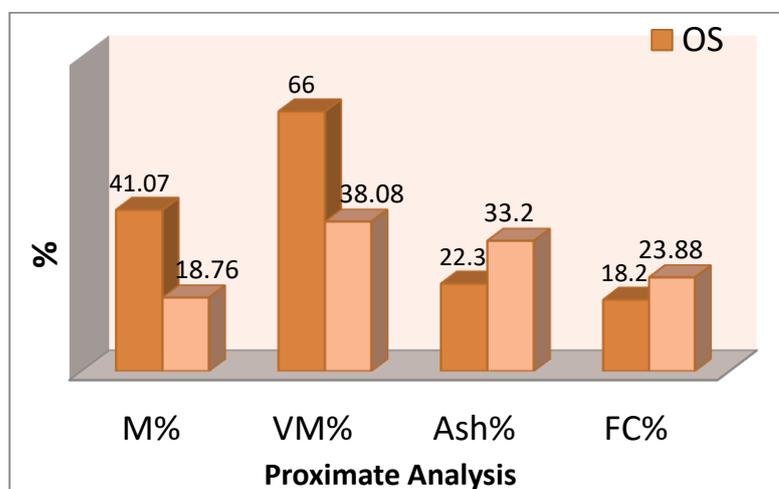


Fig. (3): Proximate Analysis for OS and AC.

### 3.3 Metal Composition of AC

The composition of OS includes a diverse range of metal contents, which were determined and analyzed in this study using AAS, as illustrated in Figure (4). The results in Figure (4) reveal that OS contains high, intermediate, and low concentrations of inorganic compounds in the form of metal compounds, including lead (Pb), cadmium (Cd), iron (Fe), zinc (Zn), and copper (Cu). Notably, Fe is the most abundant metal with a high concentration of 184.07 ppm. Other metals, such as Zn and Cu, exhibit intermediate concentrations of 11.88 and 8.08 ppm, respectively. In contrast, metals like Pb and Cd display low concentrations at 0.42 and 0.286 ppm, respectively. The high concentration of iron (Fe) found in this study's OS sample, which is significantly higher than conventional crude, may be attributed to the unique characteristics of Iraqi-origin sludge and the contamination from storage tanks [50]. Similarly, the intermediate concentrations of zinc (Zn) and copper (Cu) found in the OS sample are also considerably higher than what is typically found in conventional crude oils. Metal concentrations were measured, analyzed, and categorized into low (0.1 g/kg), intermediate (1 g/kg), and high (>1 g/kg) concentrations based on their levels[51]. A detailed examination of these concentrations can be found in the supporting material. The literature has extensively investigated metal concentrations, with some metals tending to be more concentrated[51]. Due to the waste's heterogeneity, metal content can vary significantly. By comparing the concentration levels obtained in this study with those in previous research, a good agreement with most prior results is evident. According to a report from the American Petroleum Institute[27], metal content in oily sludge is often lower than the levels reported in this study. However, this type of sludge, originating from crude oil storage tanks, is characterized by higher concentrations of certain metals compared to other sludge types, such as oil drilling or waste motor oil sludge [52]. Islam[5] also mentioned that oil sludge contains these inorganic contaminants. The elevated concentrations of heavy metals in the OS sample, compared to conventional crude oil, underscore the need for effective remediation strategies and stringent regulatory oversight to prevent environmental damage and protect public health. Furthermore, the results emphasize the importance of understanding the composition and potential hazards associated with Iraqi-origin oily sludge to develop targeted solutions for its safe disposal, treatment, and potential reutilization.

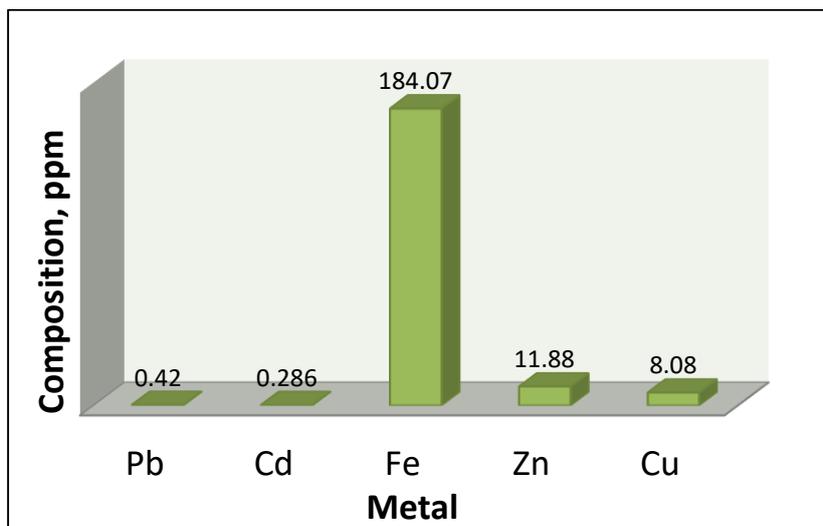


Fig. (4): Heavy metals for AC.

### 3.4 Characterization of AC Produced

#### 3.4.1 Specific Surface Area (BET)

The impregnation ratio (i.e., the weight ratio of KOH to the weight of OS Char) and activation temperature are critical factors in the production of activated carbon (AC)[53]. The standard activation temperatures for AC preparation using potassium hydroxide (KOH) range from 450-850°C, while impregnation ratios commonly fall between 1-7. In this study, the AC surface area, prepared from oily sludge (OS) via chemical activation using KOH, was 350 m<sup>2</sup>/g. The activation temperature was 850°C, with a 5°C/min heating rate, 80-minute residence time, and a 2:1 KOH/OS char ratio, under a nitrogen atmosphere. Alkali metal compounds like KOH and sodium hydroxide (NaOH) are used for activating charcoal. KOH chemical activation often yields a better surface area and performance for various industrial applications compared to NaOH. Chemical activating agents can penetrate the carbon structure, create small pores, and increase the surface area. The results obtained are consistent with previous studies [37, 54]. Increasing KOH amounts plays a crucial role in pore formation. The pores formed on the AC surface are about 25 nm (mesoporous). The KOH dosage influences pore formation on the AC surface, with further increases in KOH dosage leading to the development of microporous structures and a decrease in mesoporous pores. However, continued increases in KOH dosage can cause dehydration and degradation of mesopores, reducing adsorption capacity due to a decreased surface area. While increasing the KOH/Char ratio from 1-7 can increase surface area, a ratio of 8:1 will cause the surface area to decrease. Typically, the KOH/Char ratio ranges from

3-7. Nevertheless, increasing the KOH/Char ratio has drawbacks, such as higher preparation costs, environmental concerns, and corrosion issues due to acid washing. Activation with KOH serves as a catalyst, increasing the positive charge on the AC, which is favorable for adsorption processes. The potential reactions occurring during the activation process with potassium hydroxide are shown in equations (6-9) [55, 56]. Activation with KOH results in a high surface area and pore volume, but a lower yield (10-40%) compared to phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and zinc chloride (ZnCl<sub>2</sub>). (6-9) below [55, 56]. Finally, activation with KOH results in a high surface area and pore volume, but a lower yield (10-40%) compared to phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and zinc chloride (ZnCl<sub>2</sub>).



### 3.4.2 Fourier Electron Scanning Electron Microscopy (FESEM)

Raw OS has a heterogeneous, non-porous surface. The AC surface undergoes physical modification due to pyrolysis and chemical activation, leading to the creation and growth of pores as a result of a chemical agent's interaction with the raw material (Demiral & Aydin, 2016). After pretreatment and activation, the OS sample was crushed into powder for analysis. The morphology and micro-structure of carbonaceous materials were examined using Fourier electron scanning electron microscopy (FESEM) micrographs, as shown in Fig. 5a-d. These images reveal distinct surface morphologies between AC and carbonized intermediates. The porosity of the product sample was influenced by the raw OS's nature and the activation process used. FESEM micrographs in Figures (5(a), 5(b), 5(c), and 5(d)) show AC prepared from oily sludge using the KOH activation method. The surface texture of the AC prepared was rough, uneven, and undulating, with little pores on the surface. However, large, and well-developed pores were found on the surface of AC prepared, after activation treatment compared with the original char. According to the FESEM micrographs, it can be seen that the surface of the AC produced is quite rough without voids on its external surface. Cavities formed on the external surface of AC samples during the carbonization and activation procedures, which improved the porosity.

The KOH activation method was effective in creating pores on the surface of the AC,

hence leading to AC with a good porous structure. Creating pores during carbonization is so important since it would increase the surface area and pore volume of the AC. During carbonization and oxidation with KOH, the surface became porous as shown in Figures 5(b) and (d). The carbonized intermediates had a more compact surface structure, indicating that KOH as an activator destroyed the surface, leading to its collapse and generating numerous pores. The intermediate surface consisted of aggregates of small irregular balls and appeared relatively smooth, possibly due to molten semi-coke after pre-oxidation. After heavy metal adsorption, pores were exhausted with contaminants. Micro- or mesopore creation in ACs is significantly influenced by activation temperature. Generally, increasing the activation temperature from 600 °C to 800 °C resulted in a more porous structure. This could be due to the interaction between KOH and the carbon surface, volatile substance evaporation, or new hole formation in raw material structure. However, further increasing the activation temperature to 900 °C caused the porous structure to constrict [57].

The FESEM micrographs reveal that the KOH activation method was effective in creating pores on the surface of the AC, leading to an AC with a good porous structure. Creating pores during carbonization is essential since it increases the surface area and pore volume of the AC. The observed pores on the AC surface are not only abundant, but they also exhibit a suitable pore size, which makes the prepared AC an ideal candidate to serve as a support for catalysts. Catalyst supports generally require a high surface area and well-defined pore structure to facilitate the dispersion of the active catalyst component, ensuring effective contact between reactants and the catalytic sites. The appropriate pore size in the prepared AC enhances mass transfer processes, enabling reactants and products to access and exit the catalytic sites efficiently. This, in turn, optimizes the overall performance and stability of the supported catalyst system. Consequently, the prepared AC's favourable pore size characteristics contribute significantly to its potential application as effective catalyst support.

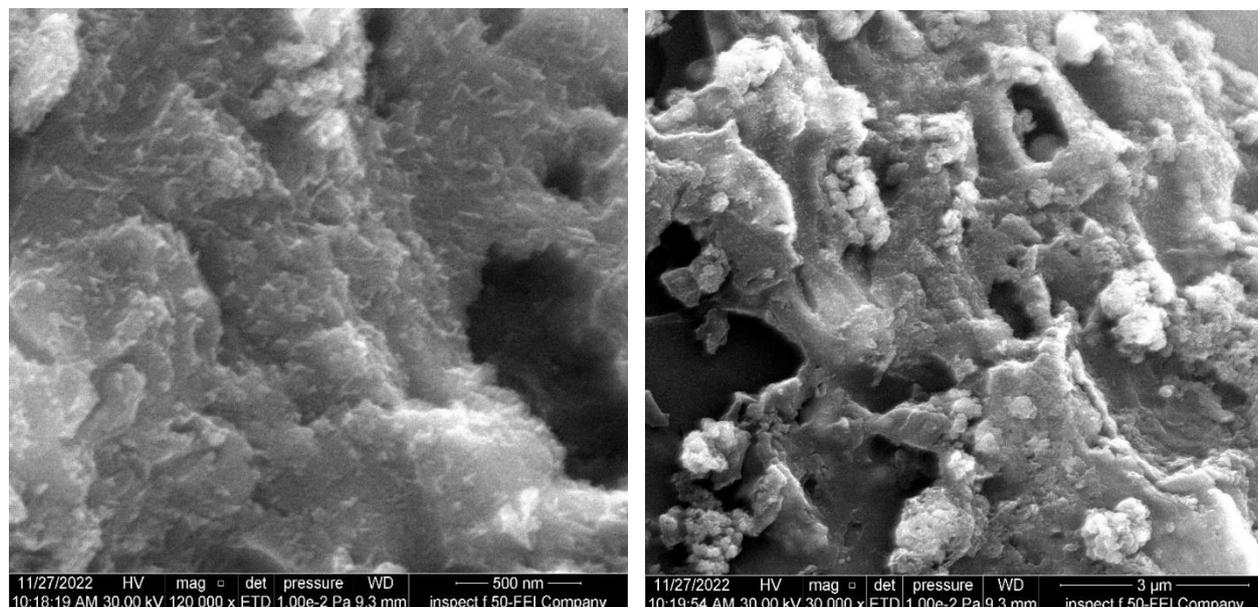
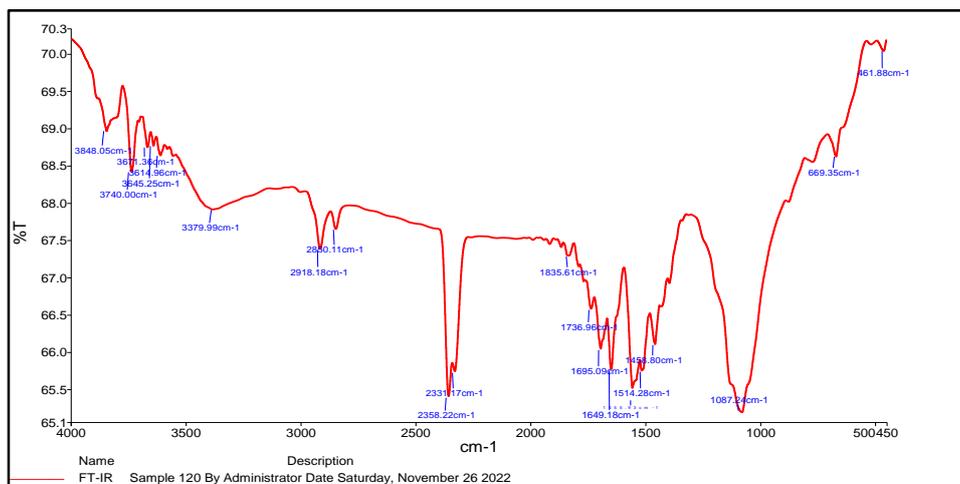


Fig. (5): FESEM images of AC

### 3.4.5 Fourier-Transform Infrared Spectroscopy (FTIR)

Carbonized intermediates exhibited a more compact surface structure, suggesting that KOH as an activator caused surface destruction, leading to its collapse and the generation of numerous pores. The intermediate surface was composed of aggregates of small irregular balls and appeared relatively smooth, possibly due to molten semi-coke after pre-oxidation. After heavy metal adsorption, pores were filled with contaminants.

The creation of micro or mesopores in ACs is significantly influenced by the activation temperature. In general, raising the activation temperature from 600 °C to 800 °C resulted in a more porous structure. This might be due to the interaction between KOH and the carbon surface, the evaporation of volatile substances, or the formation of new holes in the raw material structure. However, further increasing the activation temperature to 900 °C led to the constriction of the porous structure.



**Fig. (6): FTIR spectrum of AC.**

It can be seen from Figure 6 that the spectra of the FTIR of the prepared AC were concentrated in the range of 1000-1500  $\text{cm}^{-1}$ . These bands can be assigned to carbon-hydrogen bonding. These bands are for the symmetric and asymmetric vibration of the aliphatic hydrocarbons. can be assigned to the symmetric and asymmetric C–H stretching vibrations in the aliphatic compounds. For the higher bands intensity, 3000, 3500 and 3800 they are corresponding to oxygen-hydrogen, carbon triple bonds and which are corresponding to the OAH, C, C Triple bond, and  $\text{R}_2\text{C} = \text{N-R}$  stretching, respectively.

#### **4. Conclusions**

The conversion of hazardous oily sludge into valuable carbonaceous materials through pyrolysis has long been used as a means to minimize the impact of harmful chemicals on the environment. The environmental risks posed by Iraqi-origin oily sludge, with its high concentration of toxic contaminants, demand effective and sustainable remediation solutions. The objective of this study was to produce AC from low-cost NRC oily sludge using the KOH activation method. Chemical activation of OS with KOH was carried out at a 2:1 (KOH/OS Char) impregnation ratio, 850 °C activation temperature, 5°C/min heating rate (under  $\text{N}_2$  atmosphere), and 80 min residence time. The results demonstrated that the produced AC had a surface area of 350  $\text{m}^2/\text{g}$  and exhibited mesoporous surface texture properties. The AC generated in this study, with its advantageous pore size distribution, offers promising potential as a support for catalysts, facilitating efficient mass transfer and enhancing the overall performance of the catalyst system. Furthermore, FTIR and FESEM analyses confirmed the presence of an open-

pore morphology and various functional Based on the findings, approximately 35% of the OS sample collected from crude oil storage tanks contained oil with high levels of heavy metals. This study demonstrated that the successful recovery of the hazardous Iraqi OS and the generation of valuable products could be used as precursors in the pyrolysis process for producing high-quality AC. Given the high treatment costs associated with the OS, this process may be economically feasible for the reuse of the storage tank OS as it requires few additives and mild preparation conditions. The results indicated that there were no hazardous elements in any of the prepared AC, and that they had desirable features such as high porosity and surface area.

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