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Agricultural Waste-Based Activated Carbon for Oily Wastewater Treatment by Adsorption: A Review

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Abstract

Oily wastewater poses great risks to the ecosystem, human health and living organisms. Therefore, the development and study of sorbents using various activation techniques to remove oils from water resources is of interest to the scientific community. Here, we present a review on the use of sorbents made from agricultural waste to remove oils and hydrocarbons from aqueous media. After modification, it was found that activated carbon made from agricultural waste improves the performance of the adsorption process. The presentation also includes a comprehensive analysis of the application of isothermal models, kinetic models and thermodynamic parameters. The selectivity of the sorbent is the main focus of the adsorption kinetics and isothermal models. The process of adsorption and other parameters affecting adsorption such as contact time, solution temperature, solution pH and amount of sorbent are also studied. The use of agricultural waste as sorbents is economically and environmentally beneficial for the removal of oily pollutants.

Keywords: Oily wastewater treatment, Emulsion, activated carbon, agricultural waste, adsorption.

الكربون المنشط القائم على النفايات الزراعية لمعالجة مياه الصرف الصحي الزيتية عن طريق الامتزاز: مراجعة

الخلاصة:

تشكل مياه الصرف الصحي الزيتية مخاطر كبيرة على النظام البيئي وصحة الإنسان والكائنات الحية. لذلك، فإن تطوير ودراسة المواد الماصة باستخدام تقنيات التنشيط المختلفة لإزالة الزيوت من موارد المياه أمر يثير اهتمام المجتمع العلمي. هنا نقدم مراجعة حول استخدام المواد الماصة المصنوعة من النفايات الزراعية لإزالة الزيوت والهيدروكربونات من الوسائط المائية. بعد التعديل، وجد أنه الكربون المنشط المصنوع من النفايات الزراعية يعمل على تحسين أداء عملية الامتصاص. يتضمن العرض أيضاً تحليلاً شاملاً لتطبيق النماذج المتساوية الحرارة والنماذج الحركية والمعلومات الديناميكية الحرارية. إن انتقائية المادة الماصة هي المحور الرئيسي لحركية الامتصاص والنماذج المتساوية الحرارة. كما

تمت دراسة عملية حدوث عملية الامتصاص والمعلومات الأخرى التي تؤثر على الامتصاص مثل وقت التلامس ودرجة حرارة المحلول ودرجة حموضة المحلول وكمية المادة الماصة. إن استخدام النفايات الزراعية كمادة ماصة مفيد اقتصاديًا وبيئيًا لإزالة الملوثات الزيتية.

1. Introduction

The sea is one of the most important natural ecosystems and a key source of food. As a result, polluting this ecosystem has an immediate or indirect impact on human health while also causing irreparable environmental devastation. Present, the extraction of oily and gas in the sea, in addition to the transmission for each types of fossil fuels, had resulted in increased oily contamination in various portions of the sea [1]. Simply put, dumping oils at the water has turn out one of the most severe worldwide worries resulting in ecological issues [2]. It is worth emphasizing that addressing this environmental issue has resulted in a variety of economic challenges. Until date, a variety of procedures have been employed to eliminate this form of contamination, including biological cleansing [3]. Chemicals (e.g., on-site incineration and usage of clotting agents) [4]. And physicals (adsorbents and skimmers) [5]. A variety of factors impact the appropriate course of action, including the type of contaminated material, water nature, and contamination place. It must have been mentioned that each strategy had its merits and downsides, which influence the selection of each way [6].

The adsorption technique is one of the most well studied ways for removing oil pollutants from water. Today, using adsorbent substances is the more cost-efficient and affordable ways to elimination oily contaminates from the ground water or contaminated water supplies. In other words, this substance had the potential into transport oily from the liquid state into the solid state, allowing oily to be separated from water [7, 8]. The most important characteristics to selection of adsorbent substances for the elimination of petrochemical substances include availability, affordability, hydrophobicity, biodegradability, adsorption value, and adsorption capability [9]. Adsorbents are often classified into three types: natural organic adsorbents, metallic adsorbents, and synthetic adsorbents. Natural organic adsorbent substances are generally inexpensive and abundant, with a very high adsorption capability [10]. Moreover, poly propylene and poly urethane are the among prevalent synthetic organic substances in elimination oily contamination because their hydrophobicity [11]. Activated carbon is a porous carbon-based substance that has a highly adsorption capability and can be reactivated on the surface. It may be economically made from a range of carbon-rich organic sources, inclusive wood [12] and charcoal [13]. Because of the highly cost of precursor substances and their non-renewability, the manufacture

of carbon-effective materials employing these components are similarly costly, and their employment was limited on a wide manufacturing field [14]. As a result, in recent years, many studies have been conducted to study the cost-effective evolution of activated carbon manufacturing [15, 16, 17]. Precursors for activated carbon include plant leaves, peaches, walnut peels, almond peels, hazelnut peels, coconut peels, olive kernels, coffee peels, plum and apricot kernels, cherry kernels and grape seeds, sugar cane pulp, bamboo peels, rice hulls, pomegranate seeds, sludge, and industrial food sludge [18].

This study will concentrate on the adsorption technique that uses activated carbon obtained from agricultural wastes to treat oily wastewater as an innovative alternative to traditional approaches. The inquiry begins by tackling the issue of greasy wastewater. The characteristics that influence the stability of oil-in-water emulsions are examined. The elements that influence the elimination of oily waste from the emulsion are also examined. The kinetics and heat lines depicted in the adsorption system are also explained, and thermodynamic functions are illustrated to help readers comprehend the technical concepts and features of the adsorption process.

1.1.Oily Wastewater

Oil in wastewater is a major environmental issue that has far-reaching consequences for ecosystems, human health, and the economy. It is mostly caused by industrial operations including oil refineries, petrochemical facilities, and transportation [19]. Oil-contaminated wastewater poses major hazards because of its toxicity, persistence, and potential for ecological disturbance [20]. One of the main issues with oil in wastewater is its tendency to produce slicks on the surface, which can limit oxygen exchange, block sunlight, and kill aquatic life [21]. Furthermore, oil may pollute sediments, harming benthic creatures and altering the food chain. The presence of oil in wastewater has a negative impact on human health [22]. Consuming contaminated water or seafood from polluted locations can cause gastrointestinal disorders, organ damage, and an increased risk of cancer [23].

Furthermore, oil in wastewater can create economic losses by harming fisheries, tourism, and coastal infrastructure. Cleanup operations are costly and generally complex, especially for large-scale spills [24]. The oily phase in wastewater is often divided into a minimum of four categories based on the extent and stabilization of the oily drops. Gravity separation methods are effective for removing oily droplets larger than 150 micrometers that are floating freely. Dispersed oily, with droplet sizes ranging from 20 into 150 micrometers, may be easily removed using gravity or stabilizing agents [25,26]. Emulsified oil's droplet sizes are often smaller than 20 micrometers,

necessitating the application of advanced procedures like coagulants and surfactants [27, 28]. Dissolved oily, with droplets smaller than 5 micrometers in size, is exceedingly hard to extract, requiring sophisticated chemical and physical techniques [26, 29, 30]. Figure (1) provides an overview of oily wastewater resources, as well as the effect and benefits of treatment.



Fig. (1): Oily wastewater sources: physical shape, influence, and treatment benefits

1.2. The emulsions

Polluted wastewater comprises both light and heavy hydrocarbons, grease, petroleum-based fats, tars, hydraulic oil, cutting oils, waxy substance, and other chemicals [31]. As oils get entirely miscible in water, surfactants and ions combine to produce an emulsion [32]. An emulsion is a system in which one immiscible phase of liquid is spread as drops (dispersed phases) in another immiscible liquid phase (continuous phases) [33]. Fluid emulsions are classified into three categories: water/oil, oil/water, and multiplex emulsify. A water-in-oil emulsion is generated when water droplets are scattered throughout the continuous oil phase, as seen in Figure (2a). Oil drops are spread throughout the continuous water phase to form an oil-in-water emulsion (Figure 2b) [34]. A multiple emulsion is a complicated system in which water-in-oil or oil-in-water emulsions are dispersed across another immiscible phase [34]. This kind of emulsion comprises oil/water/oil Figure (2c) and water/oil/water Figure (2d). [34]. According to the usage, these emulsions may be advantageous or unfavorable. Figure (2) shows the types of emulsions.

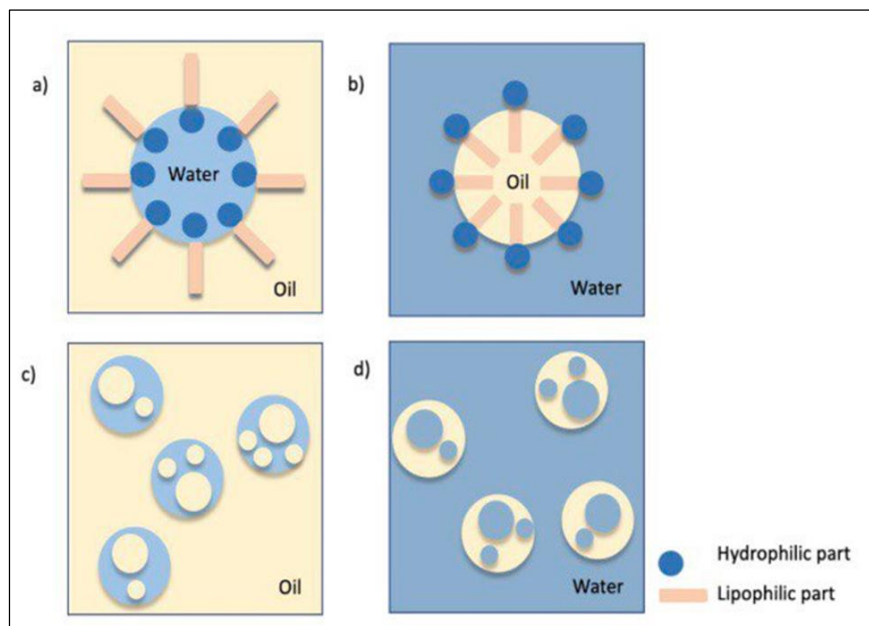


Fig. (2): Four emulsions: a) water/oily; b) oily/water; c) oily/water/oily; and d) water/oily/water [32]

1.3. Effective influences on the stabilization of an oily-in-water emulsion

There are several factors that influence the stabilization of an oily in an aqueous emulsion, include salt content (salinity) of the water, sand, tiny fragments, pH value, the existence of an emulsifier or surface, as well as the amount of oily in the solution. Within oily-in-water emulsion, the oily particles are diffused through a continuous aqueous stage. Therefore, the amount of oil in the emulsion directly affects its stabilization. Emulsions with an oil content greater than 5% V/V are often unstable. Additionally, the existence of particular ions like sodium chloride (NaCl) and magnesium chloride (MgCl_2) in the emulsion helps to improve the stability of it due to these ions establish a stratum among drops of oily and particles of water, which causes an immersion of oily droplets in the water phase [35,36].

The addition of a surfactant or emulsifier is also important in enhancing the stabilization of an emulsion. These chemicals improve the stability of an emulsion by altering its surface characteristics. As the crude oily and petroleum chemicals sectors, inhibitions, and chemicals employed at several stages of the procedure step inside waste streams and assist stabilize the oil-in-water emulsion. Furthermore, other components in the emulsion, such as dust and tiny particles, affect its stability [37,38].

1.4. Adsorption as a treatment method for oily wastewater

It is vital to eliminate oily and hydrocarbon components from effluents prior to their discharge into the environment [39, 40]. Adsorption has become one of the fundamental ways for separating oil from oil/water emulsion. Several researches in the scientific literature have employed inexpensive adsorbents to successfully eliminate oil from oily wastewater [41;39,40]. Adsorption occurs when oil molecules adhere to the surface of a solid adsorbent upon coming into contact. The adsorbent is critical in the process of adsorption because various adsorbents might engage different adsorption processes, resulting in variances in adsorption effectiveness [42]. In general, activated carbon in crushed or grainy form has a considerable adsorption ability for organic or non-organic contaminants because of its porosity and specific exterior area [43,44,45].

1.5. Activated carbon (AC) as Adsorbent

Activated carbon is a porous carbon substance that has several implementations in water desalination, water and wastewater treating, and air cleaning because of its unparalleled features [46]. It is a flexible adsorbent substance with a highly porous grade and a large surface area, with as much as 90% of the carbon surface area [47]. Activated carbon's ideal adsorption characteristics were due to its outer surface structure, which comprises several functional groups such as carbonyl, carboxyl, phenol, quinone, and lactone. Additionally, to the presence of hydrogen, oxygen, sulfur, and nitrogen, these functional groups were discovered to be responsible for the pollutants' adsorption into the activated carbon adsorbent material. These functional groups were generated by precision, activation processes, and thermal purification [48]. The raw materials required to manufacture activated carbon should be affordable, abundant, and safe [49]. Cellulosic materials have recently emerged as one of the most extensively utilized substances in activated carbon manufacturing [50].

2. Methods:

2.1. Activation methods to activate AC

The activation technique seeks to improve the pore assets and activated locations. AC can be developed by either chemical or physical activation. Activation has led to a raise in the size of these highly developed pores [51].

2.2. Chemical activation

Firstly, the lignocellulosic biomass is supplied with activation chemicals as part of the chemical activation (CA). The common activating chemicals include H_3PO_4 , NaOH , and ZnCl_2 . To avoid hydrocarbons decomposed on the carbon superfices through activating, chemical agents are generally utilized into breakdown or dehydrate organic particles [52]. As impregnating operation takes place concurrently using the activating and pyrolysis stages. The main feature of this technology is that it can end the operation at less temperature in a single stage [53]. Activation by chemicals is an economical and ecologically favorable method as chemical reagents might be recycled and reused. Chemical reagent kinds, impregnating attributions, activating temperatures, and interaction times all influence the CA [54]. The key elements impacting chemical activation are the kind of activating agent, mixing method, mass ratio of activating agent to carbon precursor, and heating technique [55].

2.3. Physical Activation

The carbonating and activating were both steps towards physical activity. Lignocellulosic substances are carbonized in an inert atmosphere, then activation with carbon dioxide, vapor, or a mixture (300-800 degrees Celsius) [56]. Later carbonization, activation takes place at a high temperature ranging from 600-900 degrees Celsius [57]. Through the first stage of the carbonization process, certain bonds in the lignocellulosic biomass structure are broken, resulting in the product of volatile chemicals. Despite the lack of porous characteristics, the resultant activated carbon precursor can generate aromatic carbon structure. The production of volatiles can occur in condensing and re-polymerization processes, which might block or fill it up while this occurs. As a result, the major purpose of the primary phase is to produce charcoal from lignocellulosic biomass raw materials. [58]. The second step of the activating process may improve the porosity composition of activated carbon by removing undesirable products from the precursor [59]. This can be accomplished using an appropriate gas, vapor, or a combination of both. Based on various research, carbon dioxide (CO_2) may give finer control and more pronounced outcomes since it is cleanly, produces outstanding results, has a delayed response rate, and has less reactivity under higher temperatures [60]. A longer activating period produces more mesoporous and macro-pores than a decrease in pore volume and surface area [61]. Activation reagents serve an important apart in producing memorable, cost-effective, and environmentally beneficial activated carbon. Chemical activation is more efficient in producing activated carbon since it takes least time than the physical activation technique. Furthermore,

chemical activating uses least power from physical activation as it might be done at lower temperatures [62]. Research has revealed that the majority of specialists feel that activated carbon obtained from chemical activation consistently produces greater amounts, more advanced pore characteristics, and a distinctive structure. Nevertheless, on an industry scale, physical activation is better since it does not employ chemicals, reducing the cost of processing and pollutants. As a result, it may improve the carbonization operations using simple techniques to boost the pore characteristics [63].

2.4. Physicochemical activation

Several previous research has explored both kinds of activation processes, to be particular, both chemical and physical [64]. According to the method utilized, the activated carbon produced by these procedures may have higher porosity or smaller surface area [65]. To get the required results, physical and chemical activation must be combined. Carbon activation via chemical and physical approaches can enhance surface quality [66]. The surface area of the activated carbon produced contributes to its environmental impact [67]. The activation stage uses chemical and physical activators to heat-break down the cellulosic biomass, allowing for a combined physical and chemical activation process [68]. It was discovered that the combined procedure allows the substance pores to expand, which serves into increase the porous adsorbent product's capacity to adsorb [69].

2.5. Microwave facilitated activation

A wide range of equipment can be used for physical and chemical activation, inclusive fluidized bed boilers, rotary kilns, and multi-hearth furnaces [70]. Microwave heating is of great interest to scientists due to its capability to transfer heat at the molecular level. As a result, heat conduction from the hot source seems quicker and more uniform [70]. Microwave heating, physical activation, and chemical activation can be combined to produce activated carbons with higher performance utilizing one- or two-step activation procedures [71,72]. In rare situations, microwave radiation can be used as the major heating technique for carbonization and activation [73].

Some of the elements that have a direct impact on the final qualities of activated carbon products include raw material kinds and sources, decomposition temperature, microwave radiation energy, reaction duration, and the type of additives employed in the process [74]. Microwave heated was preferred for its ability and versatility, as its changeable qualities stay constant. Given the

suitable input circumstances, it is the best technique to add into the activated carbon production process to assure improved pore structure and surface quality in activated carbon [70]. Microwave radiation may be utilized as a heating source in the carbonizing & activating stages of the activated carbon manufacturing procedure. The energy provided by microwave radiation for activating the activated carbon precursors may be controlled through the sample's total weight, which is determined by its rate of heating and temperature. The resultant carbon-based substance was found to have improved porosity and surface area. Extensive study has been undertaken to investigate the observed variances among alternative and conventional activated techniques in terms of AC parameters such as surface area, pore volume, and hole shape [70, 75]. The Figure (3) shows the main methods for producing and activating activated carbon.



Fig. (3): Main ways to activate the process.

In general, there have been few investigations on the treatment of oily wastewater utilizing activated carbon derived from agricultural waste using various activation procedures as presented in Table (1).

Agricultural waste from Buckthorn plant twigs was applied for successfully preparing activated carbon by microwave chemical activation to remove diesel oil from aqueous solution. The crushed sample was mixed with 60% phosphoric acid as an activating agent, and the mixture was transferred into a glass reactor put in a microwave oven for irradiation using various microwave power and activation times [76], and the maximum removal efficiency and adsorption capacity were obtained 96.0823%, 380.069mg/g respectively.

Another study investigated the efficacy of two activated carbon adsorbents manufactured from walnut shell and peach pulp to treat oily effluent including diesel, gasoline, or oil using two chemical and two physical approaches [4].

Based on another study, palm kernels were used to develop activated carbon (AC), which acts as an adsorbent for treating oil-contaminated groundwater. Palm kernel-derived biochar (BPK) was produced by directly pyrolyzing the raw material at 600 °C for 90 minutes (under oxygen-limited conditions). The activated carbon (ACPK) supplied identical pyrolysis conditions to biochar with subsequent impregnation in H_2SO_4 (as an activating agent) at an acid-to-biochar ratio of (1:1). The COD elimination effectiveness of the BPK and ACPK samples were 82.5% and 95.1%, respectively, whereas the BOD was the same (97%) for the two samples [77]. Coconut coir waste with potassium hydroxide to produce activated carbon [78]. Coconut residues were treated with potassium hydroxide to produce activated carbon. The samples were rinsed with distilled water before being dried in a laboratory oven at 105 degrees Celsius for one day. The dried sample was then crushed and sieved to produce smaller particles. The crushed material was carbonized in an oven at 600 degrees Celsius for 120 minutes in the presence of oxygen. The carbonized material had been pretreated using potassium hydroxide (KOH) at a ratio of 1:2 [78]. Coconut showed a high value for adsorption capabilities and crude oil removal rate.

In another study, pomegranate peel powder was used as a low-cost adsorbent to remove crude oil from simulated produced water [79]. The pomegranate peel was thoroughly cleansed with twice distilled water and air-dried for one day. They were pulverized to particle sizes ranging from 2 to 3 mm and dried in a fluid bed dryer at 60 degrees Celsius. Then the shredded peel was immersed in n-hexane solution for 2 h to remove soluble and hydrophobic organic matter and colored pigments. The pretreated pomegranate peels were thoroughly washed with deionized water twice

before drying in the fluid bed dryer. An electric grinder was used to produce fine PPP, which was screened through a 150-500-micron sieve. Lastly, the fine PPP had been rinsed with twice deionized water and dried in a vacuum oven at 80 degrees celsius for one day [79].

Table (1) Adsorption efficiency and maximum adsorption capacity of agricultural waste-based activated carbon for oil removal from wastewater

Feedstock	Adsorbate	Removal	Adsorption capacities	Ref.
Buckthorn plant twigs	Diesel Oil	96.0823%	380.069mg/g	[76]
walnut shell and peach pulp	oily wastewater including diesel, gasoline, or oil	---	---	[4]
Date palm kernels	COD and BOD water sample	95.2%	---	[77]
Coconut coir waste KOH	crude oil	99.98457%	4859.25mg/g	[78]
pomegranate peel	crude oil	92 %	555 mg/g	[79]

2. Results

3.1. Factors affecting the removal of oily wastewater from emulsion by activated carbon for agricultural waste

Several factors influence oil removal from wastewater, including temperature, contact time, pH solution, activated carbon dose, and concentration pollutant content [80,81].

3.1.1. Effect of Temperature

Temperature may be one of the most important factors affecting oil elimination of produced water [79]. One of the experiments investigated the impact of temperature on the adsorption of crude oily on CCAC_{KOH} at various temperatures [78]. The adsorption capability and crude oil removal ratio increased with temperature. This has been linked to the weakening of hydrogen bonds and van der Waals attraction under high temperatures, causing enhanced physical contact between the active sites of crude oil molecules and the sorbent. Furthermore, when the temperature raised the diffusion rate of crude oil particles between the outer boundary layer and the inner holes of the adsorbent increased due to a decrease in the solution's viscosity and an

increase in the solubility of crude oils in water [82,83]. Furthermore, a raise in both rate eliminations of crude oily and adsorption ability at high temperatures was possibly because a raise in kinetic strengths; that is, the mobility of the crude oil species inside the adsorbent matrix, as well as a raise in the porosity and amount to hole volume of the adsorbent [84]. Their result is shown in the Figure (4).

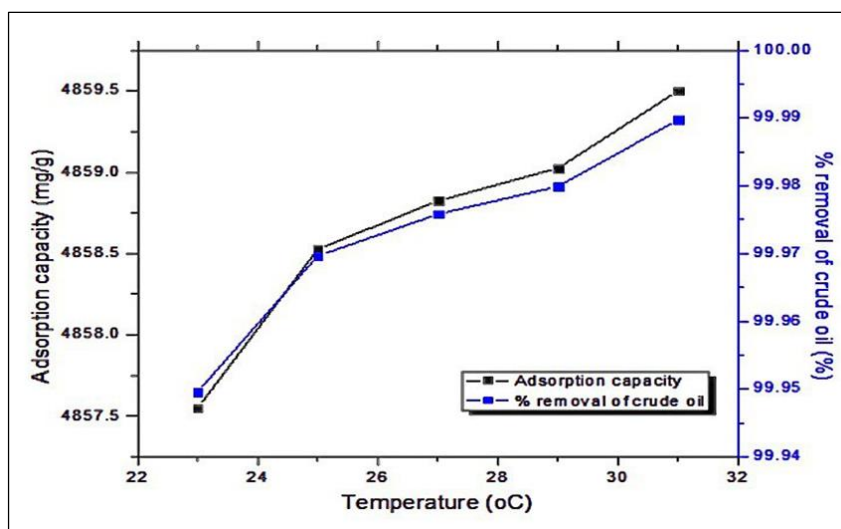


Fig. (4): Effect of Temperature [78]

3.1.2. Contact of Period

Contact period is an important factor in removing oily and other pollutions from wastewater. Execution the absorption practicability in a short period is an important agent in decrease operation price [85]. In one of the research, the effect of diesel oil content and contact time on activated carbon (Buckthorn plant twigs) was evaluated using response surface analysis [76]. The elimination efficiency was shown to increase with increasing diesel oil content and communicate or mixture time. The highest elimination effectiveness occurred at 400 mg. L-1 with a communicate period of 180 minutes. The elimination efficiency reduced with diesel oily concentration and time. It is evident that the adsorption proportion of diesel oily rose substantially over time at initially because the abundance of active sites on the sorbent surfaces. Then, when concentration grew over time, the adsorption proportion reduced because the restricted unoccupied sites and the raising repulsive interactions among the adsorbent molecules along the surfaces of the sorbents and the bulk sol [86, 87,88]. Their result is shown in the Figure (5).

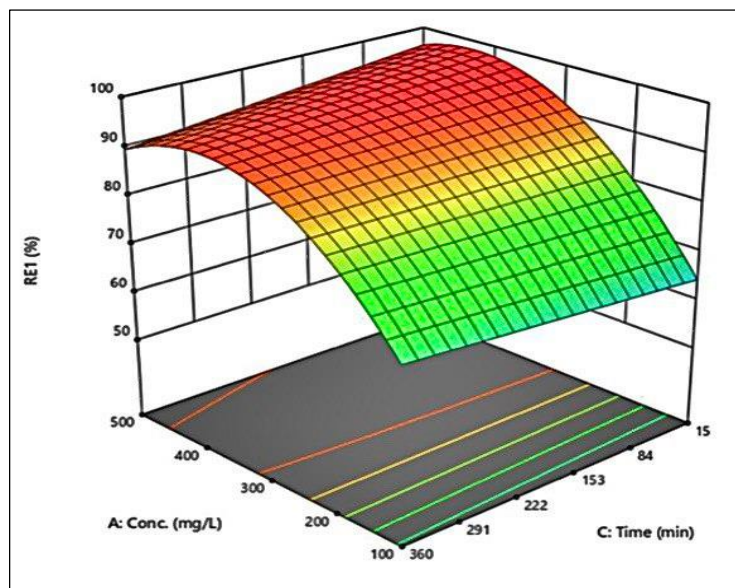


Fig. (5): 3D Plot of initial concentration and contact time [76]

3.1.3. Effect of pH

The pH of wastewater plays a significant role on pollutant uptake. At low pH, aqueous medium has a positive charge (H^+), whereas at high pH, it has a negative charge (OH^-) [89]. Thus, the charge of the pollutant has been a considerable influence on the sorption procedure. Certain pollutants have been negative shipments, whereas others possess positive charge. Furthermore, certain pollutions have no charge on their particles. To do that, a contest emerges among the shipment on the pollutant and the shipment on the sorbent [90]. The influence of diesel oily concentration with solution pH on the elimination efficiency using activated carbon was studied, and it was observed that the elimination efficiency increased with the increase of the initial diesel oily concentration with solution pH, reaching the maximum elimination efficiency at a certain point of concentration and pH (400 mg. L^{-1} and pH 7), then decreasing with the increase of the initial diesel oil concentration with solution pH. This indicates that higher acid and alkaline solutions are unsuitable for diesel oily adsorption on the adsorbent's surface. This suggests that a significant number of protons were accessible at low pH levels, resulting in the saturation of the adsorbent sites and increasing the cationic quality of the adsorbent surface [91]. As the solution pH increased above 7, an excess abundance of hydroxyl ions (OH) competed with the contaminants on the active adsorption sites, resulting in a decrease in diesel oily adsorption [92]. Their result is shown in the Figure (6).

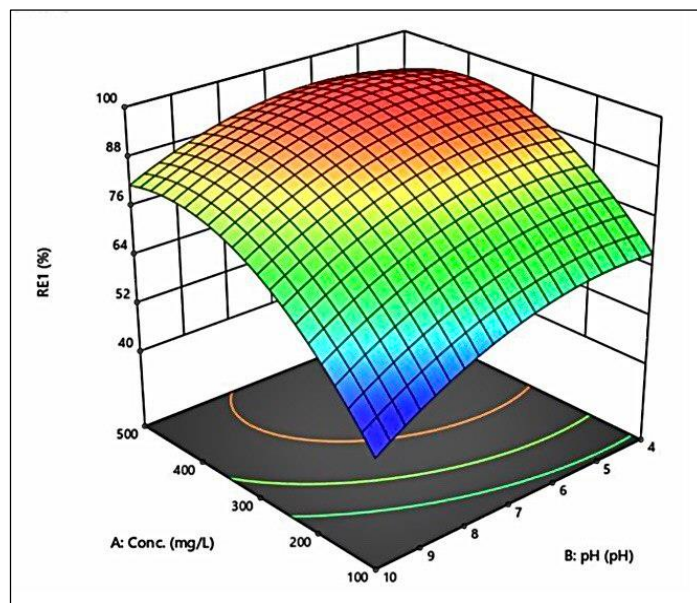


Fig. (6): 3D plot of initial concentration and pH [76].

3.1.4. Effect of dosage

The dosage of adsorbent is an important parameter since it influences the adsorption process. Because of the huge number of accessible adsorption sites on the adsorbent surface, increasing the dose of adsorbent material generally improves removal efficacy. [50]. The impact of diesel oily concentration with sorbent dosage on the elimination efficiency using activated carbon was researched, and it was discovered that the improvement in elimination efficiency mostly dependent on the rise of initial diesel oily concentration compared to sorbent dosage. This indicates that the lowest sorbent dose was adequate for all diesel concentrations. When a result, the greatest removal efficiency was obtained at 400 mg. L⁻¹ diesel oily with the minimal amount concentration (0.1 mg in 200 mL); nevertheless, when the diesel oily concentration increased, the removal efficiency declined significantly for all sorbent dosages [76]. Adsorption rate decreases with increasing oil content due to fewer unoccupied sites and higher repulsive interactions between sorbent molecules along the surfaces of sorbents and bulk solution [86,88]. Their result is shown in the Figure (7).

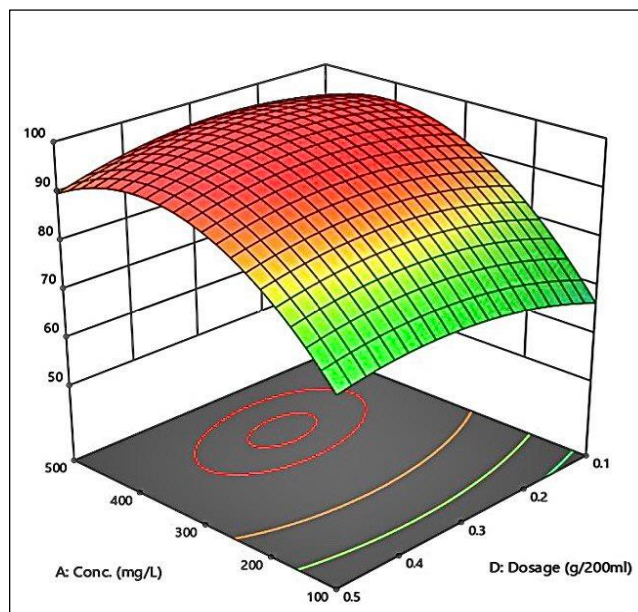


Fig. (7): 3D plot of initial concentration and dosage [76]

3.2. Adsorption isotherms

Adsorption isotherms, as well as model parameters, may be used to extract a variety of features to better understand the process [93]. Adsorption curves allow to establish the mechanism of adsorption between adsorbate molecules on the adsorbent. Models can also assist you calculate an adsorbent's maximal adsorption ability. The adsorption process can be single-layer or multi-layer depending on the nature of interactions between the adsorbates and the adsorbent, which can be easily evaluated using the Langmuir and Freundlich isothermal models [94].

3.2.1. Langmuir Isotherm Model:

Langmuir's model, often known as the ideal localized monolayer model, relies on the following key assumptions: The particles are linked to the adsorbent at certain locations. Each site may hold one molecule (monolayer); the site area is constant; the amount is regulated only by the surface form; and all sites have the same adsorption energy. Adsorbed particles, on the other hand, cannot move over the surface or interact with other molecules. Using the Langmuir isotherm model, one may estimate the maximum amount of adsorption that can be achieved if the adsorbent is completely covered with a single monolayer [95].

Equation 1 shows the linear equation for the Langmuir isotherm model. q_m (mg/g) represents the maximal adsorption capability, C_e represents the concentration at the equilibrium state, q_e (mg/g) is the equilibrium adsorbent concentration, The Langmuir constant K_L , is related to the strength

of molecule adsorption on the adsorbent surface. As a result, the bigger K_L , the more surface is covered by adsorbed molecules [96]. As shown in “Equation (1)”, a linear plot of C_e/q_e versus C_e can be used to check the validity of the Langmuir model in terms of experimental data reproduction.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (1)$$

3.2.2. Freundlich Isotherm Model:

In contrast to the Langmuir isotherm, the Freundlich isotherm model incorporates the adsorption of adsorbate molecules onto energetically heterogeneous sites. This model describes the multilayered adsorption of the adsorbate [94]. Equation 2. describes how the isotherm Freundlich model may be utilized. where n and K_F are the Freundlich isotherm temperature-depending on constants. The equation's constants, n and K_F , may be derived by charting $\ln q_e$ in terms of $\ln C_e$ and determining the intercept and slope, as shown in “Equation (2)”.

$$\ln q_e = \frac{\ln C_e}{n} - \ln K_f \quad (2)$$

K_f is the capacity of the adsorbent, it has evident that if $n = 1$, the Freundlich equation will be linear, and that the bigger the (n) number, the extra the isotherm deviates from the linear state and will have a non-linear behavior [97]. Table (2) shows the constants of the isothermal models for different absorbent materials, while Figure (8) shows the curves of the Langmuir and Freundlich models.

3.3. Kinetic models

Adsorption kinetic models are generalized by a number of controlling processes, including mass transfer coefficient, chemical reaction, and diffusion control. Kinetic studies aid in identifying the optimal reaction conditions for conducting an adsorption experiment in a full-scale batch operation. Adsorption kinetics reveals the rate of solute absorption and the mechanism by which this rate governs adsorbate residence duration at the solution interface. There are several models that may be used to analyze kinetic data, including pseudo-first-order and pseudo-second-order [94].

3.3.1. Pseudo -first-order model

The pseudo-first-order model determines the adsorption kinetics of molecules in an adsorbent surface by the following ordinary first-order differential “equation (3)” [98].

$$\ln(q_e - q_t) = \ln(q_e) - K_1 t \quad (3)$$

Where q_e and q_t are the adsorption capacity the amount of adsorbate in the adsorbent at equilibrium and any time (measured in mg. g⁻¹), K_1 : is the rate constant of (PFO) (min⁻¹); t time (min).

3.3.2. Pseudo-second-order model

Adsorption takes happen on two surface sites in pseudo-second order kinetics (some authors name it "Blanchard's model"), and hence may be described by the following second-order differential "equation (4)" [99].

$$\frac{1}{q_t} = \frac{1}{K_2 + q_e^2} + \frac{1}{q_e} t \quad (4)$$

Where q_e and q_t are the adsorption capacity the amount of adsorbate in the adsorbent at equilibrium and any time (measured in mg. g⁻¹). K_2 is the rate constant of (PSO) (g. mg⁻¹. min⁻¹), t time (min)

Adsorption rate studies are part of adsorption kinetics. Based on the results of the assessment of the relevant literature, the efficacy of treating effluent is regulated by the rate of which adsorbents take in adsorbate, which then influences the design and operation of the adsorption system [100, 101, 102].

Table (2) presents the kinetic model coefficients for various absorbent materials, whereas Figure (9) depicts the kinetic model curves.

3.4. Thermodynamics Study

Thermodynamic parameters give further information on the intrinsic energy changes connected with the adsorption process [103].

Adsorption procedures are strongly reliant on the operating temperature, that is influenced by thermodynamics factors such as the standard enthalpy change (ΔH° , KJ/mol), the standard entropy change (ΔS° , J/mol. K), and the standard Gibbs free energy change (ΔG° , KJ/mol). These parameters are calculated using the Gibbs-Helmholtz "equation (5)" [104]:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (5)$$

Temperature is a crucial variable in deciding either the adsorption process was either endothermic or exothermic [105]. As the temperature of the solution rises, the solution viscosity decreases, increasing the diffusive movement of adsorbate species from the bulk phase to the solid/liquid interface via pore diffusion [106]. Adsorption capacity rises with increasing sol

temperatures, showing the endothermic nature of the adsorption process caused by a raised in the kinetic transport of adsorbate solutes and a quicker diffusional rate [107]. The surface functional groups determine how temperature affects agricultural adsorbent capacity [108].

Previous investigations of the sorbents (CCAC_{KOH}) [78] and (Buckthorn plant twigs) [76]. show that increasing the temperature enhances the removal rate and adsorption capacity of oily wastewater, suggesting that the process is endothermic (Table 3). The negative ΔG° values show that adsorption was thermodynamically and spontaneously achievable. The reduction in ΔG° values with rising temperature demonstrates the feasibility of adsorption at higher temperatures [109]. A high ΔS° value implies that the oil droplet arrangement at the absorbent-solution interface becomes more random during absorption [110].

Table (3) Thermodynamic studies on oily wastewater treatment using CCAC_{KOH} and sea buckthorn twigs.

Table (2) Indicates the varied isotherms models constants for different adsorbents.

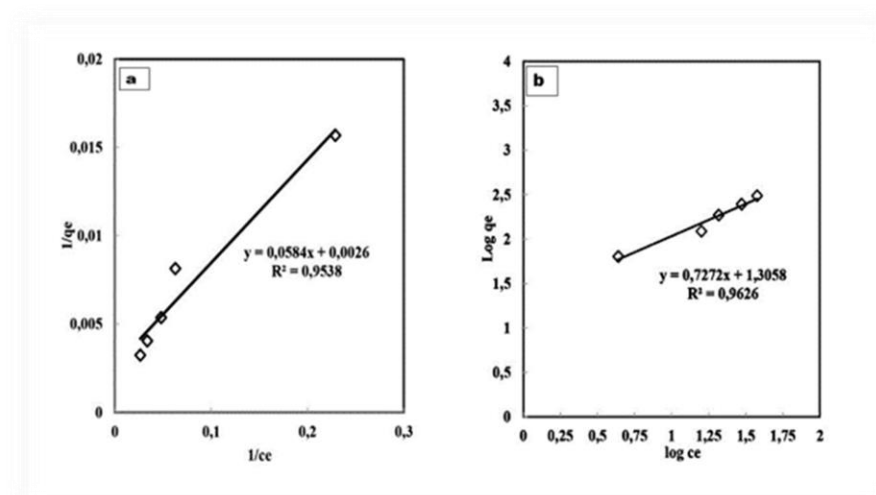
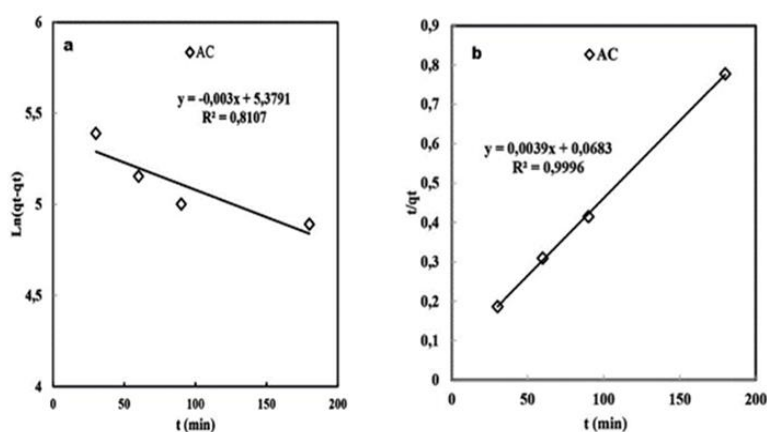
Adsorbents	Adsorbate	Langmuir			Freundlich			Refer
		Q _m (mg/g)	K _L (L/mg)	R ²	K _f (mg/g)	N	R ²	
Buckthorn plant twigs	Diesel Oil	380.068	0.045	0.9538	3.9604	1.4518	0.962	[76]
Coconut coir CCAC _(KOH)	Crude Oil	1.39 x 10 ⁴	0.2440	0.986	2.82 x 103	1.63	0.999	[78]
pomegranate peel (AC)	Crude Oil	555.56	0.0284	0.989	5.1454	2.1299	0.915	[79]

Table (3) Indicates the kinetic models parameters for different adsorbents

Adsorbents	Adsorbate	Pseudo-first order		Pseudo-second order		Refer
		K ₁ 1/min	R ²	K ₂	R ²	
Buckthorn plant twigs	Diesel Oil	0.003	0.9538	0.00022	0.9995	[76]
Coconut coir CCAC_(KOH)	Crude Oil	0.430698	0.846	0.00659	0.999	[78]
pomegranate peel (AC)	Crude Oil	0.0339	0.9366	0.000275	0.9903	[79]

Table (4) Thermodynamics studies on the removal of oily wastewater using CCAC_{KOH} and Buckthorn plant twigs

Adsorbents	Temperature (K)	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J/mol.K)
Buckthorn plant twigs	298	-5.249	28.940	0.1139
	308	-6.007		
	318	-6.837		
	328	-8.769		
CCAC _{KOH}	298	-20.067		0.5172
	300	-20.769		
	302	-21.377		
	304	-23.206		

**Fig. (8):** The isotherm adsorption (a) Langmuir and (b) Freundlich models [76].**Fig. (9):** The kinetic adsorption (a) Pseudo-first-order and (b)Pseudo-second-order [76].

3.5. Mechanism of adsorption

It is critical to understand the mechanism of adsorption of oily wastewater using activated carbon from agricultural waste. The emulsion is composed of water, crude oil, and an emulsifier. The emulsifier significantly decreases surface tension among the oily and water status. Through detracting the surface tension, the oil drops can be easily dispersed in water, stabilizing the emulsion. The primary way to remove an oily-in-water emulsion is to reduce the surface tension, which can be achieved by acidifying the emulsion. Thus, by reducing the surface tension, oil drops may more easily disperse in water, stabilizing the emulsion. The primary method for removing an oily emulsion from water is to reduce the surface tension, which can be achieved by acidifying the emulsion. To accomplish that purpose, drops of oil shift into the adsorbent's hydrophobic surface. Nonpolar molecules migrate from the oil due to the adsorbent's hydrophobic properties. The functional groups on the adsorbent's surface can help eliminate the emulsion. Furthermore, metal ions in the adsorbent composition may physically interact with the emulsion's additives, causing them to adsorb. The adsorption process is further impacted by the hydrophobic interaction between the adsorbent and electrostatic forces [11].

Agricultural waste comprises a lot of lignin and hemicellulose, which have important active functional groups. According to research, the adsorption process is influenced by two major factors. The first is the content of OW, which includes hydrocarbons, benzene, aromatic compounds, and so on; the second is the functional groups on the adsorbent's outer surface. These functional groups are likely to cause the adsorption of OW molecules. Electrostatic interaction, π - π interaction and hydrogen bonding are likely to occur. The Figure (10) shows the adsorption mechanism.

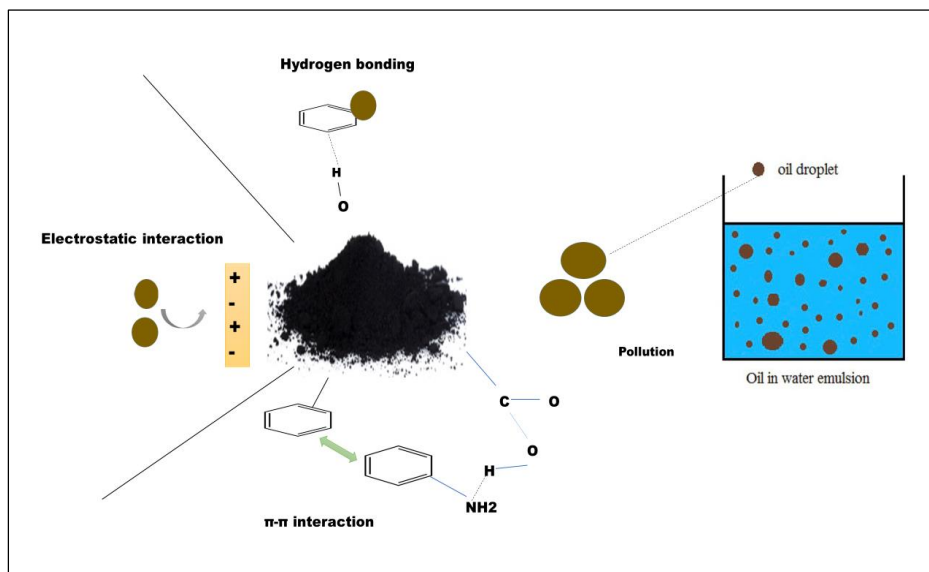


Fig. (10): The adsorption mechanism between activated carbon and oily wastewater

4. Conclusions

Oily wastewater pollution has become a global phenomenon, causing harmful environmental and health risks to ecosystems. Adsorption technology is designed to mitigate this risk, and the implementation of this technology provides an effective method for treating oily wastewater. This article provided an overview of the manufacture of activated carbon via agricultural residue utilizing several activation procedures: chemical activation, physical activation, physicochemical activation, and microwave-assisted activation. The influence of contact period, temperature, pH, and adsorbent quantity on the elimination of oily wastewater was investigated.

Thermal, kinetic, and thermodynamic models were studied. The two kinetics and thermal modeling give details on the reaction, helping to understand the procedure for adsorption. It is concluded that activated carbon can be a good option for removing hydrocarbons from wastewater due to its porosity, high adsorption capacity, environmental friendliness, and high removal efficiency. Therefore, it is suggested to carry out further work on treating oily waste using activated carbon prepared with other materials from solid waste and with different activation techniques and comparing it with commercial activated carbon and the like.

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