

Oil Removal from Polluted Seawater using Carbon Avocado Peel as Bio-Absorbent

Rana N. Malhas and Kingsley W. Amadi

Abstract — Oil spills are a very dangerous occurrence for the marine ecosystem as the marine life-form's existence gets unnecessarily threatened. Since the exploration of oil from marine resources has become a must and oil spills end up occurring accidentally, as a result, it becomes important to employ various oil spill cleanup methods. The purpose of the current work was to evaluate the oil sorption capacity of dried carbonized avocado peel (AP) waste. AP was dried under the sun and microwaved to have the activated carbon AP. In this study, batch adsorption studies were conducted to remove different oil types (Crude oil, Diesel, Kerosene, and Gas oil) from polluted seawater using AP. The effect of various important parameters, namely, mixing time, adsorbent dose, oil dose, oil types, and reusability on the oil uptake, and their optimum conditions for maximum sorption efficiency was studied. Batch studies indicated that an adsorbent dosage of 7 g, mixing time of 20 minutes under a mixing rate of 45–50 revolutions/min, 1 g of oil and provides maximum oil removal efficiency in the present study. Based on the data fit result of the adsorption; the 7 g AP at 20 min (90%) had better oil retention than the 1.5 g (66%), 3 g (77%), and 5 g (82%) AP. The results indicated that the maximum oil adsorption percentage upon increasing the adsorbent dose (1.5 g, 3 g, 5 g, and 7 g peel) was 66-90% for Crude oil, 45-68% for Diesel, 35-56% for Kerosene, and 19-45% for Gas oil at 20 min using 1 gram oil. The results revealed that sorption capacity decreased as the oil got lighter. Increasing the oil dose reduce the adsorption capacity (Crude oil 90-66%, Diesel 64-45%, Kerosene 50-39%, and Gas oil 40-12%). The oil sorption capacities of the AP sorbents reduce gradually from 90-64% after 10 cycles, with about 72%, since the oleophilic nature of the peel surface was affected during the regeneration process. The kinetic data was analyzed for all adsorbent doses. The pseudo-first order kinetic model was found to agree well with then experimental data found. The result showed that AP biosorbent followed pseudo-first order kinetics. According to the results presented, the cheap efficient AP oil spill sorbent could be developed as a potential material to be used in seawater treatment for oil removal. The avocado carbon displayed excellent adsorption properties for the simulated seawater effluents containing oil.

Keywords — Activated Carbon AP, Adsorption, Avocado Peel, Oil-Spill Cleanup, Kinetic.

I. INTRODUCTION

Oil spills are considered one of the world's most pressing issues, posing significant harm to the environment and aquatic life. Spills can occur from a variety of causes, including oil transportation, energy sources, disposal of waste, accidents, and the environment. The extraction of oil from several sources is associated with human activity. Every year, over 5 million tons of Crude oil are carried around the

world by water, putting the ecology under threat [1]. Oil leaks harm biodiversity and aquatic species, notably birds, coastlines, shellfish, mosses, and sea animals [2]. Environmental scientists have a significant problem in treating oil spills from manufactured water. Immediate action for the prevention of oil pollution is required and for this reason, several oil spill clean-up techniques were used. These include the use of booms and skimmers, oil pumping, in-situ burning, bioremediation, and the use of chemical agents, such as dispersants, solidifiers, and sorbents which are considered high-cost [3]. Oil spills are still one of the key challenges that are facing the petroleum industry nowadays.

The adsorption process is a physical adhesion of the polluting chemicals on the surface of a solid. Adsorption is often regarded as the most recommended approach for pollutant removal since it is a simple, ecologically acceptable, and low-cost procedure. Several researchers have shown an interest in using agricultural wastes or by-product components in recent decades [4], [5]. Adsorption processes have received special attention for contaminants removal to their capability to generate effluents with high quality as well as their simple design [6].

There is currently a rising interest in the manufacturing of sorbent materials utilizing natural organic sorbents for wastewater remediation, including banana, rice husk, avocado, banana, orange, lemon, pomegranate, garlic, and onion peel. The use of cheap and eco-friendly adsorbent was studied as an alternative substitution of adsorbent for removing of oils from the water [7], [8]. Although adsorbents can gather and convert liquids to semi-solid and solid states, they can remove oil from polluted water using an appropriate technique without oil draining out [9]. The production of fruit and vegetables has recently increased significantly due to the growing population and changing eating habits, with a greater number of people shifting to vegetarian-based diets [10]. The increased production coupled with poor handling of fruits and vegetables and the behavior of retailers and consumers towards wastage has led to huge quantities of loss and waste of vital agri-food commodities [11], [12].

Avocado is considered a very good oil adsorbent for dyes, toxic heavy metals removal, and organic pollutants [6], [13]. The peels of avocados, like other fruit peels, are commonly discarded, not knowing their potential use [14]. The increased demand for avocado, and therefore production and consumption generate large quantities of by-products such as seeds, peel, and defatted pulp, which account for approximately 30 % of fruit weight, and are commonly discarded and wasted [15]. Avocado (Persia Americana) fruit has great nutritional importance as a source of carbohydrates,

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R. N. Malhas, Australian University, Kuwait.
(e-mail: r.malhas@au.edu.kw)

K.W. Amadi, Australian University, Kuwait.
(e-mail: K.Amadi@au.edu.kw)

protein, and fiber and the avocado contains essential micronutrients for human consumption such as vitamins, minerals, and polyphenols [14]. The presence of compounds in the avocado peel makes it a very good bio-sorbent [15].

The focus of the present study is to assess the ability of avocado peel as a natural sorbent and a commonly available waste material for oil spill removal water across various factors. In the current work, the waste avocado peel is proposed to be used as an oil adsorbent for oil-contaminated seawater, as an alternative to conventional activated carbons whose use is sometimes restricted to high costs, upgraded by their exhausting after long-term operations [6]. The process used in the present study is rather simple, cost-effective, and easy to extrapolate at a larger scale for a practical application of the removal of oil. The effect of variable parameters, such as contact time, adsorbent dose, and various oil types, are also studied.

II. MATERIALS

AP (Persia Americana) was obtained from a fruit market in Kuwait. AP), which was the precursor of the carbonaceous solid to be used as adsorbent. Crude oil, Diesel, Kerosene, and Diesel were obtained from an oil company in Kuwait. Gas oil was obtained from a local gas station in Kuwait. All chemicals/reagents were of analytical grade. Seawater was taken from the Kuwaiti seawater. Microwave (Samsung 28 Liters (MC28H5015AW, 900 W), stopwatch timer (ONW0062, 0.05 kg), and mechanical blender (500 mL, 600-Watt motor base) were purchased from XCITE company in Kuwait. The microwave was used to dry the sorbent materials (AP). Separating funnels (500 mL) were used to separate the oil from water. Dichloromethane (99.6%, Fischer scientific). BSS 44 mesh with 355 microns, magnetic stirrer bar (coated with Teflon, 30 mm), Whatman filter paper (Grade 1, 150 mm Da, Cat No. 1001 150), Magnetic Stirrer Plate lab (12 × 12 cm) Enclosed heating plate, Cast aluminum Surface), Whatman filter paper (Grade 1, 90mm Da, Cat No. 1001 000), Vacuum pump, 1000 mL filtration flask and Sodium Sulfate Anhydrous (Granular/Certified ACS), Fisher Chemical™ were obtained from Abdullah Mohammed Faleh general trading & Cont., company, Kuwait. All experiments were conducted at the Australian University laboratory.

III. METHODS

A. Preparation of AP Adsorbent

Sorption studies were conducted by the batch technique. Batch experiments were carried out to determine the adsorption of oil onto the adsorbents. Fig. 1 illustrates the AP preparation. The AP obtained was washed (Fig.1a) with distilled water to remove any suspended particles. After washing, the AP was peeled (Fig.1b) then left to dry under the sun for 4–5 days (Fig.1c). A microwave was used for further drying (2 minutes) to allow the formation of activated carbon AP to have a large internal surface areas and pore volumes. The AP was allowed to cool down to ambient temperature. Later crushed using a laboratory mortar and pestle, then, the peel was ground using a mechanical blender to get the peel course. The AP was then sieved through the mesh (355 microns, Fig. 1d). The sieved peel (Fig.1e) was

packaged in pre-cleaned containers. Characteristics of powdered AP are shown in Table I.

TABLE I: CHARACTERISTICS OF POWDERED AP

Particle size (microns)	355
Moisture content (%)	8% (65.05)
pH in distilled water	6.3
Density (ρ) in (g/cm ³) Brazilian	1.326 ± 0.001
Specific gravity	1.326 ± 0.001

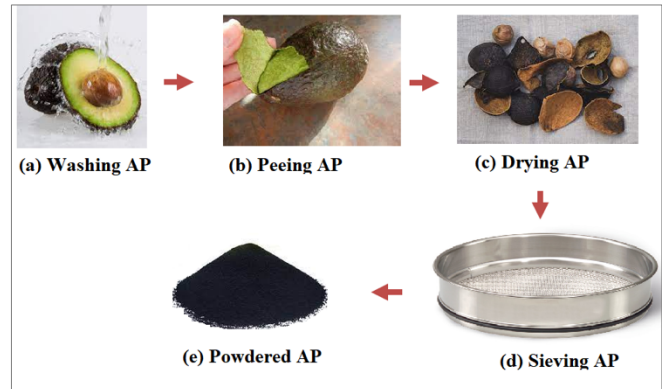


Fig. 1. AP preparation (a) Washing; (b) Peeling (c) Drying; (d) sieving using 355 Micros Sieve mesh; (e) Powdered AP.

B. Analytical Procedure

The oil content in water was measured according to the procedure for extraction recommended by the American Public Health Association using dichloromethane as the oil extraction solvent [16].

Fig. 2 shows the experimental workflow used in the study. In a 250 conical flask, the dried activated carbon AP was added and mixed for 15 minutes in 100 ml of seawater at room temperature and its final pH was measured. The oil was then added to the mixture, stirred, and left to settle for 24 hours. Then, the AP oil adsorbed was filtered using vacuum filtration. The filter paper containing the oil and the AP was left to dry for 24 hours. Then, the dry oil and AP were placed in a 100 mL beaker containing 20 mL of dichloromethane and mixed for 10 minutes. Anhydrous sodium sulfate was added to remove any water left, then filtered using Whatman filter paper. The dichloromethane (solvent) and oil were kept for 24 hours to evaporate the solvent. The weight of the beaker was measured before and after to measure the amount of oil adsorbed. The experiment was performed in triplicate, the average and standard deviation were calculated and used. The amount of oil adsorbed per unit mass of AP material is represented by the adsorption capacity. The oil sorption capacity (weight of oil adsorbed in g/ initial oil weight in g) was performed using different types of oil (Crude oil, diesel, Kerosene and Gas oil), and the percentage of oil adsorbed (oil sorption capacity *100) on AP was determined from the following expression (1):

$$\% \text{ Oil Removal} = \frac{\text{weight of oil adsorbed}}{\text{Initial oil weight}} * 100 \quad (1)$$

To determine the amount of residual oil in after filtration, the residue was then transferred to a separating funnel to which 20 mL dichloromethane was added, and the resulting mixture was shaken vigorously for 5 min and then left for 10 min to allow further separation. The dichloromethane layer

containing oil was then transferred to a beaker containing anhydrous sodium sulfate. The mixture was then filtered in a beaker and left to dry for 24 hours, and weight is measured to calculate the residual oil content. The recovery of AP was performed by washing it with distilled water for reuse.

The effects of varying values of parameters such as, mixing time, AP adsorbent dose, oil dose, oil types and reusability were studied on oil adsorption by powdered AP.

C. Synthesis of Adsorbate (Oil Polluted Seawater)

The oil-polluted seawater samples were synthesized in the laboratory by adding 1, 1.5, 3 or 5 g of crude oil in 100 mL of seawater in three conical flasks (500 mL). Each flask was stirred with a magnetic stirrer for appropriate time. The same procedure was repeated for Diesel, Kerosene, and Gas oil. All the samples were used for the sorption study.

D. Effect of Mixing Time Procedure

AP adsorption efficiency was studied as a function of time (5, 10, 15, 20, 30 and 45 min). The test solution was prepared in Erlenmeyer Flasks by adding 1 g of oil in 100 mL seawater and keeping the adsorbent dose constant for 1.5 g and varying the time. The same procedure was repeated for a different adsorbent dose of 3, 5, and 7 grams.

E. Effect of Adsorbent Dose Procedure

Oil adsorption by AP was studied as a function of AP dose (1.5, 3, 5, and 7 grams). The test solution was prepared in conical flasks by adding a fixed amount of oil (1 g) in 100 mL seawater by keeping the time constant for 20 minutes and varying the adsorbent dose. The mixture was stirred using a magnetic stirrer. The effect of adsorbent was also studied similarly for all types of oil.

F. Effect of Oil Type Procedure

Four types of oil were investigated to represent a wide variation in the ability of AP in oil spill cleanup. The oils employed in this study, namely: Crude oil, Diesel, Kerosene, and gas oil. The test solution was prepared in conical flasks by adding 1, 3, or 5 grams of crude oil in 100 mL seawater and keeping the time constant for 20 minutes and activated carbon AP weight for 7 grams. The mixture was stirred using a magnetic stirrer. The effect of oil adsorption was also repeated similarly for all oil types. With regards to more volatile components, they evaporated quickly after spreading oil spill. At the beginning of an oil spill, less volatile fractions evaporate and, as a result, the oil viscosity increases. So, to simulate the same situation of an oil spill and to reduce sorption procedure, the crude oils were put on trays for four days in open air.

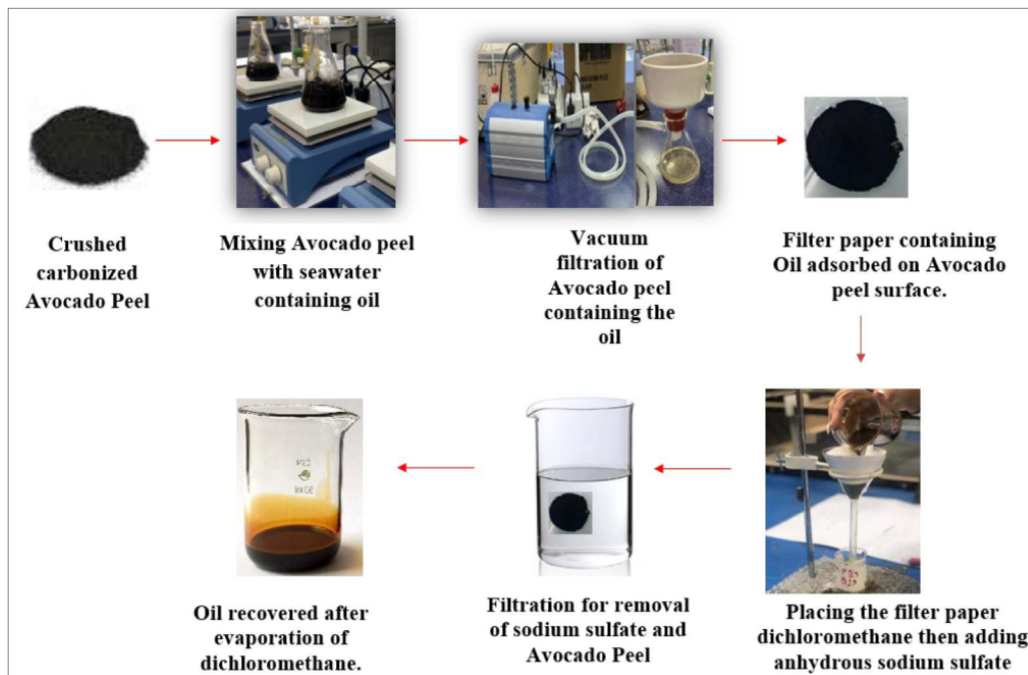


Fig. 2. Experimental workflow.

IV. RESULTS AND DISCUSSION

This section presents the results and discussions. Four types of oil were studied to observe the range of avocado adsorption capacity as an oil sorbent material. The results of API (Table II) were calculated for all oil samples (Crude oil, Diesel, Kerosene, and Gas oil) using (2). The specific gravity (2) was determined using the density (mass/volume) divided by the water density.

$$API = \left(\frac{141.5}{SG} \right) - 131.5 \quad (2)$$

TABLE II: API AND SPECIFIC GRAVITY OF OIL TYPES

Oil Type	Specific Gravity	API °
Gas oil	0.724	63.9
Kerosene	0.776	50.8
Diesel	0.808	43.6
Crude oil	0.875	30.2

A. Contact Time Effect and Sorbent Dose

The effect of mixing time is an important economic factor on oil adsorption efficiency. The test was studied using a fixed amount of crude oil (1g). Fig. 3, Table III showed the effect of mixing time (5, 10, 15, 20, 30 and 45 minutes), and AP dosage (1.5g, 3g, 5g and 7g). It was observed that oil

sorption capacity increases gradually as sorption time increases from 5 up to 20 min (18-66%), (24-77%), (25-82%) and (29-90%) for 1.5 g, 3g, 5 g and 7 g adsorption dose respectively. This can be referred to improving the diffusion of oil at the surface of the reactive medium and then, more contact between binding sites and oil in the aqueous solution.

Whereas it remains constant from 20 to 45 minutes for all adsorbents dose (66%), (77%), (82%) and (90%) respectively for 1.5 g, 3 g, 5 g and for 7 g as shown in Table III and Fig.3. It's clear that the process reaches a steady-state phase where

no further sorption occurs from 20 to 45 minutes. Table III shows the results obtained for the sorption capacity at a steady state for each sorbent. This trend represents saturation of the active sites available on the sorbents for interaction with contaminant. However, varying the sorbent dose from 1.5g to 7g (Fig. 3, Table III) up to 20 min using 1g of Crude oil revealed that the sorption capacity increased with increase in adsorbent dose 1.5 g (66%), 3 g (77%), 3 g (82%) and showed maximum adsorption capacity at sorbent dose to 7g (90%) AP.

TABLE III: EXPERIMENTAL RESULTS FOR BIOSORPTION USING AP AND 1 G OF CRUDE OIL AS A FUNCTION OF TIME AND AP DOSE

AP dosage, (g)	Contact time (min)	Residual oil (g)	Amount of oil removed (g)	Oil Removal Percentage %
0	0	1	0	0
	5	0.82	0.18	18
	10	0.62	0.38	38
	15	0.43	0.57	57
	20	0.34	0.66	66
1.5	30	0.34	0.66	66
	5	0.76	0.24	24
	10	0.52	0.48	48
	15	0.28	0.72	72
	20	0.23	0.77	77
3	30	0.23	0.77	77
	5	0.75	0.25	25
	10	0.47	0.53	53
	15	0.2	0.8	80
	20	0.18	0.82	82
5	30	0.18	0.82	82
	5	0.71	0.29	29
	10	0.39	0.61	59
	15	0.12	0.88	88
	20	0.1	0.9	90
7	30	0.1	0.9	90

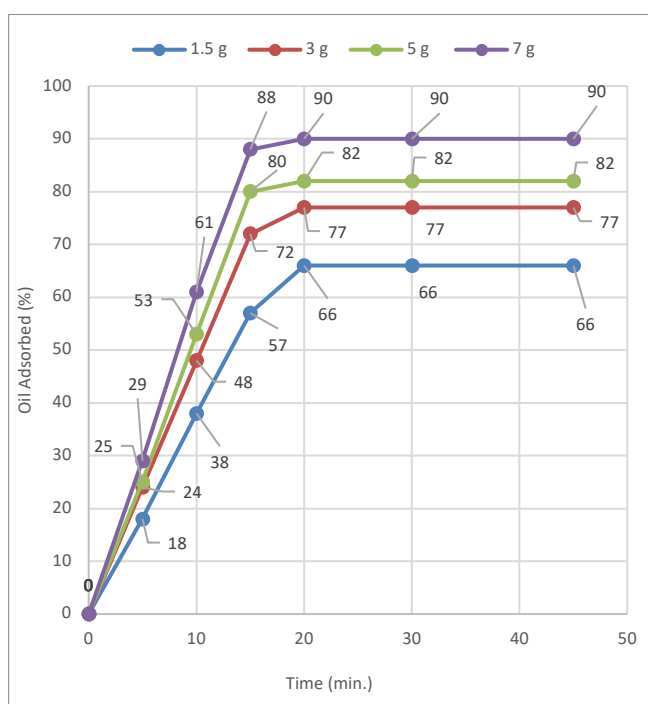


Fig. 3. Effect of contact time and adsorbent dose on adsorption.

This is shown at all mixing times from 5-45 minutes as shown in Table III. These results indicate that increasing the amount of sorbent, large amounts of oil are adsorbed due to the increased in the surface area with more adsorbent dose. In addition to that as the adsorbent dose increases will result in more adsorbent vacant site to be filled with oil particles.

This is because, at the beginning, all the binding sites on the adsorbent were vacant and the solute concentration

gradient was high. After the 20 minutes, all the vacant sites were filled, and no more adsorptions would have taken place. The weight of the residual oil was obtained to make sure of the resulted data for amount of oil adsorbed, the total of residual and amount adsorbed was equal to the oil starting weight.

B. Kinetic Modeling Study

Analysis of the adsorption data using pseudo first-order kinetic model of Lagergren pseudo-first-order model assuming that the rate of occupation of sorption sites is proportional to the number of empty sites [17] which implies that the rate of change of solute uptake with time is directly proportional to the difference in the saturation concentration and the amount of solid uptake with time.

Fig. 4 represent Q_t (amount adsorbed) versus time (min.) at 0, 5, 10 and 15 minutes for AP 0 g, 1.5 g, 3 g, 5g and 7g.

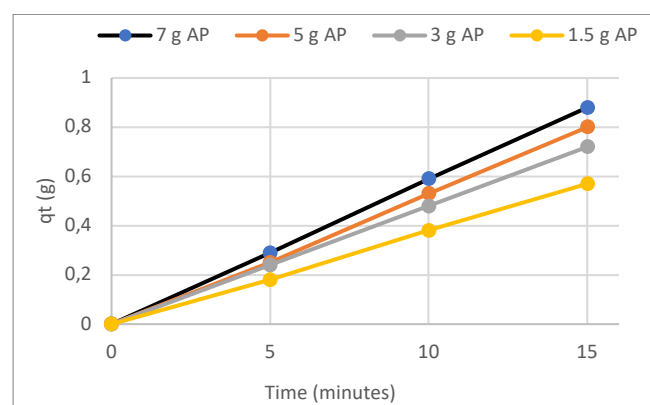


Fig.4. Plot of amount adsorbed versus time for AP.

Equation (3) express the general form of Lagergren pseudo-first-order model, where q_e is the amount of dye adsorbed at equilibrium. q_t is the amount of oil adsorbed at time t , k_1 is the first order rate constant (min^{-1}) and t is the time (minutes) and represents the rate constant of pseudo first-order adsorption. Equation (4) is the integrated form of (3).

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (4)$$

Using (4), a linear plot of $\log(q_e - q_t)$ versus t gives the applicability of pseudo-first-order kinetic model. The rate constant k_1 and equilibrium amount of oil removed q_e can be obtained from the slope ($-k_1/2.303$) and the intercept ($\log q_e$) of plot in Fig. 5. Correlation coefficient and constant values were calculated and shown in Table IV.

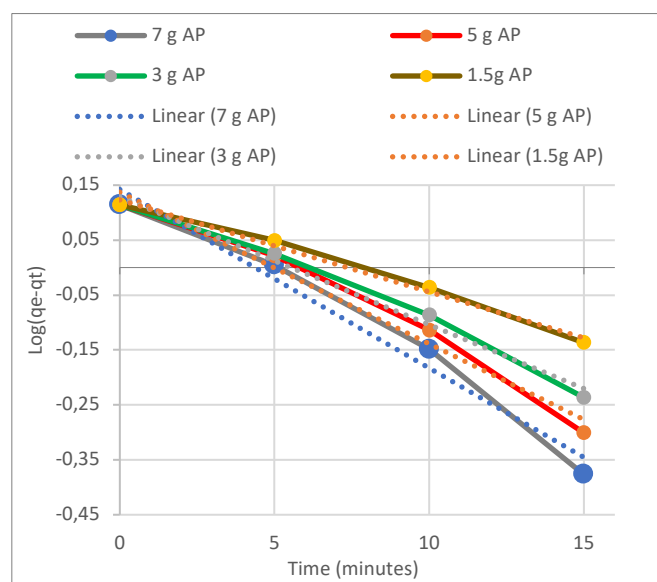


Fig. 5. Pseudo-first-order kinetics plots for the adsorption.

TABLE IV: BIOSORPTION KINETICS AND EVALUATED CONSTANTS

AP dose (g)	R ²	Intercept	slope	Calculated q _e	k ₁
1.5	0.9909	0.1232	-0.0167	1.328	0.03846
3	0.9859	0.1286	-0.0233	1.344	0.05366
5	0.9769	0.1371	-0.0276	1.371	0.06356
7	0.9738	0.142	-0.0325	1.387	0.07484

From results of Fig. 4 and Fig. 5 and Table IV, it can be deduced that the oil sorption from sea water using 1g, 1.5g, 3 g, and 5 g AP follows pseudo first-order kinetics since all R² values for all AP doses was close to 1. In addition to that the estimated q_e (1.3) value and the calculated value (1.328-1.387) was very close irrespective to the amount of the (R²) correlation coefficient, so the mechanisms will be physical adsorption.

C. Effect of Different Oil Types on Sorbent Dose

The effect of different oil types with varying the adsorbent dose at 20 min mixing time since a maximum adsorption percentage was obtained at this time. Fig. 5 illustrates the sorption capacity for Crude oil, diesel, Kerosene and Gas oil with different AP adsorption dose (1.5 g to 7 g). The results

showed that the adsorption percentage increases with increasing AP sorbent dose for all type of oil and optimum adsorption parentage was shown utilizing 7g AP.

It was further observed in Fig. 6 that the Crude oil showed the highest sorption than all other oil types. In Fig. 6 the oil adsorption percentage using 1.5 g, 3 g, 5 g and 7 g AP was for crude oil 66-90%, for Diesel oil 45-68%, for Kerosene 35-56% and for Gas oil 19-45%. This indicate that, as the oil gets lighter, the oil sorption capacity decreases. This was proven by oil loss for all oil types studied. The oil loss that is present in the filtrate was obtained for all oil types and it showed 10-36% for crude oil, 35-55%, Diesel 50-65%, Kerosene and 60-81% for Gas oil using AP peels 1.5g, 3g, 5g and 7g respectively.

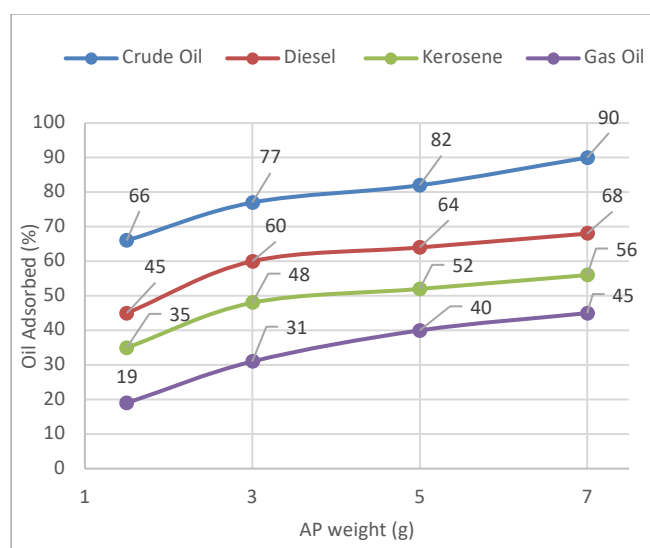


Fig. 6. Effect of sorbent dose for different oil types on sorption capacity.

D. Effect of oil dose on different oil types

Oil adsorption by AP adsorbent depends on amount of oil used. The oil adsorption percentage for different oil (Crude oil, Diesel, Kerosene and Gas oil) weight using 7g peel at 20 min for 1g, 1.5g, 3 g, and 5 g oil dose was studied. In Fig. 7 it's clear that the crude oil has a maximum impact on adsorption parentage although it drips to (90-66%) upon increasing the crude oil dose from 1g to 5 g. Similarly, the AP sorption capacity drips for Diesel fuel (64-45%), Kerosene (50-39%) and Gas oil (40-12%) quicker than for Crude oil. This could be attributed of increasing oil dose made the AP active adsorption sites over the saturation limit that can hold and become less available for oil uptake. This trend was repeated for all oil types used as oil weight increased making actual adsorption more difficult. This was due to the fact K-values are inversely proportional to the kinematic viscosity of the oil [18]. Several factors contribute to sorption, and these include high surface area and highly reactive sorbates and sorbents; organic sorbates chemically bond to the sorbent, if the sorbate and sorbent have mutually reactive moieties [19]. Variety of different types of attractive forces between the sorbate and sorbent results in sorption and the extent of these intermolecular attractions depends on molecular chain length and on surface area available for interaction [20]. The AP sorbent and the sorbates (oil) are composed mainly of hydrocarbons; in order words both have mutual reactive moieties, hence will interact together.

This was reflected in the higher sorption capacity with the crude oil than Diesel, Kerosene and Gas oil, since more and lengthier hydrocarbon content in the heavier crude oil. The capacity of the crude oil removal is related to the chemical composition and surface properties. Fig. 7 showed that adsorption capacity decreased when oil amount increases. AP adsorbent would act as a molecular sieve, whereby the oil mesopores would perpendrate the adsorbent micropores.

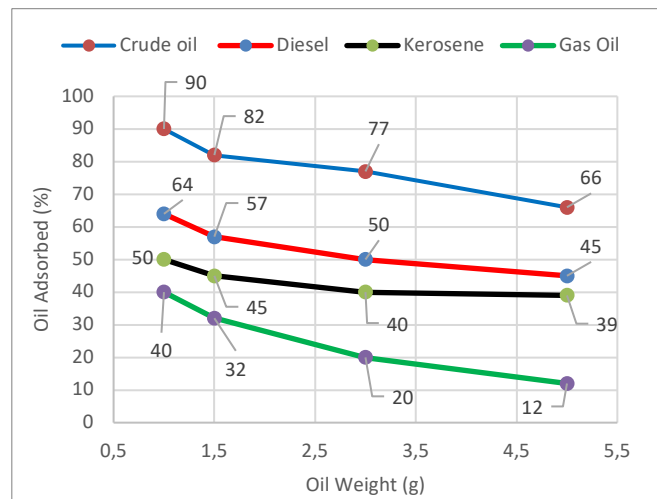


Fig. 7. Effect of oil weight with different oil types on sorption capacity.

E. Reusability of AP Sorbent

Fig. 8 shows the varying values of sorption capacities of the AP sorbents for crude oil at oil–water interface when the sorbents are subjected to successive sorption cycles.

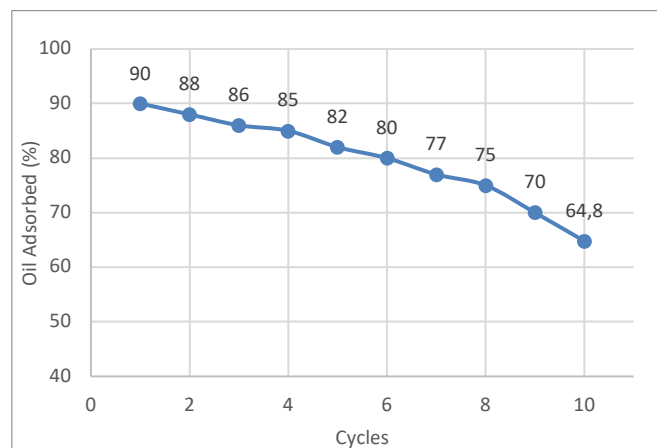


Fig. 8. Reusability and oil retaining ability of the AP sorbent.

The experiment was performed using 7 g AP at 20 min. mixing time. In general, oil sorption capacities of the AP sorbents reduce gradually from 90-64% after 10 cycles, with about 72% oil sorption capacity remaining.

V. CONCLUSION

Fruit peels, such as avocado peel, are not generally consumed and are therefore discarded. After an investigation on the oil adsorption percentage of oil adsorption on activated carbon AP, it was observed that it can be used as a source of oil sorbent, a method was suggested as a way of reusing these discarded peels. It is also available in large scale and expected to become promising candidate for spilled oil cleanup

applications to replace the commercial sorbent which is being widely used nowadays. Based on the data fit result of the adsorption; the results evaluated that increasing the amount of oil result in a negative impact of adsorption capacity. The sorption capacity showed maximum for the heavy oil (Crude oil) with 64-90% and decline toward the lighter Diesel. The reusability of AP for Crude oil reduces by 72% for the 10 cycles, due to the decline of the oleophilic nature of the peel surface during the regeneration process. According to the results presented, dried activated carbon AP waste is a potentially cheap efficient oleophilic oil spill sorbent. The kinetic data was analyzed using pseudo-first order, and it was found to agree well with the experimental data for AP oil adsorbent. Avocado Sorbents have been demonstrated to have a good hydrophobicity and absorbing capacity of oil from water surface. Recommendations Since activated carbon is becoming more popular in many industrial applications, it is recommended to carry out optimization experiments with different activation methods and the results compared. Characterization to be done to determine the pore volume, surface area and structure and surface functional groups. Validation of the methodology used is recommended to determine its suitability.

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CONFLICT OF INTEREST

Authors declare that they do not have any conflict of interest regarding the publication of this paper.

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committees including senior project, project-based learning.



applications.

Kingsley W. Amadi is a Researcher at Drilling & Well Construction research group and a Senior Instructor of Petroleum Engineering in Australian University, Kuwait. He holds an M.Sc. in Drilling and Well Engineering from the Robert Gordon University, Aberdeen. His main research interests are Directional drilling, risk quantification and decision analysis for autonomous drilling and well



Rana N. Malhas born in Kuwait on 23 Feb. 1969. Mrs. Malhas is an assistant professor at Australian University in Kuwait, Ph.D. was in the Chemistry field and application in the environment in 2006 from Kuwait University.

She has 30 years of experience in teaching and research, she published several papers in water and waste treatment using different conventional methods, ultrafiltration membrane and nanoparticles applications.

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Dr. Malhas is a member of Kuwait chemical society and received 4 awards in water treatment. Dr. Malhas joined several department