Journal of Chemical Engineering

Vol. ChE 31, No. 1, January 2023

Article

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To cite the article:
S. M. Anisuzzaman, S. Abang, S. E. B. M. Azraley (2023), "Crude Oil Spills Clean-up from Water Surface Using Modified Commercial Activated Carbon", Journal of Chemical Engineering, IEB, ChE 31 (1), pp. 13-19.

The Institute of Engineers, Bangladesh (IEB)
Chemical Engineering Division

Journal of Chemical Engineering, IEB
Vol. ChE 31, No. 1, January 2023

Crude Oil Spills Clean-up from Water Surface Using Modified Commercial Activated Carbon

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Received: 15 March 2022; Accepted: 11 August 2022; Published: 30 April 2023

Abstract: Petroleum products and their derivatives are considered as a major source of pollution and spills of those products have devastating effects towards the environment. The objectives of this study were to modify the commercial activated carbon (AC) by impregnation method with 85% w/v phosphoric acid (H_3PO_4) solution and to remove crude oil spills from water surface using modified AC (MAC). Fourier transform infrared spectroscopy (FTIR) was used to check the functional group in the unmodified AC and MAC. The effect dosage of adsorbents, temperature and the effect of contact time towards the adsorption process has been carried out, where the results showed that MAC has a higher percentage of adsorption compared to unmodified AC. For the kinetic study, pseudo-first order was chosen for the best kinetic model to express the sorption of crude oil spills on MAC as it shows the R^2 value closest to 1. Meanwhile, for the adsorption isotherm, the result indicates that Freundlich was the most suitable model for describing the sorption equilibrium of crude oil on AC and MAC.
Keywords: Adsorption; modified activated carbon; crude oil spills; oil sorption capacity

1. Introduction

Due to exploration, transportation and production of petroleum fractions, oil spill causes various environmental pollution [1,2]. The impact of the oil spills can cause pollution towards four categories and these pollution are towards soil, aquatic systems, atmospheric pollution due to volatile components and lastly land-based spills of oil [3,4]. Coral reefs are one of the major fields affected by oil spills [5]. Other than reefs, humans can also be affected by oil spills. Due to variation of petroleum substances, such as gasoline, kerosene, diesel and petroleum waxes, different substances penetrate the skin at different rates. Some of the constituents of petroleum products are proven to be associated with being carcinogenic for instance benzene and some polycyclic aromatic hydrocarbons [3].

According to Demirel *et al.,* [6], there are four ways to combat oil spills which are burning, booms and skimmers, chemical dispersants and sorbents. Traditional methods often called for chemical dispersant methods to manage the oil spills. Generally sorbents are used due to their effectiveness, inexpensive, as well as safe. Adsorbents are promising methods for the removal of oil spill as compared to other methods when dealing with oil spills in water [1,6]. Adsorption capability can be depicted from cellulose based activated carbon (AC). The Absorption capacities of the AC from alpha-cellulose was able to adsorb H_2S was 7.29 mg/g which is more than what methyl cellulose precursor can adsorb [7]. Doshi *et. al.,* [8] conducted a study on the effectiveness of N,O-carboxymethyl chitosan for the removal of oil spills. Other than chitosan, natural adsorbents such as sawdust, straw, wool and peat also have been studied [9].

Activated carbon (AC) is an amorphous carbonaceous material derived from from biomass, lignite and hard coal, synthetic materials and others. [10,11]. AC can be used as an effective adsorbent due to their high adsorptive capacity, high surface area and substantial pore volume. It can be used in a water treatment process, purification of air by removing the trace amount of unwanted substances [12]. AC can also be used to remove volatile organic compounds, namely benzene, toluene and methanol [13]. Modifications of AC are further made to increase surface adsorption and removal capacity [14,15]. According to Kim *et al.,* [16], impregnation of AC with phosphoric acid (H_3PO_4) results in a high adsorption capacity for selected volatile organic compounds such as benzene, toluene, p-xylene, methanol and etc. It has been also found that an increase in impregnation ratio will result in an increase in the ash content and percentage yield until it reaches an optimum value [15].

The objective of this study was to modify the commercial AC by impregnation method using H_3PO_4 and to remove crude oil spills from water surface using modified AC (MAC). Fourier transform infrared spectroscopy (FTIR) was used to check the functional group in the unmodified AC and MAC. The effect dosage of adsorbents, temperature and the effect of contact time towards the adsorption process has been carried out.

2. Materials and Methods

2.1 Preparation of AC using H_3PO_4

The AC (NORIT) was purchased from Sigma-Aldrich, which is a coconut shell based in powder form with ~100 mesh particle size. 85% of H_3PO_4 (Merck) was used for impregnation of AC. In the impregnation process, 10 g of AC was impregnated with 40% w/v of H_3PO_4 solution. The conical flasks containing the mixture were enclosed with aluminium foil. A few holes were punched onto the foil in order to let the vapours evaporate. Then, the mixture was set for three days to dissolve the solution by using a shaking water bath at standard room temperature. The chewy liquid was further dried at 120ºC for 24 h in the oven. The impregnated AC was placed in a muffle furnace (Carbolite RHF 1500) at 500ºC for 2 h for carbonization. After the AC heated, the AC cooled to room temperature. Then, the MAC was refluxed 3 times

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for 3 h to remove any inorganic impurities such as metal ions, on the surface. Lastly, the MAC was dried at 110ºC for 24 h [15,17].

2.2 Fourier transform infrared spectroscopy (FTIR) analysis

After the impregnation of AC using H_3PO_4, changes in the functional group of both unmodified AC and MAC were compared and the spectra was recorded within 400 to 4000 cm^{-1}. The characterization of unmodified and MAC was done by using Fourier – transform infrared spectroscopy (FTIR) (Perkin Elmer).

2.3 Oil adsorption

The sorption of oil on the surface of water was conducted using methods from Nwadiogbu *et. al.*, [17]. 1 g of MAC was placed in a 250 ml beaker containing 5 g of crude oil which was collected from Sabah basin, Malaysia displaced in 100 ml of water at room temperature. The samples were left in the mixture for an approximation of 2 min with minimum agitation. The sorbents were removed from the beakers using sieve nets and the oil-loaded sorbents were then dried at 60°C for 30 min. The oil sorption capacity was calculated using equation 1:

$$\text{Oil sorption capacity } \left({}^{g}/_{g}\right) = \frac{(S_{st}-S_o)}{S_o} \quad (1)$$

where, S_o is the initial mass of the dry sorbent, S_{st} is the mass of the sorbent with oil at the end of the sorption test.

The amount of crude oil adsorbed (q_e) was calculated using the equation 2:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (2)$$

where, C_o is the initial concentration (mg/l); C_e is the equilibrium oil concentration (mg/l); V is the volume of the solution (l); W is the mass of adsorbent (g)

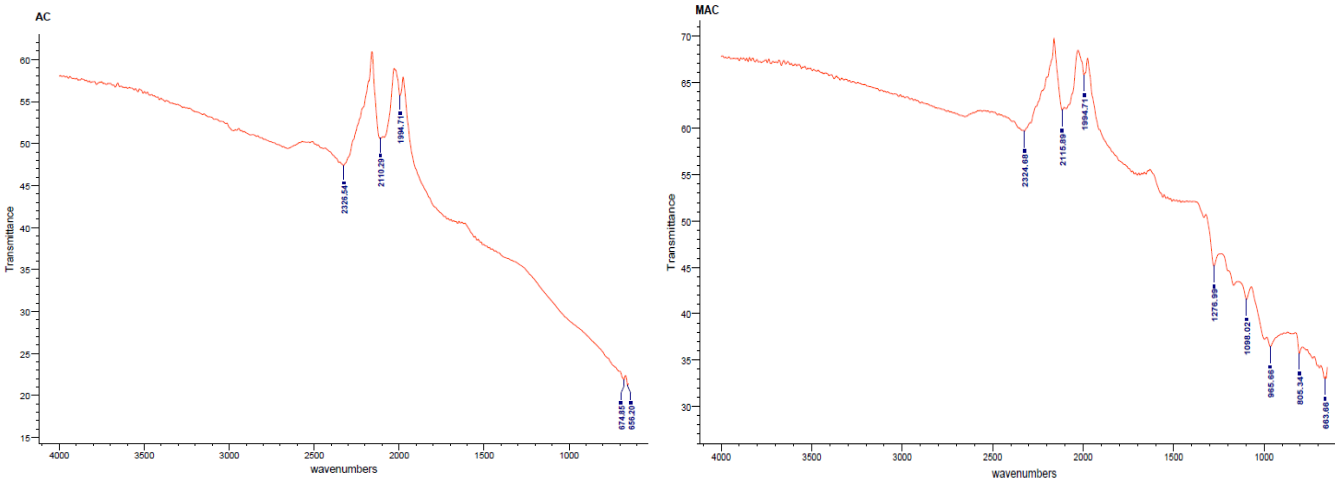
2.4 Adsorption equilibrium study

Adsorption isotherm is the relationship between adsorption capacity and concentration of the remaining adsorbent at constant temperature. Langmuir and Fruendlich equations were used as mathematical expressions to describe the isotherm of the adsorption [120 -22]. To analyse the rate and mechanism of oil sorption toward AC and MAC, kinetic models were applied as Lagergren pseudo-first order and pseudo-second order [17,23].

3. Results and Discussion

3.1 Fourier transform infrared spectroscopy (FTIR) analysis

Figure 1 (a,b) shows the FTIR spectra for both unmodified AC and MAC. As observed, there is less difference in the peaks occurred in around 2500-2000 cm^{-1} and strong peaks are detected in MAC around 1500-1000 cm^{-1}. The AC and MAC shows a similarity in a strong peak at 2326.54 and 2324.68 cm^{-1} respectively which indicates that a C≡C exists in both of them caused by the stretching vibrations of the alkyne groups. Other than that, a peak was detected at 1300-1200 cm^{-1} in the MAC graph which indicates the C-O-C group stretches in alcohols, phenols, esters, ethers and acids. At 980-950 cm^{-1} of the MAC graph, P-O-C carbon peak stretches towards the area. This is due to the acid phosphates formation in the samples which were modified using H_3PO_4 [20]. Meanwhile, in both unmodified AC and MAC graphs, peaks that arise in the range of 800 – 700 cm^{-1} may be caused by the existence of C-H [24].



(a) (b)

Figure 1. FTIR spectra of (a) unmodified AC (b) MAC

3.2 Effect of sorbent dosage towards oil sorption capacity

Table 1 shows the effect of oil sorption capacity towards the sorbent dosage. It can be observed that MAC has higher sorption capacity than AC at any given sorbent dosage. A trend was observed with an increase in sorbent dosage but a decrease in adsorption capacity. It was found that sorption capacity decreased 83.8% for unmodified AC and 83.2% for MAC with an increase in sorbent dosages.

Table 1. Effects of sorbent dosage towards oil sorption capacity on unmodified AC and MAC

Sorbent dosage, g	Oil sorption capacity, g/g	
	Unmodified AC	MAC
0.1	25.61	29.10
0.3	9.44	10.08
0.5	5.43	6.26
0.7	4.15	4.87

The decrease in sorption capacity may be due to the overlapping of AC, which results in a decrease in effective surface area for the adsorption process. It can be observed that the oil sorption capacity decreases with increasing sorbent dosage. It was also observed that after a certain dosage, at 0.5 g to 0.7 g, the efficiency of adsorption did not increase significantly. Therefore, the optimum amount of AC and MAC is 0.1g for both and was kept constant for the next adsorption experiments [25].

3.3 Effect of temperature towards oil sorption capacity

Table 2 shows the effect of temperatures towards the oil sorption capacity on both unmodified AC and MAC. Contact time and sorbent dosages were kept constant throughout the experiment meanwhile the temperatures were manipulated. It can be observed that MAC has higher oil sorption capacity than AC at any selected temperature.

Table 2. Effects of temperature towards the oil sorption capacity on unmodified AC and MAC

Temperature, ºC	Oil sorption capacity, g/g	
	Unmodified AC	MAC
25	25.61	29.10
30	25.68	27.90
35	26.05	28.03
40	25.50	28.07

MAC has higher oil sorption capacity than AC due to the modification of H_3PO_4. The modification enhances the porosity structure and sizes of the pores which consequently provides a better adsorption than unmodified AC [15]. The highest oil sorption capacity recorded for MAC was at a temperature of 25°C. The inconsistencies of the oil sorption capacity for both AC and MAC from 30°C to 40°C may be due to the increasing temperature which causes the oil to be very light which then leads to release of the oil from pores again [26]. According to El-Din *et al.,* [26], with the increase in temperature, the Brownian motion of oil particles is accelerated and increased proportional to the temperature.

3.4 Effect of contact time towards the oil sorption capacity

Table 3. shows the oil sorption capacity against contact time on unmodified AC and MAC.

The sorption capacity increases as time increases from 2 to 8 min. It was found that sorption capacity for unmodified AC was increased 5.8% and 12.4% for MAC with an increase in contact time. As observed, the maximum oil sorption capacity was recorded on the 8 min of contact time with a result of 27.10 g/g for AC and 32.71 g/g for MAC.

Table 3. Effect of contact time towards the oil sorption capacity on unmodified AC and MAC

Contact time, min	Oil sorption capacity, g/g	
	Unmodified AC	MAC
2	25.61	29.10
4	26.15	31.02
6	27.00	31.90
8	27.10	32.71

Figure 2 shows the regression plot of oil sorption capacity against contact time for both unmodified AC and MAC. According to the regression equation, for every 1 min increase in time, the oil sorption capacity for AC increases by 1%. Meanwhile, for the MAC, the oil sorption capacity increases by 2%. These results show that contact time does affect the oil sorption capacity of the modified and unmodified activated carbon.

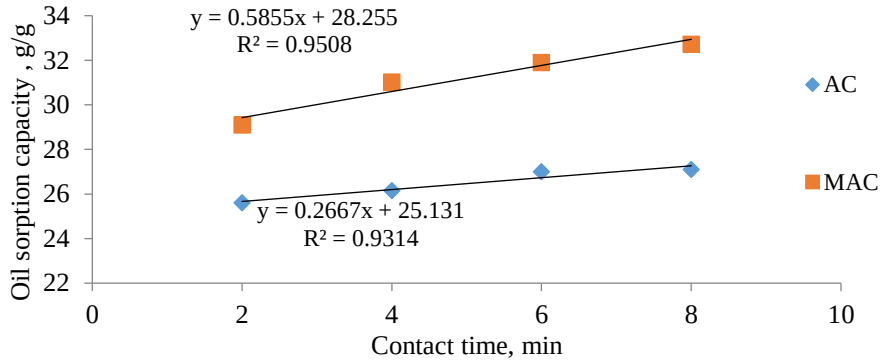


Figure 2. Regression plot of oil sorption capacity against contact time for both AC and MAC

3.5 Adsorption kinetic study

Figures 3 and 4 show the pseudo-first order and pseudo-second order kinetics for unmodified AC and MAC

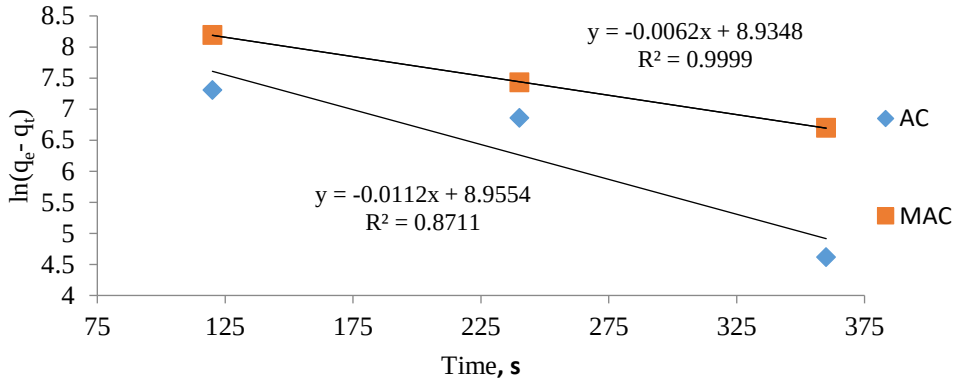


Figure 3. Pseudo-first order kinetics for unmodified AC and MAC

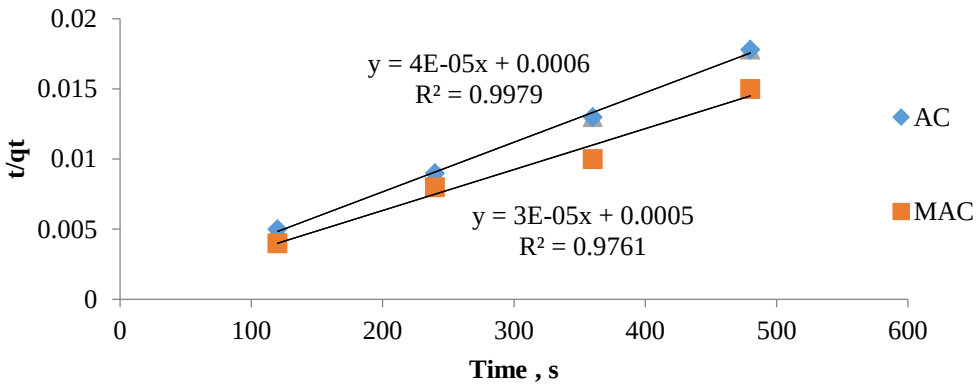


Figure 4. Pseudo-second order kinetics for AC and MAC

Table 4 shows the kinetic parameters data calculated from the Figures 3 and 4 for pseudo-first order and pseudo-second order models.

Table 4. Pseudo-first order and pseudo-second order parameters for AC and MAC

Kinetic Models	AC	MAC
Pseudo-first order:		
k_1 (s^{-1})	-0.0112	-0.0062
R^2	0.8711	0.9999
Pseudo-second order:		
k_2 (s^{-1})	$4x10^{-4}$	$1.3x10^{-6}$
R^2	0.9979	0.9761

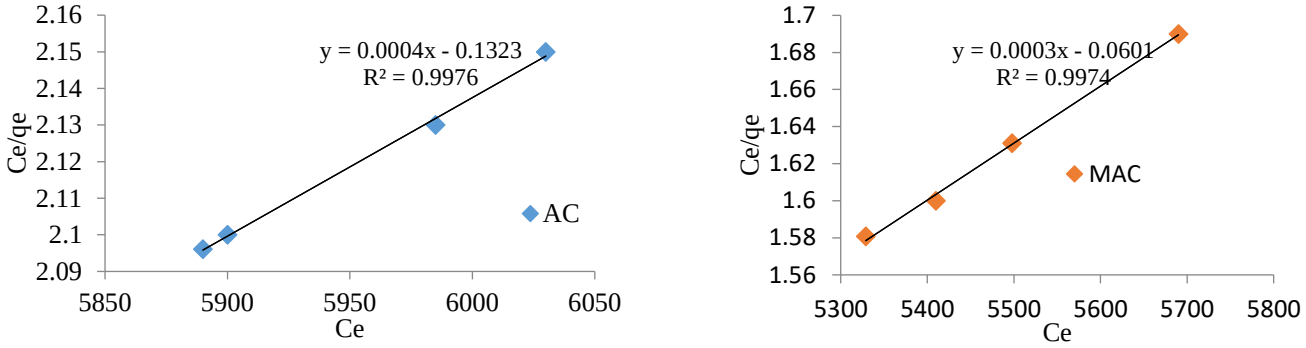
Based on the result in Table 4, both kinetic models showed a good fit of kinetic to the data. However, for MAC the comparison between the first and second order, pseudo-first order expression provided an excellent fit to the experimental data as the regression coefficient (R^2) value was closer to 1 than pseudo-second order expression. The regression

coefficient (R^2) of MAC for the pseudo-first order was 0.9999. On the other hand, the regression coefficient (R^2) for pseudo-second order was 0.9761 for MAC. Hence, the pseudo-first order was chosen for the best kinetic model to express the sorption of crude oil on MAC [28].

3.6 Adsorption equilibrium study

Sorption isotherms are the basic representation of the relationship between amounts of adsorbate removed from the liquid phase and the mass of adsorbent at a constant temperature [19].

Figure 5 shows the Langmuir isotherm for AC and MAC.



(a) (b)

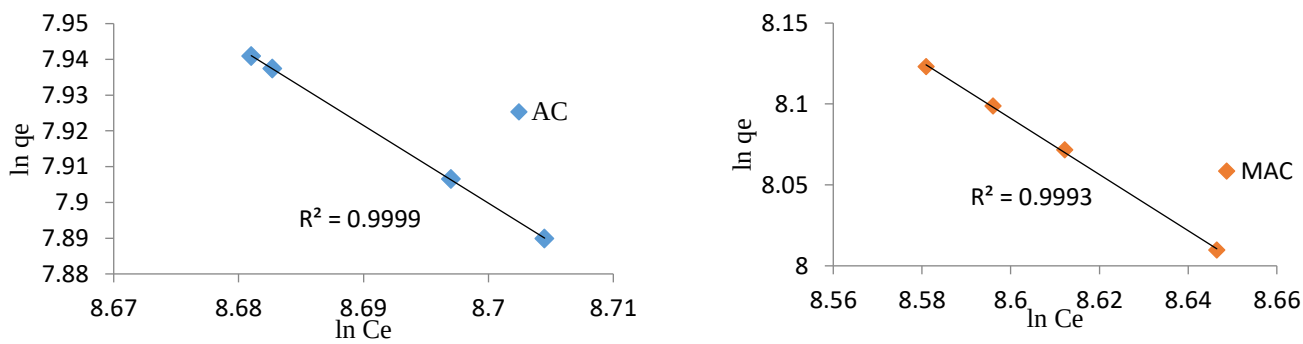
Figure 5. Langmuir isotherm (a) for AC (b) for MAC

Error! Reference source not found.5 shows the Langmuir isotherm constants obtained from this study.

Table 5. Langmuir isotherm models of AC and MAC

Isotherm models	AC	MAC
Langmuir:		
q_0	2500	3333
b	3.02x10^{-3}	4.99 x10^{-3}
R_L	0.0367	0.0225
R^2	0.9976	0.9974

As shown in Table 5, the regression coefficient (R^2) was 0.9974 for MAC and 0.9976 for AC, which indicates the monolayer adsorption isotherm can provide a proficient fit for the sorption of crude oil onto the AC. The main concern of Langmuir isotherm is the separation factor (R_L). As mentioned by Nwadiogbu *et al.*, [19] that the sorption is considered irreversible if the R_L = 0, favourable if the value of R_L ranges from 0 to 1, linear if R_L = 1, or unfavourable if the R_L value is more than 1. From the experimental data it was found that the R_L for both AC and MAC are 0.0367 and 0.0225 respectively, which indicates that the sorption of crude oil on both AC and MAC is favourable. Figure 6 shows the Freundlich isotherm for AC and MAC.



(a) (b)

Figure 6. Freundlich isotherm (a) for AC (b) for MAC.

Error! Reference source not found.6 shows the Fruendlich isotherm constants obtained from this study.

Table 6. Fruendlich isotherm models of AC and MAC

Isotherm models	AC	MAC
Freundlich:		
K_F	4.3084x10^{11}	9.7839x10^{9}
$1/n$	2.1722	1.7341
R^2	0.9999	0.9993

The value of the regression coefficient in the Freundlich isotherm for AC and AC was 0.9999 and 0.9993 respectively. This isotherm obtained was higher than Langmuir model. Therefore, the result indicates that Freundlich is the most suitable model for describing the sorption equilibrium of crude oil on AC and MAC [28].

4. Conclusion

The FTIR spectra indicate that the number of pores found on the surface of MAC is higher than AC. The optimum sorbent dosage for both AC and MAC was found to be 0.1 g. Meanwhile for temperature effect, it was found that with higher temperature, oil sorption capacity decreases for both AC and MAC. As for the contact time effect, the maximum oil sorption capacity was recorded on the 8 min of contact time with a result of 27.10 g/g for AC and 32.71 g/g for MAC. For the kinetic study, pseudo-first order was chosen for the best kinetic model to express the sorption of crude oil on MAC as it shows the R^2 value closest to 1. Meanwhile, for the adsorption isotherm, the result indicates that Freundlich is the most suitable model for describing the sorption equilibrium of crude oil on AC and MAC. In this study, the equilibrium data was obtained from the batch test which may not be suitable for the real application. Hence, further study is recommended to simulate the performance of MAC to clean-up crude oil spills from water surface, using Aspen Adsorption® based on data from batch experiments.

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