Oil Spill Remediation by Adsorption Using Two Forms of Activated Carbon in Marine Environment

*Tasnia Hassan Nazifa
Faculty of Civil Engineering
Universiti Teknologi Malaysia
Skudai, Johor, Malaysia
thnazifa@gmail.com

A S M Shanawaz Uddin
Faculty of Civil Engineering
Universiti Teknologi Malaysia
Skudai, Johor, Malaysia
asm.shanawaz@gmail.com

Rashidul Islam
Faculty of Built Environment
Universiti Teknologi Malaysia
Skudai, Johor, Malaysia
mrislam1080@gmail.com

Tony Hadibarata
Faculty of Engineering and Science
Curtin University, CDT 250
Miri, Sarawak, Malaysia
hadibarata@curtin.edu.my

*Salmiati
Centre for Environmental Sustainability and Water Security
Universiti Teknologi Malaysia
Skudai, Johor, Malaysia.
salmiati@utm.my

Azmi Aris
Centre for Environmental Sustainability and Water Security
Universiti Teknologi Malaysia
Skudai, Johor, Malaysia.
azmi.aris@utm.my

***Abstract*: The removal of diesel oil from water by activated carbon and magnetically modified activated carbon (MAC) produced from agricultural waste like banana stem was investigated. Batch adsorption technique was followed by varying pH (2 to 10), adsorbent dosage (0.05 to 1.5 gm), contact time (5 to 70 min) and initial concentration (200 to 4500 mg/L) to obtain optimum parameters. The magnetized activated carbon exhibited a greater removal (97%) compared to non-magnetized activated carbon (83%). FTIR (Fourier transform infrared spectroscopy), FESEM and XRD were used to characterize the adsorbents. Kinetic and isotherm studies were also executed. The experimental result fitted well with Freundlich model ($R^2 = 0.99$) and pseudo second order kinetic model ($R^2 = 0.99$) for MAC.**

***Keywords: Oil spill, Activated carbon, Magnetic activated carbon, Remediation, Diesel*.**

I. INTRODUCTION

Environmental catastrophes like Exxon Valdez (Alaska, 1989), Prestige (Spain, 2002) or Deepwater Horizon by British Petroleum (Gulf of Mexico, 2010) brought to the limelight claiming urgent step to control the deliberate oil release and accidental oil spill onto open waters or ocean. This contamination of oil with water are not only restricted to large scale and well-known spill incidents but also more frequently occurred small-scale oil spills [1]. For example, approximately sixteen oil spill incidents are found to report daily in water routes of the USA [2], more than hundred oil spills have been yearly reported in Nigeria [1]. However, oil pollution in marine environment not only originated from oil tanker collision during transportation but also from run-offs of onshore facilities. According to [3], from 2010 to 2015, oil tanker collision contributed about 235715 barrel of oil contamination into marine environment all over the world. The most recent spill incident recorded in January 6, 2018 in East China sea; spilled approximately 138,000 tonnes of oil due to oil tankers collision. On 2nd October 2016, 105 tonnes of oil spilled in North sea, Shetland, UK. Therefore, the clean-up of oil spills has turned into a global challenge.

After analyzing the consequences of oil spills in the marine environment, it has been found that oil spill incidents cause long duration damages to aquatic ecosystems as well as induces a huge loss [4]. To reduce environmental effect of oil spill rapidly an environment friendly & efficient oil remediation method is remarkably demanded. Conventional techniques for oil spill clean-up comprises of skimming, sorption, bioremediation and in situ burning [3]. Among these mentioned treatments, adsorption process attracted enough consideration because of possessing high surface area, ease and high removal efficiency. Adsorbents sorb pollutant moles by providing a huge surface area for chemical and physical interaction. However, one of the major limitations of using adsorbents for remediation of oil polluted sites are huge capital cost as well as comparatively low efficiency of adsorption and capacity of adsorbent materials.

Carbon based adsorbents are widely used for water pollution treatment. Among different carbon materials, activated carbons are being widely applied as sorption material in the oil pollution treatment [5]. Although graphene, carbon nanotubes, commercial activated carbon can offer a high adsorption uptake, they are much costly to be applied in the oil clean-up process [3]. However, the agricultural waste based activated carbon in this case can demonstrate very cheap, environment friendly bio-material. Compared with many other bio-materials, agricultural waste needs little or sometimes no processing, comfortable to use and plentiful in nature. Based on past research, adsorption that employs activated carbon has achieved the best technique to treat water pollution [6].

Magnetic modification makes it achievable to efficiently separate as well as recover activated carbon by using a simple external magnetic process [7]. Recently preparation and utilization of magnetized activated carbon have been gained more attention. Microporous Fe-Carbon nanocomposite, porous carbon iron oxide nanocomposite from metal organic framework (MOF), ENR-magnetized nanoparticle, magnetic carbon nanotube sponges, epoxidized natural rubber, iron oxide composite from palm shell based activated carbon, exfoliated magnetic graphite, core−shell $Fe_2O_3@C$ nanoparticles had been studied previously for oil removal by magnetic separation. The adsorbents mentioned above such as magnetic polyurethane foam, porous carbon iron oxide nanocomposite from metal organic framework (MOF), Microporous Fe-Carbon nanocomposite, ENR magnetite nanoparticle etc. are effective for oil removal capacity. Nevertheless, the synthesis of these compounds is comparatively complex as well as costly with the low yield.

978-1-5386-4904-6/18/$31.00 ©2018 IEEE

Hence cost effectiveness for a bulk amount generation for real time application is not possible [7, 8].

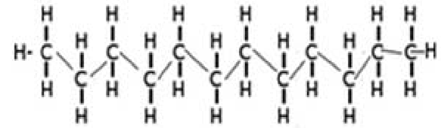
In Malaysia, Banana (*Musa* sp) trees are widely cultivated and claim to be second major fruit after durian. Therefore, banana stems are abundantly grown and contain no well-known commercial or industrial importance, rather creates severe environmental problems. The aim of this research paper is to present the adsorption ability of AC and magnetically modified AC made from agricultural waste like banana stem for the remediation of oil spills in marine environment. The resultant magnetic activated carbon (MAC) and activated carbon (AC) were characterized by FESEM and FTIR. The impact of pH, dosage, time and initial concentration on adsorption uptake and removal rate were also investigated.

II. EXPERIMENTAL SECTION

A. Material and Chemicals

All the chemicals and reagents used in this experiment are maintained AR grade and purchased from QRec, Malaysia. Dry banana leaf stems were procured from university area, Johor, Malaysia. Diesel fuel oil has been brought from BHPetrol station in Johor. Physiochemical characteristics of diesel oil are show in Table I.

TABLE I. PHYSIOCHEMICAL CHARACTERISTICS OF DIESEL OIL

Structure	
Molecular formula	$C_{10}H_{20}$ to $C_{15}H_{28}$
Appearance	Slightly brown viscous liquid
Molecular weight	178.6
Elemental analysis	carbon 85.9% (ww^{-1}), hydrogen 13.1% (ww^{-1}), nitrogen 0.3 % (ww^{-1})
Boiling point	180-360 °C
Aqueous solubility (15 °C)	0.005 g/L
Density	0.87 to 0.96 g/cm^3

B. Activated Carbon (AC) Preparation

Table II summarizes the physio-chemical properties of banana stem used in this study. The raw dry precursors were manually collected, cut into 1-2 inches length and rinsed exhaustively with water to eliminate surface dirt and air dried at 105 ^{0}C in the oven. The dried stems were soaked with 1:1 $ZnCl_2$ solution for one day. The $ZnCl_2$ solution was then drained off and the impregnated banana stems were kept inside an oven to remove moisture before carbonization. A horizontal furnace has been used for carbonization (2.5 L/minute N_2 flow, 400 ^{0}C for 2 hour). The carbonized stems were then ground to fine powder and stored in air tight container.

TABLE II. PROPERTIES OF BANANA LEAF STEM

Property	**Value**
Volatile Matter	89-89
Fixed carbon	0.2-0.3
Ash	8.65-11
Moisture	8.46 - 10.2
Elemental analysis (mf wt.%)	
Carbon	36.83-37.93
Hydrogen	5.19-4.46
Nitrogen	0.93-1.87
Chemical analysis (mf wt.%)	
Lignin	15.07-37.3
Hemi-cellulose	0.77-17.5

C. Magnetically Modified Activated Carbon (MAC)

Magnetized activated carbon was prepared by impregnating prepared AC with magnetic particles [9]. A solution of Fe_{3+}/Fe_{2+} was added in a ratio of 20 g $FeSO_4$ in 150 mL distilled water and 18 g $FeCl_3$ in 1300 mL distilled water solution. These two solutions were vigorously stirred to mix well at 60 ^{0}C. After that AC solution (30-40 g AC in 500 mL distilled water) were slowly poured inside the Fe_{3+}/Fe_{2+} solution and stirred for half an hour for proper mixing. At the end of 30 min, 10 M freshly prepared NaOH solution was added slowly to make the final pH 10-11. At this condition the solution was stopped for further NaOH mixing and aged at 25 ^{0}C for one day. The MAC was then filtered and dried (105 ^{0}C) until all moistures are evaporated. This magnetization procedure is followed because of its simplicity in preparation and cost effectiveness compare to procedure shown by [8], where CNT sponge was magnetized using chemical vapor deposition applying dichlorobenzene and ferrocene as the precursors.

D. Characterization

The surface morphology of AC and MAC has been tested through FESEM. Surface functional groups liable for adsorption has been detected by FTIR in the range of 400 to 4000 cm^{-1}. XRD analysis of MAC was evaluated by Bruker D8 Advance diffraction system for a 2θ angle between 5 ^{0}-90 ^{0}.

E. Adsorption Test

A pre-determined amount of AC or MAC (0.1 g) was added to 100 mL artificially created oil spill of 1000 g/L concentration. The solution was then agitated for 100 rpm for a specific time up to 70 minutes. At pre-determined time, all samples containing solutions were withdrawn from the mechanical shaker and AC solution was filtered using Whatman no1 filter paper. However, solution containing magnetized adsorbents (MAC) were separated by external magnet followed by filtration. The residual oil concentration was calculated by GC-FID (column type HP5, Agilent 7820A, 3.0 ml/min He rate). The temperature of oven was set at 35 ^{0}C, hold for 2 minutes at 35 ^{0}C and then at the rate of 12 ^{0}C/min reached to a temperature of 290 ^{0}C.

The mathematical equation for removal efficiency (%R) and adsorption uptake (qt) of diesel fuel oil are presented as [6]:

$$\% \text{ Removal} = (C_0 - C_f) * 100 / C_0 \quad (1)$$

$$\text{Adsorption capacity, } qt = \frac{(C0 - Cf)}{W} * V \quad (2)$$

Where, C_i and C_f are expressed as initial and final concentration of oil in 'mg/L' before and after adsorption test.

'V' is the volume of working solution in 'L' and amount of adsorbent used is expressed as 'w' (g).

III. RESULTS AND DISCUSSION

A. Characterization

The FTIR spectrum of AC and MAC for identifying the surface chemistry of adsorbents through bond structure are demonstrated in Fig. 1 The strong and broad peak detected at 3434 cm^{-1} and 3454 cm^{-1} belongs to the O-H group of alcohol or phenol. The presence of C=O vibration bands were detected around 1620 cm^{-1} in AC which has been found to shift 1628 cm^{-1} after magnetization in MAC. The peak found between 1210 to 1320 cm^{-1} was ascribed to C-O stretching [10]. A new peak detected over a range of 500 cm^{-1} to 700 cm^{-1} corresponds the iron particles (Fe-O) bonding due to impregnation [7].

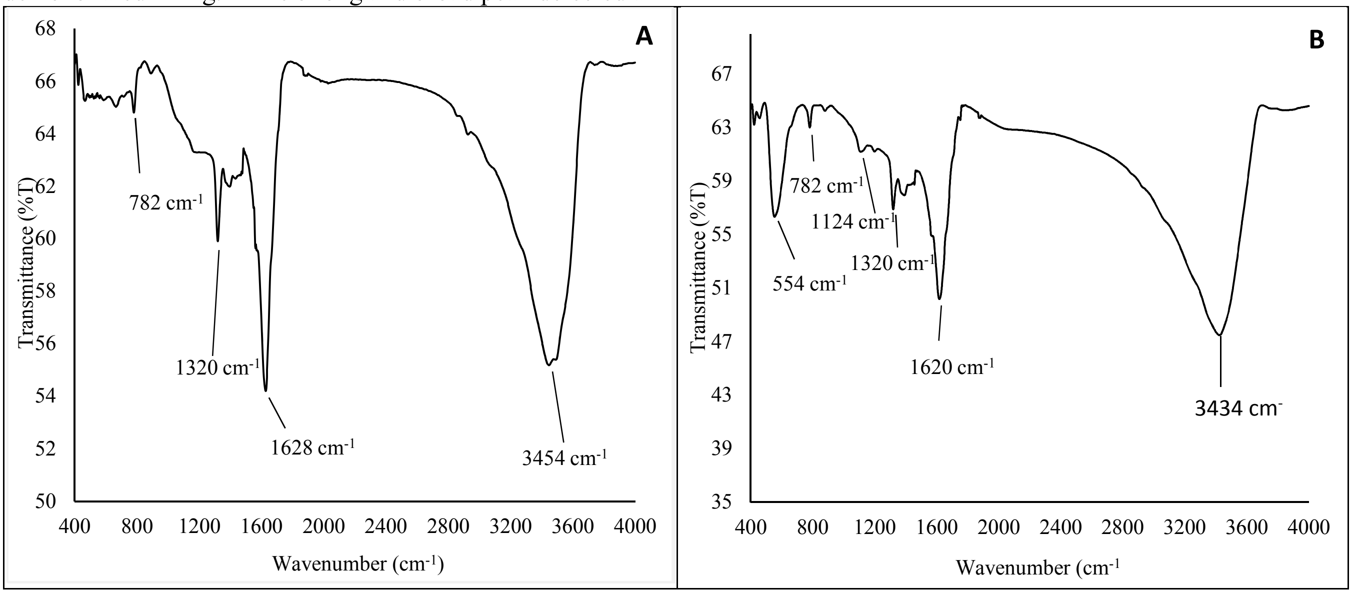


Fig. 1. FTIR spectrum of (A) Banana stem activated carbon (AC), (B) MAC before oil adsorption.

The FESEM photographs of AC and MAC are shown in Fig.2. Visible difference between AC and MAC can be observed through these images. Based on the Fig.2A, banana stem based activated carbon (AC) are well equipped with small pores with a non-organized structural pattern which still contain few original banana stem morphologies. The micropore size dispersions possess average pore diameter ranging from 5 to 10 µm. The porous structure has been developed due to $ZnCl_2$ impregnation and temperature used in the pyrolysis process [11]. A successful deposition of magnetic particles onto activated carbon can be seen on MAC surface in Fig 2B. After iron particle impregnation, AC has been turned into a porous spongy texture which suggests the well dispersed magnetic particles covering AC. Most of the carbon pores seem to contain magnetic particles as reported previously [9].

The XRD patterns shown in Fig. 3 demonstrates many sharp peaks which agrees with the existence of iron oxide. The major peaks were detected at 2Θ = 30.2º, 35.6º, 43.35º, 57.4º, 62.9º illustrate the domain of iron species exist as a crystalline form in our prepared MAC adsorbent. The magnetized phase attributes the formation of Fe_3O_4 (magnetite) and γ-Fe_2O_3 (maghemite). Magnetite or maghemite is commonly used as magnetic particles and difficult to characterize separately by analysis. Both the γ-Fe_2O_3 and Fe_3O_4 may have the same phase in XRD analysis and their properties are also acceptable since both of them have magnetic peak.

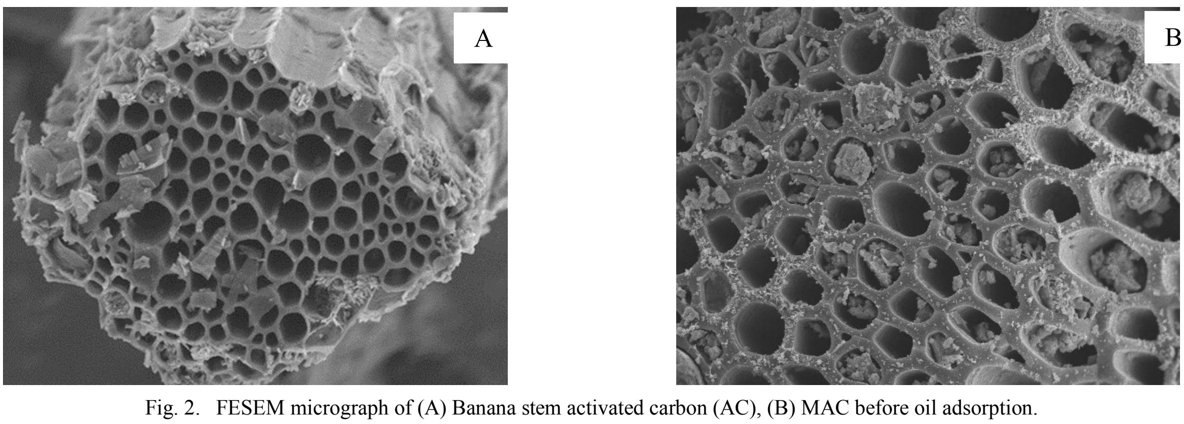


Fig. 2. FESEM micrograph of (A) Banana stem activated carbon (AC), (B) MAC before oil adsorption.

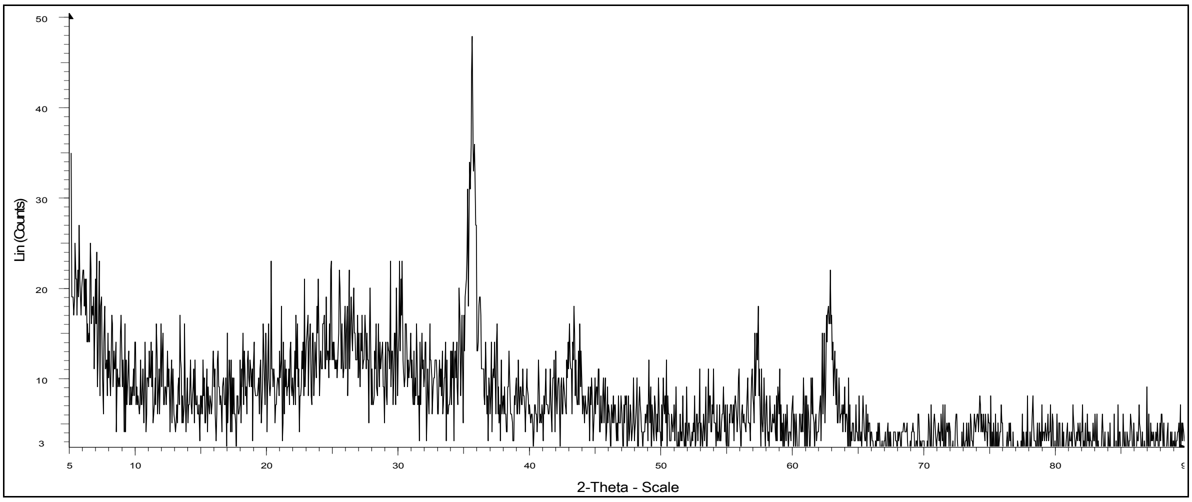


Fig. 3. XRD pattern of MAC

B. *Effect of pH*

The adsorption of diesel oil was explored from pH 2 to pH 10 (Fig. 4). The study on pH effect would determine the value of optimum pH. For MAC, the percentage of removal (%R) increased gradually from low pH but remained approximately constant after pH 6. In case of AC, similar increasing trend has been followed from pH 2 to pH 5. However, the decrease of removal at a higher value of pH could be assigned to lower positive charges on the surface [9].

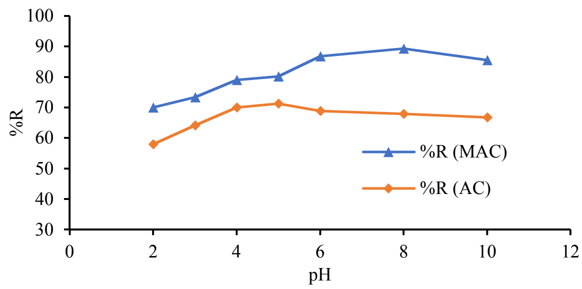


Fig. 4. Effect of pH on adsorption of diesel on AC and MAC (1,000 mg/L diesel oil, 0.1 gm adsorbent, 10 min, 80 rpm)

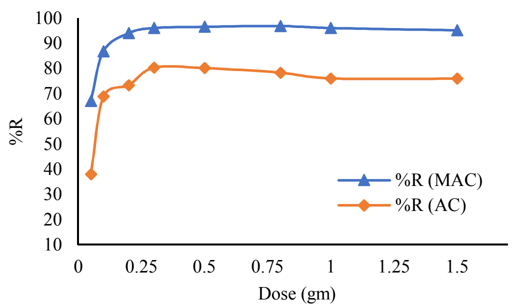


Fig. 5. Effect of adsorbent dose on adsorption of diesel onto MAC and AC (pH 6, 1000 mg/L diesel oil, 80 rpm, 10 min, 25 °C)

C. *Effect of dose*

Artificially created oil contaminated solution was further treated with 8 different doses of adsorbents at 80 rpm and 10 min contact. The initial oil concentration was 1000 mg/L. Fig. 5 shows the percentage of removal towards different AC and MAC dosage. It can be noticed, when the adsorbents dose increased, efficiency of oil adsorption increased. The optimum dosage of AC & MAC was chosen 0.3 g (80% removal) and 0.2 g (94% removal) for further experiments.

D. *Effect of Contact Time*

The impact of time was investigated by varying contact duration and from the experimental results (Fig. 6) the oil removal efficiency reached equilibrium at 30 min for MAC and 40 min for AC. It shows 30 minutes of contact at 80 rpm, MAC could remove 97% of oil from the solution whereas for AC it took 40 minutes to remove 83%. AC requires a longer time of contact compared to MAC. After half an hour of contact, MAC achieved a maximum removal of 97% however, for AC the removal increased when the duration elapsed.

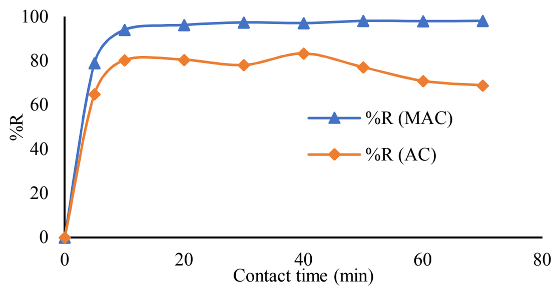


Fig. 6. Effect of time on adsorption of diesel on AC and MAC (pH 6, 1000 mg/L diesel oil, 80 rpm, 0.2 g MAC, 0.3 g AC at 25ºC)

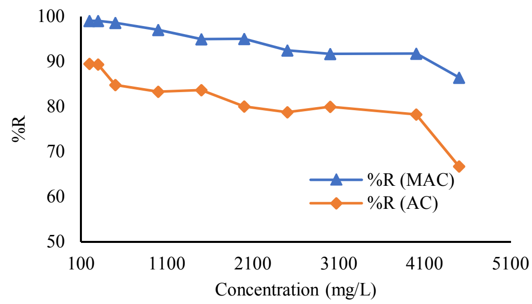


Fig. 7. Effect of concentration on adsorption of diesel on AC and MAC (pH 6, 100 rpm, 0.2 g MAC, 0.3 g AC, 30 min for MAC, 40 min for AC at 25 ºC)

E. Effect of Concentration

A range of concentration starting from 200 mg/L to a final value of 4500 mg/L has been illustrated in Fig. 7, where it clearly depicts that lower initial concentrations (below 500 mg/L) of diesel oil in the solution provides higher removal. Thereafter the removal efficiency drops and maintains a constant value with the further increase of initial oil concentration.

F. Adsorption Isotherm Models

Adsorption isotherm models are important to describe how solutes incorporate with the adsorbents. To identify the appropriate isotherm model for equilibrium, performances at various initial concentrations were assessed using Langmuir and Freundlich models as referred earlier [12].

Freundlich isotherm equation is express as:

$$\ln qe = \ln K_F + (1/n) \ln Ce\ 1/n \quad (3)$$

Langmuir isotherm equation as:

$$Ce/qe = (1/k_L\ qm) + (1/qm)\ Ce \quad (4)$$

TABLE III. LANGMUIR & FREUNDLICH ISOTHERM MODEL CONSTANT & CORRELATION COEFFICIENT

Adsorbent Type	Langmuir isotherm			Freundlich isotherm		
	KL	qm (mg/g)	R^2	Kf	n	R^2
MAC	0.011	2000	0.94	80.6	1.935	0.9914
AC	0.0017	1428	0.9313	7.18	1.397	0.0832

Table III lists all the calculated isotherm results. Freundlich model fits well for AC and MAC under the same range of concentration. Correlation coefficients (R^2) value was 0.9914 and 0.9831 for magnetized activated carbon (MAC) and activated carbon (AC). According to [12], values n>1 represent favourable adsorption state. Table III shows that the value of 'n' is greater than 1 for both adsorbent with1.93 and 1.39, respectively. Banana stem based activated carbon and magnetically modified activated carbon are considered as porous biopolymers; henceforth pores are compatible to let the residual oil (diesel) ions through.

G. Kinetic Studies

Table III (isotherm) affirms that the adsorption of diesel by MAC was faster in compare to AC but the controlling mechanisms were still unclear. Hence, to determine the adsorption controlling mechanism for example chemical reaction and mass transfer, following kinetic models were used to test the obtained experimental data.

Pseudo-first-order Lagergren's equation [7]

$$\text{Log}\ (q_e - q_t) = \log\ (q_e) - \frac{K_1 t}{2.303} \quad (5)$$

Pseudo-second-order Lagergren's equation

$$t/\ q_t = 1/k_2 q_e^2 + t/\ q_e \quad (6)$$

Table IV summarizes calculated result of experimental data for both kinetic isotherm models. The R^2 values (correlation co efficient) for second order kinetic model were found greater than the first order model. Hence, the adsorption of diesel oil was represented by second order equation which designates to chemisorption process as rate limiting stage.

TABLE IV. KINETIC CONSTANT FOR LINEAR KINETIC MODELS OF DIESEL OIL ADSORPTION

Adsorbent Type	Experiment value, q (mg/g)	Pseudo-first-order model			Pseudo-second-order model		
		qe (mg/g)	K_1	R^2	qe (mg/g)	K_2	R^2
MAC	490	160.14	0.1135	0.8017	500	0.0033	0.9998
AC	277	332.43	0.0147	0.4822	263.15	0.0096	0.998

Ahmad et al., [12] reported that the process of chemical adsorption was governed by second-order model. Higher chemisorption can occur onto adsorbents having higher surface area. Therefore, better removal and adsorption is achievable by adsorbents having large surface area. The chemical sorption process occurs between the oil particles and adsorbents through exchange or sharing of electrons. Table V compares the diesel oil removal capacities of adsorbents in this study with other oil sorbents. Based on the results provided in Table V, it can be seen that the magnetic adsorbent as well as activated carbon used in our experiment provides a higher efficiency of removal of oil from water in compare to other previously studied adsorbents. Activated carbon derived from corncob could remove oil less than 25%. Another agricultural waste like palm fibre also demonstrated poor oil removal efficiency and not more than 60%.

TABLE V. COMPARISON OF DIESEL OIL REMOVAL CAPACITIES OF DIFFERENT ADSORBENTS

Adsorbent	**Oil removal**	**Referenc**
Corncob activated carbon	22.82%	[13]
Palm fibres	59%	[14]
Acid treated palm fibre	57-59%	[14]
Alkali treated palm fibre	57-59%	[14]
Banana stem activated carbon	83%	This study
Banana stem magnetized activated	97%	This study

IV. CONCLUDING REMARKS

As a concluding remark of this findings, the diesel oil contaminated water remediation has been successfully performed by applying agricultural waste-based AC and MAC. It illustrates an increment for the efficient oil adsorption from artificially produced diesel oil spill. Experimental results demonstrate that adsorption process depends on dosage, pH, time and initial concentration. The optimum value of pH was 5 for AC and 6 for MAC. 0.2 g of MAC and 0.3 g of AC provided maximum removal percentage at respective equilibrium time. All the isotherm data was fitted by Freundlich equation which concludes AC and MAC both have favourable adsorption characteristics. In addition, kinetic study reveals that both adsorbents follow pseudo second order kinetic model. This model establishes that rate of adsorption of residual oil onto MAC were better in compare to AC. Activated carbon & magnetically modified AC which are made from mass produced agricultural waste would be useful and low cost as a residual oil adsorbent for oil spill treatments.

ACKNOWLEDGEMENT

We are grateful to the AUN/SEED Net collaborative research program for financial assistance.

REFERENCES:

[1] Pinto, J., Athanassiou, A., & Fragouli, D., 2018. Surface modification of polymeric foams for oil spills remediation. Journal of environmental management. 206, 872-889.

[2] Fingas, M., 2012. The basics of oil spill cleanup, Third ed. CRC press, New York.

[3] Xu, C., Jiao, C., Yao, R., Lin, A., & Jiao, W., 2018. Adsorption and regeneration of expanded graphite modified by CTAB-KBr/H 3 PO 4 for marine oil pollution. Environmental Pollution. 233, 194-200.

[4] Lin, M., 2016. Marine environmental protection: A highly efficient method of degradation of heavy oil pollution on coastal beaches. Hydrology Current Research. 7, 1-3.

[5] Yu, C., Li, X.-h., Qiu, J.-s., & Sun, Y.-f., 2007. Removal of sulfur-containing compounds from oil by activated carbon adsorption. Journal of Fuel Chemistry and Technology. 35(1), 121.

[6] Nazifa, T. H., Habba, N., Aris, A., & Hadibarata, T., 2017. Adsorption of Procion Red MX□5B and Crystal Violet Dyes from Aqueous Solution onto Corncob Activated Carbon. Journal of the Chinese Chemical Society.

[7] Raj, K. G., & Joy, P. A. 2015. Coconut shell based activated carbon–iron oxide magnetic nanocomposite for fast and efficient removal of oil spills. Journal of Environmental Chemical Engineering. 3(3), 2068-2075.

[8] Gui, X., Zeng, Z., Lin, Z., Gan, Q., Xiang, R., Zhu, Y.,Tang, Z., 2013. Magnetic and highly recyclable macroporous carbon nanotubes for spilled oil sorption and separation. ACS applied materials & interfaces. 5(12), 5845-5850.

[9] Mohan, D., Sarswat, A., Singh, V. K., Alexandre-Franco, M., & Pittman, C. U., 2011. Development of magnetic activated carbon from almond shells for trinitrophenol removal from water. Chemical Engineering Journal. 172(2), 1111-1125.

[10] Wirasnita, R., Hadibarata, T., Yusoff, A. R. M., & Lazim, Z. M., 2015. Preparation and characterization of activated carbon from oil palm empty fruit bunch wastes using zinc chloride. Jurnal Teknologi. 74(11), 77-81.

[11] Rahmat, N. A., Ali, A. A., Hussain, N., Muhamad, M. S., Kristanti, R. A., & Hadibarata, T., 2016. Removal of Remazol Brilliant Blue R from Aqueous Solution by Adsorption Using Pineapple Leaf Powder and Lime Peel Powder. Water, Air, & Soil Pollution. 227(4), 105.

[12] Ahmad, A., Sumathi, S., & Hameed, B., 2005. Adsorption of residue oil from palm oil mill effluent using powder and flake chitosan: equilibrium and kinetic studies. Water Research. 39(12), 2483-2494.

[13] Maulion, R. V., Abacan, S. A., Allorde, G. G., & Umali, M., 2015. Oil Spill Adsorption Capacity of Activated Carbon Tablets from Corncobs in Simulated Oil-Water Mixture. Asia Pacific Journal of Multidisciplinary Research. 3(5), 146-151.

[14] Abdelwahab, O., Nasr, S. M., & Thabet, W. M., 2017. Palm fibers and modified palm fibers adsorbents for different oils. Alexandria Engineering Journal. 56, 04.