

**COMPARATIVE STUDY OF THE ADSORPTION OF CRUDE OIL FROM SURFACE
WATER USING ESTERIFIED RICE HUSK AND SAW DUST**

ABSTRACT

The comparative adsorption of crude oil from water surface using sawdust and rice husk absorbents was carried out. The sawdust and rice husk were carbonized and further modified with stearic acid. The prepared adsorbents were characterized using Scanning electron microscopy (SEM), Fourier Transform Infra-red (FTIR) Spectroscopy, proximate and physiochemical analysis. Batch experiments were carried out to investigate the effects of the initial oil concentration, the dosage of the adsorbents, temperature, pH and contact time on the adsorption capacities of the adsorbents and percentage sorption of the crude oil. The characterization results obtained showed that the surface modification through carbonization and stearic acid activation improved the physiochemical properties of sawdust and rice husk respectively. The FTIR results revealed that the biomass samples have numerous functional groups and the major functional groups present are O-H, N-H, N-CH₃, C=C-C, C-Cl, Si-O-Si. The SEM results also showed that carbonization and stearic acid activation of the saw dust and rice husk were able to effect surface modification of the prepared adsorbents by the removal of volatile matters; improvement of porosity hence the improvement of their surface areas respectively. The process parameters investigated were found to influence the adsorption capacity of the absorbents respectively and subsequently the percentage sorption of the crude oil. Meanwhile, the results of the percentage sorption of sawdust and rice husk samples, based on the average weight of oil adsorbed; show 96.577% and 67.327% as their respective adsorption efficiency. Hence, the comparative adsorption efficiency of the carbonized and esterified saw dust and rice husk absorbents, showed that esterified saw dust adsorbent performed better than the esterified rice husk adsorbent.

Keywords: Percentage adsorption; adsorption capacity, crude oil, saw dust, rice husk.

1. INTRODUCTION

Over years, crude oil spill and its alarming pollution have been in front burner in environmental issues over the world and in particular the oil rich Niger Delta of Nigeria [1]. One of the main

sources of water pollution is crude oil spill. Oil and petroleum products such as diesel, gasoline, kerosene etc., can pollute sources of water such as seas, oceans, rivers, or underground waters. Oil spills over the oceans and seas require prompt attentions due to their environmental and economic impacts [2, 3]. Crude oil has become one of the most frequently detected underground and surface water pollutants caused by leakages from underground storage tanks, pipelines vandalization, petroleum products trucks accidents and other components of crude oil distribution systems [1, 4]. In view of the aforementioned, there has been a growing concern regarding the treatment of contaminated water and wastewater in recent years. Generally, the conventional method of water and wastewater treatment technologies including flocculation, ultrafiltration, biological treatment and coagulation [5 - 8] do not seem to be economically viable[1].

Effective decontamination and clean-up are necessary after a spill for the protection of the environment and human health. Sorption techniques are one of the most effective approaches for the treatment of oil spills [9]. Among the various sorbents that have been employed for oil spill remediation, synthetic materials, such as polypropylene and polyurethanes are the most commonly used commercial sorbents due to their oleophilic and hydrophobic properties [9, 10]. However, these materials are not biodegradable, which is a major disadvantage. Landfill disposal is environmentally undesirable, and incineration is expensive [11, 12]. Therefore, there is a renewed interest in natural sorbents and a wide variety of organic vegetable products, such as rice straw, peat moss, wood, cotton, which have been employed as sorbents in oil spill clean-up [9,11,12].

Rice husk and saw dust are agro-waste and lumber industry waste respectively found abundantly in Enugu and Ebonyi States, Nigeria. Due to their abundance and easy accessibility, these materials can be used as cheap adsorbents for crude oil sorption in aqueous medium. Some authors have carried out studies on the suitability and effectiveness of agrowaste adsorbents for crude oil and petroleum products contaminated water adsorption. Banerjee et al.[13], reported the treatment of oil spill by sorption technique using fatty acid (oleic acid, stearic acid and decanoic acid), Angelova et al. [14], studied the kinetics of oil and oil products adsorption by carbonized rice husk; and Robabeh et al.[15], studied the acetylation (acetic acid modification) of corn silk and its application for oil sorption.

Although, Onoh et al. [16] studied the kinetics, isotherm and thermodynamics of adsorption of crude oil from surface water using rice husk and saw dust, the work did not compare the adsorbents capacities. This work therefore, aims at comparing the performance of the carbonized-cum-esterified rice husk and saw dust adsorbents for the adsorption of crude oil from surface water.

2.0 MATERIALS AND METHODS

2.1 Materials

The materials used for this work include rice husk (RH), saw dust (SD), crude oil, distilled water, sulphuric acid (H_2SO_4), hydrochloric acid (HCl), stearic acid, sieving net, n-hexane. The rice husk and saw dust were washed with water to remove unwanted materials and oven dried at 110°C for 2hrs. The dried rice husk and saw dust were carbonized in a muffle furnace at 600°C for 8 hours respectively. After the carbonization, the samples were cooled and stored in dry transparent containers for further use [14].

2.2 Methods

Modification of the carbonized samples by esterification

2.0g of carbonized rice husk and sawdust were treated differently with 0.4g of fatty acid (stearic acid) in 200 ml of n-hexane containing two drops of concentrated H_2SO_4 as catalyst. The mixture was refluxed in dean stark apparatus at $65 \pm 2^\circ\text{C}$ for 4 hrs. After reaction, the esterified acid-grafted sawdust and rice husk were washed severally with n- hexane. The stearic acid grafted sawdust and rice husk were dried in an oven at 110°C for 2hrs respectively [13]. They were then kept in dry tightly closed bottles respectively.

Surface Morphological Studies

The surface morphology of the rice husk (raw and modified) and saw dust (raw and modified) was studied using Carl Zeiss Sigma Field Emission Scanning Electron Microscope and the images at 1mm and 150 magnifications.

Batch Adsorption Experiment

The isotherm study was carried out in batch experiments. Five sets of constant initial concentration of 20g/l of crude oil-water mixture were prepared. Onto the floating crude oil, different weights of adsorbents of 0.2g, 0.4g, 0.6g, 0.8g and 1.0g were added and filtered after 60 minutes at ambient temperature and constant pH of 7 with a sieving net, they were air dried overnight and weighed. This process was repeated for the two adsorbents by increasing their concentration progressively from 10 g/l to 50 g/l. The experiments were also carried out at varied time intervals of 20 minutes to 100 minutes; at varied temperatures of 30°C, 40°C, 60°C, 80°C and 100°C, and varied pH of 2, 4, 6, 8 and 10.

$$\% \text{ removal} = \frac{C_o - C_e}{C_o} \times 100 \quad 2.1$$

$$q_e = \frac{C_o - C_e}{M} V \quad 2.2$$

Where q_e is adsorption capacity, C_o is initial crude oil concentration in g/l, C_e is the equilibrium concentration, V is the volume of the adsorption mixture, and M is the mass of the adsorbent.

2.3 Effect of Process Parameters on Crude oil Adsorption

A. The Effect of Time

The effect of time on the adsorption of crude oil from surface water using the carbonized and esterified rice husk and sawdust respectively were investigated. Five sets of initial concentration of 20g/l of crude oil-water mixture were prepared. Onto the floating crude oil, a constant weight of 0.4g of sawdust and rice husk adsorbent were added respectively at a varied time interval of 20 minutes, 40 minutes, 60 minutes, 80 minutes and 100 minutes at a pH of 7 and ambient temperature.

B. The Effect of Temperature

The effect of temperature was investigated by keeping constant the initial crude oil-water concentration at 20g/l, time at 60 minutes, pH at 7, and constant adsorbent dosage of 0.4g at varied temperatures of 30°C (room temperature), 40°C, 60°C, 80°C and 100°C respectively. After which they were filtered and air dried overnight and weighed.

C. The Effect of Adsorbents Dosage

The dosage effect on the adsorption capacity, q_e of the adsorbents and their respective crude oil percentage sorption were carried out at varying dosage of 0.2g 0.4g 0.6g, 0.8g and 1.0g of the carbonized-esterified sawdust and rice husk respectively, at constant initial concentration of 20g/l of crude oil-water mixture, 60 minutes time, pH 7, and ambient temperature.

D. The Effect of pH

The effect of pH on the adsorption capacity and the percentage sorption of crude oil using a 0.4g constant dosage of carbonized and esterified rice husk and sawdust respectively. The pH was varied from 2, 4, 6, 8, and 10 while other process parameters were kept constant at 20g/l crude oil-water mixture, 60 minutes time and ambient temperature.

E. The Effect of the Initial Concentration of Crude oil

The effect of the initial concentration was investigated by increasing the concentration of the crude oil/water progressively from 10g/l, 20g/l, 30g/l, 40g/l and 50g/l at constant time of 60 minutes, pH of 7, dosage of 0.4g of carbonized-esterified rice husk and sawdust respectively, and ambient temperature. After which, they were filtered with sieving net and air dried overnight, weighed and adsorption capacity and percentage sorption calculated.

3.0 Results and Discussion

3.1 Characterization Studies

Table 1: Proximate analysis of rice husk and saw dust [16].

Adsorbents/ Parameters	Rice husk (RH)			Saw dust (SD)		
	Raw	Carbonized	Esterified	Raw	Carbonized	Esterified
Fixed carbon (%)	10	50.3	70.38	9.9	53.37	56.6
Ash content (%)	6	4.83	3.52	2.2	4.83	2.97
Surface area (cm ² /g)	769	801	820.1	778	900.34	935
Bulk density (g/cm ²)	0.43	0.87	0.44	0.41	0.52	0.52
Iodine number (mg/g)	588	714	733.42	573	727.16	739
Moisture content (%)	7	1.82	2.75	37	2.41	2.46
Volatile content	50.9	43	31	77	38	38

Fourier Transformed infrared spectroscopy (FTIR)

Fourier transform infrared spectra of the raw biomass (saw dusts and rice husk), carbonized biomass (saw dust and rice husk) and stearic acid modified biomass (saw dust and rice husk) are presented in Tables 2 and 3 below. From the table, it was observed that the biomass samples have numerous functional groups and the major functional groups present are O-H, N-H, N-CH₃, C=C-C, C-Cl, Si-O-Si. It was also observed that after carbonization of rice husk and saw dust respectively; some of the functional groups were devolatilized while some were identified. Stearic acid modified saw dust has better modification with removal of the volatile matters.

Table 2: FTIR of Saw dust sample

Raw Saw dust	Carbonized Saw dust	Assignment	Stearic acid modified saw dust
Frequency (cm ⁻¹)	Frequency (cm ⁻¹)	Assignment	Frequency (cm ⁻¹)
	3712.4	O-H stretch	-
3570.8	35690.4	Hydroxyl group, H-bonded, O-H stretch	-
3183.1	3131.0	NH stretch	-
2765.7-2974.4	-	Aliphatic secondary amine, NH stretch	-
-	-	Normal "polymeric" OH stretch	3231.6
	-	Methylamino, N-CH ₃ , C-H stretch	2918.5
	2243.993-2493.429	Isocyanate (-N=C=O asym. Stretch)	-
2113.4	-	Cynaide ion, thiocyanate ion and related ions	2109.7
1982.9	-	Isothiocyanate (-NCS)	-
	1630.697-1871.593	Conjugated ketone, open-chain acid anhydride	1625.1
1565.5	1561.8	C=C-C Aromatic ring stretch	-
1401.5-1457.4	-	O-H bend	-
1330.7	1375.4	N-O asymmetric stretch	-
1244.9-1289.7		Aromatics phosphates (P-O-C stretch)	-
1028.7-1088.4	1067.259	Aromatic C-H in plane bend, Silicon -oxy compounds, Si-O-Si	1036.2
849.8-916.9	872.2	Peroxides, C-O-O- stretch	-
782.7	-	C-Cl stretch, Alkyne C-H bend	782.7
678.4	-	C-Cl stretch, Alkyne C-H bend	-

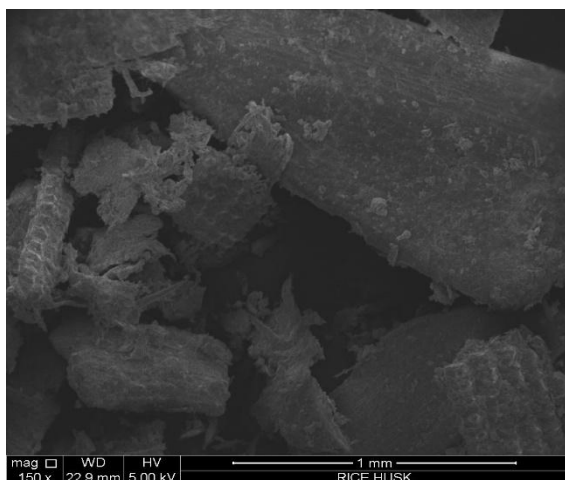
Table 3: FTIR of Rice husk sample

Raw Rice husk	Carbonized Rice husk	Assignment	Stearic acid modified rice husk
Frequency (cm ⁻¹)	Frequency (cm ⁻¹)	Assignment	-
-	3630.4	O-H stretch	-
-	3587.1	Hydroxyl group, H-bonded, O-H stretch	-
3388.2	3313.6	NH stretch	-
-	-	Aliphatic secondary amine, NH stretch	3160.8
3049	-	Normal "polymeric" OH stretch	-
-	-	Methylamino, N-CH ₃ , C-H stretch	2847.7-2918.5
2288.6	-	Isocyanate (-N=C=O asym. Stretch)	2322.1-2366.9
2094.6-2206.6	2113.4-2173.0	Cynaide ion, thiocyanate ion and related ions	2079.9
1904.7-1979.2	-	Aromatic combination	1990.4
1718.3-1804	-	Isothiocyanate (-NCS)	1804.0-1871.1
1617.7-1617.7	1630.697-1871.593	Conjugated ketone, open-chain acid anhydride	1684.8
1513.3-1576.7	1580.4	C=C-C Aromatic ring stretch	1561.8
1423.8	1423.8	O-H bend	-
-	1364.2	N-O asymmetric stretch	-
1103.3-1144.3	-	Aromatic C-H in plane bend	-
1047.4	1067.259	Aromatic C-H in plane bend,	1099.6
861	-	Peroxides, C-O-O- stretch	872.2
726.8-782.7	793.9	C-Cl stretch, Alkyne C-H bend	786.5
-	-	C-Cl stretch, Alkyne C-H bend	674.6

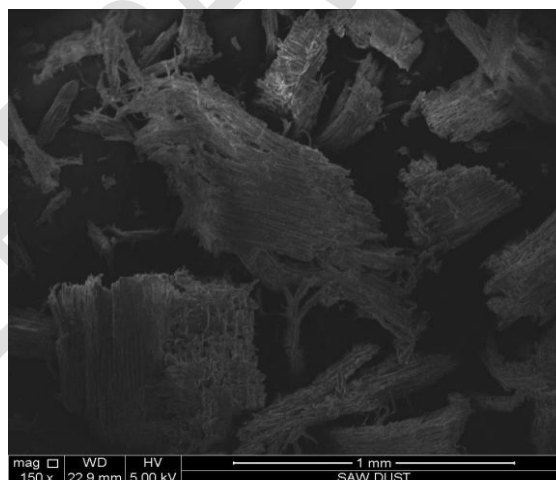
Morphology Analysis of the Adsorbents

The amount and rate of adsorption of oil into an adsorbent can be dependent on the chemical property of the adsorbent, the molecular arrangement, and the physical configuration of the adsorbent such as porosity, crimp, hollow lumen, twist and surface roughness. The oleophilicity and surface energy of the adsorbent depend on the chemical property and the surface wax [15]. The surface morphologies of the raw biomass (saw dusts and rice husk), carbonized biomass (saw dust and rice husk) and carbonized-cum-stearic acid modified biomass (saw dust and rice husk) are presented in Figures 1, 2 and 3.

Figures 2 and 3 below showed that carbonization and further surface modification of the biomass (saw dust and rice husk) with stearic acid were able to devolatilize the prepared adsorbents and improved their porosity hence increased their adsorption and retention surface areas respectively.

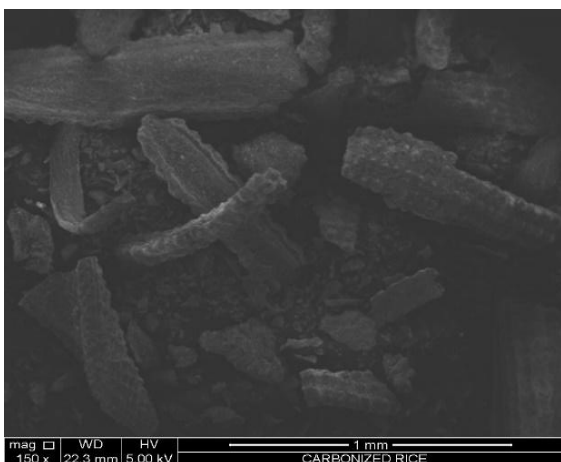


(a) Rice husk

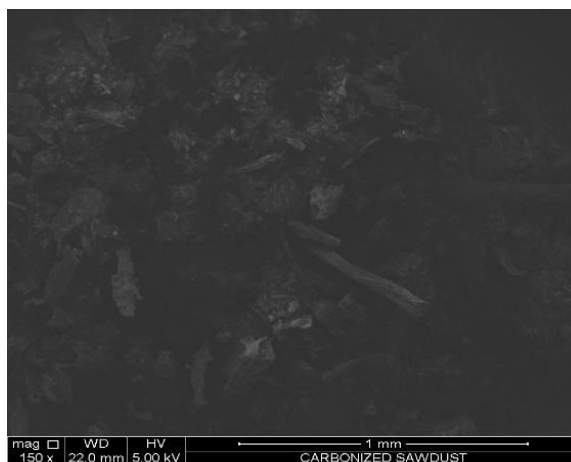


(b) Saw dust

Figure 1: Raw rice husk and saw dust

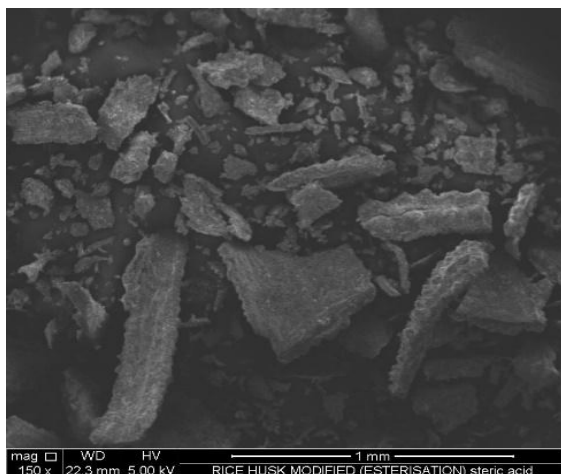


(a) Rice husk

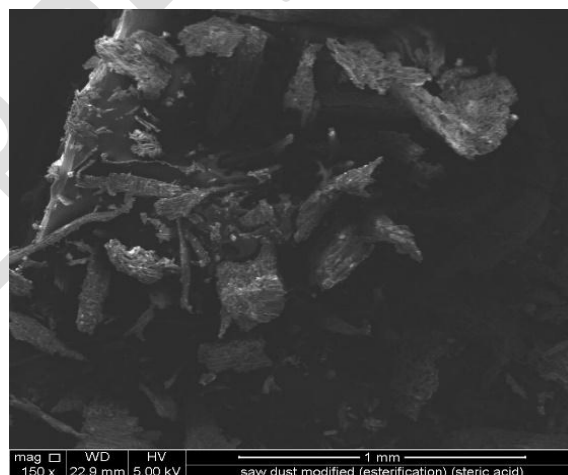


(b) Saw dust

Figure 2: Carbonized rice husk and saw dust



(a) Rice husk



(b) Saw dust

Figure 3: Stearic acid modified rice husk and saw dust

3.2 Effect of Process Parameters on Adsorption of Crude Oil

A. Effect of Time

The effect of contact time on both the adsorbents adsorption capacity and crude oil percentage sorption followed same trend as can be seen in Figures 4 and 5 respectively. Increase in contact time had a linear relationship with both adsorption capacity of the adsorbents and crude oil percentage sorption up till 80 minutes of adsorption experiments. Thereafter, the adsorption capacity and percentage sorption of crude oil remained almost constant with sawdust adsorbent,

while with rice husk adsorbent, the adsorption capacity and crude oil percentage sorption decreased infinitesimally. The constant adsorption capacity and percentage sorption for both adsorbent respectively after 80 minutes could be due to saturation of the pore spaces or limited availability of surface area or reduced oil entrapment [17]. It can be seen from the Figures 4 and 5 that the crude oil sorption using saw dust gave more adsorption capacity and percentage sorption than rice husk. This study reported a maximum uptake of crude oil at 80 minutes for both adsorbents respectively; this is in agreement with the observations of Hussien et al., [18] who studied the adsorption of crude oil using barley straw as an adsorbent.

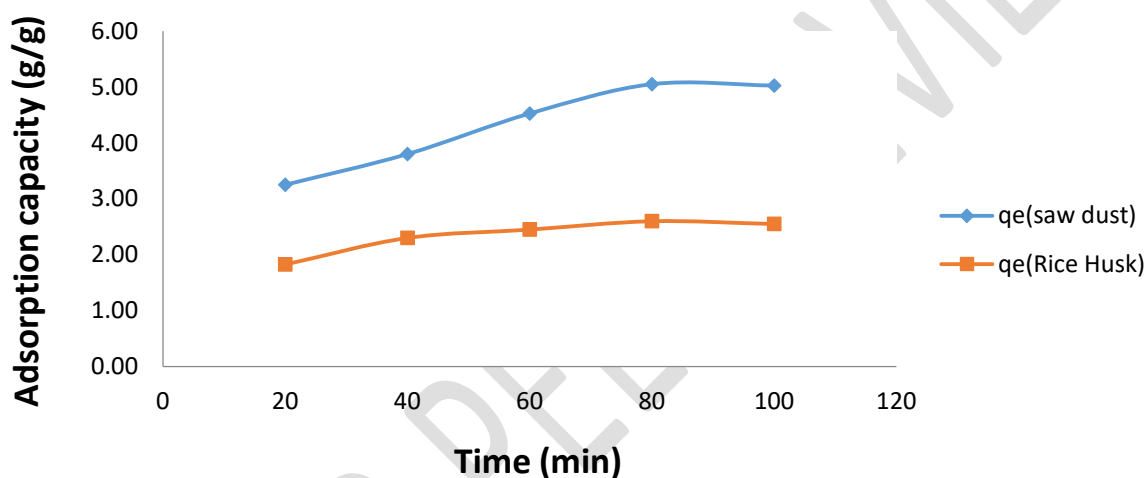


Figure 4: The effect of time on adsorption capacity

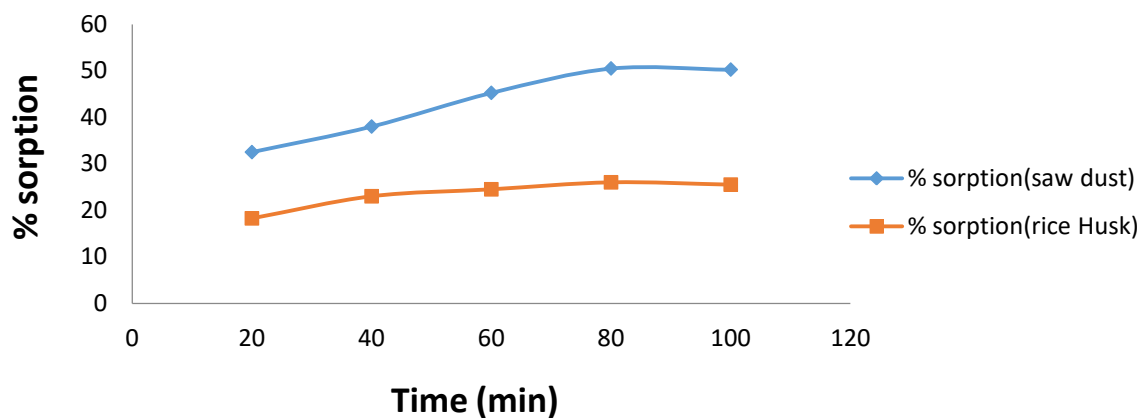


Figure 5: The effect of time on percentage sorption

B. Effect of Temperature

Temperature had similar effect on adsorption capacity of the saw dust and rice husk adsorbent respectively and percentage sorption of crude oil from surface water as can be seen in Figures 6 and 7 Adsorption capacities of the adsorbents and crude oil percentage sorption increased steadily with temperature up till 60°C and 80°C for saw dust and rice husk adsorbents respectively, and thereafter remained almost constant. It can be inferred that temperature was an important factor in the sorption process. At low temperature the adsorption capacity and percentage sorption were low. Moderate temperature should therefore be adopted as this would give the same or higher result than high temperature adsorption experiments. This is in consonance with the observation of Kudaybergenov et al., [19], adsorption capacity of the adsorbents increased as the temperature increased. Kudaybergenov et al., [19] suggested that such observation could be due to decrease in oil viscosity at higher temperature enabling penetration of oil into the pores of the adsorbent and retained between the surface roughness at temperature 60°C.

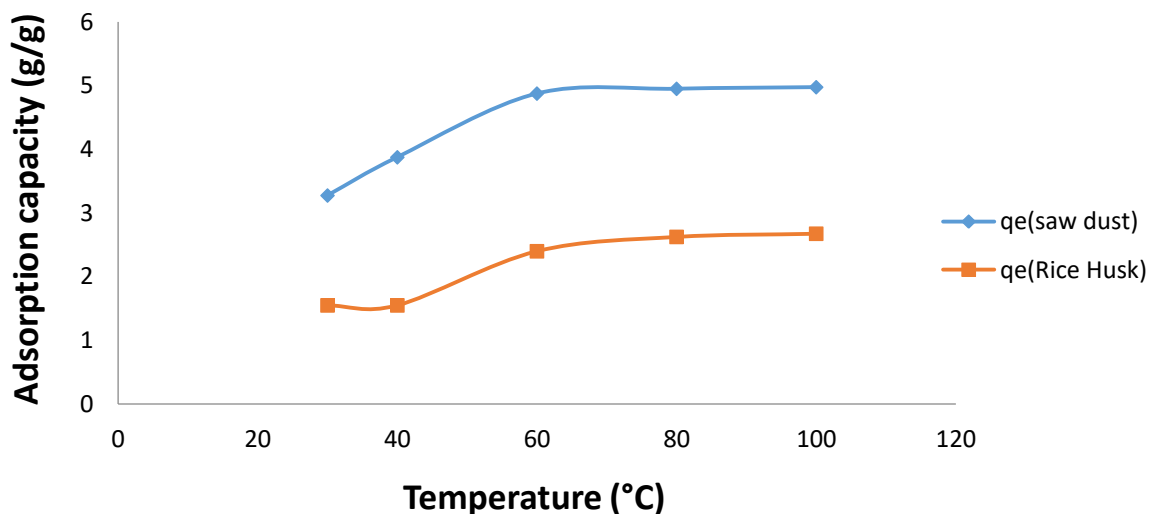


Figure 6: The effect of temperature on adsorption capacity

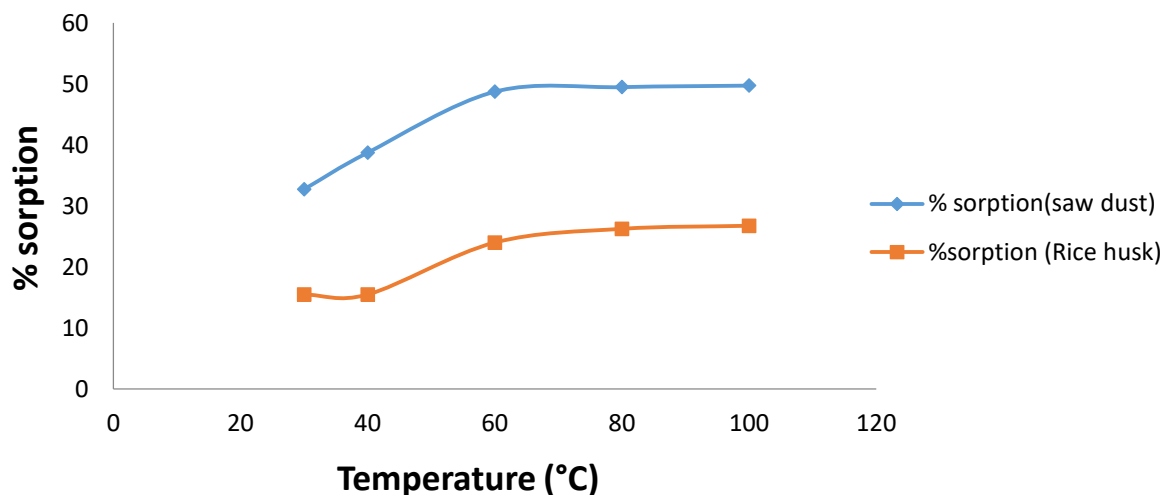


Figure 7: The effect of temperature on percentage sorption

C. Effect of Adsorbent Dosage

The effect of dosage on adsorption capacity and percentage sorption are shown in Figures 8 and 9 respectively. At low dosage, the adsorption capacity was high because of the modification but the percentage sorption of crude oil was low. The adsorption capacity of saw dust was significantly affected by dosage unlike the rice husk that shows less variation of adsorption capacity with variation in dosage. The adsorption capacity of saw dust showed inverse relationship with dosage, this could be due to increase of unsaturated oil binding site. This observation was in agreement with the report of Ibrahim et al., [20] who studied removal of emulsified oil from oily waste water using agricultural waste (barley straw). The percentage sorptions of crude oil with saw dust and rice husk respectively increased as the adsorbent dosage increased. This can be inferred to the availability of binding sites for adsorption. Based on experiment, it was also observed that 1g of sawdust adsorbent left no film of oil in the beaker, while rice husk adsorbent left a small film of the oil, but not completely cleared. This is to affirm that esterified saw dust adsorbent has a larger surface area more than the esterified rice husk adsorbent. The results were also in agreement with the results obtained by Hasanzadeh & Mazandaran, [21]. Hussien et al., [18] result showed increase in adsorption capacity of the adsorbents which differed from the result obtained in this study.

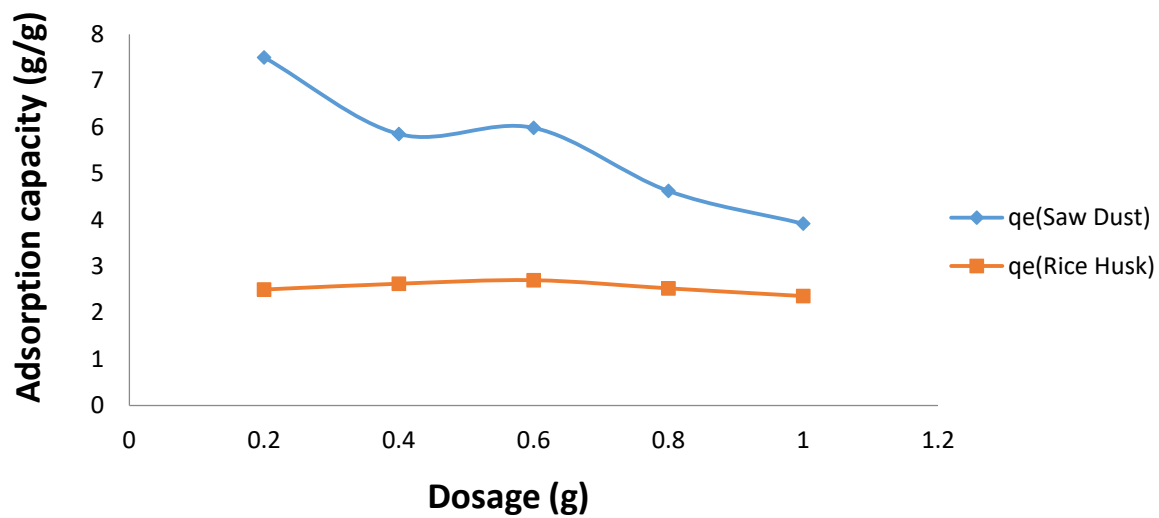


Figure 8: The effect of adsorbent dosage on adsorption capacity

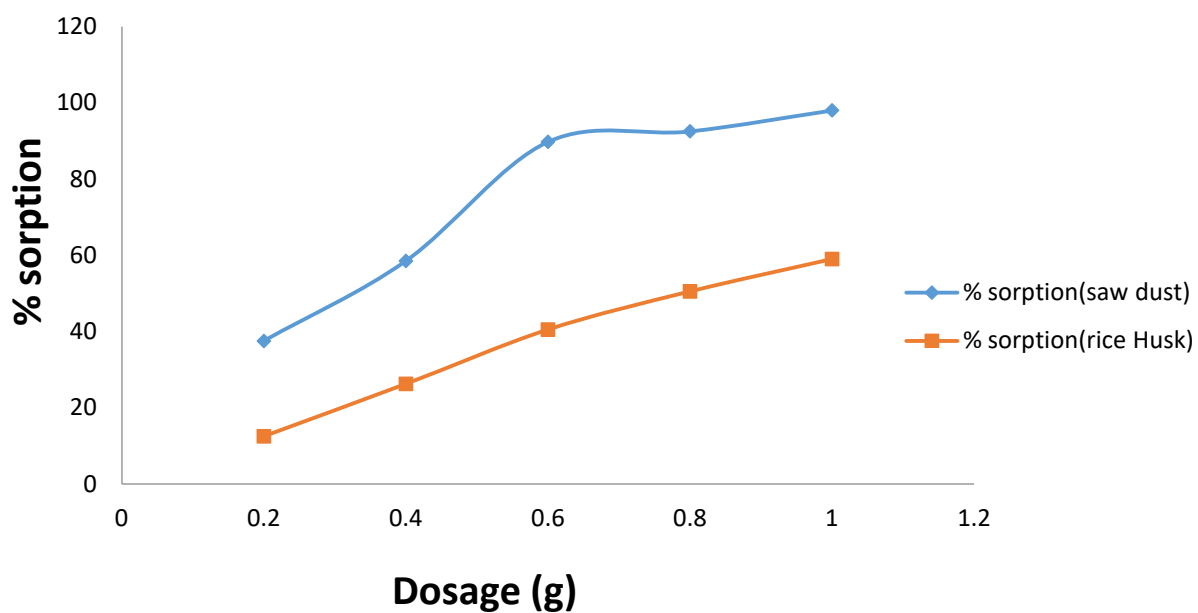


Figure 9: The effect of dosage on percentage sorption

D. Effect of pH

The effect of pH on adsorption capacity of the adsorbents respectively and crude oil percentage sorption are shown in Figures 10 and 11. The pH effect for both the adsorption capacity of the respective adsorbents and crude oil percentage sorption followed same trend. It observed that the highest adsorption capacity or percentage sorption were obtained at pH between 3 and 4, this inferred that acidic condition encouraged interaction between oil molecules and $-NH_2$ functional group in sorbents [17]. The lowest adsorbents adsorption capacity and percentage sorption were observed at pH 6 and 7. This showed that the sorption experiment was favored at mild acidic and alkaline regions. The adsorption capacity and percentage sorption declined towards the extreme alkaline region respectively. This observation could be related to saponification process whereby hydrolysis of oil in sobate occur, also it is in consonance with the report of Ahmad et al., [22], who studied the adsorption of residue oil from palm oil mill effluent using powder and flake chisotan.

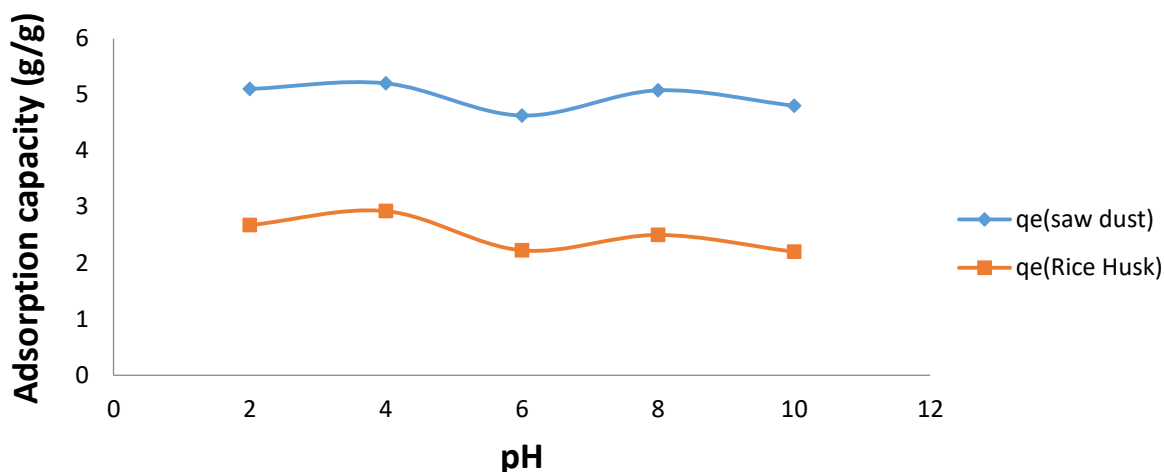


Figure 10: The effect of pH on adsorption capacity

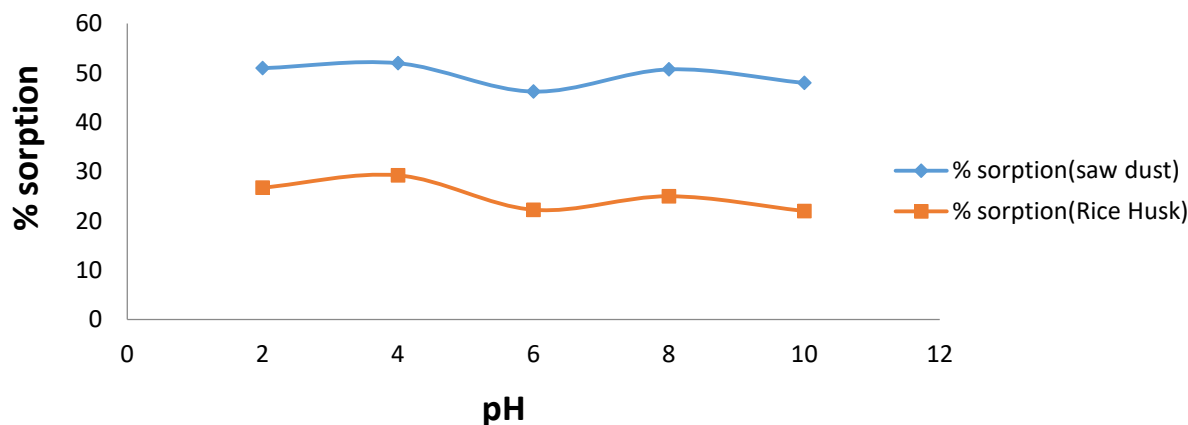


Figure 11: The effect of pH on percentage sorption

E. Effect of Initial Concentration of Crude oil

The effect of initial crude oil concentration on the adsorption capacities was different for saw dust and rice husk adsorbents respectively as can be seen in Figure 12. For saw dust adsorbent, there was an exponential increase in adsorption capacity between 10g/L to 20g/L after which the adsorption capacity decreased and became almost constant. This could be inferred to be the region of monolayer adsorption after which the adsorbent became saturated and the adsorption capacity dropped. With the rice husk, the adsorption capacity decreased at low crude oil concentration and increased after 30g/L to about 2.9g/g and remained almost constant thereafter. The effect of initial crude oil concentration on percentage sorption for both adsorbents followed the same trend (Figure 13). There was decrease in percentage sorption as the crude oil concentration increases. This could be that the available porous sites of 0.4g of the respective adsorbents used for adsorption experiments were becoming saturated with increase in crude oil concentration. This observation was in agreement with Ahmad et al., [22] who studied residual oil and suspended solid removal using natural adsorbents chitosan, bentonite and activated carbon. However, the crude oil percentage sorption with sawdust was higher than that of the rice husk adsorbent.

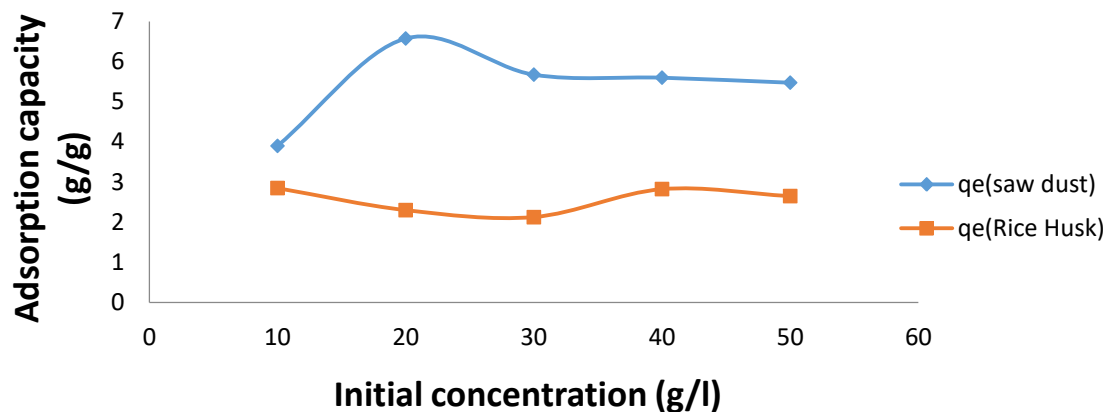


Fig. 12: The effect of initial oil concentration on adsorption capacity

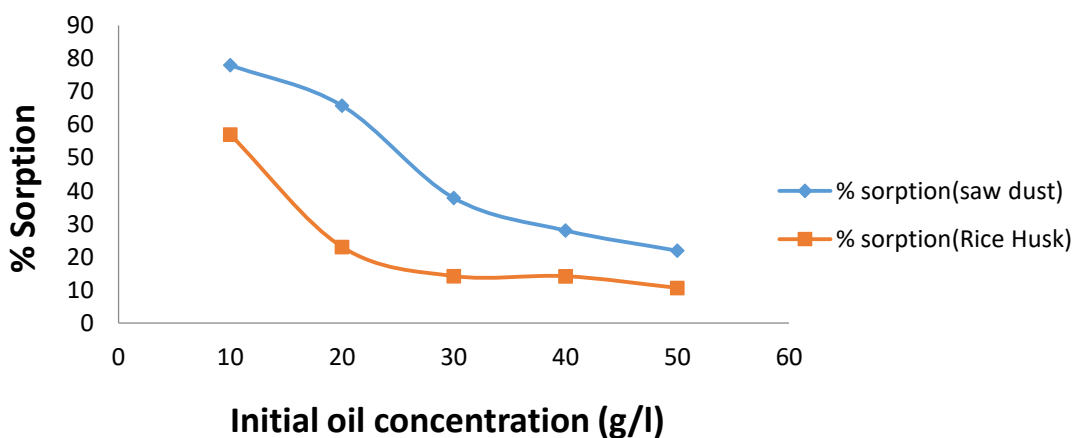


Fig. 13: The effect of initial oil concentration on percentage sorption

3.3 Comparative study of adsorbents modified

The results of the comparative study carried out on the two adsorbents are shown in Table 4. The experiments were carried out in duplicates and the oil adsorbed together with the weight of the nets was reported as final weight 1 and 2. The mean values were taken and the percentage sorption based on the average weight of oil adsorbed was reported. From Table 4, it was observed that surface modified sawdust (SD) absorbent gave higher percentage sorption of the crude oil from the surface water than surface modified rice husk (RH) absorbent. This is in line

with the work of Onoh et al[16] who reported a better kinetic findings with saw dust than rice husk.

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Table 4: Comparative Percentage Sorption of Crude oil

Adsorbent	Water (L)	Oil (g)	Dosage (g)	Final weight (W₁)	Final weight (W₂)	Average % sorption
Carbonized RH	0.2	3.36	0.98	3.93	3.86	64.900
Esterified RH	0.2	3.36	0.98	4.91	4.30	67.327
Carbonized SD	0.2	3.36	0.98	5.16	5.15	94.494
Esterified SD	0.2	3.36	0.98	5.18	5.27	96.577

4. Conclusion

The results of this study showed that both carbonized and carbonized-cum-stearic acid modified form of sawdust and rice husk can be used as economic, effective and eco-friendly adsorbents for maximum removal of crude oil from water surface. This also inferred that sorption behavior of esterified sawdust was greatly enhanced by its modification with fatty acid (stearic acid). Also, comparing the adsorption efficiencies of the adsorbents, esterified saw dust adsorbent performed better than the esterified rice husk adsorbent.

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