

## **Synthesis and Characterization of epoxidized natural rubber-chitosan (ENR-C 2h) for oil spillage sorption.**

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### **Abstract**

Pollution of marine ecosystem and land through the release of liquid petroleum hydrocarbon by accidental spillage remains one of the most significant issues to environmental researchers. In this study, chitosan from land snail shell, a biodegradable agricultural waste and epoxidized natural rubber (ENR) were synthesized. The two were compounded and used in the study of sorption of petrol and crude oil. The equilibrium isotherm data of epoxidized natural rubber-chitosan (ENR-C 2h) was also analyzed using the Langmuir, Temkin isotherms. The regression coefficients ( $R^2$ ) of Langmuir isotherm model was observed to be the highest in the experimental data. The maximum monolayer coverage ( $Q_m$ ) determined from Langmuir isotherm model was 0.8425 and the separator factor was 0.3417, thus confirming a favourable sorption. The sorbent used in this study showed a good sorption capacity while the ENR-C 2h was found to be a potential treatment for oil spills.

### **Introduction**

Crude oil is one of the major sources of energy in the world, with its refined products used in many industries. When there is a spillage of oil in water or land, the physical and chemical properties of the oil gradually change. There is a risk for spillage with the potential to cause significant environmental impact when the explored,

transported and stored oil are used with its derivative [1]. The spilled oil gives an undesirable taste and odour to drinking water and causes severe environmental damage, thus contaminated water by oil cannot be used as a municipal water supply in industry or irrigation [1, 2]. The techniques that are most extensively adopted to clean up oil spills are: chemical treatment using dispersants or emulsion breakers; in

situ burning; technical treatment using booms, skimmers, oil-water separators or sorbents and bioremediation using microorganisms or biological agents [3]. Among these techniques, sorption techniques which make use of sorbents are known to be effective in removing oil spills. Synthetic materials such as polyurethanes and polypropylene are commonly used sorbents among the various sorbents employed for oil spill remediation due to their oleophilic and hydrophobic properties [4]. Notwithstanding, these materials are not biodegradable, making it a major disadvantage. Landfill disposal is not desirable environmentally, and incineration is expensive [5, 6]. Hence, there is a need to explore natural sorbents. Sorbents that are polymers, natural material or treated cellulosic materials are used for cleaning-up of oil spillage [7].

Natural rubber (NR) is a biodegradable polymer with its inherent properties such as tear resistance, good tensile strength, high resilience, short life span, low oil resistance, poor wet skid resistance e.t.c. The low oil resistant property of NR prompted the use of NR with the expectation that modifying the NR via epoxidation will improve the resistant of NR [8]. Rubber with randomly distributed epoxy groups along with the alkenic backbone can be produced by epoxidation, which improves the degree of unsaturation in natural rubber [8, 9]. Chitosan, a biodegradable polymer is an effective bio-sorbent with high concentration of amino and hydroxyl functional groups that have a significant adsorption in removal of various water

pollutants [10, 11]. The nontoxicity, abundance in nature, biocompatibility and biodegradability of chitosan has made it to be widely accepted. Hence, in this study, chitosan served as a filler and was incorporated into the epoxidized NR to give epoxidized natural rubber chitosan (ENR-C) which is of low cost and eco-friendly for the treatment of oil spillage.

## Materials and Methods

NR latex was obtained from the Rubber Research Institute of Nigeria, Benin City, Nigeria. Land snail shell was obtained from Adeoti farm, Abeokuta. Crude oil was obtained from Dababilebu in ESE Odo Local Government Area in Ondo state, and petrol from Dambold filling station, Abeokuta, Nigeria. The reagents used in the synthesis were of analytical grade.

## Methods

### Preparation of chitosan.

Combination of the methods reported by Mohanasrinivasan and Coughlin [16, 17] were employed with slight modification. In a typical deproteinization experiment, 120 g of the powder was weighed in to a conical flask and 150 mL of 8% NaOH was added. The mixture was boiled and stirred at 100 °C for 2h in a water bath. After boiling and stirring, it was filtered and washed away. Thereafter, it was checked with red litmus paper to see if the base was completely washed away. After washing, the mixture was filtered and the residue was scraped gently into the petri dishes and dried in the oven at 100 °C for 3 h. After deproteinization, the weight of the sample reduced. Then 48 milliliters of 8% 1 M HCL was added to the deproteinized sample. The mixture was boiled and stirred for 45 min at

100 °C in a water bath. Subsequent washing was done with distilled water followed by filtration. The acidity of the mixture checked with the examination of the blue litmus paper. The residue (chitin) obtained from the above was scraped into the petri dish and dried in the oven at 100 °C for 2 h. Deacetylation reaction was thereafter followed. This was used to convert chitin to chitosan to a revised procedure of Coughlin. Briefly, the isolated chitin was soaked in 510 mL of 50% NaOH (weighing 50 g of NaOH pellets and dissolved in 100 mL of distilled water), boiled at 98.5 °C for 2 h in water bath and cooled for 36 min. The mixture was placed on a magnetic stirrer at 30 °C for 4 h, filtered, washed and examined with red litmus to check if the base was completely washed away. The mixture was filtered to retain the solid matter which is chitosan. The chitosan was oven dried at 90 °C for 24 h.

#### **Synthesis of Epoxidized Natural Rubber – Chitosan (ENR-C)**

In a typical experiment, 20 mL of latex was measured into the beaker, then 10 mL of distilled water (H<sub>2</sub>O) was added, afterwards chitosan was added. The solution was mixed and stirred. The weight ratio of rubber to chitosan was 5:1. Then the epoxidation reaction was carried out by adding 20 mL of measured latex into the beaker, then 10 mL of distilled water (H<sub>2</sub>O) was added, afterwards, 28 mL of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was added drop wisely to it and was placed on magnetic stirrer to make the solution even, under a continuous stirring for 2 hour, at temperature up to 40 °C. The rubber latex was coagulated with 8 mL of formic acid. Methanol was poured into the reaction mixture to obtain epoxidized natural rubber (ENR – 2h); 2 h represents the time of epoxidation reaction. The ENR-C was separated and pressed into thin sheet

and the sheet was dried (for 3 h) under vacuum at 50 °C.

#### **Influence of temperature on the sorption efficiency**

A series of experiments were performed to know the effect of temperature on the oil sorption efficiency by measuring the percentage absorption after 1 hr, at different temperatures of; 0 °C, 30 °C, 40 °C, 50 °C, 60 °C. Note that ENR – C 2h, was used for this study because it gave the highest level of epoxidation.

#### **Effect of pH**

pH plays a very good important role for the removal of crude oil from the aqueous solution. Three different pH conditions of the aqueous solution at pH 4, 7, and 10 were considered. 1g of the sorbent was added and the amount of crude oil that was removed from the solution was studied.

#### **Effect of contact time for the removal of crude oil from aqueous solution**

Contact time is an important parameter for practical evaluation of sorption process. Contact time effect on crude oil uptake was studied using synthesized epoxidized natural rubber and epoxidized natural rubber – chitosan at room temperature. 20 mL of petrol was taken into 250 mL beaker having 100 mL water. 1 g of the synthesized epoxidized natural rubber – chitosan was added into it. The same procedure was repeated for crude oil using 0.2 g each for the synthesized epoxidized natural rubber – chitosan. Time period ranging from 10 minutes to 60 minutes, on a 10 minutes interval was predetermined for petrol while time period ranging from 1 hour to 5 hour on a 1 hour interval was predetermined for crude oil.

## Results and Discussion

### Proximate composition:

Table 1 shows the proximate composition of the chitosan. Moisture content is the quantity of water content in a material. It is used as a measure of stability and susceptibility to microbial contamination [12]. The result showed that chitosan from snail shell has moisture content of 12.38 %. Chitosan is hygroscopic in nature [13], therefore during storage it can be affected by moisture absorption. The ash content was 9.85 %. This shows the level of inorganic content present in the sample, whereby, the total amount of minerals present could be measured. The volatile matter was 23.78 % and this shows that it is relatively stable. pH was 7.87, which shows that its weakly basic and its KOH was found to be 11.59 %.

**Table 1: Proximate Analysis of Chitosan.**

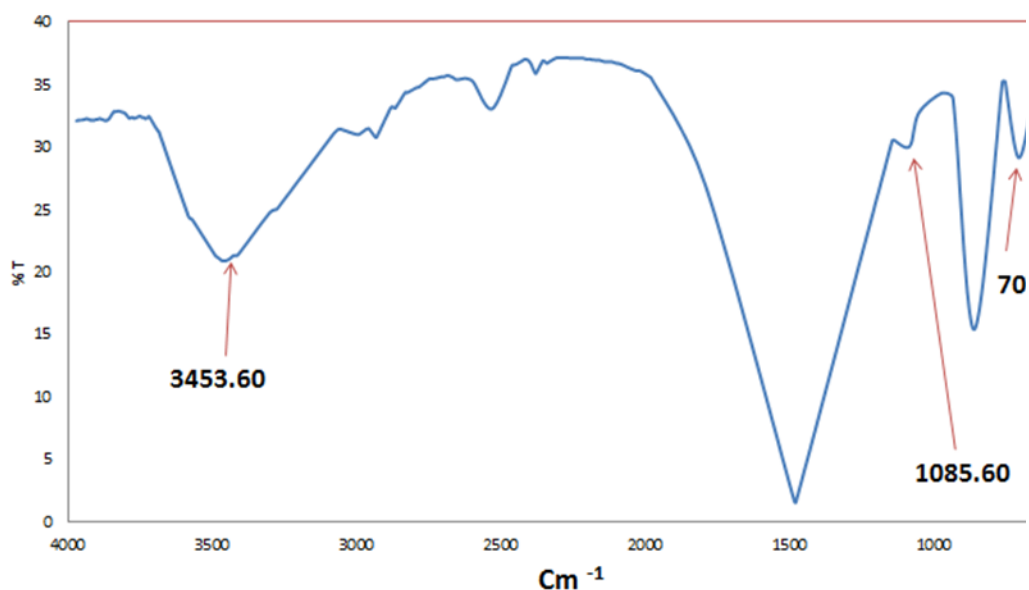
Test	Results
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Moisture	12.38 %
Ash	9.85 %
Volatile Matter	23.78 %
pH	7.87 %
KOH	11.59 %

### FTIR of Chitosan from Snail shell:

FTIR analysis was used to confirm the prepared structure of chitosan. The chitosan spectra in the region of 3453.60 shows a broad absorption band which corresponds to the stretching vibration of hydroxyls and NH stretching vibration of free amino groups as shown in figure (1). The peak observed at 2932.00  $\text{cm}^{-1}$  and 2867.00  $\text{cm}^{-1}$  can be assigned to asymmetric stretching of  $\text{CH}_3$  and  $\text{CH}_2$  in the prepared chitosan [14].

The band observed at 1794.40  $\text{cm}^{-1}$  can be attributed to C=O stretching of a carbonyl compounds. The observed peak at 1085.60  $\text{cm}^{-1}$  can be assigned to CN stretch of aliphatic amines [15]. The band at 707.20  $\text{cm}^{-1}$  can be attributed to NH bending vibration of primary amides [15].



**Fig. 1:** FT-IR spectrum of Chitosan (land snail)

### EDAX Analysis

The elemental composition of chitosan from land snail shell was studied by energy dispersive X-ray spectroscopy (EDX). The EDX graph showed the elemental analysis of the sample and the result obtained is represented in the EDX graph (Figures 2). The EDX analysis confirmed that the main peaks in the chitosan spectra are Carbon (C) and Oxygen (O) which are the principle content of chitosan. The intensity of the peaks for (C) and (O) in chitosan were minimum.

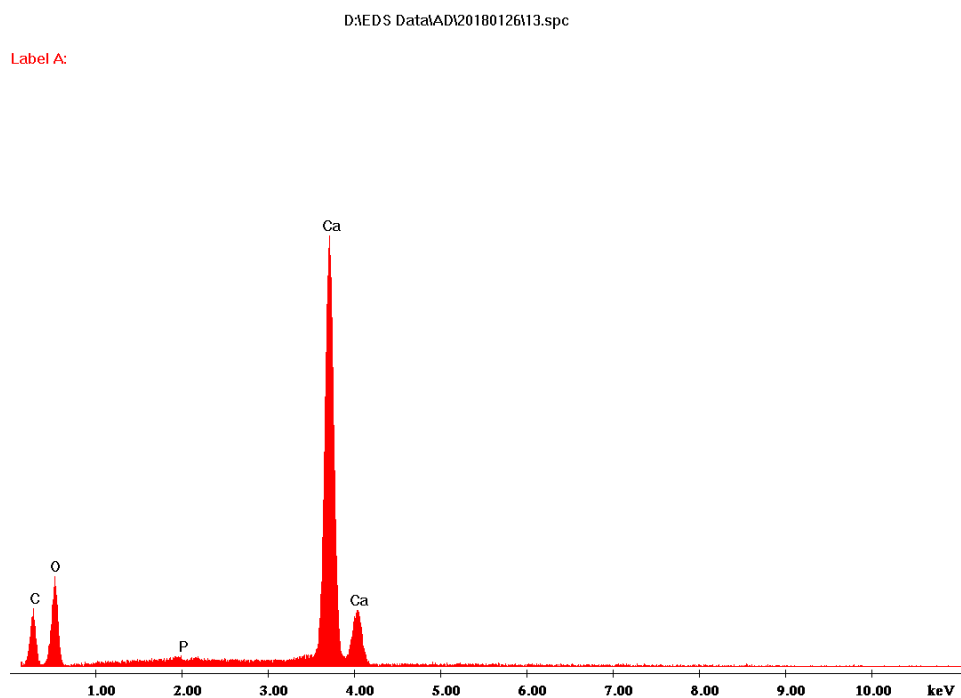
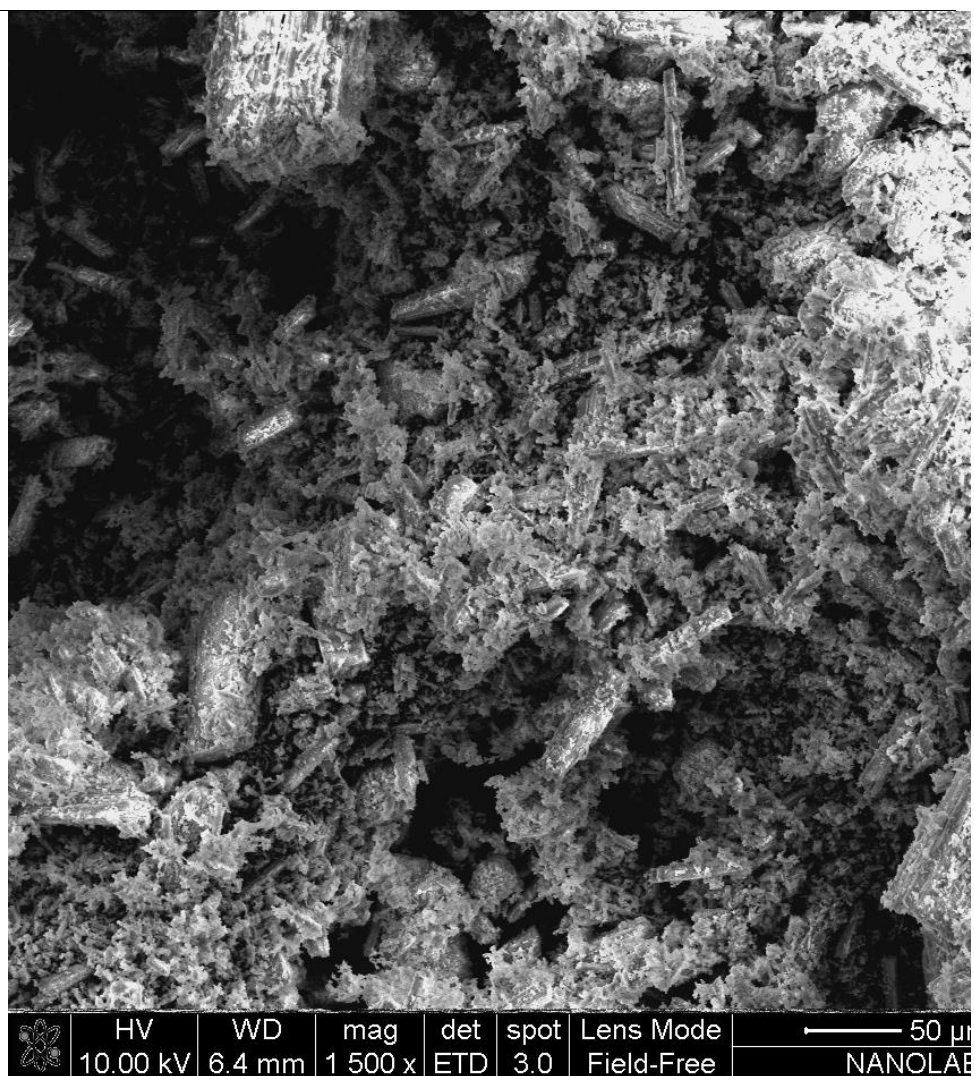


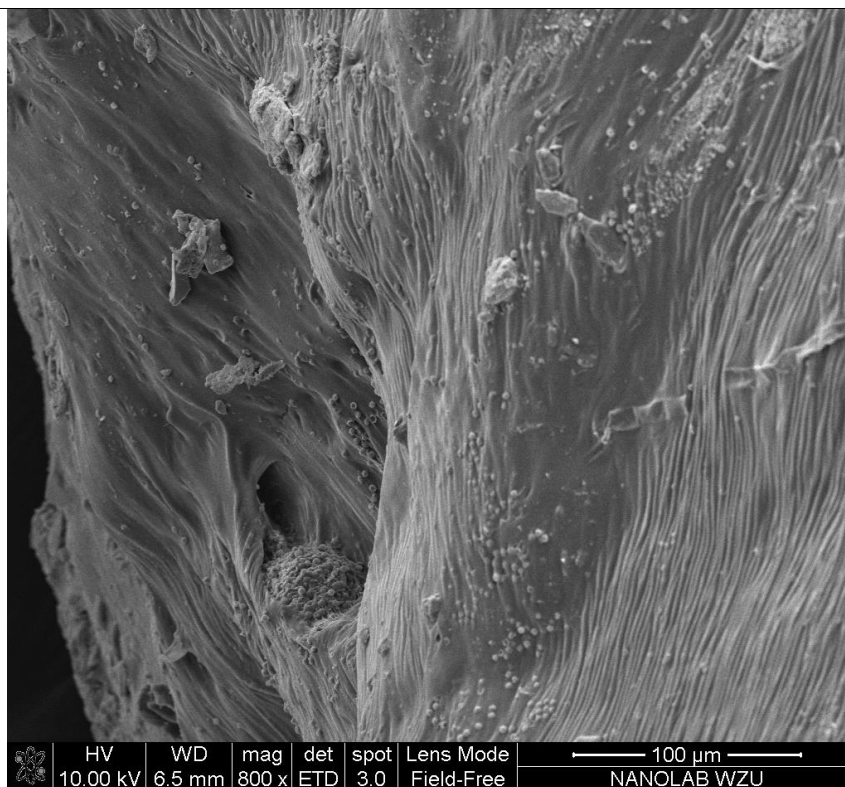
Fig. 2: EDX Graph of Chitosan from land snail shell

### Scanning Electron Microscopy (SEM) Analysis of the Samples

The surface morphology of chitosan was examined by SEM analysis. The SEM micrograph provides the morphology of prepared chitosan from snail shells. The micrograph showed a non-homogenous and non-smooth surface as shown in Fig 3. This observation was in agreement with previous work reported by Mohanasrinivasan [16] and the epoxidized natural chitosan (ENR-C 2h) showed a spongy surface morphology with good cross-linking.



**Fig 3:** SEM image of chitosan from snail shells

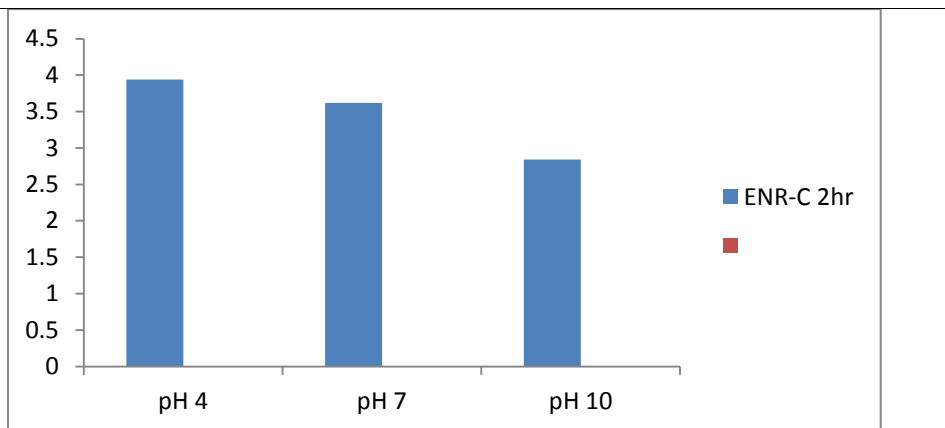


**Fig. 4:** SEM image of ENR-C 4h

### Effect of pH

pH plays an outstanding role in breaking of emulsion. The adjustment of pH on the sample was done to know the sorption efficiency of petrol on the synthesized modified natural rubbers. Three different pH conditions at 4, 7, 10 were taken into consideration. From the result, it is shown that maximum sorption of petrol occurred with ENR-C 2h at pH 4 (3.94 g/g) followed by pH 7 (3.62 g/g) and minimum sorption occurred at pH 10 (2.84 g/g). The maximum sorption takes place in the acidic medium and this could be as a result of strong acidic medium which leads to heighten the oil to unstable with the aid of the epoxidized natural rubber-chitosan and help the emulsion to be demulsified and increase the droplet size, hence promote the sorption of oil. The acidic medium of the sample act as catalyst between the molecules of oil and the sorption sites of the epoxidized natural rubber-chitosan (-COOC and -OH groups).

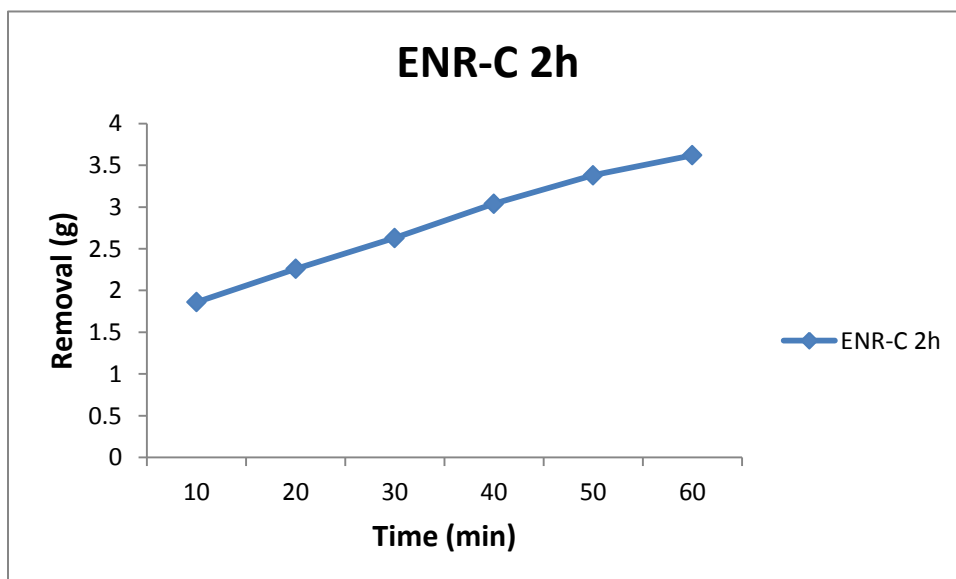




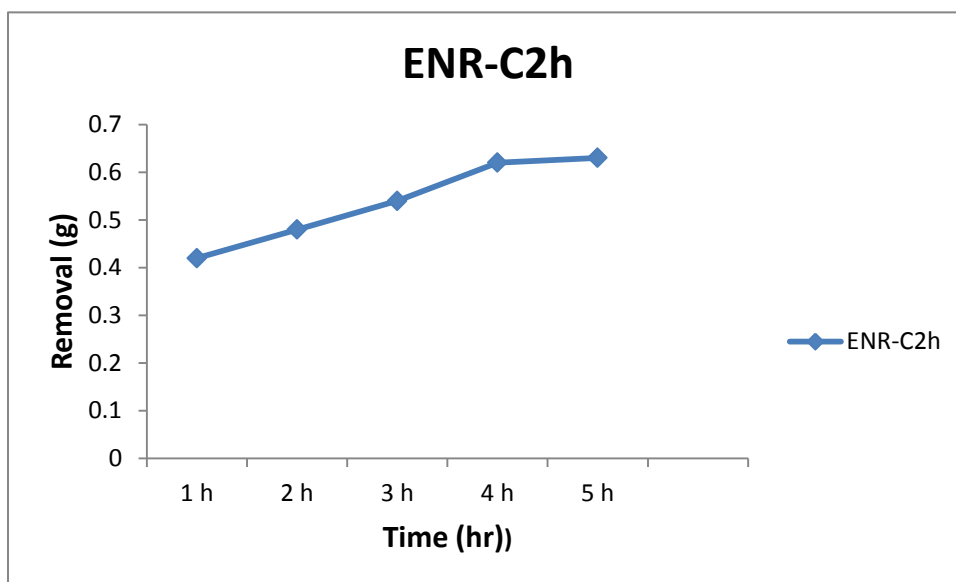
**Fig. 5: Effect of pH on sorption capacity of petrol using epoxidized natural rubber- chitosan**

#### Effect of contact time

Figure (5) show the effect of contact time on petrol and crude oil sorption on epoxidized natural rubber – chitosan (ENR-C 2h). The results show that the sorption capacity of both petrol and crude oil increases with increase in time interval.



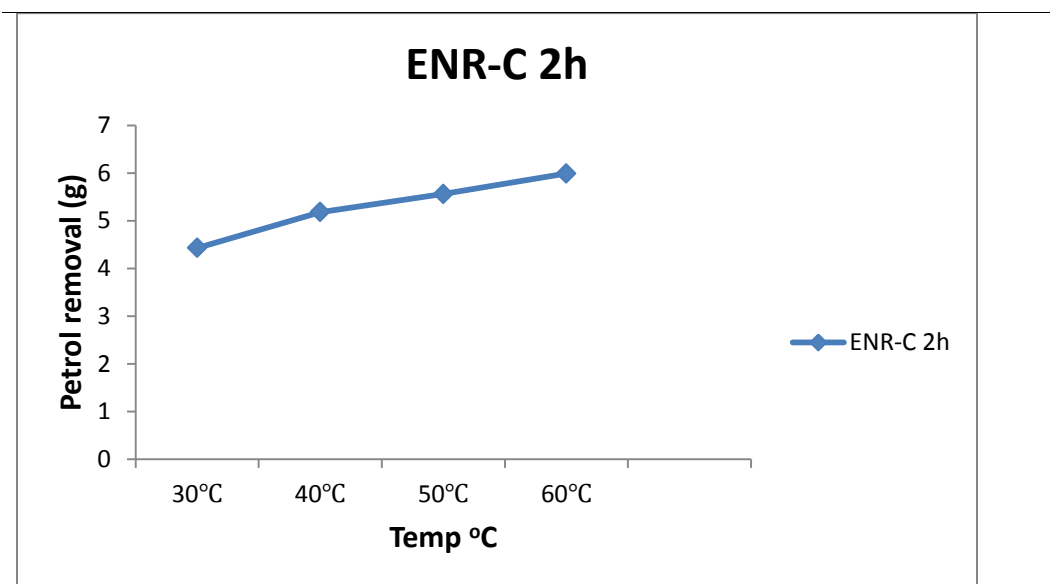
**Fig. 5.1: Effect of contact time on petrol**



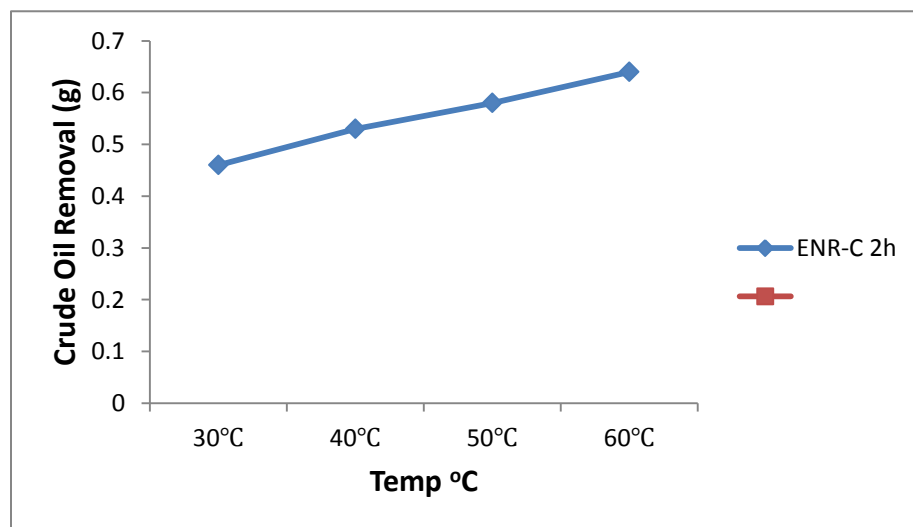
**Fig. 5.2: Effect of contact time on crude oil**

### Effect of Temperature

The effect of temperature on both petrol and crude oil were studied at temperature 30°C, 40°C, 50°C and 60°C with the values of sorption after 1 hour and was plotted against temperature in figure (6). The efficiencies of sorption of all the sorbent on petrol and crude oil were studied. The maximum uptake of petrol and crude oil increases with an increase in temperature from 30°C to 60°C. As the temperature increases from 30°C to 60°C, it is expected for the sorption of the sorbent to increase, which could be as result of more flexibility that results in breaking down of the oil molecule in order to enhance sorption. The rate of oil uptake and diffusion was directly proportional to temperature.



**Fig. 6.1: Effect of temperature on petrol sorption**



**Fig. 6.2: Effect of temperature on crude oil sorption**

**Sorption Isotherm:**

Sorption Isotherms provide information on the relationship between the unit mass of the adsorbent and the amount of the adsorbent removed from the liquid phase. Adsorption isotherms are necessary for the design of the adsorption systems. Information on sorption mechanism, affinity of the adsorbent, surface properties are sourced from the equilibrium parameters. In order to optimize the adsorption systems in removing oil from solution, determination of the most

suitable correlation for the equilibrium curve is important. Different isotherm models have been used in the literatures. In this study, Langmuir and Temkin isotherm were used to analyse the equilibrium data and table (2) show their results.

The Langmuir isotherm model has been the most frequently used isotherm describing that adsorption occurs uniformly on the active sites of the sorbents and once the site of the adsorbate had been occupied, no further adsorption takes place. The Langmuir isotherm is for monolayer adsorption on a surface that contains a finite number of identical sites.

The assumption of Langmuir isotherm are given in the following equation:

$$Q_e = \frac{Q_o K_L C_e}{1 + K_L C_e}$$

The linear form of the Langmuir model [I. Langmuir] are represented below

$$\frac{C_e}{q_e} = \frac{1}{q_o b} + \frac{C_e}{q_o} \quad \dots\dots\dots \text{Eqn}$$

Where  $C_e$  is the equilibrium concentration of the adsorbate (mg/L)

$q_e$  is the amount of oil adsorbed per gram of the adsorbent at equilibrium (mg / g)

$q_o$  is the maximum monolayer coverage capacity/ adsorption capacity of the adsorbent (mg / g),  $b$  is the Langmuir isotherm constant (L / mg) which is related to the energy of adsorption, that quantitatively shows the affinity between the adsorbent and the adsorbate.

The  $q_o$  and  $b$  constants can be determined from a linear plot  $C_e / q_e$  as a function of  $C_e$ .

Figure (7) shows the coefficient of regression ( $R^2$ ) to be 0.9552 and this indicates that the monolayer adsorption isotherm provides a good fit for the sorption of crude oil onto the epoxidized natural rubber - chitosan of 2h.

The separation factor ( $R_L$ ) known as dimensionless constant or equilibrium parameter can be used for the expression of the essential features langmuir isotherm. The following relation[18] are expressed below:

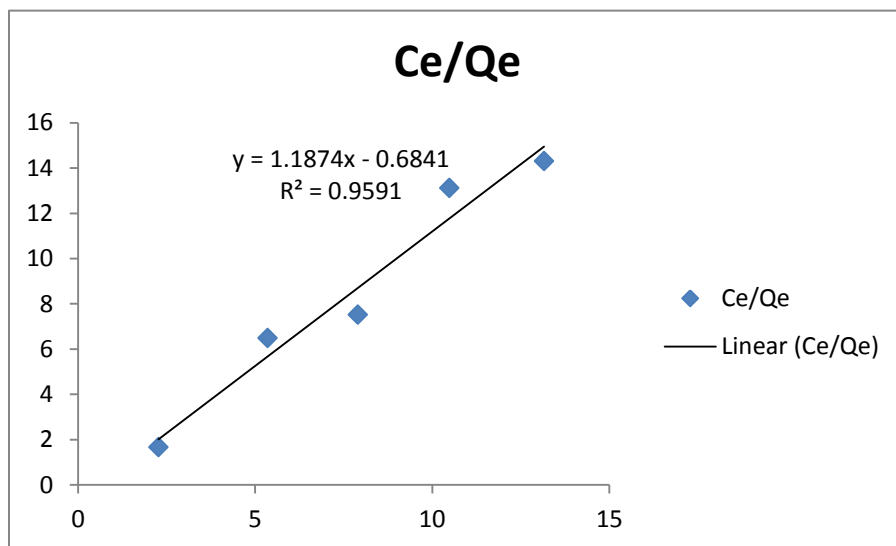
$$R_L = \frac{1}{1 + bC_o}$$

Where  $C_o$  is the initial concentration of crude oil in mg / L .

The separation factor gives information in regards to the nature of the adsorption process, indicating how favourable a sorption is. The adsorption can be referred to as irreversible ( $R_L=0$ ), favourable ( $0 < R_L < 1$ ), linear ( $R_L=1$ ) or

unfavourable ( $R_L=1$ ).

The separation factor ( $R_L$ ) obtained from this study was 0.11366 indicating that the equilibrium sorption of crude oil onto the epoxidized natural rubber-citosan (ENR-C 2h) was favourable.



**Fig. 7: ENR-C Langmuir isotherm Plot  
The Temkin Isotherm**

Temkin isotherm has a factor that take into consideration of adsorbent – adsorbate interactions. On the basis of ignoring extremely low and large value of concentrations, the model assumes that the heat of the adsorption of all the molecules in the layer would decrease linearly rather than logarithmic with coverage [19,20].

A uniform distribution binding energies (up to some more binding enrgy) was carried out by plotting the quantity absorbed  $q_e$  against  $\ln C_e$  and from the slope and intercept, the constant were determined. The model is given by the following equation [19].

$$q_e = \frac{RT}{b} \ln (A_T C_e)$$

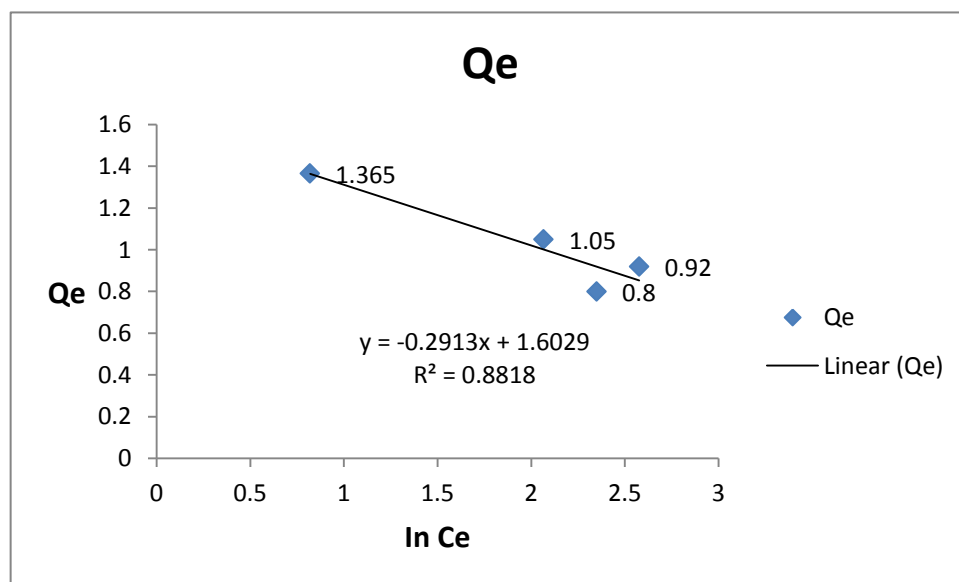
$$q_e = RT \ln A_T + \left(\frac{RT}{b}\right) \ln C_e$$

$$B = \frac{RT}{bT}$$

$$q_e = B \ln A_T + B \ln C_e \dots \dots \text{linear graph}$$

$A_T$  is the Temkin isotherm equilibrium binding constant (L/g),  $b_T$  is the temkin isotherm constant,  $R$  is the Universal gas constant (8.314 J/mol/K),  $T$  is the temperature at 298K and  $B$  is the constant related to heat of sorption (J/mol).

The following values that were estimated from the Temkin plot shown in Figure (8) are:  $A_T = 0.746$  L/g,  $B = -0.291$  J/mol and these indicate that the heat of sorption shows a physical adsorption process. The value of coefficient of regression ( $R^2$ ) was 0.8818 for temkin model is lower to the one obtained for the Langmuir model. The result in this study shows that Langmuir model is appropriate for describing the sorption equilibrium of crude oil on the epoxidized natural rubber-chitosan.



**Fig. 8: ENR-C Temkin adsorption isotherm plot**

**Table 2: ENR-C 2h Adsorption Isotherm Parameter Values**

Isotherms	Parameter	ENR-C 2h
Langmuir	Qm (mg/g)	0.8425
	a	1.7351
	Rl	0.3417
	$R^2$	0.9591

Temkin	$A_T$ (L/g)	0.746
	B(J/mol)	-0.291
	$R^2$	0.8818

in oil spill  
cleanup,  
*Desalination*  
140 (3), 259–

## Conclusion

From the observation made in this study, the synthesized epoxidized natural rubber-chitosan at two hours (ENR-C 2h) has a good sorption capacity, which could be used as sorbent for oil spillage. The equilibrium sorption on epoxidized natural rubber-chitosan at two hours was carried out and Langmuir adsorption isotherm gave the best fit out of the isotherms employed with a highest regression value and this could be deduced that ENR-C 2h is a good bio-sorption material for oil spill treatment.

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