

Performance Assessment of Ceric Induced Methacrylate Kenaf Shive Sorbents in Crude Oil Spills and Water System

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ABSTRACT

With the global challenge that casted the attention of most environmentalist of recent is the crude oil spillage, and the need for extensive research to improving and developing viable natural sorbents for oil clean-up arose. This paper aimed at the synthesis of crude oil sorbents from kenaf shive and investigate the effects of initiator concentration, monomer ratio and particle sizes -in the domain of 0.5-2.5 wt%, 0.5-2.0 wt % and 125-1000 μm respectively- on the grafting efficiency and crude oil sorption. The effects of the individual and combine factors were carried out using a statistical experimental design matrix of five-level central composite design (CCD). Respond surface methodology (RSM) was used to optimise and develop equations for synthesis navigation. The optimal sorption 7.0 g/g was achieved at initiator concentration, monomer ratio and particle size of 1.25wt %, 1.50 wt % and 562 μm respectively. FIRT, DT-TGA and XRD analyses were carried out on the optimised sorbent. Further computations for grafting efficiency (GE), homopolymers and density were carried out.

Key words: Kenaf shive, Grafting, Respond Surface Methodology (RSM), Crude oil, Sorption.

1.0 Introduction

Oil spillage is the release of a liquid petroleum hydrocarbon into the environment due to human activity, and is a form of pollution. The term often refers to marine oil spills, where oil is released into the ocean or coastal waters. Oil spills include releases of crude oil from tankers, offshore platforms, drilling rigs and wells, as well as spills of refined petroleum products (such as gasoline, diesel) and their by-products, and heavier fuels used by large ships such as bunker fuel, or the spill of any oily substance refuse or waste oil. Spills may take from a month up to years to clean up. Oil also enters the marine environment from natural oil seeps (Adelana *et al.*, 2011). Oil spills are usually transported by wind, current, temperature, weathering and salinity increases the transportation consequently, accumulate on sea surfaces or sediment at the debris [9-10]. This effect of oil spill is not restricted to human body directly alone, but could affect the plants within the community and water sources [11,12]. Furthermore, these menaces affect aquatics consequently, affect the hygiene of the communities' citizenry through the inhalation of toxicants [13-15].

The approaches used in recent years toward super hydrophobicity of cellulosic materials can be

classified into two categories, based on the generation of roughness:

- (1) Roughness offered by coating cellulosic substrates, which include:
 - a. Chemical grafting to modify the surface chemistry and surface morphology of cellulosic fibre/surface simultaneously.
 - b. Sol-gel processes to render cellulose fibre/surface with porous outer-layer and to reduce surface energy by post-treatment or by mixing precursors with low surface energy side chains.
 - c. Nanoparticle deposition, for example by using metal, metal oxide, mineral and polymers that modify the morphology of the cellulosic fibre/surface, followed by surface energy reduction by post-treatment.
 - d. Chemical vapor deposition.
- (2) Roughness offered by regeneration or fragmentation of cellulosic materials, which among others include: Electro spinning and electro-spraying, use of nanocellulose (cellulose nano crystals and nano fibrillated cellulose) and use of cellulose composites (Junlong and Orlando, 2013).

The sorbent technique are examples for physical methods however, biological methods using

microorganisms and chemical methods using in-situ burning and dispersants are also feasible and practicable also, the two latter are not viable [23]. The industrially acceptable physical methods for crude oil recovery are by using synthetic materials which are now considered hazardous owing to their non-biodegradability and are capital intensive [18,25-27].

For sustainable and renewable-of course-cheap sorbents, bio-mops would need to be considered first. Kenaf plants adapt to different climatic changes and the bast is largely used in paper pulping, agro-packages etc. therefore, if such plant shive is modified for oil spill remediation is a long-way in research. The preeminent properties imbibe by kenaf shive are: low cost, high efficiency and biodegradable properties of natural sorbents gained a high exploration. A high number of natural organic oil sorbents were reported, namely: wood chips, sugarcane bagasse, cotton and jute [28,29]. Jute plant having many common properties with kenaf plant deems to be investigated. Jute and kenaf constitute of cellulose, hemicellulose (82-85%) and lignin [15,30,31].

In this work, optimisation of kenaf shive graft-modified sorbent would be developed by taking the advantage of methylmethacrylate monomer, aftermath, study the sorption mechanism of the sorbent in crude oil spill/water system. Other analyses would be carried to ascertain the performance.

2.0 Materials and methods

2.1 Materials preparation

All chemicals are analytical grades and used as it was received without further purification, except for the monomer (acrylonitrile) which inhibitors were removed by washing it severally with 5 % concentration of NaOH. Dried Kenaf stalks were obtained from National Research Institute for Chemical Technology (NARICT), Zaria. The crude oil sample used for the sorption test was obtained from Petroleum Research Laboratory, Warri, Delta state, Nigeria. The raw crude oil was kept at room temperature and the adsorption test was carried out at 40 °C after the grafting of the acrylonitrile onto the kenaf shive. Table 1 shows the significant properties of the oil that perhaps affect the oil sorption.

2.2 Experimental

2.2.1 Extraction of the kenaf shive

The obtained dried kenaf stalks were subjected to chemical retting in 1 % w/v NaOH for 2 hrs in order to extract its shive from the two components (shive and bast fibres). The product was washed with distilled water until neutrality was achieved and further drying took place for 72 hrs at room temperature. The extracted shive was ground into different particle sizes as prescribed by the DoE software result sheet.

2.2.2 Synthesis of the sorbent

Synthesis of the grafted sorbent was done by adopting methods reported by Salisu, *et al.*, [32], only that the monomer used here was Acrylonitrile. Briefly, a requisite quantity (1.00 g) of kenaf shive was soaked in 5 mls of distilled water for 24 hrs. The mixture was transferred to reaction kettle and 1.00 ml of 2% acetic acid, 10.00ml of 0.4 M of nitric acid and 0.5 ml of the weight percent of the requisite quantities of initiator as well as monomer concentration as were added, however, the monomer was added after purging nitrogen gas for 5 min. The reaction continued for 3hrs at 60 °C. The sample was then washed, filtered and oven dried at 40 °C. Three neck flask was quarterly filled with about 25ml of acetone for homopolymers removal. The initial weight of the thimble was taken after which the thimble plus grafted shive was noted. The latter was inserted into the extractor for the extraction process. This was done at 60 °C for 24hrs in which the homopolymers weight were calculated. The experimental processes were repeated for twenty samples using requisites regressors. The oil sorption capabilities of extracted grafted sorbents were tested using 0.10 g sorbent in 5 mls of the oil. However, the effect of homopolymer was assessed on the optimized sorbent. This was done at 40 °C for 5 mins to achieve proper sorption.

2.2.3 Characterisation of the samples

Infrared spectra of the sorbent in KBr pellets was analysed and scanned from 4000 – 400 cm⁻¹ using Shimadzu FTIR-8400S. The test was carried out on the raw (unmodified) and modified optimized sorbent (unextracted homopolymers). The modification was inferred from FITR plots by taking the advantage of the unique vibration/stretching property for each functional group. The sorbent crystallinity was determine using Shimadzu XRD 6000 (Tokyo, Japan) with CuK α radiation (λ = 1.542 Å) operated at 30 kV and 30 mA. Surface area was determined using Brunauer, Emmette and Teller (BET) technique by (Quantachrome Instruments, Model Nova1000e series, USA), however, the heat

properties was not set aside but determine using DTA-TGA60 Shimadzu, Japan.

2.2.4 Experimental design, data analysis and process optimisation

There are several variables which potentially affects the grafting efficiency and absorption. Response surface method (RSM) would be of tremendous important in the analysis of such multivariate system. The objective of using RSM is to get a quick insight in the interaction amongst the investigated variables, facilitate the optimisation conditions and locate optimal response in the region of interest [31, 32]. For these purposes, a reduction empirical model describing the process was developed for predicting and determining future responses in such system. The generated results of the responses from the experimental runs was be obtained by employing Eq. 1 through fitting with a second-polynomial equation to predict the studied variable factors as independent variable and interaction between them:

$$Y = b_0 + \sum_{i=1}^k b_i X_i + \sum_{i=1}^k b_{ii} X_i^2 + \sum_{i=1}^k \sum_{j=2}^K b_{ij} X_i X_j + \varepsilon \dots\dots\dots (1)$$

where, Y is the predicted dependent variable, b_0 is constant coefficient, b_i , b_{ii} are regression coefficient, i and j are index numbers, k is number of patterns, X_i 's are independent variables and ε is the random error. The analysis of variance (ANOVA) was used to assess the significance and adequacy of the model. The fitness of the polynomial model was expressed by coefficient of determination, R^2 , R_{adj}^2 and R_{pred}^2 . The main indicators that were used to show the significance of the model were Fisher Variation Ratio (F-value), probability value (Prob > F) with 95% confidence level and adequate precision. The final model for each response was obtained after elimination of insignificance term ($p > 0.05$) base on F-test and 3D plots were presented. In addition, the optimum values of the independent variables were identified and further development of the absorbent was carried out at this condition to confirm the regression models.

Characterisations

Infrared spectra of the sorbent in KBr pellets was analysed and scanned from 4000 – 400 cm^{-1} using Shimadzu FTIR-8400S. The test was carried out on the raw (unmodified) and modified optimized unextracted sorbent that bears the highest oil sorption to confirm the modifications by taking the advantaged of the unique vibration/stretching

property for each functional group. The sorbent structure was determined using Shimadzu XRD 6000 (Tokyo, Japan) with $\text{CuK}\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$) operated at 30 kV and 30 mA whereby the ground sorbent was scanned at rate of 0.05°/min at angle range of $3^\circ \leq 2\theta \leq 90^\circ$. The generated raw data were used to replot the diffractogram aided by Origin Pro 9.0 16 Bit, Fig. 3. Surface area was determined using Brunauer, Emmette and Teller (BET) technique by (Quantachrome Instruments, Model Nova1000e series, USA), however, the heat properties was not set aside but determine using DTA-TGA60 Shimadzu, Japan.

2.4 Adsorbability Measurement

Oil adsorption capability for both preliminaries and the optimized extracted as well as unextracted sorbent of the modified kenaf shive fibers was investigated. According to ASTM F-726-12, the adsorption capacity formula is expressed as follows [15,31,32]:

$$S_w = \frac{S_{wt} - S_o}{S_o} \quad (1)$$

where; S_w is the sorption rate (g (liquid) /g (sorbent)), S_o is the quality of the shive fibre before sorption, and S_{wt} is the quality of the kenaf shive fibre after sorption. 1 g of raw and modified shive fibres was immersed into a beaker, and a measurement was recorded after every 5 min. According to ASTM F-726-12, the test measures the rapid adsorption capacity (15 min soaking) and 24 h adsorption capacity. The sea water used for this test is natural seawater not simulated.

2.5 Batch Experiments

Equal mixture of 15 mL petroleum ether and 1 mL of 1+1 sulfuric acid were shaken in a reparatory funnel for 15 mins. The lower aqueous organic layer was released after settling for about 10 min. The organic layer was poured into a beaker containing 1.2 g of drying agent (anhydrous sodium sulfate), then the mixture was drain into glass funnel. Consequently, the solution was filtered into the colorimeter coupled with 25 mL of petroleum ether (this was repeated with the same quantity of petroleum ether). The residual oil concentration was determined by filtering the sorbent and analysed using UV-Vis spectroscopy.

Adsorption kinetics were performed by immersing 1 g of developed sorbent a mixture of oil/sea water at room temperature. Samples and crude oil concentration were, respectively, weighed and

measured at different time interval, between 1-90 min.

Isotherm studies were carried out at room temperature (298 K) by varying the initial concentrations 5-30 g/L at interval of 5 g/L using the aforementioned procedure. The adsorption thermodynamics and activation energies (E_a) were determined via the batch experiments at different temperatures (298, 303, 313 and 323 K). The crude adsorption capacity at equilibrium (Q) is calculated by the following formula:

$$Q = \frac{(C_o - C_e)V}{S} \quad (2)$$

where, C_o and C_e are, respectively, the initial and equilibrium concentrations of crude oil (g/L) at any time t . V is the volume of the solution (L), and S is the mass of the adsorbent (g).

2.6 Adsorption Kinetics

2.6.1 Pseudo first-order model

The pseudo-first-order model is represented by the following equation [15,31]:

$$\frac{dQ_t}{dt} = K_1(Q_e - Q_t) \quad (3)$$

When boundary conditions are reached, $t = 0$, $Q = 0$ and $t = t$, $Q = Q_t$, the equation can change to:

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \quad (4)$$

this is simplified as:

$$Q_t = Q_e(1 - e^{-K_1 t}) \quad (5)$$

where, k_1 is the pseudo first-order rate constant; Q_e and Q_t are the adsorption capacities of the adsorbent at equilibrium.

2.6.2 Pseudo second-order model

The pseudo second-order model is represented as follows [15,33,34]:

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \quad (6)$$

The linearized-integrated form of the equation is:

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \quad (7)$$

where k_2 is the pseudo second-order rate constant.

2.6.3 Intra particle diffusion model

The intraparticle diffusion model can be used to analyze the removal of pollutants by an absorbent during a diffusion process. This is expressed as the following equation [34,35]:

$$Q_t = k_p t^{0.5} + C \quad (8)$$

where k_p is the intraparticle diffusion rate constant; and C is a constant related to the bounding layer thickness.

2.7 Adsorption Isotherm

2.7.1 Langmuir isotherm model

The Langmuir isotherm model assumes that adsorption occurs at a specific uniform location on the adsorbent surface. According to this model, the adsorbent forms a molecular monolayer.

The equation is as follows [15,31,35]:

$$Q_e = \frac{k_1 Q_o C_e}{1 + k_1 C_e} \quad (9)$$

where Q_o is the maximum adsorption capacity of the adsorbent (g/g); and K_l is the Langmuir constant of equilibrium adsorption.

2.7.2 Freundlich isotherm model

The Freundlich isotherm model assumes that multilayer adsorption takes place at heterogeneous surfaces with different adsorption energies and characteristics. Here, the adsorption of the surface is calculated by the following equation:

$$Q_e = k_2 C_e^{1/n} \quad (10)$$

where K_2 (mg/g) (L/mg) $1/n$ is the Freundlich constant; and n is the adsorption intensity.

2.8 Adsorption Thermodynamics

The adsorption thermodynamics of the crude oil adsorption process need to be further investigated. Various thermodynamic parameters such as enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) can be obtained by isothermal adsorption studies [31,36]. ΔG of adsorption can be represented by the classical Van't Hoff equation:

$$\Delta G = RT \ln K_o \quad (11)$$

where K_o can be calculated by the following equation:

$$K_o = Q_e / C_e$$

The apparent enthalpy (ΔH) of adsorption and the entropy (ΔS) are calculated as follows:

$$\ln\left(\frac{Q_e}{C_e}\right) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (12)$$

where ΔG is in (kJ/mol); ΔH is in (kJ/mol); ΔS is in (kJ/(molK)); R is the universal gas constant (8.314 J/mol); T is the adsorption temperature (K).

2.9 Activation Energy

The activation energy can be determined from the change of the absorption rate constant, k with

temperature, $T(K)$ using the Arrhenius equation [33]:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (13)$$

where A is the pre-exponential factor obtained from the intercept plot of $\ln k$ (kinetic rate constant of the best fitted model) versus $1/T$ and R is the gas constant (8.314 J/mol K). By plotting $\ln[k]$ against $1/T$, E_a can be calculated from the slope. Where I_{22} and I_{16} are, respectively, the crystalline and amorphous intensities at 2θ scale close to 22 & 1

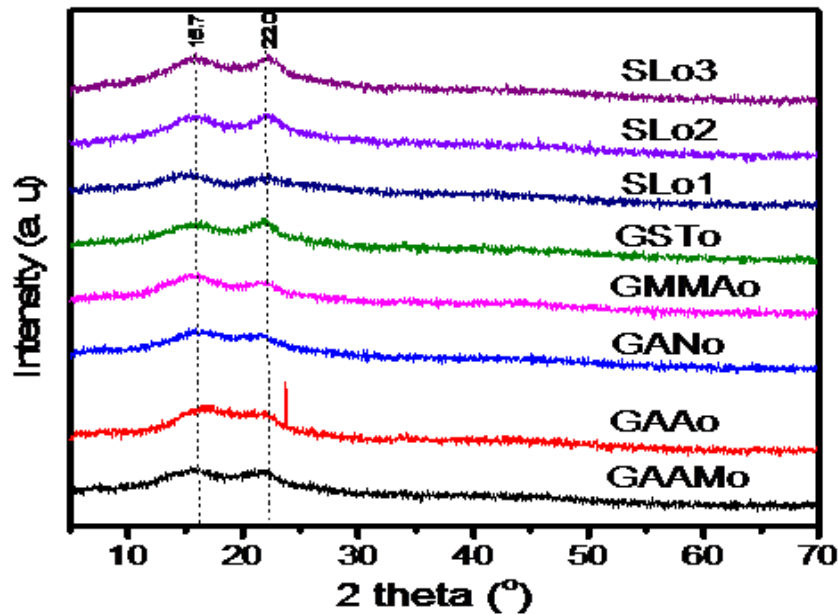


Figure 4.1 X-ray Diffractogram

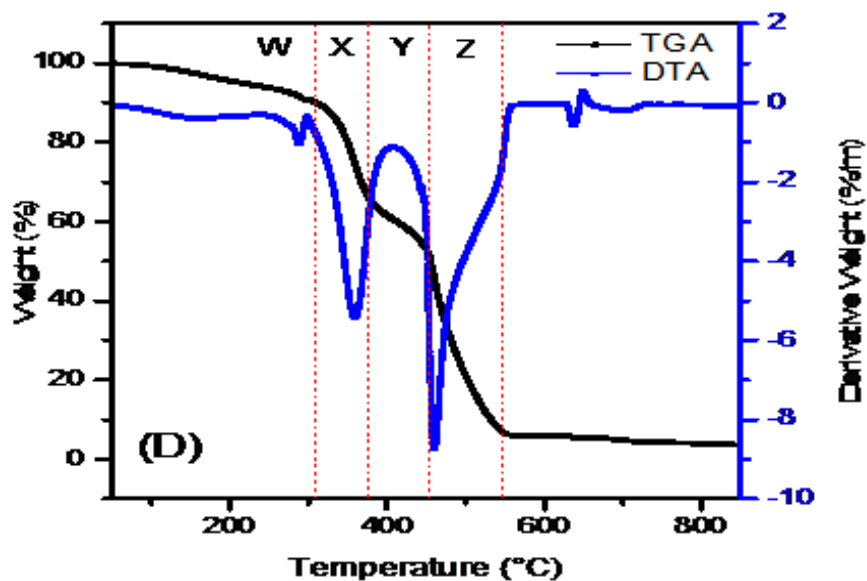


Figure 4.2- TG-DTA plots for D: GMMA

Table 1 shows the significant properties of the oil that perhaps affect the oil sorption.

Sorbent Code	I ₂₂	I ₁₆	% Crystallinity (%Cr)	Crystallinity index (C.I)
GAAo	2800	2100	57.14	0.250
GAAmo	1650	1300	55.93	0.212
GANo	2300	1850	55.42	0.196
GSTo	1400	1100	56.00	0.214
GMMAo	2000	1650	54.80	0.175
SL1,o	1400	900	60.87	0.360
SL2,o	1700	1100	60.71	0.350
SL3,o	1750	1000	63.00	0.430

Table 2: Thermogravimetric data of the optimised kenaf shive sorbents

Sample code	Decomposition stages	Temperature range (°C)	T _{max} (°C)	Weight loss (%)	Residue (%)
GMMAo	First	200-320	280	5	25
	Second	320-400	350	21	
	Third	400-500	440	9	
	Fourth	600-700	620	40	

X-ray diffraction (XRD) analysis was conducted to compare the XRD patterns of the kenaf shive sorbents. The crystallinity index (CrI) and percentage crystallinity of the developed sorbents were calculated using equation (6 and 7) in the experimental section, as reported by Nur Inani *et al.*, (2014). Figure 4.1 shows XRD diffractogram. The patterns exhibited an intense peak at around $2\theta = 22^\circ$ for the sorbents. This peak corresponds to the crystallinity region in the fibre. The non-crystalline region of the fiber is shown by the plateaus between the peaks which were assigned as around $2\theta = 16^\circ$ for all the developed sorbents it shows element of crystallinity at around $2\theta = 22^\circ$. The peaks at approximately 16° corresponds to planes 101 and 10-1. Additionally, peak at 22° corresponds to plane 002, these are characteristic attributes of cellulose I (Duong *et al.*, 2017; Li *et al.*, 2009). Moreover, the peak at 22° is as result of Van der Waal or amorphous halo (Li *et al.*, 2009). Besides, the pattern show amorphous behaviors as depicted in Table 2. Furthermore, gives the particle sizes to play an important role of adsorption. Taylor, (2012) reported that natural fibres adsorb maximally at a length equal or closer to its original strand length. GMMAo after been the best oil sorption in its kind after optimising. This perhaps could be as result of the aforementioned facts.

4.0 Conclusion

A crude oil sorbents was achieved and optimise from kenaf shive by grafting modification using multivariate factors of monomer ratio, particle size and initiator concentration based on the statistically designed experimental matrix. The succeeded sorbent was tested for oil recovery, the result was sound if compared with the control (ungrafted). The former shows a low retention and high swelling while the latter has high retention which is an indication for poor recovery. The optimization conditions were achieved at 1000um, 5%, 0.50 % w/v of particle sizes, monomer ratio and initiator concentration, respectively, gives the higher oil sorption capability of 7.02 (g/g).

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