

# **Abstraction and regeneration potential of temperature enhanced rice husk-montmorillonite combo for oil spill**

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## **Abstract**

Chemical modification of montmorillonite though popular may be expensive, environmentally noxious and can result in secondary contamination. Therefore, the need for eco-friendly and efficient treatment techniques. The use of thermally enhanced rice husk montmorillonite combo (TRMC) for aqueous crude oil pollution was evaluated. The physical characterization of the sorbate revealed a light crude oil. Scanning electron microscopy of TRMC and untreated montmorillonite (UM) showed efficient utilization of the pores for crude oil sequestration. Temperatures, pH, initial oil concentration, dosage of sorbent and time were found to be significant in the batch sorption investigation. The heterogeneous surface nature of TRMC was elucidated by the Freundlich and scatchard model analysis. Langmuir monolayer maximum sorption capacity was 5.8 and 9.7 g/g for UM and TRMC respectively and the later found to be higher than most reported sorbents. The pseudo first order model gave better fit than pseudo second order, Bangham and Elovich model in kinetics based on regression and chi-square analysis. Thermodynamics showed a spontaneous, feasible, endothermic and physical sorption process. Regeneration and reusability studies using n-hexane as eluent showed TRMC as suitable, environmental friendly sorbents for oil spill remediation.

**Keywords:** Desorption, petroleum, oil spill, rice-husk montmorillonite, thermal treatment.

## **Introduction**

Nigeria is known to be one of the largest host and exporter of crude oil in the world. In addition its refinery is usually associated with wastewater as by products. The recent bombing of oil pipelines by agitating militants in the south Niger Delta areas of Nigeria has led to high rate of oil spills. These have contaminated environmental water bodies, extending to farms and domestic areas as well. Oil spill also arises from discharge of petroleum products from ships, offshore operations, tankers, accidents in pipelines and effluents from refineries (Ibrahim et al. 2010). Oil spill is a major environmental challenge because most components of crude oil are toxic to aquatic lives and humans (Gammoun et al. 2007).

The cleanup of oil spill from contaminated water can be performed by biological, mechanical or chemical techniques. This involves the use of skimmers, trunk vacuums, surface washing and collecting agents, dispersants, nutrients and enzyme additives and microbiological cultures (Zhou et al. 2008; El-Gendy and Nassar 2015). However, most of these methods are faced with the disadvantages such as low removal efficiency, high cost and secondary contamination (Ibrahim et al. 2010). The cleanup of oil spill using sorption technique has been said to be the most effective in terms of high sequestration percentages, safety and affordability (Mishra and Mukherji 2012). An ideal sorbent used for treatment should be cheap, oleophilic, reusable, biodegradable, have high oil selectivity and sorption capacity (Abdelwahab et al. 2017). Many natural cheap sorbents such as straws, cotton, onion peel, banana trunk fibers, coconut fibers, walnut shell, rice straw, corn cobs, sand and clay minerals have been found to be effective for oil spill treatment (Kenes et al. 2012; El-Gendy and Nasar 2015; Abdelwahab t al. 2017). The use of montmorillonite as a natural sorbent for oil spill cleanup has been established (Warr et al. 2009; Ugochukwu et al. 2014a). Montmorillonite present in large deposits in Nigeria can be harnessed for oil spill treatment. A suitable treatment means of improving the sorption capacity of montmorillonite for oil is desired. Chemical treatments using acid and alkaline is popular in the treatment of different sorbents for improved removal of heavy metals and dyes (Gautam et al. 2014; Akpomie et al. 2017). However, it was reported that modification of sorbents by acid and alkaline have little effect in enhancing sorption capacity for crude oil (Ugochukwu et al. 2014b; Abdelwahab et al. 2017). Moreover, even if these chemicals were effective, their use increases the process cost, is noxious to the surrounding and results in secondary contamination. Therefore, cheap, efficient and eco-friendly means of modifying clays

for improved sorption of crude oil is important. The use of clay-hybrid composites materials for decontamination of heavy metals, dyes and other contaminants is presently the preferred technique due to the higher uptake capacities (Huang et al. 2015; Ismadji et al. 2015; Liu et al. 2015; Olu-owolabi et al. 2016; El-korashy et al. 2016; Akpomie et al. 2018; Chukwuemeka-okorie et al. 2018). However, such treatment has seldom been applied to crude oil sorption experiments. Clay–biomass composites are preferred to the synthetic chemical-clay hybrids due to the lower cost and environmental friendliness. Also, utilizing biomass materials in oil spill treatment is desirable since they are easily available, biodegradable, cheap and have high oil sorption capacities (Brandao et al. 2010). Rice husk and its thermally treated form have been tested and found to be effective for the removal of crude oil from oil spill (Kenes et al. 2012). Therefore, a combination of thermally treated rice husk-montmorillonite sorbent may offer good potentials for oil spill treatment. Interestingly, the use of such temperature treated rice husk-montmorillonite combo was more effective than acid and alkaline modified montmorillonite in the sorption of heavy metals (Akpomie and Dawodu 2015). However, this sorbent has not been applied for oil spill remediation. This study was thus performed to evaluate the crude oil sorption potential of thermally enhanced rice husk-montmorillonite combo for attenuation of crude oil from aqueous media. Regeneration and reusability studies of the sorbent were also evaluated.

## **Materials and Methods**

### **Sorbent preparation, sorbate collection and characterization**

The montmorillonite was collected from ugwuoba, Enugu state, Nigeria and prepared as described (Akpomie et al. 2015) to obtain the untreated montmorillonite (UM). The temperature treated rice-husk montmorillonite composite was prepared (Akpomie and Dawodu 2015). Briefly, collected rice husk were washed, sundried, oven dried and pulverized. The material was sieved through 100  $\mu\text{m}$  mesh screen and 40% added to montmorillonite (60%). Distilled water was added and the mixture, then compounded properly using a laboratory mortar and pestle. It was sundried then calcined in a muffle furnace at 300  $^{\circ}\text{C}$  for 2 hr, sieved through 100  $\mu\text{m}$  screen to obtain the temperature treated rice husk-montmorillonite combo (TRMC) sorbent. The sorbent was characterized to determine its surface morphology before and after crude oil sorption by the scanning electron microscope (SEM, Hitachi S4800).

Crude oil (sorbate) was obtained from a petrol station in Port Harcourt, Nigeria and characterized by standard ASTM methods as shown in Table 1.

### **Sorption, desorption and reusability studies**

Batch sorption method was applied by weighing different amounts of crude oil into 250 mL beakers containing 150 mL de-ionized water. The solution was mixed at 100 rpm for 10 min using an orbital shaker to obtain crude oil concentrations (1.0 – 3.0 g/L). 0.2 g sorbent was added at the oil water interface, agitated gradually for 1 min and left for 60 min at room temperature of 300 K. the sorbents were then removed from the beaker using sieve nets, which were left for 10 min to drain off excess crude oil then dried overnight at 60 °C then weighed. The influence of initial pH (3.0 – 9.0), dosage of sorbent (0.2 – 1.0 g), time of contact (5 – 60 min) and temperature (300 – 323 K) were studied by varying the parameter of interest while keeping others constant. A thermostat temperature water bath was utilized to study temperature influence were the beakers were placed. The pH was controlled by the use of 0.1 M NaOH and 0.1 M HCl with the help of a pH meter (Toledo Model MP 220). Controls were carried out under the performed experimental conditions using the sieve nets without any sorbent material to ensure that any sorption effect of the sieve net in the removal process was eliminated.

Regeneration reusability studies were evaluated by contacting 1.0 g of crude oil loaded sorbent with 450 mL of n-hexane taking 150 mL aliquot at a time. After 10 min of extraction the sorbents were dried at 60 °C in an oven before reuse for treatment. Sorption was conducted using 2.0 g/L of crude oil solution at a contact time 60 min and temperature 300 K. Three desorption-sorption cycles was performed.

The crude oil sorption percentage removal (PR) and the sorbent sorption capacity (SSC) of UM and TRMC were calculated from the equations respectively:

$$PR = M_s/M_o \quad (1)$$

$$SSC = (S_s - S_o)/S_o \quad (2)$$

Where  $M_s$  and  $M_o$  is the weight of adsorbed oil and initial weight of oil used (g) respectively.  $S_s$  (g) is the weight of the dried saturated sorbent after sorption (sorbent + oil) and  $S_o$  (G) is the initial dry weight of sorbent before sorption. All the experiments were done in triplicate and the average value calculated. For quality assurance, experiments were repeated for rejected values which deviated with over 10% from the mean of the three runs.

### Sorption isotherm modeling

The isotherm model of removal of crude oil by the sorbents was performed by the application of non-linear Langmuir, Freundlich, Flory-Huggins and Scatchard equations given respectively (Foo and Hameed 2010; Gulistan et al. 2015)

$$q_e = (q_L K_L C_e) / (1 + K_L C_e) \quad (3)$$

$$q_e = K_F C_e^{1/n} \quad (4)$$

$$\theta / C_i = K_{FH} (1 - \theta)^{n_{FH}} \quad (5)$$

$$q_e = b C_e (q_s - q_e) \quad (6)$$

Where  $q_L$  (g/g) is the langmuir monolayer sorption capacity,  $K_L$  (L/g) is the sorption constant,  $n$  Freundlich sorption capacity,  $K_F$  (L/g) intensity,  $\theta = (1 - C_e/C_i)$  is the extent of coverage,  $C_e$  and  $C_i$  in g/L are the equilibrium and initial crude oil concentrations respectively,  $K_{FH}$  (L/g) is the Flory-Huggins model constant,  $n_{FH}$  the model exponent,  $q_s$  (g/g) and  $b$  (L/mg) are the Scatchard model sorption constants (Akpomie et al. 2017).

### Kinetic and thermodynamic analysis

Kinetic modeling of crude oil sorption on UM and TRMC was analyzed by the use of the non linear pseudo first order (PFO), pseudo second order (PSO), Bangham and Elovich equations given respectively (Largitte and Pasquier 2016; Akpomie and Dawodu 2015):

$$q_t = q_e [1 - \exp(-K_i t)] \quad (7)$$

$$q_t = (q_e^2 K_2 t) / (1 + q_e K_2 t) \quad (8)$$

$$q_t = (1/\beta) (\ln \alpha \beta t) \quad (9)$$

$$\ln [C_i / (C_i - q_t m)] = (K_O m / V) t^{a_B} \quad (10)$$

Where  $q_t$  (g/g) is the sorption capacity at time  $t$  (min),  $K_i$  ( $\text{min}^{-1}$ ) is the PFO rate constant,  $K_2$  (g/g/min) represents the PSO rate constant,  $\beta$  (g/mg) corresponds to chemisorptions surface coverage and activation energy,  $\alpha$  (mg/g min) is the initial removal rate,  $V$  (ml) represents the volume of solution,  $K_O$  (g) and  $a_B$  ( $< 1$ ) are Banghams constants.

Thermodynamic sorption parameters changes in Enthalpy ( $\Delta H^\circ$ ), free energy ( $\Delta G^\circ$ ), and Entropy ( $\Delta S^\circ$ ) were evaluated to provide information on the feasibility, spontaneity and heat change of the sorption using the equations:

$$\Delta G^\circ = - RT \ln K_c \quad (11)$$

$$\ln K_c = - (\Delta H^\circ / RT) + (\Delta S^\circ / R) \quad (12)$$

Where  $K_c = C_a / C_e$  is the distribution coefficient,  $C_a$  and  $C_e$  in g/L is the concentration of crude oil sorbed and that left in solution at equilibrium respectively,  $R$  the ideal gas constant and  $T$  (K) absolute temperature of sorption.

### **Validation of kinetic and equilibrium models**

Apart from the coefficient of determination ( $R^2$ ), the chi-square ( $\chi^2$ ) error analysis was used to validate the best fit kinetic or equilibrium model. The model with smaller  $\chi^2$  value implies better fit. The  $\chi^2$  is calculated from:

$$\chi^2 = \Sigma[(q_{e_{\text{exp}}} - q_{e_{\text{cal}}})^2 / q_{e_{\text{cal}}}] \quad (13)$$

Where  $q_{e_{\text{cal}}}$  and  $q_{e_{\text{exp}}}$  represents the equilibrium uptake capacity gotten from model calculations and experiment respectively (Akpomie et al. 2018).

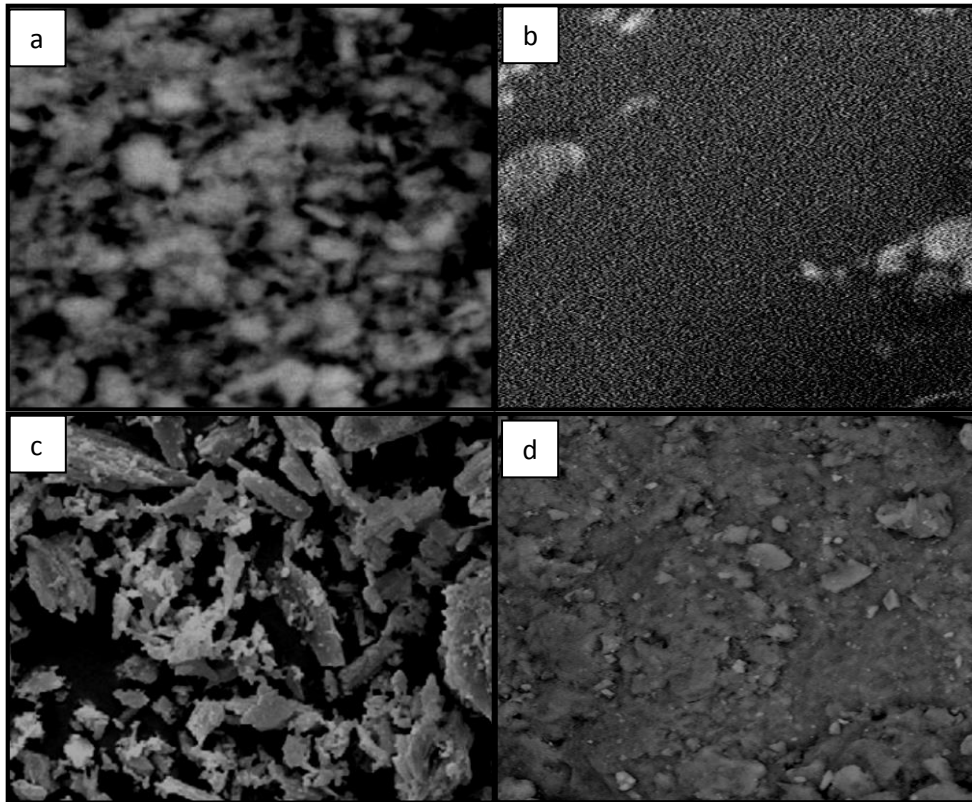
## **Results and Discussion**

### **Characterization of sorbate and sorbent**

Some physical properties of the crude oil determined are presented in Table 1. The  $^\circ\text{API}$  gravity is a very important property which helps in the classification of crude oil. Crude oil having  $^\circ\text{API}$  gravity are classified as very light crudes ( $40-45^\circ$ ), light crude ( $34-39^\circ$ ), medium crude ( $22-33^\circ$ ) and heavy crude oil ( $< 22^\circ$ ) (Nwadinigwe and Alumona 2015). The value of the crude oil obtained fell in the classification of light crude oil suggesting the crude utilized in this study is a light one. The scanning electron microscopy (SEM) image of the sorbents before and after crude oil sorption is shown in Fig.1. The surface morphology of UM and TRMC after crude oil sorption was clearly different from the surface of the sorbents before sorption. Also, the porosity of the oil loaded sorbents was reduced. This is an indication of the presence of crude oil on the porous structure of the used sorbents, suggesting efficient utilization of the active sites in the removal process. It has been reported that high crude oil removal is usually obtained by sorbents with porous structure (Kenes et al. 2012).

**Table 1.** Physical properties of the crude oil

<b>Properties</b>	<b>Method</b>	<b>Value</b>
Viscosity	ASTM D-445	4.03
Density (g/cm <sup>3</sup> )	ASTM D-1298	0.861
<sup>0</sup> API gravity (degrees)	ASTM D-287	34.2
Kinematic viscosity at 50 °C (mm <sup>2</sup> /s)	ASTM D-445	3.61
Total acid number (mg KOH gm)	ASTM D-2896	0.252
Total base number (mg KOH gm)	ASTM D-974	2.793
Ash content (wt%)	ASTM D-482	0.093
Carbon residue (wt%)	ASTM D-189	2.836
Water content (ppm)	ASTM D-1744	226.8
Total sulfur (wt%)	ASTM D-4294	0.52



**Figure 1:** SEM images of UM (a) before and (b) after crude oil sorption, TRMC (c) before and (d) after crude oil sorption



### **Influence of experimental factors on crude oil removal**

The experimental factors such as, pH, sorbent dosage, initial crude oil concentration, contact time and temperature are very important as they influence the amount of sorbate removed by a sorbent. The pH of oil-water mixture on the abstraction potential of a given sorbent affects the sorbent surface charge and its interaction with the crude oil sorbate. In this regard, the influence of pH of oil-water mixture on crude oil removal by UM and TRMC was evaluated as illustrated in Fig.2. Decrease in PR and SSC with pH increase was observed on both sorbents. The composite sorbent TRMC recorded higher sorption than UM at the given pH range indicating an efficient sorbent. The trend of decrease in sorption with pH is attributed to increasing repulsion between negatively charged crude oil molecules in aqueous solution and the increasing negative charge on the sorbents as pH increases (El-Gendy and Nassar 2015). Similar pattern has been reported using cork-by-products for removal of mineral oil from aqueous solution (Souza et al. 2016). The pH 3.0 was selected and utilized in the sorption experiments due to the optimum PR and SSC obtained by UM and TRMC at this pH.

The report on the effect of sorbent dosage on the PR of crude oil and SSC of the sorbents is presented in Fig.3. Increase in the PR of crude oil on both sorbents was recorded with increase in sorbent dosage. In contrast the SSC of UM and TRMC decreased significantly. The increase in PR is due to increasing number of active sites for more crude oil uptake with increasing sorbent dosage. Since more active sites are made available at higher sorbent dosage there is the tendency of the sites to get unsaturated compared to lower doses leading to decrease in SSC per unit mass of sorbent. The decrease may also be attributed to under utilization of the active sites resulting from aggregation of the sorbent particles which is a phenomenon common with clay minerals. The sorbent dosage of 0.2 g was taken for efficient utilization of sorption sites. Similar reports have been documented (Peng et al. 2013; Abdelwahab et al. 2017).

The influence of initial crude oil concentration on the SSC of UM and TRMC and the PR of crude oil is also presented in Fig.3. The PR of crude oil was found to decrease with increase in concentration for both UM and TRMC. Such trend was attributed to the variation in interfacial tension in the oil spill solution and the surface of sorbent at high oil concentration (Gulistan et al. 2015). The decrease may also be due to the saturation of the active sites on the sorbents as the concentration of crude oil increased which resulted in limited active sites for efficient removal. However, the SSC of the sorbents increased with increase in crude oil concentration. The

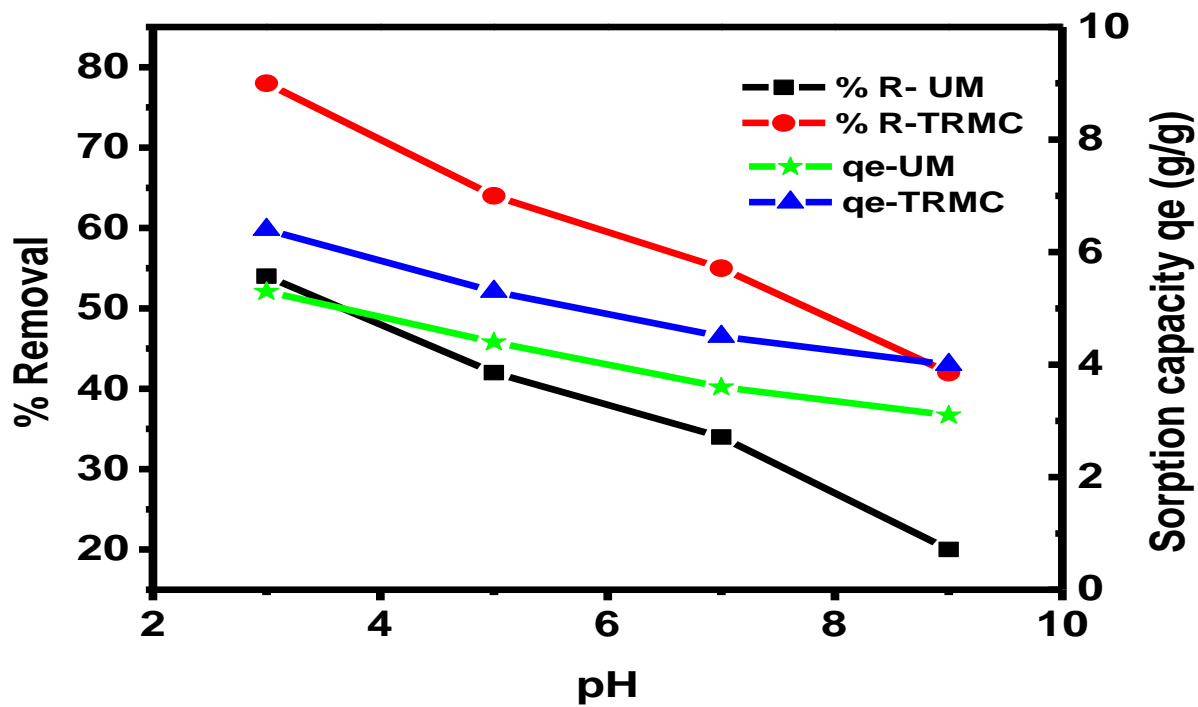
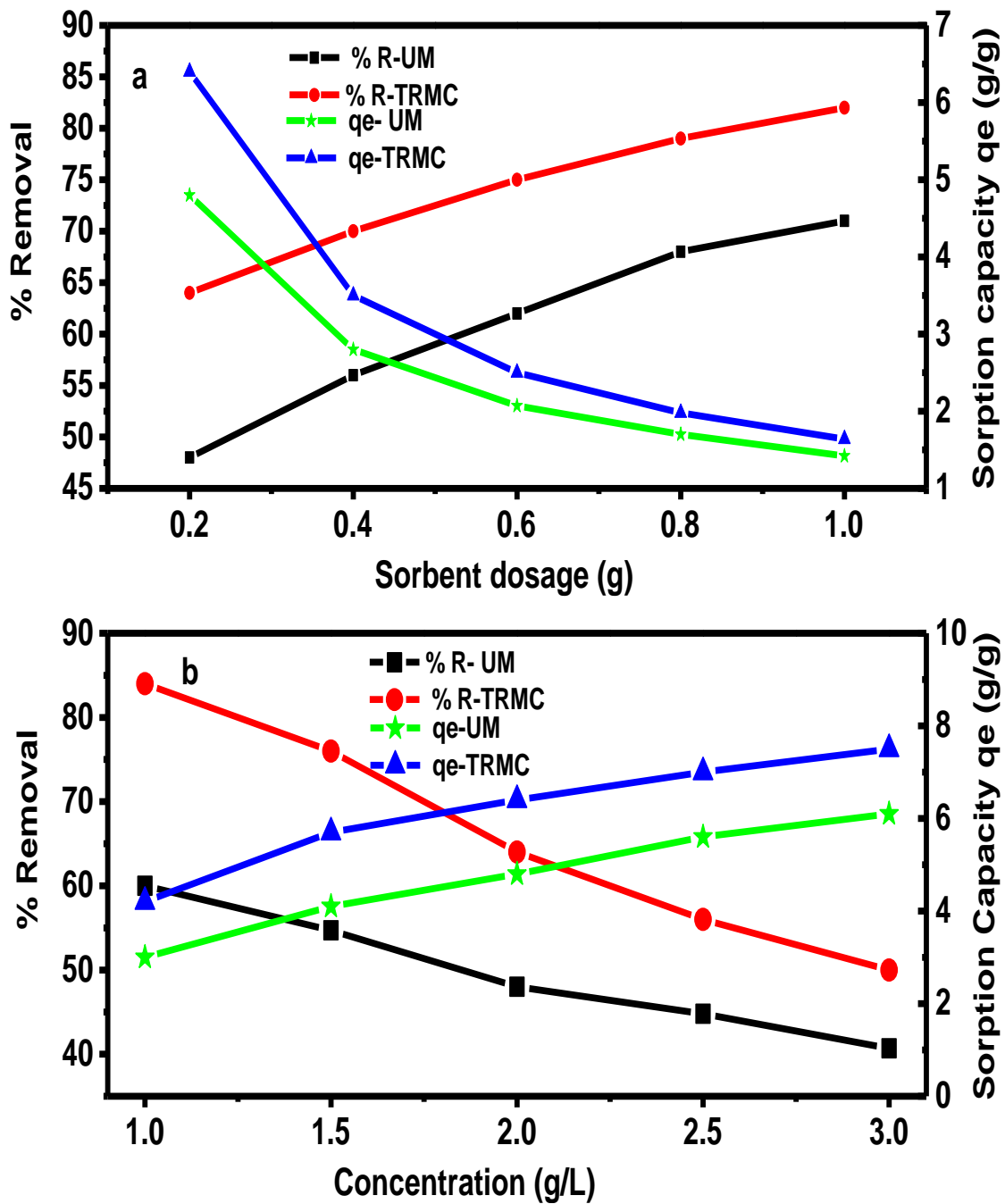


Figure 2: Influence of pH on the remediation of crude oil polluted water.

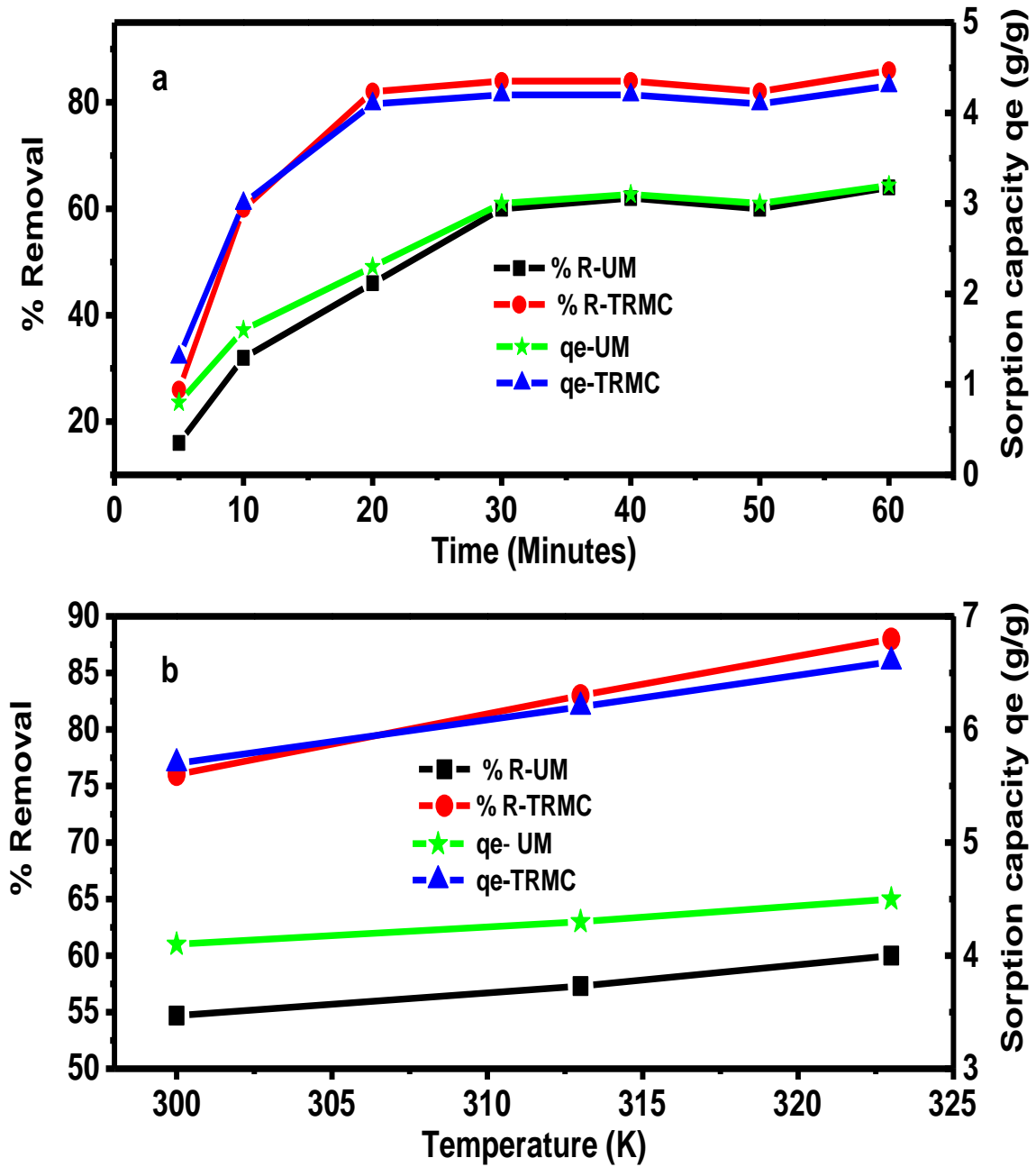


**Figure 3:** Influence of (a) sorbent dosage and (b) initial crude oil concentration on the remediation of crude oil polluted water.

phenomenon is attributed to increasing driving force at higher concentration resulting in higher mass transfer of crude oil for better interaction with the sorbent. Similar trend was reported by El-Gendy and Nassar (2015) in the study of the effectiveness of spent waste sugarcane bagasse on the removal of crude oil hydrocarbons from water.

The sorption of crude oil on UM and TRMC as a function of contact time is shown in Fig.4. An increase in the PR and SSC with time was obtained initially after which it became constant at equilibrium. TRMC was found to have higher sorption of crude oil than UM again indicating the effectiveness of thermal rice husk modification of montmorillonite. Equilibrium sorption was achieved at 20 min for TRMC and 30 min for UM. The faster rate of crude oil removal by TRMC may be due to inclusion of the hydrophobic component of rice husk for better, faster and more efficient interaction with crude oil. This faster rate of attenuation is desirable in sorption studies which is an advantage of the modified sorbent. The initial fast sorption and later slow process attaining equilibrium was attributed to the fact that initially the sorbent removed crude oil by macropores resulting in penetration into micropores (a slower process) until equilibrium attainment (Kenes et al. 2012). Also due to the vacant active sites on the sorbent and high crude oil concentration at the initial stages, the high concentration gradient is rapidly sorbed by the abundant vacant sites. As the process progresses it becomes difficult for the remaining vacant sites to be occupied due to repulsions between crude oil already adsorbed and the remaining in solution. Similar sorption trend have been observed previously (Aisien and Aisien 2012; Zou et al. 2015).

Temperature of sorption is a very important factor since it varies with seasons and areas where oil spillage may occur. Fig.4 shows the effect of temperature on the PR and SSC of UM and TRMC for crude oil. Increase in the sorption of crude oil with increase in oil spill temperature from 300 to 323K was obtained for both sorbents. This suggests the endothermic nature of the removal process. This is due to the fact that as temperature increases oil viscosity decreases. The decrease in viscosity enables mass transfer and enhanced diffusion of crude oil to the surface for interaction with the active sites and pores (Li et al. 2013). This increase in removal of crude oil with temperature may be an advantage in temperate regions like Nigeria where temperatures can be high in certain periods favoring the oil spill cleanup by the sorbents. The fact that TRMC had higher PR and SSC than UM under all external factors like initial concentration, dosage, time and temperature clearly indicates the success of our modification of



**Figure 4:** Influence of (a) contact time and (b) temperature on the remediation of crude oil polluted water.

montmorillonite for oil spill cleanup. The high potency of TRMC as an efficient sorbent was supported by the high removal efficiencies also recorded for heavy metals in a previous study (Akpomie and Dawodu 2015).

### **Sorption isotherm and kinetics of crude oil removal**

Sorption isotherm helps to establish the interaction between the sorbent and sorbate at constant temperature in a given sorption process. In this experiment the Langmuir, Freundlich, Flory-Huggins and scatchard isotherm models were used to analyze equilibrium data. The isotherm parameters obtained for the removal of crude oil from oil contaminated solution by UM and TRMC are given in Table 2. The best fit model is judged by the linear regression coefficient ( $R^2$ ) value closest to one and the model with the smallest  $\chi^2$  value. The  $R^2$  and  $\chi^2$  presented by the Langmuir model was the highest (0.988) and lowest (0.08) respectively for UM sorbent. The implication of the best fit of Langmuir model is that the surface of UM is homogenous in nature and involves a monolayer sorption of crude oil (El-Gendy and Nassar 2015). Also the maximum monolayer sorption capacity corroborated the higher SSC of TRMC (9.7) than UM (5.8) which showed enhanced montmorillonite capacity with rice husk and thermal treatments. The nature of sorption can be obtained from a Langmuir separation factor  $R_L$  given by

$$R_L = 1/[1 + K_L C_I] \quad (13)$$

Where  $C_I$  (g/L) represents the initial crude oil concentration in solution. The  $R_L$  values indicate a favorable ( $0 < R_L < 1$ ), irreversible ( $R_L = 0$ ), linear ( $R_L = 1$ ) and unfavorable ( $R_L > 1$ ) sorption process (Zou et al. 2015). The  $R_L$  values for sorption of crude oil on UM and TRMC was in the range 0.608 - 0.823 and 0.556 - 0.789 respectively which showed a favourable sorption process or good interaction between the sorbent and sorbate. Furthermore, the  $R^2$  (0.999) and  $\chi^2$  (0.05) presented by the Freundlich model gave the best fit for sorption on TRMC. This suggested a multilayer sorption of crude oil on a heterogeneous TRMC surface (El-Gendy and Nassar 2015). The in-cooperation of rice husk to montmorillonite tends to introduce a different type of active site in the combo adsorbent. The sorbent is thus composed of rice husk sites as well as montmorillonite sites which would likely increase the affinity for different kind of pollutants. Furthermore, values of  $n > 1$  represents favorable sorption process (Ho and Mckay, 1998). The  $n$  values obtained corroborated the Langmuir  $R_L$  values of a favorable sorption of crude oil on UM

**Table 2.** Isotherm parameters for sorption of crude oil on UM and TRMC

<b>Isotherm model</b>	<b>UM</b>	<b>TRMC</b>
Langmuir		
$q_L$ (g/g)	5.8	9.7
$K_L$ (L/g)	0.215	0.266
$R^2$	0.998	0.973
$\chi^2$	0.08	0.76
Freundlich		
$K_F$ (g/g)	3.02	2.47
$n$	2.89	1.98
$R^2$	0.924	0.999
$\chi^2$	2.27	0.05
Flory–Huggins		
$K_{FH}$	0.04	0.11
$n_{FH}$	1.68	1.79
$R^2$	0.975	0.961
$\chi^2$	1.22	1.24
Scatchard		
$q_s$ (g/g)	15.9	19.8
$b$ (L/g)	0.21	0.38
$R^2$	0.997	0.811
$\chi^2$	0.11	3.45

and TRMC sorbent. The  $R^2$  and  $\chi^2$  values presented by the Flory-Huggins model although high and low respectively did not give good fits as the Langmuir (for UM) and Freundlich (for TRMC) models and thus was not considered further. The scatchard plot analysis also called independent site oriented model was applied to verify the homogenous or heterogeneous surface nature of the sorbents (Anirudhan and Suchithra 2010). The  $R^2$  and  $\chi^2$  obtained from the scatchard model further corroborated the homogenous surface of UM (indicated by the good fits) proposed by Langmuir model and the heterogeneous nature of TRMC (indicated by poor fits) suggested by the Freundlich model.

The kinetic mechanism of sorption was evaluated by the PFO, PSO, Elovich and Bangham kinetic rate equations. The kinetic constants obtained from the sorption of crude oil on UM and TRMC are presented in Table 3. It was observed that both the PFO and PSO models gave good fit ( $R^2 > 0.963$ ) to the sorption process. However, the PFO model was found to present the best for the kinetics of sorption based on higher  $R^2$  and lower  $\chi^2$  values obtained for both sorbents. This implies chemisorptions may not likely be the mechanism of removal process; this is because chemisorption is assumed when the PSO model provides the best fit (Ho and Mckay 1999). Also both the PFO and PSO rate constants of  $K_1$  ( $0.086 \text{ min}^{-1}$ ) and  $K_2$  ( $4.2 \times 10^{-4} \text{ g/gmin}$ ) for TRMC were higher than those  $K_1$  ( $0.021 \text{ min}^{-1}$ ) and  $K_2$  ( $3.6 \times 10^{-4} \text{ g/g min}$ ) of UM. This supported the faster rate of sorption or equilibrium attainment by TRMC compared to UM. This fast sorption rate of crude oil on TRMC could be utilized in the design of large scale adsorption systems with shorter residence time using TRMC as sorbents which is desirable, as equilibrium removal of crude oil in such systems would be achieved in a shorter time. The  $\chi^2$  presented by the Elovich chemisorptions were high ( $> 6.70$ ) compare to the PFO and PSO, which further suggest that chemisorptions is not the dominant mechanism of crude oil removal on the sorbents. Also, the highest  $\chi^2$  values (11.24 and 16.03) presented by the Bangham kinetic model for UM and TRMC respectively suggests that intraparticle diffusion is not the major mechanism of diffusion rather boundary layer diffusion from the bulk to the sorbent surface must have played a major role (Akpomie et al. 2017). The SSC of UM and TRMC were compared with those of other sorbents in literature as shown in Table 4. It was observed that although the maximum monolayer SSC of TRMC was not high compared to some of the sorbents, it was however, higher than most sorbents reported. This showed the suitability of TRMC as an efficient sorbent



**Table 3.** Kinetic parameters for sorption of crude oil on Um and TRMC

<b>Kinetic model</b>	<b>UM</b>	<b>TMRC</b>
Pseudo-first order		
$q_e$ (g/g)	2.21	4.77
$K_i$ ( $\text{min}^{-1}$ )	0.021	0.086
$R^2$	0.985	0.992
$\chi^2$	1.73	1.16
Pseudo-second order		
$q_e$ (g/g)	2.13	4.57
$K_2$ (g/g min)	$3.6 \times 10^{-4}$	$4.2 \times 10^{-4}$
$R^2$	0.973	0.964
$\chi^2$	3.44	4.38
Elovich		
$\alpha$ (g/g min)	0.231	0.317
$\beta$ (kg/min)	0.021	0.047
$R^2$	0.917	0.904
$\chi^2$	6.71	8.39
Bangham		
$a_B$	0.163	0.231
$K_o$	1.88	2.94
$R^2$	0.901	0.883
$\chi^2$	11.24	16.03

**Table 4.** Comparison of sorption capacities of sorbents with others in literature

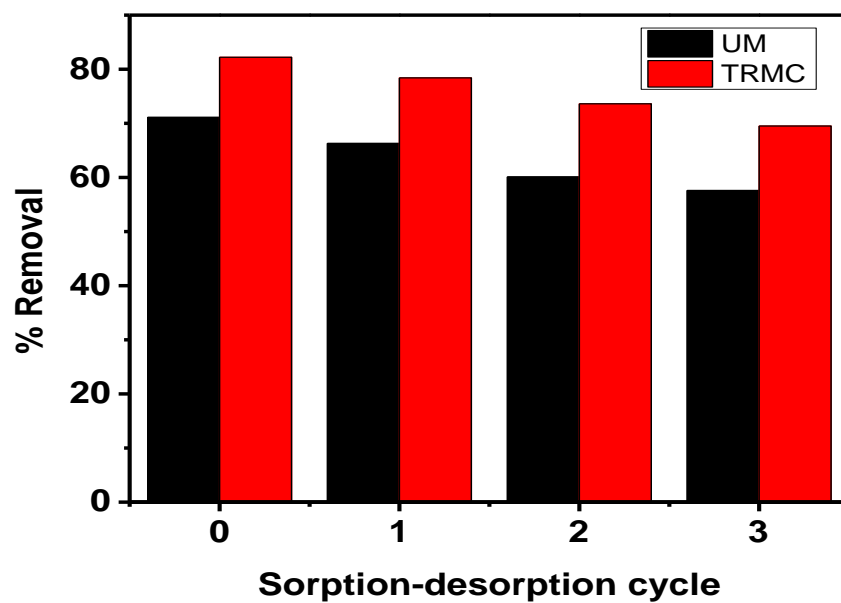
<b>Sorbent</b>	<b><math>q_{\max}</math> (g/g)</b>	<b>Reference</b>
Expanded perlite	3.25	(Teas et al. 2001)
Corncob	0.0043	(Nwadiogbu et al. 2016)
Acetylated corncob	0.0768	(Nwadiogbu et al. 2016)
Macroporous organogel	18.2	(Tuncaboylu and Okay 2009)
Polyester pads	9.0	(Nikkhah et al. 2015)
Polypropylene pads	8.0	(Nikkhah et al. 2015)
Treated perlite	8.0	(Nikkhah et al. 2015)
Peat moss	3.0	(Nikkhah et al. 2015)
Polyurethane foam	18.5	(Nikkhah et al. 2015)
Clay modified polyurethane	21.5	(Nikkhah et al. 2015)
Palm fibers	22.73	(Abdelwahab et al. 2017)
Eggplant peels	0.833	(Gulistan et al. 2015)
Chitosan hydrogel	2.0	(Sokker et al. 2011)
Bentonite	7.12	(Okiel et al. 2011)
Deposited carbon	9.23	(Okiel et al. 2011)
Powdered activated carbon	2.58	(Okiel et al. 2011)
Unmodified montmorillonite	5.8	This study
Rice husk montmorillonite	9.7	This study

for oil spill treatment. UM and TRMC could then be utilized as suitable alternatives to sorbents with lower SSC, since our proposed sorbents are low cost and environmentally friendly.

### **Thermodynamics and regeneration of UM and TRMC**

Thermodynamic parameters were calculated in order to classify the physical or chemical nature of sorption and determine the spontaneity and feasibility of sequestration. Thermodynamic values  $\Delta G^\circ$ ,  $\Delta S^\circ$  and  $\Delta H^\circ$  for sorption of crude oil on UM and TRMC are given in Table 5. The spontaneous and feasible nature of sorption process was established by negative  $\Delta G^\circ$  values and showed increase in feasibility of the process with temperature increase. Positive  $\Delta S^\circ$  showed high affinity of the sorbents for crude oil and random increase in particulate movement at the interface of sorption. The endothermic nature of sorption process was clearly established by positive  $\Delta H^\circ$  values which supported the increase in crude oil uptake with temperature on the sorbents. Furthermore, the fact that  $\Delta H^\circ$  obtained for both UM and TRMC were within the range of 2.1 to 20.9 kJ/mol verified the physical nature of sorption (Tan et al. 2008). This supports the assumption (physisorption) established due to higher fit of PFO model than PSO model for attenuation process. The physical nature may enhance easy crude oil desorption from UM and TRMC surfaces for regeneration and reuse.

The ability of the sorbent to be regenerated and reused is a very important criterion if the material is to be selected and applied. The reusability studies of UM and TRMC after three cycles of regeneration is shown in Fig.5. A decrease in the initial sorption of crude oil from 71.1 to 57.6% and 82.2 to 69.5% for UM and TRMC respectively showed the reusability of the sorbents for oil spill cleanup. The decrease however was quite significant when compared to that reported by Zou et al. (2015) where they used magnetic pomelo peel for up to ten cycles of regeneration sorption experiments. In general, the decrease in sorption of crude oil after each progressive cycle may be due to decrease in the number of active sites due to irreversible binding or aggregation of oil within the sorbents. Also, certain sorbent weight loss during washing with n-hexane can be a possible cause of reduction. Similar results have been reported by other workers (Likon et al. 2013; Gulistan et al. 2015).



**Figure 5:** Percentage removal of crude oil by UM and TRMC after three cycles of sorption-desorption experiment

**Table 5.** Thermodynamic parameters for sorption of crude oil by the sorbents

<b>Thermodynamic parameters</b>	<b>UM</b>	<b>TRMC</b>
300 K ( $\Delta G^\circ$ ) (KJ/mol)	- 1.17	- 2.56
313 K ( $\Delta G^\circ$ ) (KJ/mol)	- 1.86	- 3.11
323 K ( $\Delta G^\circ$ ) (KJ/mol)	- 2.33	- 3.73
$\Delta H^\circ$ (KJ/mol)	12.7	17.5
$\Delta S^\circ$ (J/mol K)	48.6	60.4

## Conclusions

The present study revealed that the modified sorbent (TRMC) was more efficient in treatment of oil contaminated solution than unmodified sorbent (UM). Process parameters such as pH, temperature, initial crude oil concentration, and time of contact and dosage of sorbent influence the sorption process significantly. The heterogeneous nature of TRMC was revealed by the Freundlich and scatchard model while UM showed a homogenous surface from Langmuir evaluation. The maximum sorption potential of TRMC was found to be higher than other reported sorbents used for crude oil remediation. The kinetics was more fitted by the pseudo first order model and thermodynamics revealed a physisorption mechanism. The good regeneration of the sorbents using n-hexane and reusability showed the effective of these low cost materials for oil spill cleanup.

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