

Oil Removal from Produced Water Using Surfactant Modified Eggshell

Muhammad, Idris Misau ¹⁺, Usman Aliyu El-Nafaty ¹, Surajudeen, Abdulsalam ¹ and Yusuf Isa Makarfi ²

¹ Department of Chemical Engineering, Faculty of Engineering and Engineering technology, AbubakarTafawaBalewa University, Bauchi-Nigeria

² Chemical Engineering Department, Federal University of Technology, Minna-Nigeria

Abstract. Produced water discharged into surrounding waters and/or oil spillage during transportation, storage, and handling poses a major threat to aquatic life and causes havoc to the environment. This paper aims at reporting a low-cost waste material replacing the expensive chemical dispersant in the removal of oil from oil polluted waters. Eggshell was used as the treating agent by surface treatment or modification with hexadecyl-trimethyl-ammonium-bromide surfactant solution (HDTMA-Br). The surface modified eggshell (SMES) was used in the removal of oil from laboratory synthesized oil-water mixture. At an equilibrium dose of 1600 mg/L, the SMES was able to remove 91.21% of the oil within the first five minutes and the total oil (194mg/L) in 25 minutes. The effect of contact time on oil removal using SMES by batch biosorption was also investigated at constant pH (7.4), stirring speed (700rpm) and temperature (28°C). From the batch sorption study using SMES, data generated were tested on two commonly used isotherms; Freundlich and Langmuir. From the data fit, the Freundlich isotherm fitted better than the Langmuir isotherm. Several other kinetic models were also tested using the time dependent data generated. The pseudo-second order kinetic model fitted the data best with coefficient of regression of 0.965.

Keywords: surfactant, surface modification, eggshell, isotherm, kinetics model.

1. Introduction

Energy is the prime mover for all developed and developing nations. Crude oil is the measure global source of energy. However, its exploration has resulted in serious environmental pollution. These range from air, water, and soil pollutions. The result of crude oil activities leaves most of our surface waters heavily contaminated with several pollutants including dissolved and dispersed oils. These pollutants pose threat to our aquatic life and make our soil infertile. Most of the oil producing companies discharge this produced water to the water bodies without proper treatment. Those treated are partial and not pollutant free. However, there is a regulatory body which controls the discharge of pollutants to the surroundings. This depends upon the set targets.

The result of agricultural activities has resulted in a number of agricultural wastes being thrown away as wastes which eventually litter the environment. Many researchers have reported the use of several bio-waste materials in the conditioning of some pollutants associated with crude oil activities. It was reported that the removal of oil from produced water using raw eggshell was very effective [1]. In their findings, they discovered that raw eggshell effectively removed oil from water at an equivalent dosage of 1800 mg eggshell/liter produced water.

The oil concentration in water was as high as 194 ppm. Sorption of heavy crude, nujol, and Vaseline oils using CPC modified barley straw were investigated. It was discovered that the CPC modified sorbent has different sorption capacity depending upon the sorbate used. The adsorption capacity for heavy crude was

⁺Corresponding author. Tel.: + (2348034293848);
E-mail address: idrismisau@gmail.com

found to be 11.6 mg oil/g sorbent, nujol oil was 4.8 mg oil/g sorbent, while 2.7 mg oil/g sorbent was discovered for Vaseline oil [2]. In the same manner, activated carbon and bentonite were tested in the treatment of palm oil effluent. The researchers found out that activated carbon removed 70% of the palm oil after an hour contact time and 60% removal at a contact time of 30 minutes. On the contrary, bentonite was able to remove 65% and 50% at contact times of 1 hour and 30 minutes respectively [2]. Fatty acid grafted sawdust was used in the treatment of oil spill and 54.2% [3] was the sorption capacity. Carbonized rice husk was used as sorbent for crude oil and 20% sorption capacity was recorded by the researchers [4]. Canola and cutting oils were removed using walnut shell achieving sorption capacities of 0.51 mg canola oil/g walnut shell and 0.58 mg cutting oil/g walnut shell [5]. Carbonaceous hibiscus cannabilus L. was used to remove diesel and cooking oils realizing sorption capacities of 35 and 30 mg oil/g sorbent respectively [6]. In the removal of canola oil using raw and surfactant modified barley straw were able to achieve 90.5% and 90.7% respectively [7]. This indicates that surfactant modification of the barley straw did not bring appreciable increase in the sorption capacity. High calcium fly ash was tested in the removal of crude oil from spill and were able to record a sorption capacity of 1.5 mg oil/g sorbent [8]. In the treatment of oilfield produced water used activated carbon and bentonite and found out that 93.54% of the oil was removed by activated carbon while 98.30% was removed by bentonite under the same conditions [9]. Rice husk was used as sorbent and was reported to have a sorption capacity of 5 mg diesel oil/g sorbent [10]. Fatty acid grafted banana trunk was used as sorbent for kerosene oil. 12.30 mg oil/g sorbent [5]. Banana pseudostem fiber was tried in the treatment of palm oil effluent. It was reported to have a sorption capacity of 97.8% [11].

In Nigeria, the riverine areas, especially where petroleum exploration activities are currently taking place, most of the waters are polluted with oil resulting from either pipeline vandalisation or discharge of produced water into the water streams. The treatment process employed by the oil companies are either not effective or sometimes dangerous to the aquatic life and affect food (cold food) production. The purpose of this article is to report on the discovery of converting waste to wealth in the treatment of oil from oil polluted water. We have earlier on reported the use of raw eggshell in removal of oil from produced water. This paper reports the oil removal using surfactant modified eggshell and the findings as to whether or not it can be utilized for general purpose treatment.

2. Materials and Method

2.1. Materials

Eggshells were collected from Yelwa, quarters, Bauchi Nigeria. Crude oil was obtained from Kaduna Refinery and Petrochemical Company, Kaduna-Nigeria. 1,1,1-tri-chloroethane was purchased from Chuzz Bond International, Jos-Nigeria and cationic surfactant (HDTMA-Br) was imported from Suzhou Enhao Trade Limited, China. All chemicals/reagents were of analytical grade. Distilled water was produced in Gubi Dam Water Treatment Plant Laboratory, Bauchi-Nigeria. The oven was used to dry the sorbent materials was manufactured by Regaterm, Italy. Separating funnels were used to extract the oil from water and DR/2000 spectrophotometer (HACH, Colorado, U. S. A) was used to quantify the oil content in the extract. Hanna pH meter was used to determine the pH of the mixture. A JJ-4 Six couplet digital electric mixer (Search Tech Instrument, England) was used for the sorption study. Laboratory mortar and pestle were used to convert the eggshell to powder and sieve was used to collect a fraction of 212 microns. A Perkin Elmer Spectrum 100 FTIR spectrometer was used for the infra-red spectroscopic studies at wave numbers 4000-400 cm^{-1} . The X-ray diffractometry was done on a BRUKER AXS D8 Advance (Cu-K α radiation $\lambda_{\text{K}\alpha_1}=1.5406\text{\AA}$) 40 kV. The Hitachi X-650 Scanning Electron Microscope (Tungsten filament, EHT 20.00kV) and LEO 1450 Scanning Electron Microscope (Tungsten filament, EHT 20.00kV) were used for the SEM imaging. The chemical composition was determined using energy dispersive spectroscopy (EDS) and surface area and pore sizes were determined using TriStar 3000 V6.05.

2.2. Methods

2.2.1. Eggshell preparation

Eggshell was first crushed, washed with water several times and then sun-dried. The dried eggshell was further ground, sieved through 212-63 microns sieve and washed with distilled water till negligible turbidity. 0.1 molar solution of hexadecyl-trimethyl-ammonium-bromide (HDTMA-Br) was prepared and the washed eggshell powder mixed with it for an hour contact time. This was washed severally to remove any unbound HDTMA-Br from the surface. The washed eggshell was then dried in an oven at temperature of 70°C for 24 hours and later stored in air tight sealed plastic containers as surfactant modified eggshell (SMES).

2.2.2. Batch adsorption experiment

The experiments were carried out by taking 300 mL of 194 mg/l produced water and different quantities of SMES in a 600 ml beaker. The contents were then agitated at 700 rpm for 30 minutes using mechanical shaker at room temperature. The biosorbent and sorbate were separated using a 63 micron sieve. Studies on the effects of agitation time, and biosorbent dose were carried out by using known amounts of biosorbent of size 212-63 microns. Oil solutions (300 mL) with different amounts of biosorbent were taken to study the effect of adsorbent dosage on the removal of oil. The biosorption experiments were carried out at room temperatures.

The laboratory synthesized produced water (oil-in-water mixture) was prepared by mixing crude oil with distilled water. The pH was kept constant during the experiment. The prepared oil-water mixture samples were treated differently with various quantities of SMES for a period of 30 minutes and a stirring speed of 700 rpm. At the end of the treatment, SMES was removed from the oil/water mixture by passing through 63microns sieve; the residual oil in the water was determined using 1-1-1-tri-chloroethane as solvent. The extract was analyzed for oil content using HACH DR/2000 spectrophotometer at a wavelength of 450 nm. The test was repeated until optimum loading point was identified. With the optimum loading kept constant, the time was varied to determine the effect of contact time on the batch sorption study.

2.2.3. Characterization

The surfactant modified eggshell (SMES) biosorbent was characterized using FT-IR and BET in order to identify the functional groups and to measure the surface area respectively.

3. Results and Discussions

3.1. Characterization using FTIR

FTIR spectroscopy method was used to show the functional groups present on the surface of the bio-waste. Many functional groups were present on the material surfaces. All assignments to peaks were made according to Coates [12]. The SMEB was observed to have a shift between 409-465 cm^{-1} which was attributed to polysulfide (S-S stretch), at 544-583 cm^{-1} aliphatic iodo-compounds. At 716 cm^{-1} , the peak was assigned to aliphatic chloro-compounds while the peak at 877 cm^{-1} was assigned to aromatic C-H out-of-plane bend. Absorption at 1356 cm^{-1} was assigned to primary or secondary OH in plane bend. In the same manner, there was a peak at 1428 cm^{-1} which was assigned to phenol or tertiary alcohol (-OH) bend. At 1572 cm^{-1} the peak was assigned to carboxylic acid salt and alkenyl C=C stretch was assigned to peak at 1664 cm^{-1} . A peak was observed at 1985 cm^{-1} which was assigned to aromatic combination band. At 2046 cm^{-1} , the observed peak was as a result of CO bending in which the peak at 2188 cm^{-1} was as a result of C≡C stretching. Sulphite vibration (S-H) was observed at 2516 cm^{-1} and at 3040 cm^{-1} C=C-H for unsaturated or aromatic ring vibration was observed to be the cause of the peak. At 3295 cm^{-1} the peak observed was due to hydroxyl group H-bonded OH stretch.

3.2. Surface area measurement

The Surface area of the modified eggshell (SMES) was measured using Brunauer, Emmett, and Teller, method (BET) and was found to be 0.0232 m^2/g . Surface area measurement by Langmuir method revealed the area to be 0.0261 m^2/g with a pore volume 0.00218 cm^3/g , and a pore size of 484.8494 nm. As reported by [1], the surface area of raw eggshell was 0.002357 m^2/g . It could be seen that surface modification of eggshell increased the surface area about 10 fold. This modification could be vital considering that surface area is an important factor in sorption processes.

3.3. Sorption experiment

Table 1 presents the results obtained from batch studies undertaken with SMES at a stirring speed of 700 rpm, pH of 7.4 and room temperature. It could be seen that the equilibrium dosage for complete removal of oil from the water was 1600 mg oil/g SMES. This value when compared to the one obtained from sorption using raw eggshell by [1] for complete oil uptake as 1800 mg oil/g eggshell. This showed that SMES has better efficiency compared with raw eggshell.

Table 1: Determination of maximum loading of SMES on oil removal from produced water

Dosage, (mg)	Residual oil C_e (mg/l)	Oil removed X, (mg)	Oil Removal (%)
0.00	194.00	0.00	0.00
200.00	79.00	115.00	59.27
400.00	75.00	119.00	61.34
600.00	49.00	145.00	74.74
800.00	20.80	173.20	89.27
1000.00	17.00	177.00	91.23
1200.00	13.00	181.00	93.29
1400.00	2.20	191.80	98.86
1600.00	0.00	194.00	100.00
1800.00	0.00	194.00	100.00

3.4. Equilibrium modeling

The equilibrium sorption isotherm is fundamentally important in the design of biosorption systems. Equilibrium studies in biosorption gives the capacity of the sorbent adsorbed. It gives a relationship between sorbent and sorbate are described by adsorption isotherms, usually the ratio between the quantity sorbed and that remaining in the solution at a fixed temperature at equilibrium [13].

3.4.1. The freundlich isotherm

Freundlich presented the earliest known sorption isotherm equation [14]. This empirical model has been applied to non-ideal sorption on heterogeneous surfaces as well as multilayer sorption [15]. The Freundlich isotherm model is the well-known earliest relationship describing the adsorption process. This model applies to adsorption on heterogeneous surfaces with the interaction between adsorbed molecules; the application of the Freundlich equation also suggests that sorption energy exponentially decreases on completion of the ‘sorptional centers’ of an adsorbent. This isotherm is an empirical equation and can be employed to describe heterogeneous systems and is expressed as follows:

$$q_e = a_f C_e^{b_F} \quad (1)$$

where, q_e is the amount of adsorbate adsorbed at equilibrium (mg/g) calculated from equation 6, a_f Freundlich isotherm constant; C_e solution phase oil concentration at equilibrium, mg dm^{-3} ; and b_F is the heterogeneity parameter. Although, the smaller the value of b_F , the greater the expected heterogeneity. Freundlich equation is strictly valid only for ion adsorption at low concentration. The Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution. It is often criticized for lacking a fundamental thermodynamic basis since it does not reduce to Henry’s law at low concentrations. The linearized Freundlich equation was used (Eq. 2) for the SMES with the generated data from Table 1 and Fig. 1 resulted. The n or $1/b_F$ value indicates the degree of non-linearity between solution concentration and adsorption as follows: if $1/b_F = 1$, then adsorption is linear; if $1/b_F < 1$, then adsorption is a chemical process; if $1/b_F > 1$, then adsorption is a physical process [16].

$$\ln q_e = \ln a_f + b_F \ln C_e \quad (2)$$

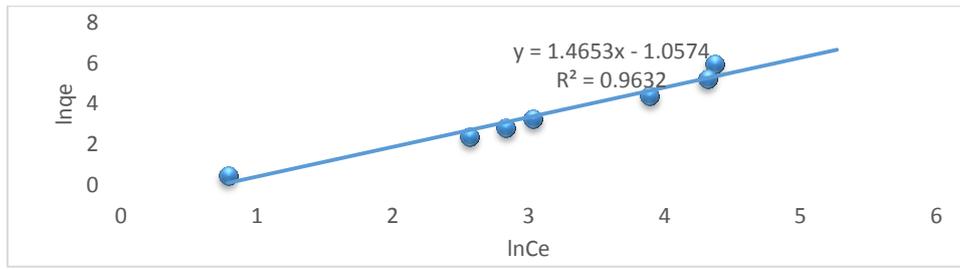


Fig. 1: Freundlich plot of SMES

3.4.2 The langmuir isotherm

The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. Once a site is filled, no further sorption can take place at that site. As such the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved. The Langmuir adsorption isotherm equation was initially developed to describe the adsorption of gases onto clean solids. It is often used to describe the sorption of solute from solution. This equation can be derived theoretically based on evaporation and condensation rates. The Langmuir isotherm equation is (Eq. 3):

$$q_e = \frac{k_L b C_e}{1 + k_L C_e} \quad (3)$$

where, b is the Langmuir constant related to the energy of biosorption (L/mg), k_L is the maximum sorption capacity corresponding to complete monolayer coverage (mg/g), and C_e is the equilibrium solute concentration (mg/L). The Langmuir adsorption isotherm can be transformed to linear form thereby allowing the parameters to be estimated graphically or with linear regression.

$$\frac{C_e}{q_e} = \frac{1}{k_L b} + \frac{1}{k_L} C_e \quad (4)$$

The favorable nature of adsorption can be expressed in terms of dimensionless separation factor of equilibrium parameter, R_L which is defined by Eq. (5)

$$R_L = \frac{1}{1 + b C_0} \quad (5)$$

where, C_0 is the highest initial solute concentration, b the Langmuir's adsorption constant (L/mg). The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). R_L is a positive number whose magnitude determines the feasibility of the adsorption process [17].

where, C_e is the equilibrium concentration of the sorbate (milligrams per liter), q_e is the amount of sorbate per unit mass of biosorbent (milligrams per gram), k_L is a constant representing the strength with which the solute is bound to the substrate (L/mg) and b is the adsorption capacity of the substrate (gram solute/gram adsorbent). When $\frac{C_e}{q_e}$ was plotted against C_e for SMES a straight line with slope $\frac{1}{k_L}$ was obtained and an intercept $\frac{1}{b k_L}$ as in Figure 3 while q_e is expressed as given in Eq. 6

$$q_e = \frac{V(C_i - C_e)}{m} \quad (6)$$

where, V is the biosorption volume (liters), C_i is the initial concentration of the sorbate (milligrams/liter), and m is the mass of biosorbent (gram). Use of Langmuir isotherm implies a finite number of uniform

adsorption sites and absence of lateral interactions. Using the Langmuir reciprocal plot (Eq. 4) the data generated were fitted into the linear isotherm for SMES (Fig. not shown).

Table 2: Freundlich and Langmuir constants determined from the isotherms plotted and evaluated parameters

Isotherm	R ²	Slope	Intercept	b _F	n	k _L	b	R _L
Freundlich	0.963	1.465	-1.057	0.347	2.882	-	-	-
Langmuir	0.919	-69	91.77	-	-	-0.014	-1.579E-4	1.0001

From Table 2, the values of coefficient of regression analysis (R²) showed that the generated data from the sorption experiment fitted better in the Freundlich isotherm 0.963 as against the Langmuir isotherm plot (0.919). From the evaluated value of degree of non-linearity (n), sorption with SMES is a physical process and the oil can be recovered. The value of dimensionless separation factor (R_L) from the Langmuir isotherm, an indication that the sorption is unfavorable since R_L is greater than 1.

3.5. Effect of contact time

The effect of contact time on biosorption of oil from produced water by surfactant modified eggshell at C_o = 194 mg/L for optimum biosorbent dosage was studied. It was observed that rapid biosorption of oil takes place within the first 5 minutes and thereafter, the rate of biosorption decreases gradually and reaches equilibrium in about 25 min. About 91.21% of oil removal was obtained in the first five (5) minutes. This may be due to strong attractive forces between the oil molecules and the adsorbent. Fast diffusion on the external surface was followed by fast pore diffusion into the intra particle matrix to attain rapid equilibrium [18]. Further increase in contact time showed gradual decrease in the oil removal until equilibrium was reached or total oil removal took place. Table 3 depicts the results obtained after determining the optimum time for oil using SMES.

Table 3: Equilibrium time oil sorption for SMES

Time (min)	Oil concentration C _e (mg/L)
0	194.00
5	17.05
10	10.66
15	4.26
20	2.20
25	0.00

3.6. Adsorption kinetics

Many kinetic models have been proposed to elucidate the mechanism of solute adsorption. These kinetic models are useful for the design and optimization of effluent treatment processes.

In order to investigate the mechanism of oil biosorption by SMES, the following kinetic models were considered. Pre-equilibrium kinetic profiles were characterized in order to determine the rate limiting steps involved in the process of biosorption of oil onto SMES. The first order (Eq. 7), Lagergren pseudo-first order (Eq. 8), second order (Eq. 9), pseudo-second order (Eq. 10) and Elovich (Eq. 11) kinetic models were applied. In the biosorption of nickel on spent activated clay [19], reactive black 5 dye by *Aspergillus foetidus* [20] biosorption of Acid Red 57 by dried *Cephalosporium aphidicola* cells [21] and biosorption of Cu²⁺ unto banana peel [22] some of these kinetic models were used.

$$\frac{1}{q_t} = \frac{1}{q_e} + \frac{k_1}{q_e t} \quad (7)$$

Kinetic investigation was done to find the stage which plays a decisive role to the adsorption rate. Therefore, the use of kinetic models to fit the time dependent experimental data is one of important steps for the adsorption study. The first order kinetic model hence, the integrated linear form of pseudo first order kinetic model the model proposed by Lagergren was tried (Eq. 8).

$$\ln(q_e - q_t) = \ln q_e - kt \quad (8)$$

where, q_e is the amount of oil adsorbed at equilibrium (mg/g), q_t is the amount of oil adsorbed at time t (mg/g), k_1 is the first order rate constant (min^{-1}) and t is the time (min). Hence, a linear trace is expected between the two parameters $\log(q_e - q_t)$ and t , provided the biosorption follows first order kinetics. The values of k_1 and q_e can be determined from the slope and intercept. Even though q_e and the R^2 value suggest that the biosorption data badly fitted to pseudo first order kinetics. Hence, the biosorption of oil onto SMES may not follow the pseudo first order rate expression.

The linear plot using the Lagergren pseudo-first order kinetic model (Fig. not shown) becomes worse than the first order kinetic based on their coefficient of regressions. The second order kinetic model was tested on the generated data. The biosorption may also be described by a second order or pseudo second order kinetic model. The linearized form of the second order and pseudo second order models are:

$$\frac{1}{C_e} = k_2 t + \frac{1}{C_0} \quad (9)$$

The data fitted better than the first and pseudo-first order kinetic models. These can be seen from their R^2 values. The R^2 value for the second order kinetic was 0.885 and greater than the previously tested kinetic models. The pseudo-second order kinetic model can also be used to test the data generated (Eq. 10).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e t} \quad (10)$$

where, k_2 is the second order rate constant (g/mg min). A plot of $1/q_e$ vs t and t/q_t vs t should be linear if the adsorption follows second order or pseudo-second order. q_e and k_2 can be calculated from the slopes and intercepts of the plots. The plot of this kinetic is shown in Fig. 7.

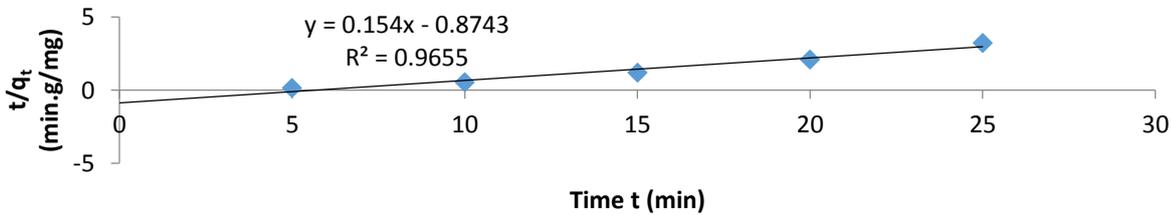


Fig. 2: Pseudo-second-order kinetic of SMES

As seen from the plot (Fig. 2), the R^2 value is very much appreciable ($R^2=0.965$). This showed that the data generated from the use of SMES on the removal of oil fitted into the pseudo-second order kinetic model. However, in order to see if a better fitted kinetic model, the Elovich model (Eq. 11) was used as in Figure 8. The Elovich model is mainly applicable for chemisorptions processes. The equation is often valid for systems in which the adsorbing surface is heterogeneous. The Elovich model is generally expressed as

$$q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln t \quad (11)$$

where, 'a' is the initial biosorption rate (mg/g min) and b is related to the extent of surface coverage and the activation energy for chemisorptions (g/mg). A plot of q_t vs $\ln t$ gives a straight line with a slope of $1/b$ and an intercept of $1/b \ln(ab)$ with good correlation coefficients.

The R^2 value is less than that of the pseudo-second order plot but better than the remaining models. The constants evaluated from the plot of the models can be seen in Table 4.

Table 4: Evaluated constants obtained from the kinetic models tested

Kinetic model	R ²	Slope	Intercept	Rate constant	Other constants
First order	0.821	-0.554	0.129	-4.295	q _e =7.752
Pseudo-first order	0.795	0.012	4.452	0.012	q _e =1.493
Second order	0.885	0.021	-0.045	0.021	C ₀ =22.222
Pseudo-second order	0.965	0.154	-0.874	-48.237	q _e =6.493
Elovich	0.946	-15.900	58.070	b=-0.063	a=20.556

4. Conclusion

SMES was used in the removal of oil from laboratory synthesized oil-water mixture. It was found that SMES was an effective sorbent for oil. At an equilibrium dose of 1600 mg/L, the SMES was able to remove all oil present in water as high as 194 mg/L in 25 minutes. During the first five minutes, 91.21% of the oil was removed. The effect of contact time on oil removal using SMES was investigated. From the sorption study using SMES, data generated were tested on the two commonly used isotherms of Freundlich and Langmuir. From the data fit, Freundlich isotherm fitted the data very well as against the Langmuir. The various isotherm constants were evaluated and were compared with values obtained by [1]. It was finally concluded that sorption with SMES is a physical process from the evaluated value of degree of non-linearity ('n') from the Freundlich isotherm. The effect of modifying the eggshell with HDTMA-Br reduces the loading of the sorbent and increased its surface area. Several kinetic models were tested using the time dependent data generated. The pseudo-second order kinetic model fitted the data best with coefficient of regression 0.965. All rate constants and other kinetic constants from the models were evaluated. The kinetic rate constant for the best fitted model was -48.237 g/mg min and the value of q_e was 6.493 mg/g. SMES has proven to be a good oil sorbent provided the concentration did not exceed 194 mg/L in water. Hence, it could be suitable for use in the treatment of produced water.

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