

## Removal of Oil from Oil Produced Water Using Eggshell

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### Abstract

The presence of dissolved crude oil in water poses significant environmental hazards to aquatic lives. Components of dissolved oil, BTEX which are carcinogenic can cause cancer after a long time of exposure. Eggshell, a potential biosorbent was used to remove both dissolved and dispersed oil in produced water. It was conditioned to provide good oil uptake in its natural form. The biosorbent material was characterized using FT-IR, SEM, XRD, BET and EDS techniques. The results showed that eggshell contains calcium, carbon and oxygen in proportions of 37.4, 48.5 and 14.1 atomic percent respectively. Biosorption experiments with the eggshell biosorbent showed that it can be used for crude oil removal from produced water providing almost 100% at concentration of 1.8 g eggshell/L of produced water and oil concentration as high as 194 mg/l. Several kinetic models were tested and it was discovered that the biosorbent followed pseudo-second order biosorption kinetics. The value of  $q_e$  deduced from the slope of the curve was 108.69 mg/g and the value of rate constant ( $k_2$ ) was found to be 0.019  $\text{g.mg}^{-1}\text{min}^{-1}$ . This result showed that eggshell is a good biosorbent for crude oil removal in produced water. It will provide a cheap way of cleaning oily contaminated water environment thus safeguarding human health, aquatic lives, and soil fertility.

**Keywords:** eggshell, oil removal, produced water, environment, biosorption, biosorbent

### 1.0 Introduction

With the ever-increasing use of water for municipal and industrial purposes, it has become necessary to appraise water quality on a continuous basis. Water treatment process selection is a complex task involving consideration of many factors which include, available space for the construction of treatment facilities, reliability of process equipment, waste disposal constraints, desired finished water quality and capital and operating costs. The treatment of wastewaters to make them suitable for subsequent use requires physical, chemical and biological processes. A number of technologies are available with varying degree of success to control water pollution. Some of them are coagulation, foam flotation, filtration, ion exchange, aerobic and anaerobic treatment, advanced oxidation processes, solvent extraction, adsorption, electrolysis, microbial reduction, and activated sludge. However, most of them require substantial financial input and their use is restricted because of cost factors overriding the importance of pollution control (Bhatnagar and Sillanpää, 2010). Among various available water treatment technologies, adsorption process is considered better because of convenience, ease of operation and simplicity of design.

Oil is one of the most important energy sources in the developed world. However, oil spill accidents often take place during the oil utilization process, resulting in energy loss as well as threats to the environment (Lin *et al.*, 2011). Oil transportation is a risky business and oil spills require immediate attention. It is important that after an oil spill the marine cleanup operation should collect or adsorb quickly a major part of the oil spilled, especially in coastal areas. Oil-polluted water often contains other substances as well as oil (Pasila, 2004). Therefore the existing cleaning processes are complex and may consist of different water purification units.

Oil and chemical spill accidents can be caused by human mistakes and carelessness, deliberate acts such as vandalism, war and illegal dumping, or by natural disasters such as hurricanes or earthquakes (Angelovaa *et al.*, 2011). Offshore and shoreline waters can be polluted by oil drilling operations, accidents involving oil tankers, runoffs from offshore oil explorations and productions, and spills from tanker loading and unloading operations. Massive marine oil spills have occurred frequently and resulted in a great deal of damage to the marine, coastal and terrestrial habitats, economical impacts on fisheries, mariculture and tourism, and loss of energy source. Inland water bodies can be polluted by leaking of oil through pipelines, refineries, and storage facilities, runoff from oil fields and refinery areas and, in some cases, process effluent from petroleum refineries and petrochemical plants.

A number of materials have been extensively investigated as adsorbents in water pollution abatement. Some of the important ones include silica gel, activated alumina, zeolites and activated carbon (Khaled *et al.*, 2011). One of the most economical and efficient methods for combating oil spills is oil removal by sorbents. Oil sorbents are able to concentrate and transform liquid oil to the semi solid or solid phase, which can then be removed from the water and handled in a convenient manner without significant oil draining out. The preferable sorbent materials are those which, besides being inexpensive and readily available, demonstrate fast oil sorption rate, high oil sorption capacity (oleophilicity or

lipophilicity), low water pickup high oil retention capacity during transfer, high recovery of the absorbed oil with simple methods, good reusability, high buoyancy, and excellent physical and chemical resistances against deformation, photodegradation, and chemical attacks.

There are three major classes of oil sorbents, namely, inorganic mineral products, organic synthetic products and organic natural products (Lim and Huang, 2007). At present, most of the commercially available oil sorbents are organic synthetic products such as polypropylene (PP) and polyurethane (Gao *et al.*, 2011). However, they are non-biodegradable and can be difficult to deal with after use due to their xenobiotic nature (Lin *et al.*, 2011). The mineral products used as oil sorbents include perlite, exfoliated graphite, vermiculites, organoclay, zeolite, silica aero gel, and diatomite. Most of them have poor buoyancy and oil sorption capacity. In addition, they are difficult to handle on site due to their granular or powder forms. Most of them also exhibit poor reusability and oil recovery. Due to inadequate hydrophobicity, they may also experience collapse of their microstructure due to sorption of water (Lim and Huang, 2007).

While exfoliated graphite and silica aero gel are excellent oil sorbents, they are fairly expensive. The limitations of the mineral products and organic synthetic products have led to the recent interest in developing alternative materials, especially biodegradable ones such as natural agro-based products. Agricultural products which have good oil absorbency are rice straw (Vlaev *et al.*, 2011), corn cob, peat moss, cotton, cotton grass (Suni *et al.*, 2004), barks, milkweed, kenaf, and kapok (Lim and Huang, 2007). These agricultural products and residues are inexpensive and available locally. Some are waste materials and hence their reuse will result in savings in disposal fee. The cellulosic products which exist in fibrous form can be easily formed into mats, pads, and nonwoven sheets for convenient applications.

In this study, eggshell was used in the biosorption of dissolved and dispersed oils from oil contaminated water. The optimum loading capacity and optimum biosorption time were determined. The egg shell was characterized by FT-IR spectroscopy, scanning electron microscope (SEM), and electron dispersion spectroscopy (EDS) was also used to determine the elemental analysis of the sorbent material. The surface area of the eggshell material was determined using BET method.

## 2.0 Materials

Eggshells were collected from Yelwa, quarters, Bauchi Nigeria. Crude oil was obtained from Kaduna Refinery and Petrochemical Company, Kaduna-Nigeria. Tri-chloroethane was purchased from Chuzz Bond International, Jos-Nigeria. All chemicals/reagents were of analytical grade. Distilled water was produced in Gubi Dam Water Treatment Plant Laboratory, Bauchi-Nigeria. Oven was used to dry the sorbent materials (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 classify it into different sizes (212-63 microns). A Perkin Elmer Spectrum 100 FTIR spectrometer was used for the infra-red spectroscopic studies at wave numbers 4000-400  $\text{cm}^{-1}$ . The X-ray diffractometry was done on a BRUKER AXS D8 Advance (Cu-K $\alpha$  radiation  $\lambda K\alpha_1=1.5406\text{\AA}$ ) 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 A BET equipment.

## 3.0 Methods

### 3.1 Biosorbent Preparation

REB 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 till negligible turbidity. The washed eggshell was then dried in an oven at temperature of 70°C for 24 hours which was then stored in air tight sealed plastic containers.

### 3.2 Characterization

The egg shell biosorbent was characterized using FT-IR, SEM, and EDS. The spectrograms were presented in figures 1, 2, and 3 respectively.

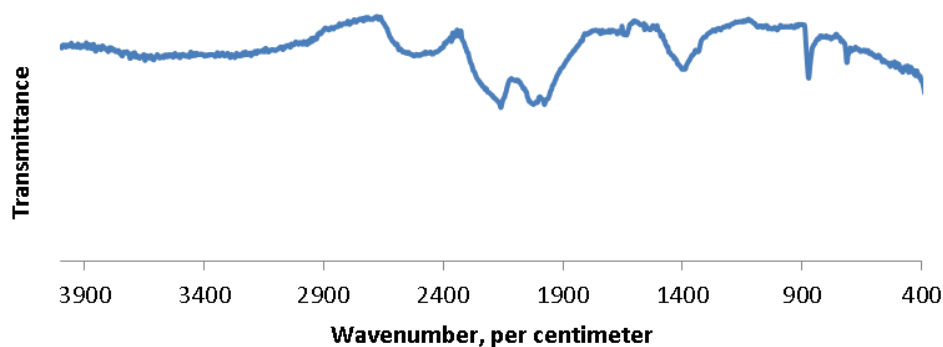


Figure 1: FT-IR Spectrum of REB

FTIR spectroscopy method (Figure 1) was used to show the functional groups present on the surface of the bio-wastes. As could be seen from the FTIR spectra, many functional groups were present on the material surfaces. All assignments to peaks will be made according to Coates, (2000). Looking at the eggshell spectra, it shows that there is a band shift at  $661\text{ cm}^{-1}$  and was assigned to C-OH stretching, at  $715\text{ cm}^{-1}$  was assigned to C-H out of plane bend or long linear aliphatic chain, at  $876\text{ cm}^{-1}$ , the absorption was assigned to skeletal C-C vibrations. The absorption at  $1423\text{ cm}^{-1}$  was assigned to C=C stretching in aromatic ring carbonate ion, while  $1684\text{ cm}^{-1}$  was assigned to C=C stretching. Absorption at  $1993\text{ cm}^{-1}$  was assigned to aromatic combination band. At  $2050\text{ cm}^{-1}$  the absorption was associated with CO group. Absorption took place at  $2187\text{ cm}^{-1}$  and was associated with C=C stretching while absorption at  $2570\text{ cm}^{-1}$  was associated with hydrides vibration. The absorption at  $2714\text{ cm}^{-1}$  was assigned to C-H stretching and that of  $2995\text{ cm}^{-1}$  was as a result of C-H stretching of aliphatic compounds.

Dissolved oil from the produced water (BETX) polarizes in water. The charged particles initiate a reaction by opening the double bonds in the eggshell structure and exchange their ions to neutralize the charges. Where the pollutants do not dissociate in solution, adsorption is by affinity of the surface to bind with the pollutant through the porous structure of the sorbent material.

Elemental analysis using electron dispersion spectroscopy, the egg shell was found to contain Carbon, Oxygen, and Calcium only in proportion stipulated in Table 4. The spectroscopy is as shown in Figure 2.

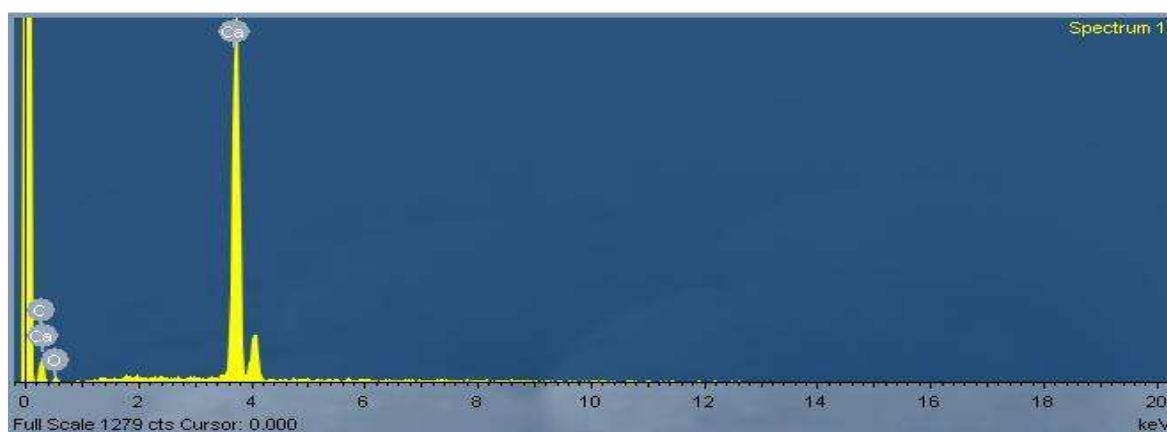


Figure 2: Electron Dispersion Spectrum of Egg shell Biosorbent

Electron dispersion spectroscopy (EDS) analysis of the eggshell (Figure 2) reveals that the chemical compositions and available on the surface were carbon (C) has 48.5 atomic %, 14.1% atomic oxygen (O), and 37.4% atomic calcium (Ca) as summarized in Table 1.

**Table 1: Elemental analysis of egg shell biosorbent**

Element	Weight, g	Weight %	Atomic %
C	1.85	25.31	48.50
O	0.71	9.71	14.10
Ca	4.75	64.98	37.40
Totals	7.31	100	100

It is always better for sorption studies to investigate the surface morphology of the sorbents under high magnification as it plays a vital role in knowing the presence of pores that can allow sorption to take place in a substance. This was made possible using scanning electron microscope under 16000 magnifications. Eggshell is a semi permeable bio-membrane with an intricate poly porous structure. As can be seen in Figure 3, the SEM image shows that it is a micro porous network with pore diameters of 1.5-10  $\mu\text{m}$  as explained by Liu, *et al.*, (2005). For the present study, it consisted of pores from 8-17  $\mu\text{m}$  in diameter and which is composed of interlaced protein fibres with an average diameter of about 2  $\mu\text{m}$ . Most of the eggshell material is  $\text{CaCO}_3$  which account for about one tenth of the egg's weight. Surface areas were measured and found to be ranging from 9-28 micrometer square. Particle sizes were determined and were found within the range 23.739-42.687 micrometer and area range of 25-44 micrometer.

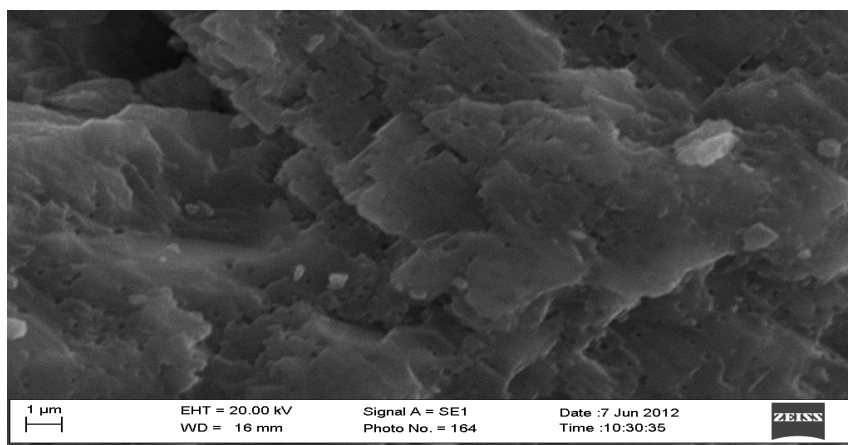


Figure 3: Scanning Electron Microgram of egg shell Biosorbent

### 3.3 Batch adsorption experiments

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

#### 3.3.1 Sorption Experiment

The laboratory synthesized produced water (oil-in-water mixture) was prepared by mixing crude oil with distilled water and its pH was measured. pH was kept constant during the experiment. The already prepared oil-water mixture was treated differently with various quantities of REB for a period of 30 minutes and a stirring speed of 700 rpm. At the end of the treatment, REB was removed from the oil/water mixture by passing through 63microns sieve and 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. The results are presented in Table 2. With the optimum loading kept constant, the time was varied to determine the optimum time of the sorption study and the results are presented in Table 3.

## 4.0 Results and Discussion

### 4.1 Results

Tables 2 and 3 present the results obtained on biosorption of oil from water using REB.

**Table 2: Experimental values for oil biosorption using REB**

Biosorbent dosage M, (mg)	Residual oil C <sub>e</sub> (mg/l)	Amount of oil removed X, (mg)	Oil Removal (%)
0	194	0	0
200	43	151	77.83
400	41	153	78.86
600	34.2	159.8	82.37
800	30	164	84.53
1000	20.8	173.2	89.27
1200	6	188	96.90
1400	6	188	96.90
1600	4	190	97.93
1800	0	194	100.00
2000	0	194	100.00

**Table 3: Variation of oil biosorption with time using optimum loading dosage of REB**

Sorption time t, (min)	Residual oil C <sub>e</sub> (mg/l)	Amount of oil removed X, (mg)	Oil Removal (%)
0	194	0	0
5	17.05	176.95	91.21
10	12.79	181.21	93.41
15	10.66	183.34	94.51
20	4.26	189.74	97.80
25	0.00	194.00	100.00
30	0.00	194.00	100.00

## 4.2 Adsorption isotherm

Among several models that have been published in the literature to describe experimental data of adsorption isotherms, Langmuir, Freundlich, Temkin-Pycher, and Dubinin-Radushkevich isotherm models were used to describe the data generated.

### 4.2.1 Langmuir isotherm

The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent, and it has been used successfully for many adsorption processes of monolayer adsorption. The linearized Langmuir equation is:

$$\frac{1}{q_c} = \frac{1}{q_0} + \frac{1}{b \cdot C_e} \quad \text{--- 1}$$

Where, C<sub>e</sub> is the equilibrium concentration of the adsorbate (mg/L), q<sub>c</sub> is the amount of adsorbate adsorbed per unit mass of adsorbate (mg/L) and q<sub>0</sub> and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. As required by equation (1), plotting  $\frac{1}{q_c}$  against  $\frac{1}{C_e}$  does not give straight line (Figure 4), indicating that the biosorption of oil on raw eggshell biosorbent (REB) did not follow the Langmuir isotherm. The Langmuir constants ‘b’ and q<sub>0</sub> were evaluated and their values recorded in Table 4.

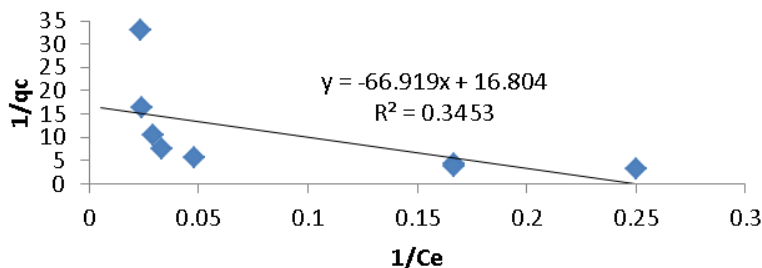


Figure 4: Langmuir isotherm of REB

The fact that the Langmuir isotherm did not fit well in the experimental, biosorption on REB may not be a homogeneous distribution of active sites on the REB biosorbent surfaces.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter,  $R_L$  which is defined by.

$$R_L = \frac{1}{1 + bC_0} \quad \dots 2$$

Where,  $C_0$  is the highest initial solute concentration, 'b' the Langmuir's adsorption constant (L/mg). The value of  $R_L$  indicated the type of the isotherm to be either unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favourable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ).

#### 4.2.2 Freundlich model

The Freundlich isotherm which is an empirical equation used to describe heterogeneous systems can be expressed in its logarithmic form as:

$$\log_e(q_c) = \frac{1}{n} \log_e C_e + \log_e k_f \quad \dots 3$$

Where,  $K_f$  and  $1/n$  are Freundlich constants related to adsorption capacity and adsorption intensity of the biosorbent respectively.  $q_c$  is the amount adsorbed at equilibrium (mg/g),  $C_e$  is the equilibrium concentration of the adsorbate. The values of  $K_f$  and  $\frac{1}{n}$  are calculated from the intercept and slope respectively and are recorded in Table 3. The plot of  $\log q_c$  versus  $\log C_e$  gave straight line (Figure 5) with correlation coefficients 0.7483 showing that the biosorption of oil follows the Freundlich isotherm more closer than that of the Langmuir isotherm.

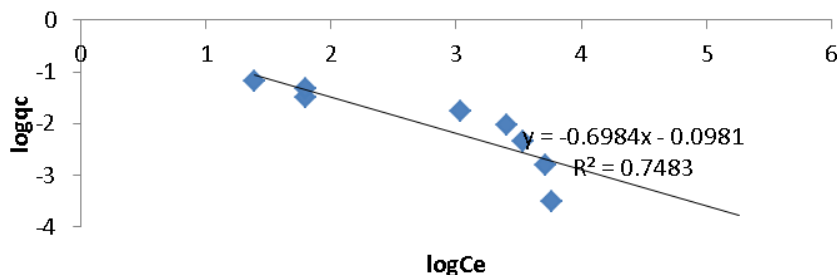


Figure 5: Freundlich isotherm of REB

#### 4.2.3 Dubinin – Radushkevish isotherm

The Dubinin – Radushkevish isotherm was chosen to estimate the characteristics porosity of the biomass and the apparent energy of adsorption. The model is represented as:

$$q_c = q_D \exp \left( - B_D [RT \ln (1 + 1/C_{e,q})]^2 \right) \quad \dots 4$$

Where,  $B_D$  is related to the free energy of sorption per mole of the sorbate as it migrates to the surface of the adsorbent from infinite distance in the solution and  $q_D$  is the Dubinin-Radushkevich isotherm constant related to the degree of sorbate sorption by the biosorbent surface. The Linear form of equation (5) is given as:

$$\ln q_c = \ln q_D - 2B_D RT \ln (1 + 1/C_e) \quad \dots 5$$

The plots of  $\ln q_c$  against  $RT \ln(1 + 1/C_e)$ , yielded a straight line and indicates a good fit of the isotherm to the experimental data. The values of  $q_D$  and  $B_D$  calculated from the intercepts slopes of the plots respectively are shown on Table 4. The apparent energy (E) of adsorption from the Dubinin-Radushkevich isotherm was calculated using equation (6) and found to be 65.5403. The higher the values of  $q_D$ , the higher the adsorption capacity and the better are the biosorbents (Venkateswaran and Parimaladevi, 2011).

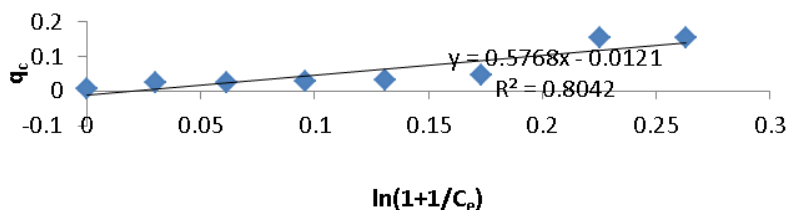


Figure 6: Dubinin-Radushkevich isotherm for REB

$$E = 1/(2B_D)^{1/2} \quad \dots 6$$

#### 4.2.4 The Temkin Isotherm

The derivation of the Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm has generally been applied in the following form (Ho *et al.*, 2001):

$$q_c = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e \quad \dots 7$$

Where, R is the universal gas constant, T is the absolute temperature, A and b are constants based on the biosorbent. A plot of  $q_c$  vs  $\ln C_e$  is a straight line with slope  $\frac{RT}{b}$  and intercept  $\frac{RT}{b} \ln A$ . The values are deduced from the curve in figure 7.

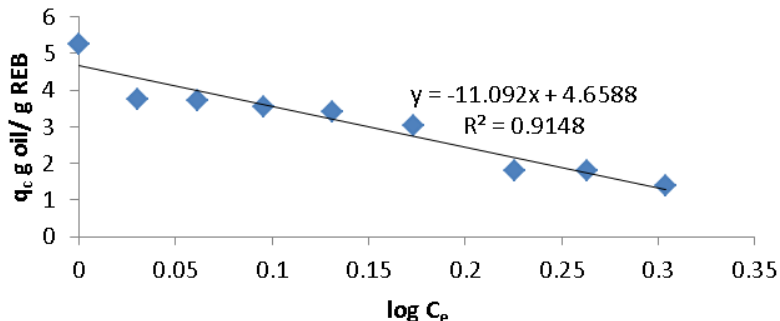


Figure 7: Temkin-Pycher isotherm plot of REB

From Table 4, it can be seen that the data generated in this work fitted in better in the Temkin-Pycher isotherm model with  $R^2=0.9148$  followed with the Dubinin-Radushkevich model ( $R^2 = 0.8042$ ). However, the dimensionless equilibrium parameter ( $R_L$ ) evaluated from equation 2, indicated that a favourable adsorption took place by Langmuir model.

#### 4.3 Kinetics of biosorption

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 process.

In order to investigate the mechanism of oil biosorption by REB, the following five (5) 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 REB. The first order (Eq. 8), Lagergren pseudo-first order (Eq. 9) and pseudo-second order (Eq. 10) kinetic models were applied in the biosorption of nickel on spent activated clay (Mahmoud *et al.*, 2012), reactive black 5 dye by *Aspergillus foetidus* (Patel and Suresh, 2008), biosorption of Acid Red 57 by dried *Cephalosporium aphidicola* cells (Kiran *et al.*, 2006).

$$\frac{1}{q_t} = \frac{1}{q_e} + \frac{k_1}{q_e t}$$

... 8

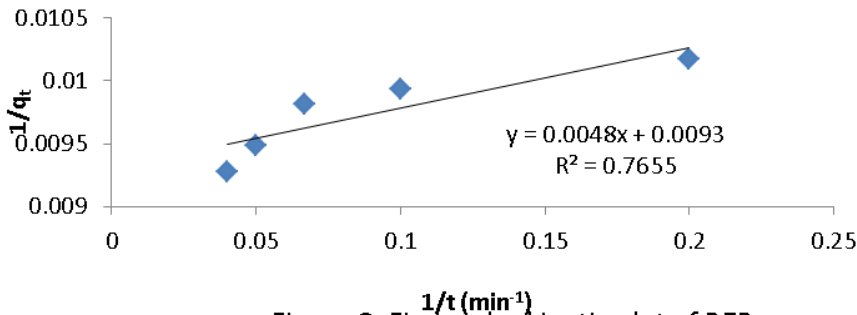


Figure 8: First order kinetic plot of REB

#### 4.3.1 Pseudo first order kinetic model

The integrated linear form of pseudo first order kinetic model the model proposed by Lagergren is

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

... 9

Where,  $q_e$  is the amount of dye 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 ( $\text{min}^{-1}$ ) and  $t$  is the time (min). Hence, a linear trace is expected between the two parameters  $\ln(q_e - q_t)$  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 fitted poor to pseudo first order kinetics. Hence, the biosorption of oil onto REB may not follow the pseudo first order rate expression.

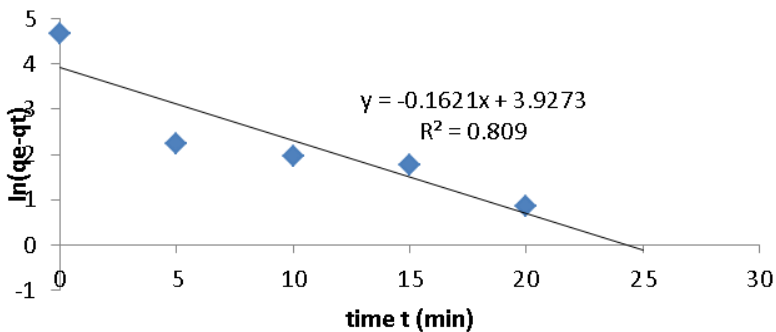


Figure 9: Pseudo-first-order kinetic model of REB

#### 4.3.2 Second order and Pseudo second – order kinetics

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:

$$\frac{1}{q_e} = k_2 t + \frac{1}{q_e} \quad .10$$

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad .11$$

Where,  $k_2$  is the second order rate constant (g/mg min). A plot of  $1/C_e$  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.



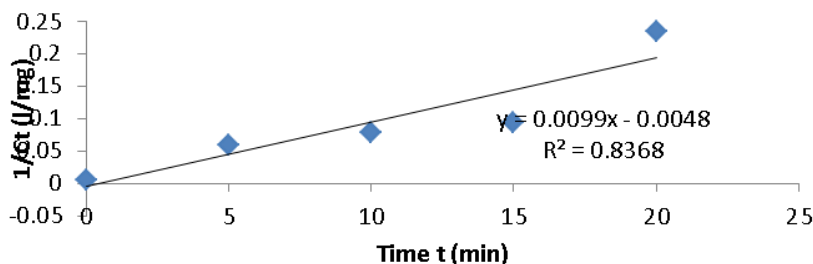


Figure 10: Second Order Kinetic Model of REB

Figure 11, shows the pseudo second order plot for the biosorption of oil by REB at various oil concentrations. The equilibrium sorption capacity,  $q_e$  and initial sorption rate,  $h$  increases and the pseudo second order rate constant decreases with increase in initial oil concentration. From the results it can be suggested that pseudo second order kinetics describes the adsorption of oil by REB much better than pseudo first order model.

Table 4: Evaluated isotherms constants

Isotherm	Slope	Intercept	$R^2$	Constants evaluated							
				$B_D$	A	n	$q_0$	K	b	$R_L$	
Langmuir	-66.919	16.808	0.3453	-	-	-	0.05945	-0.2513	-0.01494	0.07979	
Freundlich	-0.6984	-0.0981	0.7483	-	-	-1.4318	-	1.1031	-	-	
Dubinin-Radushkevich	0.25768	-0.0121	0.8042	1.164E-4			1.01217			-	
Temkin-Pycher	-11.092	4.6588	0.9148		1.522					-223.365	

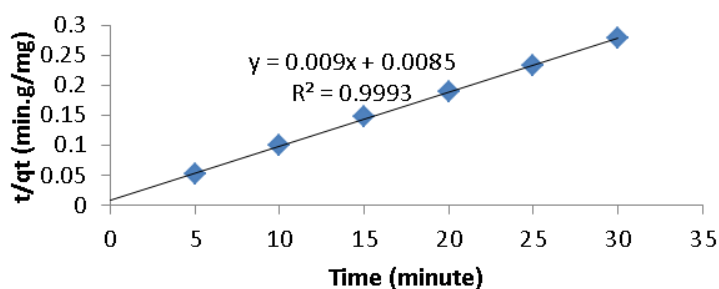


Figure 11: Pseudo-second-order kinetic model of REB

#### 4.3.3 Elovich model

The Elovich equation is mainly applicable for chemisorption process. The equation is often valid for systems in which the adsorbing surface is heterogeneous. The Elovich model is generally expressed as

$$q_t = \frac{1}{b} \ln(ab) - \frac{1}{b} \ln t \quad \dots 12$$

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 chemisorption (g/mg). A plot of  $q_t$  vs  $\ln t$  gave a straight line with a slope of  $1/b$  and an intercept of  $1/b \ln(ab)$  with good correlation coefficients.

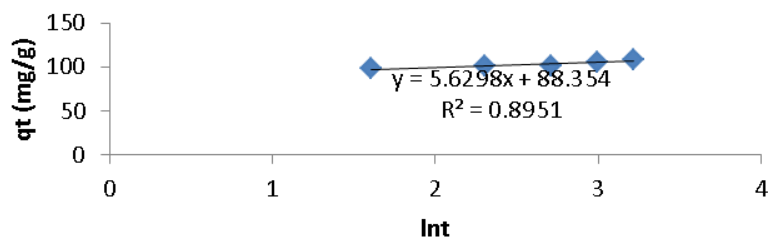


Figure 12: Elovich kinetic model of REB

#### 4.3.4 Intra particle diffusion study

In the batch mode adsorption process, initial adsorption occurs on the surface of the adsorbent. In addition, there is a possibility of the sorbate to diffuse into the interior pores of the adsorbent. Weber and Morris suggested the following kinetic model to investigate the adsorption is intra particle diffusion or not. The relationship may be given as

$$q_t = k_{id} t^{1/2} \quad \dots 13$$

Where,  $k_{id}$  is the intra-particle diffusion rate constant and is calculated by plotting  $q_t$  vs  $t^{1/2}$  (Fig. 10). The linear portion of the plot for wide range of contact time between biosorbent and sorbate does not pass through the origin. This deviation from the origin or near saturation may be due to the variation of mass transfer in the initial and final stages of adsorption. Such a deviation from the origin indicates that pore diffusion is the only controlling step and not the film diffusion.

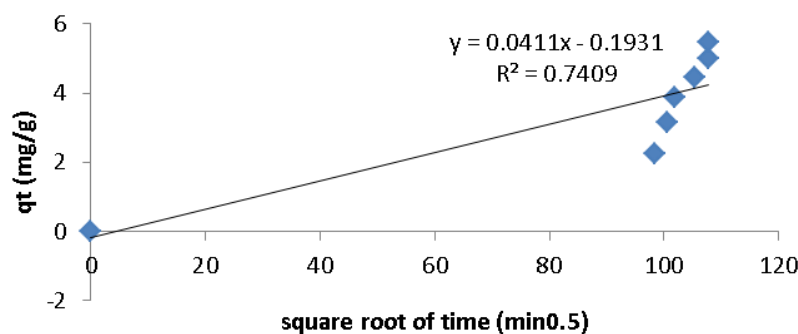


Figure 13: Intra Particle Kinetic Model of REB

Table 5: kinetic parameters of various kinetic models using REB

Kinetics	Slope	Intercept	R <sup>2</sup>	Kinetic constant (k)
First order	0.0048	0.0093	0.7655	82.312
Pseudo-first order	-0.162	3.9273	0.809	0.162
Second order	0.0099	-0.0048	0.8368	0.0099
Pseudo-second order	0.009	0.0085	0.9993	0.00953
Elovich	5.6298	88.354	0.8951	1.162Exp+6
Intra-particle diffusion	0.04111	0.1931	0.7409	0.0411

From Table 5, it can be seen that pseudo-second-order kinetic model has the highest regression coefficient ( $R^2$ ) signifying that the biosorption can well be described by the kinetic model.

#### 5.0 Conclusion

Egg shell was used as biosorbent for oil removal from produced water. Various isotherms and kinetic models were tested with the data generated. The sorption from the isotherm studies showed that it was a favourable biosorption as indicated by the value of  $R_L$  ( $0 < R_L < 1$ ) from the Langmuir isotherm study (0.07979). However, the study does not favour mono layer as suggested by the Langmuir isotherm. The isotherm study showed that Temlin-Pycher isotherm is the most favourable isotherm with  $R^2 = 0.9148$ . Several biosorption kinetic models were tested. The most favourable kinetic model is pseudo-second order with initial oil take up of  $117.647 \text{ mg.g}^{-1}\text{min}^{-1}$ . The REB proved to be effective in oil clean off from water as it

virtually removed the oil from it. Upon characterization, the REB was found to contain Calcium, Carbon and Oxygen. The study revealed that oil pollution in whatever form can be removed even at a very lower concentration.

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