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Full Length Research Paper

Modeling the biosorption of crude oil in water using plantain pseudo stem as the adsorbent

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Biosorption is a technique that can be used for the removal of pollutants from waters. A variety of biomaterials are known to bind these pollutants, including bacteria, fungi, algae, and industrial and agricultural wastes. In this work, the biosoption abilities of plantain pseudo stem towards crude oil are emphasized. Experimental and theoretical approach was used to monitor and predict the rate of biosorption using plantain pseudo stem obtained from Erema town in Ogba/Egbema/Nndoni Local Government Area of Nigeria. The rate of adsorption of Bonny light crude oil by plantain pseudo stem as adsorbent of different thicknesses were used for the process for which it was observed that the adsorbent of 1 cm thickness agreed very closely with theoretical data. Thus, this article revealed that plantain stem is useful in enhancing effective remediation of oil polluted water environment.

Key words: Modeling, biosorption, crude oil, water, plantain pseudo stem, adsorbent.

INTRODUCTION

The major problem associated with oil exploitation is the spillage of petroleum hydrocarbon during transportation, offshore drilling and even during routine maintenance. Crude oil is a complex mixture of hydrocarbons and other organic compounds, including some organometallic constituents' (Butler and Mason, 1997; Mandelbaum et al., 1997; Reddy and Chinthamreddy, 1999; Page and Page, 2002). Investigation conducted by various research groups revealed that the Petroleum hydrocarbon contains hundreds and thousands of aliphatic compounds as well as branches based on the reaction in which aromatic hydrocarbons formed are toxic to living organisms (Prince, 1993; Wang et al., 1998). Crude oil spillage can thus be defined as the accidental discharge of petroleum hydrocarbons into the environment and this spillage can damage ecosystems, including plants and animals, and contaminate water for drinking and other purposes (Virkutyte et al., 2002; Toyoda and Inagaki, 2003; Carberry and Wik, 2001; Pamukeu et al., 2004; Reed et

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al., 1995). When the contamination is deposited in water environment, fishes can suffocate by the thick sludge of oil formed on the water surface, and bottom-dwelling fish can develop liver disease, as well as reproductive and growth problems (Safe drinking water formulation, 2000). Also, plants that grow on water and near the water can be harmed by oil pollution, which when spited on plant leaves can block the sunlight needed for photosynthesis, thus impeding growth as well leading to the death of the plant. Investigation conducted revealed that oil spillage results in closed beaches and harbors' high level of contaminants (Desehamps et al., 2003; Jacman et al., 2001; FRTS, 2000; Shapiro and Probstein, 1993; USEPA, 1999). It in like manner, affects fishing and hunting, which is especially detrimental for people who rely on hunting and fishing, such as many rural communities. Water sources that are intended to provide drinking water can become contaminated (Ukpaka, 2005, 2006, 2007, 2008, 2010; Wei et al., 2003; Teas et al.,



Figure 1. Pore size in the adsorbent.

2001; USDOD, 1994; USEPA, 2000).

There are some areas that are more sensitive to oil pollution than others, for example, coral reefs, mangroves and marshes are more sensitive than sandy beaches and sea-grass beds. Currents and wind can sometimes carry the oil far from the spill location, causing damage to the vegetation, birds and marine animals. Crude oil constitutes a potential threat to humans especially, when fat soluble components may accumulate in the organs of animals and may be enriched in the food chain such that prolonged exposure and high oil concentration may cause the development of liver and kidney disease, possible damage to the bone marrow and an increased risk of cancer. One of the most notable oil spills in the US and even in the world was in March, 1989, when a large tanker, Exxon Valdez spilled thousands of tons of crude oil (Paine et al., 1996; Albaiges et al., 2006; Butter and Mason, 1997; Gottz et al., 2001; Acar and Alshawabkeh, 1993; Cerniglia, 1997; Morgan and Watkinsons, 1992; Pamucks, 1997; Prince, 1993).

Engineering methods has been put in place using different approach in solving the pollution problem due to this almost inevitable occurrence, difference means of removing, reducing and remediating these problems caused by petroleum hydrocarbons spills were developed. These methods can be grouped into physiochemical remediation and bioremediation (Jain et al., 2011; Reynold et al., 2001; O'Connor et al., 2003; Ribeiro et al., 2005; Van Cauwenberghe, 1997; Roszak and Colwell, 1987; Colwell et al., 1978).

This work engulfs effective, efficient and economic preliminary means of remediating water bodies by biosorption of petroleum hydrocarbons using pseudostem of plantain as a biosorbent or adsorbent. It also gives a head-start for further research on ways to improve the process. This project will demonstrate: how adsorbent enhances bioremediation, the effect of size of adsorbent on bioremediation, development of a model that describes the rate of adsorption of crude oil in water using plantain pseudo stem as adsorbent, the effect of moisture on biosorption, determination of the physical properties of adsorbents relevant to this work, determination of the physical properties of crude oil relevant to this work, development of a model of rate of adsorption of crude oil, determine the constants from experiment and test the model for its deviation from experimental data. This project will be carried out within the above stated framework due to funds insufficiency, limited time specified for the project to be carried out and equipment available.

MATERIALS AND METHODS

Developing the model

The mathematical model for this research work was developed by considering an adsorbent of area (A) and thickness (Z) as well as assuming the pore arrangement within the adsorbent to be like cylindrical pipes of constant volume arranged parallel to each other and adsorption occurring due to bulk flow and diffusion, taking into consideration only axial gradient in volume of the substance (in this case oil) to be adsorbed, the rate of adsorption is given in the Figure 1.

Applying the principal of conservation of mass which states that:



where 'A' is total mass/moles or component mass/moles.

Analyzing each term in the Equation (1) for the material balance of oil and representing oil as component a, thus:

Accumulation of

$$\frac{component'a' within the system}{Time} = \frac{\partial m_a}{\partial t}$$
(2)

$$\frac{\text{Inflow of a quantity 'a'}}{\text{Time}} = M_a + (-D \nu A) \frac{\partial \frac{m_a}{mrv}}{\partial z} \quad (3)$$

$$\frac{Outflow of a quantity S}{Time} = m_a + \frac{\partial m_a}{\partial z} + (-Dv)A \frac{\partial \frac{m_a}{mrv}}{\partial z} + \frac{\partial}{\partial z} \left((-Dv)A \frac{\partial \frac{m_a}{mrv}}{\partial z} \right)$$
(4)

$$\frac{Amount of a quantity S generated}{consumed within the system} = 0$$
(5)

The last term above is zero since no reaction occurred during the time of observation of the process. Substituting the Equations, (2), (3), (4), and (5) into Equation (1) gives:

$$\frac{\partial m_a}{\partial z} = m_a + (-Dv) \frac{\partial m_a}{\partial z} - \left(m_a + \frac{\partial m_a}{\partial z} dz + (-DvA)A \frac{\partial \frac{m_a}{mvv}}{\partial z} + \frac{\partial}{\partial z} \left((-Dv)A \frac{\partial \frac{m_a}{mvv}}{\partial z} \right) \partial z \right)^{(6)}$$

Equation (6) can be written as;

$$\frac{\partial m_a}{\partial z} = -\left(\frac{\partial m_a}{\partial z} + \frac{\partial}{\partial z}\left((-Dv)A\frac{\partial \frac{m_a}{mrv}}{\partial z}\right)\right) \quad (7)$$

From Equation (7) considering Mr and V as constant as well as insignificance to the process, therefore Equation (7) can be written as;

$$\frac{\partial m_a}{\partial z} = -\left(\frac{\partial m_a}{\partial z} + \frac{(-Dv)A}{mrv} \frac{\partial^2 m_a}{\partial z^2}\right) \tag{8}$$

The above expression, Equation (8) is the model for the rate of adsorption crude oil in water using a adsorbent (plantain pseudo stem).

where, Ma = mass of crude oil (a) uptake (g), -Dv = the diffusivity of adsorbent (plantain stem) (m²s⁻¹), Mr = the molecular weight of crude oil (a) (g/gmol), A = the surface area of adsorbent (m²), V = the volume the adsorbent (m³).

The developed expression is based on oil adsorbed by the adsorbent that is mass balance for water was not taken into consideration because it is assumed that only oil is adsorbed as the adsorbent, plantain stem has a high affinity for just oil, that is, the only fluid flowing into the adsorbent, which is consider as the control volume, is oil.

Solving the model

The model was further resolved by considering the following operations:

Let
$$\frac{(-Dv)A}{mrv} = q$$
 (9)

Therefore substituting Equation (9) into Equation (7) we have:

$$\frac{\partial m_a}{\partial z} = -\left(\frac{\partial m_a}{\partial z} dz + q \frac{\partial^2 m_a}{\partial z^2} \partial z\right)$$
(10)

Putting $M_a = f(z)g(t)$ as the solution of the above model thus

$$\frac{\partial m_a}{\partial z} = f(z)\frac{\partial g}{\partial t}$$
(11)

$$\frac{\partial m_a}{\partial z} = g(t) \frac{\partial f}{\partial z}$$
(12)

$$\frac{\partial^2 m_a}{\partial z^2} = g(t) \frac{\partial^2 f}{\partial z^2}$$
(13)

Substituting Equations (11), (12) and (13) into Equation (10) becomes

$$f(z) \frac{\partial g}{\partial t} = -g(t) \frac{\partial f}{\partial z} - g(t) q \frac{\partial^2 f}{\partial z^2}$$
(14)

Dividing through Equation (14) by f(z)g(t) we have

$$\frac{1}{g} \frac{\partial g}{\partial t} = -\frac{1}{f} \frac{\partial f}{\partial z} - q \frac{1}{f} \frac{\partial^2 f}{\partial z^2} = k$$
(15)

Equation (15) can be expressed as

$$\frac{1}{g} \frac{\partial g}{\partial t} = k \text{ and } -\frac{1}{f} \frac{\partial f}{\partial z} - q \frac{1}{f} \frac{\partial^2 f}{\partial z^2} = k \quad (16)$$

Therefore Equation (15) can be written as

$$\frac{\partial g}{\partial t} = k \,\partial t \tag{17}$$

Integrating both sides of the Equation (17) we have

$$\int_{0}^{g} \frac{\partial g}{\partial t} = \int_{0}^{t} k \, \partial t \tag{18}$$

$$g = e^{kt+d}$$
(20)

$$q = C^{ekt}$$
(21)

In the same vein, Equation (16) can be expressed as

$$-\frac{1}{f}\frac{\partial g}{\partial t} - a\frac{1}{f}\frac{\partial^2 f}{\partial z^2} = k$$
(22)

$$-\frac{1}{f}\left(\frac{\partial f}{\partial z} + q \; \frac{\partial^2 f}{\partial z^2}\right) = k \tag{23}$$

Putting $f = e^{hZ}$ as the solution of the Equation (23), then

$$\frac{\partial f}{\partial z} = h e^{hz} \tag{24}$$

$$\frac{\partial^2 f}{\partial z} = h^2 e^{hz} \tag{25}$$

Substituting Equations (24) and (25) into Equation (23) and resolving gives

$$(he^{hz} + qh^2 e^{hz}) = -ke^{hz}$$
(26)

Further rearrangement of Equation (26) yields

$$e^{hz} (h + qh^2) = -ke^{hz}$$
 (27)

Canceling the exponential terms on both sides gives the quadratic equation below

$$(h+qh^2) = -k \tag{28}$$

$$qh^2 + h + k = 0 (29)$$

Using the formula for quadratic equations to solve Equation (29), gives

$$h = \frac{-1 \pm \sqrt{1 - 4qk}}{2 q}$$
(30)

Substitute the value of h into f to obtain the solution to the second order differential equation thus,

$$f = P_e \left(\frac{-1 \pm \sqrt{1 - 4qk}}{2 q} \right) z + N_e \left(\frac{-1 - \sqrt{1 - 4qk}}{2 q} \right) z$$
(31)

Substitute Equations (31) and (23) into the expression for Ma gives

$$Ma = Ce^{kt} \left(P_e \left(\frac{-1 \pm \sqrt{1 - 4qk}}{2 q} \right) z + N_e \left(\frac{-1 - \sqrt{1 - 4qk}}{2 q} \right) z \right)$$
(32)

where CP=A and CP=B, thus Equation (32) becomes

$$Ma = e^{kt} \left(A_e \left(\frac{-1 + \sqrt{1 - 4qk}}{2 q} \right) z + B_e \left(\frac{-1 - \sqrt{1 - 4qk}}{2 q} \right) z \right)$$
(33)

Equation (33) is the solution to the model for the rate of adsorption of crude oil using plantain pseudo stem as adsorbent

Equipment/materials used

The materials used for this experiment includes: Weighing balance, Plantain pseudo stem, Plastic cans, measuring cup, tooth pick, stainless steel bowl, Bonny light crude oil, Machete, cutter, detergent, wipes, desiccators, oven, and water.

Sample collection and preparation

The plantain pseudo stem was collected from a plantain plantation in Erema town in Ogba/Egbema/Ndoni Local Government Area (ONELGA) in Rivers State. The stem was first cut from the living tree laterally with the aid of a machete in the form of a log. The log-like stem's outer back (impermeable part) was peeled, further cut through its middle, longitudinally, and then an area of 9 cm³ (3 x 3 cm) and thickness of 1 cm³ was measured out with a ruler and cut. Four other samples of equal volume (3 x 3 x 1 cm) were cut using the same procedure as stated above. Each sample was labeled 1 to 5.

The above steps were carried out for adsorbents of thickness of 2 and 3 cm, given a total number of 15 samples of the sorbent realized and used for the experiment, whereby adsorbents of thickness of 1, 2, and 3 cm had 5 samples each. Due to the nature of the stem, the samples were held in place with tooth picks. 15 empty plastic cans were weighed using an electronic weigh balance and each labeled accordingly based on the samples obtained stating from sample 1 for 1cm thickness, sample 2 for 1 cm thickness, down to sample 5 for 3 cm thickness. The adsorbent were placed in their corresponding cans and the gross weights were obtained. The weight of the empty measuring cup and crude oil (bonny light) of 25ml was also obtained

Adsorption process

Five bowls were filled with water and polluted with 25 ml of crude oil each. The five samples of 1 cm thickness were placed all at the same time in the individual bowls. Using a stop watch to monitor the process, sample 1 was removed and placed in its plastic can after 30 s, sample 2 after 1 min, down to sample 5 which was removed after 2 min 30 s. The new weights of the samples were obtained. The five bowls were washed with detergent, filled with water, polluted with 25 ml crude and the process repeated for samples of thickness 2 and 3 cm.

Moisture content

Seven (7) samples of thickness 2 cm and area 9 cm³ were obtained as explained under the subheading of sample collection and preparation. An oven was preheated to 70°C and all seven samples were placed on a metal tray, and then put into the oven to dry. Sample 1 was removed after 20 min, and placed in a desiccator to cool and dry before weighing again. This step is repeated for samples 2 and 3 after which the remaining four samples (4 and 5) were removed after every 6 min. After cooling and weighing the samples, the 7 samples were placed all at the same time in 7 bowls of water polluted with 25 ml of crude oil for 2 min. All samples were removed at the same time and weighed again.

RESULTS AND DISCUSSION

The results obtained from the research work are presented in Figures and Tables. Tables 1, 2 and 3 contain few physical properties relevant to this study. These properties include the mass of all 15 samples and the mass of oil adsorbed by each with respect the time of contact with the oil. In Table 1 the 5th sample, the sample with longest contact time, adsorbed oil about its own weight with the difference between its weight and the oil adsorbed being (5.96 - 5.12 = 0.84 g). This is pretty impressive and promising as it can be said that the adsorbent has the ability to utilize its entire volume for the sole purpose and aim of the work, which is adsorbing crude oil in water.

Weight of empty	Weight of can +	Weight of	Adsorption	Weight of can +	Weight of oil
can (g)	adsorbent (g)	adsorbent (g)	time (s)	Adsorbent + oil (g)	(g)
36.04	43.04	7.00	30	45.13	2.09
39.54	46.12	6.58	60	48.74	2.62
40.60	47.70	7.10	90	50.98	3.28
13.57	19.29	5.72	120	23.39	4.10
20.60	26.56	5.96	150	31.68	5.12

Table 1. The rate of adsorption of crude oil using 1 cm thickness adsorbent.

Table 2. The rate of adsorption of crude oil using 2 cm thickness adsorbent.

Weight of empty	Weight of can +	Weight of	Adsorption	Weight of can +	Weight of
can (g)	adsorbent (g)	adsorbent (g)	time (s)	adsorbent+ oil (g)	oil (g)
36.04	49.69	13.65	30	56.80	7.11
39.54	54.68	15.14	60	59.50	4.82
40.60	53.46	12.86	90	58.77	5.31
13.57	28.11	14.54	120	35.12	7.01
20.60	28.11	15.08	150	33.80	5.69

Table 3. The rate of adsorption of crude oil using 3 cm thickness adsorbent.

Weight of empty	Weight of can +	Weight of	Adsorption	Weight of can +	Weight of
can (g)	adsorbent (g)	adsorbent (g)	time (s)	adsorbent+ oil (g)	oil (g)
36.04	52.36	16.32	30	66.39	4.72
39.54	54.38	14.84	60	66.39	12.01
40.60	58.71	18.11	90	21.02	2.91
13.57	29.30	15.73	120	37.39	8.09
20.60	38.64	18.04	150	49.75	11.11

On the other hand, Table 4 shows the effect of moisture content on the rate of adsorption of crude oil using 2 cm thickness adsorbent at various drying times. The samples were exposed to drying within a time limit of 30 to 150 s

The result presented in Figure 2 illustrates the relationship between the mass of oil adsorbed and the time taken for adsorption process using adsorbent of 1 cm thickness. The variation in the mass adsorbed can be attributed to the variation in time as well as the adsorbent thickness as presented in Figure 2. Increase in the rate of oil adsorbed was observed with increase in time, that is the rate of adsorption is directly proportional to time.

From Figure 3, it is seen that the mass of oil adsorbed decreases with increase in time for a period of 30 to 60 s and later increase with increase in time. The variation in the mass of oil adsorbed can be attributed to the variation in time as well as adsorbent thickness.

Figure 4 illustrates the relationship between the mass of oil adsorbed by the adsorbent per unit time. Increase in

the rate of adsorption of oil with the time period of >30 s <60 s was observed and later decreased with the time range of >60 s <90 s and finally increased with increase in time. The variation in mass of oil adsorbed can be attributed to the variation in the time as well as the adsorbent thickness.

A linear curve was observed within the time range of 20 to 40 min and later a decrease in mass of oil adsorbed was experienced with increase in time. The mass of oil adsorbed can be attributed to the variation in time as well as adsorbent thickness as presented in Figure 5.

Determining the constants of the model

Recalling Equation (33) which states that;

$$Ma = e^{kt} \left(A_e \left(\frac{-1 + \sqrt{1 - 4qk}}{2 q} \right) z + B_e \left(\frac{-1 - \sqrt{1 - 4qk}}{2 q} \right) z \right)$$

Weight of empty can (g)	Weight of can+ adsorbent before drying (g)	Weight of adsorbent (g)	Drying time (min)	Weight of can + adsorbent after drying (g)	Moisture content (g)	Weight of can + adsorbent+ oil (g)	Weight of oil (g)
36.04	56.93	20.89	20	45.02	11.91	49.02	4.00
39.54	55.42	15.88	40	42.55	12.87	46.53	3.98
40.60	55.14	14.54	60	40.91	14.23	43.89	2.98
13.57	28.72	14.97	66	14.52	14.20	17.50	3.30
20.60	40.26	19.66	72	23.25	17.01	26.35	3.10
12.45	28.86	16.41	74	13.67	15.19	16.76	3.09
13.65	28.78	15.13	80	13.66	15.12	16.64	2.98

Table 4. Illustrates the effect of moisture content on the rate of adsorption upon the influence of drying.



Figure 2. Graph of the relationship between mass adsorbed and the time taking for the adsorption process using adsorbent of 1 cm thickness.

Using the result data in Table 1 to determine the constants in the developed model shown in Equation (33) gives values of some functional parameters as shown in Table 5.

Substituting the result presented in Table 5 into the Equation (33) and resolving mathematically gives,

$$2.09 = e^{30k} \left(A_e^{0.01} \left(\frac{-1 + \sqrt{1 - 4qk}}{2 q} \right) + B_e^{0.01} \left(\frac{-1 - \sqrt{1 - 4qk}}{2 q} \right) \right)$$
(34)

$$2.62 = e^{60k} \left(A_e^{0.01} \left(\frac{-1 + \sqrt{1 - 4qk}}{2 q} \right) + B_e^{0.01} \left(\frac{-1 - \sqrt{1 - 4qk}}{2 q} \right) \right)$$
(35)

Dividing Equation (35) by (34) gives,

$$\frac{2.62}{2.09} = \frac{e^{60k}}{e^{30k}} \tag{36}$$

Resolving Equation (36) mathematically we have

$$1.2536 = e^{30k} \tag{37}$$

Taking the natural log of both sides of the Equation (37) gives,

$$0.2260 = 30k$$
 (38)

Therefore, Equation (37) becomes

$$k = \frac{0.2260}{30}$$

$$k = 0.0075$$



Figure 3. Graph of the relationship between mass adsorbed and the time taking for the adsorption process using adsorbent of 2 cm thickness.



Figure 4. Graph of the relationship between mass adsorbed and the time taking for the adsorption process using adsorbent of 3 cm thickness



Figure 5. Graph of the relationship between mass adsorbed versus the drying time for a adsorbent of 2 cm thickness.

Table 5. Values of some functional parameters.

Component	Ma (g)	t (s)	z (m)
Sample 1	2.09	30	0.01
Sample 2	2.62	60	0.01

Table 6. Values for functional parameters for various thicknesses of adsorbent.

Functional parameter	Values of functional	parameters for	different thicknesses
Z (m)	0.01	0.02	0.03
M (g)	3.442	5.988	7.768
T (s)	90	90	90

To check if the value of 'k' is correct then

$$\frac{2.09}{e^{30k}} = \frac{2.62}{e^{60k}} = \frac{3.28}{e^{90k}} = \frac{4.10}{e^{120k}} = \frac{5.12}{e^{150k}}$$
$$\frac{2.09}{e^{30k}} = 1.6689$$
$$\frac{2.62}{e^{60k}} = 1.6706$$
$$\frac{3.28}{e^{120k}} = 1.6700$$
$$\frac{4.10}{e^{120k}} = 1.6669$$
$$\frac{5.12}{e^{150k}} = 1.6622$$

These values are acceptable as errors are expected due to the assumption made during the development of the model. To determine other functional parameters that govern the rate of adsorption of adsorbent in oil, Tables 2 and 3 are required. Due to the irregularities in both data the average will be used instead. Note that this will bring about errors as approximated values (the averages) are being used.

Substituting the values in the Table 6 into Equation (33) gives,

$$3.442 = e^{0.0075 (90)} \left(A_e^{0.01} \left(\frac{-1 + \sqrt{1 - 4qk}}{2 q} \right) + B_e^{0.01} \left(\frac{-1 - \sqrt{1 - 4qk}}{2 q} \right) \right)$$
(39)

$$1.7525 = \left(A_e^{0.01} \left(\frac{-1 + \sqrt{1 - 4qk}}{2 q}\right) + B_e^{0.01} \left(\frac{-1 - \sqrt{1 - 4qk}}{2 q}\right)\right)$$
(40)

$$1.7525 = (Ae^{0.01} + Be^{0.01b})$$
(41)

$$5.988 = e^{0.0075(90)} \left(A_e^{0.02} \left(\frac{-1 + \sqrt{1 - 4qk}}{2 q} \right) + B_e^{0.02} \left(\frac{-1 - \sqrt{1 - 4qk}}{2 q} \right) \right) \quad (42)$$

$$3.049 = \left(A_e^{0.02} \left(\frac{-1 + \sqrt{1 - 4qk}}{2 q}\right) + B_e^{0.02} \left(\frac{-1 - \sqrt{1 - 4qk}}{2 q}\right)\right)$$
(43)

$$3049 = (Ae^{0.02a} + Be^{0.02b})$$
(44)

7.768
$$e^{0.0075(90)} = \left(A_e^{0.03}\left(\frac{-1+\sqrt{1-4qk}}{2q}\right) + B_e^{0.03}\left(\frac{-1-\sqrt{1-4qk}}{2q}\right)\right)$$
 (45)

$$3.9551 = \left(A_e^{0.03} \left(\frac{-1 + \sqrt{1 - 4qk}}{2 q}\right) + B_e^{0.03} \left(\frac{-1 - \sqrt{1 - 4qk}}{2 q}\right)\right)$$
(46)

$$3.9551 = (Ae^{0.03a} + Be^{0.03b}) \tag{47}$$

where

$$a = \left(\frac{-1 + \sqrt{1 - 4qk}}{2 q}\right) \tag{48}$$

$$b = \left(\frac{-1 + \sqrt{1 - 4qk}}{2 q}\right) \tag{49}$$

Multiplying Equation (41) by $e^{0.02a}$, gives

$$1.7525e^{0.02a} = (Ae^{0.03a} + Be^{(0.02a + 0.01b)})$$
(50)

Multiplying Equation (44) by $e^{0.01a}$, gives

$$3.049e^{0.01b} = (Ae^{0.03a} + Be^{(0.01a + 0.02b)})$$
(51)

Resolving Equations (41) and (44) simultaneously gives, $3.049e^{0.01a} - 1.7525e^{0.02a} = B\left(e^{0.01a + 0.02b} - e^{(0.02a + 0.01b)}\right) (52)$

Making B subject of the formula from Equation (52) gives,

$$B = \frac{3.049 \ e^{0.01a} - 1.7525 \ e^{0.02a}}{(e^{0.01a + 0.02b)} - e^{(0.02a + 0.01b)})}$$
(53)

Substituting Equation (53) into Equation (47) gives,

$$3.9551 = \left(A e^{0.03a} + \frac{3.049 e^{0.01a} - 1.7525 e^{0.02a}}{\left(e^{(0.01a + 0.02b) - e(0.02a + 0.01b)}\right)} e^{0.03b}\right)$$
(54)

Making A subject of formula in Equation (54) gives,

$$3.9551 = \left(e^{(0.01a + 0.02b)} - e^{(0.02a + 0.01b)}\right) = \left(Ae^{0.03a} \left(e^{(0.01a + 0.02b)}\right)^{-} e^{(0.02a + 0.01b)} + (3.049 \ e^{0.01a} - 1.7525 \ e^{0.02a}) \ e^{0.03b}\right)$$

$$A = \frac{3.9551 \left(e^{(0.01a + 0.02b)} - e^{(0.02a + 0.01b)} - (3.049 \ e^{0.01a + 0.03b}) - 1.7525 \ e^{0.02a + 0.30b}\right)}{\left(^{(0.04a + 0.02b)} \ e^{-(0.05a + 0.01b)}\right)}$$
(55)

Substituting the values of A and B obtained above into Equation (41)

$$1.7525 = \frac{3.9551 \left(e^{(0.01a + 0.02b)} - e^{(0.02a + 0.01b)} - (3.049 e^{0.01a + 0.03b}) - 1.7525 e^{0.02a + 0.30b} \right)}{\left(^{(0.04a + 0.02b)} e^{-(0.05a + 0.01b)} \right)}$$

$$e^{0.01a} + \frac{3.049 e^{0.01a} - 1.7525 e^{0.02a}}{\left(e^{(0.01a + 0.02b)} - e^{(0.02a + 0.01b)} \right)} e^{0.01b}$$

$$1.7525 \left(e^{(0.01a + 0.02b)} - e^{(0.02a + 0.01b)} \right) = 3.9551 \left(e^{(0.01a + 0.02b)} - e^{(0.02a + 0.01b)} \right)$$

$$1.7525 \left(e^{(0.01a + 0.03b)} - 1.7525 e^{(0.02a + 0.03b)} \right) e^{0.01a + \left(3.049 e^{(0.01a + 0.02b)} - 1.7525 e^{(0.02a + 0.01b)} \right)}$$

$$1.7525 \left(e^{(0.04a + 0.02b)} - e^{(0.05a + 0.01b)} \right) = 3.9551 \left(e^{(0.02a + 0.02b)} - 1.7525 e^{(0.02a + 0.01b)} \right)$$

$$1.7525 \left(e^{(0.04a + 0.02b)} - e^{(0.05a + 0.01b)} \right) = 3.9551 \left(e^{(0.02a + 0.02b)} - e^{(0.03a + 0.01b)} \right)$$

$$(3.049 e^{(0.02a + 0.03b)} - 1.7525 e^{(0.03a + 0.03b)} \right) + (3.049 e^{0.04a + 0.01b} - 1.7525 e^{0.05a + 0.01b})$$

$$(59)$$

Rearranging Equation (59) by collecting like coefficient terms gives

$$1.7525 \left(e^{(0.04a + 0.02b)} - e^{(0.05a + 0.01b)} \right) = 3.9551 \left(e^{(0.05a + 0.01b)} - e^{(0.03a + 0.03b)} \right)$$
$$= 3.9551 \left(e^{(0.02a + 0.02b)} - e^{(0.03a + 0.01b)} \right) + 3.049 \left(e^{0.04a + 0.01b} - e^{0.02a + 0.03b} \right)$$
(60)

Further simplifying of Equation (60) yields

$$1.7525 \left(e^{(0.04a + 0.02b)} - e^{(0.03a + 0.03b)} \right) = 3.9551 \left(e^{(0.02a + 0.02b)} - e^{(0.03a + 0.01b)} \right) + 3.049 \left(e^{(0.04a + 0.01b)} - e^{(0.02a + 0.03b)} \right)$$
(61)

$$1.7525 (e^{(0.04a + 0.01b)} - e^{(0.02a + 0.03b)}) = 3.9551 (e^{(0.04a + 0.01b)} - e^{(0.02a + 0.03b)})$$

$$(61$$

$$(0.04a + 0.02b) = \frac{-0.04 + 0.04\sqrt{1 - 4q} \ (0.075)}{2q} + \frac{-0.02 - 0.02\sqrt{1 - 4q} \ (0.075)}{2q}$$
(62)

$$(0.03a + 0.01b) = \frac{-0.02 + 0.01\sqrt{1 - 0.03q}}{q}$$
(66)

$$(0.04a + 0.01b) = \frac{-0.05 + 0.03\sqrt{1 - 0.03q}}{2q} \quad (67)$$

$$(0.02a + 0.03b) = \frac{-0.05 + 0.01\sqrt{1 - 0.03q}}{2q}$$
(68)

Substituting Equations (68) into Equation (60) gives

$$1.7525 \left(e^{\left(\frac{-0.03 + 0.01\sqrt{1 - 0.03q}}{q}\right)} - e^{\frac{-0.03}{q}} \right) = 3.9551 \left(e^{\left(\frac{-0.02}{q}\right)} - e^{\left(\frac{-0.02 + 0.01\sqrt{1 - 0.03q}}{q}\right)} \right)$$

$$3.049 \left(e^{\left(\frac{-0.05 + 0.03\sqrt{1 - 0.03q}}{2q}\right)} - e^{\left(\frac{-0.05 - 0.01\sqrt{1 - 0.03q}}{2q}\right)} \right)$$

$$1.7525 e^{\frac{-0.03}{q}} \left(e^{\left(\frac{0.01\sqrt{1 - 0.03q}}{q}\right)} - 1 \right) = 3.9551e^{\left(\frac{-0.02}{q}\right)} \left(1 - e^{\left(\frac{0.01\sqrt{1 - 0.03q}}{q}\right)} \right)$$

$$+ 3.049e^{\left(\frac{-0.05}{2q}\right)} \left(e^{\left(\frac{0.03\sqrt{1 - 0.03q}}{2q}\right)} - e^{\frac{-0.01\sqrt{1 - 0.03q}}{2q}} \right)$$

$$(70)$$

$$f (q) = 1.7525e^{\frac{-0.03}{q}} \left(1 - e^{\left(\frac{0.01\sqrt{1 - 0.03q}}{q}\right)} \right) + 3.9551e^{\left(\frac{-0.02}{q}\right)} \left(1 - e^{\left(\frac{-0.02 + 0.01\sqrt{1 - 0.03q}}{q}\right)} \right)$$

$$f (q) = 1.7525e^{\frac{-0.03}{q}} \left(1 - e^{\left(\frac{0.01\sqrt{1 - 0.03q}}{q}\right)} \right) + 3.9551e^{\left(\frac{-0.02}{q}\right)} \left(1 - e^{\left(\frac{-0.02 + 0.01\sqrt{1 - 0.03q}}{q}\right)} \right)$$

$$+ 3.049e^{\left(\frac{-0.05}{2q}\right)} \left(e^{\frac{0.03\sqrt{1 - 0.03q}}{2q}} - e^{\frac{-0.01\sqrt{1 - 0.03q}}{2q}} \right)$$

$$(71)$$

(63)

(64)

(65)

Collecting like terms from Equation (71) and simplifying gives

 $(0.04a + 0.02b) = \frac{-0.03 + 0.01\sqrt{1 - 0.03q}}{2q}$

 $(0.03a + 0.03b) = \frac{-0.03}{q}$

 $(0.02a + 0.02b) = \frac{-0.02}{q}$

$$f(q) = \left(1.7525 e^{\frac{-0.03}{q}} + 3.9551 e^{\left(\frac{-0.02}{q}\right)}\right) \left(1 - e^{\left(\frac{0.01\sqrt{1 - 0.03q}}{2q}\right)}\right) + 3.049 e^{\left(\frac{-0.025}{q}\right)}$$

$$\left(e^{\frac{0.015\sqrt{1-0.03q}}{q}} - e^{\frac{-0.005\sqrt{1-0.03q}}{q}}\right)$$
(72)

Using iteration method to solve Equation (72), this can be

achieved by making one of the q's in Equation (72) the subject of the formula then taking initial conditions as well as rearranging Equation (72) by dividing through by $\left(\frac{-0.025}{2}\right)$

$$3.049 e^{\left(-q^{-}\right)}$$
 gives

$$\frac{\left(1.7525 e^{\frac{-0.03}{q}} + 3.9551 e^{\left(\frac{-0.02}{q}\right)}\right) \left(1 - e^{\frac{\left(\frac{0.01\sqrt{1-0.03q}}{2q}\right)}{2}}\right)}{+ 3.049 e^{\left(\frac{-0.025}{q}\right)}} = \left(e^{\frac{0.005\sqrt{1-0.03q}}{q}} - e^{\frac{0.015\sqrt{1-0.03q}}{q}}\right)$$
(73)
$$\frac{\left(1.5748 e^{\frac{-0.005}{q}} + 1.2972 e^{\left(\frac{-0.005}{q}\right)}\right) \left(1 - e^{\frac{\left(\frac{0.01\sqrt{1-0.03q}}{2q}\right)}{2}}\right)}{+ 3.049 e^{\left(\frac{-0.025}{q}\right)}} = \left(e^{\frac{-0.005\sqrt{1-0.03q}}{q}} - e^{\frac{0.015\sqrt{1-0.03q}}{q}}\right)$$
(74)
Dividing Equation (74) by $\left(1 - e^{\frac{\left(\frac{0.01\sqrt{1-0.03q}}{2q}\right)}{2}}\right)$ gives
$$\left(0.5748 e^{\frac{-0.005}{q}} + 1.2972 e^{\left(\frac{0.005}{q}\right)}\right) = \frac{\left(e^{\frac{-0.005\sqrt{1-0.03q}}{q}} - e^{\frac{-0.015\sqrt{1-0.03q}}{q}}\right)}{\left(1 - e^{\frac{\left(\frac{0.01\sqrt{1-0.03q}}{2q}\right)}{2}}\right)}$$
(75)
$$\frac{0.005\sqrt{1-0.03q}}{2}$$

Multiply all through by e

q

$$e^{\frac{0.005\sqrt{10.03q}}{q}} \left(0.5748 e^{\frac{-0.005}{q}} + 1.2972 e^{\left(\frac{0.005}{q}\right)} \right) = e^{\frac{0.005\sqrt{1-0.03q}}{q}} \frac{\left(e^{\frac{-0.005\sqrt{1-0.03q}}{q}} - e^{\frac{-0.015\sqrt{1-0.03q}}{q}}\right)}{\left(1 - e^{\left(\frac{0.01\sqrt{1-0.03q}}{2q}\right)}\right)}$$
(76)
$$\left(0.5748 e^{\frac{-0.005+0.005\sqrt{1-0.03q}}{q}} + 1.2972 e^{\frac{0.005+0.005\sqrt{1-0.03q}}{q}} \right) = \frac{\left(1 - e^{\frac{-0.02\sqrt{1-0.03q}}{q}}\right)}{\left(1 - e^{\left(\frac{0.01\sqrt{1-0.03q}}{2q}\right)}\right)}$$
(77)

$$\left(0.5748e^{\frac{-0.005+0.005\sqrt{1-0.03q}}{q}} + 1.2972e^{\frac{0.005+0.005\sqrt{1-0.03q}}{q}}\right) = \frac{\left(1 - e^{\frac{-0.01\sqrt{1-0.03q}}{q}}\right)\left(1 - e^{\frac{0.01\sqrt{1-0.03q}}{2q}}\right)}{\left(1 - e^{\left(\frac{0.01\sqrt{1-0.03q}}{2q}\right)}\right)}$$
(78)
$$\left(0.5748e^{\frac{-0.005+0.005\sqrt{1-0.03q}}{q}} + 1.2972e^{\frac{0.005+0.005\sqrt{1-0.03q}}{q}}\right) = \left(1 + e^{\frac{0.01\sqrt{1-0.03q}}{2q}}\right)$$
(79)

Equation (79) can be written as shown in Equation (80) considering the RHS of Equation (79) results in

$$q = \frac{0.01\sqrt{1 - 0.03q}}{\ln\left[\left(0.5748 \ e^{\frac{0.005 + 0.005\sqrt{1 - 0.03q}}{q}} + 1.2972 \ e^{\frac{0.005 + 0.005\sqrt{1 - 0.03q}}{q}}\right) - 1\right]}$$
(80)

Considering the initial value of q=1, the iteration provides no solution for q and thus another q in Equation (80) is made the subject of the formula. Resolving Equation (80) algebraically for another expression for q,

$$q = \frac{1 \frac{q^2}{0.0001} \left[In \left(0.5748 e^{-0.005 + 0.005\sqrt{1 - 0.03q}} + 1.2972 e^{\frac{0.005 + 0.005\sqrt{1 - 0.03q}}{q}} \right) - 1 \right]^2}{0.03}$$
(81)

Considering the initial value of q=1, the iteration provides no solution for q and thus another q in Equation (80) is made the subject of the formula. Resolving Equation (80) algebraically for another expression for q,

Stating with initial value of q=1 and after 89 iterations the value of q calculated for is q = 0.008665668397. Substituting the value of q = 0.008665668397 into Equation (80) gives

$$\left(0.5748\,e^{\frac{-0.005+0.005\sqrt{1-0.03q}}{q}}+1.2972\,e^{\frac{0.005+0.005}{q}}\right) = \left(1+e^{\frac{0.01\sqrt{1-0.03q}}{q}}\right) = 4.170309018 \quad (83)$$

Substituting the value q = 0.008665668397 into equations (41), (44), (47), (48) and (49) to determine the values of a, b, A and B

Commonant	Values of functional parameters for adsorption of oil				
Component –	Time (s)	Z (m)	Ma-model (g)	Ma-experiment (g)	
Sample 1	30	0.01	2.42	2.09	
Sample 2	60	0.01	3.03	2.62	
Sample 3	90	0.01	3.79	3.28	
Sample 4	120	0.01	4.75	4.10	
Sample 5	150	0.01	5.95	5.12	

Table 7. Experimental and theoretical values of the functional parameters for 1cm thickness of adsorbent.

Table 8. Experimental and theoretical values of the functional parameters for 2 cm thickness of adsorbent.

Common ant	Values of functional parameters for adsorption of oil					
Component	Time (s)	Z (m)	Ma-model (g)	Ma-experiment		
Sample 1	30	0.02	4.32	7.11		
Sample 2	60	0.02	5.41	4.84		
Sample 3	90	0.02	6.77	5.31		
Sample 4	120	0.02	8.48	7.01		
Sample 5	150	0.02	10.615	5.69		

$$a = \left(\frac{-1 + \sqrt{1 - 4 \ (0.008665668397) \ (0.0075)}}{2 \ (0.008665668397)}\right) = -0.007500487507$$

$$b = \left(\frac{-1 - \sqrt{1 - 4 \ (0.008665668397) \ (0.0075)}}{2 \ (0.008665668397)}\right) = -115.390407$$

$$A = \frac{3.9551 \left(e^{-2.307883145} - e^{(-1.1540540\$}\right) - (3.049 e^{-3.46178215} - 1.7525 e^{-3.4618622})}{\left(e^{(-2.3081081\$} - e^{-1.154279094}\right)}$$

$$A = 4.14410287$$

$$B = \frac{3.049 e^{-0.000075004\$507} - 1.7525 e^{-0.000150009501}}{\left(e^{(-2.3788314\$} - e^{(-1.1540540\$})\right)} = -7.006344672$$

Substituting the determined functional parameters of q, a, b, A, and B into the developed model yielded the general solution for this project work.

$$M_a = e^{0.0075} \quad (4.14410287 \ e^{-0.00750048767z} - 7.006344672 \ e^{-115.390407z}) \quad (84)$$

Equation (84) is the Candy-Ukpaka's Model equation for the adsorption of crude oil using plantain pseudo-stem as adsorbent.

Testing the model

The following functional parameters were determined from the theoretical model developed in this project work.

The model used is known as Candy-Ukpaka's model for adsorption of crude oil using plantain pseudo stem as adsorbent. The results obtained are presented in the Tables 7, 8, 9 and Figure 6.

The graph presented in Figure 6 illustrates the comparison of experimental results with theoretical results in terms of mass of oil adsorbed for adsorbent of 1 cm thickness. Increase in the mass of oil adsorbed is observed with increase in contact time. Both

0	Values of functional parameters for adsorption of oil					
Component -	Time (s)	Thickness (m)	Ma-experiment (g)	Ma-model (g)		
Sample 1	30	0.03	4.19	4.72		
Sample 2	60	0.03	6.15	12.01		
Sample 3	90	0.03	7.71	2.91		
Sample 4	120	0.03	9.65	8.09		
Sample 5	150	0.03	12.08	11.11		

Table 9. Experimental and theoretical values of the functional parameters for 3 cm thickness of adsorbent.



Figure 6. Comparison of experimental and theoretical values of mass of oil adsorbed versus time for 1 cm thickness of adsorbent.

experimental and theoretical results obey this rule as shown in Figure 6. The results illustrated in Figure 6 shows a good match for the comparison of experimental and theoretical result. Therefore the model developed can be found useful in monitoring and predicting the rate of adsorption using plantain pseudo-stem for effective remediation of polluted water environment.

Figure 7 illustrates the comparison of the experimental and theoretical result on the mass of adsorbed oil using plantain pseudo-stem as an adsorbent for 2 cm thickness. An intersection was obtained at time t=57 s, Ma=5.2 g as shown in Figure 7.

The results obtained for the model indicate increase in mass of adsorbed oil with increase in contact time, whereas for the experimental results, a decrease was observed with the contact time range of 30 to 60 s and sudden rise in the mass of oil adsorbed within 60 to 120 s as well as sudden decrease in the mass of oil adsorbed within time range of >120 s to <150 min as shown in Figure 6. The comparison of the experimental and theoretical results indicates a poor match.

In Figure 8, the experimental and theoretical results are presented for the rate of mass of oil adsorbed using adsorbent of 3 cm thickness. From the result presented in Figure 8 the mass adsorbed, based on the calculation from the developed model, increases with increase in contact time. On other hand, the experimental result for mass adsorbed increases and decreases in an irregular pattern, that is the mass of oil adsorbed increase within the time range of 30 to 60 s and later dropped within the time range of >60 to<90 s, and a sudden increase was observed within the time range of >90 s. This indicates that the experimental behavior of the rate of the mass of oil adsorbed did not initial obey the model but later followed the sequence of the model developed in this project.

General discussion

Figure 1 is a plot of the mass adsorbed by an adsorbent of 1cm thickness against time. The graph shows that an increase in the contact time increases the amount of oil



Figure 7. Comparison of experimental and theoretical values of mass of oil adsorbed versus time for 2 cm thickness of adsorbent.



Figure 8. Comparison of experimental and theoretical values of mass of oil adsorbed versus time for 3 cm thickness of adsorbent.

been adsorbed by the adsorbent. This indicates that the adsorbent of 1 cm thickness is effective and thus can be used in facilitating remediation of an oil spilt site (in water environment). On the other hand, Figure 3 is more irregular, as the mass of oil adsorbed increases and decrease with time. This is expected, as it was previously stated in the literature review that plantain pseudo stem, as the name implies, is a false stem because it looks like a stem, but rather is made up of clustered cylindrical aggregation of the plantain leaf stalk. So for higher thicknesses say 2 cm and above, the possibility of having a adsorbent with pore spaces running without obstruction by an impermeable layer (which is a thin layer covering the front and back of the leaf stalk), from top to bottom is slim which is not only dependent on the nature of the leaf but also depends on the way the adsorbent was cut. Also it is true that the sample of 2 cm thickness with the highest amount oil adsorbed was probably hollow from top to bottom, as this is the only possible reason.

Likewise, Figure 4 shows a more irregular pattern than

the former, which proves that the higher the thickness of the adsorbent, the lower the possibility of having an adsorbent without impermeable layers. Figure 4 shows the relationship between mass of oil adsorbed by an adsorbent of 2 cm thickness with varying drying times against the drying time. From the plot, it is observed that mass adsorbed by the adsorbent decreases with an increase in the drying time of the adsorbent. This is anticipated as heating not only denatures the plant but also destroys the cellulose in the plant which is the main component responsible for the retention capability of plantain stem. That is, though the porosity of the stem aids adsorption by capillary action and diffusion, the adsorbent should have the ability to retain its adsorbed content which is the function of the cellulose, so by heating the adsorbent it becomes less or no longer effective.

Figures 6, 7 and 8 shows the relationship between experiment data and data estimated by the model for 1, 2 and 3 cm thickness of adsorbent respectively. In Figures 6, the deviation of model values from experiment is minimal as compared to the two other graphs. These errors arose as a result of assumption made in course of simplification, certain approximations and the method used for determining q. On the other hand, Figures 7 and 8 show the graphs estimated from the model for adsorbents which take into consideration the absence of a layer restricting adsorption in the direction of major concern (z-direction) based on this study. This implies that the model developed for this biosorption process with plantain stem as the adsorbent, characterizes to a great extent, oil adsorption process using adsorbent of 1 cm thickness and even smaller thicknesses, judging by the nature of the adsorbent. Deviations of a rather unacceptable magnitude are noted in the use of this particular model for adsorbents of 2 cm thickness. A rather outrageous set of results are got for adsorbents of 3 cm thickness. These errors can be attributed to the irregularity of the stem structure, which is of a variation from the model structure assumption. Also drying the adsorbent as a treatment step to enhance adsorption proved otherwise as drying reduces the effectiveness of the adsorbent.

Conclusion

Accidental spillage of crude is a major problem to mostly petroleum exploring nation and means of effectively remediating the polluted site at cheap rates is the target. On the bright side, plantain pseudo stem which is a major agricultural waste, as it is recorded in literature, has the desired specification required of every adsorbent, as it is clearly shown from this study that plantain pseudo stem can adsorb as much oil as its own weight. Also the problem associated with biosorbents adsorbing as much oil as water, is not the case for plantain pseudo stem as it has a high affinity for oil (oleophilic).

The Candy – Ukpaka's model,

$$M_{a} = e^{0.0075} \quad (4.14410287 \ e^{-0.00750048767z} - 7.006344672 \ e^{-115.390407z})$$

On the other hand, it is useful for monitoring and predicting the amount of oil adsorbed for a given size of the adsorbent and time of contact required to remove a particular amount of oil spilt. It must be also be noted that plantain pseudo stem as an adsorbent is mainly a primary remediating material as it merely adsorbs the crude and removes it from the uncontrolled polluted site to a site where recovery or degradation of the crude oil can be deliberately carried out.

Nomenclature: c, solute concentration in the pore of the biomass (mg/L); T, solute concentration in the non biomass layer (mg/L); **c**_b, solute concentration in the bulk solution (mg/L); r, radial variable in the biomass core (cm); R, radius of the biomass core (cm); KR, radius of immobilized biomass particle (cm); Q. solute concentration in the biomass (mg/g); A, apparent biomass core porosity core (mg/L) (mg/g); D, effective solute diffusivity in the pore of the biomass core (cm²/s); P, apparent biomass core density (g/cm³); D, effective solute diffusivity in the non biomass layer (cm2/s); δ , non biomass layer thickness (KR - R)(cm); k, external fluid film mass transfer coefficient (cm/s).

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