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EGG SHELL AS A POTENTIAL OIL SORBENT FOR CRUDE OIL SPILL REMEDIATION

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ABSTRACT

Oil pollution has been the major environmental effect in oil producing countries particularly where crude oil exploration tales place. In Nigeria, the problem is more pronounced in the Niger-Delta region. Poultry farming is a very lucrative business in Nigeria where both chickens (layers and broilers) are found particularly in the northern part of the country. The eggshells are usually thrown and allowed to liter the environment. A column study was used to test the ability of the eggshell granules in the removal of crude oil from oil polluted water from as high as 187 ppm to 1.5 ppm. Effects on water flow rate, and bed height were investigated. The result showed that as the bed height increased from 5 cm to 30 cm, the oil removal varies from 88 to 99% and the service time varies from 876 to 3702 s. The effect of flow rate on oil removal showed that the higher the flow rate, the lower the amount of oil removed.The pattern by which oil was removed from polluted water was based on an equation of a polynomial order of 5 degree.Bed depth service time was used to evaluate the values of the sorption capacity of the bed N_o and the bed depth service constant K_a. The values of N_o and K_a are 36.88mg/L and 0.000068 L/mg/sec respectively. The critical bed depth Z_0 determined was 3.04cm. By the values of N_0 and $K_a$it is anindication that the eggshell is highly efficient for biosorption of oil from oil polluted water.

Keywords: eggshell, column, oil, pollution, exploration, oil spill, remediation

1. INTRODUCTION

Agriculture employs about two-thirds of Nigeria's total labor force, contributed 42.2% of Gross Domestic Products (GDP) in 2007 and provides 88% of non-oil earnings (Onwukwe, 2012). More than 90% of the agricultural output is accounted for by small-scale farmers with less than two (2) hectares under cropping. It is estimated that about 75% (68 million ha) of the total land area has potential for agricultural activities with about 33 million hectares under cultivation. Similarly, of the estimated 3.14 million hectares irrigable land area, only about 220,000 ha (7%) is utilized (Onwukwe, 2012).

The total poultry population in Nigeria has been estimated at between 133 – 165 million (Onwukwe, 2012). However, there is consensus that about 90% of the figure derives from the local poultry stocks which is in turn composed of chickens (91%), guinea fowl (4%), ducks (3%), turkeys and others (2%) (Onwukwe, 2012). Those that are of commercial or economic importance given the trade in poultry, however, are chicken, guinea fowls and turkeys, amongst which the chickens predominate. Poultry meat and eggs play a very useful role in bridging the protein gap in Nigeria. They are palatable and generally acceptable. This acceptability cuts across nearly all cultural and religious boundaries in Nigeria. Poultry birds mature earlier than most breeds of livestock and can bring economic returns within relatively short periods of about 10-12 weeks (Onwukwe,

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2012). The poultry sub-sector is the most commercialized (capitalized) of all the sub-sectors of the Nigerian agriculture. In communities where food shortages are uncommon, chickens are kept to supplement the meals or to honor a guest.

The word poultry applies to all domestic fowl raised for their eggs, their meat, or both. Poultry includes chickens, turkeys, ducks, geese, guinea fowl, pheasants, quail and pigeons. Chickens by are far the most popular poultry raised today. More than 50 billion chickens are reared annually as a source of food, for both their meat and their eggs (Onwukwe, 2012). However, poultry Industry, being an important sector of Nigerian livestock production is expected to play a vital role in national development through generation of revenue. About 85% and 5% of Nigeria's poultry population estimated at 190 million were reared extensively in rural and urban areas, respectively, while 10 % were managed intensively nation-wide.

Fossil oil is beyond any doubt currently the most important raw material and energy source worldwide. There have been numerous occasions whereby oil was unintentionally introduced into the environment during production, transportation, and refining process causing adverse effects on sea life and human economic activities (Sathasivam, et al., 2010). Furthermore, oil spill may also cause strong odor to be felt miles away, and the excessive growth of green algae may alter the color of sea and landscape. This has prompted academic and industrial interests in developing methods for marine oil spill recovery. One of the most economical and efficient methods for combating oil spill is using eggshell as a natural hollow hydrophobic–oleophilic sorbent (Muhammad, et al., 2014;Muhammad, et al., 2012). Oil spill leaves detrimental effects to environment, living organisms, and economy. As such, it is of considerable interest to find an effective, simple, and inexpensive method to treat this calamity.

The oil-bearing areas of the Niger Delta have the largest mangrove forests in Africa and the third largest in the world. The inhabitants of the area derive a wide range of natural resources from the mangrove forest; including herbal medicine, fish, timber, and vital ecosystem services like stable soil and a flourishing habitat for a variety of wildlife, such as several endangered species, such as the Delta elephant, the white-crested monkey, and the river hippopotamus. In other words, the Niger Delta mangrove provides the means of sustenance to the people, who live largely on a subsistence basis. It also provides an important spawning habitat for Nigeria's commercial fisheries.

However, the advent of oil production in the Niger Delta has led to deforestation and ecological degradation, threatening the renewable natural resources and the ecosystem services in a number of ways. The oil-bearing areas have faced so many environmental problems caused by pollution arising from oil activities such as drill cuttings, drilling mud, fluids used in production, chemicals injected to control corrosion or to separate oil from water, and general industrial waste. Added to this are problems of gas flaring and incidents of oil spills and blow outs. While spills inevitably accompany oil production, in Nigeria they occur with an alarming frequency and magnitude because most of the oil delivery infrastructure is obsolete and inadequate. Also, sabotage of pipelines is a persistent problem, and spills and pipelines leaks are poorly monitored and often not reported and repaired on time.

In addition, oil exploration and production are linked to poorly designed causeways and canals that the oil industry uses. These affect the hydrology of the seasonally flooded fresh water swamp and the brackish water of the mangrove forest, killing crops, destroying fishing grounds and damaging the drinking water supply.

While it is evident that the environmental effects of oil production are great, it is important to point out that there are also some environmental problems not related to oil exploitation. The recent United Nations development report on the Niger Delta identified certain environmental problems that are not attributable to the oil industry activities, but rather a result of the natural terrain and hydrology of the Niger

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Delta. They are flooding, siltation, occlusion, erosion and the shortage of land for development. However, oil-related environmental effects compound and overshadow these others.

The Niger Delta region is a sensitive and fragile ecosystem. In spite of this vast resource endowment and its immense potential for socio-economic growth and contributions to the overall development of Nigeria, the oil-bearing areas within the Niger Delta remain under threat from rapidly deteriorating economic and environmental conditions as well as social tensions. Some critics suggest that the situation has worsened in recent years. The perception of local people living in the oil communities is that the government is acting negligently, while the valuable ecosystems on which they depend for their livelihood are devastated by oil extraction. As a result, the situation degenerates into violence and this draws a disproportionate reaction from the government, deepening the people's resentment and sense of alienation(Babatunde, 2010).

In spite of the damaging impact of oil exploitation on the environment and livelihoods of the host communities, scientific data on the overall and long-term effects of oil exploitation on the area are only beginning to emerge. Environmentalists and other experts have focused attention on the environmental degradation resulting from oil activities and a major bone of contention is the implication of the environmental impact on the livelihood of the people of the oil-bearing areas of the Niger Delta.

The importance of environmental sustainability cannot be overemphasized. This is fundamental to the people's welfare and development as their existence to a large extent relies on subsistence endeavors, which depend on natural resources. While there have been many intricate poverty strategies that have been designed and implemented in the Niger Delta region, and while all these schemes have their own validity depending on the environment, the stark reality in the oil-bearing areas is that decades of these schemes and programs have not mitigated the crucial problems of exclusion and human deprivation.

As a result, more germane to the survival of the indigenous people is the danger of oil exploitation obliterating their source of livelihood since they rely solely on their immediate environment for survival. Hence, anything that alters their environment threatens their very existence. Oil exploitation has created life-threatening ecological hazards and deterioration of health and social fabrics of the inhabitants of the oil-affected communities. The implication is that the oil industry has exploited the ecosystems for resources beyond the level of sustainability. The ecological problem is a reality that has to be tackled. This will reduce the vicious cycle of poverty and prevent the endemic social conflict that has pervaded the oil-bearing areas of the Niger Delta.Various organic wastes have been used as adsorbents (Angelova, et al., (2011); Shariff, et al., (2010);Asha & Thiruvenkatachari, (2008); Vlaev, et al., (2011);Pasila, (2004);Sathasivam, et al., (2010);Cambiella, et al., (2006);El-Nafaty, et al., (2013) and some inorganic materials (Khaled, et al., 2011) . During the last years of searching for new materials for the preparation of adsorbents greater attention is paid to the utilization of renewable resources such as agricultural wastes or wastes from the food-processing industry. Plant-processing wastes can be used directly for purification of sea water from oil spills, or after some thermal retreatment, increasing their adsorption capacity several times.

2. Materials and Method

2.1 **Materials**

The following are the materials used during the conduct of this study;

Distilled water, 1,1,1- trichloroethane, Pestle and mortar, Sieves (425 microns, 600 microns, 1.18 mm mesh size), Separating funnel, DR 2000 spectrophotometer, Retort stand, Plastic bucket, Meter rule, Long column, Plywood, Rubber band, Valves, Beakers (GG-17,500 ml), pH meter (Hanna Italia, model type-800-276868). All reagents are of the analytical grades. The column used was same as we reported (Aliyu, et al., 2015).

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2.2 **Method**

2.2.1 Eggshell preparation

The eggshell was prepared according to (Muhammad, et al., 2012)and(Muhammad, et al., 2014). It was characterized as we earlier reported (Muhammad, et al., 2012).

2.2.2 Sorption study

The column was packed with the sorbent material (eggshell) to a height of 5cm using a meter rule attached to the column. A control valve was slightly opened to allow the oil polluted water to flow into the column such that the water would have a proper contact time with the sorbent before passing through the bed. The treated water was collected using a beaker below the column. The experiment was repeated for different bed heights of 10, 15, 20, 25, and 30 cm respectively at a constant flow rate of 0.33ml/sec. Each of the samples in the respective heights was collected separately and labeled properly in a plastic sample bottle and DR/2000 spectrophotometer was used to quantify the oil content effluent in the water.The experiment was repeated for the bed height that give the best performance in oil removal with different flow rate by adjusting the flow regulator.

3. Results and Discussion

Table 1 presents the results obtained following the variation of bed height from 0 to 30 cm, while Table 2 shows the effect of flow rate on oil removal.

Table 1: Effect of bed height on oil removal from oil polluted water

Bed-Height (cm)	Bed-Height (m)	Oil Removal (%)	Service time(sec)
5	0.05	87.93	876.0
10	0.1	91.82	1520.4
15	0.15	93.78	2022.0
20	0.2	96.65	2575.2
25	0.25	98.72	3204.0
30	0.3	99.01	3702.0

Table 2: Effect of flow rate on oil removal from oil polluted water

FLOWRATE (ml/s)	Residual Oil Concentration(mg/L)	% Removal
1.3	14.72	92.13
3.3	22.57	87.93
3.8	26.91	85.61
5.7	54.55	70.83
7.6	68.24	63.51
9.1	88.19	52.84

Table 1 showed that an increase in the bed height, which is directly related to bed mass, allows to treat a larger volume of emulsion, until a critical bed height value is reached. At critical height, the pressure drop across the bed increases exponentially with time, while for shorter beds, the pressure drop remains constant or increases linearly. The exponential increase in pressure drop suggests the occurrence of surface straining or clogging in a deep layer of the bed. As the bed height is increased, higher inlet pressures are needed to maintain a certain flow rate of the feed emulsion. Hence, the bed porosity is reduced, the void spaces become smaller and the velocity is increased. An increased velocity increases the drag forces between the liquid and the granular media. In conclusion, the oil droplets are not easily retained but driven deeper into

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the bed, coalescing and reaching a size large enough to cause clogging of an inner layer. At that moment, the linear increase of pressure with time shifts suddenly to an exponential increase and the filtration must be discontinued.

From Table 2, it can be seen that the eggshell media performs better at low flow rates. This might be explained because the oil droplets coalesce to a droplet size large enough to be entrapped, as a result of longer residence times in the bed. Also, at a certain flow rate, the void spaces are progressively clogged by the retained oil, and hence the local velocity of the liquid phase increases, weakening the interaction forces and driving the disperse phase droplets more deeply into the bed. This entrainment ensures a better use of the eggshell bed layers and filtration runs take longer time. However, a flow rate is reached above which the eggshell bed is not able to retain the oil present in the feed and it goes through with the outlet effluent. Moreover, the head loss across the granular media itself is a linear function of velocity, regardless of the degree of clogging, supporting the suitability of low flow rates, when it is possible. Finally, it is worth to notice that liquid–liquid phase separations are more sensitive than the corresponding liquid–solid to the influence of flow rate, because of the fact of droplet deformation. This was also explained by some authors (Cambiella, et al., 2006).

3.1 Bed depth service time (BDST) models

The bed depth service time (BDST) model describes the relationship between $\frac{C_b}{C_o}$ and t in a continuous system. The experimental data can be modeled by establishing a term called service time, which was defined as the time required for the effluent concentration to reach 1 mg/l of the oil. The bed height (z) and serviced time (t) have a linear relationship given by BDST model (Padmesh, et al., 2006).

$$t=\frac{N_o Z}{C_o U}-\frac{1}{K_a C_o}\ln\left(\frac{C_o}{C_b}-1\right) \quad \dots \quad (1)$$

Where C_o is the initial oil concentration (mg/g), C_b is the break through oil concentration (mg/g), u is the linear velocity (cm/min), N_o is the sorption capacity of bed (mg/L), k_a is the rate Constant in BDST model column. Eq. (1) can be rewritten in the form of a straight line.

$$t=aZ-b \quad \dots \quad (2)$$

Where

$$a=\text{slope}=\frac{N_o}{C_{oU}} \quad \dots \quad (3)$$

$$b=\text{intercept}=\frac{1}{K_a C_o}\ln\left(\frac{C_o}{C_b}-1\right) \quad \dots \quad (4)$$

The critical bed depth (Z_o) is the theoretical depth of the sorbent sufficient to ensure that the outlet solute concentration does not exceed the break through concentration, $C_{b,}$ at time t = 0. Z_o can be calculated by setting t = 0 and solving Eq. (1) for Z:

$$Z_o=\frac{U}{K_a N_o}\ln\left(\frac{C_o}{C_b}-1\right) \quad \dots \quad (5)$$

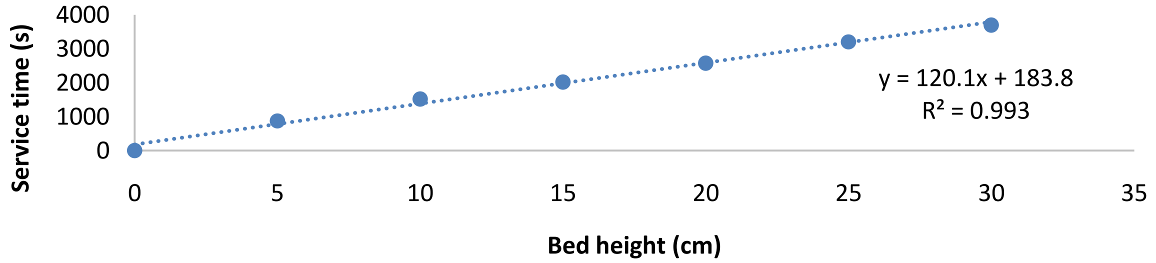

Figure 1: Plot of bed height against service time for oil removal from polluted water

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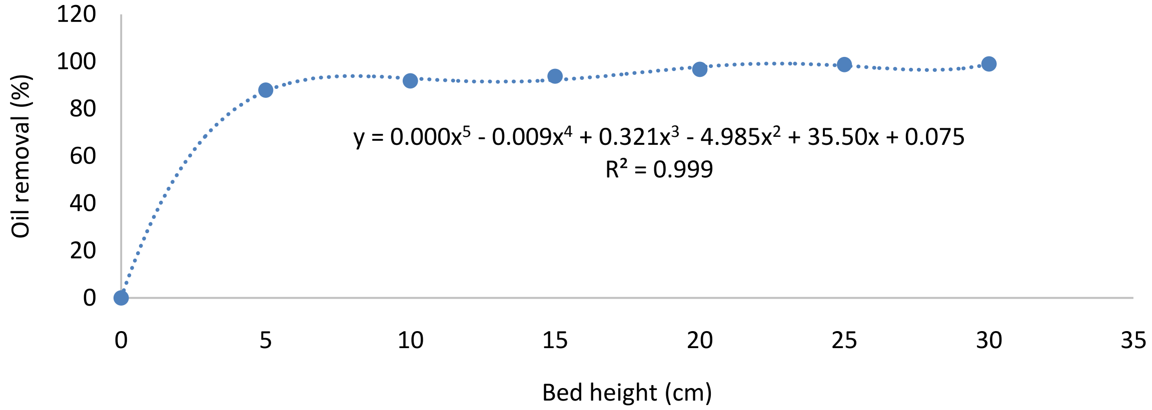

Figure 2: Patern followed by oil removal using eggshell in continuous column

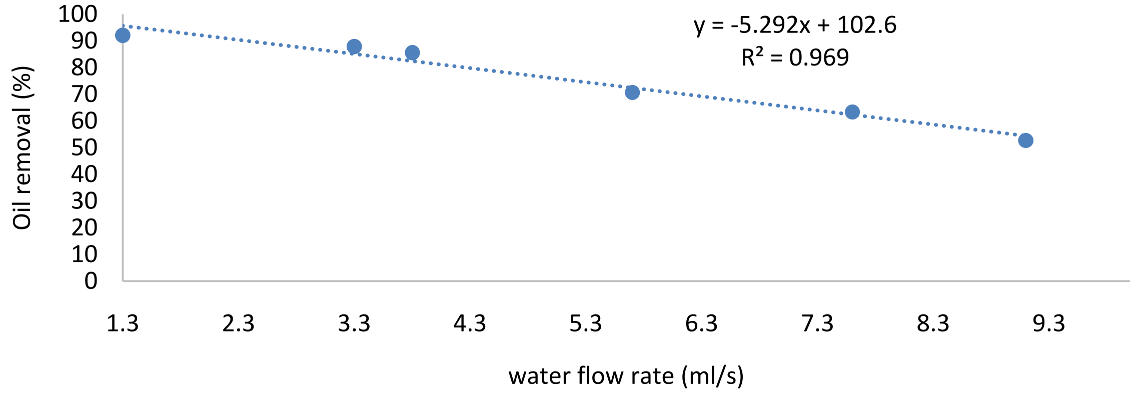

Figure 3: Effect of flow rate on oil removal using eggshell

From the results obtained, it was observed that as the bed height increases the bed service time increases. This was due to the more availability of sorbent sites for the sorption to occur. The plot of service time against bed height in Fig. 1 was used to calculate the values of the sorption capacity of the bed N_o using equation (3) and the bed depth service constant K_a was also calculated using equation (4). The values of N_o and K_a are 36.88mg/L and 0.000068 L/mg/sec respectively. The critical bed depth Z_0 determined was 3.04cm. The values of N_0 and $K_a$indicated that the eggshell is highly efficient for biosorption of oil from oil polluted water. The value of R^2=0.9932 obtained in Fig. 1 showed that the variation of the service time with bed height is highly linear for the system thus, indicating the validity of the bed depth service time model when applied to continuous column studies.

4. Conclusion

Eggshell was used to remediate crude oil polluted water in a continuous manner. Effects of bed height was investigated from 5 to 30 cm. Within the range of investigation, oil removal and service time were seen to increase with bed height increased. The eggshell sorption capacity was found to be 36.88 mg/l while the bed time service constant was evaluated as $6.8*10^{-5}$ l/mg with the critical bed depth found to be 3.04 cm. Increase

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in flow rate from 0.13 to 0.93 was seen effect oil removal negatively from 92.13 to 52.84%. This showed that at higher flow rate, oil removal is minimal due to less contact time between the sorbent and the sorbate.The value of R^2=0.9932 obtained in Fig. 1 showed that the variation of the service time with bed height is highly linear for the system thus, indicating the validity of the bed depth service time model when applied to continuous column studies.

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