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Petroleum Produced Water; Characterization and Adsorption Properties on Coconut Shell Carbon.

[1]Akpoturi Peters and [2]Usuolori O.B.A
[1,2]Department of Petroleum Engineering
[1]Federal University of Petroleum Resources, Effurun
[2]Delta State university of Science and Technology, Ozoro

ABSTRACT
In the course of most activities in the petroleum industry, enormous amounts of polluted wastewater of various types are produced and discharged. Produced water is the name commonly given to water discharged as a result of oil production. It is known to contain organic compounds derived from crude oil, inorganic compounds and many metals that are toxic to the environment.
Most of the available treatment technologies for removal of these toxic components from produced water effluent are capital intensive and require long term investments for effective operation; hence innovative approaches and new methodologies for protecting water resources from pollution are necessary.
The application of adsorption techniques for the removal of organic, inorganic and metallic contaminants from wastewater has been well established.
Activated carbon is universally used for treatment of industrial effluents by adsorption. However, the exorbitant cost of its preparation and regeneration has led to a search for alternative sorbents especially in the developing countries.
This paper examines the characteristics of produced water from some Nigerian oil fields and the use of Coconut Shell Carbon (CSC) as an alternative low cost sorbent derived from organic waste material for the removal of toxic contaminants from produced water.
The results of the batch adsorption studies have indicated the efficiency of contaminant removal by CSC, which was comparable to that of commercially available activated carbon.
The optimum sorptive capacity (Sc) of CSC for organic, inorganic and metallic contaminant removal was found to be 45.7 mg/g. 20.9mglg and 13.8 mg/g respectively (Table 60).
Subsequent recovery of the removed contaminant from the surface of the sorbent was also attempted.
Keywords; *produced water, waste water, crude oil, toxic , environment, organic compound, petroleum industry and Adsorption*

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I. INTRODUCTION

Environmental management is one of the most pressing issues as the upward trend in industrialization continues globally. Among the challenges faced by the managers of industrial establishments is the need to ensure a functional and sustainable wastewater management system. Highly technical conventional wastewater treatment systems that require large capital investments demand high maintenance costs are not feasible for widespread use in developing nations.

The oil industry in Nigeria is the chief foreign exchange earner and the single most important source of pollution in the country. Notwithstanding, the oil industry must of necessity co-exist with our fragile environment.

Most activities in the petroleum industry release enormous amounts of polluted liquids of various types into the environment. Most of these contaminants if not treated before discharging into the environment, will have adverse effects on the ecosystem. Within the last fifteen years, a number of methods for the treatment of this oily wastewater have been introduced in Nigeria.

Some researchers have been conducted on the adsorption capability of carbonized and activated carbons from coconut shell. Cheremisinoff and Ellerbush (1978) reported the ability of granular carbon produced from coconut shell to purify water. They showed that controlled processes of dehydration, carbonization and oxidation of coconut shell gave an active product with high adsorption capability. Hassler (1994) also reported that carbons from wood and coconut shell could be used for purification of water at low cost. Kovach (1978) reported the production of steam-activated coconut carbons with superior properties for krypton — Xenon adsorption. Yoshida et al (1996) observed that activated carbon prepared from coconut shell by steam activation has a high adsorptive ability for the adsorption of mercury metal.

Activated carbon is gaining prominence in the removal of contaminants from drinking waters and wastewater (Burke eta1., 1980; Wu, 1978; Ramalho, 1977).

Activated carbon works by attracting and holding certain chemicals as water passes through it. Activated carbon is a highly porous material; therefore, it has an extremely high surface area for contaminant adsorption. The equivalent surface area of pound of Activated carbon ranges horn 60 to 150 acres.

Activated carbon is made of tiny clusters of carbon atoms stacked upon one another (Figure 6.0). The carbon source is a variety of materials, such as peanut shells of coconut shell. The raw carbon source is slowly heated in the absence of air to produce a high carbon material. Passing oxidizing gases through the material at extremely high temperatures activates the carbon, The activation process produces the pores that result in such high adsorptive properties.

The adsorption process depends on the following factors: physical properties of the Activated carbon, such as pore size distribution and surface area; the chemical nature of the carbon source, or the amount of oxygen and hydrogen associated with it chemical composition and concentration of the contaminant; the temperature and p1-1 of the water; and the flow rate or time exposure of water to Activated carbon. (Bruce et al., 1992).

Despite the various reports on the activity of activated carbon, not much work has been reported on the adsorptive capability of powdered and granular forms of carbon from coconut shell obtained in Nigeria and the application of this carbon to the treatment of petroleum produced water. Therefore, one of the main objectives of this investigation was to produce a powdered as well as granular form of carbons from coconut shell and compare their capabilities to adsorb specific contaminants from produced water, Other objectives include determination of the adsorption characteristics of the produced carbons, which could be used for carbon adsorption column design.

The commercial feasibility of this work seems evident since the raw material (coconut shell) is cheap and readily available.

II. MATERIAL AND METHODS

Waste water:

The produced water effluent (PWE) used for the studies were obtained from two major Oil producing company locations in Nigeria. Samples were collected at different time intervals. At the end of the sampling period, adding together equal volumes of samples collected at different sampling points made a composite sample. This was done to accommodate the cyclic and intermittent variations occurring at the various sampling points along the production stages. MI samples were quickly transferred to the laboratory for analysis.
The characteristic of the Nigerian petroleum produced water obtained is shown in Table 10.

Preliminary Treatment Processes:

The unit processes used for the preliminary treatment of the PWE water in the studies were as shown in Figure 1.0.

The PWE Wastewater collected was passed through iron screens placed at an inclined position across the flow to remove coarse materials. The effluent then enters a settling tank made up of iron sheet with the floor sloped at 30. The dimensions of the setting tank is 30cm square and 40cm deep and generally holding about 12.5 x 102 cm^3 PWE wastewater. The PWE wastewater sample was allowed to settle the 30 minutes. The supernatant liquid was then treated with commercial alum. A12 (S04)3. 14H20 at its optimum dosage of 10 percent volume by volume (Figure 20). The mixture was agitated mechanically for 2 minutes at 210r.p.m. for effective coagulation and then for 20 minutes at 21rpm. to ensure good flocculation. It was allowed to settle for about I hour. The supernatant liquid was then filtered through a sand bed of 1.0mm grading in a cylindrical column of 15cm in diameter and 40cm depth. The clarified PWE wastewaters were analyzed for pH, Temperature. Conductivity, Total - Suspended Solids (TSS), Biochemical Oxygen Demand (B0D5), Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), Oil/Grease Content and Zinc content (Zn2+) (Table 2.0). The analysis was carried out using standard methods (APHA, 1975). The clarified PWE wastewater was then subjected to the Fixed Bed carbon treatment unit and the Fluidized Bed carbon treatment unit.

Powdered carbon:

The coconut shells used in this study were collected from different locations around Warri. The coconut shells were then oven-dried, ground to pass through laboratory test sieves of 1400 tm and 425 gm respectively for granular and powdered forms. It was then carbonized in a muffle furnace at 600CC ± 20C. 2.0 of the powdered and granular coconut shell was calcimined at this temperature in an enclosed environment inside the muffle furnace for a period of 180 seconds. The carbons produced were characterized (Table 3.0) and their adsorption capacity for organic, inorganic and metallic contaminants removal was determined (Table 4.0).

Fixed bed carbon Adsorption Treatment:
Ten litres of 10-percent-alum-clarified PWE wastewater were placed in the Fixed Bed containing two grammes of the powdered carbon. The filtrate was obtained and analyzed. The results were as shown in Table 5.0.
Fluidized Bed carbon Adsorption Treatment:
Ten litres of 10-percent-alum-clarified PWE wastewater were placed in the fluidized and containing two grammes of powdered carbon. Blowing air into the fled for agitation at the rate of 300cm3min-l by using an air compressor fluidized the bed. It was fluidized for 10 minutes (Ademoroti, 1986). The filtrate obtained was analyzed and results were as shown in Table 5.0.

Measurement of Langmuir Constants:
The Langmuir coefficients K and b were determined using the Langmuir equation which describe the equilibrium relationships between adsorbent and adsorbate by plotting I/(X/M) versus 1/C.
The equation is given as:

$$X/M = \frac{KbC}{(1+KC)}$$

Where X = Weight of solute adsorbed, mg
M = Weight of adsorbent, g
K = Equilibrium constant
C = Equilibrium concentration of solute,
mg/l, b = Constant

The Langmuir constant was measured for adsorption of organic, inorganic and metallic contaminant by powdered carbon. Values obtained were as shown in Table 4.0.

III. RESULTS AND DISCUSSIONS

The results of all the PWE wastewater analysis carried out are presented in Tables 1.0-5.0 and Figures 1.0-5.0. The results have shown that carbon produced from coconut shell in Nigeria can efficiently reduce the contaminant concentration.

The additional improvement caused to the PWE wastewater through the application of the Fluidized Bed technique is clearly illustrated by the comparative performance shown in Table 5.0. The fluidized bed technique not only has the advantage of improved effluent quality but also has the potential of reducing the total east of treatment.

The optimum Aluminum Sulphate concentration used for clarification before carbon treatment was found to be 10 percent. (Figure 2.0).

The result obtained for the adsorption is well represented by the Langmuir Isotherm. This is shown by the correlation coefficient values obtained (Table 4.0). The results also show that the adsorption of these contaminants on coconut carbon is relatively high. The k and b values obtained compared with those reported for foreign activated carbon as reported by Zytner (1992) (Table 6.0). The values also reveal the relative adsorption capacities tor these different contaminants in PWE wastewater.

Table 3.0 show results obtained for the characterization of the powdered and granular carbon samples, which were produced from the coconut shell.

The final effluents obtained in the studies were comparable with FEPA standards on effluent limit, for discharge into the environment without fear of pollution (Table 2.0).

The optimum adsorption capacity (Sc) of the coconut shell carbon for organic, inorganic and metallic contaminant removal was found to be 45.7 mg/g, 20.9 mg/g and 13.8 mg/g respectively. Subsequent recovery of the removed contaminant from the surface of the sorbent through the use of Soxhlet extraction method shows that 62.9% of the contaminants was recovered.

IV. CONCLUSION

Treatment of all kinds of effluents including PWE wastewater prior to discharge into the environment is desirable so as to avoid pollution. In Nigeria today, billions of naira are spent on importing highly engineered technologies for the treatment of effluent. This investigation has shown the ability of a cheap and locally sourced treatment method to remove various waste contaminants from PWE wastewater, which can then be safely discharged into the environment.

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Table 1.0: Characteristics of PWE Wastewater used in the studies

Characteristics	Range	Mean
PH	4.9 - 8.3	7.4
Temperature, ^oC	25.0 - 27.8	26.2
Conductivity, µS/cm	2,750 - 35,500	6250
Total Suspended Solids (TSS), mg/l	40.3- 219.0	82.6
Biochemical Oxygen Demand (BOD), mg/l	38.0 - 516.0	209.0
Chemical Oxygen Demand (COD), mg/l	55.3- 705.1	374.0
Total Organic Carbon (TOC), nigh	4.185 - 7062	2.532
Lead Content (Pb^{2+}), mg/l	0.026 - 0.550	0.125
Zinc Content (Zn^{2+}) mg/l	42.08-70.10	33.65

Table 2.0 : Characteristics of the Produced Water Effluent from different units of the Treatment Units

	Raw PWE	**Screening**	**Alum Clarified Effluent**	**Carbon Treatment of Effluent**		**FEPA STANDARD**	**WHO STANDARD**
				Fixed Bed (2g)	Fluidized Bed (2g)		
PH	7.1	7.1	6.3	6.8	6.8	6.5-8.5	6.5-9.2
Temperature	26.2	26.2	26.2	26.1	25.9	30	N.S
Conductivity	28,500	25,250	480	400	275	N.S	N.S
Total Suspended Solids (TSS), mg/l	86.9	31.4	12.6	Nil	Nil	30	25.0
Biochemical Oxygen Demand (BOD), mg/l	407.0	109.2	28.3	9.5	7.4	10	N.S
Chemical Oxygen Demand (COD) mg/l	791.0	206.4	115.2	23.8	17.6	40	N.S
Total Organic Carbon (TOC), mg/l	5.480	4.238	2.065	Nil	Nil	N.S	N.S
Lead Content (Pb^{2+}), mg/l	0.212	0.190	0.113	0.029	0.015	0.050	0.50
Zinc Content (Zn^{2+}), mg/l	58.36	37.36	27.80	0.201	0.117	1.00	15.0

Table 3.0: Properties of the Granular and Powdered Carbon Samples from Coconut Shell

Characteristics	Granular Carbon	Powdered Carbon
Packed Density * (gcm^3)	0.45	0.42
Total Pore Volume* (cm^3g^{-1})	0.66	0.63
Raw Material Surface*(m^2g^{-1})	901	1187
Particle Size (µm)	425	1400
*Data determined using standard methods		

Table 4.0: Langmuir Constants for the Adsorption of Organic, Inorganic and metallic contaminant from PWE Wastewater

Contaminant Type	K value	b value	Correlation Coefficient ®
Organic (COD)	1.50	0.62	0.99
Inorganic (Conductivity)	0.87	0.49	0.98
Metallic (Zinc)	0.62	0.45	0.98

Table 5.0: Relative Efficiency of different modes of a single carbon treatment of Clarified Produced Water Effluent

Characteristics	Clarified PWE Initial Value	Fixed Bed Technique		Fluidized Bed Technique	
		Final value	Percentage Reduction	Final Value	Percentage Reduction
Conductivity µS/cm	480.0	395.0	17.7	225.0	53.1
Chemical Oxygen Demand (COD), mg/l	115.2	23.8	79.3	17.4	84.9
Zinc Content (Zn^{2+}), mg/l	27.80	0.20	99.3	0.12	99.6

Table 6.0: Degree of contaminant removal achieved by different sources of Activated Carbon

Contaminant Type/Test Parameter	Nigerian Produced Carbon			American Produced Carbon			European Produced Carbon		
	% Reduction	K value	B value	% Reduction	K value	B value	% Reduction	K value	B value
Organic (COD, mg/l)	84.9	1.50	0.62	87.3	1.54	0.64	86.2	1.52	0.63
Inorganic (Conductivity, µS/cm)	53.1	0.87	0.49	55.6	0.91	0.51	57.5	0.94	0.53
Metallic (Zinc Content, mg/I)	99.6	0.62	0.45	99.8	0.62	0.45	99.8	0.62	0.45

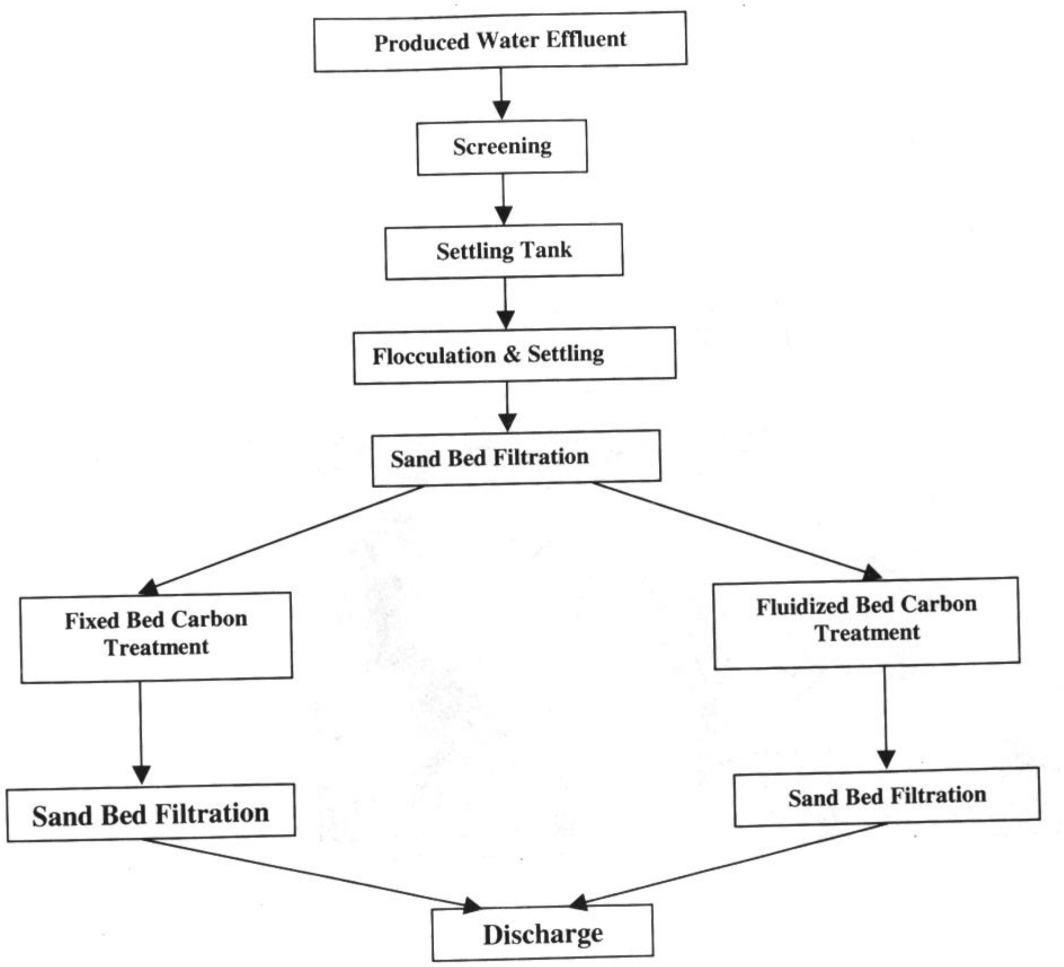

Figure 1.0: Unit Processes for the Integrated Treatment of Produced Water Effluent

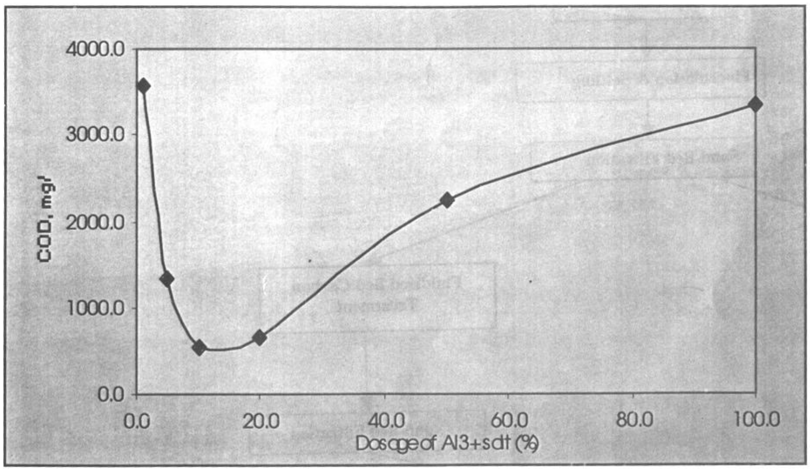

Figure 2.0: Effect of dosage of Aluminum Sulphate on the flocculation of PWE Wastewater

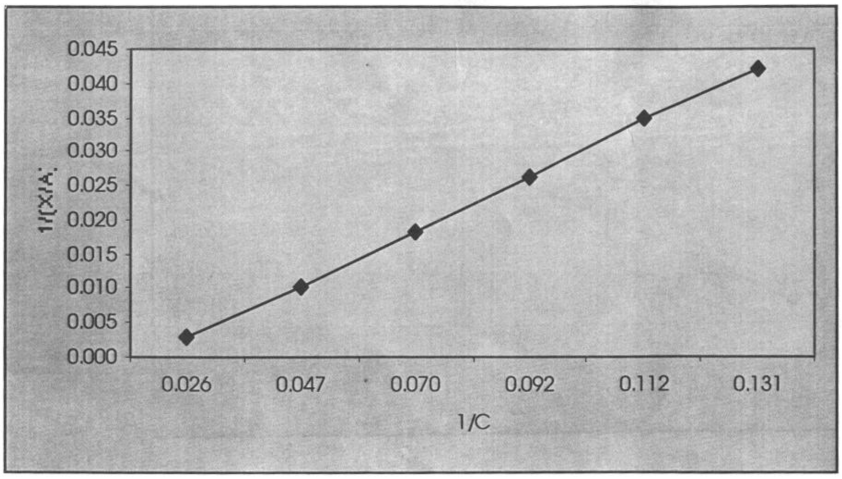

Figure 3.0: Langmuir Isotherm for the adsorption of COD, mgl^{-1} (Organic Contaminant) from the PWE Wastewater

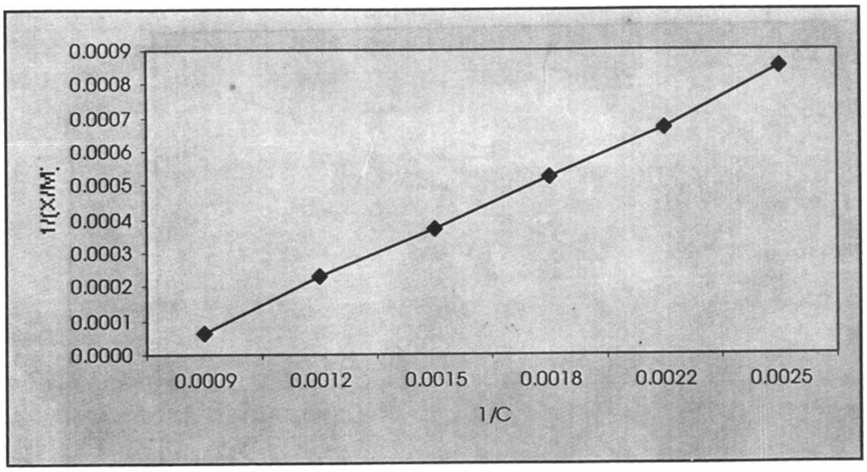

Figure 4.0: Langmuir Isotherm for the adsorption of Conductivity, μScm^{-1} (Inorganic Contaminant) from the PWE Wastewater

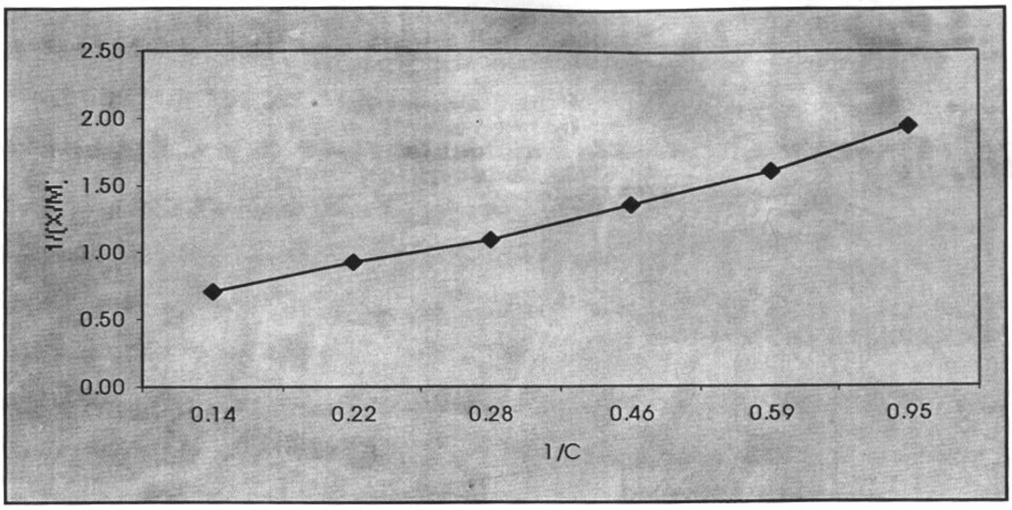

Figure 5.0:Langmuir Isotherm for the adsorption of Copper, mgl^{-1} (Metallic Contaminant) from the PWE Wastewater

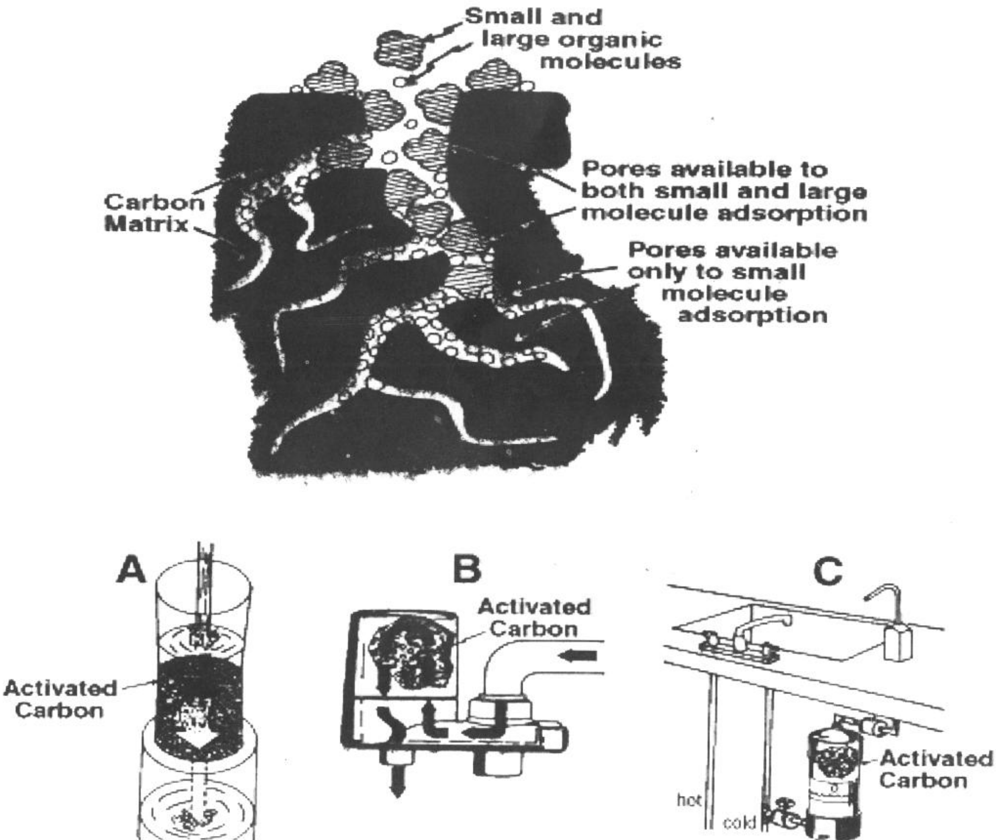

Figure 6.0: Molecular screening in the micropores of an activated carbon filter and application processes (G.L. Culp and R.L. Culp)

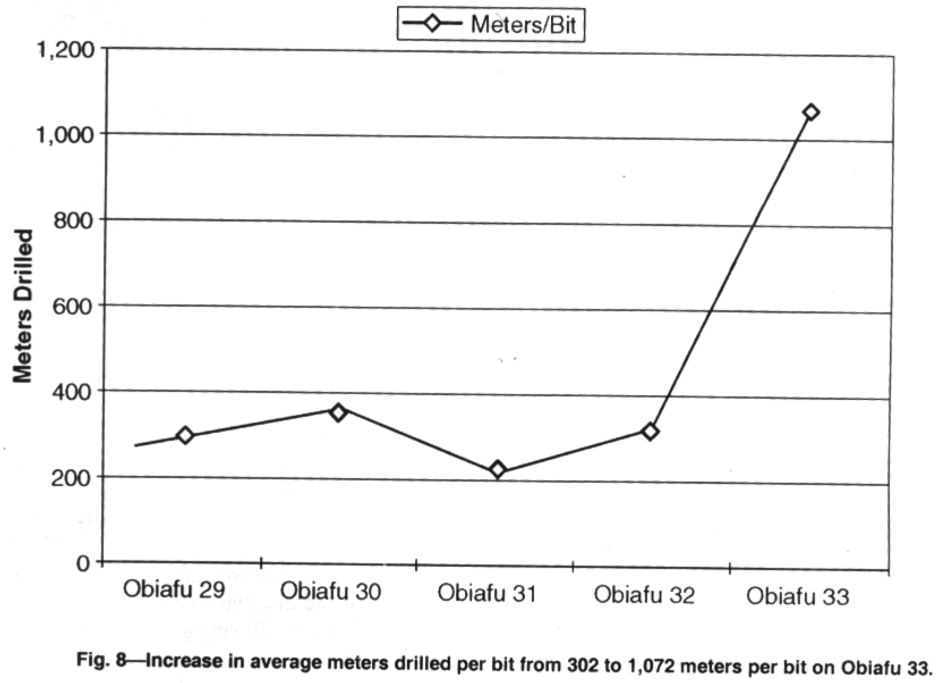

Fig. 8 - Increase in average meters drilled per bit from 302 to 1,072 meters per bit on Obiafu 33.