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Application of Locally Produced Activated Carbons for Petroleum Produced Water Treatment

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Abstract: The treatment of petroleum produced water before discharge has been made a legal requirement to protect water resources and avoid acute and chronic toxicities. Activated carbon (AC) has been widely used worldwide as an effective medium for the adsorption of biological and chemical contaminants in advance waste water, but its use is limited by its high cost. This study aimed to apply locally prepared activated carbons from coconut and palm kernel shells waste for the abatement of chemical oxygen demand (COD), turbidity, total alkalinity and conductivity in petroleum produced water. Chemical analyses of the petroleum produced water were done to establish the characteristics of the water before and after contacting with the activated carbons for 60 min. The results revealed the COD was reduced to 9.38% by PKSAC, 15.63% by CNTAC and 45.31% by ZC at the 45th min. The total alkalinity reduction was 27.27% for both PKSAC and CNTAC, and 36.36% for ZC. Also, turbidity of the waste water was reduced to 3.48% for CNTAC, 5.56% for PKSAC at the end of 60 min but an anomaly was observed for ZC, where the percentage turbidity of the water increased from 2.78% to 5.36% from the first 45th to the 60th min. The reduction of conductivities of the solution occurred in the first 15 min. The anomalous behaviours observed by all the carbons are an indication of the consumption of vacant active sites on the surface of the carbons for further uptake. This study has revealed some latent facts about the usefulness and effectiveness of granular activated carbons produced from agricultural waste materials which advances existing knowledge in the use of local agro-waste materials for AC preparation.

Keywords: Produced Water, Activated Carbon, Adsorption, Waste Water Treatment

1. Introduction

Oilfields like most production activities generate large volumes of liquid waste called produced water [1, 2]. The constituents of produced water are broadly classified into organic and inorganic compounds which includes dissolved and dispersed oils, grease, heavy, metals, radionuclides, treatment chemicals, formation solids, dissolved gases, scale products, waxes, microorganisms and dissolved oxygen [1, 3, 4]. Disposal of untreated produced water into water bodies results in environmental and human health effects in addition to the pollution of surface water, ground water and soils [1, 5]. One notable impact of the release of produced water is "chronic pollution" which is a phenomenon that results in limiting the breeding and reproduction of seabirds [6]. It is estimated that globally over seventy (70) billion barrels of produced water is generated by the petrochemical industries annually [1, 6]. In Ghana, total oil deposit is estimated to be about 800 million barrels with an upside potential of 3 billion barrels of oil. Consequentially, oil production in Ghana can be estimated to produce an average of 2400 million barrels of produced water [7, 8].

For this reason, the treatment of petroleum produced water before discharge has been made a legal requirement to protect water resources and avoid acute and chronic toxicities [9, 10].

A variety of management options for produced water exists, but the selection of an option is dependent on factors like regulatory acceptance, site location, technical feasibility,

and cost of equipment and availability of infrastructure [1, 9, 11]. The management practices have to be environmentally protective while the method used in managing produce water depending on the composition of produced water, location, quantity and availability of resources can be in the following forms [1, 11]:

(1) Avoiding produced water production onto the surface by using polymer gels and in the process separate water from oil or gas streams down-hole and re-inject it into the suitable formation.
(2) Re-injection of produced water into the same formation or another suitable formation to enhance recovery process.
(3) Treatment of produced water to meet onshore and offshore regulation before discharge.
(4) Treatment for reuse in drilling, simulation and work over in the oil and gas operation.
(5) Treatment for beneficial uses such as irrigation, animal consumption and drinking water.

Thus a careful study to determine the best treatment technology and set the disposal method is required. The traditional treatment of the wastewater effluents from the refinery and petrochemical plants are usually based on the mechanical, physicochemical and biological methods. The conventional processes that are applied for the treatment of petrochemical wastewater can only partially remove the contaminants. Often, the existing regulations governing the reuse and/or discharge of petrochemical effluents require the adoption of advanced treatment techniques [10, 12]. Among the advanced treatment techniques adsorption on activated carbons for waste water treatment has been found superior compared to other chemical and physical methods in use in terms of its capability for efficiently adsorbing a broad spectrum of pollutants, and its simplicity in design [13]. But, the high cost of the traditional commercial activated carbons produced from coal, lignite and peat wood limits its application in many parts of the world, especially those from the developing world [14 - 17]. As such, there is a rapidly growing research interest for the production of activated carbons from locally sourced materials like agricultural and industrial wastes [13, 18].

It is estimated that more than 4.2 million tons of agricultural residue are generated yearly in Ghana after the harvest season [19]. Traditionally, agro-forestry waste either ends up in landfills, openly burnt or left to decompose naturally causing environmental degradations.

The present study aimed at carrying out experiments using granular activated carbons prepared locally from palm kernel and coconut shells for the abatement of chemical oxygen demand (COD), turbidity, total alkalinity and conductivity in petroleum produced water, and to advance research in the use of local agro-solid wastes for the preparation of activated carbons.

2. Materials and Methods Used

2.1. Activated Carbon Preparation

Palm kernel and coconut shells used for the preparation of activated carbons were obtained locally. The procedure used to prepare the activated carbons was referred to in our previous work [20]. The precursors were first washed to remove mud from the surfaces and were then dried overnight in an oven at 105°C. The dried precursors were crushed and sieved to a desired particle size of 1-5 mm. 1 kg of the reduced raw materials per batch was loaded into a gas fired pyrolysis-gasification reactor to produce activated carbons.

The first step in activating is to carbonise the shells to drive out the volatiles out of the precursor to create carbonaceous mass full of tiny pores at 900°C. This carbonised base material in the second stage was activated at a temperature of 900°C under the flow of steam at 30 ml/min for different durations of 3 and 6 h for coconut shells (CNTAC) and palm kernel shells (PKSAC) respectively.

2.2. Characterisation of Activated Carbons

The porous structural characteristics of the prepared activated carbons were obtained by adsorption of liquid nitrogen at temperature (-195.6°C) adsorption isotherms, which was later used to obtain the surface area. These were carried out using an automatic adsorption unit, Autosorb -1 (Quantachrome). Surface area (S_T) values were calculated from the experimental adsorption isotherm over a relative pressure range of 0.04 to 0.2 using the standard BET (Brunauer, Emmett and Teller) method and assuming an average micropore activated carbon. The iodine number test was employed to determine the adsorption capacities of the activated carbons and the surface morphology of the carbons examined by a scanning electron microscopy to visualise the porous nature of the adsorbents [21 - 25].

Produced water used for the adsorption studies was collected from Zeal Environmental Limited in Western Region of Ghana. Samples of the water (100 ml) were mixed with carbon (1.0 g) in 250 ml Erlenmeyer flasks in batches. The mixtures were shaken at 200 rpm in a temperature controlled shaker (Vacutec Cat N° 10 ×400××2) at (25 ± °C) for 2 h then filtered using a Whatman filter paper N° 1 size 15 to remove the carbon. The characteristics of the petroleum produced water was analysed before and after treatment with the derived activated carbon. The chemical analysis included determination of chemical oxygen demand (COD), conductivity, total alkalinity and turbidity following the America Public Health Association standard methods for the examination of waste water [26, 27]. The percentage removal of contaminants was calculated by the following equation:

$$\text{Removal}\% = \frac{(C_o - C)}{C_o} \times 100$$

Where C_o is the initial concentration of the contaminant (mg/l) of the wastewater sample and C is the final concentration of contaminant (mg/l) after the adsorption period. The abatement of the selected contaminants in the produced water by the prepared activated carbons was compared with that of a commercial activated carbon (ZC) in use.

3. Results and Discussion

3.1. Characterisation of Activated Carbons

The results of the BET surface area and Iodine Number tests of the derived activated carbons and the commercial one (ZC) are shown in Table 1.

The BET surface area is an important property of activated carbons which indicate the adsorption capacity. Comparing the BET surface areas and iodine numbers of the prepared carbons study and the commercial carbons, the palm kernel shells activated carbon (PKSAC) has the highest BET surface area and iodine number followed by the ZC, and then the CNTAC. The iodine numbers and BET surface areas are in agreement with the nitrogen adsorption-desorption isotherms shown in Figure 1.

Table 1. *BET Surface Area of Prepared Carbons and Commercial ZC.*

Sample ID	BET Surface Area m2/g	Iodine Number mg/g
CNTAC	819.23	621.83
PKSAC	1160.97	1020.01
ZC	1117.82	1014.41

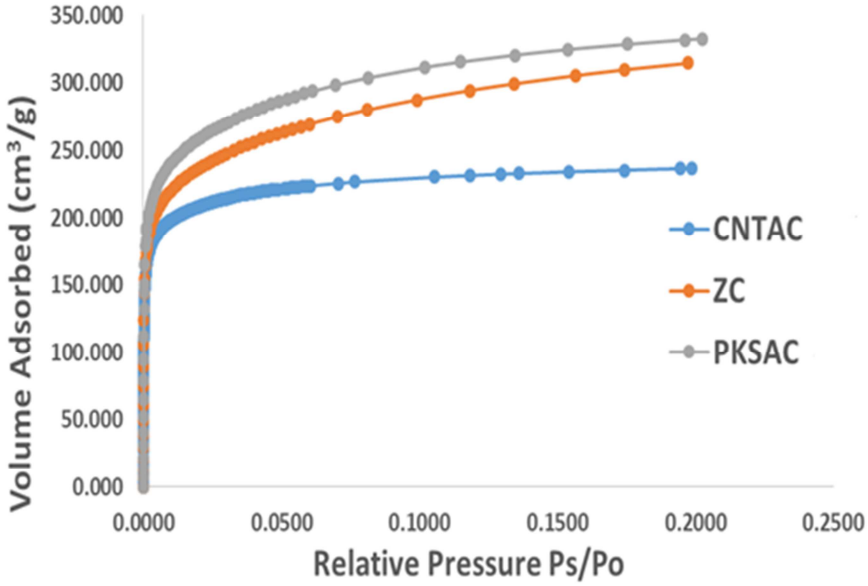

Figure 1. *Nitrogen Adsorption-Desorption Isotherms for the Prepared Activated Carbons and the Commercial ZC.*

The scanning electron micrographs (SEM) of the raw coconut and palm kernel shells and the prepared activated carbons derived from each material showing the surface morphology are shown in Figures 2 and 3 respectively. This demonstrated that activation removes hydrocarbons and tars, which enhances the adsorption capacity of activated carbons. Comparison of SEM images has also been reported in literature to be used in the determination of differences between precursors. The SEM results indicated that the nature of precursor influences the porous development and structure of the derived activated [28 - 30].

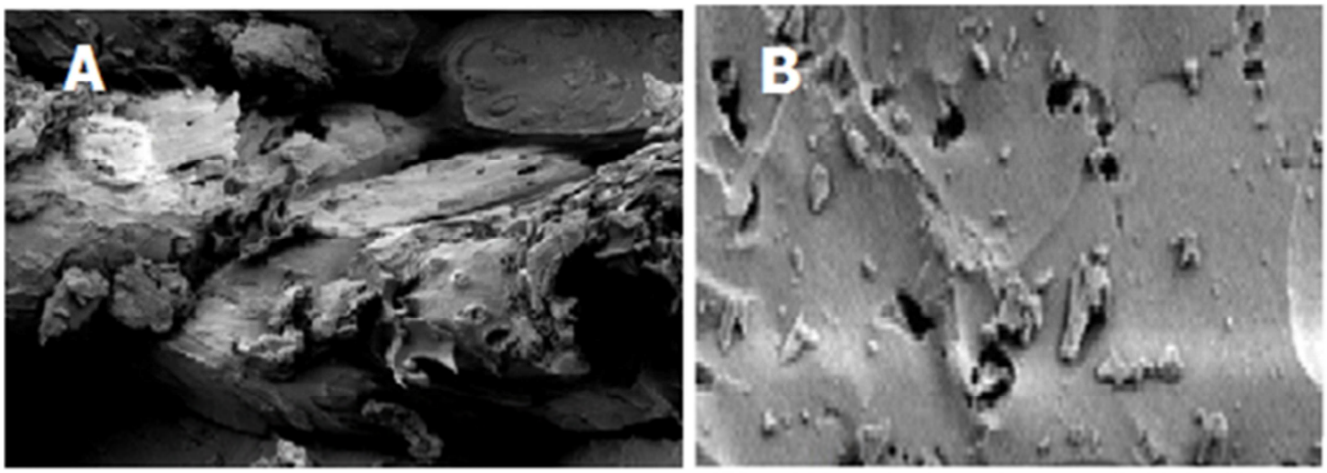

Figure 2. *Scanning micrographs of the Raw Coconut shells (A) and the Prepared Coconut Shell Activated Carbons (B).*

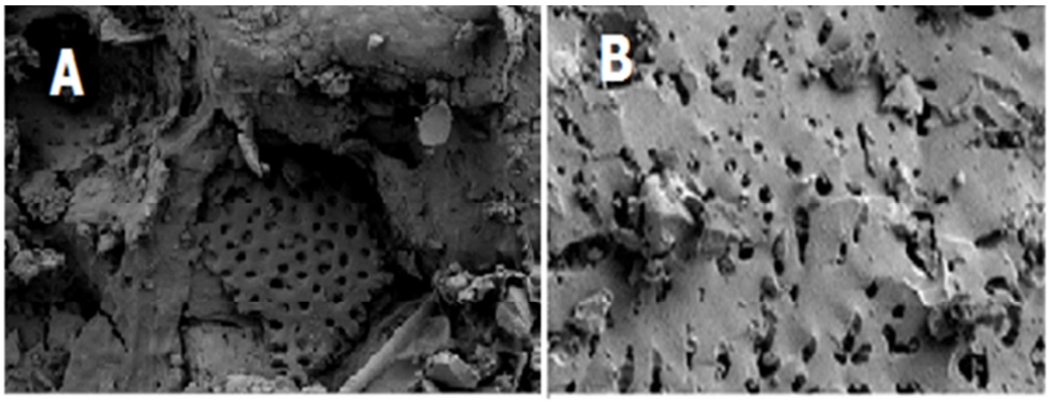

Figure 3. *Scanning micrographs of the Raw Palm Kernel shells (A) and the Prepared Palm Kernel Shell Activated Carbons (B).*

3.2. Adsorptions of the Selected Parameters of the Produced Water by the Activated Carbons

The percentage removal of the contaminants of the produced water after contacting with the prepared activated carbons and the commercial one at various times are presented in Figures 4 – 7.

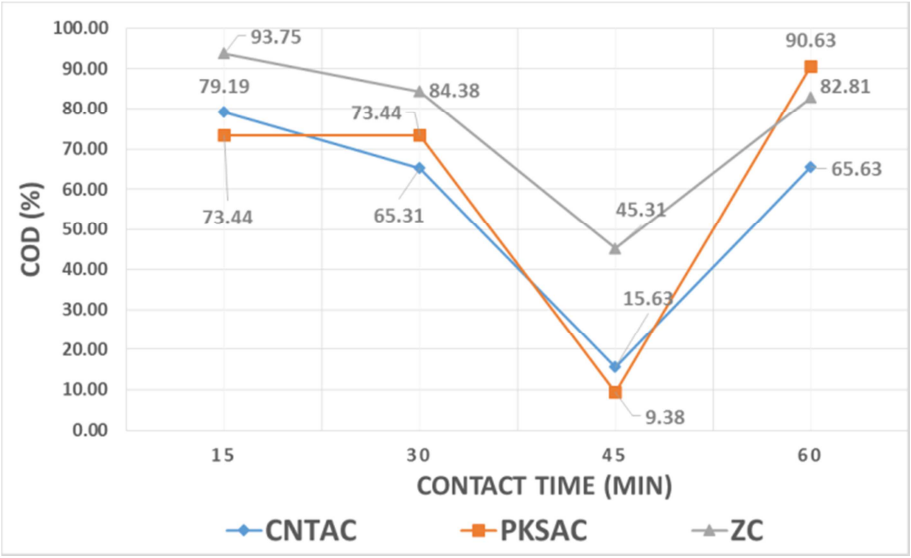

Figure 4. *Reduction of COD of Petroleum Produced Water by the Prepared Carbons and Commercial Carbons (ZC).*

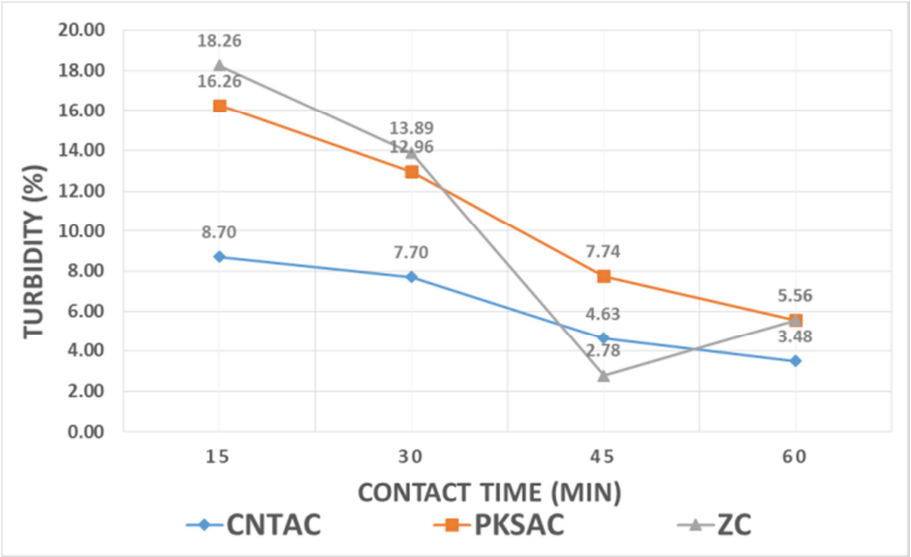

Figure 5. *Reduction of Turbidity of Petroleum Produced Water by the Prepared Carbons and Commercial Carbons (ZC).*

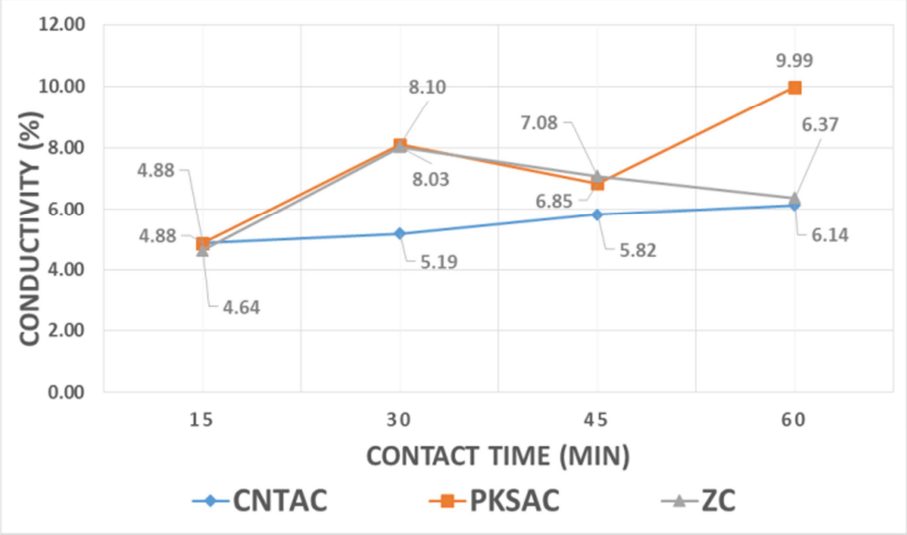

Figure 6. *Reduction of Conductivity of Petroleum Produced Water by the Prepared Carbons and Commercial Carbons (ZC).*

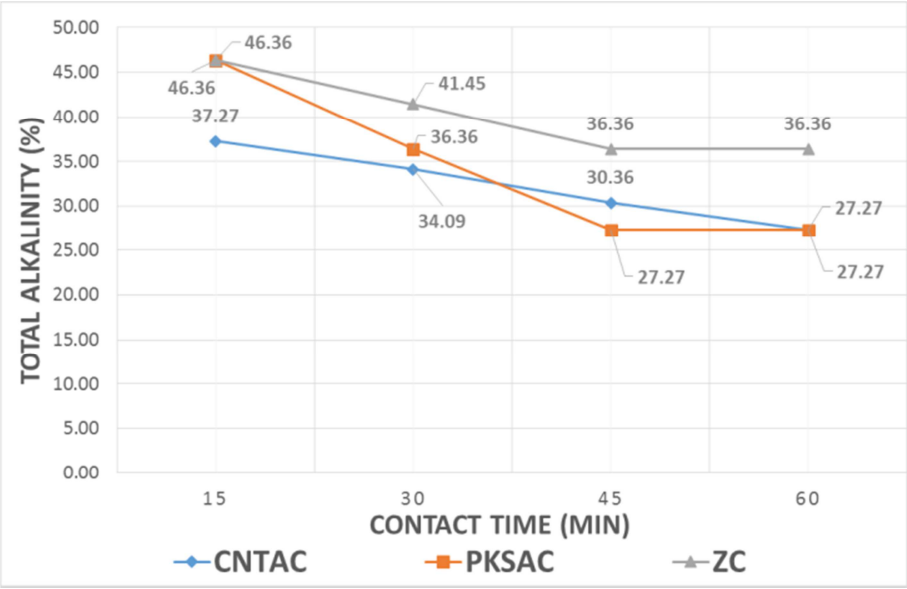

Figure 7. *Reduction of Total Alkalinity of Petroleum Produced Water by the Prepared Carbons and Commercial Carbons (ZC).*

The trends obtained from Figures 4, 5 and 7 indicate that the prepared local activated carbons were able to reduce the concentrations of the contaminants in the waste water especially within the first 45 mins of contact time. The COD at the 45th min was reduced to 9.38% by PKSAC, 15.63% by CNTAC and 45.31% by ZC. The anomalous behaviours observed by all the carbons after the 45th min is an indication of the consumption of vacant active sites on the surface of the carbons for further COD uptake [31]. The total alkalinity reduced to 27.27% for both PKSAC and CNTAC and 36.36% for ZC. The turbidity of the waste water was also reduced to 3.48% for CNTAC, 5.56% for PKSAC at the end of 60 min but an anomaly was observed for ZC, where the percentage turbidity of the water increased from 2.78% to 5.36% from the first 45th to the 60th min. The Figure 6 indicates that reduction of conductivities of the solution occurred in the first 15 min. The nature of the trends can be attributed to the larger number of active surface sites available for adsorption during the initial stage and with the passage of time decreased resulting in decrease in adsorption. The increase in the conductivities of the water samples in contact with the carbons may be attributed to the adsorption and desorption of the ions of the dissolved solids in the solution.

4. Conclusions and Recommendations

Palm kernel and coconut shells were used as precursors to successfully prepared activated carbons locally. The pores revealed by the SEM images indicated that the nature of precursor influences the porous development and nature of pores. The results of the BET surface area and iodine numbers obtained indicated that the prepared activated carbons are micro porous activated carbons. More so, the adsorption tests clearly revealed that the locally prepared activated carbons can be used as effective and low cost adsorbents. Further analysis needs to be conducted to test the

adsorption data with various isotherms and also the adsorption kinetics.

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Biography

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