

Full Length Research Paper

Degradation of anthracene: Influence of adsorbents from inorganic activation

Owabor C. N.* and Saniyo E.

Department of Chemical Engineering, University of Benin, Benin City, Nigeria.

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The use of rice and melon husks in their raw, carbonized (at 400 °C and 600 °C) and activated (using 10%, v/v orthophosphoric acid) form to catalyze the degradation of anthracene in sandy soil was investigated. Rice husk carbonized at 600 °C and activated was found to be a better adsorbent than melon husk under same condition. After five weeks of degradation experiment the anthracene reduced from an initial concentration of 5000 to 1009.7 and 1200.2 µg/g soil for rice and melon husks, respectively, while the control reduced to 2671.0 µg/g soil. Result of the batch degradation process of anthracene was found to follow first order heterogeneous kinetics with rice husk carbonized at 600 °C and activated having the fastest reaction rate constant of 0.0018 h⁻¹ followed by melon husk with 0.0016 h⁻¹ while the control had 0.0009 h⁻¹. The regression coefficients obtained from the analysis of the experimental data used to test the order of reaction were greater than 88% showing a good reliability of the data obtained.

Key words: Degradation, polycyclic aromatic hydrocarbon, anthracene, rice husk, melon husk.

INTRODUCTION

The presence of polycyclic aromatic hydrocarbons (PAHs) in the environment is becoming a problem of increasing magnitude because of their widespread distribution, their persistence and their known toxic properties (Pfaender and Roper, 2001). Concern with regards to the potential negative health effects of polycyclic aromatic hydrocarbon exposure is evident in the recent inclusion of 16 polycyclic aromatic compounds in the environmental protection agency priority contamination list (ATSDR, 1995).

Environmental anthracene contamination originates from a number of anthropogenic sources/practices such as manufacturing of dyes, production of synthetic fibers, plastics and pesticides, petroleum spills as result of pipeline rupture, tanker failure, land transport accidents, and incomplete combustion of fuel (such as coal, oil, gas). Due to the fact that anthracene has been implicated

as a mutagenic and carcinogenic substance, it poses potential hazard to man's health, thus methods need to be devised to eliminate or reduce their concentration in soil and water to a tolerable level. Degradation of anthracene, which is its conversion into both carbon dioxide and water (mineralization), or another organic substance (degradation product) which is not toxic, is one of the inexpensive way of removing large concentration of anthracene from soil and water. (Mette, 2001). Various methods have been improvised to accelerate this degradation process. These include addition of nutrients (Bedessem et al., 1997), use of hydrogen peroxide, use of iron (III) as catalyst (Anderson et al., 2000), and use of surfactants (Eyre, 1999).

Active carbon manufactured from carbonaceous materials, usually carbohydrates; wood, coal, nutshell, husks (coconut, rice), lignite, vegetable matter and other carbon-containing materials such as peat moss have been used as effective adsorbent for removal of dissolved organic substances from water (Vernon et al., 1967). In this work, activated carbon from rice and melon husks were used as catalysts in the degradation of anthracene.

*Corresponding author. E-mail: owabor4you@yahoo.com.

EXPERIMENTAL

Materials

Sandy soil was collected from uncultivated site at the Nigeria Institute for Oil and Palm Research (NIFOR) near Benin City Edo state. The soil sample was air dried. Rice husk was collected from a rice mill at Ekpoma, Edo state, while the melon husk was collected from New Benin Market, Benin-city, Edo state. The husks were dried and ground to smaller sizes by a blender. All chemicals used were of analytical grade.

Methods

The organic carbon content of the soil was determined by employing the method of Walkley and Black (1934), as described by Black (1965). The rice and melon husks were carbonized at 400 and 600°C before the raw and carbonized husks were activated using a 10% (v/v) H₃PO₄. The iodine number of the husks was determined by the procedures described by Philip (1992). The moisture content, pH and bulk densities of the husks were determined using the procedures described by the American Society for Testing Materials (D2867-95, D3838-80 and D2854-96) respectively.

Degradation experiment

Batch degradation study was carried out with 100 g of sandy soil in 13 different cylindrical reactor flasks (1500 ml). 1000 ml of the anthracene solution (prepared by adding 15 g of anthracene to 30 ml of methanol and the resulting solution added to 1000 ml of distilled water and properly stirred) was added. Due to the low final concentration (0.1%, v/v) of the carrier solvent (methanol), it was assumed to have no effect on the degradation process (Benny et al., 2000). 10 g of the 12 variations of carbonaceous materials were weighed and added to each of the cylindrical flask containing sand and was vigorously stirred and allowed to stand. The remaining container without any carbonaceous material was used as a control sample to monitor natural degradation. 20 ml of the settled mixture was taken from the top layer of the solution from each cylinder to determine the amount (concentration) of anthracene. Thereafter, on a weekly basis, 20 ml of solution was taken from the top layer of each of the settled mixture to determine the concentration of anthracene. The procedure was repeated for 5 consecutive weeks. Kinetic analysis of the data obtained was carried out by employing the 1st order heterogeneous equations (Octave, 1999).

Determination of the concentration of anthracene

The quantification of anthracene was done using a Hewlett Packard Gas Chromatography (HP 5890 series 11). The gas chromatograph is equipped with flame ionization detector and nitrogen was used as carrier gas at a pressure of 60-65 psi. The injector and detector temperatures were 250 and 320°C, respectively. The column temperature was 40 to 300°C programmed at 10°C /min with computer interphase and a Chem Station.

Developing the rate equation for the degradation

Since more than one phase is present, the movement of materials from phase to phase must be considered in the rate equation. Thus the rate expression in general will incorporate mass transfer terms in addition to the usual chemical kinetics term. The model assumptions were as follows:

The polycyclic aromatic hydrocarbon is adsorbed from the solution through a stagnant film onto the surface containing the activated carbon and the soil.

The micro-organism present in the soil degrades the PAHs sorbed from the pores.

The degradation product diffuses back to the main stream free the pores of the carbon for further adsorption.

Reaction rates written on a unit volume of fluid.

The adsorption and degradation steps are in series.

The adsorption step is linear in concentration.

Thus by adsorption, the sorption of PAHs to the surface is

$$-r_{A1} = (1/V) (dN=1/dt) = K_L (C_{AL} - C_{AS}) \text{-----(1)}$$

Degradation process with respect to a based on unit volume of fluid is

$$-r_{A2} = (1/V) (dNA/dt) = K_R C_{AS}^n \text{-----(2)}$$

At steady state the sorption to the surface is equal the degradation rate at the surface (step in series)

$$\text{Therefore } r_{A1} = r_{A2}$$

$$\text{And } K_L (C_{AL} - C_{AS}) = K_R C_{AS}^n \text{-----(3)}$$

Where C_{AL} = concentration of PAHs in solution

C_{AS} = concentration of PAHs at the surface of solid

K_L = absorption rate constant

K_R = degradation rate constant

n = order of reaction

If the degradation process follow a first order kinetics, the $n = 1$ and equation 3 becomes

$$K_L (C_{AL} - C_{AS}) = K_R C_{AS}$$

$$K_L C_{AL} = (K_L + K_R) C_{AS}$$

$$C_{AS} = (K_L / (K_L + K_R)) C_{AL} \text{----- (4)}$$

Substituting equation 4 in equation 2

$$-r_{A2} = K_R C_{AS} \quad (n = 1)$$

$$-r_{A2} = \frac{K_R K_L}{K_L + K_R} C_{AL}$$

$$-r_{A2} = \frac{1}{1/K_L + 1/K_R} C_{AL}$$

$$\text{If } K = 1$$

$$1/K_L + 1/K_R$$

Therefore equation 5 becomes

$$-r_{A1} = -r_{A2} = K C_{AL}$$

$$\text{Since } -r_{A2} = -dC_{AL}/dt$$

$$-dC_{AL}/dt = K C_{AL}$$

$$-dC_{AL} / C_{AL} = K dt$$

Table 1. Iodine number of the various husks.

Husk	Iodine number (mg I ₂ /g carbon)
Raw melon husk	8.9
Raw rice husk	11.45
Carbonized melon husk at 400 °C	19.08
Carbonized melon husk at 600 °C	21.62
Carbonized rice husk at 400 °C	29.26
Carbonized rice husk at 600 °C	31.8
Activated raw melon husk	24.168
Activated raw rice husk	31.8
Carbonized and activated rice husk at 400 °C	35.616
Carbonized and activated rice husk at 600 °C	38.16
Carbonized and activated melon husk at 400 °C	27.984
Carbonized and activated melon husk at 600 °C	31.8

On integrating

$$\ln (C_{AL} / C_A) = K t$$

Thus a graph of $\ln (C_{AL}/C_A)$ versus t will give a straight line starting from the origin.

RESULTS AND DISCUSSION

Characterisation of the various husks

Results obtained for the characterization of various carbonaceous materials clearly shows that the activation or treatment of carbonaceous materials by chemical or thermal or both processes enhances the adsorptive qualities of the carbonaceous materials (Table 1). The progressive increase in iodine number as the temperature was increased can be attributed to the fact that an increase in carbonization temperature is accompanied by respective increase in pore volume and pore diameter and a decrease in non carbonaceous material that retard its adsorptive properties.

The activated raw melon and rice husk show similar properties with various carbonized rice and melon husk with respect to iodine number, with the activated raw melon and rice husk having a slight advantage. This infer that what can be achieved by carbonization at elevated temperatures can also be achieved with use of activating acid like orthophosphoric acid since both thermal and chemical activation serve to remove non-carbonaceous material from the husks.

Batch degradation study

On the batch degradation studies, it can be seen from Figures 1 to 3 that with carbonaceous material present or

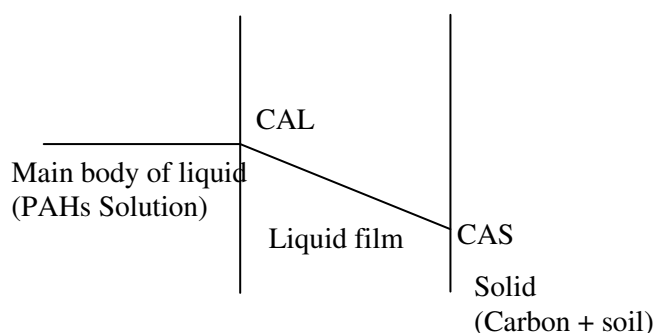


Figure 1a. Movement of anthracene from solution unto the solid surface.

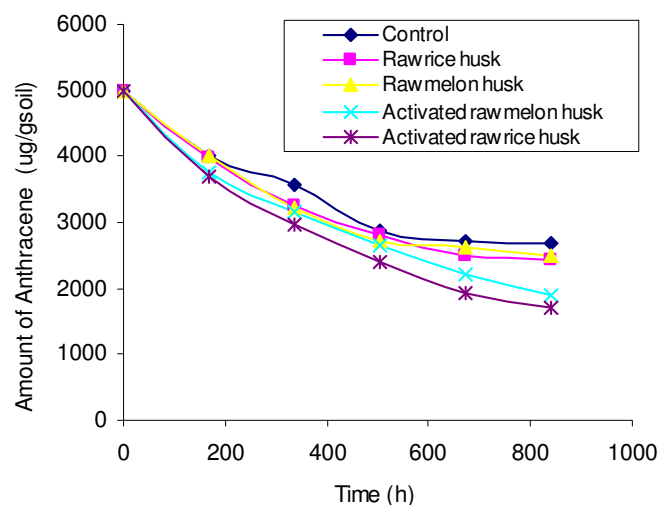


Figure 1b. Degradation curves of anthracene using raw and activated rice and melon husks.

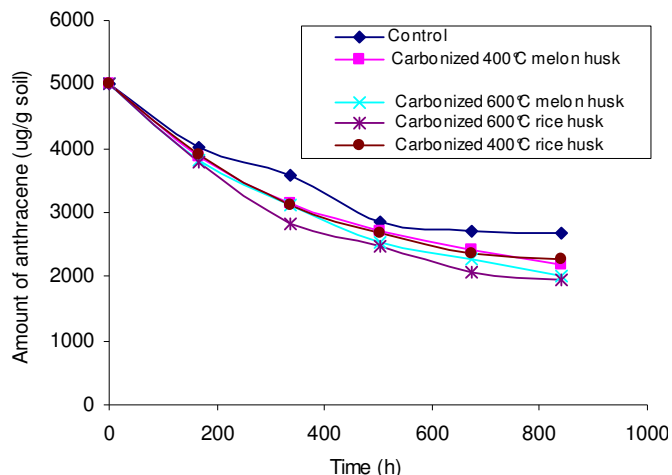


Figure 2. Degradation curves of anthracene using carbonized rice and melon husk.

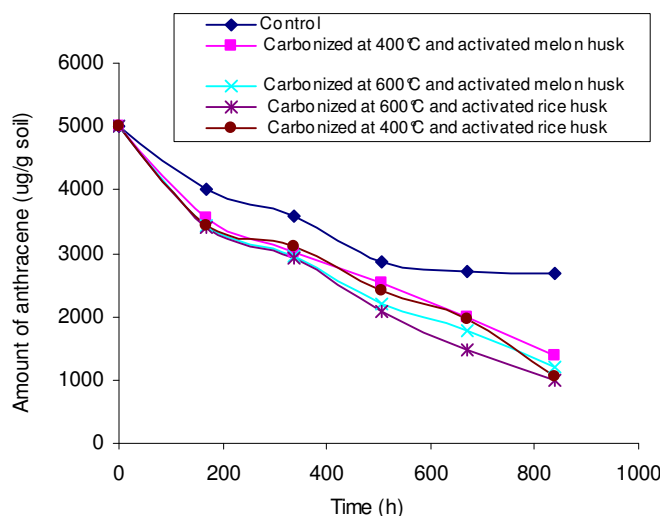


Figure 3. Degradation curves of anthracene using carbonized and activated rice and melon husk.

not, degradation of the anthracene occurs. This corresponds to the fact that natural degradation of polycyclic aromatic hydrocarbon does occur. From the figures, it can be observed that for the first week of experiment, there was drastic reduction in the amount of anthracene in solution for all samples. This is attributed to the fact that all the adsorptive sites i.e. internal surface area are still available for adsorption of the adsorbate (anthracene) and with the additional degradation of the anthracene by microorganism, the rate of removal of anthracene from solution was more. For the subsequent weeks (week 2, 3, 4, and 5), there was a reduction in concentrations of anthracene in solution. This can be attributed to the fact that all the pores available for

anthracene to be sorbed onto in the adsorbent have been occupied during the first week and as such require the microorganism to degrade these sorbed anthracene from the pores before more anthracene molecule from the solution can be sorbed to that pore thereby reducing the rate of removal of anthracene from solution. After five weeks of degradation experiment, the concentration of anthracene left in solution was recorded and it can be seen that various concentration of anthracene was obtained for various husks added to the anthracene solution in soil, with the control sample having the highest concentration of anthracene, while rice husk carbonized at 600°C and activated with 10% (v/v) orthophosphoric acid had the least concentration of anthracene in solution.

The pattern of the degradation of anthracene in soils containing raw melon husk, raw rice husk, activated raw melon husk, activated raw rice husk and control is shown in Figure 1. The figure shows that there was a significant difference in the degradation in the presence and absence of carbonaceous material. The degradation of anthracene in soil using activated raw rice husk was fastest followed by activated raw melon husk, raw rice husk, raw melon husk and control. Also from the curve, the degradation process using raw rice husk, raw melon husk and control were fast approaching a “plateau” (uniform or constant) concentration after 600 h while the others were far from that. The degradation of anthracene in soils using carbonized melon and rice husks at various temperatures is depicted in Figure 2. The curves clearly show that as the carbonization temperatures increased for a particular material, the degradation process became faster with carbonized rice husk at 600°C showing the fastest degradation followed by rice husk carbonized at 400°C. Figure 3 shows the degradation process using carbonized melon and rice husk which were activated. The degradation process using these set of carbonaceous materials resulted in the presence of minimal amount of anthracene at termination time.

It was observed that the degradation process with the various forms of carbonaceous materials were faster than without any carbonaceous material (control). This is because one of the factors hindering the effective degradation of PAHs by microorganisms in soil is the availability of PAHs for microbial degradation. By sorption mechanism, the large, readily accessible surface area of these carbonaceous materials has made the PAHs available for microbes by adsorbing the anthracene (sorbate) from the soil.

The rate of degradation was determined by testing the fitness of the data obtained at the termination of the batch studies to kinetics of a 1st order heterogeneous reaction. Straight line plots starting from the origin were obtained for all samples of carbonaceous material used, and regression coefficient (R^2) greater than 88% obtained, thereby verifying the reliability of the data and the graph

Table 2. Regression coefficients for the 1st order disappearance of anthracene.

Sample Type	Regression Coefficients (R ²)
Control	0.8971
Raw melon husk	0.8801
Raw rice husk	0.922
Activated raw melon husk	0.9801
Activated raw rice husk	0.9764
Carbonized melon husk at 400 °C	0.9188
Carbonized melon husk at 600 °C	0.9149
Carbonized rice husk at 400 °C	0.9539
Carbonized rice husk at 600 °C	0.9324
Carbonized and activated melon husk at 400 °C	0.9823
Carbonized and activated melon husk at 600 °C	0.9864
Carbonized and activated rice husk at 400 °C	0.9422
Carbonized and activated rice husk at 600 °C	0.9898

plotted. The reaction rate constants are as shown in Table 2.

The graphs show that the degradation process follow a first order heterogeneous reaction kinetics with the control having the least reaction rate constant of 0.009 h^{-1} while the carbonized at 600°C and activated rice husk had the fastest reaction rate constant of 0.0018 h^{-1} . The melon husk at the same condition had a rate constant of 0.0016 h^{-1} . These results show that the degradation rate was twice faster when the carbonized at 600°C and activated rice husk was added compared to the soil without an adsorbent. Using this first order kinetic data it implies that to obtain an acceptable treatment end point of soil contaminated with anthracene from $5000 \mu\text{g/g}$ soil, it will take 10 g of carbonized (at 600°C) and activated rice husk 135 days while natural degradation will take 267 days.

CONCLUSIONS

From the investigation of the influence of various carbonaceous materials prepared from rice and melon husks in the degradation of anthracene in soil, it can be deduced that as the carbonization temperature increased from 400°C to 600°C , the yield for rice and melon husk decreased while the iodine number increased implying an increase in surface area. The effect of treatment of raw rice husk and melon husk with 10% (v/v) orthophosphoric acid was approximately the same as carbonizing these husks at a temperature of 600°C . The carbonization and activation of rice and melon husks improved the properties (iodine number) of these husks than either carbonization or activation alone. The degradation of anthracene using carbonaceous materials prepared from melon and rice husk at the various specified conditions

was faster than degradation without any adsorbent. Rice husk carbonized at 600°C and activated with 10% (v/v) orthophosphoric acid was found to degrade the anthracene faster than any other carbonaceous material produced. Rice husk was found to be a better carbonaceous material than melon husk in the degradation of anthracene. Finally, the degradation of anthracene in soil using carbonaceous material follows first order kinetics.

REFERENCES

- Agency for Toxic Substances and Disease Registry (ATSDR). (1995). Toxicology profile for polycyclic aromatic hydrocarbons (PAHs), Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service. E-mail ATSDRI@cdc.gov.
- American Society for Testing Material (ASTM). www.ASTM.org.
- Anderson TR, Rooney VJN (2000). "Aromatic and Polycyclic Aromatic Hydrocarbon Degradation under Fe (III) Reducing Conditions" University of Massachusetts. Amherst. Ma 01003. pp. 1-7.
- Bedessem ME, Swoboda CNG (1997). "Naphthalene Mineralization Coupled to Sulfate Reduction in Aquifer – Derived Enrichments" FEMS Microbiol. Lett. Vol.152, pp. 213–218.
- Benny C, Ashish PD, Hatcher GP (2000). "Pyrene Sorption by Natural Organic Matter" Environ. Sci. Technol. Vol. 34, pp. 2925–2933.
- Black CA (1965). "Organic Carbon Determination by the Chronic Acid Wet Oxidation Method", Methods of soil Analysis. pp. 1372-1376.
- Mette B (2001). "Natural Degradation of Polycyclic Aromatic Hydrocarbons in Soil and Ground Water" Environmental project no 582 Danish EPA.
- Octave L (1999). "Chemical Reaction Engineering" McGraw hill Book Company, 3rd edition, New York. pp. 369 – 373.
- Pfaender F, Roper CJ (2001). "Pyrene and Chrysene fate in surface soil and sand" Environ. Toxicol. Chem. Vol. 20, issue 2, pp. 223–230.
- Phillip Process Engineering (1992) "Philip's Process Company Laboratory Manual for NNPC" TRW broading Bartlesville, Oklahoma 74000 pp. C2–C9.
- Vernon IS, Weber WJ Jr. (1967). "The Surface Chemistry of Active Carbon" American Water Works Vol.1, pp. 228-233.
- Walkley A, Black IA (1934). "An Examination of the Degtjareff Method for Determining Soil Organic Matter and a Proposed Modification of the Chromic Acid Titration Method" Soil Sci. Vol. 37, pp. 29–38.