Full Length Research Paper

Application of adsorbent as a novel technique during biodegradation of a polycyclic aromatic hydrocarbon (anthracene)

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The use of an alternative technique as a management strategy for the decontamination of hydrocarbon-based pollution in soil has been advanced in this work. The study investigated the degradation of anthracene, a three-ringed benzene derivative, in clay soil at ambient conditions under the influence of hydrophilic compound (carbon), thermally activated at temperatures of 300, 500, 700 and 900°C. The soil (500 g) was impacted with 1:1 of the contaminant anthracene and activated carbon from groundnut shell in a water medium at a flow rate of 5.0 ml/min. Experimental results revealed that there was a significant reduction in the level of anthracene in the soil matrix with time. The percentage reduction was found to be directly dependent on the activation temperature. The estimated reaction rate constant was found to be 0.014/h (control sample without activated carbon) while for the experimental samples, the values ranged from 0.018 - 0.051/h. The study therefore affirms that the presence of activated carbon in microbial degradation of anthracene, elicits an enhanced disappearance rate of the hydrocarbon.

Key words: Anthracene, management strategy, activated carbon, groundnut shell, microbial degradation.

INTRODUCTION

The increased reliance on technology by man to obtain and maintain the desired standard of existence has resulted in the overlooking of the best possible monitor of the quality of life itself which is the environment. Most of the pollutant currently bedeviling our environment are mainly organic in origin and are of great concern due to their presence in detectable quantities in various compo-nents of the ecosystem (Boonchan et al., 2000), their persistence, toxicity and their tendency to bioaccumulate (Owabor, 2007).

Generally, the Nigerian environment has been sub-jected to a barage of sustained and unmitigated pollution of its air, land and sea. Some of the spills have been known to seep into the ground and contaminate ground-water (Asuquo et al., 2004). In recent times, soil pollution resulting from industrial activities such as exploration, production and refining of crude oil is been given signifi-

cant attention (Layokun et al., 1987; Amadi and Antai, 1991; Odokuma and Dickson, 2003). Soil pollution can also result from the discharge of solid waste, particu-larly, agricultural waste. It is now generally recognized that land deserves the same attention and protection as water and air. This recognition has arisen because of the increased incidence of scarcity of farmlands in the Niger-Delta and other regions where pollution due to oil and petroleum spillages are recurrent and increased aware-ness about the potential long term negative health effects (Nwilo and Badejo, 2001; Kinigoma, 2001).

A major pollutant that has been subject of many excellent reviews over the years is the polycyclic aroma-tic hydrocarbons (PAHs). They are generally referred to as "priority pollutant" (Karthikeyan and Bhandari, 2001). Due to their lipophilic nature, PAHs have a high potential for biomagnification through trophic transfers. They are also known to exert acutely toxic effects and/or posses mutagenic, teratogenic or carcinogenic properties (Kanaly and Harayama, 2000). The overwhelming report-ed literature and articles have shown that stimulation and augmentation of indigenous microorganisms present in

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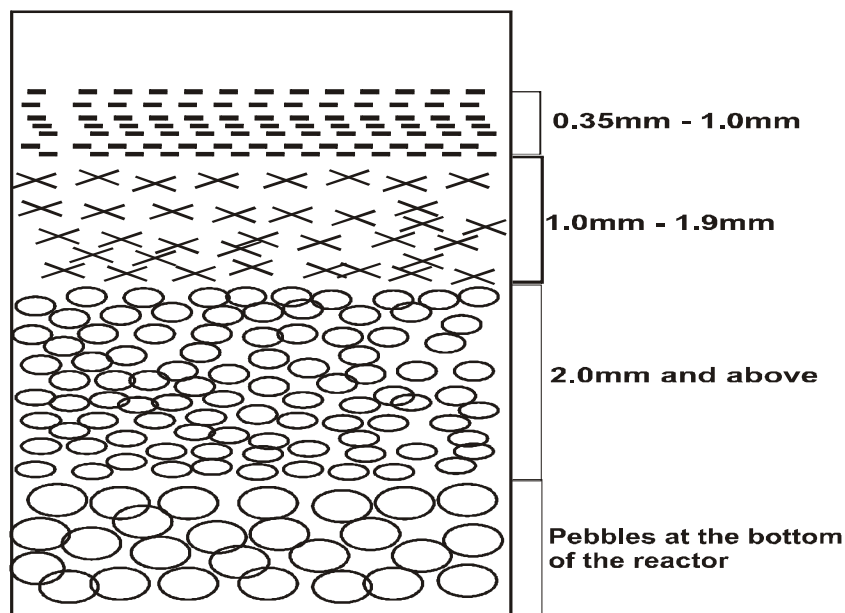
Figure 1. Schematic representation of particle size distribution within the soil matrix.

contaminated soil essentially increases the rate of degradation so as to eliminate as quickly as possible both long and short term effects of these contaminants that compromise the integrity of the environment (Bouchez et al., 1996; Ahn et al., 1999; Reardon et al., 2002; Bogan et al., 2003; Xu and Obbard, 2004). To this end, bioremediation has become successful over the years in harnessing the natural activity of microorganisms.

The purpose of this study is to assess the capacity of adsorbents in ex-situ bioremediation processes. This paper therefore, investigates the use of adsorbent (activated carbon) prepared from groundnut shells to accelerate the bioremediation of PAH-contaminated soil while reducing the menace posed by the agricultural waste (groundnut shell) by transforming it into a more economically viable use.

MATERIALS AND METHODS

Materials

Fresh groundnut shells were obtained from New Benin market in Benin City, Edo State while the clay soil was collected from Enerhen River in Warri, Delta State. Sampling was done around a sampling point to a depth of 0 – 15 cm. The chemicals/reagents used were of analytical grade and were obtained from Chemical Engineering Laboratory, University of Benin, Benin City. Distilled water was used for sample dilution and preparation. Carbonization of the groundnut shell at the varying temperatures of 300, 500, 700 and 900°C was carried out according to the method of Owabor and Iyasele (2006) and Owabor and Ogunsakin (2006). Solvent extraction was carried out using n-hexane and dichloromethane (HPLC grade). A Hewlett Packard gas chromatograph (HP 5890 series II) was used for the quantitative determination of the concentration of anthracene in the reacting medium. The soil sample

and extracts for chromatographic analysis were preserved following the procedure described by Owabor and Irheren, (2006).

Batch degradation studies

The aerobic degradation studies was conducted by spiking 500 g of clay soil containing 50 mg of the carbonized groundnut shell with 50 mg of anthracene dissolved in 1 L of distilled water. A control sample which did not contain activated carbon was set up along side the experimental samples following the same procedure.

A column reactor constructed using a 20 mm thick plastic glass (transparent material) with the dimensions 20.32 cm height by 10.16 cm width by 8.5 cm length with a holding capacity of 10 L was used to simulate reaction conditions occurring in the depth from which soil samples were collected. The soil was arranged according to the particle size distribution within the soil matrix. A schematic representation is as shown in Figure 1.

The temperature and pressure of the reacting system were monitored throughout the period of experimentation using a digital multimeter and pressure gauge. The nutrient level of the reaction media (both control and experimental) were not boosted as no nutrient supplement was introduced. Thereafter, samples were taken on a weekly interval and analyzed for anthracene concentration with the gas chromatograph after solvent extraction.

RESULTS AND DISCUSSION

A general decrease in the concentration of anthracene was observed with time in the experimental and control samples presented in Figure 2. These results indicate that anthracene naturally degraded in the samples due to the presence of the microorganisms present in the soil. However, comparing the degree of degradation following the degradation curves for soil without adsorbent to that containing adsorbent carbonized at the varying tempera-
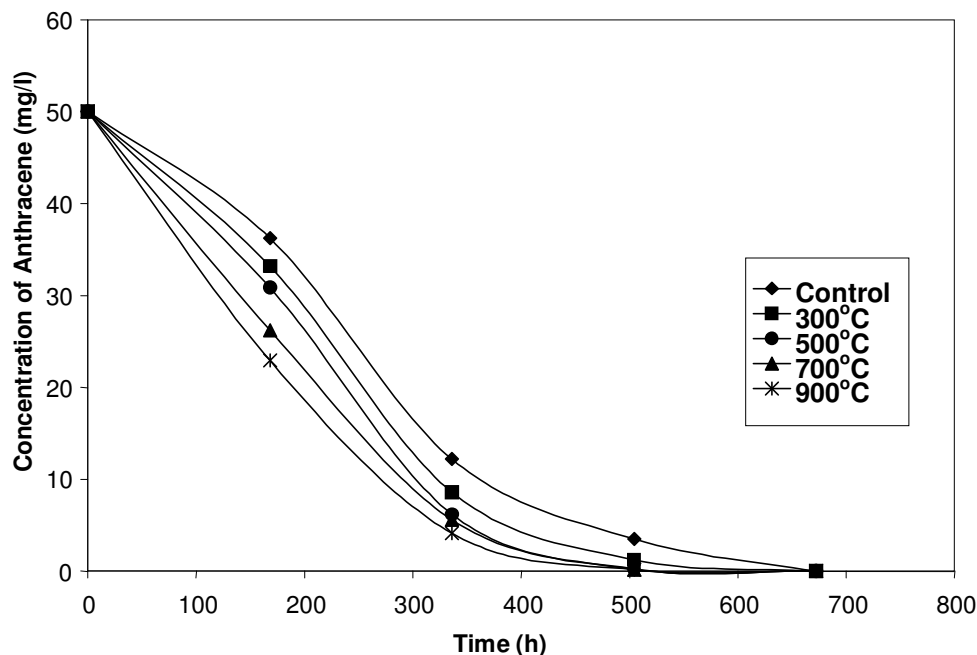
Figure 2. Degradation of anthracene in soil containing activated carbon at different temperatures.

tures under investigation (300, 500, 700 and 900°C) showed that degradation was faster in the latter than the former.

The observed trend maybe attributed to the presence of the adsorbents and the effects of carbonization. As carbonization occurs, the number of sites available for adsorption also increases. This results in the removal of anthracene from the liquid phase onto the solid which is the adsorbed phase. The overall effect is an increase in the decay rate of anthracene in the samples with adsorbent. This observation can be related to the result of the experimental study conducted by Owabor and Iyasele, (2006) and Owabor and Ogunsakin (2006) where it was reported that activation and carbonization of agricultural waste materials improves their adsorptive capacity. The positive influence of adsorbents in the biodegradation process of contaminants of organic origin is further strengthened by the results of the investigation carried out by Takashi et al. (2002) and Ruchi et al. (2004).

The variation in the degradation rates for clay soil with adsorbent at the different temperatures of carbonization was determined by calculating the percentage reduction of anthracene. The results shown in Figure 3, suggest that the higher the temperature of carbonization of the activated carbon, the better the adsorptive capacity of the adsorbent and hence the greater the rate of disappearance of anthracene. The result of this study is significant as it confirms the effectiveness of the use of adsorbents as an alternative to the introduction of supplements in the form of bioaugmentation and/or biostimulation of the indigenous microbes during the remediation of contami-

Table 1. Estimated reaction rate constant for control and experimental clay soil sample.

Sample type	Rate constant k (h⁻¹)
Control (Soil without adsorbent)	0.014
Soil with adsorbent at 300°C	0.018
Soil with adsorbent at 500°C	0.024
Soil with adsorbent at 700°C	0.03
Soil with adsorbent at 900°C	0.051

nated soils.

Modelling of the consumption rate of anthracene was achieved by subjecting the data from experiments to the Michaelis-Menten kinetics using the Lineweaver-Burk double reciprocal plot. The results are shown below in Table 1. The estimated reaction rates constant (k) was found to be lower for the natural degradation process. These estimates further confirms the earlier deduction that biodegradation is enhanced in the presence of activated carbon. For biodegradation in the presence of the hydrophilic component (activated carbon), the trend was in the order: $900 > 700 > 500 > 300$°C. The yield of the activated carbon from the groundnut shell was found to decrease with increasing temperature of activation as shown in Table 2.

The observation is predicated on the fact that as the temperature of carbonization increases, some of the carbon content becomes ashed. This result is consistent with literature finding of Tharapong et al. (1999), in which it was reported that the higher the temperature of carbo-
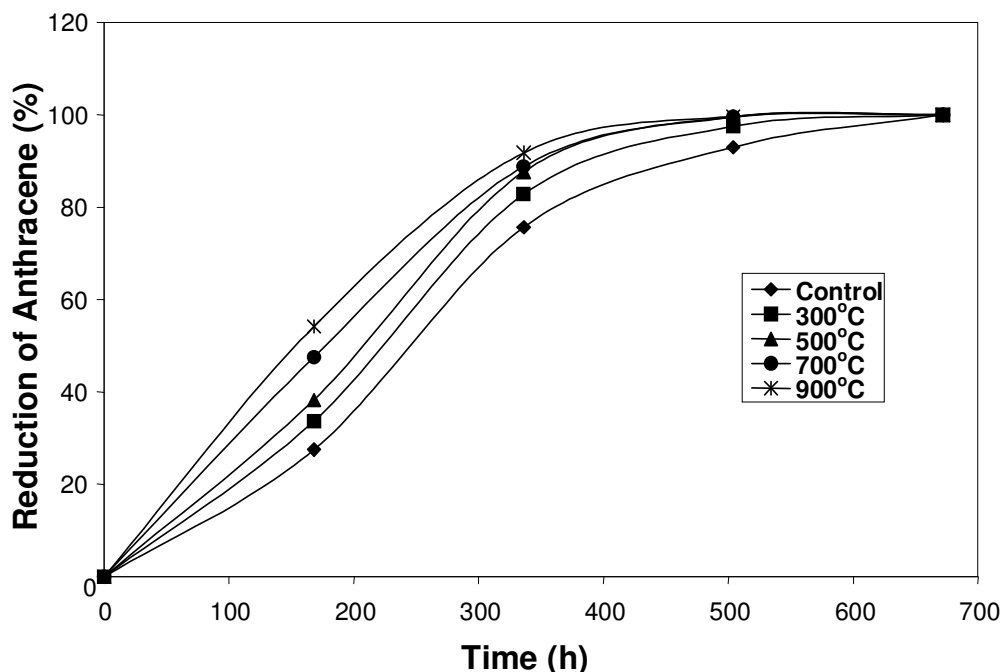
Figure 3. Percentage reduction of anthracene in clay soil.

Table 2. Yield of activated carbon from groundnut shell at varying temperatures.

Temperature (^{o}C)	Original weight (g)	Final weight (g)	Carbon yield	% Carbon yield
300	150	125	0.8180	81.80
500	150	43.8	0.2920	29.20
700	150	36.3	0.2420	24.20
900	150	35.3	0.2353	23.53

nization, the lower the yield and the better the performance of the adsorbent.

Conclusion

The rate of biodegradation of anthracene in the soil is a function of the microbial content of the soil as well as conditions that favour their activity. The rate of biodegradation of clay soil spiked with anthracene can be further enhanced by the addition of activated carbon. The higher the temperature of carbonization (optimum), the greater the adsorptive capacity of the adsorbent and hence the more anthracene removed from the aqueous phase onto the adsorbed solid phase for biodegradation. However, there is the need to further investigate the optima temperature for the carbonization that will enhance the overall performance of this novel technique. The success recorded in this work serves as a benchmark and as an alternative technology for cleaning up oil spill in land and water.

REFERENCES

Ahn Y, Sanseverino J, Sayler GS (1999). Analyses of polycyclic aromatic hydrocarbon-degrading bacteria isolated from contaminated soils. Biodegradation 10: 149-157.

Amadi A, Antai SP (1991). Degradation of bonny medium crude oil by microbial species isolated from Oshika-Oyekama oil polluted area. Int. J. Biochemphys. 1: 10-14.

Asuquo FE, Ewa-oboho I, Asuquo EF, Udo PJ (2004). Fish species used as biomarker for heavy metal and hydrocarbon contamination for Cross River, Nigeria. The Environmentalist, 24: 1-2.

Bogan BW, Trbovic V, Paterek JR (2003). Inclusion of vegetable oils in Fenton's chemistry for remediation of PAH-contaminated soils. Chemosphere, 50: 15-21.

Boonchan ML, Sudarat B, Grant AS (2000). Degradation of high molecular weight polycyclic aromatic hydrocarbon by defined fungi-bacteria cocultures. Appl. Environ. Microbiol. 66: 1007-1019.

Bouchez M, Blanchet D, Vandecasteele VP (1996). The microbiological fate of polycyclic aromatic hydrocarbons. Carbon and oxygen balances for bacterial degradation of model compounds. Appl. Microbiol. Biotechnol. 45: 556-561.

Kanaly RA, Harayama S (2000). Biodegradation of high-molecular-weight polycyclic aromatic hydrocarbons by bacteria. J. Bacteriol. 182(8): 2059-2067.

Karthikeyan R, Bhandari A (2001). Anaerobic biotransformation of aromatic and polycyclic aromatic hydrocarbons in soil microcosms: A

review. J. Hazard. Subst. Res. 3: 1-7.

Kinigoma BS (2001). Effects of drilling fluid additives on the Niger Delta environment: A case study of the Soku oil fields. J. Appl. Sci. Environ. 5(1): 57-61.

Layokun SK, Umoh EF, Solomon A (1987). Kinetic model for the degradation of dodecane by pseudomonas flourescens isolated from Warri in Nigeria." J. Niger. Soc. Chem. Eng. 6: 49-52.

Nwilo PC, Badejo OT (2001). Soil sediment and water: Impacts of oil spills along the Nigerian coast. The Association for Environmental Health and Sciences (AEHS).

Odokuma LO, Dickson AA (2003). Bioremediation of crude oil polluted tropical rain forest soil. Glob. J. Environ. Sci. 2: 29-40.

Owabor CN (2007). Substrate bioavailability and biodegradation of naphthalene, anthracene and pyrene on contaminated aqueous-soil matrix, Ph.D Thesis, University of Lagos, Nigeria.

Owabor CN, Irheren MO (2006). Effect of nutrient and moisture content variation on the bioremediation of anthracene contaminated soil. Niger. J. Biomed. Eng. 4(1): 9-14.

Owabor CN, Ogunsakin NO (2006). Sorption interactions of a polycyclic aromatic hydrocarbon (naphthalene) on suspended carbonaceous materials using alkali activator, J. Sci. Eng. Technol. 13(1): 6619-6626.

Owabor CN, Iyasele NO (2006). Sorption interactions of a polycyclic aromatic hydrocarbon (naphthalene) on suspended carbonaceous materials using acidic activator, J. Sci. Eng. Technol. 13(1): 6571-6578.

Reardon KF, Mosteller DC, Rogers JB, Duteau N, Kim K (2002). Biodegradation kinetics of aromatic hydrocarbon mixtures by Pure and mixed bacterial cultures. Environ. Health Persp. 110: 1005-1011.

Xu R, Obbard JP (2004). Biodegradation of polycyclic aromatic hydrocarbons in oil-contaminated beach sediments treated with nutrients amendments. J. Environ. Qual. 33: 861-867.