

PETROLEUM CONTAMINATED GROUND-WATER: REMEDIATION USING ACTIVATED CARBON

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Abstract

Ground-water contamination resulting from the leakage of crude-oil and refined petroleum products during extraction and processing operations is a serious and a growing environmental-problem in Nigeria. Consequently, a study of the use of activated carbon (AC) in the clean up was undertaken with the aim of reducing the water contamination to a more acceptable level. In the experiments described, crude-oil contamination of ground-water was simulated under laboratory conditions using ground-water samples collected from existing hand-dug wells at Eagle Island, Port Harcourt, Nigeria. Different masses of the absorbent (i.e. activated carbon) were then added to the samples of ground-water. The so treated water samples were left to equilibrate for 7 days, after which the total petroleum hydrocarbon (TPH) contents of the samples were measured. Adsorption isotherms were derived for the two forms of activated carbon used namely granular activated-carbon (GAC) and powdered activated-carbon (PAC). Results of the TPH analyses showed that activated carbon is an excellent means for the stripping-off of the contaminant: there were decreases in contaminant concentration from an initial concentration of 9,304.70 mg/litre to average final concentrations of 361.00 mg/litre and 12.37 mg/litre, that is, 96% and 99.9% resulting from the same amounts of GAC and PAC applications respectively. The results of this study revealed that the powdered form of AC would be very effective in the remediation of petroleum-hydrocarbon contaminated ground-water and its use is therefore recommended.

Keywords: Activated carbon, ground-water remediation, petroleum contamination.

Nomenclature

| | |
|-------------------|--|
| AC | Activated carbon |
| CaCO ₃ | Calcium carbonate |
| Ce | Equilibrium concentration of adsorbate |
| Co | Initial concentration of adsorbate |
| E | East |
| GAC | Granular activated-carbon |

| | |
|------|------------------------------|
| m | Mass of adsorbent (grams) |
| N | North |
| NaCl | Sodium chloride |
| NTU | Nephelometric turbidity unit |
| PAC | Powdered activated-carbon |
| TPH | Total petroleum hydrocarbon |
| % | Percentage |

The problem

With the increasing dependence of Nigerian agriculture, industry and private households within urban and rural areas on having readily-available potable ground-water supplies, reported cases of ground-water contamination by hydrocarbons are on the increase. A study carried out in 1987 showed that the ground-water in Port Harcourt area had a hydrocarbon contamination of 1.8 mg/litre rather than the maximum of 0.1mg/litre recommended by the World Health Organization [1]: the situation has worsened subsequently. This has prompted research into methods for remediating petroleum-contaminated ground-water. One commonly used technique for removing organics dissolved in water involves the process of adsorption, which is the physical adhesion of the polluting chemicals onto the surface of a solid. The most commonly-used adsorbent is the highly-porous activated carbon, which has a relatively small volume, yet an enormous surface area per unit mass, i.e. $\sim 1000 \text{ m}^2/\text{g}$ [2]. Activated carbon includes a wide range of amorphous carbon-based materials produced with high porosities and extended inter-particulate surface areas. It occurs commercially in two forms, granulated activated-carbon (GAC) and powdered activated-carbon (PAC). GAC by definition is composed of ultra-small particles [3]. Norit and Ultra Carbon are common trade names for this material [4].

Activated carbon (AC) treatment systems usually consist of a series of large vessels (i.e. the contacting basins), partially filled with the adsorbent. Contaminated water enters the top of each vessel, trickles down through the AC (in granular or powdered form) and is released at the bottom. After a period of time, equilibrium is reached and the carbon is allowed to settle at the bottom of the vessel: the treated water is then removed [5]. Equilibrium is attained when the rate of adsorption of contaminant molecules onto the surface of the adsorbent is the same as the rate of desorption of contaminant molecules from the surface of the adsorbent. An adsorption isotherm is a function expressing the relationship between the amount of contaminant adsorbed and its concentration at a constant temperature. The Freundlich adsorption-isotherm is the most commonly used in the literature.

Hubbert [6] concluded that when dealing with crude-oil accumulation in subterranean water, the immiscibility of the fluids is a salient feature. This leads to a consideration of distinct fluid-fluid interfaces, which influence the treatment process to be used. In the experiments described in this paper, contactors which reflected the distinct oil-water interfaces were employed and the two forms of activated carbon, granular-activated

carbon (GAC) and powdered-activated carbon (PAC), were used to demonstrate the utility of the material in the treatment of petroleum-contaminated ground-water. The pertinent adsorption isotherms were determined. This study was undertaken with the aim of ascertaining the effectiveness of activated carbon in adsorbing petroleum hydrocarbons from contaminated ground-water systems.

Location from whence came the test specimens

The ground-water samples were collected from an existing well at Eagle Island in Port Harcourt, in the Niger Delta of Nigeria; the latter lies between latitudes 4° 15' N and 6° 30' N and longitudes 5° 00' E and 8° 00' E. Port Harcourt city is within the tropical-rainforest belt of the country. The city receives an annual rainfall of about 3,000 mm and experiences an annual average temperature of 27°C [1].

Experimental procedure

Ground-water samples from an existing well were collected in pre-rinsed 12-litre plastic containers, sealed and transported to the laboratory for analysis. The sampling and handling of the ground-water conformed with the Directorate for Petroleum Resources (DPR) Guidelines and Standards [7].

Six glassware (contactors) were used for the five sets of treatment plants together with a total of thirty-two carbon contactors. The contactors were filled with the required volumes of sampled water and contaminated with a fixed volume of crude-oil (i.e. the adsorbate). Contactor O was the control volume which was not subjected to any treatment, Contactors A, B, C, D and E were treated with 5g, 10g, 15g, 20g and 25g of activated carbon respectively. The entire procedure was accomplished first with PAC and subsequently with GAC.

Treatment description

The samples treated with PAC were measured into 200ml volumes, after which two different volumes of Bonny light-crude-oil (2ml and 20ml), were poured into the water samples. The water samples treated with GAC were measured into 200ml and 20,000ml volumes, which were contaminated with 2ml and 200ml respectively of the crude-oil. Greater masses of PAC and GAC were added thereafter. The treated water samples were left to equilibrate for 7 days. A polyelectrolyte (sodium-chloride salt) was added to the samples on the 8th day. It served as a coagulant to aid in the removal of fine carbon particles as suggested by Tchobanoglous et al [8]. Physicochemical parameters of representative samples such as pH value, electrical conductivity, turbidity, total dissolved solids (TDS), chloride, sulphate, total alkalinity, as well as total hardness, calcium and magnesium concentration were determined after periods of 7 and 10 days using methods described by the American Public Health Association (APHA) [9]. The total petroleum hydrocarbon (TPH) analysis was undertaken using the procedure described by Concawe [10].

The test results (see Tables 1→5)

The physicochemical characteristics of the ground-water used for this study were outside the prescribed ranges by the World Health Organization (WHO) [11]. This occurs because of the numerous industrial activities located within the Niger Delta region: Horsfall and Spiff [1] and Odu et al [12] made similar observations.

The results shown in Tables 2→4 are evidence of the ability of the adsorbent to strip-off the contaminant. However, the adsorptive property of the two forms of the material varied greatly. This may have been influenced by factors, such as particle size distribution, concentration of the adsorbent, surface area and contact time. After the seven-day period, it was observed that the PAC adsorbed more of the contaminant than the GAC. Henning and Degel [13] made a similar observation and reported that a faster rate of adsorption ensues when finer particles of activated carbon (AC) are used.

An increase in the concentration of the PAC adsorbent led to a greater adsorption of the contaminant - see Tables 4 and 5. However, the samples treated with GAC did not strictly follow this trend. There was a decrease in the concentration of the adsorbate when 5 →15g of the adsorbent was used, after which the concentration increased (see Tables 2 and 3). This could be attributed to the inability of the adsorbent to be attached to the contaminant molecules at an available adsorption site when higher concentrations of GAC were employed. Snoeyink and Summers [14] made a similar observation.

Furthermore, the surface area of the adsorbent affected the adsorption kinetics. That is why the adsorption was greater with the PAC than with GAC treatment, because PAC has a greater surface-area-to-volume ratio than GAC. Also, the final concentration of the adsorbate, after ten days, was far less than the concentration obtained after the 7-day period (see Tables 2→5): this reveals the importance of determining the optimal contact-time and the use of a coagulant in the adsorption kinetics. The coagulant aided the settling of the carbon particles to the bottom of the vessel [8].

The Freundlich isotherms (see Figures 1 and 2) revealed that the general adsorptive property of the treatment process was a function of the characteristics of both the carbon used and the solute (namely crude-oil). This could be observed from the performance of the AC tests which followed the trend with respect to the amount of adsorption, namely PAC (Test 3) > PAC (Test 4) > GAC (Test1) > GAC (test 2), - see Tables 2 → 5.

Table 1: Physicochemical Characteristics of the well water

| Parameters | Value | WHO International Standard (1985) |
|---|--------|-----------------------------------|
| pH | 5.5 | 6.5→8.5 |
| Conductivity. :S/cm | 155 | 0→40 |
| Turbidity, NTU | 2 | 1 |
| Total dissolved solids, mg/litre | 108.50 | 0→500 |
| Chloride, mg/litre | 790.4 | 250 |
| Sulphate mg/litre | 15.23 | 150 |
| Total alkalinity, mg of CaCO ₃ per litre | 20.00 | Ns |
| Total hardness, mg of CaCO ₃ per litre | 7.66 | 200→250 |
| Calcium, mg/litre | 30.60 | 75→200 |
| Magnesium, mg/litre | 2.80 | 30→150 |

* Ns – No specification

Table 2: Unadsorbed-oil contents arising from the treatment with GAC in 200ml of water and 2ml of oil (Test 1): initial concentration, Co, of adsorbate in the water=9304.70 mg/litre

| Contactors | Mass of adsorbent, m (g) | Final concentration of adsorbate after day 7 (mg/litre) | Final concentration of adsorbate after day 10 with NaCl (mg/litre) |
|------------|--------------------------|---|--|
| O | 0 | 9304.70 | 9304.70 |
| A | 5 | 1140.55 | 473.51 |
| B | 10 | 1007.07 | 409.81 |
| C | 15 | 830.29 | 289.08 |
| D | 20 | 958.54 | 297.88 |
| E | 25 | 1001.01 | 335.19 |

Table 3: Unadsorbed-oil contents for the treatment with GAC in 20,000ml of water and 200ml of oil (Test 2): initial concentration, C_0 , of adsorbate in the water=9304.70 mg/litre

| Contactor | Mass of adsorbent, m (g) | Final concentration of adsorbate after day 7 (mg/litre) | Final concentration of adsorbate after day 10 with NaCl (mg/litre) |
|-----------|--------------------------|---|--|
| O | 0 | 9304.70 | 9304.70 |
| A | 5 | 1560.67 | 634.73 |
| B | 10 | 1173.92 | 462.59 |
| C | 15 | 532.36 | 187.31 |
| D | 20 | 600.60 | 252.34 |
| E | 25 | 855.41 | 192.62 |

Table 4: The unadsorbed-oil contents arising from the treatment with PAC in 200ml of water and 2ml of oil (Test 3) : initial concentration, C_0 , of adsorbate in the water=9304.70 mg/litre

| Contactor | Mass of adsorbent, m (g) | Final concentration of adsorbate after day 7 (mg/litre) | Final concentration of adsorbate after day 10 with NaCl (mg/litre) |
|-----------|--------------------------|---|--|
| O | 0 | 9304.70 | 9304.70 |
| A | 5 | 201.48 | 19.72 |
| B | 10 | 187.46 | 14.86 |
| C | 15 | 141.96 | 14.14 |
| D | 20 | 18.74 | 8.74 |
| E | 25 | 14.37 | 4.37 |

Table 5: Unadsorbed-oil contents arising from the treatment with PAC in 200ml of water and 20ml of oil (Test 4) : initial concentration, C_0 , of adsorbate in the water=9304.70 mg/litre

| Contactor | Mass of adsorbent, m (g) | Concentration of adsorbate after day 7 (mg/litre) | Concentration of adsorbate after day 10 with NaCl (mg/litre) |
|-----------|--------------------------|---|--|
| O | 0 | 9304.70 | 9304.70 |
| A | 5 | 197.16 | 159.86 |
| B | 10 | 148.17 | 140.60 |
| C | 15 | 141.36 | 115.27 |
| D | 20 | 138.94 | 87.36 |
| E | 25 | 128.00 | 43.68 |

Table 6: Adsorbate concentrations (Test1): initial concentration, C_0 , of adsorbate in the water=9304.70 mg/litre

| Equilibrium concentration of adsorbate (C_e) (mg/litre) | $C_0 - C_e$ (mg/litre) | Mass of adsorbent, m (g) | $(C_0 - C_e) / m$ (mg/g) |
|---|------------------------|--------------------------|--------------------------|
| 9304.70 | 0.00 | 0 | – |
| 473.51 | 8831.19 | 5 | 1766.24 |
| 409.81 | 8894.89 | 10 | 889.49 |
| 289.08 | 9015.62 | 15 | 601.04 |
| 297.88 | 9006.82 | 20 | 450.34 |
| 335.19 | 8969.51 | 25 | 358.78 |

Table 7: Adsorbate concentration (Test 4): initial concentration, C_0 , of adsorbate in the water=9304.70 mg/litre

| Equilibrium concentration of adsorbate (C_e) (mg/litre) | $C_0 - C_e$ (mg/litre) | Mass of adsorbent, m (g) | $(C_0 - C_e) / m$ (mg/g) |
|---|------------------------|----------------------------|--------------------------|
| 9304.70 | 0.00 | 0 | – |
| 159.86 | 9144.84 | 5 | 1828.97 |
| 140.60 | 9164.10 | 10 | 916.41 |
| 115.27 | 9189.43 | 15 | 612.63 |
| 87.36 | 9217.34 | 20 | 460.87 |
| 43.68 | 9261.02 | 25 | 370.44 |

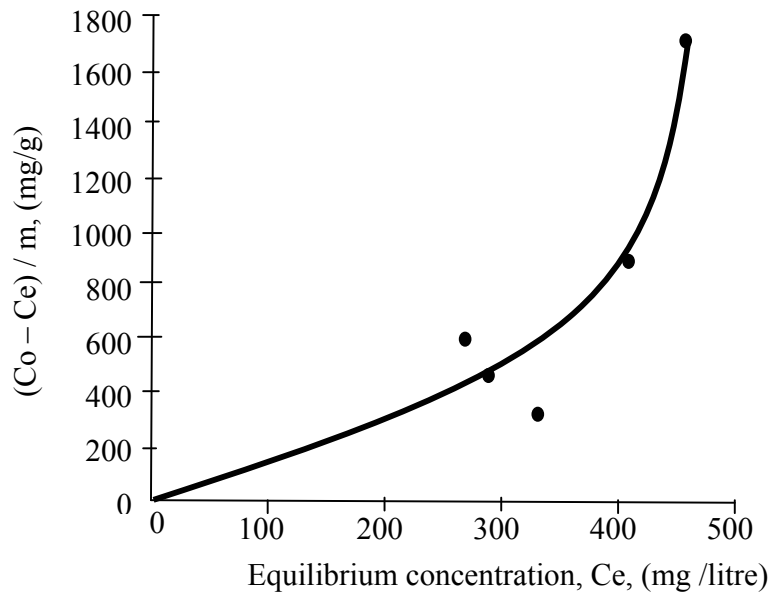


Figure 1: Freundlich Adsorption Isotherm for GAC used

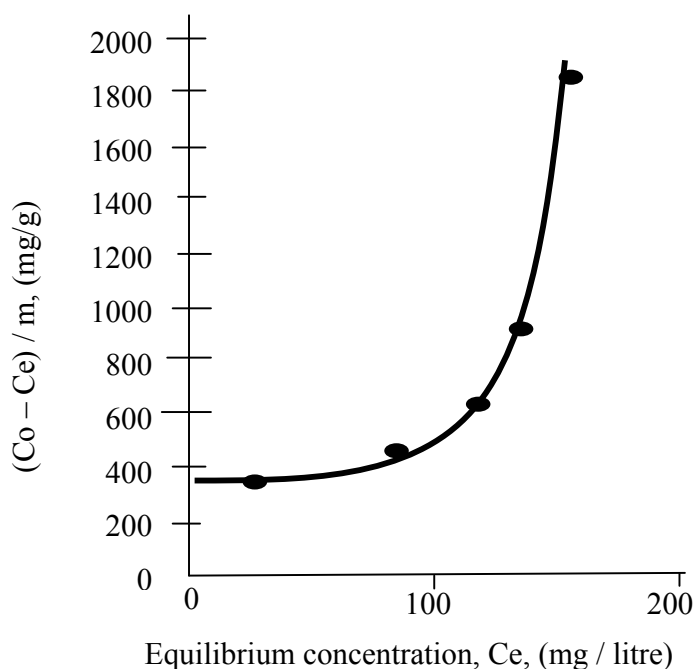


Figure 2: Freundlich adsorption isotherm for the PAC used

Conclusion and recommendations

The use of activated carbon (AC) is effective in the remediation of petroleum-hydrocarbon contaminated ground-water. Decreases in contaminant concentration from an initial value of 9304.70 mg/litre to average final concentrations of 361.00 mg/litre and 12.37 mg/litre were achieved by employing similar amounts of GAC and PAC respectively. This indicates 96% and 99.9% contaminant removal by GAC and PAC respectively. It also reveals that the powdered form of activated carbon is more effective than the granular form: hence the former is recommended for use in ground-water clean-up procedures.

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