

ENHANCEMENT OF HYDROCARBON RECOVERY BY MODIFIED SOLVENT EXTRACTION

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ABSTRACT

Sixty water samples collected in January and March, 2002 from the Qua Iboe River and its associated Creeks were used in this investigation. In January, 2002 thirty water samples were collected from 10 stations consisting of 3 samples per station. In March, 2002 another batch of thirty water samples were similarly collected. The samples were subjected to different hydrocarbon extracting solvents and extraction conditions. Of the three extracting solvents, hexane yielded the highest concentration of hydrocarbon (mean concentration of 58.93 ± 31.50 mg/l) while dichloromethane yielded the least (mean concentration of 31.63 ± 13.68 mg/l). Under different conditions of extraction with hexane, the highest concentration of hydrocarbon was obtained in batch I with a mean concentration of 63.30 ± 33.84 mg/l followed by batch II with a mean concentration of 62.87 ± 33.46 mg/l and then batch III with a mean concentration of 31.49 ± 17.60 mg/l. The 100ml and 50ml of n-hexane added in batches I and II prior to sampling reduced the adsorption of hydrocarbons to the vessel walls. Thus, the amount of hydrocarbon extracted in batches I and II relative to batch III was increased.

KEYWORDS: Hydrocarbon, extraction, enhancement, batch, adsorption.

INTRODUCTION

Crude oil exploration and exploitation is usually associated with large scale environmental pollution with the aquatic environment being the final sink. Notably, in Buzzards Bay, Massachusetts, there have been two major oil spills in 1969 and 1974 respectively (Teal and Farrington, 1978); and also in 1989 about 258,000 bbls or 4 million litres of crude oil spilled from Exxon Valdez oil tanker into Prince William Sound, Alaska (Bence et al 1996).

So also in Nigeria, the oil producing region of the Niger Delta has a history of medium to large scale oil pollution arising from well accidents, pipeline rupture, tanker accidents and chronic spills from flow stations among others. In 1998, an underwater oil pipeline belonging to Mobil Producing Nigeria Unlimited ruptured spilling over 40,000 barrels of crude oil into the overlying water with the adjacent Qua Iboe River and environs being the worst affected (Akpan et al., 1998).

Oil pollution has a large scale negative impact on the aquatic environment ranging from aesthetic quality modifications to death of sensitive species. Tainting and elimination of commercial fish species have impacts on the social economy and nutrition of coastal settlements. Destruction of wild life and tourism sites have direct impacts on ecological stability and national economy.

After oil spills or as part of monitoring programme crude oil analysis from water is required. Whatever the final method of analysis, quantitative extraction of the oil from the polluted media is usually a prerequisite for further analysis.

In a third world country like Nigeria where the instrumental methods of analysis have not gained prominence due to high cost of the analytical instruments, the basic classical methods in use right now have to be improved upon. The aim of this work therefore is to examine the effectiveness of three different solvents and methods of hydrocarbon recovery from water by solvent extraction using the Qua Iboe River system as a case study.

The Qua Iboe River (Fig. 1) lies within latitude $4^{\circ}31'$ to $4^{\circ}45'N$ and longitude $7^{\circ}31'$ to $8^{\circ}00'E$ on the South Eastern coastline of Nigeria. The River originating from Umuahia hills, traverses mainly sedimentary terrains of Cretaceous to recent

ages and develops into extensive meanders before emptying into the Atlantic Ocean within the Gulf of Guinea (Ekwere et al., 1992). The Qua Iboe River is fronted by several offshore oil well pipelines and flanked to the East by other oil producing facilities of Mobil Producing Nigeria Unlimited including gas flaring. Because of the intensive oil activities in the area, the Qua Iboe river system is selected for this study.

MATERIALS AND METHODS

Procurement of distilled water

1,500mls of distilled water were obtained from the technology unit of the Department of Pure and Applied Chemistry, University of Calabar, Nigeria.

Sample and Sampling

In January, 2002 water samples were collected in triplicates from ten different sample stations in the Qua Iboe River and Douglas Creek (Fig. 1). Samples were collected in batches of 500ml each into ten pre-cleaned glass stoppered bottles.

In March, 2002 water samples were collected from the same ten sample stations in triplicates. In the first batch of the water samples n-hexane (100ml) was added to each sample bottle prior to sample collection. In the second batch n-hexane (50ml) was added while in the third batch no n-hexane was added.

The water samples were each preserved with 2ml of chloroform until laboratory analysis after 56 hours.

METHOD

Solvent extraction

Solvent extraction involves the distribution of a solute between two immiscible liquid phases. A blank run was first carried out by extracting three samples of distilled water (500ml) each with dichloromethane (CH_2Cl_2), hexane (C_6H_{14}) and chloroform ($CHCl_3$) to investigate possible presence of residual solvent after evaporation under ambient condition of the laboratory.

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Table 1: Total hydrocarbon concentration (mg/l) in water with different solvents.

Sample No.	Dichloromethane (CH ₂ Cl ₂)	Hexane (C ₆ H ₁₄)	Chloroform (CHCl ₃)
Distilled water (Blank)	0.0040	0.0025	0.0055
1	10.7212	19.2608	13.4487
2	50.1411	122.5073	49.9803
3	43.8203	93.7125	57.6342
4	20.1400	40.2672	31.6257
5	11.2412	21.7903	14.8441
6	35.6343	43.1677	40.6252
7	40.2671	59.2818	43.7134
8	42.4184	60.2623	50.6278
9	30.2672	70.1342	36.3818
Mean	31.63 ± 13.68	58.93 ± 31.50	37.65 ± 14.56

Table 2: Total hydrocarbon concentration (mg/l) in water using hexane under different conditions.

Sample No.	Batch 1	Batch II	Batch III
1	20.1000	20.0001	10.0031
2	123.4200	122.9041	70.0400
3	100.0000	97.2013	24.0204
4	42.3101	42.0700	31.3041
5	21.2012	21.1201	10.0413
6	36.0130	36.0173	20.0441
7	69.0222	68.7014	40.2051
8	77.0103	76.8025	40.8103
9	80.6021	81.0521	36.9001
Mean	63.30 ± 33.84	62.87 ± 33.46	31.49 ± 17.60

Batch 1 - no other volume of n-hexane used other than the 100ml n-hexane added prior to sample collection.

Batch II - 50ml n-hexane used in addition to the 50ml n-hexane added prior to sample collection.

Batch III - 100ml n-hexane used as no volume of n-hexane was added prior to sample collection.

concentration of hydrocarbon recovery perhaps because it is an unsubstituted saturated hydrocarbon and the least polar of the three solvents. Chloroform is the most polar of the three solvents and has the highest molar mass. Thus, it may possibly extract only polar compounds which may relatively be low in concentration in a petroleum polluted water system like Qua Iboe River and its associated Creeks. Besides, it may extract, mostly heavier or waxy hydrocarbons due to its polarity and these do not solubilize in water easily but get attached to solid particles and then settle to become part of the bottom water sediment (ATSDR, 2004). Hence, the relatively poorer recovery yield. Dichloromethane, a substituted saturated hydrocarbon has about the same molar mass with hexane but is of intermediate polarity between hexane and chloroform. Besides, the opposing inductive effect of the two chloro-substituents which accounts for its very low polarity also tends to moderate its hydrocarbon extracting ability. Hence, the very low yield.

The statistical analyses of the concentrations of the hydrocarbon obtained by the three solvents using t-test at 0.05 confidence level gave the calculated t-values for dichloromethane and hexane as 2.25; dichloromethane and chloroform as 0.82 while chloroform and hexane was 1.74. The table t-value at 0.05 confidence level and 16 degrees of freedom is 2.12. These show that a significant difference exists in the effectiveness of hydrocarbon extraction between dichloromethane and hexane while between dichloromethane and chloroform and between chloroform and hexane there were no significant differences in the effectiveness of their hydrocarbon extraction.

Table 2 shows the total hydrocarbon concentration obtained with hexane under different experimental conditions. Batch 1 (extracted with 100ml n-hexane added prior to sample collection) gave the highest recovery yield of hydrocarbon with a concentration of $63.30 \pm 33.84\text{mg/l}$ followed by batch II (extracted with 50ml n-hexane in addition to the 50ml added prior to sample collection) with a concentration of $62.87 \pm 33.46\text{mg/l}$ and then batch III (extracted with 100ml n-hexane as no volume of n-hexane was added prior to sample collection) with a concentration of $31.49 \pm 17.60\text{mg/l}$.

The 100ml and 50ml of n-hexane respectively added prior to sampling may have reduced the adsorption of the hydrocarbons to vessel walls thereby keeping the hydrocarbons in the water prior to extraction. This contributed to the relatively high yield of hydrocarbons in batches I and II.

The statistical analyses of the concentrations of the hydrocarbon obtained with hexane under the three different experimental conditions using t-test at 0.05 level of confidence gave the calculated t-values for batch I and batch II as 0.03; batch I and batch III as 2.36 while batch II and batch III was 2.35. The table t-value at 0.05 level of confidence and 16 degrees of freedom is 2.12.

These t-values show that a significant difference exists between the hydrocarbon concentration of batch I and batch III as well as batch II and batch III but there was no significant difference between batch I and batch II. This suggests that about 50ml of n-hexane were enough to prevent the adsorption of hydrocarbons on the vessel walls for the volume of water used. Batch III suffered from strong adsorption of hydrocarbons to the vessel wall with a resultant low hydrocarbon concentration relative to batches I and II. Although 100ml of n-hexane was used for the extraction in batch III and the time of contact the same as in batches I and II (56 hours), part of the hydrocarbons already adsorbed on the vessel walls could not be desorbed giving rise to the relatively low hydrocarbon yield in batch III. Perhaps the volume of n-hexane (100ml) added and the duration of the extraction may not have been enough to overcome the adsorptive force binding the hydrocarbons on the walls of the sample bottles

and at the same time extracting a relatively high amount of the hydrocarbons in the water sample. Therefore, it is easier and better to prevent hydrocarbons from adsorption on the vessel walls than to desorb them.

CONCLUSION

In quantitative works such as solvent extraction, the investigation of the extracting powers of different solvents and the variation of conditions of extraction influence the concentration of hydrocarbon recovery.

The addition of the extracting solvent in the sample bottle prior to sampling influences the concentration of the hydrocarbon recovered. It takes more solvent and time to desorb hydrocarbons from vessel walls than to prevent the adsorption of the hydrocarbons on the vessel walls.

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