



# MANAGEMENT OF PETROPORPHYRINS IN A CRUDE OIL POLLUTED ENVIRONMENT

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The ability of three chemical oxidants (Fenton's reagent, Potassium permanganate and Potassium persulfate) to degrade one of the recalcitrant non-hydrocarbon components of crude oil- the porphyrins at three different pH media was investigated in this work and the results showed that the oxidants removed less than 10% of the porphyrins on the average, after two months of treatment. The porphyrins were found to experience degradation of 5%, 7% and 4% on the average for the acidic, neutral and basic soils respectively for the vanadyl ( $\text{VO}^{2+}$ ) porphyrins and a reduction of 7%, 15% and 7% on the average for the acidic, neutral and basic soils respectively for the Nickel ( $\text{Ni}^{2+}$ ) porphyrins. This highlighted the recalcitrant nature of porphyrins, but also showed that they are not perfectly so in the presence of chemical oxidants.

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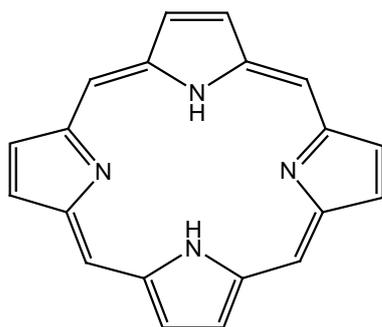
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## Introduction

The largest source of hydrocarbons is crude oil. Crude oil contains different types of hydrocarbons – aliphatic (saturated and unsaturated) and aromatic (isolated rings and condensed ringed) hydrocarbons. Some crude oil components are non-hydrocarbon and are highly recalcitrant, remaining essentially undegraded many years after crude oil spillage. Prominent among these degradation-resistant components of crude oil are the porphyrins or more specifically the petroporphyrins or metalloporphyrins. They are highly conjugated heterocyclic organometallic compounds found in crude oil. The porphyrins consists of four pyrrole rings joined at  $\alpha$ -carbon atoms by four methine bridges to give a highly conjugated macromolecule.



A porphyrin molecule

They are aromatic and can form intensely coloured complexes with metals at the centre of the molecule called metalloporphyrins. For example, in association with iron they form a metalloporphyrin called haem, a component of haemoglobin found in red blood cells. When they complex with magnesium they form a derivative of chlorophyll, the green colouring matter in plants that is used in photosynthesis. In combination with cobalt, they form vitamin B<sub>12</sub> complex and when they combine with vanadium

and nickel, they form complexes called petroporphyrins because they are found in abundance in coals, bitumen and heavy crude oils.<sup>1,2</sup>

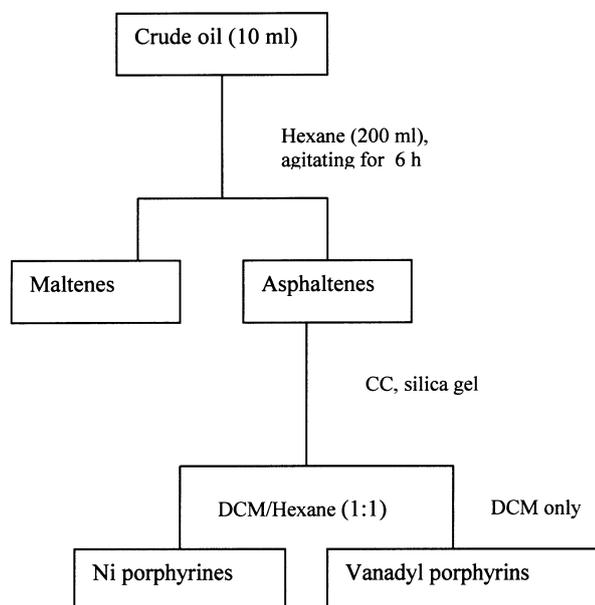
The petroporphyrins are stable and resistant to weathering and biodegradation unlike chlorophyll and haem. In fact, they have been said to be the products of haem and chlorophyll transformation. They are the last to degrade in petroleum among the petroleum residues. They are responsible for the formation of tar balls and other degradation resistant deposits at coastal shores long after oil spills. Thus, they are always used as biomarkers in the study of the origin/source and migration of petroleum residues.<sup>3</sup> They exist predominantly as vanadyl ( $\text{VO}^{2+}$ ) and nickel ( $\text{Ni}^{2+}$ ) compounds of two structural types; deoxyphyloerythroetioporphyrins (DPEP) and etioporphyrins (ETIO).<sup>4</sup>

Their highly conjugated nature makes it possible for them to be studied using u.v/visible spectroscopy.<sup>5-7</sup> Studies on the degradation and stability of petroleum products and components cannot be complete without these compounds. They are very resistant to degradation by microorganisms and do not volatilize from crude oils. A good understanding of their nature and behaviour will be very useful in the management of crude oil polluted soils and waters. The use of chemical oxidants in the remediation of crude oil / hydrocarbon polluted environments is an emerging trend that has received international acclaim.<sup>8,9</sup> Its advantages cannot be overemphasized. Researches in this area is ongoing and is yielding good results.

## Experimental

Ten millilitres of vacuum distilled crude oil (500 °C) in ten 50 ml volumetric flasks are treated with three oxidants (Fenton's reagent, potassium permanganate and potassium persulfate) at different pH ranges and left to stand for two months. An untreated sample exposed to the same conditions was made to act as control. Subsequently the samples were separated into the soluble maltenes and the insoluble asphaltenes. This was done by dissolving the samples in hexane, agitating them in a mechanical shaker for six hours and allowing it to stand overnight. The

dissolved samples are then filtered with a sintered glass funnel and a 342-whatman filter paper using a vacuum pump. The residue (asphaltenes) are then eluted with dichloromethane (DCM) and hexane in a glass column (50 ml x 1 cm) packed with silica gel according to the outline in Scheme 1.



**Scheme 1.** Steps involved in the extraction of the vanadyl and nickel porphyrins from the crude oil sample.

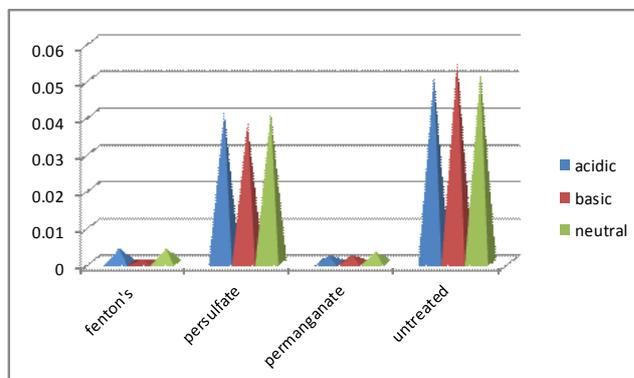
The different porphyrins are determined using uv-visible spectrophotometer at (550 nm-570 nm). The concentration of the nickel and vanadylporphyrins calculated using coefficient of extinction of  $2.7 \times 10^4$  and  $2.9 \times 10^4 \text{ L}^{-1}(\text{mole}\cdot\text{cm})$  respectively.<sup>7,10</sup>

## Results and discussion

The results of the absorbance of nickel and vanadyl porphyrins are presented in Tables 1 and 2 respectively. The results show that the porphyrins decreased in concentration after two months of treatment with the oxidants. This supports the generally accepted view that porphyrins are recalcitrant or resistant to degradation.<sup>11</sup> It is worthy of note that this reduction in the amount of porphyrins was noticed after the sample was treated with the oxidants for two months. Thus, it might be that after a prolonged period of time, the effect may become pronounced. Porphyrins have been fingered as the main constituents of tar balls – a dark and hard ball deposited at shore lines after incidents of oil spillage in rivers and oceans.<sup>7</sup> Therefore oil spillage in water bodies managed with chemical oxidants like Fenton's reagent and potassium permanganate may prevent formation of tar balls.

**Table 1.** Absorbance of the  $\text{VO}^{2+}$  porphyrins from the oil samples treated with the different oxidants at the different pH media.

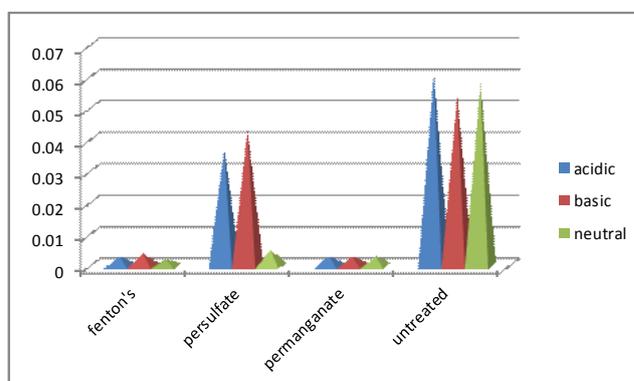
Oxidant	pH=5	pH=7	pH=9
Fenton's reagent	0.004	0.001	0.004
$\text{K}_2\text{S}_2\text{O}_8$	0.041	0.038	0.041
$\text{KMnO}_4$	0.002	0.002	0.003
Untreated	0.051	0.055	0.052



**Figure 1.** Chart showing the effect of the different oxidants on the  $\text{VO}^{2+}$  porphyrin concentration at the different pH media

**Table 2.** Absorbance of the  $\text{Ni}^{2+}$  porphyrins from the oil samples treated with the oxidants at different pH media

Oxidant	pH=5	pH=7	pH=9
Fenton's reagent	0.003	0.004	0.002
$\text{K}_2\text{S}_2\text{O}_8$	0.037	0.043	0.005
$\text{KMnO}_4$	0.003	0.003	0.003
Untreated	0.061	0.054	0.058



**Figure 2.** Chart showing the effect of the different oxidants (Fenton's reagent, potassium persulfate and potassium permanganate) on the  $\text{Ni}^{2+}$  porphyrin concentration at the different pH media

Although all the oxidants used had a slight effect on the amount of the porphyrins, the inactivity is more pronounced in the use of persulfate as oxidant (Tables 1 and 2). This seems to explain why persulfate were ineffective in the removal of the PAHs from the soil samples at all pH media.<sup>12</sup> Since PAHs and porphyrins dominate asphaltic crude oils, it implies that persulfates may not be the right oxidants for the remediation of asphaltic crude oils.

## Conclusion

This study has shown that even though the petroporphyrins are recalcitrant in the environment, they can be removed with time using Fenton's reagent and potassium permanganate as chemical oxidants.

The study also revealed that potassium persulphates may not remove petroporphyrin when used as oxidants even after a long period of time.

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