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Hydrocarbon removal from bilgewater by a combination of air-stripping and photocatalysis

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HIGHLIGHTS

- Bilge water is an oily effluent that contaminates oceans and seas (MARPOL73/78).
- Hydrocarbon removal was studied by photocatalysis and air-stripping, together used.
- Both aqueous and gaseous phases were monitored by GC–MS during the process.
- The combined process showed a better efficiency and a synergistic effect.
- N-Alkanes ($N_C > 15$) appeared as being the most refractory compounds.

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ABSTRACT

In order to prevent hydrocarbon discharge at sea from the bilge of ships, the International Maritime Organization (IMO) enacted the MARPOL 73/78 convention in which effluents are now limited to those with maximum oil content of 15 ppmv. Thus, photocatalysis and air-stripping were combined for the hydrocarbon removal from a real oily bilgewater sample and an original monitoring of both aqueous and gaseous phases was performed by GC/MS to better understand the process. Our results show that the hydrocarbon oil index [HC] can be reduced to its maximum permissible value of 15 ppmv (MARPOL) in only 8.5 h when photocatalysis and air-stripping are used together in a synergistic way, as against 17 h when photocatalysis is used alone. However, this air-assisted photocatalytic process emits a large quantity of volatile organic compounds (VOC) and, within the first four hours, *ca.* 10% of the hydrocarbon removal in the aqueous phase is actually just transferred into the gaseous one. Finally, we highlight that the n-alkanes with a number of carbon atoms higher than 15 ($N_C > 15$) are those which most decrease the rate of [HC] removal.

1. Introduction

Bilgewater, a polluted effluent with a smell of hydrocarbons and rotten eggs is a corrosive mixture from the bilge of ships that mainly originates from seawater infiltration and leakage of engine oil and fuel. Each year, two thousand tons of hydrocarbons from bilge are discharged at sea and this huge quantity is a major pollution problem for marine ecosystems and more or less directly for human health, causing the International Maritime Organization (IMO) to enact MARPOL 73/78 convention in which effluents from ships are now limited to a maximum oil content of 15 ppmv [1].

However, because on-board storage of bilgewater is not always feasible, remediation is required and different kinds of treatment have been proposed. Of these, physical processes are currently the most commonly-used techniques. The oil-in-water separators with which ships have to be equipped [2] make the remediation of a huge quantity of oil possible. However, there are still some engineering problems for this kind of reactor and, in the presence of some particles or coupled with a failed detector, discharge at sea may take place even when the oil content is higher than 15 ppmv. Other problems are (i) the extremely long time required for the separation process which can favour the irreversible dissolution of organic materials, and (ii) the presence of detergents that promote emulsion formation. Filtration techniques, sometimes combined with reverse osmosis [3], have been proposed to enhance the separation

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Abbreviations: %w, percentage (weight ratio); IMO, International Maritime Organization; ASP, air-stripping photocatalytic; MS, mass spectrometry; BTEX, benzene-toluene-ethylbenzene-xylene(s); MTBE, methyl tert-butyl ether; DAPR, diffused aeration photocatalytic reactor; NC, number of carbon atoms; ETBE, ethyl tert-butyl ether; PAB, polyalkyl-benzene; GC, gas chromatography; ppmv, part per million (volumic ratio); H_{CC}, The Henry constant; RT, retention time; HC/[HC], hydrocarbon/hydrocarbon oil index; UV, ultraviolet; IC, ionic chromatography; VOC/[VOC], volatile organic compound/concentration.

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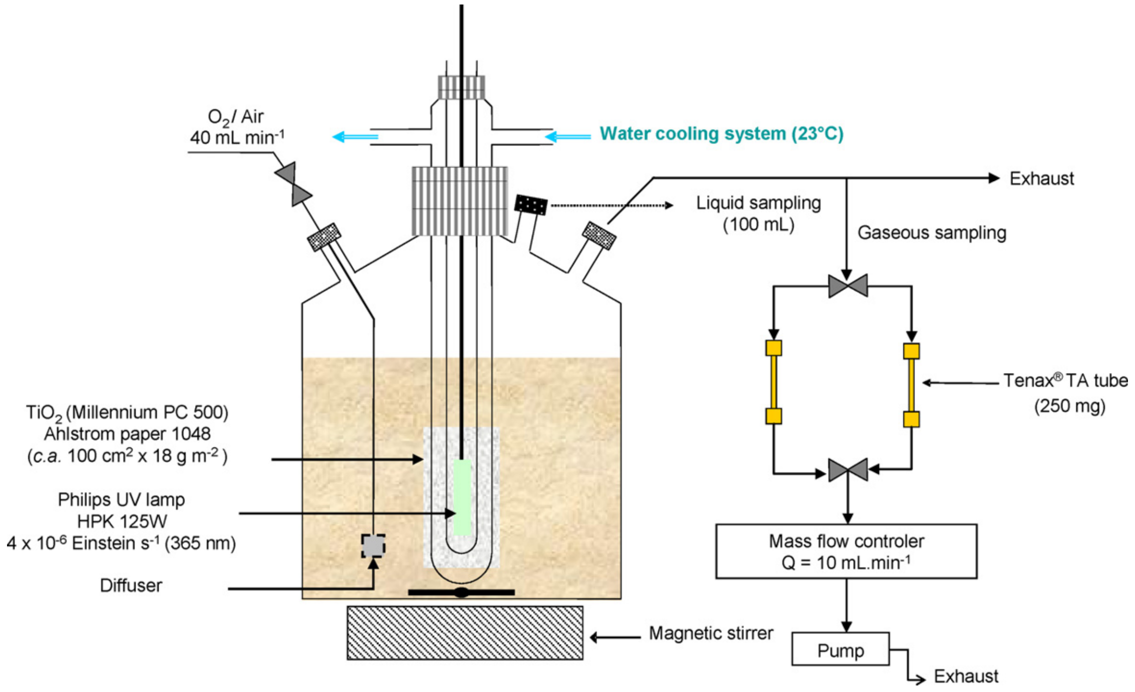

Fig. 1. Schematic of the 1 L batch photoreactor.

of aqueous and organic phases [4,5]. Such physical processes do not degrade the pollutants but only separate them.

To counter this, biological processes have been proposed as a degrading method for the removal of hydrocarbons from this kind of effluent. A pilot bioreactor containing microorganisms was tested aboard the Caps Lobos MARAD motor vessel in combination with a physical process. Results showed that more than 300 m^3 could be treated each month in this way [6]. More recently, the presence of some *Pseudomonas* species in bilge oil was also highlighted and biodegradation was studied using these organisms [7]. These bacteria are able to degrade 70% of the hexane-extractable organics and 90% of the aromatic compounds. The efficiency of this process can also be improved by using cyclodextrins as carrier molecules for increasing the water solubility of the low water soluble hydrocarbons [8]: *e.g.* after 120 h of treatment, only 15% of hexadecane remained undegraded as against 43% when cyclodextrins were not used.

Many other techniques have been studied in order to degrade hydrocarbons from bilgewater. We can cite for example, wet air oxidation [9], electrochemical purification [10,11] and photocatalysis [12,13].

Photocatalysis is an advanced oxydation processes with which any sample contaminated by an organic substrate can be remediated until mineralisation, by using a semiconductor (*e.g.* TiO_2) and a source of photons like a UV lamp or sunlight [14–17]. Promising results have been obtained for polar compounds in water [18–20] as well as for hydrocarbons [13,18,21–23]. In order to treat bilgewater samples, Karakulski et al. [12] coupled a filtration process to a photocatalytic one and achieved a total decomposition of the oil after 50 h of ultrafiltration (the chemical oxygen demand was removed by *ca.* 96% in the permeate) followed by 2 h of UV illumination using a K-TiO_2 photocatalyst. Lair also worked on the treatment of bilgewater by photocatalysis but limitations due to a lack of dissolved oxygen appeared since $[O_2]$ did not exceed 1 mg L^{-1} [13]. Indeed, the photocatalytic process needs a constant supply of oxygen toward the photocatalyst in order to oxidize all the organic compounds and to avoid undesirable electron–hole recombination [24].

Aeration therefore appears to be a good means of improving photocatalytic performance in this case. In addition, aeration favours the air-stripping phenomenon which is based on the principle that dissolved volatile compounds can be carried away by a gas stream that shifts the equilibrium from aqueous to gaseous phase. The gas–liquid partitioning behaviour of volatile solutes obeys Henry's law, which states that the partial pressure of a component in the gas phase is proportional to its concentration in the liquid phase under equilibrium conditions. The dimensionless form of Henry's law constant (H_{CC}) can be expressed as:

$$H_{CC} = \frac{C_{i,G}}{C_{i,L}} \tag{1}$$

where $C_{i,L}$ and $C_{i,G}$ are the concentrations of the compound in moles per volume of solution and gas, respectively. Staudinger and Roberts published a compilation of various H_{CC} of organic compounds [25] which has proved to be very useful when studying the air-stripping phenomenon, the latter being already used in water treatment [26] especially in the case of surfactant-containing wastewater [27,28].

This work reports on the combination of photocatalysis and air-stripping for bilgewater remediation. Since aeration would play various roles during the photocatalytic treatment, a synergistic effect is expected, and in order to better evaluate the efficiency of the combined process, the behaviour of both aqueous and gaseous phases were monitored with an original experimental set up.

2. Experimental

2.1. Bilgewater preparation

Once received from a French military ship, samples were first well mixed during one hour and then settled for 30 min in order to obtain after separation (i) a realistic and reproducible oily aqueous phase of bilgewater (hereinafter called *the bilgewater sample*) from one hand and (ii) a 100% organic phase from another hand. So the *bilgewater sample* was used immediately to prevent instability during any storage. Where needed, different initial concentrations