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ORIGINAL PAPER

Applications of advanced oxidative processes for the recovery of water from bilge water

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Abstract

In the present study, two different advanced oxidation processes, the Fenton reaction and titanium dioxide photocatalysis process, were tested and compared with the aim of water recovery from bilge water. A suitable analytical method was developed in order to evaluate the efficiency of the processes. Wastewater and process products were characterized using analysis of the total carbon content, elemental analysis and permanganometry. The experimental tests were performed both on synthetic samples and on the real matrix. The percentages of carbon abatement in bilge water after the Fenton reaction and titanium dioxide photocatalysis were 67% and 64%, respectively. The Fenton reaction efficiency increased to 95% when the bilge water aqueous phase was pretreated by flocculation using a polyelectrolyte. This combined process can be considered as a valid method to treat bilge water which can then be discharged directly into the sea, sewer, or may be reused as gray water.

Keywords Advance oxidative process · Bilge water · Fenton reaction · TiO_2-based photocatalysts · Flocculation

Introduction

Marine transportation represents more than 90% (by weight) of the global commerce. Based on the type of load transported, it can be mainly classified in cargo-carrying commercial shipping such as merchant marine and non-cargo commercial shipping such as ferries, cruise ships, but also military ships, tugs, and fishing vessels (Walker et al. 2018). In the period between 1990 and 2019, the global seaborne trade volume exponentially increased from 4 to 11 billion tons (Statista Research Department 2021). Although marine transportation is one of the most common way to transport goods, different environmental issues are related to shipping (Andersson et al. 2016). In particular, the impacts of shipping on the marine environment are listed into three main categories: discharges to water (e.g., ballast water, bilge water, oil spills), physical impact (e.g., noise and resuspension of sediments) and air emissions (e.g., ejection of sulfur oxides (SO_x), nitrogen oxides (NO_x) and greenhouses gases through exhaust fumes) (Yang 2011; Church et al. 2019). Oil spills are one of the major sources of oil released into the marine ecosystem. An additional source of hydrocarbons is represented by vessel operational discharges, including discharge of ballast water and bilge water (Motoyoshi and Nishi 2020; McLaughlin et al. 2014; Shen et al. 2020).

Bilge water is accumulated in the lower internal part of the ship (bilge) and its composition depends on the type of ship and its operation mode (Peng et al. 2005; Byrnes and Dunn 2020). Bilge water is generally composed of a mixture of seawater with different compounds including oily fluids and other pollutants such as metals, surfactants and solvents, which come from the mechanical part of the ship (McLaughlin et al. 2014; Tiselius and Magnusson 2017). It can be described as a two-phase dispersion system where seawater is the continuous phase and the oil is the dispersed one (Tomaszewska et al. 2005). The physicochemical properties of marine oily wastewater are as follows: salty, alkaline, indecomposable and serious emulsification (Han et al. 2019). The dispersed oil is present in four physical states depending on the size of the droplets: floating oil (> 100 µm), dispersed oil (10–100 µm), emulsified oil (0.1–10 µm) and dissolved oil (< 0.1 µm) (McLaughlin et al. 2014; Han et al. 2019).

Although the amount of hydrocarbons discharged during normal maritime operations is lower compared to the

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amount spilled during maritime accidents, the operational discharge occurs constantly from numerous vessels (Motoyoshi and Nishi 2020). For this reason, the International Maritime Organization (IMO) sets the standards for developing regulations regarding treatment and disposal of oily bilge water to reduce the negative effects of oily wastewater to the marine environment system. For achieving this parameter, ships are equipped with oil/water separators (OWS) as requested in Annex I of MARPOL (73/78) (International Maritime Organization (IMO) 1978; Amran and Mustapha 2021; Gryta 2020). Although the OWSs technology is efficient with floating oil and dispersed oil, with emulsion oil droplets and dissolved oil the removal effectiveness decreases. Indeed, the presence of surfactants in water increases the emulsion stability due to the formation of a film on oil droplets surface which avoids the coalescence (Maiti et al. 2011; Gryta 2020; Eskandarloo et al. 2018). Therefore, the physical methods (gravity OWS and centrifugal OWS) are inefficient to remove oil droplets with a particle size below 20 µm, but also colloidal metals and soluble compounds which are present in bilge water (McLaughlin et al. 2014; Penny and Suominen-Yeh 2006; Aini Amran and Nor Adibah Mustapha 2021).

In the last decades, several bilge water treatment technologies have been developed to decrease the discharge of oily wastewater and drastically reduce the related environmental damages (Yu et al. 2017; Han et al. 2019; Amran and Mustapha 2021). As reported in the review of Han et al. (2019), these studies can be mainly classified into physical treatments by using different separation methods (Shen et al. 2020; Sun et al. 2010; Tomaszewska et al. 2005; Gryta 2020; Lu et al. 2018; Cortese et al. 2014), chemical technologies such as adsorption (Rahmani et al. 2018; Turco et al. 2017; Furlan et al. 2017; Wang et al. 2014; Gupta and Kandasubramanian 2017) and electrochemical oxidation (Körbahti and Artut 2013; Ulucan and Kurt 2015; Carlesi et al. 2014; Bilgili et al. 2016) and biological treatments (Sun et al. 2009; Chanthamalee et al. 2013; Crisafi et al. 2016; Zhang et al. 2018; Putatunda et al. 2019). Due to the different physicochemical properties of marine oily wastewater, in the last years also combined treatments were studied (Eskandarloo et al. 2018; Akarsu et al. 2016; Mancini et al. 2017; Moslehyani et al. 2016a; Moslehyani et al. 2016a, b).

Advanced oxidation processes (AOPs) are based on the formation of hydroxyl radicals ($^{\bullet}OH$) by using ultraviolet (UV) radiation, ozone (O_3), hydrogen peroxide (H_2O_2), and oxygen (O_2), among others (Luo et al. 2021; Ribeiro et al. 2015; Wang and Zhuan 2020). The most commonly employed AOPs are classified as homogeneous and heterogeneous processes depending upon occurring in single phase (such as O_3-based processes, Fenton-based processes, wet oxidation and wet peroxide oxidation) or using heterogeneous catalysts such as carbon materials, metal supported catalysts or semiconductors such as titanium, zinc and tungsten oxides (Ribeiro et al. 2015; Ma et al. 2021). Heterogeneous processes include heterogeneous photocatalysis, irradiated with UV and/or Vis-light, catalytic wet peroxide oxidation (CWPO), catalytic ozonation and others (Ribeiro et al. 2015; Ma et al. 2021). As mentioned above, AOPs generate hydroxyl radicals, which can destroy organic pollutants into less complex compounds with high reaction rates (about 109 L mol^{-1} s^{-1}). The kinetic rate depends on the concentration of organic fraction (Ribeiro et al. 2015; Luste and Sillanpää 2020; Ma et al. 2021). Regarding hydroxyl radicals' characteristics, AOPs are considered a clean and efficient treatment for polluted water (Ribeiro et al. 2015). $^{\bullet}OH$ is a non-selective agent and it is the strongest oxidant with $E^{\circ} = 2.80$ V, after fluorine (Pera-Titus et al. 2004; Liu et al. 2019). After the generation of hydroxyl radicals, they would attack organic chemicals by radical addition, hydrogen abstraction and electron transfer, oxidizing almost all organic compounds to carbon dioxide and water (Pera-Titus et al. 2004). Moreover, hydroxyl radicals have a short lifetime and need to be generated in situ through the combination of oxidizing agents, irradiation and catalysts (Gautam et al. 2019).

The aim of this study is to develop a process to recover water from bilge water. The recovery treatments have been conducted by comparing two different AOPs: the Fenton reaction (homogeneous process) and titanium dioxide (TiO_2) photocatalysis (heterogeneous process). Both processes are efficient and have been selected to treat several organic wastes (Ma et al. 2021). Because bilge water is a complex matrix, it was necessary to develop a suitable analytical method to evaluate the efficiency of wastewater treatment and characterize the final product. In the first part of the work, the experiments were carried out on bilge water synthetic solutions prepared considering the composition of the real one. The experiments performed on synthetic solutions allowed improving the methods of analysis to examine the oxidation processes. In addition, these experiments allowed testing the process efficiency on categories of substances typical of bilge water, but also of other types of wastewater.

The developed analytical methods and processes were afterward tested on the real matrix. The ultimate purpose of the study was to obtain water having physicochemical parameters suitable to the MARPOL 73/78 limit, so that it can be directly discharged into the sea as well as in surface waters.

The research activity reported in this paper has been performed in the ENEA laboratory facilities (Rome, Italy) during year 2019.

Materials and methods

Synthetic stock solutions were prepared using sodium dodecyl sulfate as a surfactant (SDS, Sigma Aldrich), due to its wide employment in the formulations of commercial detergents, and nonane as a hydrocarbon (C_9H_{20} Nonane Reagent plus® 99%, Sigma Aldrich), as it is a short-chain hydrocarbon contained in ship fuels.

Solutions of SDS were prepared at different concentrations (from 10^{-1} to 10^{-4} mol L^{-1}), by dissolving SDS in ultra-pure water. C initial content was 30 mg L^{-1} (sample 1), 280 mg L^{-1} (sample 2), 3900 mg L^{-1} (sample 3) and 30,700 mg L^{-1} (sample 4), respectively. Nonane was used as received.

The bilge water sample was collected from "Norwegian Jade" docked at Civitavecchia port (Italy). Samples were stored in plastic tanks at room temperature. After 24 h, due to gravitational separation, the bilge water gave a two-phase system (water and oil). Oil was then separated from the water phase by pumping. Tests were performed on this water phase, which was used throughout the whole investigation.

Different analytical methods were employed to determine the concentration of organic *C*: total organic carbon (TOC) analysis by TOC-V_{CPN} (Shimadzu), volumetric analysis using potassium permanganate ($KMnO_4$) as titrant (also known as Kubel method) and elemental analysis through the Elemental Macro Vario Cube analyzer.

The experimental tests on synthetic and real samples were performed 5 times. Each analysis was repeated 3 times. The obtained results were averaged, and the repeatability was always < 5%.

All reagents were of analytical grade and were used as received. The glassware utilized was class A Pyrex glass.

Treatment by Fenton reaction

Synthetic solutions

The Fenton reaction is based on the production of •OH radicals by employing H_2O_2 and Fe^{2+} salts, as shown in Eq. 1:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + \cdot OH \quad (1)$$

The degradation efficiency depends on several parameters such as aqueous phase pH, concentration of Fenton reagent and initial organic concentration; in particular, the pH range of 2–4 allows achieving the best treatment efficiency (Zhang et al. 2019).

The Fenton reaction was performed by using solutions of ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, Mallinckrodt Baker) 0.024 mol L^{-1} and hydrogen peroxide (H_2O_2) 30% w/v (Panreac).

The following parameters were controlled during each test: temperature to be 19 ± 1 °C, pH = 2.36—2.41 and $FeSO_4$ solution/synthetic solution volume ratio = 1/1; these operative conditions were selected because allowed obtaining the lowest reagents consumption, as assessed during preliminary tests.

Regarding the surfactant, the experiments were conducted by adding 250 mL of $FeSO_4 \cdot 7H_2O$ solution to 250 mL of SDS solution, under magnetic stirring; subsequently, 15 mL of H_2O_2 was added drop by drop. Kinetic tests were carried out (1, 2 and 24 h), and samples were analyzed by TOC-V_{CPN} before and after the reaction to determine *C* concentration and therefore the effectiveness of the process.

The solutions were centrifuged at 3500 rpm (Nüve NF800 centrifuge), and the supernatant was filtered with 0.2 µm Sartorius Stedim polyether sulfone (PES) membrane filters and analyzed by TOC-V_{CPN}. The precipitate was washed, dried and weighed to determine the amount of produced sludge. In addition, iron concentration was analyzed by atomic absorption spectrophotometry (AA-6300, Shimadzu) before and after the Fenton reaction.

Regarding the hydrocarbon, 20 mL of nonane (Reagent Plus® 99%) was put under magnetic stirring in a beaker with 20 mL of $FeSO_4 \cdot 7H_2O$ solution; subsequently 1.5 mL of H_2O_2 was added drop by drop. Nonane is insoluble in water, so a biphasic organic phase (nonane)/aqueous phase (Fenton reactive) system was formed during the reaction. Kinetic tests were carried out (1, 2 and 24 h). The organic phase was separated, adsorbed on Celite®545 AW (Sigma Aldrich) and placed inside a tin crucible. The percentage of C was determined with a CHN analyzer. The aqueous phase was filtered with 0.2 µm PES membrane filters and analyzed through the TOC-V_{CPN}.

Bilge water

The treatment methods described above were then tested on the real bilge water matrix. Fenton reaction experiments were conducted under magnetic stirring, adding 80 mL of $FeSO_4 \cdot 7\ H_2O$ solution and 5 mL of H_2O_2 poured drop by drop to 80 mL of de-oiled aqueous phase (DAP). Kinetic tests were carried out (1, 2 and 24 h). Samples were centrifuged and C content was analyzed by TOC-V_{CPN}. The sludges produced during the reaction were separated from the aqueous phase by centrifugation, dried at 40 °C and weighed with an analytical balance.

Further tests were performed combining a flocculant process by using a polyelectrolyte before the AOPs treatments studied. The flocculation produced suspension flakes which

were separated from the aqueous phase, dried at 40 °C and weighed with an analytical balance. C content in the supernatant solution was determined by TOC–V_{CPN}. Chemical analysis of bilge water before and after flocculation treatment was executed via inductively coupled plasma optical emission spectroscopy microwave plasma atomic emission spectroscopy (MP-AES). In addition, inductively coupled plasma optical emission spectroscopy (ICP-OES) measurements were performed to confirm metal values below MP-AES detection limit (LOD).

Treatment by TiO_2 photocatalysis

Synthetic solutions

In photocatalytic processes, semiconductor materials (such as TiO_2) are irradiated with UV light which causes migration of electrons from the valence band to the conduction band, resulting in the formation of an oxidizing and a reducing site, as shown in Eqs. 2, 3, 4 and 5). The organic compounds are thus oxidatively degraded into reaction products such as CO_2 and H_2O (Dhanjai et al. 2019).

$$TiO_2 + hv \rightarrow TiO_2\left(e^- + h^+\right) \quad (2)$$

$$OH^- + h^+ \rightarrow \cdot OH \quad (3)$$

$$H_2O + h^+ \rightarrow \cdot OH + H^+ \quad (4)$$

$$\cdot OH + \text{organic compounds} \rightarrow CO_2 + H_2O \quad (5)$$

SDS solutions and anatase titanium oxide (Sigma Aldrich, ≥ 99% trace metals basis, powder, − 325 mesh) were placed inside a quartz glass reactor and irradiated with a Helios Italquartz UV lamp, with wavelengths ranging from 380 to 10 nm under magnetic stirring. The lamp was equipped with a quartz cooling tube which allowed keeping the samples exposed at a constant temperature. Air at a pressure of 55 bar was used to cool down the lamp and maintain the temperature at 40 °C.

The experimental tests were performed by using a TiO_2/SDS solution ratio equal to $25{\cdot}10^{-3}$ g mL^{-1}; as in the case of Fenton reaction, this value was selected because allowed obtaining the lowest reagents consumption, as assessed during preliminary tests. 200 mL of a known concentration of SDS were put in the quartz reactor with about 5 g of TiO_2, and the sample was stirred at 200 rpm.

Kinetic tests were carried out (1, 2 and 24 h) to study the efficiency of the process. Samples were filtered with 0.2 µm PES filters, and C content was analyzed using the TOC-V_{CPN} and by the Kubel method.

Regarding the hydrocarbon, 6 mL of nonane samples was put into the quartz reactor and stirred at 200 rpm with about 600 mg of TiO_2. Kinetic tests were carried out (1, 2 and 24 h), and C content was analyzed using the Kubel method.

Bilge water

The analytical methods described above were tested on the real bilge water matrix.

TiO_2 photocatalysis experiments were carried out adding 5 g of TiO_2 to 200 mL of DAP. Samples were placed in the reactor and collected after 1, 2 and 24 h, filtered with 0.2 µm PES filters and C content was analyzed by the TOC-V_{CPN}.

Further tests were performed combining a flocculant process by using a polyelectrolyte before the photocatalysis treatment. The flocculation produced suspension flakes which were separated from the aqueous phase, dried at 40 °C and weighed with an analytical balance. C content in the supernatant solution was determined by TOC—V_{CPN}.

Results and discussion

Treatment by Fenton reaction

Synthetic solutions

The results of the Fenton reaction treatment on synthetic SDS solutions are reported in Table 1. It was found that the reaction is already efficient within a short time (1 h) as reported in the literature (Ma et al. 2021). The percentage of mineralization varied between 80 and 90% for SDS synthetic solutions 1, 2 and 3, while for sample 4 the value was 62%. The difference between the C depleted in the four SDS synthetic solutions can be due to insufficient quantities of Fenton reagents, compared to the surfactant concentration, even though Fenton oxidation is particularly suitable for organic wastewater that would be hard to biodegraded or treated with conventional chemical techniques (Zhang et al. 2019).

The produced sludge was 320 mg L^{-1} on average. Its production depends mainly on the Fenton reactant (Zhang et al. 2019). To confirm this, iron concentration before and after the reaction was determined through AAS and it was found that the amount of Fe in the solution decreased of about 90%.

Regarding nonane, it is a highly hydrophobic hydrocarbon; therefore, it was not possible to determine *C* content

Table 1 *C* removal percentage in the SDS and nonane synthetic solution after Fenton reaction

SDS solution		
Sample	Time (h)	*C* removal (%)
1	0	–
	1	89
	2	87
	24	87
2	0	–
	1	83
	2	80
	24	79
3	0	–
	1	80
	2	74
	24	74
4	0	–
	1	62
	2	57
	24	57
Nonane		
Celite + C_9H_{20} (mg)	Time (h)	*C* removal (%)
50.01	0	–
50.07	1	31
50.1	2	32
50.05	24	33

within the solutions by using the liquid TOC. For this reason, elemental analysis was employed through the Elemental Macro Vario Cube analyzer. In addition, nonane is a highly volatile liquid hydrocarbon; thus, it was adsorbed on a solid support to prevent sample weight variability. Tests by using several supports such as glucose (D—(+)—glucose, Sigma Aldrich), glass wool (amorphous silicates) and celite®545 AW (Sigma Aldrich) were performed to determine the optimum adsorbent. To reduce evaporation, the sample was weighed directly in the tin crucible, where the adsorbent was inserted and immediately closed.

To determine the most efficient sample/adsorbent ratio, tests were carried out with different quantities of hydrocarbon for the same quantity by weight of adsorbent. For each experiment, sample blank with the adsorbent alone was firstly determined as internal standard (Table 2). It was observed that the optimum conditions are achieved with 50 µL of nonane and 15 mg of adsorbent.

In addition, Table 2 shows that the optimal measurement conditions are achieved using Celite®545 AW as adsorbent, when comparing the percentage of measured C content to the percentage of expected C content. Indeed, for 50 µL of nonane in 15 mg of celite, the expected value of *C* was 59% and the measured value of C was 59% as well.

After the validation of C content measuring method for the nonane, tests were carried out through the Fenton reaction. *C* content was determined collecting the sample after 1, 2 and 24 h (Table 1). The results show that the Fenton

Table 2 Determination of sample *C* content through the elemental macro vario cube analyzer, analyzing different solid supports

Sample	Adsorbent (ADS)	ADS weight (mg)	Expected C_9H_{20} weight (mg)	Expected weight ADS + C_9H_{20} (mg)	Measured weight ADS + C_9H_{20} (mg)	Expected *C* content (%)	Measured *C* content (%)
C_9H_{20} 10 µL	Glucose	15	7	22	12	54	3
	Fiberglass	15	7	22	13	27	5
	Celite	15	7	22	14	27	4
C_9H_{20} 20 µL	Glucose	15	14	29	20	62	16
	Fiberglass	15	14	29	20	41	20
	Celite	15	14	29	20	41	20
C_9H_{20} 30 µL	Glucose	15	21	36	30	66	25
	Fiberglass	15	21	36	31	50	24
	Celite	15	21	36	32	50	23
C_9H_{20} 40 µL	Glucose	15	28	43	37	69	29
	Fiberglass	15	28	43	39	55	40
	Celite	15	28	43	39	55	40
C_9H_{20} 50 µL	Glucose	15	36	51	50	71	61
	Fiberglass	15	36	51	50	59	59
	Celite	15	36	51	50	59	59

reaction has the maximum efficiency after 1 h, as seen for SDS, with a carbon abatement of about 32%.

Comparing the results on SDS and nonane, it was found that Fenton reaction is more efficient for the surfactant with a *C* % removed between 62 and 90%, depending on *C* concentration. In the case of nonane, the *C* % removed was about 32%, which can be due to the higher oxidation resistance of hydrocarbons (Tomaszewska et al. 2005; Eskandarloo et al. 2018) and to the higher *C* concentration of nonane. Therefore, the oxidative process efficiency depends on both pollutants concentration and their oxidation resistance.

Bilge water

Four aliquots were collected from the aqueous phase of bilge water and C content was measured by TOC-V_{CPN}. The value obtained was 316.3 mg L^{-1} on average with a percentage error < 5%. *C* content is comparable to the SDS 10^{-2} mol L^{-1} synthetic sample, where the efficiency of the Fenton reaction was > 80%.

The aqueous phase was treated by Fenton reaction and it was found that the percentage of carbon removed reaches the value of 66% after 1 h and remains constant if the reaction time is increased up to 2 h, as already occurred for the experiments with the SDS synthetics solutions with a C concentration of 10^{-2} mol L^{-1}.

The result obtained with the aqueous phase was low if compared to the experiments carried out with SDS 10^{-2} mol L^{-1}, where more than 80% of the C present in the solution was demineralized. This phenomenon depends on the bilge water composition as it is a heterogeneous matrix containing hydrocarbons and oils that are more resistant to oxidation, in addition to the surfactant (Eskandarloo et al. 2018; Tomaszewska et al. 2005).

The sludges produced during the reaction were separated and weighted and the quantity was 322 mg L^{-1} on average. This value is comparable to the results obtained with the SDS standard solution (320 mg L^{-1} on average). The constant amount of solid residue demonstrated that the sludge is mainly coming from the Fenton reagents (M. Zhang et al. 2019).

To decrease the amount of the fraction that is more resistant to oxidation, a possible scenario is to pretreat bilge water with a flocculant (Han et al. 2019).

Four aliquots of bilge water were collected and treated by using a polyelectrolyte as described in 2.1.2. Carbon content was measured by TOC—V_{CPN} and the value obtained was found to be 291.3 mg L^{-1} on average with a percentage error < 5%. Comparing the results measured before (316.3 mg L^{-1}) and after (291.3 mg L^{-1}) the flocculation treatment, a decrease in carbon content of 8% was observed. The percentage of carbon removed after 1 h was 95%, and this value was higher compared to the results obtained by treating the aqueous phase of bilge water directly with the Fenton reaction (66%).

In Table 3, the chemical analyses of some chemical species before and after the flocculation process are presented. Although the flocculation process decreased the carbon content of about 8%, this method allows to purify the solution from other chemical species and, in particular, from metals. The combined method (flocculation process + Fenton reaction) gives the possibility of water reuse as well as its direct discharged into the sea or surface water. In addition, the quantity of reaction sludge was determined. The value was 2.5 g L^{-1} on average for the flocculation, while for the Fenton reaction was 321 mg L^{-1} on average (comparable with the results obtain with SDS synthetic solutions).

Treatment by TiO_2 photocatalysis

Synthetic solutions

The experimental tests were performed by using a SDS synthetic solution with a concentration of 10^{-2} mol L^{-1} as the *C* concentration in the real matrix. Oxygen consumption (VO_2) was determined in the solution through permanganometry, in particular with the Kubel method. For each sample, three titrations were carried out. VO_2 derives from the oxidation of organic substances in solution using potassium permanganate and was determined according to Eq. 6:

$$\frac{(v \cdot N \cdot 8) \cdot 1000}{V} \tag{6}$$

where v is the volume of permanganate solution, N is the normality of the $KMnO_4$ solution (0.01210 N), 8 is the mass

Table 3 Bilge water chemical analysis via MP-AES, before and after flocculation treatment (*values measured by ICP-OES)

Element	Before flocculation (mg L^{-1})	After flocculation (mg L^{-1})
Al	54	1
Ba	3	1
Cd	< 1	< 0.01*
Total Cr	69	< 0.01*
Fe	650	1
Mn	14	1
Ni	40	1
Pb	9	< 0.01*
Cu	9	< 0.01*
Sn	< 1	< 0.01*
Zn	20	< 0.01*

in grams of one equivalent of oxygen, 1000 is a conversion factor (*g*mg) and *V* is the volume of the analyzed sample.

It was found that the VO_2 was 117 mg L^{-1} on average.

The SDS solutions were placed in the reactor with TiO_2 to be irradiated. For each experiment, two samples were collected after 1, 2 and 24 h. In the first one, oxygen consumption was determined using the Kubel method; in the other one, C content was determined by TOC-V_{CPN}.

Oxygen consumption was determined in 15 mL of SDS synthetic solution treated with the photocatalysis and it was 39.80 mg L^{-1}, which represented 65% of VO_2. This consumption is attributable to the abatement of organic substances caused by photocatalysis oxidation that oxidizes the surfactant into CO_2 and H_2O. Similarly to Fenton reaction, it was found that the photocatalysis reaction reaches the maximum efficiency within a short time reaction (1 h), as also reported by Chen et al. 2020. Moreover, the samples were analyzed through TOC—V_{CPN} to evaluate C concentration before and after TiO_2 photocatalysis; the results confirmed that the reaction was efficient after 1 h with a percentage of carbon removal of about 67%. Although the consumption of oxygen and the quantity of residual carbon are two different parameters, the obtained values are comparable and both can be used to evaluate the efficiency of the process. Hydroxyl radicals generated during the TiO_2 photocatalysis reaction oxidized almost all the organic compounds to carbon dioxide and water. Therefore, C content decreases due to the reaction and consequently the oxygen consumption is also reduced, allowing correlation between the two parameters.

Regarding TiO_2 tests on nonane hydrocarbon, a number of experiments were carried out to determine the VO_2 with Kubel method. From the analysis, the oxygen consumption value was about 447 mg L^{-1}. Comparing the VO_2 value of nonane to the VO_2 value of SDS 10^{-2} mol L^{-1} (117 mg L^{-1}), it was found that the VO_2 of nonane is higher than the VO_2 of SDS. This depends on C concentration of nonane which was 599 g L^{-1}, while *C* present in the SDS solution was 3.94 g L^{-1}.

The nonane solutions were placed in the reactor with TiO_2 to be irradiated. The samples were collected after 1, 2 and 24 h and the oxygen consumption was determined using the Kubel method. It was not possible to determine the *C* content through TOC—V_{CPN}, because nonane is a strong hydrophobic hydrocarbon. TiO_2 photocatalysis reaches the equilibrium after 1 h, as SDS experiments confirmed, with an oxygen consumption of 75%.

Bilge water

Four samples were collected from the aqueous phase of bilge water and placed inside the reactor with TiO_2. Samples were collected after 1, 2 and 24 h, and the *C* content was analyzed through TOC—V_{CPN}. TiO_2 photocatalysis reaction is efficient after 1 h and the percentage of C removal was 64% and this is comparable to the demineralization of SDS 10^{-2} mol L^{-1} synthetic solutions. The poor affinity of photocatalysts toward organic pollutants could be an explanation for the results obtained through TiO_2 photocatalytic process. As Lee et al. (2018) presented in their work, slow photocatalytic degradation rates were caused by low adsorption of organic pollutants on the TiO_2 surface. Photocatalyst immobilization on an inert matrix could solve the selective affinity issue (Lee et al. 2018; Chen et al. 2020).

In addition, tests were also carried out to verify the possibility of reusing TiO_2 during the photocatalysis experiments. The values obtained after the process with the recycled TiO_2 showed that the oxide was still efficient with a percentage of reduced carbon of 63%.

Further tests were performed combining a flocculant process by using a polyelectrolyte before the photocatalysis treatment. Four samples were collected, treated by using a polyelectrolyte and centrifuged. Subsequently, the supernatant was demineralized with TiO_2 photocatalysis. Samples were collected after 1, 2 and 24 h, and the carbon content was determined via TOC-V_{CPN}. It was found that TiO_2 photocatalysis is efficient after 1 h and the percentage of *C* removal was about 63%: the effect of the photocatalysis on the sample after flocculation process produces then similar results to those obtained after the oxidation process on the aqueous phase.

Conclusion

In this paper, water recovery from bilge water is presented by comparing two different advanced oxidation processes: the Fenton reaction and TiO_2 photocatalysis.

All the oxidative processes tested on both synthetic solutions and bilge water showed that the highest efficiency is achieved already after one hour with comparable oxidation yields. The surfactants oxidation in both oxidative processes achieved a C depletion higher than 90% compared to hydrocarbons (30%). This difference is due to the higher resistance to oxidation of hydrocarbons (Tomaszewska et al. 2005; Eskandarloo et al. 2018). Therefore, the oxidative process

efficiency depends on both concentration and pollutants oxidation resistance.

The oxidative process yields obtained on bilge water are lower compared to the synthetic solutions ones (about 60%). Furthermore, it was found that the oxidative processes efficiency increases when the bilge water aqueous phase is pretreated by flocculation (95% of C depleted in the case of Fenton reaction).

The processes here presented allowed obtaining water having chemical-physical parameters which allow its direct discharge into the sea as well as in surface waters. It is concluded that the AOPs treatments can be applied to a matrix with a similar composition to bilge water. Furthermore, analytical methods such as analysis of the total carbon content, elemental analysis and Kubel method proved to be efficient to evaluate the effectiveness of the processes.

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Declarations

Conflict of interest There are no conflicts of interest to declare.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

References

Akarsu C, Ozay Y, Dizge N, Gulsen HE, Ates H, Gozmen B, Turabik M (2016) Electrocoagulation and nanofiltration integrated process application in purification of bilge water using response surface methodology. Water Sci Technol 74(3):564–579. https://doi.org/10.2166/wst.2016.168

Amran NA, Mustapha SNA (2021) Oil-water separation techniques for bilge water treatment. Resour Water 32:137–44. https://doi.org/10.5772/intechopen.91409

Andersson K, Brynolf S, Landquist H, Svensson E (2016) Methods and tools for environmental assessment. In: Andersson K, Brynolf S, Lindgren J, Wilewska-Bien M (eds) Shipping and the environment. Springer, Berlin Heidelberg. https://doi.org/10.1007/978-3-662-49045-7_9

Bilgili MS, Ince M, Tari GT, Adar E, Balahorli V, Yildiz S (2016) Batch and continuous treatability of oily wastewaters from port waste reception facilities: a pilot scale study. J Electroanal Chem 760:119–126. https://doi.org/10.1016/j.jelechem.2015.11.024

Byrnes TA, Dunn RJK (2020) Boating-and shipping-related environmental impacts and example management measures: a review. J Mar Sci Eng 8(11):1–49. https://doi.org/10.3390/jmse8110908

Carles C, Ramírez NG, Carvajal D, Hernández MC, Fino D (2014) Electrochemical treatment of bilge wastewater. Desalin Water Treat 54(6):1556–1562. https://doi.org/10.1080/19443994.2014.887040

Chanthamalee J, Wongchitphimon T, Luepromchai E (2013) Treatment of oily bilge water from small fishing vessels by PUF-immobilized gordonia sp. JC11. Water Air Soil Pollut 224:1601. https://doi.org/10.1007/s11270-013-1601-6

Chen D, Cheng Y, Zhou N, Chen P, Wang Y, Li K, Huo S, Cheng P, Peng P, Zhang R, Wang L, Liu H, Liu Y, Ruan R (2020) Photocatalytic Degradation of organic pollutants using TiO_2-based photocatalysts: a review. J Clean Prod 268:121725. https://doi.org/10.1016/j.jclepro.2020.121725

Church J, Lundin JG, Diaz D, Mercado D, Willner MR, Lee WH, Paynter DM (2019) Identification and characterization of bilgewater emulsions. Sci Total Environ 691:981–995. https://doi.org/10.1016/j.scitotenv.2019.06.510

Cortese B, Caschera D, Federici F, Ingo GM, Gigli G (2014) Superhydrophobic fabrics for oil-water separation through a diamond like carbon (DLC) coating. J Mater Chem A 2(19):6781–6789. https://doi.org/10.1039/C4TA00450G

Crisafi F, Genovese M, Smedile F, Russo D, Catalfamo M, Yakimov M, Giuliano L, Denaro R (2016) Bioremediation technologies for polluted seawater sampled after an oil-spill in taranto gulf (Italy): a comparison of Biostimulation, Bioaugmentation and use of a washing agent in microcosm studies. Mar Pollut Bull 106(1–2):119–126. https://doi.org/10.1016/j.marpolbul.2016.03.017

Eskandarloo H, Selig MJ, Abbaspourrad A (2018) In situ H_2O_2 generation for De-emulsification of fine stable bilge water emulsions. Chem Eng J 335:434–442. https://doi.org/10.1016/j.cej.2017.10.174

Furlan PY, Ackerman BM, Melcer ME, Perez SE (2017) Reusable magnetic nanocomposite sponges for removing oil from water discharges. J Ship Prod Des 33(03):227–236. https://doi.org/10.5957/JSPD.33.3.160017

Gautam P, Kumar S, Lokhandwala S (2019) Advanced oxidation processes for treatment of leachate from hazardous waste landfill: a critical review. J Clean Prod 237:117639. https://doi.org/10.1016/j.jclepro.2019.117639

Gryta M (2020) Bilge water separation by membrane distillation. Sep Purif Technol 237:116332. https://doi.org/10.1016/j.seppur.2019.116332

Gupta P, Balasubramanian K (2017) Directional fluid gating by janus membranes with heterogeneous wetting properties for selective

oil-water separation. ACS Appl Mater Interf 9(22):19102–19113. https://doi.org/10.1021/acsami.7b03313

Han M, Zhang J, Chu W, Chen J, Zhou G (2019) Research progress and prospects of marine oily wastewater treatment: a review. Water 11(12):1–29. https://doi.org/10.3390/w11122517

International Maritime Organization (IMO) (1978) International Convention for the Prevention of Pollution from Ships, as Modified by the Protocol of 1978, (MARPOL 73/78). 1978. https://www.imo.org/en/About/Conventions/Pages/International-Convention-for-the-Prevention-of-Pollution-from-Ships-(MARPOL).aspx

Körbahti BK, Artut K (2013) Bilge water treatment in an upflow electrochemical reactor using Pt anode. Sep Sci Technol 48(14):2204–2216. https://doi.org/10.1080/01496395.2013.791852

Lee CG, Javed H, Zhang D, Kim JH, Westerhoff P, Li Q, Alvarez PJJ (2018) Porous electrospun fibers embedding TiO_2 for adsorption and photocatalytic degradation of water pollutants. Environ Sci Technol 52(7):4285–4293. https://doi.org/10.1021/acs.est.7b06508

Liu B, Zhan Y, Xie R, Huang H, Li K, Zeng Y, Shrestha RP, Oanh NTK, Winijkul E (2019) Efficient photocatalytic oxidation of gaseous toluene in a bubbling reactor of water. Chemosphere 233:754–761. https://doi.org/10.1016/j.chemosphere.2019.06.002

Lu D, Liu Q, Zhao Y, Liu H, Ma J (2018) Treatment and energy utilization of oily water via integrated ultrafiltration-forward osmosis-membrane distillation (UF-FO-MD) system. J Membr Sci 548:275–287. https://doi.org/10.1016/j.memsci.2017.11.004

Luo H, Zeng Y, He D, Pan X (2021) Application of iron-based materials in heterogeneous advanced oxidation processes for wastewater treatment: a review. Chem Eng J 407:127191. https://doi.org/10.1016/j.cej.2020.127191

Luste S, Sillanpää M (2020). UVC irradiation–based water treatment. In Advanced water treatment, Elsevier. p 95–128. https://doi.org/10.1016/B978-0-12-819225-2.00003-X

Ma D, Yi H, Lai C, Liu X, Huo X, An Z, Li L, Fu Y, Li B, Zhang M, Qin L, Liu S, Yang L (2021) Critical review of advanced oxidation processes in organic wastewater treatment. Chemosphere 275:130104. https://doi.org/10.1016/j.chemosphere.2021.130104

Maiti S, Mishra IM, Bhattacharya SD, Joshi JK (2011) Removal of oil from oil-in-water emulsion using a packed bed of commercial resin. Colloids Surf A Physicochem Eng Asp 389(1–3):291–298. https://doi.org/10.1016/j.colsurfa.2011.07.041

Mancini G, Panzica M, Fino D, Cappello S, Yakimov MM, Luciano A (2017) Feasibility of treating emulsified oily and salty wastewaters through coagulation and bio-regenerated GAC filtration. J Environ Manag 203:817–24. https://doi.org/10.1016/j.jenvman.2016.07.014

McLaughlin C, Falatko D, Danesi R, Albert R (2014) Characterizing shipboard bilgewater effluent before and after treatment. Environ Sci Pollut Res 21(8):5637–52. https://doi.org/10.1007/s11356-013-2443-x

Moslehyani A, Mobaraki M, Isloor AM, Ismail AF, Othman MHD (2016a) Photoreactor-ultrafiltration hybrid system for oily bilge water photooxidation and separation from oil tanker. React Funct Polym 101:28–38. https://doi.org/10.1016/j.reactfunctpolym.2016.02.003

Moslehyani A, Mobaraki M, Matsuura T, Ismail AF, Othman MHD, Chowdhury MNK (2016b) Novel green hybrid processes for oily water photooxidation and purification from merchant ship. Desalination 391:98–104. https://doi.org/10.1016/j.desal.2016.01.003

Motoyoshi M, Nishi Y (2020) Statistical modeling of bilge water discharge from ships during normal operation. J Mar Sci Eng. https://doi.org/10.3390/JMSE8050320

Peng H, Tremblay AY, Veinot DE (2005) The use of backflushed coalescing microfiltration as a pretreatment for the ultrafiltration of bilge water. Desalination 181(1–3):109–120. https://doi.org/10.1016/j.desal.2004.12.040

Penny RL, Suominen-Yeh M (2006) Biological bilge water treatment system. Nav Eng J 118(3):45–50. https://doi.org/10.1111/j.1559-3584.2006.tb00462.x

Pera-Titus M, García-Molina V, Baños MA, Giménez J, Esplugas S (2004) Degradation of chlorophenols by means of advanced oxidation processes: a general review. Appl Catal B: Environ 47(4):219–256. https://doi.org/10.1016/j.apcatb.2003.09.010

Putatunda S, Bhattacharya S, Sen D, Bhattacharjee C (2019) A review on the application of different treatment processes for emulsified oily wastewater. Int J Environ Sci Technol 16(5):2525–2536. https://doi.org/10.1007/s13762-018-2055-6

Rahmani Z, Shafiei-Alavijeh M, Kazemi A, Rashidi AM (2018) Synthesis of MIL-101@nanoporous graphene composites as hydrophobic adsorbents for oil removal. J Taiwan Inst Chem 91:597–608. https://doi.org/10.1016/j.jtice.2018.06.015

Ribeiro AR, Nunes OC, Pereira MFR, Silva AMT (2015) An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched directive 2013/39/EU. Environ Int 75:33–51. https://doi.org/10.1016/j.envint.2014.10.027

Shen Y, Yao J, Son J, Zhu Z, Yu X-Y (2020) Liquid ToF-SIMS revealing the oil, water, and surfactant interface evolution. Phys Chem Chem Phys 22(21):11771–11782. https://doi.org/10.1039/d0cp00528b

Sinha DA, Zhao H, Chen J, Mugo SM (2019) Determination of chemical oxygen demand: an analytical approach. In: Worsfold P, Poole C, Townshend A, Miró M (eds) Encyclopedia of analytical science, 3rd edn. Academic Press, Oxford, pp 258–270. https://doi.org/10.1016/B978-0-12-409547-2.14517-2

Statista Research Department (2021). Transport Volume of Seaborne Trade from 1990–2019. https://www.statista.com/statistics/264117/tonnage-of-worldwide-maritime-trade-since-1990/

Sun C, Leiknes TO, Weitzenböck J, Thorstensen B (2009) The effect of bilge water on a biofilm-MBR process in an integrated shipboard wastewater treatment system. Desalination 236(1–3):56–64. https://doi.org/10.1016/j.desal.2007.10.051

Sun C, Leiknes TO, Weitzenböck J, Thorstensen B (2010) Development of an integrated shipboard wastewater treatment system Using biofilm-MBR. Sep Purif Technol 75(1):22–31. https://doi.org/10.1016/j.seppur.2010.07.005

Tiselius P, Magnusson K (2017) Toxicity of treated bilge water: the need for revised regulatory control. Mar Pollut Bull 114(2):860–866. https://doi.org/10.1016/j.marpolbul.2016.11.010

Tomaszewska M, Orecki A, Karakulski K (2005) Treatment of bilge water using a combination of ultrafiltration and reverse osmosis. Desalination 185(1–3):203–212. https://doi.org/10.1016/j.desal.2005.03.078

Turco A, Primiceri E, Frigione M, Maruccio G, Malitesta C (2017) An innovative, fast and facile soft-template approach for the fabrication of porous PDMS for Oil-Water separation. J Mater Chem A 5(45):23785–23793. https://doi.org/10.1039/C7TA06840A

Ulucan K, Kurt U (2015) Comparative study of electrochemical wastewater treatment processes for bilge water as oily wastewater: a kinetic approach. J Electroanal Chem 747:104–111. https://doi.org/10.1016/j.jelechem.2015.04.005

Walker TR, Adebambo O, Del Aguila Feijoo MC, Elhaimer E, Hossain T, Edwards SJ, Morrison CE, Romo J, Sharma N, Taylor S, Zomorodi S (2018). Environmental effects of marine transportation. In: World seas: an environmental evaluation Volume III: ecological issues and environmental Impacts. Second Ed. Elsevier Ltd. https://doi.org/10.1016/B978-0-12-805052-1.00030-9

Wang J, Zhuan R (2020) Degradation of antibiotics by advanced oxidation processes: an overview. Sci Total Environ 701:135023. https://doi.org/10.1016/j.scitotenv.2019.135023

Wang G, Zeng Z, Wu X, Ren T, Han J, Xue Q (2014) Three-dimensional structured sponge with high oil wettability for the clean-up of oil contaminations and separation of oil-water mixtures. Polym Chem 5(20):5942–5948. https://doi.org/10.1039/C4PY00552J

Yang M (2011) Shipping and maritime transport. Encycloped Environ Health. https://doi.org/10.1016/B978-0-444-52272-6.00315-9

Yu L, Han M, He F (2017) A review of treating oily wastewater. Arab J Chem 10:S1913–S1922. https://doi.org/10.1016/j.arabjc.2013.07.020

Zhang W, Wei Y, Jin Y (2018) Full-scale processing by anaerobic baffle reactor, sequencing batch reactor, and sand filter for treating high-salinity wastewater from offshore oil rigs. Processes 6(12):256. https://doi.org/10.3390/pr6120256

Zhang M-h, Dong H, Zhao L, Wang D-x, Meng D (2019) A Review on fenton process for organic wastewater treatment based on optimization perspective. Sci Total Environ 670:110–121. https://doi.org/10.1016/j.scitotenv.2019.03.180