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# Novel green hybrid processes for oily water photooxidation and purification from merchant ship

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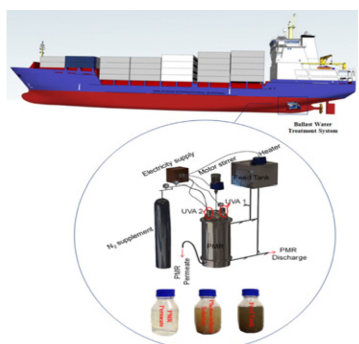
## HIGHLIGHTS

- Photoxidation of oily water by two different photocatalytic reactors (PR-UF and PMR)
- Immobilizing TiO2 in the HNT surface via AEAPTMS silan and embedded on the PVDF polymer matrix
- Over 80% TOC degradation has been achieved via PR-UF process.

## GRAPHICAL ABSTRACT




Two hybrid systems for photooxidation and separation of oily water from merchant ship have been investigated in this study.

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## ABSTRACT

Two hybrid photooxidation systems consisting of two different reactors; photocatalytic reactor-ultrafiltration (PR-UF) and photocatalytic membrane reactor (PMR) have been investigated and compared for photolysis and separation of oily water. In both, oily water was irradiated by ultraviolet (UV) light. In PR, UV irradiation was made on the $TiO_2$ photocatalyst suspended in oily water, followed by ultrafiltration (UF) to remove $TiO_2$ particles and hydrocarbon residues. On the other hand, $TiO_2$ was immobilized on the halloysite nanotube (HNT) and embedded in the UF membrane in PMR. In both systems, hydrocarbon concentration, chemical oxygen demand (COD), total dissolved solid (TDS), and hydrocarbon concentration were measured at each step of photooxydation and filtration. In UF, membrane flux, reduction in solute concentration, flux decline and flux recovery by backwashing were investigated. The experimental results showed that the reduction in TOC by PR-UF was ~10% higher than PMR. On the other hand, reduction in hydrocarbon concentration, COD and TDS was higher for PMR. The $TiO_2$ concentration in UF permeate was 8 ppm and 0.2 ppm, respectively, for PR-UF and PMR.



## 1. Introduction

Merchant ships' water filter including small feeder ships, car carrier ships, giant container vessels, oil tankers, warships, and cruise ships have given many advantages to human life via huge carrying capacity and low cost shipping compared to other vehicles [1–4]. However, their oily water discharge is known to have a negative impact on the marine ecosystem. In particular, one merchant ship crew practice is using their clean ballast water for washing out ship oil or fuel tanks, which makes oil emulsion in ballast water [5,6]. Afterward, that oily ballast water will be pumped offshore without proper treatment. This

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practice results in the spillage of oily ballast offshore, causing extensive ecological and economic damages to the aquatic ecosystems around the world, along with serious human health issues including death due to the discharge of toxic waste to the environment. This negative impact of merchant ship on marine and human life has become a subject for green global organizations since the late 1980s. Accordingly, the International Maritime Organization (IMO) adopted the Ballast Water Management (BWM) convention in February 2004, and its ratification is under way for having green environment. Prior to BWM, marine pollution (MARPOL) was made by England in 1978 to prevent pollution from all types of ships [7]. The marine pollution 1973–1978 (MARPOL 73–78) conventions have regulated that merchant ships install a water purification system for their wastewater in order to purify water on board such that their oily wastewater discharge contains no more than 15 mg of oil per liter. In particular, merchant ships should store their retentate of treated oily ballast water or untreated oily ballast water in their segregated ballast tanks (SBT) until the vessel reaches a reception facility in the port [8]. Regarding these regulations, the merchant ship industry has been looking forward to having green and advanced on board oily ballast water treatment. Hence, companies specializing in water and wastewater treatment systems are providing ballast water treatment systems and processes for merchant ships [7]. Currently, the potable ultraviolet (UV) irradiation application as the greenest and most advanced process is of interest to the merchant ship industries due to their promising performance [9]. Schematic diagram of a 20,000 deadweight (dwt) merchant ship elements are shown in Fig. 1.

The UV irradiation system is one of the AOPs [10,11]. It consists of UV reactor, UV lamp and photocatalyst or photocatalyst support (e.g. photocatalytic membrane) [12,13] and can photooxidize the toxic components to non-toxic or lower level toxic components via photoreaction [14–16]. The factors that affect the performance of a UV irradiated photocatalytic system are photocatalyst type [17] and loading [18], contaminants concentration [19], UV wavelength and UV intensity [20,21]. Titanium dioxide ($TiO_2$) is well-accepted as a photocatalyst due to its high degradation performance, recovery capability via heating up to the temperature of 250 °C for 5 or more degradation cycles and low cost [22,23].

In a photocatalytic reactor (PR) system ultrafiltration (UF) can be combined with photocatalyst either separately, called PR-UF system, or as a photocatalytic membrane reactor, called PMR system, in which both photocatalytic reaction and filtration take place [4]. However, in the latter system, membrane flux may decrease with the filtration time due to the deposition of oil [24], or catalyst particles or agglomerate of the catalyst particles [25–27]. Hence, a number of suggestions were made to address the problem, e.g. backwashing of the membrane or immobilization of photocatalysts to the surface of nanofillers [28].

The objective of this research is to develop a novel photooxidation-filtration system for the treatment of oily wastewater. To this end, two hybrid photooxidation systems, photocatalytic reactor- ultrafiltration (PR-UF) and photocatalytic membrane reactor (PMR), were constructed and compared. In both systems, UV irradiation was made on $TiO_2$ photocatalyst. The catalyst particles were suspended in the oily water in PR and ultrafiltered by UF hollow fibers in the PR-UF system. On the other hand, the catalyst particles were incorporated in UF hollow fiber membrane in PMR.

## 2. Materials and methods

### 2.1. Materials and chemicals

Polyvinylidene fluoride (PVDF) Solef 6012 from Solvay Advanced Polymers was used as polymer and the solvent was dimethylacetamide (DMAc, >99.5%) from Merck. Halloysite nanotubes (HNTs) clay with inner tube diameter of 5–15 nm from Sigma Aldrich and titanium-dioxide ($TiO_2$) P25 nanoparticles with specific surface area of $50 \pm 15\ m^2g^{-1}$ from Evonik Degussa were used, respectively, as the nanofiller and the photocatalyst. N-β-(aminoethyl)-γ-aminopropyltrimethoxysilane (AEAPTMS) from Merck was used to immobilize $TiO_2$ on the surface of HNTs.

### 2.2. System design

Fig. 2a and b show the schematic diagram of the PR-UF and PMR systems, respectively, used in this study. The same stainless steel vessel with a maximum liquid loading of 22 L was used as the UF separator and the membrane reactor, respectively, for the PR-UF and PMR systems. Two UV lamps (type A of HITACHI, Japan; 18 W, ~340 nm, OD ~25 mm, length ~ 60 cm), a stainless steel stirrer (50 rpm) and two hollow fiber bundles (diameter, ½ in., length 30 cm) containing 120 hollow fibers were installed in the vessel.

### 2.3. Photocatalyst preparation

In the PR of the PR-UF system $TiO_2$ nanoparticles were used as photocatalyst without any treatment. For PMR $TiO_2$ was chemically

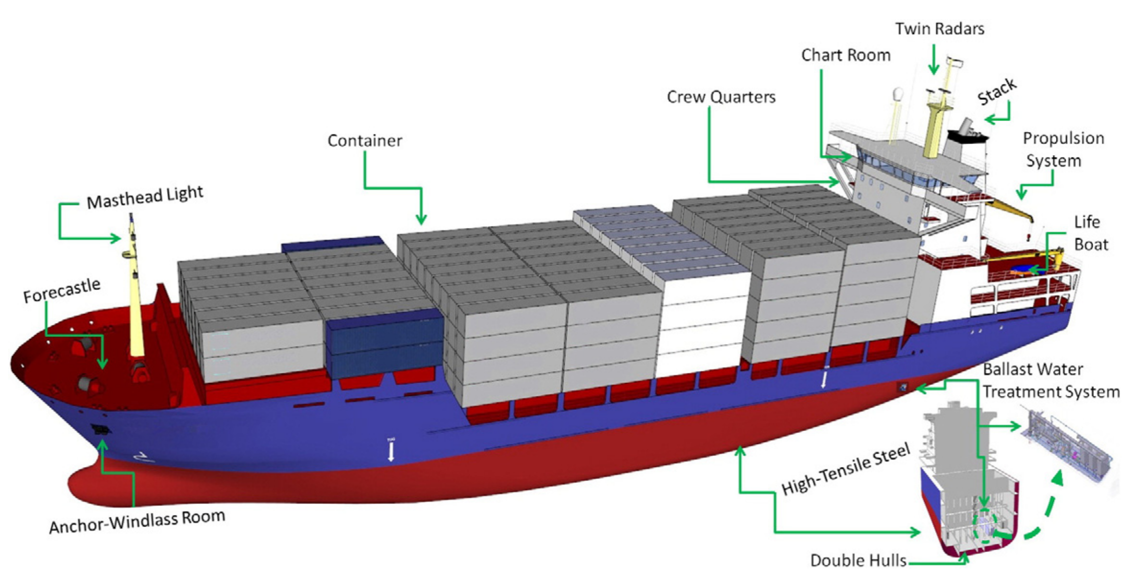


**Fig. 1.** Schematic diagram of oil tanker.