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Marine environmental protection: An application of the nanometer photo catalyst method on decomposition of benzene

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ABSTRACT

Bioremediation is currently extensively employed in the elimination of coastal oil pollution, but it is not very effective as the process takes several months to degrade oil.
Among the components of oil, benzene degradation is difficult due to its stable characteristics. This paper describes an experimental study on the decomposition of benzene by titanium dioxide (TiO_2) nanometer photocatalysis. The photocatalyst is illuminated with 360-nm ultraviolet light for generation of peroxide ions. This results in complete decomposition of benzene, thus yielding CO_2 and H_2O. In this study, a nonwoven fabric is coated with the photocatalyst and benzene. Using the Double-Shot Py–GC system on the residual component, complete decomposition of the benzene was verified by 4 h of exposure to ultraviolet light. The method proposed in this study can be directly applied to elimination of marine oil pollution. Further studies will be conducted on coastal oil pollution in situ.

1. Introduction

Marine environmental protection is one of the main duties of the Coast Guard Administration (CGA) (Lin and Kuo, 2013). This protection includes prevention and control of marine oil and chemical pollution that can lead to marine accidents and sometimes environmental catastrophes. Marine accidents are still frequent in spite of effective ship design. The most famous accident off the coast in Taiwan occurred involving the Greek cargo vessel *M/V Amorgos*, which ran aground off the coast of southern Taiwan and caused severe marine pollution. The Indonesian chemical tanker *Dewi Bunyu* collided at sea off Keelung, and the South Korean benzene ship *Samho Brother* collided at sea off Hsinchu (Lin, 2011). Moreover, these accidents occur consecutively, generally as a result of human error or mechanical failures. Despite the heavy monetary penalties in force, oil and oil-contaminated water are discharged overboard due to several reasons including accidents. Although such penalties may have contributed to a decrease in the frequency of accidents or incidents, one must continuously seek ways to recover the spilt oil in order to reduce the damage to the environment.

Unarguably, marine environmental protection is crucial for the survival of the marine ecosystem and the sustenance of marine life, and prevention of oil pollution contributes significantly toward this objective.

Among the components of oil, the aromatic compound (benzene) does not decompose easily due to its stable characteristics. Yet, the decomposition of benzene is a requisite for the decomposition of oil and thus protection of the marine environment.

Marine oil pollution is conventionally eliminated by cleanup with cotton or chemical treatment (Lin, 2010). However, these methods require considerable manpower and material resources, thus resulting in a labor-intensive, low-efficiency process and a longer recovery cycle. Moreover, with little experience in treating chemical pollution, for example, with benzene, governments have had difficulty in developing successful policies that adequately address such cleanups (Lin, 2011).

Research focus on the microbial degradation of oil pollutants in coastal waters has considerably increased in recent years. Bioremediation involves natural microbial degradation processes and is currently used to restore oil-polluted environments (Atlas, 1991; Leahy and Colwell, 1990; Seo et al., 2009). The literature focused on accelerating the rate of degradation has been reviewed (Pucci, 2011). A series of studies on the physical and chemical effects of degradation of hydrocarbons have been investigated, which suggest improved methods to increase the rate of degradation, including addition of fertilizers, air supply, temperature control, etc.

Despite successful biodegradation of oil, the following limitations are noted: First, biodegradation yielded mostly unsatisfactory results due to its relatively low efficiency, irrespective of the efforts taken to improve results. Second, various microbes have an affinity toward specific hydrocarbons. Hence, using a single type of microbe results in poor degradation of oil due to the diverse range of oils and

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hydrocarbon mixtures. Finally, similar to plants, greater efficiencies can be achieved only by setting up the optimal conditions for microbial activities. Hence, the photodegradation method is proposed to replace biodegradation.

Apparently, the typical characteristics of benzene are different from those of fuel oil, with respect to the degree of volatility and purity. The former is both volatile and pure, whereas fuel oil is not as volatile and is impure. There exists, however, some degree of similarity between them: (1) both are hydrocarbons, and (2) upon complete oxidation, both yield H_2O and CO_2. Water is not harmful to human life, and carbon dioxide is not directly harmful to human life either. It is well known that benzene is a primary ingredient of fuel oil, and has a hexagon wreath structure at the molecular level; its structural stability makes its natural decomposition difficult (Peng et al., 2008). Benzene is also toxic to humans.

Combustion is a type of rapid oxidation. While burning fuel oil, complete breakdown of the wreath structures present within the fuel oil is more difficult, unlike chain structures of other molecules. This suggests that complete breakdown of the wreath structures imply easy decomposition of fuel oil. The titanium dioxide nanophotocatalyst used in this study to decompose benzene yielded positive results.

2. Theorem of titanium dioxide nanometer photocatalyst

A series of studies using a titanium dioxide (TiO_2) nanophotocatalyst based on its application in daily life have been conducted (Chen and Mao, 2007; Fujishima et al., 2000). It has been used as a self-cleaning agent and a medical disinfectant (Huang et al., 2000) and also in the purification of air and water. Sakthivel and Kisch (2003) presented the use of a titanium dioxide nanophotocatalyst as a semiconductor. Several semiconductors are presently available with different photocatalytic properties, and their abilities are distinct from those observed under ultraviolet light. The TiO_2 photocatalyst has been found to exhibit properties; its low toxicity, low cost, and stability further make it highly marketable. It is a waterproofing agent with strong oxidation properties even upon exposure to ultraviolet light (Fujishima and Zhang, 2006).

A TiO_2 nanophotocatalyst in an aqueous solution and under ultraviolet light exhibits behavioral characteristics similar to other semiconductors, particularly in generation of positive holes for the production of hydroxyl radicals (•OH) (Carp et al., 2004). The hydroxyl radicals, with strong oxidizing power, will decompose hydrocarbons into CO_2 and H_2O. The following reaction process of TiO_2 occurs (Bilmes et al., 2000):

$$TiO_2 + h\nu \rightarrow h^+ + e^- \quad \text{(positive hole and electron)}$$

$$H_2O + h^+ \rightarrow H^+ + \bullet OH \quad \text{(hydroxyl radical)}.$$

Basically, hydrocarbons consist of C–C, C–H, or O–H bonds having energy values of about 80–100 kcal/molecule. The hydroxyl radicals, with a high energy of 120 kcal/molecule, can easily break the hydrocarbon bonds.

Decomposition reactions occur when O_2 meets the excited electrons in air; they yield $\bullet O_2^-$ ions, which upon binding with H^+ form peroxides H_2O_2. These peroxides are unstable and thus yield H_2O. The decomposition sequence is as follows:

$$2e^- + O_2 \rightarrow \bullet O_2^-$$

$$\bullet O_2^- + H^+ \leftrightarrow HO_2\bullet$$

$$HO_2\bullet + O_2^- + H^+ \rightarrow H_2O_2 + O_2$$

$$HO_2\bullet + HO_2\bullet \rightarrow H_2O_2 + O_2$$

$$\bullet O_2^- + \bullet O_2^- + 2H^+ \rightarrow H_2O_2 + O_2.$$

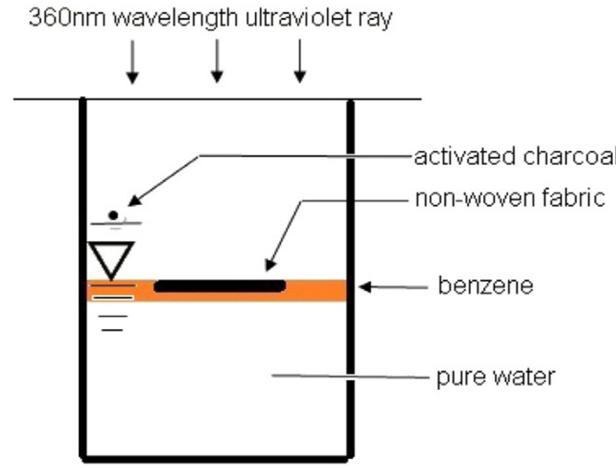

Fig. 1. Simplified schematic of decomposition.
Source: Authors' own work.

Benzene possesses a hexagon wreath structure with stable bonds such as C–C, C═C, and C–H. When the TiO_2 nanophotocatalyst comes in contact with any hydrocarbon, with either a chain or a hexagon wreath structure, under ultraviolet light, the highly active hydroxyl radicals released from oxidized water destroy the hydrocarbon bonds and yield CO_2 and H_2O (Yamashita et al., 2002; Khataee and Kasiri, 2010; Kim and Anderson, 1994; Kaneco et al., 2004). Thus, the TiO_2 nanophotocatalyst, in accordance with this process, can play a vital role in eliminating marine oil or chemical pollutants (Wold, 1993).

Research on using titanium dioxide nanophotocatalysts is common; however, there is a lack of studies on the application of its properties in eliminating oil and chemical pollution.

3. Experimental method

First, the samples selected were 100% standard benzene. Fig. 1 shows a simplified scheme of the calibration system. In the calibration procedure, different concentrations of benzene (0.01%, 0.02%, 0.03%, 0.04%, 0.05%, and 0.1%) were chosen and enclosed in beakers without a photocatalyst and ultraviolet light exposure to check any leakage. The enclosed samples were left for 4–8 h and then drawn out to the Double-Shot Py–GC system to recheck their concentrations.

The linear distribution graph obtained with the resulting data is shown in Fig. 2. Reduction in concentrations would have yielded a random distribution rather than linear. It is thus evident that the concentrations of the enclosed samples were constant. There were no losses or difficulties in the testing procedure. Hence, the results of the study are reliable. The sample analysis system is shown in Fig. 3.

Moreover, benzene (0.01%; 0.02%; 0.03%; 0.04%; 0.05%, and 0.1%) was enclosed in beakers again with 7 nm TiO_2 photocatalyst solution and bathed in ultraviolet light for 4–8 h. Fig. 3 shows the components of the decomposition system. These beakers form a closed system

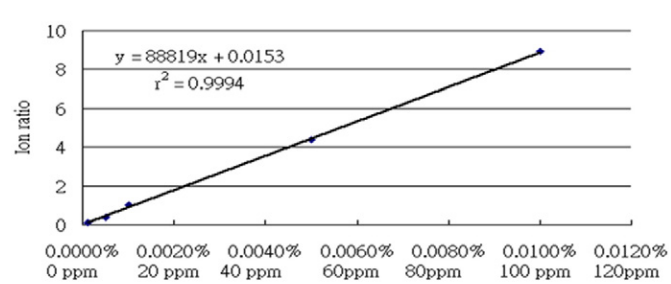

Fig. 2. Results of test for simplified scheme. Benzene concentrations analyzed from Py-GC system appear as a linear distribution.
Source: Authors' own work.