Photo catalytic degradation of spill oils on TiO_2 nanoparticles in the strait of Singapore

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List of Symbols

XRD	X-ray diffractometer
TEM	transmission electron microscope
λ	wavelength
R^2	coefficient of determination

Abstract

The TiO_2 nanoparticles with anatase form was prepared and analysed by X-ray diffractometer (XRD) and transmission electron microscope (TEM). In this study, TiO_2 was used with and without sunlight for the degradation toluene. About 37.8% of toluene (representing aromatics in the oil spills) in sea water (strait of Singapore) can be photocatalytically degraded under sunlight after 120 min. On an average, , the effectiveness of TiO_2 for photocatalytic degradation of toluene in the oil spill sea water is around 0.38 mg toluene/g TiO_2 h under sun light radiation. It is expected that oil spills in the harbors or seashores can be adsorbed and photocatalytically degraded with the TiO_2 nanoparticles.

Keywords: Oil spill, TiO_2 nanoparticle, toluene, photo catalyst, degradation.

1. Introduction

The heterogeneous photo-catalysis has been the subject of a vast amount of studies related to environmental abatement in both liquid and gas phase environments[2,7,8,12,14]. Photocatalytic decomposition of water contaminants on semiconductor catalysts, such as TiO_2, is a potential technique for improving indoor air quality[4]. Recently, a large quantity of work has been devoted to this field[3], because of its low-cost production, high specific surface area, and many applications in photo catalytic process. Among different semiconductors nanorod with wide band gaps and titanate or titanium oxide have been prepared over the past decades[15].

The primary oil pollutant in ocean may be caused by leaking of oil from the shipwreck, prospecting and excavating of oil from the sea, subsidence of oil gas in the atmosphere, shipping maintenance industry and offshore industry or harbour contamination[1]. In addition to the release of the toxic substances from oil spills , the oil slick may cover the sea surface to reduce the photosynthesis of alga and dissolve oxygen therein[5]. The negative impacts of oil spill to the ecosystem of ocean or environment of sea surface may be very serious and unexpected[13].

The fate and behaviour of spilled oil in the environment depends on a number of physicochemical and biological factors including evaporation, dissolution, microbial degradation, photo oxidation, interaction between oil and sediments[13]. Many previous studies revealed toluene as one of the most hazardous compound present in the oil[5]. In this study, TiO_2 was used for the degradation of toluene in oil under two conditions: with and without sunlight. The Singapore Strait is 105-kilometer long, 16-kilometer wide strait between the Strait of Malacca in the west and south China Sea in the east. The Malaysia-Singapore border lies along the length of the straits and one oil spill took place in 2010, so for the current research seawater was selected from this area.

2.0 Materials and Methods

2.1 Characterization of Titanium Oxide

Titanium Oxide was characterized for its shape, size and distribution. The phase recognition was done using X-ray diffractometer (XRD, Bruker D-8 Advance) using the Cu Kα radiation of wavelength $\lambda = 1.5406A^{\circ}$. Fine powder of titanium nanoparticles was applied for sample preparation, at first the sample was put in a sample holder and then the powder was pushed into the trough with a glass side to get an even dispensation of the powder.

The transmission electron microscopy (TEM) was performed to get high resolution images of the specimen. During the sample preparation, the samples were first diluted and then a droplet of the liquid sample was directly placed on a copper microscope grid covered with a carbon film. The size, shape, distribution and poly dispersity of the maghemite nano particles were verified using JEOL-JSM 639OL.

2.2 Photo catalyst Experimentation

2.2.1 Solution of seawater and toluene preparation

The solution preparation was carried out using sea water and then, toluene that is considered to be one of the most toxic and hazardous material in the oil was added to seawater samples with various ratios of (5, 10 and 15%V/V) in the laboratory.

2.2 Photo catalytic Activity

All the reactions were performed under sunlight irradiation.1g of TiO_2 was placed in 100 ml of seawater which includes oil in a 250 ml conical flask. 5 ml of sample was withdrawn at every 20 minutes up to l20 minutes and were analysed for oil concentration. The prepared samples prepared were then tested for oil concentration using model of Jenway 6300 spectrophotometer. Toluene wavelength for spectrophotometer is 365nm from before studies[5]. Furthermore, all the reactions were carried out without sunlight for comparing degradation result of toluene. The photo catalyst set up is shown in Fig. 1.

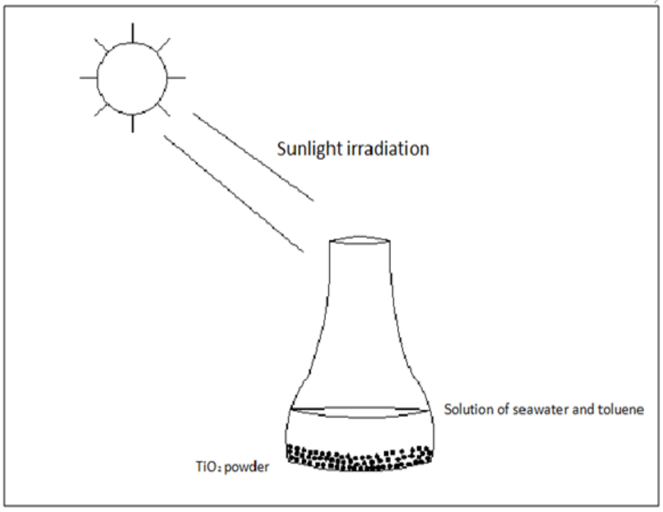

Fig. 1. Schematic diagram of photo catalytic activity under sunlight irradiation

3.0 Result and discussion

3.1XRD and TEM analysis

The XRD patterns of the powders obtained from the hydrothermal treatment are shown in Fig. 2. The peaks of the powdered material are identified to originate from (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 1 3), (1 1 6), (2 1 5) and (3 0 3) reflections. All the reflection of peaks can be readily indexed to anatase TiO_2 with lattice constants of a = 3.784 ˚A and c = 9.512 ˚A (JCPDS: no. 84-1286). No characteristic peak was associated with other crystalline forms as detected in the XRD pattern.

The low and high magnification FESEM images of the prepared powder sample are shown in Fig. 3(a, b). The nanoparticles are uniformly distributed throughout the sample and the sizes of the particles are relatively small. To find the average size HRTEM study was performed. The low and high magnification HRTEM images of the sample are shown in Fig. 3 (c,d) respectively, which shows the uniform formation of TiO_2 nanoparticles. The average particle size was ˷ 12 nm as seen from Fig. 3(d). The minimum and maximum particle sizes are lying closer to the average particle size. The inset of Fig. 3(d) shows the lattice image of TiO_2 nanoparticles with d value (3.52A˚) corresponding to (1 0 1) planes.

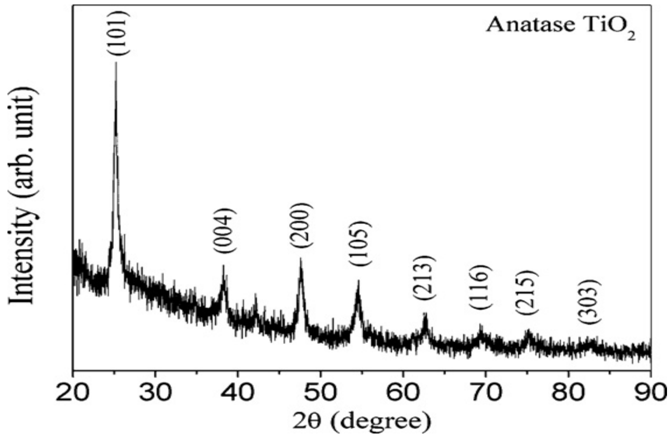

Fig. 2. XRD patterns of the prepared TiO_2 nanoparticles

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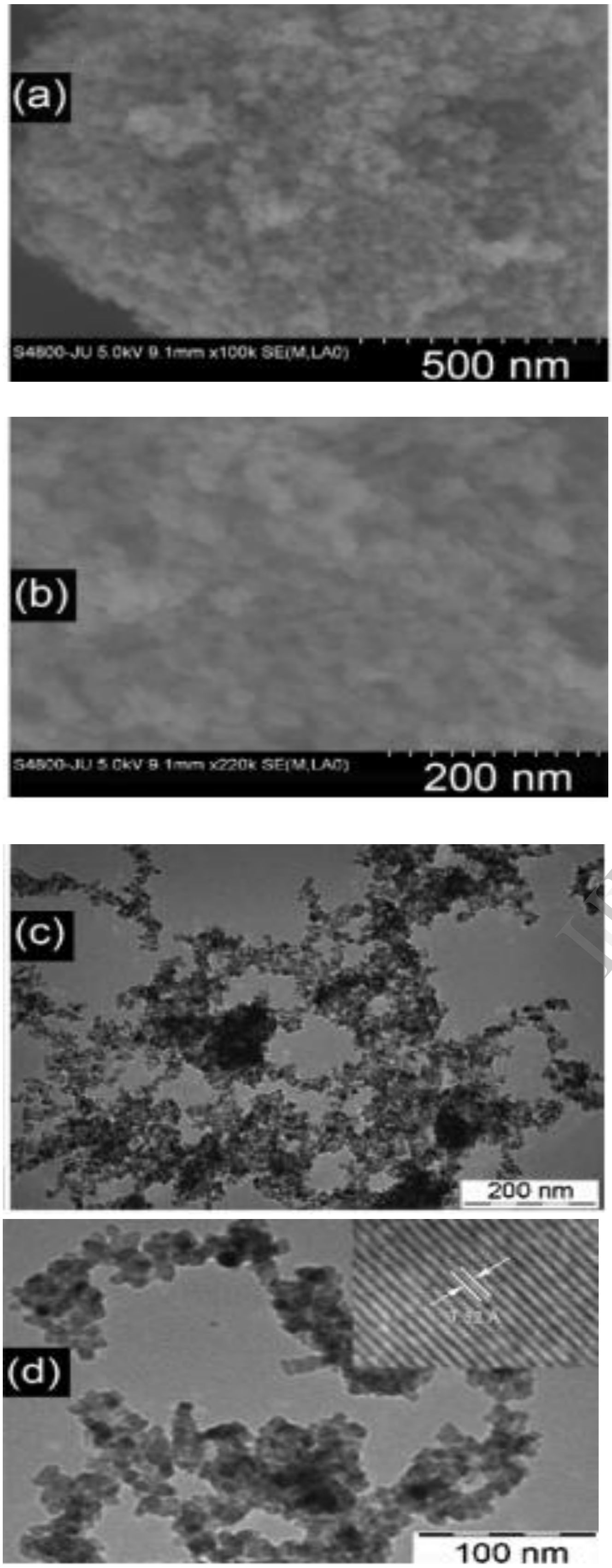

Fig. 3. The different magnification of TiO_2 nanoparticles (a), (b) FESEM images (c), (d) TEM images

3.2 Determining the concentration of characterized Substance

The standard concentration curve of solution was constructed by measuring the absorbance of several different known concentrations of the solution and graphing the results by plotting absorbance on the Y-axis and concentration on the X-axis. The spectrophotometer can be used to measure the absolute or relative concentration of a characterized substance in solution[9,11]. To determination of the absolute concentration of a pure substance was carried out, by constructing a standard concentration curve from known concentrations and then taking the absorbance reading of the unknown concentration. The unknown concentration was further determined from the standard curve by drawing a horizontal line on the graph parallel to the X-axis and through the point on the Y-axis which corresponds to the absorbance. This line will intersect the standard curve; at this intersection, a vertical line was dropped to the X-axis and the concentration is read from the X-axis as shown in (Table 1 and Fig. 4).

Table 1. Amount of absorbance for toluene based on 365nm wavelength

Toluene concentration (%)	Absorbance from spectrophotometer (nm)
0	0
5	0.635
10	1.21
15	1.48
20	1.78

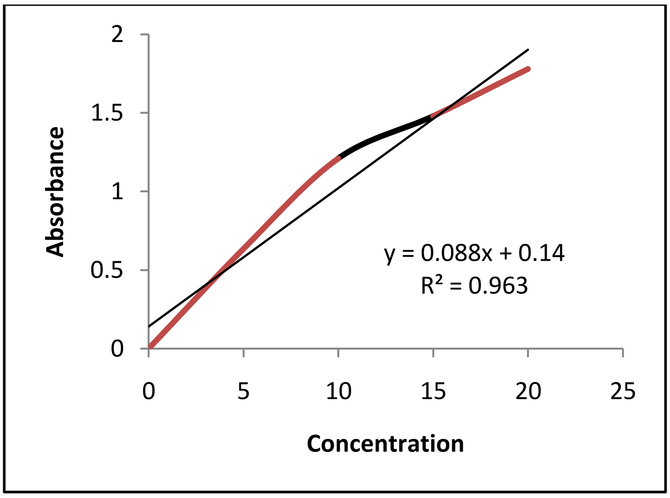

Fig. 4. Concentration absorbance chart of toluene

4.2 Photo catalytic activity with sunlight

The photo reduction of toluene in the absence and presence of TiO_2 is shown in Table 2. It is observed that the concentration of toluene is constant and unchanged under sunlight irradiation in the absence of TiO_2. However in the presence TiO_2 nanoparticles, toluene was found be degraded after 20 min of exposure to sunlight irradiation. The addition of titanium oxide nanoparticles has enhanced degradation of toluene within 20 minutes, and 37. 8% of the toluene was degraded. If the system was not exposed to sunlight irradiation, the toluene reduction was only about 26.6% (Fig. 5). The results illustrated that illumination energy is significant in determining the toluene degradation [6].

Table 2. The results of toluene degradation with and without sunlight irradiation

Type of light	Toluene (%)	Time (min)	Concentration of toluene (mg/L)	Degradation of toluene (%)
TiO_2 with sun light	5	0	5	0
		20	3.89	22.1
		40	3.74	25.2
		60	3.56	28.7
		80	3.44	31.2
		100	3.27	34.6
		120	3.11	37.8
	10	0	10	0
		20	8.19	18.1
		40	7.68	23.2
		60	7.36	26.4
		80	7.02	29.8
		100	6.84	31.6
		120	6.66	33.4
	15	0	15	0
		20	12.5	16.3
		40	12.0	19.9
		60	11.5	23
		80	11.1	25.9
		100	10.8	27.7
		120	10.6	29.1
TiO_2 without sun light	5	0	5	0
		20	4.24	15.1
		40	4.05	19
		60	3.91	21.7
		80	3.79	24.1
		100	3.72	25.5
		120	3.67	26.6
	10	0	10	0
		20	8.78	12.2
		40	8.51	14.9
		60	8.32	16.8
		80	8.07	19.3
		100	7.95	20.5
		120	7.71	22.9
	15	0	15	0
		20	13.5	9.9
		40	13.1	12.1
		60	12.9	13.5
		80	12.6	15.8
		100	12.4	17.1
		120	12.2	18.3

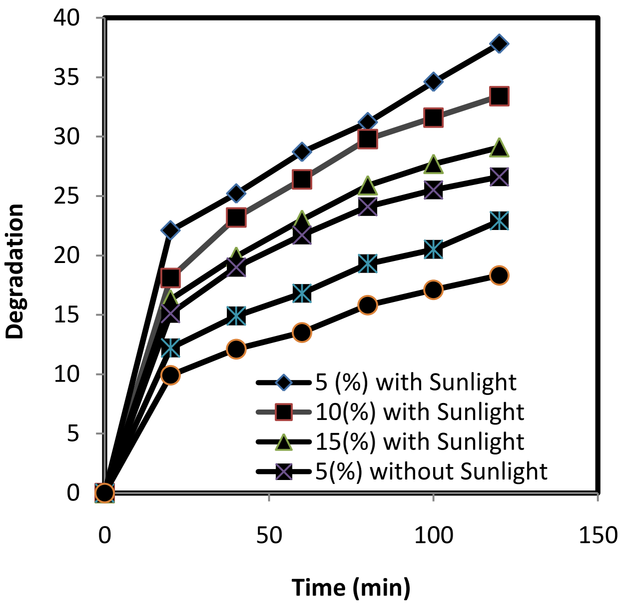

Fig. 5. The degradation for TiO_2 at various time intervals

4. Conclusion

The overall findings of this study are very attractive as titanium dioxide exhibits excellent photo catalytic activity. From the experiments performed it clearly shows that TiO_2 prepared are far more superior in terms of performance and robustness. A series of batch experiments were performed in two conditions; titanium dioxide with and without sunlight. The light energy seems to be vital in oil degradation, as it has significant inference on the photo catalytic activity. As it is visible, with the increasing amount of toluene in solution the effects of photo catalytic activity for degradation also decreased. The overall finding shows that the effect of titanium dioxide on degradation line slopes of toluene. The increment of toluene from 5 to 10 and 10 to 15 percent degradation had declined from 22.1 to 18.1 and 18.1 to 16.3 in 20 minutes of sunlight exposure time, also without sunlight exposure is from 15.1 to 12.2 and from 12.2 to 9.9 respectively.

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