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Photocatalytic degradation of spilled oil in sea water using maghemite nanoparticles

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ABSTRACT

Maghemite nanoparticles (γ-Fe_2O_3) were successfully synthesized by co-precipitation method as to remove toluene from sea water. The obtained sample was characterized with X-ray diffraction and transmission electron microscopy which showed that the size of particles was in the average of 9 nm. Further, Fourier transform infrared spectroscopy was performed to ensure successful coating process. The influence of other physico–chemical parameters such sunlight, initial toluene concentrations (5, 10, and 15% V/V), and equilibrium contact time (120 min) were also studied. The results showed that 90% of toluene could be removed within a period of 120 min and the toluene solution with initial concentration of 5 mg/L has shown to have the best removal efficiency.

Keywords: Spilled oil; γ-Fe_2O_3; Toluene; Photocatalyst; Degradation; Nanoparticles

1. Introduction

Maghemite nanoscale particles have already been known for over 50 years; however, their potential applications in science are now a hot topic in this domain of research. The unique blending of high magnetization and paramagnetic behaviors allow these materials to be used for a very wide range of applications [1]. Iron oxide nanoparticle belongs to the most widely used materials in this field. It has lower saturation magnetization, maghemite properties, and its specific damage power is lower than that of Fe and Co nanoparticles. Iron oxide has just started to gain attention for environmental purposes [2]. Also, iron oxides have some advantages over Fe and Co nanoparticles, such as having better oxidative stability and nontoxicity [3,4]. Among the small molecules available, citric acid ($C_6H_8O_7$) (i.e. a biocompatible short-chained tricarboxylic acid) has been widely applied in the synthesis of aqueous stable iron oxide nanoparticles in environmental applications [5].

In recent years, increasing concern about the effect of toxic metals in the environment has resulted in implementing strict environmental regulations [6]. In this framework, the biosorption process, which uses cheap and nonpollutant materials, may be an alternative technology in the wastewater treatment [7]. The search for new biosorbents is now receiving special

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attention by many researchers. The main objective is to obtain higher adsorption capacities within a shorter period of time. Many materials of natural origin have been studied as adsorbents to remove various heavy metals from wastewater [8].

The primary oil pollutant of the ocean may be caused by leaking of oil from the shipwreck, prospecting and excavating of oil on the sea, subsidence of oil gas in the atmosphere, shipping maintenance industry, and offshore industry, or harbor contamination. In addition to the release of the toxic substances from spilled oil, the oil slick may cover the sea surface to reduce the photosynthesis of alga and dissolve oxygen therein. The negative impacts of oil spillage to the ocean ecosystem and environment can be tremendous and unimaginable [9].

To determine the efficiency of photocatalytic degradation of hazardous compounds (such as aromatics) in the spilled oil, the present study, and experiments were performed using toluene. In the present work, γ-Fe_2O_3 nanoparticles have been synthesized by co-precipitation method and also the γ-Fe_2O_3 photocatalysts have been modified by coating with trisodium citrate to enhance their efficiency under visible light radiation.

Variety of inorganic ions exists in sea water like a Cl^- ion (major anion). Investigation of the effects of dissolved inorganic salts in sea water is very important to use photocatalytic reaction in and/or on sea water. The special effects of dissolved inorganic salts in sea water on photocatalytic reaction have not been investigated in this study, but major inorganic materials in sea water such as H_2O_2 on photocatalytic degradation has been studied before [10–12].

2. Materials and methods

2.1. Materials

Iron (II) chloride ($FeCl_2$, 98%) and Iron (III) chloride solution ($FeCl_3$, 45%) were purchased from Sigma-Aldrich and Riedel-de Haen company. Hydrochloric acid (HCl, 37%), nitric acid (HNO_3, 65%, v/v), acetone, potassium dichromate ($K_2Cr_2O_7$, 99.9%), and 1,5-diphenylcarbazide (DPC, 98%) were purchased from QReC and ammonia solution (NH_3, 25%, w/v) was provided by Merck Company. Sodium alginate was obtained from Fluka. All the above materials were used in their current form without further purification and distilled–deionized water was used throughout the experiment.

2.2. Methods

2.2.1. Preparation of maghemite nanoparticles

The employed maghemite material used was a ferrofluid composed of maghemite nanoparticles (γ-Fe_2O_3) dispersed in an aqueous solution. They were synthesized according to the process described by Massart [13] and improved according to the method of [14]. This method allows controlling the size and superficial charge of the nanoparticles. The particles were synthesized by alkaline co-precipitation of stoichiometric mixture of ferrous and ferric chloride in an ammonium hydroxide solution. The magnetite (Fe_3O_4) precipitate obtained was acidified by nitric acid (to provoke a reversion of the surface charges) and oxidized into maghemite (γ-Fe_2O_3) in a solution of ferric nitrate at 100°C, which allowed the nanoparticles to stabilize [7]. At this stage, nanoparticles of γ-Fe_2O_3 are polydispersed in size of $5\,nm < d < 20\,nm$ and exist in two-phase solution. The supernatant composed of smaller size particles which were removed by suction. The fraction with larger particles was carefully washed several times, in order to decrease the ionic strength of the acidic anionic ferrofluid (pH 2) [15].

2.2.2. Coating γ-Fe_2O_3 nanoparticles with trisodium citrate

To obtain stable maghemite dispersion compatibility, nanoparticles were coated with citrate anions. 50 ml of maghemite nanoparticles were mixed with 10 g of trisodium citrate which was dissolved in 100 ml deionized water. This solution was stirred for 30 min in a maghemite stirrer and thus, two layers were formed. Further, 50 ml acetone was added to the residue and was put on the maghemite bar. After precipitation with acetone, coated particles were dispersed in water to obtain a stable ferrofluid with pH of 7.

2.2.3. Characterization of the maghemite nanoparticles

XRD Siemens D5000 was used in this study to recognize the elements present in the maghemite nanoparticles. Fine powder of maghemite nanoparticles was used in sample preparation and placed in a sample holder. Then, the catalyst powder was pressed into a trough with a glass side in order to get an even distribution.

Transmission electron microscopy (TEM, JEOL-JSM-6360) was applied to determine the maghemite nanoparticles' characteristics such as morphology and particle size. The measurements were performed for both the coated nanoparticles and uncoated nanoparticles.

Fourier transform infrared spectroscopy (FTIR) spectrum which was used in this experiment can function as a preliminary quantitative analysis of major functional groups. For the maghemite nanoparticles (γ-Fe_2O_3), the FTIR spectrum (400–4,000 cm^{-1}) and dehydrates of citrate ferrofluid were crushed and mixed with KBr to reveal the band from the iron citrate spectrum [16].

2.2.4. Preparation of toluene and sea water solution

The sea water samples were taken for preparation of solution because the experiment was mainly focused on the degradation of oil in and around Malaysia, especially in the south of Malaysia in the Strait of Singapore. Toluene, that is one of the most toxic and hazardous material in the oil was added to sea water samples in sunlight and without sunlight for various ratios of toluene (5, 10, and 15% V/V) in laboratory.

2.2.5. Photocatalyst experiment

All the reactions were performed under sunlight irradiation, 1 g of maghemite nanoparticles coated with trisodium citrate was placed in 100 ml of solution (mixing of sea water and toluene) in a 250 ml corneal flask. 5 ml of samples were taken every 20 min until l20 min and were analyzed to determine the toluene concentration using Jenway 6300 spectrophotometer. The spectrophotometer wavelength for toluene was set at 365 nm as suggested by Hsu et al. [9].

3. Results and discussion

3.1. Characterization of nanosized γ-Fe_2O_3

The TEM image of the particles in Fig. 1 shows that the maghemite nanoparticles synthesized in this study were multi-dispersed with an average diameter of 9 nm. The electron diffraction pattern indicated that the maghemite nanoparticles were highly crystalline in nature. The identity and purity of the maghemite nanoparticles were also verified by X-ray diffraction (XRD) (Fig. 2). The obtained XRD peaks of the nanocrystallite matched well with the standard γ-Fe_2O_3 and it is known that maghemite particles of less than 30 nm will exhibit paramagnetism [17].

The FTIR spectrum was run through wavelengths of 4,000–400 cm^{-1} (Fig. 3). The 1,700 cm^{-1} peak is assigned to C=O vibration (–COOH group from citric acid shifts to 1,600 cm^{-1} for maghemite–citric acids) [7], which reveals the binding of the citric acid to the maghemite surface through the chemical bonding of carboxylate chemisorption.

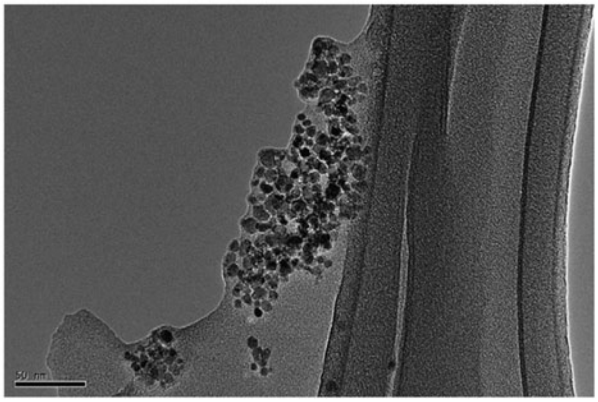

Fig. 1. TEM image of maghemite nanoparticles.

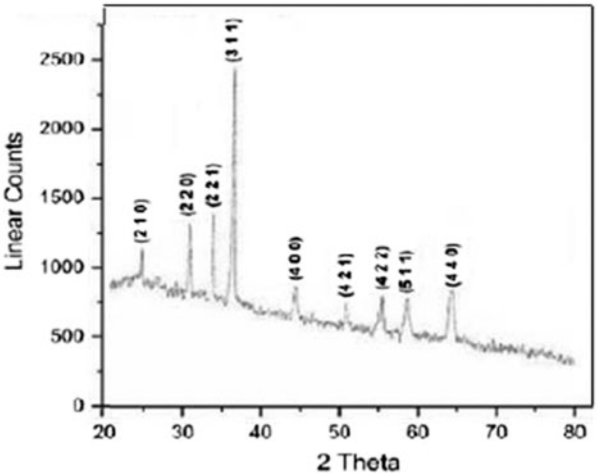

Fig. 2. XRD patterns of maghemite nanoparticles.

3.2. Determining the concentration of characterized substance

The spectrophotometer can be used to measure the absolute or relative concentration of a characterized substance in a solution. To determine the absolute concentration of a pure substance, it is necessary to first construct a standard concentration curve (curved line in Fig. 4) from known concentrations and then take the absorbance reading of the unknown

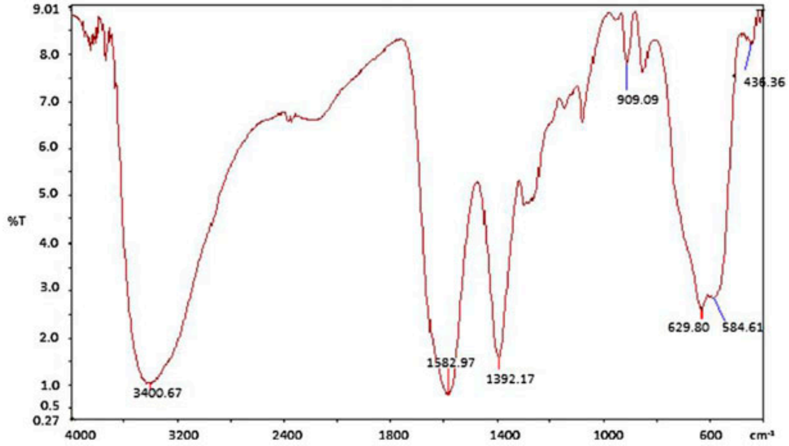

Fig. 3. FTIR analysis of maghemite nanoparticles.

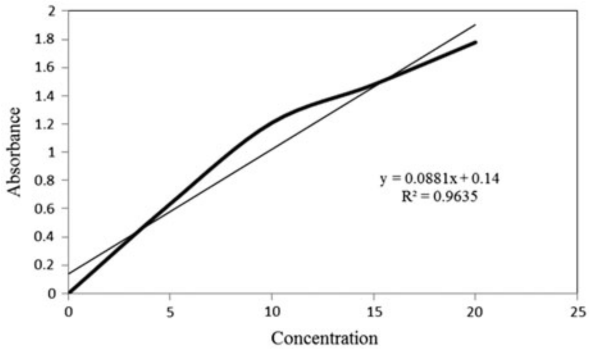

Fig. 4. Concentration-absorbance chart of toluene (Standard concentration curve).

concentration. The unknown concentration can be 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.

The maximum absorption should be used and absorbance should be plotted instead of percent transmittance, because absorbance is directly proportional to the concentration and not to the transmittance (Fig. 4). As it can be perceived in the aforementioned experiment, the amount of absorbance demonstrates an ascending trend with the enhancement of toluene percentage. Through the experiment, with 0% of toluene, no absorbance was recorded. By deploying 5% toluene, the portion of absorbance reached 0.635. Meanwhile, 1.21 and 1.48 were the established absorbance for 10 and 15% of toluene, respectively. Eventually, the absorbance factor hit the peak of 1.78 after implementing 20% toluene (Fig. 4).

3.3. *Photocatalytic activity under sunlight*

To determine the efficiency for photocatalytic degradation of hazardous compounds (such as aromatics) in the spilled oil, toluene which is hazardous was used to investigate the photocatalytic behavior of the maghemite nanoparticles. Photocatalytic degradation of toluene at various concentrations (5, 10, and 15% V/V) in sea water with maghemite nanoparticles is shown in Fig. 5.

Table 1 illustrates the photoreduction of toluene by maghemite nanoparticles in the presence and absence of sunlight. In the presence of maghemite nanoparticles, toluene can be degraded after 120 min of exposure to sunlight irradiation resulting in 90% reduction. If the system was not exposed to sunlight irradiation, the toluene reduction was found to be only 50% (Fig. 5). The results suggest that illumination energy is significant in toluene degradation [15]. With the increments of toluene from 5 to 10% and 10 to 15%,

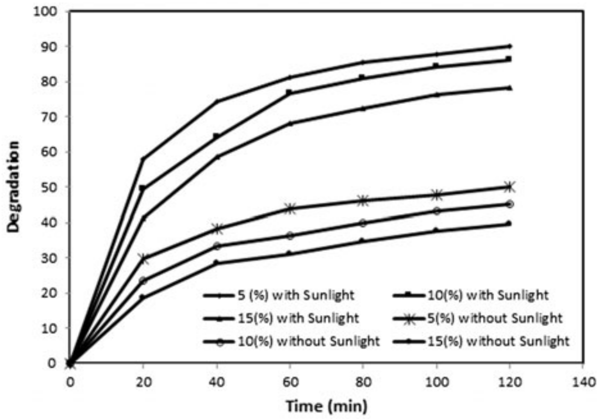

Fig. 5. Photo catalytic degradation of toluene for different toluene concentrations and exposure to sunlight.

Table 1
The result of photocatalytic activity

Toluene (%)		5							10							15						
Time (min)		0	20	40	60	80	100	120	0	20	40	60	80	100	120	0	20	40	60	80	100	120
Degradation (%)	Sunlight	0	58	74	81	85	88	90	0	49	64	77	81	84	86	0	41	59	68	72	76	78
	Without Sunlight	0	30	38	44	46	48	50	0	23	33	36	40	43	45	0	19	28	31	35	38	40

degradation had declined from 90 to 86% and 86 to 78% in 120 min of sunlight exposure time. Also, without sunlight exposure, it declined from 50 to 45% and from 45 to 40%, respectively. Also, in this study the effect of synthetic solution by using deionized water and toluene as benchmark on degradation of toluene was investigated. The results revealed that for the best condition (5% with sunlight in 120 min) synthetic solution showed more degradation (96%), when compared with the original solution (90%). It can be explained by this fact that the presence of inorganic materials in sea water can prevent the complete degradation of toluene [10–12].

4. Conclusion

The procedure for fabricating maghemite nanoparticles with co-precipitation method with particle size of 9 nm was illustrated. Toluene, a hazardous pollutant in sea water, was degraded within 120 min under a sunlight irradiation around 90% for 5% of toluene. The results showed that without sunlight, photocatalytic activity of maghemite nanoparticles reaches no more than 50% degradation for the same percent of toluene. Also, it suggests that hexadecane which is another hazardous compound present in sea water can be degraded with this method using maghemite nanoparticles.

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