Application of Fe$_2$O$_3$/ZrO$_2$ loaded polyhedron ball on photocatalytic degradation of diesel pollutants in seawater under visible light
Liping Wang, Xiaocai Yu, Jiaqi Liao, Bining Xue, Siyao Tian and Wanting Zhu

ABSTRACT
Fe$_2$O$_3$/ZrO$_2$ nanocomposite photocatalyst was successfully prepared by coprecipitation method for the degradation of diesel pollutants in seawater under visible light. The effects of doping ratio, calcination temperature, photocatalyst dosage, initial diesel concentration, H$_2$O$_2$ concentration, and reaction time on the photocatalytic removal efficiency were investigated. Moreover, the optimal conditions for Fe$_2$O$_3$/ZrO$_2$ nanocomposite photocatalyst to degrade marine diesel pollution were determined. The removal efficiency of diesel by nanocomposite photocatalyst could reach 97.03%. A photocatalyst-loaded polypropylene polyhedral ball was prepared, and the removal efficiency of diesel by photocatalyst-loaded polypropylene polyhedral ball decreased from 99.35 to 68.84% after four recycling cycles.

Key words | diesel pollutants, Fe$_2$O$_3$/ZrO$_2$ nanocomposite photocatalyst, photocatalytic degradation, polyhedron ball, visible light

HIGHLIGHTS
• Fe$_2$O$_3$/ZrO$_2$ nanocomposite photocatalyst was successfully prepared by coprecipitation method for the degradation of diesel pollutants in seawater under visible light.
• Photocatalyst-loaded polypropylene polyhedral ball was prepared, and the removal efficiency of the photocatalyst-loaded polypropylene polyhedral ball on diesel decreased only slightly for the first three recycles and then by nearly a third after the fourth recycle.

GRAPHICAL ABSTRACT
INTRODUCTION

In recent decades, with the rapid development of industry, the exploitation and utilization of oil energy continues to increase. Especially, diesel energy is indispensable in various fields for its high-power export, reliability and durability (Kumar & Saravanan 2016). However, unfortunately, the huge demand for diesel causes massive amounts of diesel pollutants to be released into the marine environment, which has a strong impact on the marine ecosystem (Qiu et al. 2019). Nowadays, a variety of treatments are taken for removal or degradation of diesel pollutants, such as the use of booms, skimmers, dispersants, bacteria or fungi (Si-Zhong et al. 2009). All these common physical, chemical and biological ways show limitations in diesel pollutant treatment, like high cost, long processing period, low reaction rate and secondary pollution (Hsu et al. 2008; Zhu et al. 2013). Thus, a rapid, green and economical method is required. The photocatalytic method has gained wide interest for its excellent efficiency, environment-friendliness and easy operation (Peng et al. 2015; Wang et al. 2016).

Due to the advantage of the light-stimulated degradation, semiconductor photocatalytic materials have gained great attention recently. Among diverse metal oxide semiconductors, ZrO2 is a p-type semiconductor, which can generate oxygen vacancies and exhibit corrosion-resistant properties (Zhang et al. 2013). Similar to the traditional photocatalytic material TiO2, ZrO2 with acid-base, redox and stable photochemistry properties is considered as a promising photocatalyst (Neppolian et al. 2007; Zheng et al. 2009). However, the band gap energy of ZrO2 is around 3.64 eV and wide band gap energy causes short wavelength photoluminescence, which limits the application of the photocatalyst in visible light (Fakhri et al. 2016). Therefore, how to reduce the band gap energy of ZrO2 is necessary. Fe2O3 has relatively low band gap energy of 2.2 eV, which causes the absorption spectrum of Fe2O3 to approximate to that of visible light and makes better use of solar energy (Belaidi et al. 2019). Otherwise, electron-hole pairs of Fe2O3 demonstrate short lifetime and are prone to be corroded, resulting in low catalytic activity. Considering the above factors, a compound of ZrO2 and Fe2O3 is a realizable way to combine the advantage of ZrO2 and Fe2O3, which can lead to an extension of the light absorption range of the photocatalyst and improve the efficiency of the photocatalyst.

Numerous methods are used to prepare nano-photocatalysts, including coprecipitation (Ji et al. 2017), sol-gel (Escobar et al. 2000), and impregnation (Li et al. 2006) methods. The coprecipitation method is low-cost, simple and energy-efficient among them. Importantly, the obtained colloidal precipitate could be dispersed by ultrasound, surfactant or supercritical fluid to prevent the formation of agglomerates and then control the particle size of a nanometre photocatalyst.

Especially, improving the utilization efficiency of photocatalysts is a research hotspot. Various materials (porous ceramics, molecular sieve, and crystal ball) are used for loading photocatalyst; however, they are expensive and non-recyclable. Thus, a polypropylene polyhedral ball as carrier is considered in our work. In this work, Fe2O3/ZrO2 nanocomposite photocatalyst was synthesized by coprecipitation method, the sample was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectrometry (EDS) and UV-visible diffuse reflectance spectroscopy (UV-Vis DRS). Effects of different factors on photocatalytic degradation efficiency were investigated, and the optimum technological conditions for degradation of marine diesel pollution by Fe2O3/ZrO2 nanocomposite photocatalyst were determined by orthogonal test. Removal efficiency of Fe2O3/ZrO2 photocatalyst-loaded polypropylene polyhedral ball towards diesel was investigated.

MATERIALS AND METHODS

Materials

Ferric sulfate (FeSO4) was obtained from Tianjin Quartz Clock Factory Bazhou Chemical plant. Zirconium oxychloride (ZrOCl2·8H2O) was purchased from Aladdin. Hexane (C6H14), hydrogen peroxide (H2O2), hexadecyl trimethyl ammonium bromide (HTAB), sodium hydroxide (NaOH) and ethanol (C2H5O) were supplied by Tianjin Kemiou Chemical Reagent Co., Ltd.

Preparation of photocatalysts

A certain amount of ZrOCl2·8H2O and FeSO4 were weighed (the molar ratio of Fe and Zr was 1:10, 2:10, 3:10, 4:10 and 5:10) and dissolved in 150 mL deionized water; then an appropriate amount of HTAB was added into the mixture under stirring. NaOH solution was added dropwise by an alkali burette into the mixture to produce precipitates under ultrasonic treatment for 30 min; then the precipitates were washed three times with anhydrous ethanol and deionized water, respectively. The precipitates were dried at 105 °C for 12 h in an oven and ground into powder, and finally calcined in a muffle at a certain temperature for 2 h.
Characterization

The phase composition analysis of Fe₂O₃/ZrO₂ nanocomposite photocatalyst was measured using an X-ray diffractometer (D/MAX-2500) at 2θ ranges from 0° to 80°. The morphology and microstructure were obtained by using a scanning electron microscope (Hitachi SU8010) with a working voltage of 5 kV. The elemental analysis was recorded by an energy dispersive spectrometer (IXRF Model 550i) with accelerating voltage at 15 kV. The UV-visible diffuse reflectance spectra were obtained using a solid UV-vis spectrum analyzer (Lambda 35).

The band gap energy \(E_g\) of the sample was calculated according to the following:

\[ E_g = \frac{h \times c}{\lambda} \]

where \(c\) is the velocity of light of \(3 \times 10^8\) m/s, \(h\) is Planck’s constant of \(6.63 \times 10^{-34}\) Js, and \(\lambda\) (nm) is the wavelength.

Photocatalytic experiments

Seawater was taken from Heishijiao, Dalian, China; then suspended matter was removed by pumping the seawater. A certain amount of diesel fuel was added into the seawater to get 0.2 g/L simulated diesel-polluted seawater. The photocatalytic degradation was carried out by dispersing Fe₂O₃/ZrO₂ nanocomposite photocatalysts in diesel pollution seawater at appropriate conditions. The concentration of diesel was determined by spectrophotometry with pure hexane as reference at 225 nm. The photocatalytic removal efficiency was determined as follows:

\[ \text{Removal efficiency} = \frac{C_0 - C_t}{C_0} \times 100\% \]

where \(C_0\) (g/L) represents the initial concentration of diesel fuel; \(C_t\) (g/L) represents the concentration of residual diesel in simulated seawater.

Effect of doping ratio of photocatalyst on photocatalytic degradation

Different photocatalysts were obtained at different doping ratios (1:10, 2:10, 3:10, 4:10 and 5:10) and calcination temperature of 450 °C. Then 0.2 g/L photocatalyst and 6 mg/L H₂O₂ solution were added into simulated seawater (pH was 8.0, the concentration of diesel was 0.2 g/L), and the photocatalytic reaction was carried out for 2 h under visible light conditions with magnetic stirring.

Effect of calcination temperature of photocatalyst on photocatalytic degradation

The photocatalyst was obtained at doping ratio of 3:10 and different calcination temperatures (350, 400, 450, 500, 550 and 600 °C). Then 0.2 g/L photocatalyst and 6 mg/L H₂O₂ solution were added into the simulated seawater (pH was 8.0, the concentration of diesel was 0.2 g/L), and the photocatalytic reaction was carried out for 2 h under visible light conditions with magnetic stirring.

Effect of Fe₂O₃/ZrO₂ photocatalyst dosage on photocatalytic degradation

The photocatalyst was obtained at doping ratio of 3:10 and calcination temperature of 450 °C. Then 0.2 g/L photocatalyst and 6 mg/L H₂O₂ solution were added into simulated seawater (pH was 8.0, the concentration of diesel was 0.2 g/L), and the photocatalytic reaction was carried out for 2 h under visible light conditions with magnetic stirring.

Effect of initial diesel concentration on photocatalytic degradation

The photocatalyst was obtained at doping ratio of 3:10 and calcination temperature of 450 °C. Then 0.2 g/L photocatalyst and 6 mg/L H₂O₂ solution were added into simulated seawater (pH was 8.0, the concentration of diesel was 0.1, 0.3, 0.5, 0.7, 0.9 and 1.1 g/L), and the photocatalytic reaction was carried out for 2 h under visible light conditions with magnetic stirring.

Effect of H₂O₂ concentration on photocatalytic degradation

The photocatalyst was obtained at doping ratio of 3:10 and calcination temperature of 450 °C. Then 0.2 g/L photocatalyst and different concentrations of H₂O₂ solution (0, 2.0, 4.0, 6.0, 8.0, 10.0 and 12.0 mg/L) were added into simulated seawater (pH was 8.0, the concentration of diesel was 0.2 g/L), and the photocatalytic reaction was carried out for 2 h under visible light conditions with magnetic stirring.

Effect of reaction time on photocatalytic degradation

The photocatalyst was obtained at doping ratio of 3:10 and calcination temperature of 450 °C. Then 0.2 g/L photocatalyst and 6.0 mg/L H₂O₂ solution were added into simulated seawater (pH was 8.0, the concentration of diesel was 0.2 g/L), and the photocatalytic reaction was carried out for 2 h under visible light conditions with magnetic stirring.
seawater (pH was 8.0, the concentration of diesel was 0.2 g/L), and the photocatalytic reaction was carried out for 1, 2, 3, 4, 5 and 6 h under visible light conditions with magnetic stirring.

**Preparation of Fe$_2$O$_3$/ZrO$_2$ photocatalyst-loaded polypropylene polyhedral ball**

The titanate coupling agent was mixed with anhydrous ethanol (the weight ratio of titanate and anhydrous ethanol was 1.5:1); then a dry polypropylene multi-faceted ball (white) was placed in the mixture, which was then stirred for 30 min. A given amount of Fe$_2$O$_3$/ZrO$_2$ photocatalyst (doping ratio was 3:10, calcination temperature was 450 °C) was accurately weighed into a 100 mL beaker and an appropriate amount of pure water was added; then the mixture was subjected to ultrasound for 30 min to get a turbid solution of photocatalysts. Polypropylene polyhedron with coupling agent was placed into the turbid liquid under stirring, the stirring was maintained until the turbid solution became transparent, and then the ball was taken out and air-dried.

**Effect of photocatalyst-loaded polypropylene balls on degradation of marine diesel**

Photocatalysts were obtained at doping ratio of 3:10 and calcination temperature of 450 °C. Different dosage photocatalysts (0.15, 0.2, 0.25, 0.3, 0.55 and 0.4 g) were loaded on polypropylene balls and placed into 2 g/L simulated diesel seawater, then 6.0 mg/L H$_2$O$_2$ solution was added into simulated seawater, and the photocatalytic reaction was carried out for 2 h under visible light conditions with magnetic stirring.

**Effect of initial diesel concentration on degradation of marine diesel by photocatalyst-loaded balls**

Photocatalysts were obtained at doping ratio of 3:10 and calcination temperature of 450 °C. 0.3 g photocatalyst was loaded on polypropylene balls and placed into different simulated diesel seawater (1, 2, 3, 4, 5 and 6 g/L), then 6.0 mg/L H$_2$O$_2$ solution was added into simulated seawater, and the photocatalytic reaction was carried out for 2 h under visible light conditions with magnetic stirring.

**Recycle performance of Fe$_2$O$_3$/ZrO$_2$ photocatalyst-loaded polypropylene polyhedral ball**

In this work, the photocatalyst was obtained at doping ratio of 3:10 and 450 °C calcination temperature. Photocatalysts (0.3 g) were loaded on polypropylene balls and placed into 2 g/L simulated diesel seawater, then 6.0 mg/L H$_2$O$_2$ solution was added into simulated seawater, and the photocatalytic reaction was carried out for 2 h under visible light conditions with magnetic stirring. After the reaction, the ball was removed and air-dried for reuse in the next cycle of degradation experiment; this process was repeated for four times.

**RESULTS AND DISCUSSION**

**Characterization of Fe$_2$O$_3$/ZrO$_2$ nanocomposite photocatalyst**

The phase composition analysis and the conversion of Fe$_2$O$_3$/ZrO$_2$ sample were determined by XRD method. The XRD pattern of Fe$_2$O$_3$/ZrO$_2$ sample with doping ratio (molar ratio) of 3:10 is shown in Figure S1 (Supplementary Material). In Figure S1, the main characteristic diffraction peaks are located at 2θ of 28.2664°, 30.5247°, 31.5445°, 34.1971° and 50.2529°, corresponding to monoclinic and cubic phase ZrO$_2$ (JCPDS 37-1484 and JCPDS 49-1642). Consistently, the characteristic peaks appearing at 2θ of 24.1309°, 33.2417° and 35.3547° correspond to partial crystal plane stacking structure of Fe$_2$O$_3$ (JCPDS 89-0597). All the facts indicated the successful preparation of Fe$_2$O$_3$/ZrO$_2$ photocatalyst sample. Figure S1 also shows a sharp peak in the diffraction pattern, indicating high particle size of the Fe$_2$O$_3$/ZrO$_2$ nanocomposite photocatalyst.

The morphology and microstructure of Fe$_2$O$_3$/ZrO$_2$ nanocomposite photocatalyst are displayed in Figure 1, Fe$_2$O$_3$/ZrO$_2$ particles with doping ratio of 3:10 showed uniform spherical shape and smooth surface; in addition, the nanoparticles are arranged uniformly. Moreover, Fe$_2$O$_3$/ZrO$_2$ particles with doping ratio of 5:10 exhibited an agglomeration phenomenon of rod-shaped and spherical shape.

The ultraviolet-visible diffuse reflection spectrum of Fe$_2$O$_3$/ZrO$_2$ nanocomposite photocatalyst and ZrO$_2$ is shown in Figure S3. Compared with pure ZrO$_2$, the diffuse
reflection spectrum of Fe₂O₃/ZrO₂ exhibited a red shift and relatively wider light absorption in the visible light region of 400–760 nm, indicating that doping Fe₂O₃ into ZrO₂ broadened the optical response range of ZrO₂ effectively. Importantly, the band gap energy of Fe₂O₃/ZrO₂ was calculated to be 1.42 eV, which was significantly lower than that of ZrO₂ (3.64 eV).

Effect of doping ratio of photocatalyst on photocatalytic degradation

As shown in Figure 2(a), the photocatalytic degradation efficiency of diesel first increased and then decreased with the increase of doping ratio; when the doping ratio was 3:10, the efficiency reached the maximum of 88.11%. Moreover, compared with pure ZrO₂, Fe₂O₃-doped photocatalysts showed significant high removal efficiency, due to the photore response range of ZrO₂ being broadened by Fe₂O₃, and the degradation of diesel process could be implemented in visible light. Meanwhile, Fe₂O₃ is a photocatalyst with high performance that could participate in the degradation process of diesel. However, excessive Fe₂O₃ could physically cover the surface of ZrO₂ and caused agglomeration of the photocatalyst (Josephine & Sivasamy 2014). Therefore, when the doping ratio was more than 3:10, the removal efficiency of diesel decreased apparently.

Effect of calcination temperature of photocatalyst on photocatalytic degradation

As illustrated in Figure 2(b), when the calcination temperature was 450 °C, the removal efficiency of Fe₂O₃/ZrO₂ nanocomposite photocatalyst for diesel reached the maximum of 83.34%. When the temperature was lower than 400 °C, more monoclinic ZrO₂ was formed in Fe₂O₃/ZrO₂ crystal, causing relatively low photocatalytic activity. Additionally, as the temperature increased to 450 °C, tetragonal phase and monoclinic phase in the photocatalyst achieved the best mixed crystal effect, resulting in the increase of photocatalytic performance. However, Fe₂O₃ crystals showed excessive growth at high temperature, causing the destruction of ZrO₂ crystal structure and the reduction in quantity of photogenerated electron-hole pairs, hence lowering the removal efficiency of diesel oil.

Effect of Fe₂O₃/ZrO₂ photocatalyst dosage on photocatalytic degradation

It can be seen from Figure 2(c) that the removal efficiency of diesel was only 33.01% in the absence of photocatalyst; because the diesel was a light petroleum product, a small amount of volatilization of diesel existed under visible light. However, the addition of photocatalyst caused the removal efficiency to increase rapidly, indicating Fe₂O₃/ZrO₂ nanocomposite photocatalyst displayed effective degradation capability on diesel. As the amount of photocatalyst increased, the diesel removal efficiency increased rapidly and then decreased slowly. The diesel removal efficiency reached the maximum of 83.32% when the catalyst dosage was 0.2 g/L. This could be explained by the following reason. With the dosage of photocatalyst increasing, the number of electron-hole pairs increased, thereby improving the photocatalytic activity of the photocatalyst. Nevertheless, superabundant photocatalyst prevented light beams from entering the solution and caused light scattering; thus the removal efficiency was significantly reduced (Yu et al. 2018).

Effect of initial diesel concentration on photocatalytic degradation

Removal efficiency varied with the initial concentration of diesel as shown in Figure 2(d): with the increase of initial concentration of diesel, the removal efficiency of diesel first increased and then decreased. Generally, reaction rate was directly proportional to the concentration of the reactants, but when the concentration increased to more than a certain value, the diesel removal efficiency decreased instead. This was because diesel could adhere to the surface of photocatalyst and hinder the activity of the photocatalyst, which reduced the photogenerated electron pairs, thereby reducing the continuation of the photocatalytic reaction and removal efficiency.

Effect of H₂O₂ concentration on photocatalytic degradation

The removal efficiency changed with H₂O₂ concentration as shown in Figure 2(e): without the addition of H₂O₂, removal efficiency of Fe₂O₃/ZrO₂ nanocomposite photocatalyst for
diesel was poor and the removal efficiency was only 52.62%. Generally, in Figure 2(e), with the increase of H2O2 concentration of diesel, the removal efficiency of diesel first increased and then decreased. H2O2, as an oxidant, showed strong oxidizing property and could act as electron acceptor. Photogenerated electrons on the photocatalyst surface could be easily captured by H2O2, preventing recombination of the photogenerated electron-hole pair (e−/h+). However, excessive H2O2 inhibited the production of ·OH, which hindered the photocatalytic degradation process (Dionysiou et al. 2000).

Figure 2 | Effect of (a) doping ratio (T = 450 °C, Cphotocatalyst = 0.2 g/L, Chydrogen peroxide = 6 mg/L, pH = 8.0, Cdiesel = 0.2 g/L, t = 2 h), (b) calcination temperature (doping ratio = 3:10, Cphotocatalyst = 0.2 g/L, Chydrogen peroxide = 6 mg/L, pH = 8.0, Cdiesel = 0.2 g/L, t = 2 h), (c) Fe2O3/ZrO2 dosage (T = 450 °C, doping ratio = 3:10, Cphotocatalyst = 0.2 g/L, Chydrogen peroxide = 6 mg/L, pH = 8.0, Cdiesel = 0.2 g/L, t = 2 h), (d) initial diesel concentration (T = 450 °C, doping ratio = 3:10, Cphotocatalyst = 0.2 g/L, Chydrogen peroxide = 6 mg/L, pH = 8.0, t = 2 h), (e) H2O2 concentration (T = 450 °C, doping ratio = 3:10, Cphotocatalyst = 0.2 g/L, Chydrogen peroxide = 6 mg/L, pH = 8.0, Cdiesel = 0.2 g/L, t = 2 h) and (f) reaction time (T = 450 °C, doping ratio = 3:10, Cphotocatalyst = 0.2 g/L, Chydrogen peroxide = 6 mg/L, pH = 8.0, Cdiesel = 0.2 g/L) on removal efficiency. In the caption, T is calcination temperature, Cphotocatalyst is Fe2O3/ZrO2 dosage, Chydrogen peroxide is H2O2 concentration, Cdiesel is initial diesel concentration, t is reaction time.
Table 1 | Factors and levels selected for orthogonal experimental design

<table>
<thead>
<tr>
<th>Level</th>
<th>Doping ratio</th>
<th>Calcination temperature (°C)</th>
<th>Dosage of photocatalyst (g/L)</th>
<th>Initial concentration of diesel (g/L)</th>
<th>H₂O₂ concentration (mg/L)</th>
<th>Photocatalytic reaction time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:10</td>
<td>350</td>
<td>0.2</td>
<td>0.1</td>
<td>2.0</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>2:10</td>
<td>400</td>
<td>0.3</td>
<td>0.3</td>
<td>4.0</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>3:10</td>
<td>450</td>
<td>0.4</td>
<td>0.5</td>
<td>6.0</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>4:10</td>
<td>500</td>
<td>0.5</td>
<td>0.7</td>
<td>8.0</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>5:10</td>
<td>550</td>
<td>0.6</td>
<td>0.9</td>
<td>10.0</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 2 | Design matrix and experimental results for orthogonal array

<table>
<thead>
<tr>
<th>No.</th>
<th>Doping ratio</th>
<th>Calcination temperature (°C)</th>
<th>Dosage of photocatalyst (g/L)</th>
<th>Initial concentration of diesel (g/L)</th>
<th>H₂O₂ concentration (mg/L)</th>
<th>Photocatalytic reaction time (h)</th>
<th>Removal efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>72.71</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>76.48</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>72.06</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>54.73</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>69.29</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>83.15</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>1</td>
<td>54.09</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>1</td>
<td>2</td>
<td>41.64</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>4</td>
<td>5</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>85.25</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>5</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>78.47</td>
</tr>
<tr>
<td>11</td>
<td>3</td>
<td>1</td>
<td>3</td>
<td>5</td>
<td>2</td>
<td>4</td>
<td>59.66</td>
</tr>
<tr>
<td>12</td>
<td>3</td>
<td>2</td>
<td>4</td>
<td>1</td>
<td>3</td>
<td>5</td>
<td>95.40</td>
</tr>
<tr>
<td>13</td>
<td>3</td>
<td>3</td>
<td>5</td>
<td>2</td>
<td>4</td>
<td>1</td>
<td>75.96</td>
</tr>
<tr>
<td>14</td>
<td>3</td>
<td>4</td>
<td>1</td>
<td>3</td>
<td>5</td>
<td>2</td>
<td>59.82</td>
</tr>
<tr>
<td>15</td>
<td>3</td>
<td>5</td>
<td>2</td>
<td>4</td>
<td>1</td>
<td>3</td>
<td>48.71</td>
</tr>
<tr>
<td>16</td>
<td>4</td>
<td>1</td>
<td>4</td>
<td>2</td>
<td>5</td>
<td>3</td>
<td>89.79</td>
</tr>
<tr>
<td>17</td>
<td>4</td>
<td>2</td>
<td>5</td>
<td>3</td>
<td>1</td>
<td>4</td>
<td>89.41</td>
</tr>
<tr>
<td>18</td>
<td>4</td>
<td>3</td>
<td>1</td>
<td>4</td>
<td>2</td>
<td>5</td>
<td>73.99</td>
</tr>
<tr>
<td>19</td>
<td>4</td>
<td>4</td>
<td>2</td>
<td>5</td>
<td>3</td>
<td>1</td>
<td>44.45</td>
</tr>
<tr>
<td>20</td>
<td>4</td>
<td>5</td>
<td>3</td>
<td>1</td>
<td>4</td>
<td>2</td>
<td>86.79</td>
</tr>
<tr>
<td>21</td>
<td>5</td>
<td>1</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>49.29</td>
</tr>
<tr>
<td>22</td>
<td>5</td>
<td>2</td>
<td>1</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>52.69</td>
</tr>
<tr>
<td>23</td>
<td>5</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>5</td>
<td>4</td>
<td>79.30</td>
</tr>
<tr>
<td>24</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>5</td>
<td>74.62</td>
</tr>
<tr>
<td>25</td>
<td>5</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>53.26</td>
</tr>
<tr>
<td>K1</td>
<td>345.27</td>
<td>354.60</td>
<td>337.68</td>
<td>419.45</td>
<td>327.09</td>
<td>300.47</td>
<td></td>
</tr>
<tr>
<td>K2</td>
<td>342.60</td>
<td>368.07</td>
<td>332.09</td>
<td>395.32</td>
<td>348.64</td>
<td>314.02</td>
<td></td>
</tr>
<tr>
<td>K3</td>
<td>339.55</td>
<td>342.95</td>
<td>347.22</td>
<td>357.70</td>
<td>339.67</td>
<td>348.50</td>
<td></td>
</tr>
<tr>
<td>K4</td>
<td>384.43</td>
<td>318.87</td>
<td>334.82</td>
<td>280.81</td>
<td>353.32</td>
<td>361.57</td>
<td></td>
</tr>
<tr>
<td>K5</td>
<td>309.16</td>
<td>336.52</td>
<td>369.20</td>
<td>267.73</td>
<td>352.29</td>
<td>396.45</td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>75.27</td>
<td>49.20</td>
<td>37.11</td>
<td>151.72</td>
<td>26.23</td>
<td>95.98</td>
<td></td>
</tr>
</tbody>
</table>
Effect of reaction time on photocatalytic degradation

The removal efficiency changed with reaction time as shown in Figure 2(f): the removal efficiency increased rapidly and then the degradation platform emerged after 2 h. The photocatalyst could provide enough active sites at the beginning and the effective concentration of the diesel was high; as the photocatalyst degradation reaction process continued, the active sites and effective concentration of diesel decreased, thus the removal efficiency increased slowly.

Optimization of degradation conditions of Fe₂O₃/ZrO₂ nanocomposite photocatalyst

In order to determine the optimal photocatalytic degradation conditions of Fe₂O₃/ZrO₂ nanocomposite photocatalyst for diesel-polluted seawater and examine the interaction of various factors affecting photocatalytic degradation, orthogonal experiments with six factors and five levels were designed. The six factors were photocatalyst doping ratio, photocatalyst calcination temperature, photocatalyst dosage, initial diesel fuel concentration, H₂O₂ concentration, and photocatalytic reaction time (Table 1).

According to the analysis results in Table 2, the effect order of different factors on degradation of diesel-contaminated seawater was as follows: initial concentration of diesel > photocatalytic reaction time > doping ratio > calcination temperature > dosage of photocatalyst > H₂O₂ concentration. The optimal conditions for Fe₂O₃/ZrO₂ nanocomposite photocatalyst to degrade marine diesel pollution were as follows: doping ratio of Fe₂O₃/ZrO₂ nanocomposite photocatalyst was 4:10, calcination temperature was 400 °C, dosage of photocatalyst was 0.6 g/L, initial diesel concentration was 0.1 g/L, H₂O₂ concentration was 0.4 g/L, and the photocatalytic reaction time was 6 h. Verification experiments were carried out under these conditions; the results showed that the removal efficiency of diesel oil by Fe₂O₃/ZrO₂ nanocomposite photocatalyst could reach 97.03%.

Effect of photocatalyst-loaded polypropylene balls on degradation of marine diesel

Images of different photocatalyst-loaded polypropylene balls prepared by Fe₂O₃/ZrO₂ are shown in Figure 3; with the increase of loaded weight, the color of the polypropylene balls became deeper. As illustrated in Figure 4, with the amount of loaded photocatalysts increasing from 0.15 to 0.35 g, the removal efficiency of diesel showed slight drop from 99.15 to 97.86%. This result might be related to the shed of photocatalyst during the reaction; excess catalyst just adhered to the photocatalyst surface and fell off due to the shock during the reaction.

Effect of initial diesel concentration on degradation of marine diesel by photocatalyst-loaded balls

As shown in Figure 5, varying the initial diesel concentration displayed no significant change on the removal efficiency, and the removal efficiency reached the maximum at initial diesel concentration of 4 g/L. Generally, reaction rate is directly proportional to the concentration of the reactants; in this work, however, initial diesel concentration showed little effect on photocatalytic reaction, confirming Fe₂O₃/ZrO₂ photocatalyst had high activity and adequate active sites for degrading diesel oil.

Recycle performance of Fe₂O₃/ZrO₂ photocatalyst-loaded polypropylene polyhedral ball

As shown in Figure 6(a), after four recycling cycles, the Fe₂O₃/ZrO₂ photocatalyst-loaded polypropylene polyhedral ball still showed red color, indicating that the loss of recovered photocatalyst was small, and a certain amount of Fe₂O₃/ZrO₂ photocatalyst still existed on the surface of
the polypropylene polyhedral ball. Additionally, removal efficiency of diesel decreased from 99.35 to 68.84% after four recycling cycles (Figure 6(b)). Removal efficiency was only 68.84% at the fourth cycle due to the decrease of photocatalytic performance and a certain amount of photocatalysts fell off the surface of the ball, causing the significant decrease of degradation efficiency. This suggested an outstanding recycle of Fe₂O₃/ZrO₂ photocatalyst-loaded polypropylene polyhedral ball, which implies a great potential in treatment of diesel-polluted seawater.

CONCLUSION

(1) In this work, Fe₂O₃/ZrO₂ nanocomposite photocatalyst was successfully prepared by coprecipitation method. Fe₂O₃/ZrO₂ nanocomposite photocatalyst was characterized by XRD, SEM, EDS, and UV-Vis DRS. The average particle diameter of the photocatalyst was 40.32 nm, and the band gap energy of the Fe₂O₃/ZrO₂ nanocomposite photocatalyst was 1.42 eV; additionally, Fe₂O₃/ZrO₂ nanocomposite photocatalyst showed great light absorption in the visible light region of 400–760 nm.

(2) Effects of photocatalyst doping ratio, calcination temperature, photocatalyst dosage, initial diesel concentration, H₂O₂ concentration, and photocatalytic reaction time on the photocatalytic removal efficiency were studied through single-factor experiments. The optimal process conditions for Fe₂O₃/ZrO₂ nanocomposite...
photocatalyst to degrade marine diesel pollution were determined by the orthogonal experiment.

(3) The effect order of different factors on degradation of diesel-contaminated seawater was as follows: initial concentration of diesel > photocatalytic reaction time > doping ratio > calcination temperature > dosage of photocatalyst > H2O2 concentration. The optimal conditions for Fe2O3/ZrO2 nanocomposite photocatalyst to degrade marine diesel pollution were as follows: doping ratio of Fe2O3/ZrO2 nanocomposite photocatalyst was 4:10, calcination temperature was 400 °C, dosage of photocatalyst was 0.6 g/L, initial concentration of diesel was 0.1 g/L, H2O2 concentration was 0.4 g/L, and the photocatalytic reaction time was 6 h. Verification experiments were carried out under these conditions, and the results showed that the removal efficiency of diesel oil by Fe2O3/ZrO2 nanocomposite photocatalyst could reach 97.03%.

(4) Removal efficiency of Fe2O3/ZrO2 photocatalyst-loaded polypropylene polyhedral ball on diesel decreased from 99.35 to 68.84% after four recycling cycles, indicating satisfactory potential in diesel-polluted seawater treatment.

ACKNOWLEDGEMENTS

This study was supported by a grant from State Oceanic Administration People's Republic of China (201305002), Liaoning Science and Technology Public Welfare Fund (20170002), Science Foundation of Department of Ocean and Fisheries of Liaoning Province (201733), and Department of Science and Technology of Liaoning (2016LD0105).

SUPPLEMENTARY MATERIAL

The Supplementary Material for this paper is available online at https://dx.doi.org/10.2166/wst.2020.252.

REFERENCES


First received 27 March 2020; accepted in revised form 11 May 2020. Available online 22 May 2020.