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Application of nano-TiO_2 photocatalyst in marine pollution control

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ABSTRACT

Nano-TiO_2 photocatalysis technology is a new environmental pollutant purification technology. It is of great significance to control marine pollution by using nano-TiO_2 photocatalyst. Seawater is artificially distributed, and the weathered diesel is added to the simulated seawater polluted by oil in seawater. The nano-TiO_2 photocatalyst is synthesized by sol–gel method. The nano-TiO_2 photocatalyst is added into the simulated seawater and the high pressure mercury lamp is used to carry out the photocatalysis experiment of nano-TiO_2. Through scanning electron microscopy, X-ray diffraction and photocatalytic degradation performance of nano-TiO_2 under different conditions, the best nano-TiO_2 photocatalytic process for marine pollution control is determined. The experimental results show that when the pH value is 6, the dosage of nano-TiO_2 is 20 mg, the doping ratio is 16% and the illumination time is 5 h, the nano-TiO_2 photocatalyst has the best degradation efficiency and the best marine pollution control performance.

Keywords: Nano; TiO_2; Photocatalyst; Ocean; Pollution control; Photocatalytic experiment

1. Introduction

With the rapid development of society, people are not only enjoying the convenience brought by high technology, but also facing a serious environmental crisis. The random and savage discharge of pollutants such as domestic garbage, industrial wastewater and production waste gas has not only caused the environmental pollution problem in people's life and development, but also highlighted the urgency and necessity of environmental pollution control. For the treatment of environmental pollution, in addition to relying on the enhancement of people's awareness and behavior of environmental protection, it should also rely on advanced technology [1]. At present, there is still a lack of scientific, systematic, reasonable and efficient methods to deal with environmental pollution, and more methods such as simple adsorption and micro treatment are used. Although these methods have achieved certain results in some areas and some pollution types, they have little effect in controlling pollution diffusion and eradicating environmental pollution, and some methods may even produce secondary pollution [2]. Based on this, it is necessary to explore more scientific, reasonable and effective methods for degradation and elimination of environmental pollutants from the aspect of technological innovation.

With the increasing development of petrochemical industry, marine transportation and offshore oil development, marine oil spill accidents occur frequently. A large number of land-based oily wastewater is discharged into the ocean. Petroleum hydrocarbons have become one of the most important pollutants in coastal waters. There are about 1.0×10^{10} kg oil in the world every year enters the marine environment, and China's oil discharged into the ocean every year reaches 1.15 × 108 kg, with an increasing trend, so that oil has caused serious harm to the marine and nearshore environment [3,4]. In some bays, oil pollution has led to environmental degradation and biological extinction. Scholars at home and abroad have gained some experience in the process of seeking efficient, environmental protection and economic remediation methods for marine oil

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pollution. The common treatment methods include physical method, chemical method and biological method. The above methods have certain defects in technology or economy [5]. Traditional physical and chemical methods transfer organic pollutants from aqueous phase to other phases, so there is the possibility of secondary pollution. With the discovery and research of nano-TiO_2 with good catalytic ability under UV irradiation, the degradation and treatment of pollutants by photocatalyst has become a very active research direction in the environmental field. It uses photochemical method to produce strong oxidants to completely oxidize organic pollutants into inorganic small molecules, and has received good results in the treatment of a variety of wastewater [6,7].

The demand for energy in economic development is increasing, and the demand for petrochemical fuels is also increasing. The exploitation and utilization of oil has become a symbol of economic development. However, oil will leak or discharge in the process of exploitation, transportation, loading and unloading, processing and use, and oil pollution mainly occurs in the ocean, causing harm to aquatic biological resources, fisheries and human beings [8]. Although the toxicity of crude oil in each water area is less than that of refined products, the crude oil contains petroleum gas harmful to human body, and the allowable concentration is generally 500 mg/L. Polycyclic aromatic hydrocarbons in petroleum products are difficult to degrade and have long-term toxicity. They can not only cause cancer, but also easily accumulate in the environment. Therefore, in order to protect water resources and marine ecosystem, we should prevent oil pollution and strengthen the treatment of oil polluted waters. Marine oil pollution treatment generally includes physical remediation, chemical remediation, combustion, natural remediation and bioremediation. With the rise of nanotechnology and the development of application research of photocatalytic technology in environmental protection and organic synthesis, photocatalytic technology is also applied to the treatment of environmental pollution [9,10]. Under certain conditions, photocatalysis can degrade oil into H_2O and CO_2 without secondary pollution.

At present, a lot of research has been carried out on photocatalysts at home and abroad. Zhang has studied the synthesis of flake nano heterostructure photocatalysts and their photocatalytic performance under visible light irradiation [11]; Mahmoudian-Boroujerd et al. [12] studied a new visible light drive for the treatment of recombinant DNA in biopharmaceutical wastewater, realizing the effective optimization of nano photocatalyst; Khdary et al. [13] studied the synthesis of excellent nano photocatalysts driven by visible light with high surface area titanium dioxide nanoparticles; Eskandari et al. [14] studied the cross coupling reaction of supramolecular photocatalysts in dendrimers encapsulated on titanium dioxide nanoparticles. The above researches have achieved great research results, which provide a theoretical basis for the application of photocatalyst in marine pollution control. In this paper, the application of nano-TiO_2 photocatalyst in marine pollution control is studied. The simulated oil polluted seawater is taken as the research object. Through the degradation of nano-TiO_2 photocatalyst, the effects of catalytic dosage, pollutant concentration and catalytic time on photocatalytic degradation of oil pollution are studied.

2. Materials and methods

2.1. Principle of TiO_2 photocatalysis

TiO_2 contains two structures: VB full valence band and CB empty conduction band. The energy difference between the highest energy level in VB structure and the lowest energy level in CB structure is called the band gap width, while the band gap width of anatase TiO_2 is 3.3 eV. Since the light absorption threshold of TiO_2 is 398.5 nm, when it is irradiated with ultraviolet light with wavelength < 398.5 nm, the valence band electrons will be excited after absorbing certain energy, and photogenerated electron hole pairs will be generated on the conduction band and valence band respectively [15].

The photo excitation mechanism of TiO_2 is shown in Fig. 1.

It can be seen from the figure that hole pairs move to the surface under the action of electric field, in which some of them are composite inactivated (line B), some electron hole pairs are redox reacted with the substrate adsorbed on the catalyst surface (line C and line D), and a small part is composite on the catalyst surface (line A). The faster the electron hole pair migrates, the greater the chance of redox with the substrate is, the smaller the probability of recombination is, and the higher the photocatalytic activity of TiO_2 is [16].

2.2. Experimental reagent

The prepared experimental reagents of nano-TiO_2 photocatalyst and their manufacturers are shown in Table 1.

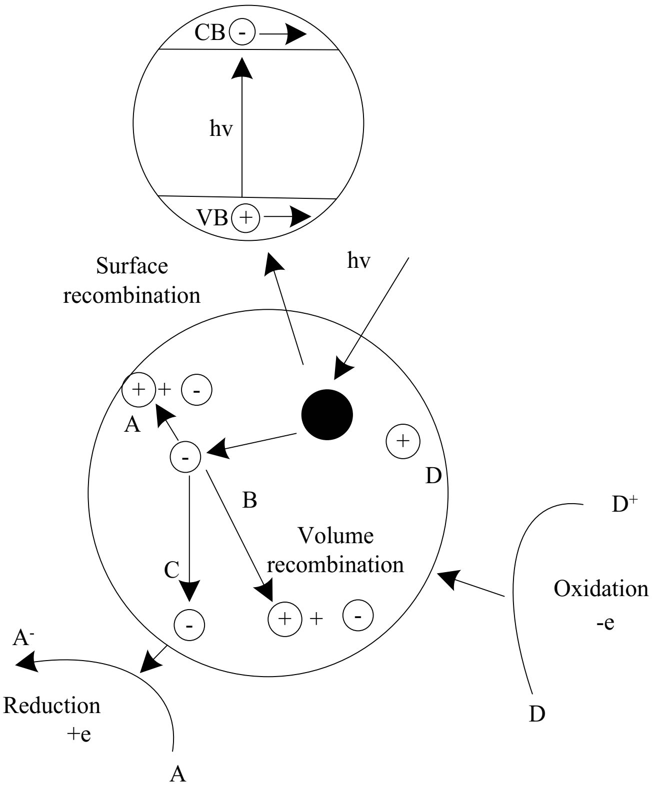

Fig. 1. Optical excitation mechanism of TiO_2.

2.3. Experimental instruments and equipment

The experimental instruments, equipment and manufacturers for the preparation of nano-TiO_2 photocatalyst are shown in Table 2.

2.4. Preparation of nano-TiO_2 photocatalyst

In this study, nano-TiO_2 photocatalyst is synthesized by sol–gel method (sol–gel).

Firstly, add 7.5 mL of tetrabutyl titanate (TBot) slowly to 20 mL of absolute ethanol to obtain solution A; then add 0.75 mL of acetic acid, 1 mL of distilled water, 1 mL of nitric acid, $CaF_2(Er^{3+})$ and thiourea into 10 mL of absolute ethanol solution to obtain solution B.

In the case of intense magnetic stirring (800 rpm), add the solution B to the solution A by drop, and continue to react until the transparent colloid suspension is obtained; continually stir for 1 h, make ultrasonic treatment for 20 min and aging at 5 h at room temperature, and dry the colloid at 10 h for 80°C, to get the gel [17]. Finally, calcine the gel in muffle furnace (adjusting T at 400°C, 500°C, 600°C, and 700°C) to obtain TiO_2 nano photocatalyst powder.

The synthesis flow chart of nano-TiO_2 photocatalyst is shown in Fig. 2.

Nano-TiO_2 photocatalyst is prepared through the above process and applied to marine pollution control.

2.5. Preparation of artificial seawater polluted by oil

The composition of artificial seawater is shown in Table 3.

Boil the purified water in an induction cooker for 20 min to remove the dissolved carbon dioxide gas in the water. According to the mix proportion in Table 3, first add sodium chloride and calcium chloride, place them overnight, and then add magnesium chloride and sodium sulfate after they are completely dissolved, dissolve and mix evenly [18].

Add an appropriate amount of weathered diesel oil to the prepared seawater to prepare oil polluted simulated seawater. The content of diesel oil in the simulated seawater is 100 mg/L. The content of petroleum hydrocarbons is determined by UV spectrophotometry.

2.6. Photocatalytic experiment

The experiment is carried out at room temperature. The photocatalytic device is composed of a magnetic stirrer, a reflux condenser, a high-pressure mercury lamp and a dark box. The quartz beaker has good permeability to ultraviolet light (UV) [19]. Therefore, the quartz beaker should be used as a glass container in the photocatalytic reaction experiment. The model of the quartz beaker is 500 mL. The light source is provided by a high-pressure mercury lamp with $P = 300$ W.

The specific experimental process is as follows: weigh 0.5 g of prepared samples into a quartz beaker, add 100 mL

Table 1
Experimental reagents and their manufacturers

Chemical reagent name	Specification	Manufacturer
Tetrabutyl titanate	CR	Jinan Jiushang New Material Technology Co., Ltd., China
Erbium-doped calcium fluoride nanopowder	CR	Jinan Jiushang New Material Technology Co., Ltd., China
Acetic acid	AR	Jinan Jiushang New Material Technology Co., Ltd., China
Nitric acid	AR	Jinan Jiushang New Material Technology Co., Ltd., China
Absolute ethanol	AR	Jinan Jiushang New Material Technology Co., Ltd., China
Methyl orange	AR	Baoji Guokang Biological Technology Co., Ltd., China
Thiourea	GR	Jinan Jiushang New Material Technology Co., Ltd., China
Distilled water	–	Baoji Guokang Biological Technology Co., Ltd., China

Table 2
Experimental instruments and equipment

Equipment name	Instrument model	Instrument manufacturer
Intelligent constant temperature digital display magnetic stirring heating pot	ZNCL-GS	Shanghai Yushen Instrument Co., Ltd., China
Constant temperature blast drying oven	VYJG-9420	Hangzhou Yijie Technology Co., Ltd., China
Electronic balance	ME204E	Shanghai Hengqin Instrument Equipment Co., Ltd., China
Refrigerated centrifuge	5424R	Shanghai Bajiu Industrial Co., Ltd., China
X-ray diffractometer	Xray	Shanghai Anzhu Optoelectronics Technology Co., Ltd., China
Multifunctional photochemical reaction instrument	CY-GHX-AC	Hangzhou Chuanyi Experimental Instrument Co., Ltd., China
UV-visible spectrophotometer	T6	Jinan Shangdi Electronic Technology Co., Ltd., China
Scanning electron microscope	S-4800	Hitachi Construction Machinery (Shanghai) Co., Ltd.
Muffle furnace	SX2-4-12A	Wuxi Marite Technology Co., Ltd., China

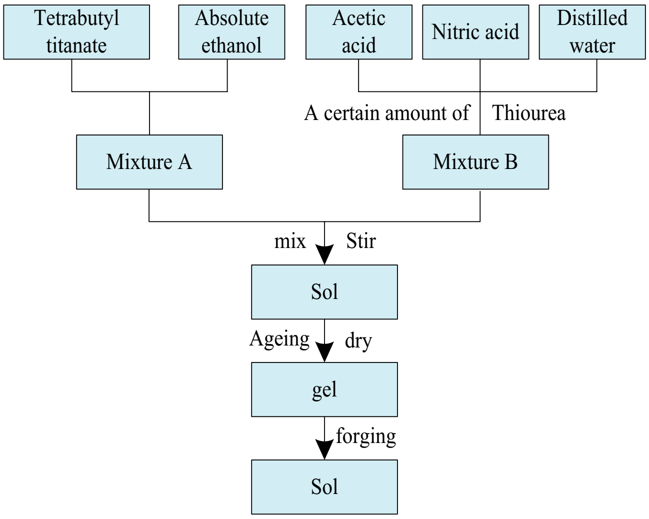

Fig. 2. Synthesis flow chart of nano-TiO_2 photocatalyst.

of prepared methyl orange aqueous solution with a mass concentration of 20 mg/L, put them on a magnetic stirrer to stir evenly, open the circulating condenser pipe to circulate the cooling water, put the whole device in a dark box, and first conduct dark treatment for 0.5 h [20]; then, irradiate the solution after dark treatment under a high-pressure mercury lamp with a power of 350 W for 5 h. During this period, about 5 mL is sampled every 0.5 h. Finally, centrifuge the sample and take out the supernatant; since the maximum absorption wavelength of MO is λ = 460 nm, at this wavelength, with distilled water as the reference solution, determine the absorbance of the sample with UV-vis spectrophotometer, and calculate the degradation rate according to the change of absorbance of the sample.

Before the high-pressure mercury lamp irradiates the quartz cup, it needs to be treated in darkness to ensure that the photocatalyst reaches adsorption equilibrium in methyl orange aqueous solution during photocatalytic degradation [21]; when the high-pressure mercury lamp irradiates the quartz beaker, it needs to be connected with condensed water. This is because the high-pressure mercury lamp will emit more heat during the irradiation process, which will increase the temperature of the whole experimental environment and affect the experimental effect. Therefore, in order to eliminate this effect, it needs to be connected with condensed water.

2.7. Test indicators

2.7.1. Characterization of samples

The surface morphology of the sample is observed by scanning electron microscope (SEM). Firstly, disperse the sample in absolute ethanol, drop it on the tin foil with a dropper, dry it, spray gold, and then observe it under the electron microscope [22]. The phase structure of the samples is determined by X-ray diffraction (XRD).

2.7.2. Oil degradation rate

The calculation formula of oil degradation rate is:

Table 3
Composition of artificial seawater

Reagent name	Content (g/L)
Magnesium chloride	12
Calcium chloride	1.7
Sodium sulfate	5
Sodium chloride	26

$$A = \frac{\left(C_0 - C_i\right)}{C_0} \times 100\% \quad (1)$$

where C_0 is the initial concentration of oil (mg/L) and C_i is the concentration of residual oil in simulated seawater (mg/L).

2.7.3. Other test indicators

In this experiment, the synthesis conditions of nano-TiO_2 photocatalyst with the best photocatalytic effect are found by controlling the calcination temperature and raw material ratio. The main research contents are as follows:

- Nano-TiO_2 photocatalyst has been synthesized by sol–gel method, which can degrade certain concentration of methyl orange solution under ultraviolet light.
- By controlling the calcination temperature and raw material ratio in the experimental preparation process, the optimal doping ratio of nano-TiO_2 photocatalyst and the optimal calcination temperature for the preparation of photocatalyst are found.
- The prepared nano-TiO_2 photocatalyst is observed under scanning electron microscope, and the microstructure of the sample surface is obtained to analyze the influence of the difference of micro morphology on the photocatalytic effect [23].
- The prepared nano-TiO_2 photocatalyst is analyzed by X-ray diffraction, and the crystal type of the experimental sample is analyzed.

3. Results

3.1. X-ray diffraction analysis

The composition and grain size of nano-TiO_2 photocatalysts with doping ratios of 0%, 6%, 12%, 18%, 24% and 30% are analyzed by X-ray diffraction. The XRD diagram characterizing the analysis results is shown in Fig. 3.

As can be seen from Fig. 3, at the Bragg angle (2θ), there are obvious peaks at 31.5°, 43.5°, 55.8°, 60.3°, 69.7°, 77.8° and 83.4°. Compared with JCPDS card, it can be seen that the sample is anatase type, and its lattice constants a, b and c are 3.8554, 3.9665 and 9.6357 Å respectively, which is very similar to the XRD pattern of TiO_2. According to the diffraction peaks, the average size of the sample is about: (a) 17.35 nm; (b) 37.52 nm; (c) 23.68 nm; (d) 30.52 nm; (e) 40.52 nm and (f) 53.85 nm. No obvious (Er^{3+}) diffraction peak is found in the XRD spectra of the above substances, which may be due to the low content of (Er^{3+}).

3.2. Scanning electron microscope

Fig. 4 lists the SEM photos of the prepared nano-TiO_2 photocatalyst with a magnification of 100,000 times.

It can be seen from Fig. 4 that the crystallinity of the photocatalyst is good, showing a cubic structure, which is consistent with the three-dimensional anatase described in XRD. The comparison shows that the volume of the crystal tends to increase, which is consistent with the phenomenon of larger particle size in XRD analysis, and the particle size is about 10–50 nm. The sample has good dispersion, only with a small amount of agglomeration, and the particle size is uniform. With the increase of $CaF_2(Er^{3+})$ doping, the agglomeration phenomenon becomes more and more obvious.

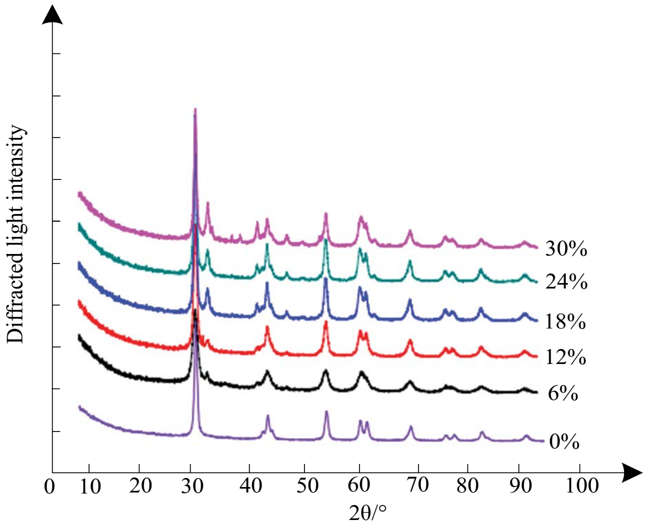

Fig. 3. XRD pattern of nano-TiO_2 photocatalyst.

3.3. Effect of nano-TiO_2 dosage on photocatalytic degradation performance

Take two parts of simulated oil polluted water, add H_2O_2 with a mass fraction of 60%, and add different amounts of nano-TiO_2 respectively, to investigate the effect of the amount of nano-TiO_2 on the treatment of oil polluted seawater according to the experimental method. The results are shown in Fig. 5.

Photocatalytic degradation of oily wastewater increased with the increase of the amount of nano-TiO_2, but when the amount of nano-TiO_2 exceeded 20 mg, the oil degradation rate begins to decline. The main reason is that with the increase of the amount of nano-TiO_2, the number of nano-TiO_2 particles participating in the photolysis reaction increases and the degradation rate also increases. However, when the amount of nano-TiO_2 increases to a certain concentration, with the increase of the amount of nano-TiO_2, the scattering of TiO_2 to light in the solution increases, the utilization of light decreases, and the number of photogenerated electrons and holes decreases.

The degradation rate of oil pollution in TiO_2/H_2O_2 photocatalytic system is significantly higher than that in TiO_2

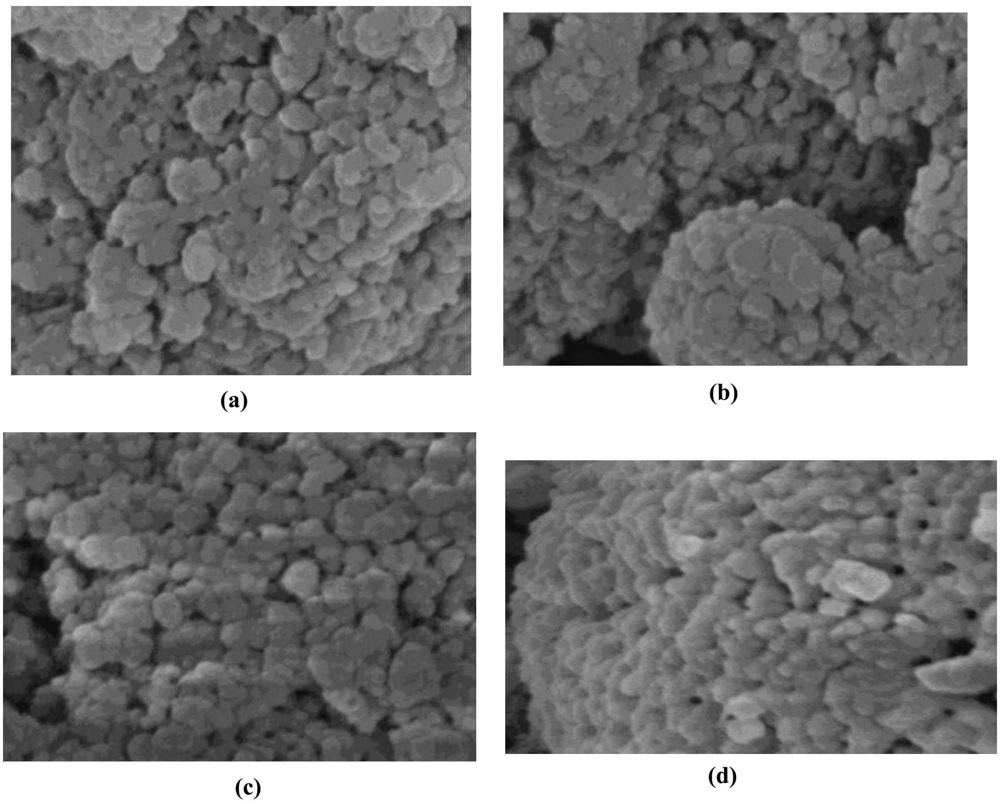

Fig. 4. SEM picture of nano-TiO_2 photocatalyst. $CaF_2(Er^{3+})$ doping amount (a) 5%, (b) 10%, (c) 15%, and (d) 20%.

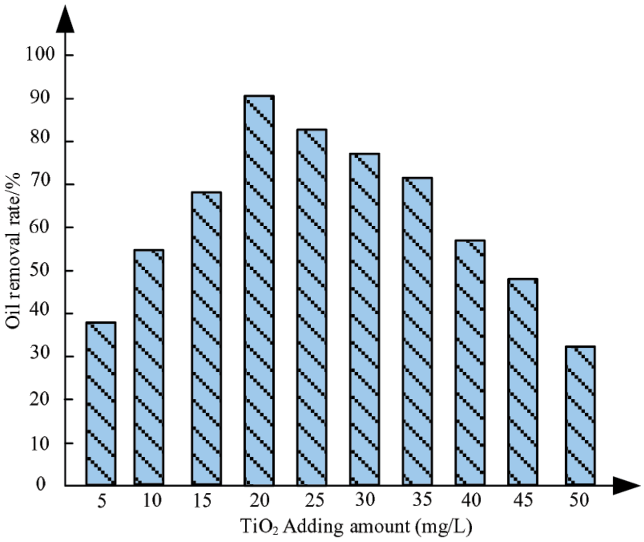

Fig. 5. Effect of the amount of nano-TiO_2 on the photocatalytic degradation performance.

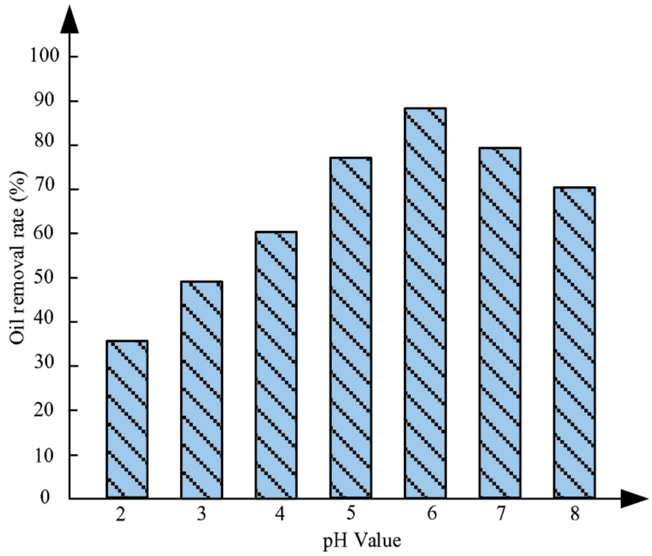

Fig. 6. The influence of pH on photocatalytic performance.

photocatalytic system. This may be because in photocatalytic engineering, in order to ensure the effective progress of reaction, it is necessary to reduce the simple recombination of photogenerated electrons and holes. Oxidant is an effective electron trapping agent, and the addition of oxidant can improve the rate and efficiency of photocatalytic oxidation. H_2O_2 plays an important role in photocatalytic reaction. Under the action of ultraviolet light, it is photolyzed to produce hydroxyl radical $^{\bullet}OH$. Firstly, it is a strong oxidant. In addition, it can also act as an electron acceptor to reduce the electron hole recombination generated on the surface of photocatalyst, so as to greatly improve the degradation efficiency in a short time.

3.4. Effect of initial pH value of solution on photocatalytic degradation performance

The pH value of the solution has a significant effect on the removal rate of organic pollutants. Under other conditions unchanged, the pH value of the solution is adjusted to 2–8. The effect of pH value on the degradation efficiency of diesel polluted seawater in TiO_2/H_2O_2 photocatalytic system is investigated. The results are shown in Fig. 6.

Fig. 6 shows that when the pH value of the photocatalytic reaction system is small, the oil pollution removal rate increases significantly with the increase of pH value, and the removal rate increases rapidly from 32.72% at pH 2 to 90.52% at pH 6. However, with the further increase of pH value of the solution, the oil pollution removal rate changes slowly and shows a decreasing trend. It shows that it is conducive to the photocatalytic degradation of oil polluted seawater in acidic medium, which may be due to the formation of strong oxidizing $^{\bullet}OH$ by the action of dissolved oxygen and excited electrons in acidic medium. Oil pollution contains a large number of neutral *n*-alkanes and dissociatable phenols, and the dissociation of phenols in the reaction system and the charge on the catalyst surface are affected by the pH value of the solution. Existing researchers have shown that when photocatalytic degradation of phenol by TiO_2, it is found that when the pH value of the solution is less than 2, the photocatalytic efficiency is poor, but when the pH increases, the degradation efficiency of phenol increases continuously. When the pH is about 6, the degradation efficiency is the highest, and when the pH continues to increase, the degradation efficiency decreases continuously. Photocatalytic degradation of oil polluted seawater is better in acidic conditions, which may be due to the fact that the substances in the degradation system are not a single phenol, but a complex organic mixture system, and the pH has different effects on various substances in the solution.

3.5. Effect of initial diesel concentration on photocatalytic oxidation of diesel

Set the initial concentration of diesel oil simulating polluted seawater as 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8 g/L respectively, adjust the pH value of wastewater to 7, and irradiate it with visible light for 2 h, and then add 40 mg of self-made nano $CaF_2(Er^{3+})/TiO_2$ photocatalyst respectively. After the reaction, measure the residual amount of diesel oil and calculate the diesel removal rate.

The effect of initial diesel concentration on diesel removal rate is shown in Table 4.

It can be seen from Table 4 that the diesel removal rate increases first and then decreases with the increase of the initial concentration of diesel. This may be because under the condition of a certain amount of catalyst, the amount of diesel is too small, the concentration of diesel is low, and the power of photocatalytic degradation is weakened, resulting in the decrease of the degradation rate of the solution with low initial concentration; with the increase of diesel concentration, the power of photocatalytic degradation is enhanced, which is conducive to the photocatalytic degradation of diesel, so as to improve the diesel removal rate. However, too much diesel may be adsorbed on the catalyst surface, hinder the injection of light, affect the excitation of light to the active potential, and reduce the generation

Table 4
Influence of the initial concentration of diesel oil on the oil removal rate

Test number	Diesel initial concentration (g/L)	Oil removal rate (%)
1	0.1	56.78
2	0.2	69.54
3	0.3	67.85
4	0.4	50.46
5	0.5	45.67
6	0.6	43.58
7	0.7	38.52
8	0.8	34.65

of photogenerated electron hole pairs. Therefore, it can consider whether the photocatalytic method is applicable to the treatment according to the different degree of diesel pollution of seawater, or determine the amount of photocatalyst through the different degree of pollution of seawater. Under the test conditions, the optimal initial concentration of diesel oil is 0.1–0.3 g/L.

3.6. Effect of catalyst doping ratio on photocatalytic oxidation of diesel

Place the simulated diesel polluted seawater with 50 mL concentration of 0.2 g/L in the beaker of 7,250 mL, and adjust the pH value of the wastewater to 7. The appropriate amount of nano $CaF_2(Er^{3+})/TiO_2$ with different doping ratios is added respectively. The influence of different doping ratios on the diesel oil removal rate is investigated by visible light 2H. The results are shown in Table 5.

It can be seen from Table 5 that the removal rate first increases and then decreases with the increase of catalyst doping ratio. When the doping ratio is 16%, the oil removal rate is the highest, which is 87.51%. When the doping ratio continues to increase, the removal rate begins to decrease. The reason is that too many upconversion materials may cover TiO_2, so that TiO_2 cannot absorb the ultraviolet light emitted by the upconversion materials, so it cannot achieve the effect of degrading pollutants. At the same time, the increase of composite content will reduce the content of TiO_2 in the new materials, which reduces the photocatalytic ability on the other hand. Under the experimental conditions, the optimum catalyst doping ratio is 16%.

3.7. Effect of illumination time on photocatalytic oxidation of diesel

Take 50 mL of simulated diesel polluted seawater with concentration of 0.2 g/L and put it into 12,250 mL beakers, adjust the pH value of wastewater to 7 with hydrochloric acid or sodium hydroxide, add 50 mg of self-made nano $CaF_2(Er^{3+})/TiO_2$ photocatalyst respectively, and react for 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5 and 6 h respectively, to investigate the influence of different illumination time on diesel removal rate. The results are shown in Table 6.

Table 5
Effect of catalyst doping ratio on oil removal rate

Test number	Doping ratio (%)	Oil removal rate (%)
1	0	76.58
2	4	82.61
3	8	78.52
4	12	74.52
5	16	87.51
6	20	85.46
7	24	81.52

Table 6
Influence of light time on oil removal rate

Test number	Light time (h)	Oil removal rate (%)
1	0.5	39.52
2	1	43.52
3	1.5	56.84
4	2	68.64
5	2.5	78.52
6	3	83.64
7	3.5	85.76
8	4	86.51
9	4.5	87.64
10	5	87.79
11	5.5	87.81
12	6	87.83

It can be seen from Table 6 that when the illumination time is 5 h, the oil removal rate is better, which is 87.79%. The reason is that the pollution of photocatalytic degradation oil is also increasing with the extension of illumination time. It can be seen that the oil removal rate increases significantly at 0.5–5 h, and reaches the maximum at 5 h. This is because the oxygen molecules in the water continuously capture electrons, resulting in the gradual increase of $^{\bullet}OH$ and highly active superoxide anion radical (O^{2-}). $^{\bullet}OH$ has strong oxidizability and can oxidize organic pollutants into inorganic substances to achieve the purpose of degradation.

4. Discussion

The application of nano-TiO_2 photocatalyst in marine pollution control is studied, and the optimal nano-TiO_2 photocatalyst process for marine pollution control is determined through experiments. With the large-scale development of the marine industry, especially the offshore oil industry, the pollution problems caused by the development of some marine resources began to increase. For example, a large amount of water pollution occurs during the exploitation, transportation and even use of oil and gas resources, and the pollution caused by a large number of oil tankers in beaches and other areas is common, which has affected the harmony of China's marine ecological environment to a certain extent. Compared with fresh water, the existence of various salt ions in seawater may lead to changes in the inactivation mechanism of photocatalysis. At present, there are few studies on the removal of organic pollutants in seawater by photocatalysis. The characteristics of organic pollution in seawater are high toxicity and very low concentration. Heterogeneous photocatalytic technology is very suitable for the removal of organic pollutants in the system. In addition, heterogeneous photocatalytic technology is also very suitable for the advanced treatment of industrial high salt wastewater with concentration of more than 10%, so as to reduce the discharge pressure from the source. There are a large number of salt ions in seawater or industrial high salt wastewater, which will not only interfere with the photocatalytic process, but also lead to the corrosion and instability of the photocatalyst. Therefore, to apply heterogeneous photocatalysis technology to the degradation of organic matter in high salt wastewater system, the catalyst must not only have structural stability, but also have very high catalytic activity and adsorption to avoid the interference of salt ions. In the seawater system, due to the interference of salt ions, the photocatalytic activity of the catalyst for the photodegradation of phenol in seawater under weak ultraviolet light is significantly weaker than that in pure water under the same conditions. This is because a large number of salt ions in the seawater system interfere with the adsorption process of the catalyst for organic pollutants. TiO_2 is loaded on the carrier that can overcome the interference of salt ions, and the strong adsorption performance of the carrier for phenol is used to resist the interference of inorganic salt ions in seawater. The seawater has a huge range and strong fluidity. In order to deal with the pollution of offshore waters, we still need to overcome the problem of how to enrich pollutants. Nano sized TiO_2 is easy to form particle aggregation under high pressure and is difficult to be used in continuous flow system. Therefore, TiO_2 nanomaterials used in offshore waters need to be compounded with carriers. On the one hand, it can resist the interference brought by salt ions in seawater, on the other hand, it can enrich organic pollutants in seawater, so that TiO_2 can react with it for photocatalytic oxidation.

Carbon nanomaterials have huge specific surface area. In addition to providing support and fixation with high specific surface area for TiO_2 particles, they can enhance the photocatalytic activity of the composites by minimizing the recombination of electrons and holes and providing reaction sites with high quality and high adsorption activity. They are an ideal carrier for the application of nano-TiO_2 in offshore waters. The super adsorption capacity of carbon nanomaterials can adsorb salt ions and organic macromolecular pollutants in seawater at the same time. The addition of nano carbon materials not only overcomes the interference of salt ions on the photocatalytic process in the seawater system, but also enriches a large number of organic pollutants with high toxicity and low concentration on the catalyst surface to increase the contact area of photocatalytic reaction, so as to achieve the ultimate goal of improving the photocatalytic performance of TiO_2.

Nano-TiO_2 photocatalyst can be applied not only to control marine pollution, but also to other applications. The main applications are as follows:

4.1. Treatment of industrial wastewater

Organic wastewater is the main type of industrial wastewater. This kind of wastewater contains a lot of harmful substances such as organic phosphorus, phenols, halogenated hydrocarbons, aromatics and their derivatives and heterocyclic compounds, which will do great harm to human body. Compared with other wastewater pollutants, there are many kinds of harmful components of such wastewater pollutants, and it is difficult to effectively prevent and control the harm to human body. At present, organic wastewater mainly comes from printing and dyeing, pesticide use and papermaking, and nano titanium dioxide degradation methods are also mainly used in the treatment of these organic wastewater. With the development of printing and dyeing industry, a large number of dyes are used in the production of textiles, plastic products, ceramics and other products, and the dyes used in these printing and dyeing activities contain a large number of harmful substances, which will cause significant pollution to the printing and dyeing water. Relevant studies show that nano titanium dioxide can better improve the decolorization rate and degradation rate of dyes, so as to degrade pollutants in printing and dyeing wastewater and purify wastewater. Although modern agricultural development has strictly controlled the use of toxic and harmful pesticides, in some rural areas, highly toxic pesticides such as organic sulfur and organic phosphorus are still used frequently, and the residues of these pesticides are difficult to decompose under conventional natural conditions, and will permeate and diffuse due to rain erosion, resulting in serious pollution of groundwater, ultimately endangering human health. TiO_2 can decompose the toxic substances in highly toxic pesticides and their residues into PO_4^{3-} and SO_4^{2-} to reduce the harm to human body. Compared with other production water pollution, papermaking wastewater is produced in a large amount and difficult to treat, so the traditional sewage treatment methods are difficult to be effective. The photocatalytic degradation of papermaking wastewater with TiO_2 can weaken the toxic substances in bleaching water and degrade them into biodegradable substances.

Inorganic pollutants in industrial wastewater, especially heavy metals, are another difficult problem in industrial wastewater treatment, because its structure cannot change, and the most environmentally friendly method is recycling. Nano-TiO_2 photocatalytic technology is an effective method to remove mercury and other heavy metals from water pollution. Under the action of laser light source with main wavelength greater than 310 nm, 99% of 100 mg/L Hg^{2+} is reduced and removed by photocatalysis within 20 min. The results of light proof comparison test show that 30% $HgCl_2$ is adsorbed on the surface of nano-TiO_2 particles, indicating that Hg^{2+} has a strong affinity for metal oxides. Photocatalysis can degrade inorganic pollutants and cyanide. Under ultraviolet light, CN^- can be oxidized to OCN^- on the surface of TiO_2, and then further reacted to produce CO_2, N_2 and NO^{3-} ions.

4.2. Drinking water

Nano-TiO_2 can not only treat environmental wastewater, but also deeply purify tap water, which solves a difficult problem of removing dissolved organic pollutants in water.

The organic matter in drinking water can be mineralized by photocatalytic oxidation, and finally simple inorganic substances such as CO_2 and H_2O can be generated to eliminate the harm to human body. In the case of interference and competitive reaction, photocatalytic oxidation has a satisfactory treatment effect on the deep purification of urban tap water with poor water quality.

4.3. Disposal of solid waste

There is a great demand for plastics in China, among which wastes such as agricultural film, packaging products, industrial and daily garbage are difficult to recycle. The existence and diffusion of these white pollutants will have a significant impact on human health. The application of nano photocatalysis technology in solid waste can achieve the effect of fast reaction speed and good catalytic effect. This catalytic method has the advantages of low cost and large-scale promotion. Nano-TiO_2 photocatalyst has more obvious catalytic degradation effect on solid waste.

4.4. Application in antibacterial and air purification

For bacteria and other pollutants composed of protein, bactericides are often used to solve them, but this aspect is easy to cause obvious secondary pollution. Compared with the conventional sterilization methods, TiO_2 photocatalytic technology can not only achieve the sterilization effect, but also degrade the toxic substances produced in the sterilization process and reduce environmental pollution. At the same time, brushing the coating containing nano-TiO_2 photocatalyst in public places such as hospitals can achieve good sterilization under the action of indoor light and make the human body in a better environment. When TiO_2 photocatalyst is used to catalyze the pollutants, *E. coli* in the pollutants can be completely eliminated after UV irradiation for 2 h. At the same time, the degradation rate of penicillin resistant yellow bacillus can be increased to 99% for 1 h, so as to achieve the effect of sterilization. In terms of air purification, the application of photocatalytic oxidation technology can eliminate formaldehyde, sulfide, oxynitride and other pollutants in the air and keep the indoor air at an excellent standard. TiO_2 can effectively degrade alcohols, ketones, chlorinated olefins, chlorinated alkanes, toluene, isopropyl benzene, isooctane and other organic pollutants in the air.

5. Conclusion

At present, there are many research contents and achievements on environmental pollutant degradation technology, which is not only the actual requirement of current ecological environment treatment, but also an effective way to deepen the application of science and technology in environmental pollution. Although there are many studies on the application of nano-TiO_2 photocatalysis technology in the degradation of marine environmental pollutants and some achievements have been made, there is still a large gap with the practical application requirements of pollutant degradation, and some achievements are still in the stage of exploration and improvement and do not have corresponding feasibility. In order to make the application of nano-TiO_2 and other photocatalytic materials in environmental protection really enter the practical stage, we should focus on the following aspects: a large number of doping, composite and other bulk phase and surface modification studies must be carried out to obtain photocatalytic composites with wide light response range and high quantum efficiency; do a good job in catalyst separation and recovery; develop a new process combining traditional sewage treatment technology and photocatalytic technology; vigorously look for low consumption and efficient energy. The utilization of solar energy has limitations, thus, finding a suitable light source has become another challenge for the application of photocatalytic technology in the treatment of marine pollutants.

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