Study on degradation of methyl orange using pelagite as photocatalyst

Jian-Qiu Chen *, Duo Wang, Mao-Xu Zhu, Cong-Jie Gao

College of Chemistry and Chemical Engineering, Ocean University of China, Yushan Road 5, Qingdao 266003, PR China

Abstract

Pelagite of East Pacific Ocean as a low-price, very high reserve photocatalyst, has been successfully used for the first time to realize total degradation and decoloration of methyl orange within 120 min through photocatalysis. The photocatalysis and degradation performance of pelagite for methyl orange under the effect of various factors has been studied. Results show that pelagite has satisfactory photocatalysis effect in degradation of organic compounds.
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1. Introduction

Pelagite is an autogenic manganese ore in deep sea bed, also referred to as manganese nodule, manganese ball and ocean polymetallic nodule, etc. Main compositions are oxides and hydroxides of manganese and iron. A number of metallic elements such as copper, nickel and cobalt are also contained. Pelagite is widely distributed at ocean bed 4000–6000 m deep in the Pacific Ocean, Indian Ocean and Atlantic Ocean. Pelagite normally takes spherical, elliptical or block shape. Diameter is 1–20 cm [1]. Manganese in pelagite is mainly amorphous MnO_2 and MnOOH. Degree of crystallization of pelagite is much lower than that of land-born natural manganese ore. Therefore, pelagite has better surface activity, stronger absorbing power and oxidation reduction activity. Synthetic nascent state MnO_2 or chemical reagent MnO_2 made from low crystallinity or amorphous natural manganese ore can be used for effective oxidation and decoloration of organic pollutants in waste water [2–4]. The special channel structure in pelagite is the masterwork of ocean microorganism [5]. Pelagite is not toxic to micro-organism; it is a good biological carrier. Experiment of dyeing waste water treatment using pelagite as biological fixing carrier shows that quality of water treated in this method is apparently better than non-fixing direct activated sludge process, and in this method, COD, BOD, SS and chroma in waste water can be effectively reduced [6].

Pelagite has huge application potential in water treatment. However, when used as absorbent to treat waste water, especially organic waste water, its absorption capability is not sufficient. As a direct oxidant, its oxidizing ability is not strong. By far, there has been no report of pelagite used as photocatalyst to degrade organic pollutant. For the first time, this paper describes use of pelagite as photocatalyst and study of its decoloration and degradation efficiency for organic dye methyl orange.

2. Experiment using pelagite as photo-catalyst to degrade organic matter

2.1. Materials and reagent

Methyl Orange (99%, made by Shanghai Chemical Reagent Co., China Medicine Group); pelagite from East Pacific Ocean (cleaned by ultrasonic method, dried, grinded and sieved by 100 mesh sieve), and triple distilled water.

2.2. Instruments

Model XPA-II photocatalytic reactor (Nanjing Xujiang Electromechanical Factory): 0.5 L volume, central light source is 500 W medium pressure mercury lamp (characteristic wavelength is 365 nm) placed in a quartz socket tube with one end closed. The system is cooled by circulating water running through an interlayer and magnetic agitation is used so that catalyst is suspended in the reaction liquid (Fig. 1); UV-2450 ultraviolet-visible light spectrophotometer (SHIMADZU,

* Corresponding author. Tel.: +86 532 82031872; fax: +86 532 82031872.
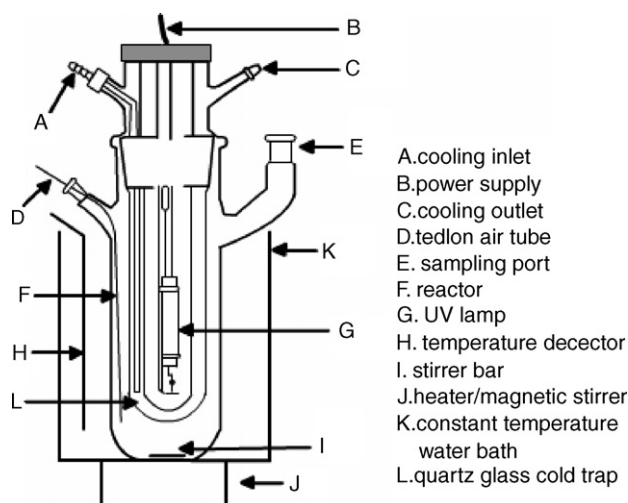*E-mail addresses:* cjqer@126.com, cjqer@163.com (J.-Q. Chen).

Fig. 1. Schematic diagram of the set-up of photocatalytic reactor.

A. cooling inlet
B. power supply
C. cooling outlet
D. tedlon air tube
E. sampling port
F. reactor
G. UV lamp
H. temperature decector
I. stirrer bar
J. heater/magnetic stirrer
K. constant temperature water bath
L. quartz glass cold trap

Japan); DELTA 3200 pH meter (METTLER TOLEDO, Switzerland); RCT temperature control magnetic agitator (IKA, Germany); AL204 precision analytical balance (0.0001 g, METTLER TOLEDO, Switzerland); Scout pro balance (0.01 g); KQ2200DB digital control ultrasonic meter (operating frequency at $40\,kHz \pm 10\%$, Kunshan Ultrasonic Instrument Ltd.); SEM: Field-Emission Scanning Electron Microscopy (FE-SEM) (JEOL-6700F, Japan Electron Co. Ltd.); Energy dispersive X-ray Microanalysis System (Oxford Instrument, UK); XRD: Bruker D8 X-ray diffraction spectrometer (Bruker Co. Ltd., Germany).

2.3. Experimental procedure and method of analysis

Five hundred milligram per liter of methyl orange solution is prepared as reserve liquid. Take certain amount of pelagite catalyst and 500 mL methyl orange solution of certain concentration and preheat to $25.0 \pm 1.0\,°C$, and mix them in the reactor. Perform ultrasonic oscillation of the mixture at constant temperature of $25.0\,°C$ for 5 min. Place the photocatalytic reactor in a water bath of constant temperature ($25.0 \pm 1.0\,°C$). Circulate air through it for 10 min or not; air circulation shall be 400 mL/min. Turn on agitator. When catalyst is fully mixed with reaction fluid, turn on 500 W ultraviolet lamp and start counting time. Take samples every 15 min, use $0.22\,\mu m$ filtering film to filter the catalyst and immediately detect photo-absorption at each characteristic wavelength of the dye and pH value.

Spectrophotometric method is used to measure decoloration rate of methyl orange. Maximum absorbing wavelength of methyl orange solution is $\lambda_{max} = 465\,nm$. Methyl orange solutions of 0, 4, 10, 20, 30 and 40 mg/L are prepared respectively for drawing operating curves. Residual content of methyl orange is calculated by the following formula:

$$\text{Residual content }(\eta)\% = \frac{C_t}{C_0} \times 100$$

In which C_t is methyl orange solution concentration at time t and C_0 is initial concentration of methyl orange.

3. Results and discussion

3.1. Representation of pelagite structure and elements

Fig. 2 is a magnified (7500×) SEM photo of 100 mesh pelagite, Fig. 3 is the X-ray energy spectrum of pelagite, and Fig. 4 is the X-ray diffraction diagram of pelagite. According to analysis based on Fig. 2, Table 1 and reference literature
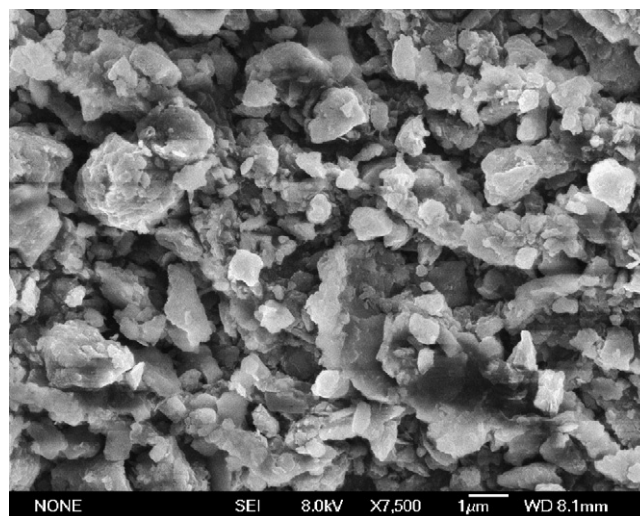

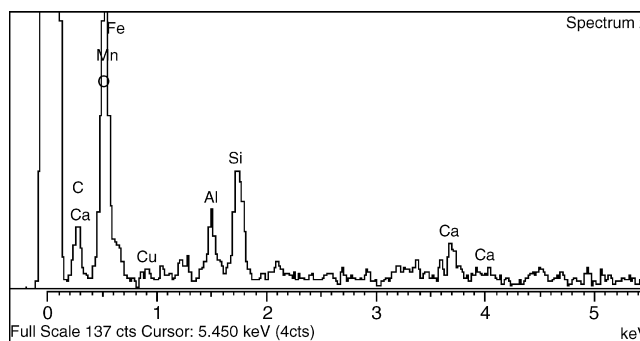Fig. 2. SEM photo of 100 mesh pelagite (magnified 7500×).
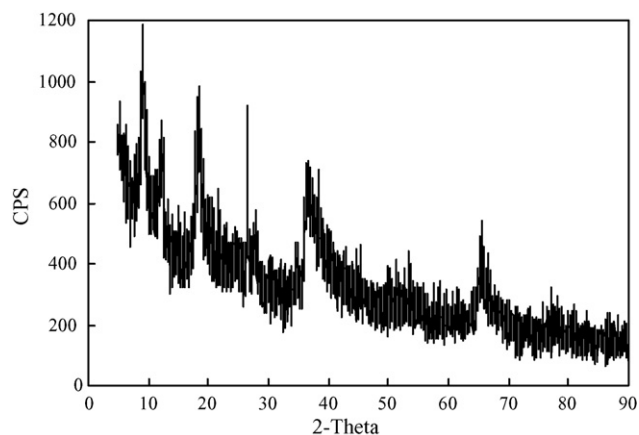

Fig. 3. X-ray energy spectrum of pelagite.

Fig. 4. X-ray diffraction diagram of pelagite.

Table 1
Contents of metal elements in the pelagite

| Element	Weight (%)	Atomic (%)
C	10.16	19.94
O	32.87	48.45
Al	3.61	3.15
Si	9.93	8.34
Ca	9.71	5.71
Mn	28.53	12.24
Fe	4.62	1.95
Cu	0.58	0.21
Total	100.00	

Fig. 5. Effect of air on photocatalysis degradation of pelagite.

Fig. 6. Effect of methyl orange concentration on photocatalysis degradation of pelagite.

[7], there is flocculated deposit on surface of this pelagite, iron/manganese mass ratio Mn/Fe > 4, and the pelagite grows in calcium, silicon or siliceous ooze area where biological activities are strong (formed by diffusion of interstitial water). Diffusion elements are mainly Fe^{3+} and Mn^{4+} from sediment. Under biological mediation, with degradation of active organics in sediment, iron and manganese ions receive electrons from organic matter and are reduced into interstitial water. Accumulation of radiolarian and diatom shells forms loose and porous surface sediment, favoring action of benthonic organism or bacteria. A silky manganese bacterium is a marine bacterium with very strong oxidizing ability. Substances that catalyze oxidation of manganese exist on its sheath and large amount of mucus can be secreted, so that both manganese and iron deposit. Therefore, it is easy to find large amount of flocculated deposit in SEM photos and, in addition, cracks.

From Fig. 4, it can be seen that with the exception of quartz (at $d = 0.335$ nm, with relative strength of 46) that has relatively high degree of crystallization, other main components in pelagite, e.g. todorokite (at $d = 0.977$ and 0.482 nm, with relative strength of 100 and 58, respectively), sodium manganite (at $d = 0.724$ and 0.359 nm, with relative strength of 71 and 34, respectively) and vernadite (at $d = 0.224$ and 0.142 nm, with relative strength of 37 and 35, respectively).

3.2. Study of photocatalyzing effect of pelagite

3.2.1. Effect of air on photocatalysis by pelagite

In the first group of experiments, method described in Section 2.3 is used to prepare 500 mL of 10 mg/L methyl orange solution, in which 0.3 g pelagite powder is added. Air of flow 400 mL/min is circulated through the solution for photocatalysis. In the second group of experiments, no air circulation is used, but other conditions remain the same.

From Fig. 5, it can be seen that air can affect photocatalysis by pelagite. After 120 min of photocatalysis, in the water sample through which air is circulated, 95.16% methyl orange has degraded and discolored by photo-catalyzing, while in the water sample through which no air is circulated, 97.85% methyl orange has degraded and discolored. Also, during the reaction, photocatalysis degradation speed is higher in the sample in which no air is used than that in which air is used. For example, at 60 min, methyl orange degradation rate under these conditions (without
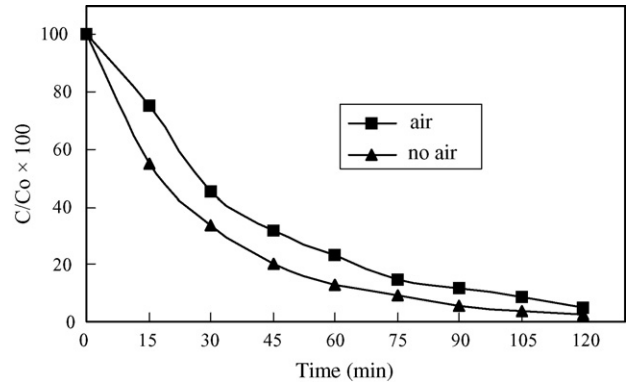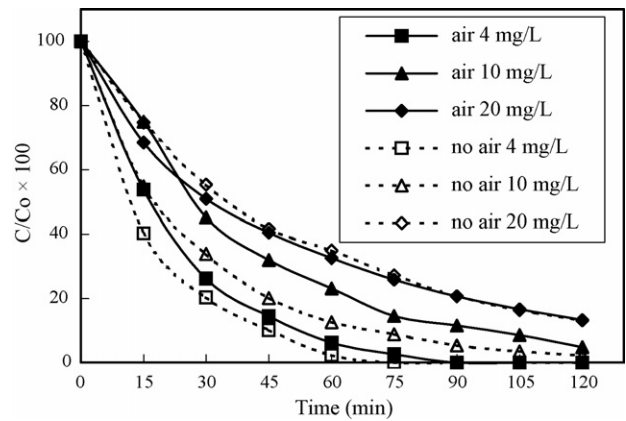
air and with air) are 87.37% and 76.88%, respectively, indicating that air does not favor photocatalysis by pelagite. It is also found that solution pH value has not changed apparently before and after reaction. For example, when air is used on 10 mg/L methyl orange solution, pH value before reaction is 7.46 and that after 120 min of reaction is 7.45, a very small change during reaction.

3.2.2. Effect of methyl orange concentration on photocatalysis by pelagite

Two groups of methyl orange solutions, i.e. 500 mL of 4, 10 and 20 mg/L concentration each, are prepared, and 0.3 g pelagite powder is added in each such solution. In the first group, air of 400 mL/min flow is used while no air is used for the second group; all other conditions are the same.

From Fig. 6, we can see that no matter air is used or not, it is easier to degrade low concentration methyl orange solution by photocatalysis. Results obtained by fitting show that photocatal-

Table 2
Kinetic constants of different concentration methyl orange (min^{-1})

	Concentration		
	4 mg/L	10 mg/L	20 mg/L
k (air)	0.0481	0.0258	0.0176
k (no air)	0.0595	0.0324	0.0173

Fig. 7. Effect of pelagite concentration on photocatalysis degradation.

Table 3
Standard electrode potentials of some common oxidation reduction reactions [8]

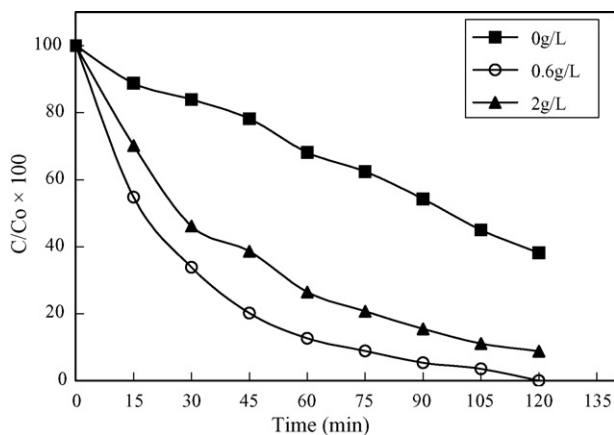| Electrode	Oxidation reduction reaction	E^0 (V)
β-MnOOH/Mn^{2+}	β-MnOOH (s) + 3H$^+$ + e$^-$ $\rightarrow$ Mn^{2+}(aq) + 2H$_2$O	1.65
γ-MnOOH/Mn^{2+}	γ-MnOOH (s) + 3H$^+$ + e$^-$ $\rightarrow$ Mn^{2+}(aq) + 2H$_2$O	1.50
γ-MnO$_2$/Mn^{2+}	γ-MnO$_2$ (s) + 4H$^+$ + 2e$^-$ $\rightarrow$ Mn^{2+}(aq) + 2H$_2$O	1.27
δ-MnO$_2$/Mn^{2+}	δ-MnO$_2$ (s) + 4H$^+$ + 2e$^-$ $\rightarrow$ Mn^{2+}(aq) + 2H$_2$O	1.29
α-FeOOH/Fe^{2+}	α-FeOOH (s) + 3H$^+$ + e$^-$ $\rightarrow$ Fe^{2+}(aq) + 2H$_2$O	0.656
γ-FeOOH/Fe^{2+}	γ-FeOOH (s) + 3H$^+$ + e$^-$ $\rightarrow$ Fe^{2+}(aq) + 2H$_2$O	0.757
α-Fe$_2$O$_3$/Fe^{2+}	α-Fe$_2$O$_3$ (s) + 6H$^+$ + 2e$^-$ $\rightarrow$ 2Fe^{2+}(aq) + 3H$_2$O	0.655

Fig. 8. Effect of air on photocatalysis degradation of pelagite.

ysis reaction by pelagite meets grade I reaction kinetics; refer to Table 2 for its kinetic constants.

From Table 2, we can see that reaction speed constant decreases with increase of methyl orange solution concentration. Under different concentrations, reaction speed when air is not used is higher than when air is used; under relatively high concentrations, these speeds tend to be the same.

3.2.3. Effect of pelagite concentration on photocatalysis effect of pelagite

Ten milligram per liter of methyl orange solutions are prepared and 0, 0.6 and 2 g/L pelagite are added respectively. When pelagite concentration is 0 g/L, under pure ultraviolet light, after 120 min, 61.85% methyl orange has degraded and discolored. When this concentration is 0.6 g/L, methyl orange has totally degraded and discolored after 120 min. However, when pelagite concentration increases to 2 g/L, degradation rate after 120 min is only 91.17%. This is because when pelagite concentration reaches certain value, the screening effect of ultraviolet light by pelagite powder arises, causing fall of degradation rate (refer to Fig. 7).

3.2.4. Effect of pH value on photocatalysis effect of pelagite

Prepare 10 mg/L methyl orange solution with pelagite concentration of 0.6 g/L. Use dilute hydrochloric acid or sulfuric acid to adjust pH value of the reaction liquid to 1.70, 7.46 and 11.15, respectively. The reaction is performed without use of air. At pH 1.70, ultrasonic dispersion of pelagite is performed. Within 10 min, 98.92% methyl orange has degraded with final pH value of 1.73. This is because under acidic condition, various minerals in pelagite containing Fe and Mn form electrode pairs of certain oxidizing ability that decomposed methyl orange. Table 3 shows standard electrode potentials of some common oxidation reduction reactions reported by literature [8].

As shown in Fig. 8, at pH 7.51, within 120 min, 97.85% methyl orange has degraded and discolored. At pH 11.15, methyl orange has totally degraded and discolored after 75 min; at this time, pH value has changed to 11.68.

Therefore, under acidic condition, pelagite can dissolve and consume H$^+$, and oxidation reduction reaction will occur. Under basic condition, due to large amount of OH$^-$, surface of pelagite has electro-negativity, favoring migration of holes toward particle surface and generation of $^\bullet$OH. Therefore, pelagite photocatalysis reaction is subject to high reaction rate under basic condition. Under neutral condition, effect of methyl orange degradation by pelagite photocatalysis is most poor.

3.2.5. Effect of salt on photocatalysis effect of pelagite

Fig. 9 reflects effect of salt on pelagite photocatalysis. Ten milligram per liter methyl orange solution is prepared. Concentration of pelagite used is 0.6 g/L. NaCl concentration is 0, 10, 30 and 50 g/L, respectively.
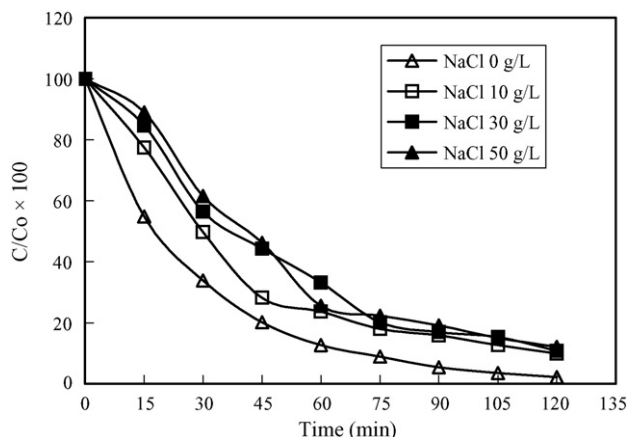

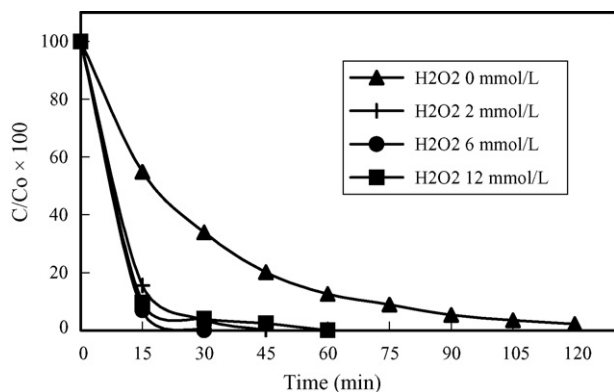Fig. 9. Effect of salt on photocatalysis effect of pelagite.

Fig. 10. Effect of H_2O_2 on photocatalysis effect of pelagite.

It can be seen from Fig. 9 that addition of NaCl can apparently affect pelagite photocatalysis effect, which is reduced with increased NaCl concentration. At 120 min of photocatalysis reaction, the effect reduces from 97.85% at NaCl concentration of 0 g/L to 90.05%, 89.25% and 87.91%, respectively. This is due to addition of inorganic ions affecting double electrode layer of pelagite in water and competing with organic matters in scrabbling of reaction absorption potential, surface holes and $^\bullet$OH, thereby baffling degradation of organic matter by photocatalysis.

3.2.6. Effect of H_2O_2 on photocatalysis effect of pelagite

Fig. 10 shows effect of H_2O_2 on photocatalysis effect of pelagite. Method of experiment: prepare 10 mg/L methyl orange solution; concentration of pelagite is 0.6 g/L, and H_2O_2 concentration is 0, 2, 6 and 12 mmol/L, respectively. Results show that addition of H_2O_2 can greatly accelerate degradation. When no H_2O_2 is added, methyl orange degradation rate at 120 min is 97.85%; when H_2O_2 content is 2 mmol/L, methyl orange has totally degraded at 45 min. When this concentration is 6 mmol/L, methyl orange has totally degraded at 30 min. This is because H_2O_2 is a very strong oxidant that can not only capture photo electrons to effectively impede combination of electron–hole pairs at surface of the catalyst, but also generate this reaction: $H_2O_2 + e \rightarrow {}^\bullet OH + OH^-$ to form strongly oxidizing $^\bullet$OH, thereby further increasing degradation rate. However, when H_2O_2 concentration reaches 12 mmol/L, total degradation and decoloration of methyl orange is deferred to 60 min, indicating a suppression effect. We postulate that too much H_2O_2 is absorbed on surface of pelagite, impeding absorption of methyl orange on such surface, and lowering degradation rate. At the same time, excessive H_2O_2 serves as a scavenging agent of $^\bullet$OH [9] with the mechanism of $^\bullet OH + H_2O_2 \rightarrow H_2O + HO_2^\bullet$ and $^\bullet OH + HO_2^\bullet \rightarrow H_2O + O_2$. Therefore, addition of H_2O_2 has an optimum quantity.

4. Conclusions

In this paper, we propose a bold method of high research significance and actual application value according to main compositions of pelagite of oxides and hydroxides of manganese and iron, in which manganese is mainly amorphous MnO_2 and MnOOH featuring low degree of crystallization, high surface activity, strong absorbing capability and oxidation reduction activity: use of pelagite as photocatalysis to degrade organic pollutants in water (in this experiment, methyl orange dye is selected). Experimental study and mechanism analysis lead to the following conclusions:

1. effect of photocatalysis by pelagite is better when no air is used;
2. lower concentration of methyl orange favors photo-catalyzing by pelagite;
3. concentration of pelagite has apparent effect on catalytic effect and optimum concentration is about 2 g/L; more accurate optimum concentration needs to be determined by further investigation;
4. photo-catalyst reaction speed of pelagite increases with increased reaction liquid pH value;
5. salinity can apparently affect photocatalytic effect of pelagite: the higher the salinity, the poorer the photo-catalytic effect;
6. as a strong oxidant, H_2O_2 concentration has the most apparent effect on pelagite photocatalytic effect and optimum salt concentration is around 6 mmol/L. More accurate optimum concentration requires further investigation.

References

[1] L.J. Zhang, The black riddle on the sea botten—pelagite, Earth 1 (2004) 11–12.
[2] J.T. Ge, J.H. Qu, Ultrasonic irradiation enhanced degradation of azo dye on MnO_2, Appl. Catal. B: Environ. 47 (2004) 133–140.
[3] H.C. Zhang, C.H. Huang, Oxidative transformation of triclosan and chlorophene by manganese oxides, Environ. Sci. Technol. 37 (2003) 2421–2430.
[4] Z.C. Ma, L.H. Jiang, L.L. Dong, Adsorptive decolourization of acid mordant yellow GG on the fresh MnO_2, Environ. Pollut. Contr. 24 (2002) 157–159.
[5] C.Y. Lin, L.Z. Bian, F.S. Zhang, Classification of the microbes and study of the beaded ultra-microfossils in pelagic manganese nodules, Chin. Sci. Bull. 41 (1996) 821–824.
[6] H.R. Li, Y.L. Feng, P. OuYang, Manganese nodules as bio-immobilized carrier to degradation dye wastewater, J. Univ. Sci. Technol. Beijing 24 (2002) 11–14.
[7] H.M. Zhang, P.D. Huang, G.D. Bao, The microstructure and composition study of ferromanganese nodule from the Pacific, J. Zhejiang Univ. 21 (1994) 315–322.
[8] K.M. Parida, B. Gorac, N.N. Das, Studies on indian ocean manganese nodules. III. Adsorption of aqueous selenite on ferromanganese nodules, J. Colloid Interf. Sci. 187 (1997) 375–380.
[9] M.W. Peterson, I.A. Turner, A.J. Nozik, Mechanistic studies of the photocatalytic behavior of titanium dioxide: particles in a photoelectrochemical slurry cell and relevance to photodetoxification reactions, J. Phys. Chem. B 95 (1991) 221–225.