Solar photocatalysis : Inactivation of bacteria by smectite catalysts

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Abstract : This study uses smectite clays as the catalyst carriers and exchange Ag^+ and Zn^{2+} onto the carriers by the method of ion exchange. Meanwhile, with photocatalytic activities under the irradiation of a sodium lamp, the cell structures of bacteria in the water can be totally destroyed to finally achieve inactivation of bacteria.

The modified smectite catalysts undergo the functional-group analysis through the Fourier Transform Infrared Spectroscopy (FTIR). The results show that high-temperature sintering does not damage the mineral structures of smectite catalysts. As for the effect on inactivation of bacteria, owing to the semiconductor properties of the modified smectite catalysts, when a sodium lamp emits light on the catalyst particles, catalyst particles can be excited to cause photocatalysis and generate •OH radicals, which would then damage the internal structures and compositions of bacterial cells, causing oxidative splitting of cell walls and membranes and overall decomposition of cells to achieve the purpose of bacterial inactivation. Meanwhile, among the different types of smectite catalysts and catalysts with different weight percentages, smectite-Ag catalyst with a 0.06 weight percent and smectite-Zn catalyst with a 0.04 weight percent can achieve highest efficiencies of bacterial inacitivation. This study shows that the possibility of shadowing effects gets higher with higher weight percentages. In other words, excessive catalysts will take over the light locations, reduce the amount of sodium light activities over the surface of bacteria, and therefore lower the efficiency of bacterial inactivation.

Keywords : Inactivation, smectite catalyst, sodium light, shielding effect.

Introduction

Recently, sunlight has been used as a method of water disinfection, where, in addition to the heating effect, the efficacy of treatment has been attributed to the production of reactive oxygen species by the UV-A photosensitization of oxygen within the water sample[1,2]. Most of the research into the effectiveness of solar disinfection has focused either on the pasteurizing effects of solar radiation at temperatures higher than 45–50 °C, or on the synergistic interaction between temperature (45–50 °C) and solar radiation[3,4]. One small-scale approach that has gained support in recent years makes use of the disinfectant properties of sunlight to treat contaminated water in transparent plastic bottles or plastic bags in a process termed solar disinfection[5,6].

During the last decade, photocatalysts have become more popular, drawing significant global interest[7]. Titanium dioxide (TiO_2) is the most widely used catalyst; it is considered to be an ideal catalyst for photocatalytic oxidation applications[8–10]. Numerous reports on the mechanisms of a photocatalytic process for disinfecting air have been published in the literature[8,11]. However, not much research has been carried out on the photocatalytic disinfection of airborne bacteria in polluted indoor air, despite its great potential to protect public health.

Because of their versatile properties, ease of preparation and low cost, zinc oxide (ZnO) and silver oxide (Ag_2O) have received a great deal of attention in materials research. Although titanium dioxide (TiO_2) is the most commonly used effective photocatalyst for a wide range

of organic compound degradation, ZnO and Ag_2O are suitable alternatives for TiO_2 because their photo-degradation mechanism is similar to that of TiO_2[12]. Furthermore, the optimum pH reported for a ZnO process is close to neutral, whereas the optimum pH for TiO_2 lies primarily in the acidic region. Hence, the ZnO process is more economical for the treatment of industrial effluents.

Over the past decade, more and more industries have adopted photocatalytic technology. Compared with the equipment used for traditional oxidizing, photocatalysis is easier to operate. Photocatalysts can also be used under room temperature with no need of subsequent treatment; this process consumes less energy and costs less as well. Photocatalysts have been widely used; for instance, they serve as construction materials, such as ceramic tiles, concrete, mortar, plaster, and so on.

The main objectives of this study are : (1) to evaluate the optimal disinfection conditions of bacteria by sodium light with smectite catalysts and (2) to explore the mechanism of disinfection and compare its efficacy between two kinds of smectite catalysts (smectite-Ag and smectite-Zn) added in different proportions of photocatalysts under visible light. The results of this work can, thus, provide a theoretical basis for the photocatalytic disinfection of persistent surface water.

Experimental

Fig. 1. shows the flowchart related to the experiment.

Test reagents :

This study adopts the following reagents : silver nitrate, JJT Baker reagent; zinc chloride, Merck reagent, GR grade; potassium dihydrogen phosphate (KH_2PO_4), Merck reagent, GR grade; magnesium chloride ($MgCl_2.6H_2O$), Merck reagent; and Tryptone Glucose Extract Agar (TGE-Agar), Merck reagent, GR grade.

Purification and preparation of saturated Na-smectite :

Take the appropriate amount of the commercially available smectite clay. Soak the smectite clay in water for a few days until it is completely inflated. Take 250 mL of smectite clay suspension and filter out the sand. Add 1 L of deionized water, shake with a stirrer, and then let it sit. Pump the top 10 cm of suspension into a cylinder for high-speed centrifuging. Add 10 mL of NaCl to the smectite clay obtained from centrifuging and stir continuously for eight hours. And then add twice of 20 mL of deionized water to remove the impurity in solution. Wash off the extra chlorine ions in the clay particles with 50% ethanol. Finally, after freezing dry, saturated smectite clay is ground into power and it becomes sodium saturated smectite clay.

Preparation of smectite catalysts :

Prepare 0.1 N $AgNO_3$ and 0.1 N $ZnCl_2$ and then add into 2% clay. Use boiling water bath treatment to maintain the temperature at 40 °C and stir evenly for 48 h. Stir at 80 °C for another 2 h and discard the upper liquid. Freeze-dry the modified smectite-Ag catalysts and smectite-Zn catalysts and take them out for grinding. Then, sinter the clays at 400 °C for 2 h in a high-temperature furnace. When they return to room temperature, they will become smectite-Ag catalysts and smectite-Zn catalysts.

Function group authentication based on Fourier Transfer Infrared Spectroscopy (FTIR) :

A Fourier Transfer Infrared Spectrometer (FTIR) is adopted in this study for analysis to make use of the movement or vibration of molecular structures to absorb radioactive rays of the same frequencies. The fingerprint area and eigen-area of the FTIR can be used to determine the homeotype substitution of the clay particle catalysts and the existence of organic molecules.

Place the clay particle catalyst and the KBr powder in the oven separately for 48 h. After drying up the clay particle catalyst and the KBr powder for 48 h, mix them at a ratio of 1 : 10, and then grind them in an agate mortar. Afterwards, produce a transparent sheet by using an oil presser with 10 tons of pressure. Then put the transparent sheet on the spectrometer to scan from 4000 cm^{-1} to 400 cm^{-1} for analysis.

Experiment on photocatalytic inactivation :

The experimental system of this study makes use of surface water in a sealed wooden box. With the sodium light and various clay particle catalysts, we address and compare the inactivation efficiency of each clay particle catalyst in the surface water. This study uses a low-voltage sodium lamp as the lighting source, and the low amount of sodium contained in the lamp begins to evaporate into gas and generate light within a few minutes after electri-
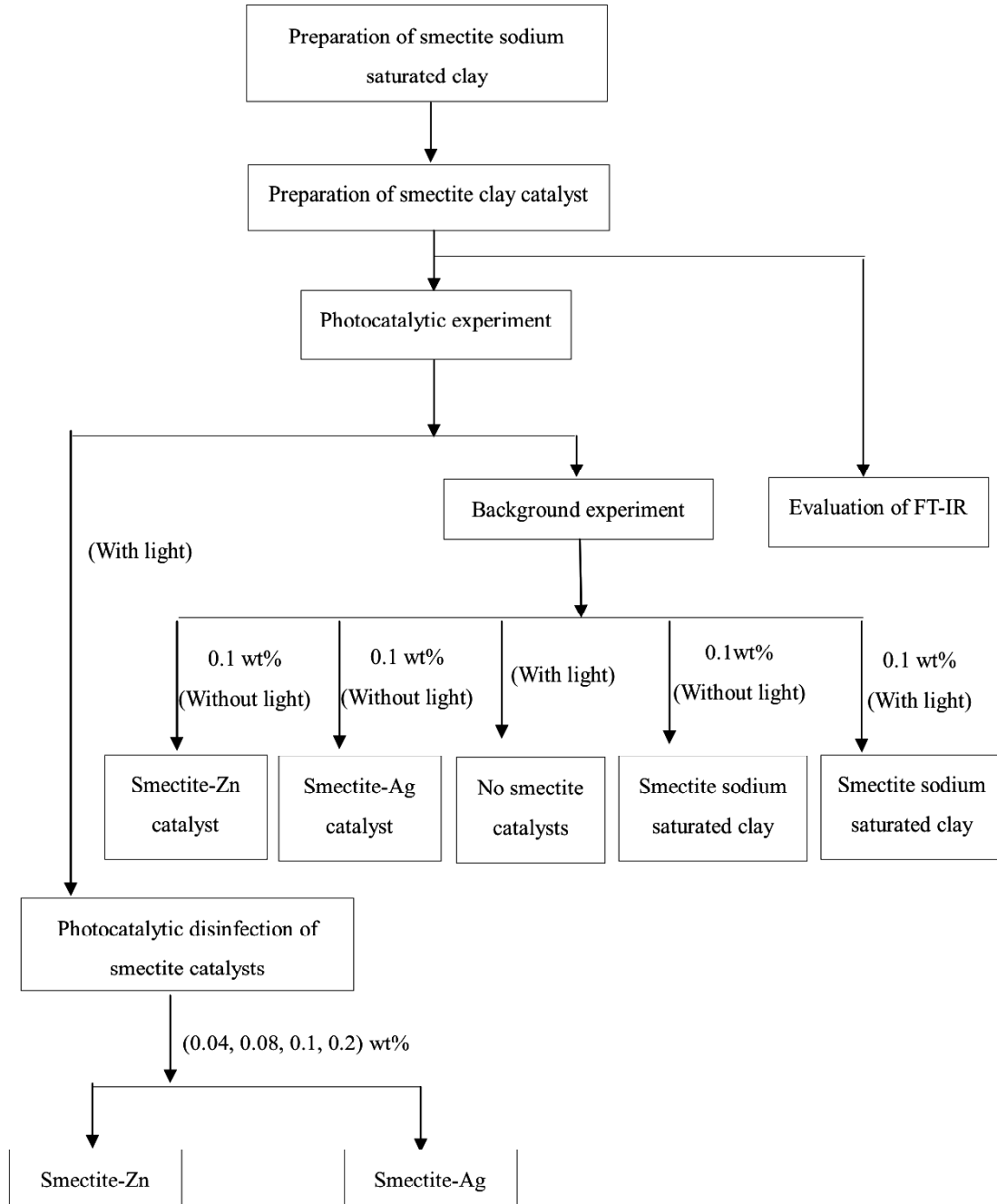
Fig. 1. Experimental flowchart of this study.

city is connected. The wavelength of sodium light is about 589.44 nm, which is close to the yellow color. The power of the lighting source of a sodium lamp ranges from 0 W to 400 W as the voltage ranges from 0 V to 260 V. The experiment are conducted according to the following steps : pour 50 mL of surface water into the beakers and add smectite catalysts with 0.04, 0.06, 0.1 and 0.2 wt%, respectively. Cover the openings of the beakers with aluminum foils and fiercely vibrate the beakers to evenly disperse the smectite catalysts in the surface water. Then, put the beakers inside a sealed wooden box and expose the beakers to the sodium light of 146 watts for 0, 20, 50,

100, 150 and 200 min. At the end, take out the abovementioned surface water containing the cultured bacteria and calcualte the amount of bacteria.

Total Bacterial Count (TBC) :

This study adopts the spread plate method to detect the Total Bacteria Count (TBC) in the water[13]. The steps of spread plate method are explained as follows :

(1) Dilution has to be carried out according to the possible range of microorganisms in the water sample; take out 10 mL of water by the micropipette aspiration technique (MAT) and mix it with 90 mL of water to form a 10-fold diluted water sample. Take the 10-fold diluted water sample to make a 100-fold dilution water sample as well as another 1000-fold dilution water sample and mix them well.

(2) Use a 1 mL micropipette to take 0.2 mL of the original water and water samples at different dilution levels on the culture mediums. Make duplicate samples for each of the dilution levels.

(3) Put a bending glass rod on the culture mediums and rotate the culture medium with hands to spread water samples evenly on the medium surface.

(4) Put the culture mediums upside down in a culture box at the temperature of 35 ± 1 °C for 48 ± 3 h.

(5) Calculate and record the count of cultured bacteria; if the count is hard to trace, then it can be marked with TNTC (too numerous to count).

Assessment of pseudo-first order kinetic model of heterogeneous photocatalytic system :

This study adopts pseudo-first order kinetic model to examine the inactivation effect of bacteria after inactivation by two types of photocatalysts under exposure to a sodium light and sunlight; the reaction equation is shown below :

$$\ln\left(\frac{C}{C_0}\right) = -k \times t$$

where, C_0 : bacteria's initial concentration (CFU/100 mL), C : bacteria's concentration after the inactivation reaction (CFU/100 mL), k : constant of reaction speed (min^{-1}) and t : reaction time (min).

Results and discussion

Evaluation of the FTIR results :

Fig. 2 shows the evaluation of the FTIR results for smectite clay minerals. In the $415 \sim 600$ cm^{-1} and $750 \sim 1170$ cm^{-1} ranges of the fingerprint areas, there are
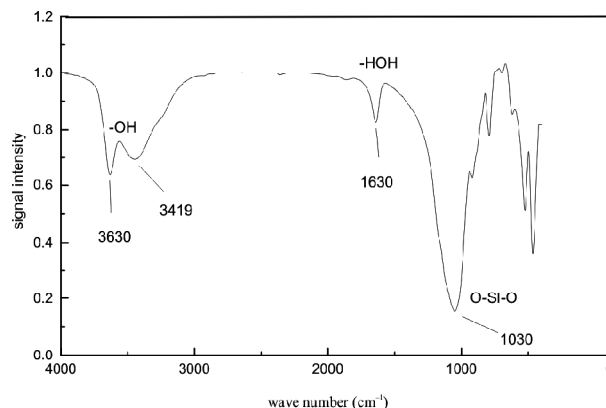
Fig. 2. FT-IR graph for smectite clay.

some significant and complicated wave peaks indicating strong bonds between impure silicates (Si-O) and pure silicates (O-Si-O). Because part of the Si^{4+} ions are replaced by the Al^{3+} ions inside of the silicate layer (tetrahedral), and many metallic ions enter the metallicion layer (octahedral) causing •OH radicals to bend, vibrate and generate different absorption characteristics. If the octahedral contains only aluminum, the absorption peak would be about 920 cm^{-1}. If the octahedral contains only iron, the absorption peak would be about 820 cm^{-1}. If the octahedral contains a combination of iron and magnesium, the absorption peak would reach $820 \sim 920$ cm^{-1}. Judging from the absorption region, we find that breakage and shifting occur in •OH radicals when the absorption peak ranges between 3200 cm^{-1} and 3700 cm^{-1}, and Al will appear to replace Si in the tetrahedron. Fig. 3 and Fig. 4 indicate smectite clays modified with Ag$^+$ and Zn^{2+} and the FTIR is introduced to conduct analysis after formation of smectite catalysts. The figures tell us that after sintering at 400 °C for 2 h, the structures of smectite catalysts remain intact with original absorption characteristics of the clay minerals.

Photocatalytic background experiment :

These experiments are conducted under a photocatalytic background to address the influential level of photocatalysis on the surface water. Background experiments
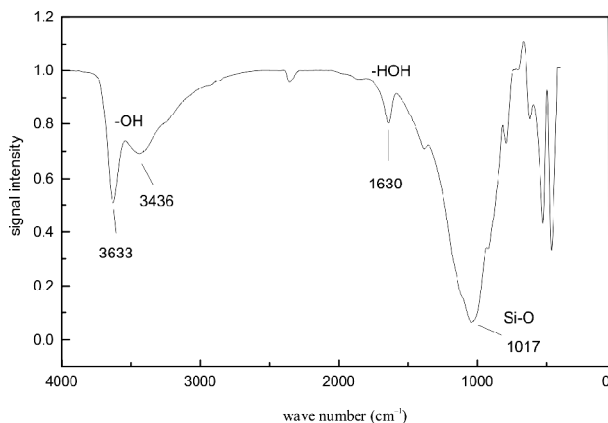
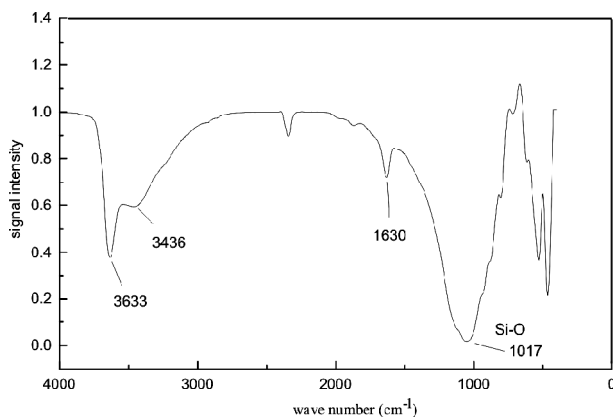**Fig. 3.** FTIR graph for smectite-Ag catalyst.

Fig. 4. FTIR graph for smectite-Zn catalyst.

include : (1) adding 0.1 wt% saturated Na-smectite with or without exposure to sodium light to verify inactivation effects; (2) adding no smectite catalysts with exposure to sodium light and (3) adding 0.1 wt% smectite-Ag catalysts and smectite-Zn catalysts in the dark to evaluate inactivation effects. These experimental results prove that after exposure to the sodium light for 200 min, the temperature of the surface water increases to 45 °C, and it is impossible to kill all bacteria. That is to say, with less than 200 min of lighting from a sodium lamp, there is no significant change to the bacteria in the surface water, and the bacteria remain at the same quantity. The effects of the three factors above shall, therefore, be ignored.

Inactivation effects of smectite-Ag catalysts with different weight percentages :

Fig. 5 shows the inactivation effects of smectite-Ag catalysts with 0.04, 0.06, 0.1 and 0.2 wt%. In this fig-
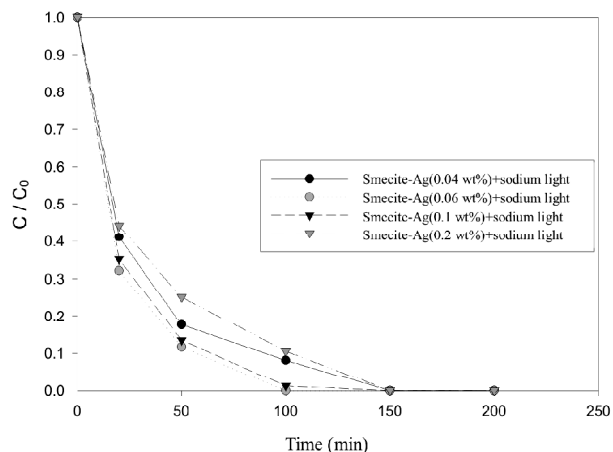

Fig. 5. Photocatalytic comparison by sodium light using smectite-Ag catalysts with different weight percentages.

ure, C_0 refers to the total amount of bacteria in the water before a photocatalytic reaction occurs; C indicates the total amount of bacteria in the water after the reaction occurs.
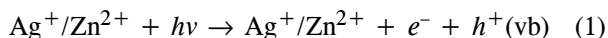
This study also makes use of pseudo-first order[14,15] to address the inactivation ratio of each smectite catalyst, and Table 1 shows the photocatalytic reaction constant, k, of each smectite catalyst. Experimental results demon-

Table 1. Photocatalytic inactivation reaction constant comparison by sodium light using smectite-Ag catalysts of different weight percentages
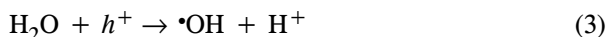
Catalysts	k (min^{-1})
Smectite-Ag (0.04 wt%)	0.0348
Smectite-Ag (0.06 wt%)	0.0430
Smectite-Ag (0.1 wt%)	0.0401
Smectite-Ag (0.2 wt%)	0.0277

strate that the best results lies in the smectite-Ag catalyst with 0.06 wt%, where k = 0.0430 min^{-1}; the second best results lies in the smectite-Ag catalyst with 0.1 wt%, where k = 0.0401 min^{-1}. When a smectite-Ag catalyst with 0.06 wt% is exposed to the sodium light for 100 min, the inactivation effects will reach 100% and then drop to 97.48% for 200 min. Ag catalyst has good inactivation effects because bacteria have mechanisms and functions of auto-defense and auto-repair[16,17]. In an ideal growing environment, bacteria undergo a great amount of replication, whereas in a poor growing environment, cells inside the microorganism will activate their auto-defense and auto-repair functions to resist damages. When being

exposed to sodium light, particles of a smectite catalyst are excited to process photocatalysis; at this moment, the energy of catalyst particles is enhanced due to the exposure to light. That results in a transition to transmit the valence band to a conduction band and generate a hole, h^+, and an electron, e^-.

$$Ag^+/Zn^{2+} + h\nu \rightarrow Ag^+/Zn^{2+} + e^- + h^+(vb) \quad (1)$$

Take the Ag catalyst as an example : On the surface, the hole interacts with OH^- and H_2O to form $^\bullet OH$ radicals.

$$OH^- + h^+ \rightarrow {^\bullet OH} \text{ or } e^- + O_2 \rightarrow {^\bullet O_2^-} \quad\quad (2)$$

$$H_2O + h^+ \rightarrow {^\bullet OH} + H^+ \quad\quad\quad (3)$$

$^\bullet OH$ radicals and O_2^- radicals are very active; in particular, $^\bullet OH$ radicals are extremely toxic and has the ability to inactivate organisms[15]. Ag catalyst has a self-catalytic function, and sodium light excites the catalyst particles to conduct photocatalysis; therefore, when exposed to sodium light in surface water, Ag catalyst releases $^\bullet OH$ radicals to oxidize microorganisms and generate cell toxicity to damage the cell structures and internal compositions[18,19] to disturb the composition of proteins. It results in overall oxidation cleavage and weaker self-defense and self-repair abilities. The longer it is exposed to the lighting source, the less ability it has to achieve inactivation effects. Thus, Fig. 5 shows that a smectite-Ag catalyst with 0.06 wt% is able to kill all bacteria after being radiated in sodium light for 100 min. It is proven that Ag is a good catalyst to achieve the inactivation effects in surface water.

Inactivation effects of smectite-Zn catalysts with different weight percentages :

Fig. 6 compares inactivation effects of smectite-Zn catalysts with different weight percentages of 0.04, 0.06, 0.1 and 0.2 wt%. Experimental results demonstrate that a smectite-Zn catalyst with 0.04 wt% have been proven to exhibit the best inactivation effects, followed by a smectite-Zn catalyst with 0.06 wt%. Smectite-Zn catalysts with 0.06 wt% and 0.1 wt% reach the same inactivation efficiency after 200 min. The curve of inactivation efficiency in the experiments indicates that, along with the increase of radiation time, the curve grows slowly; this result corresponds to the findings of previous literature[20,21] : two inactivation rates appear in the group of Zn catalysts. During photocatalysis, a Zn catalyst releases
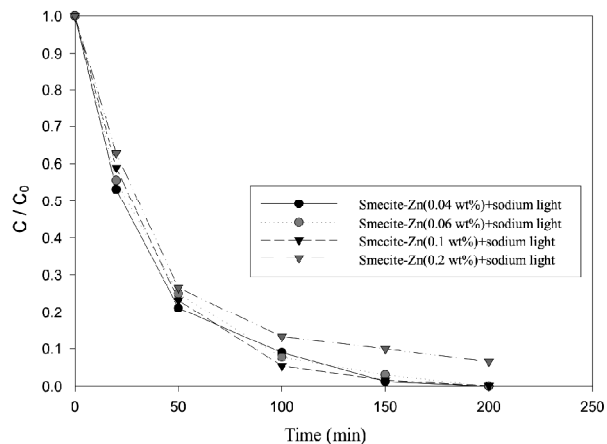

Fig. 6. Photocatalytic comparison by sodium light using smectite-Zn catalysts with different weight percentages.

intermediates that compete with $^\bullet OH$ radicals for reaction sites and reduce the sites for catalytic activities, sites for the absorption of water molecules and oxygen molecules, as well as the generation of holes. Consequently, it reduces the reaction rate of target products on the surface of Zn catalysts, which results in slower growth of inactivation in the latter part of the reaction curve. From the inactivation curve in Fig. 6, we find that after 100 min, smectite-Zn catalysts with different weight percentages exhibit a decreasing trend. Another possible reason is that due to high photo-activation of $Zn^{20,22}$, it is easy to see fewer bacteria in surface water flow to reaction sites with the same reaction time. This can be easily observed in a catalyst with 0.2 wt% (k = 0.0136 min^{-1}). It is shown that the greater the weight percentage of a Zn catalyst, the more easily it will result in a shielding effect, for intermediates to compete for $^\bullet OH$ radicals with target products and cause poor inactivation effects.

Table 2 of the photocatalytic reaction constant of the pseudo-first order kinetic model indicates that a smectite-Zn catalyst with 0.04 wt% (k = 0.0293 min^{-1}) works

Table 2. Photocatalytic inactivation reaction constant comparison by sodium light using smectite-Zn catalysts of different weight percentages

Catalysts	k (min^{-1})
Smectite-Zn (0.04 wt%)	0.0293
Smectite-Zn (0.06 wt%)	0.0234
Smectite-Zn (0.1 wt%)	0.0207
Smectite-Zn (0.2 wt%)	0.0136

best for inactivation : 1.25 times, 1.42 times and 2.15 times better than those with 0.06 wt% ($k = 0.0234$ min^{-1}), 0.1 wt% ($k = 0.0207$ min^{-1}) and 0.2 wt% ($k = 0.0136$ min^{-1}) respectively. Because the photocatalytic reaction constant shows a decreasing trend of inactivation efficiency along with the increased amount of catalysts caused by the reaction mechanism and shielding effect during a catalytic process, the greater the amount of catalysts added, the greater the influence becomes.

Conclusion

The FTIR analysis finds the modified smectite catalysts with undamaged clay mineral structures and original absorption characteristics. Due to the semiconductor properties of synthesized smectite catalysts, when exposed to sodium light, catalyst particles are excited for photocatalysis, thereby achieving inactivation.

In this study, experimental results prove that a smectite-Ag catalyst with 0.06 wt% works the best for inactivation, followed by a smectite-Ag catalyst with 0.1 wt%; smectite-Zn with 0.04 wt% has the highest efficiency and 0.06 wt% ranks second highest. Finally, the photocatalytic reaction constant in this study clearly shows that when the concentration exceeds 0.1 wt%, the inactivation efficiency is reduced owing to the shielding effect.

Photocatalytic inactivation is heterogeneous and its reaction can speed up only at activated sites. Under sodium light, the formation of hydrated electrons and $^{\bullet}$OH radicals helps inactivation of bacteria. Hence, if proper conditions for photocatalysis are provided; it would effectively eliminate germs. When research is conducted on semiconductor photocatalysis inactivation, photoelectrons and photogenerated electron-hole pairs are formed because excitation occurs once catalysts are exposed to the sun. These electrons and hole pairs react with water, so an $^{\bullet}$OH radical is generated. Then, the $^{\bullet}$OH radical reacts with cell walls, cell membranes and other substances inside the cells, inactivating cells and accomplishing effective inactivation.

The main purpose of this study was to modify smectite clay minerals by using two kinds of metallic cations that cover the surface with Ag^+ and Zn^{2+}. After modification, they form smectite clay catalysts. When these clay catalysts are illuminated by a sodium light, they can pro-

duce photocatalytic reaction and achieve a inactivation effect. Photocatalysis can be activated directly by solar energy (visible light), so it is an ideal technology in the global limelight for dealing with environmental pollution and generating clean energy. The results of this work can, thus, provide a theoretical basis for the photocatalytic inactivation of persistent surface water.

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