J. Indian Chem. Soc.,
Vol. 91, September 2014, pp. 1-13

The photocatalytical degradation of trichloroethylene in water by reaction board using clay catalyst

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Manuscript received online 02 March 2014, revised 27 March 2014, accepted 06 April 2014

Abstract : This study uses reaction boards as a smectite catalyst immobilization carrier as well as degradation generated with photocatalytic action to degrade pollutants contained within chlorine-Trichloroethylene (TCE). After a FT-IR analysis, this study finds that smectite catalysts have significant and complicated wave crests between the fingerprint area with wave numbers of 415 ~ 600 cm^{-1} and 750 ~ 1170 cm^{-1}, indicating the existence of a strong bond between impure silicates (Si-O) and silicates (O-Si-O).

Before photocatalytic action, background absorption was conducted and the results indicate that without exposure to a sodium light source, the limited effect of smectite catalysts on the absorption of 4-CP is identified. The optimal degradation efficiency of TCE is found with the addition of a 0.08% catalyst with smectite-Ti and smectite-Zn as well as 0.1% of smectite-Ag. When the addition of smectite catalysts exceeds 0.1% of weight, the degradation efficiency of TCE will be reduced suggesting the more likely shielding effect yielded by the addition of more smectite catalysts. In terms of TCE mineralization, a significant decreasing trend is shown at the beginning but grows slowly after degradation at 180 min.

At present, a heterogeneous photocatalytic system has been fully applied for use in daily life with its efficiency determined by the free radical action of electrons and holes, the generation efficiency of •OH. Furthermore, the pH level in the solution affects the feature of the photocatalytic surface and changes its absorption feature. These issues require more in-depth discussion in future studies on heterogeneous photocatalytic systems.

Keywords : Smectite catalysts, photocatalytic reaction, trichloroethylene, degradation.

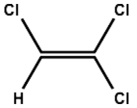
Introduction

In recent years, using a semiconductor as the photocatalyst to degrade various organic and inorganic pollutants in wastewater has become a type of water treatment technology with the best prospect of exploitation and utilization[1–5]. Since pollutants could be completely degraded into harmless matter by the photocatalysis method under room temperature and air pressure, scientists predicted that in the near future photocatalysis will become one of the most effective means in dealing with various kinds of industrial wastewater[6–11]. Among various oxide semiconductor photocatalysts, TiO_2 has proven to be the most suitable for widespread environmental applications due to its biological and chemical inertness, strong oxidizing power, low cost, and long-term stability against photocorrosion and chemical corrosion[12–14].

When a photocatalyst is used to treat pollutants in the water, it helps to degrade pollutants in wastewater completely via oxidation. However, more time and effort are required to separate water treated with nano photocatalysts. During practical applications, general photocatalysts are immobilized to solve the concerns of repeated use and separation. Basis materials generally include: glass, ceramic tile, metal, filters, fiber, and plastic. Because of the non-adherence of nano catalysts, an adhesive (such as epoxy resin, PVC, and waterproof lacquer paint) is often needed for catalyst immobilization. Although nano catalysts may break some basis materials or binders, separation between photocatalysts and basis materials is required and a proper adhesive shall be used[15–17]. Photocatalysts after immobilization sometimes only need to be dried or heated to complete the required crystalling phase and composition or adhere to basis materials.

Moreover, many photocatalyst systems have been proposed in literature[18,19], such as SnO_2, TiO_2, and ZnO. Among these systems, TiO_2 is the one with the most potential for practical applications. TiO_2-based photocatalysis could directly photodegrade organic pollutants (e.g. alkanes, alcohols, phenols, dyes and pesticides) into CO_2, H_2O and innocuous inorganic species[14,20,8]. However, due to the high value of the TiO_2 band gap (E_g = 3.2 and 3.0 eV for anatase and rutile phases, respectively), the TiO_2 photocatalyst could only be activated by ultraviolet radiation (the wavelength of which is < 387 nm), and only 4–6% of the solar radiation reaching the earth is available[21].

Trichloroethylene (TCE) is a volatile, halogenated organic compound that was once a widely used degreasing agent. TCE is also a popular industrial solvent that is colorless, poisonous, transparent, fluid, non-inflammable, volatile, and an aromatic solution. It anesthetizes the nerves. Two decades ago, over 200 million pounds of TCE were produced in the United States each year[22]. Although the majority of TCE lost to the environment is due to volatilization, large plumes of TCE have been reported in various groundwater systems[23]. Since concentrations of TCE can be above the solubility limit in water (1000–1100 ppm), a majority of TCE is often present in the form of a dense, nonaqueous phase liquid (DNAPL), particularly at high depths. The molecular structure of TCE is shown below :



Bentonite is a term in petrology because it is named after the Fort Benton Formation in Rock Creek, Wyoming. Bentonite, montmorillonite, and smectite have different definitions. They are alternatively used, but in fact, they are different. Bentonite mainly contains montmorillonite, a type of clay mineral of the Smectite series. The smectite series, according to the position of its metal ion, can be categorized into montmorillonite, saponite, and nontronite (montmorillonite belongs to the smectite series). This study uses montmorillonite of the smectite series. This study discusses the addition of various types of adjusted smectite catalysts to TCE from the application of a heterogeneous photocatalytic; meanwhile, exposure to visible light (sodium lamp) is introduced in order to observe the degradation efficiency of TCE for the evaluation and comparison of the best suitable mix proportion of smectite catalysts at different degradation speeds and weight percentages as well as the understanding of the TCE efficiency of wastewater treatment via smectite catalysts.

Experimental

Experiment reagents :

Trichloroethylene (99.5%, J. T. Baker Chemical Co.); methanol (99.7%, Merck); $TiCl_4$ (99%, Showa); $ZnCl_2$ (96%, Merck); $AgNO_3$ (99.8%, Merck).

Experiment devices :

(a) Photocatalytic reactor : This study uses a low voltage sodium lamp as a source light with a wave length of 589.44 nm and distance range between 0 ~ 400 W (100 W in this study). The sodium lamp is placed inside an airtight wooden box with a length and width of 75 cm and 33 cm, respectively.

(b) High-performance liquid chromatography/UV-Vis detector (Hitachi, L-2420) : This is used to measure the concentration of TCE. The mobile phase is methanol : ultra pure water (80% : 20%), water flow speed of 1 mL/min, column dimension of RP18 (MIGHISIL) and wavelength of detection of 240 nm.

(c) Analysis of total organic carbon :

This study uses a Total Organic Carbon Analyzer (model number TOC-50000) manufactured by Shimadzu of Japan to measure the concentration levels of organic and non-organic carbon in the samples. After photocatalytic degradation, surface water generates final products such as inorganic carbon. Researchers, thus, use the relationship between organic carbon and inorganic carbon to show concentration changes in surface water after disinfection.

Fourier-transform infrared spectrometer – Function group authentication :

A Fourier-transform infrared spectrometer (FT-IR) is adopted to analyze the move or vibration of molecular structures that absorb radiation with the same frequency[24]. The fingerprint area and Eigen-area of FT-IR are used to determine the homeotype substitution of the clay catalyst and the existence of organic molecules.

Place the clay catalyst and KBr powder in the oven separately to dry for 48 h and mix them at 1 : 10, and then grind them in an agate mortar. Use an oil presser to produce a transparent sheet with 10 tons of high pressure and put it on the spectrometer to scan from 4000 cm^{-1} to 400 cm^{-1} for analysis.

X-Ray diffraction analysis, XRD :

X-Ray diffraction analysis utilizes an X-ray diffractometer coded with Rigaku RINT 2000[19]. CuK_{α} is used as a photo source to separately analyze the crystalline forms of smectite clay and the other three smectite catalysts after modifications in order to explore the layer spacing for these materials. The wavelength of the X-ray produced is 1.5418 Å and 10 mA for testing operational current, 20 kV for voltage, and 5 deg/min for a scanning rate with a scanning angle of $2\theta = 2 \sim 40^{\circ}$.

Measurement of the specific surface area :

Ethylene glycol is used to measure the total specific surface area of smectite clay and smectite catalysts. The followings are the steps of this experiment : place 0.5 g catalyst on an aluminum plate and leave it is still in a P_2O_5 drying box after vacuuming for one hour; weigh the sample on a gauge and obtain W_1. Drip 1.5 mL of ethylene glycol on the sample and place the sample still on the $CaCl_2$ drying box after vacuuming for 45 min to achieve the balance level. Then obtain W_2 for the measurement of the specific surface area of the sample.

$$A = \frac{W_a}{(W_s \times K)} \tag{1}$$

A : Specific surface area (m^2/g); W_a ($W_2 - W_1$) : Difference of the weight before and after absorption of ethylene glycol; W_s : Weight (g) before absorption of ethylene glycol; K : 0.00031.

Source and purification of sodium saturated smectite clay[25] :

The main clay photocatalyst carrier, which is modified, comes from Wyoming smectite minerals. Wyoming smectite minerals are from a colloid corporation in the U.S. Its purification steps are as follows : put 60 g smectite in a 2 L beaker, in which 1.8 L deionized water is added to make it fully swollen; obtain 250 mL smectite suspension and filter the sand particles by wet sieve of 300 mesh; move the filtered liquid to the 1 L settling cylinder and add the deionized water to 1 L; rigorously churn it with the agitating vane and then keep it so still as to make it settle down naturally; pump the top 10 cm of suspension in the cylinder for high-speed centrifuging. Then add the proper amount of NaCl to the smectite clay obtained from centrifuging and stir continuously for eight hours; wash off the extra chlorine ions in the clay particles with 50% ethanol. Finally, after freezing dry, ground the saturated smectite clay into power and it becomes sodium saturated smectite clay.

Preparation of smectite catalysts :

Smectite catalysts are prepared as follows : separately prepare the 0.1 *N* $AgNO_3$ solution, 0.1 *N* $ZnCl_2$ solution, and 0.1 *N* $TiCl_4$ solution at 100 mL each (i.e. take 2 g of smectite sodium saturated clay into 100 mL solution), keep the temperature at 40 °C with a water bath; agitate it evenly for 48 h and then churn it evenly at 80 °C before putting it still by the upper layer solution; remove the extra chlorine ions with 50% ethanol; dry the finished smectite catalyst by freezing and drying; take it out, grind it and sinter it for two hours in the calcination furnace at 400 °C. When the temperature is lowered to room temperature (25 °C), the smectite catalysts will be obtained after grinding.

Photocatalytic experiment procedure :

Background absorption of smectite catalysts :

TCE at proper concentration level is prepared and various smectite catalysts are added (at 0.1 wt%); the absorption experiment is conducted to examine the adhesive characteristics of TCE to various smectite catalysts during action without exposure to the sodium light source.

The best suitable mix proportion of smectite catalysts, degradation efficiency and mineralization.

Three different types of smectite catalysts with various weight proportions of 0.05, 0.08, 0.1 and 0.5% are added to a TCE solution. Under the sodium lamp at 589 nm, TCE degradation at different intervals is observed to identify the best suitable mix proportion as well as their degradation and mineralization. The maximum power of the sodium lamp is approximately 100 watts (68,300 Lumen).

Photocatalytic degradation experiment of smectite catalyst immobilization :

Clear paint is sprayed on a chemical resistant reaction board. Prepared smectite catalysts are poured on a mesh filter. Smectite catalysts are evenly distributed on the board through patting. After drying, smectite catalysts are added to the TCE solution. A sodium lamp with 589 nm is used for the facilitation of the photocatalytic reaction.

Results and discussion

Result of FT-IR evaluation :

Fig. 1 shows the evaluation of the FT-IR result of the smectite mineral. In the range of 415~600 cm^{-1} and 750~1170 cm^{-1}, there are some significant and complicated wave peaks indicating strong bonds between impure silicates (Si-O) and silicates (O-Si-O). Because of the inside silicates layer (tetrahedral), part of Si^{4+} is replaced by Al^{3+} and many metal ions in the metal ion layer (octahedral) enter the inner layer to promote bent and vibration of -OH and to form different absorption characteristics. If only aluminum is found on the octahedral, then the absorption peak will reach 920 cm^{-1}; while iron will reach approximately 820 cm^{-1} and the combination of iron and magnesium will reach 820~920 cm^{-1}. Judging from the absorption region, we find that between the range of 3200~3700 cm^{-1} breakage and shift occur in the -OH absorption peak and Al^{3+} replaces Si in tetrahedral.

Figs. 2 to 4 indicate smectite modified by Ag^{+}, Zn^{2+}, and Ti^{4+}. FT-IR is introduced to conduct analysis after the formation of the smectite catalysts. These figures show that after being sintered at 350 °C for two hours, the structure of the smectite catalysts remains undamaged with the original characteristic absorption of clay minerals.

Result of XRD evaluation :

Fig. 5(a) shows the evaluation of the XRD result of the smectite mineral. The smectite mineral consists of a layered structure[14]. The layers are bounded by the Van der Waals force and there are exchangeable positive ions. Thus, adhesive balance can be reached with an exchange between various positive ions and sodium ions between the layers of the smectite mineral. On the crystallization surface of regularly arranged silicate (001), the angle of diffraction is $2\theta = 6.91°$. By using Bragg's law, $2d \sin\theta = n\lambda$, we acquire the position of the first angle of diffraction as $n = 1$ and λ, and the wavelength of the copper plate material as 1.5405 Å. The results indicate that the layer distance of the smectite mineral at room temperature is 1.2782 nm.

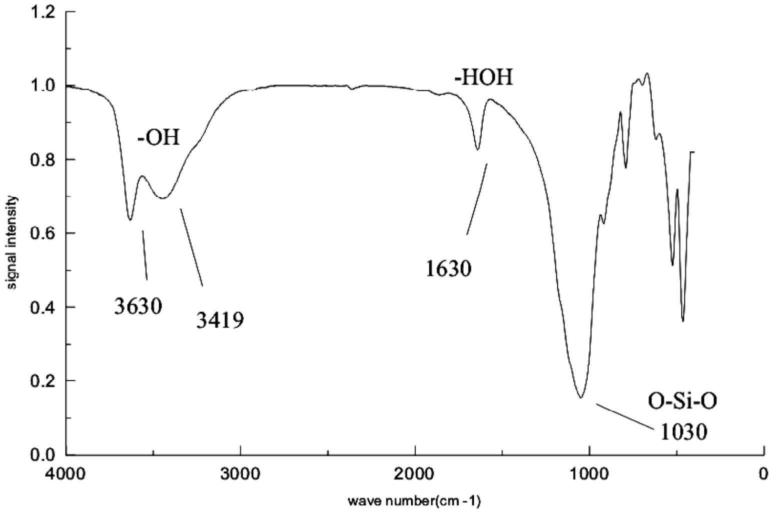


Fig. 1 FT-IR evaluation of smectite.

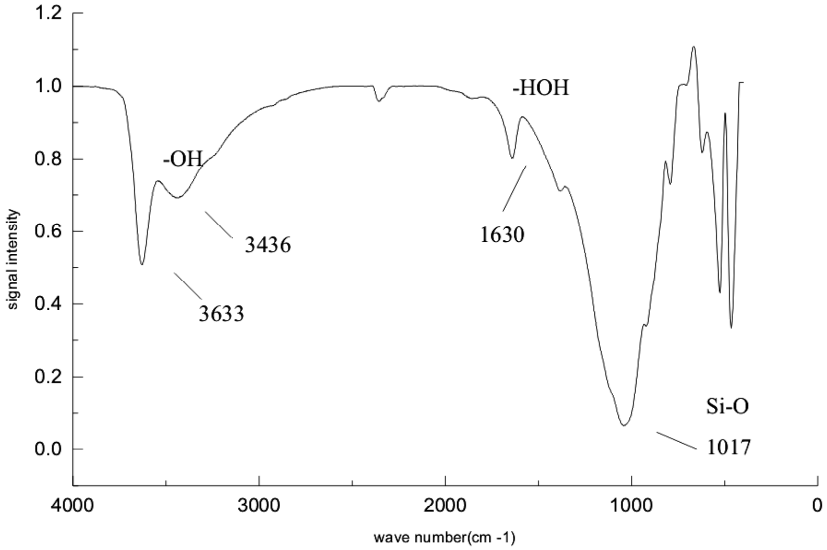


Fig. 2. FT-IR evaluation of Smectite-Ag.

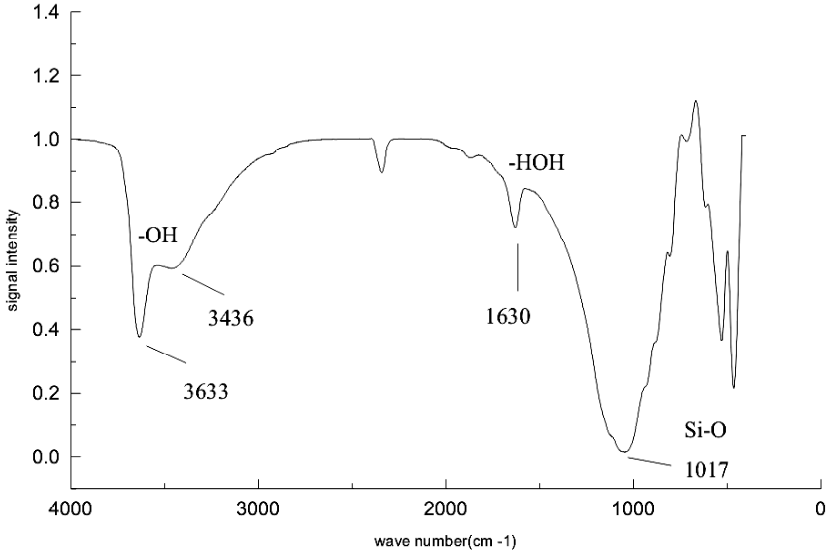


Fig. 3. FT-IR evaluation of Smectite-Zn.

Fig. 5(b) ~ 5(d) show XRD results of various smectite catalysts after grinding at 350 °C. As shown in Fig. 5(b), the layer distance of smectite-Ag is shortened to 1.2653 nm, Fig. 5(c) smectite-Zn to 1.2608 nm and Fig. 5(d) smectite-Ti to 1.2616 nm. Among them, Fig. 5(d) shows a peak of smectite-Ti at 25 °C indicating the main composition of TiO_2. Smectite is an inflating mineral at the moisture ratio of 2 : 1. It is vulnerable to environmental moisture and water molecules can easily exist in the layered structure. After the regulation of various metal ions, layers of smectite then shrink due to the loss of water content.

Determination of the specific surface area of smectite mineral and different smectite catalysts :

This study utilizes ethylene glycol to determine the specific surface area of the smectite mineral and different smectite catalysts. The result is shown in Table 1. The specific surface area of the smectite mineral is bigger

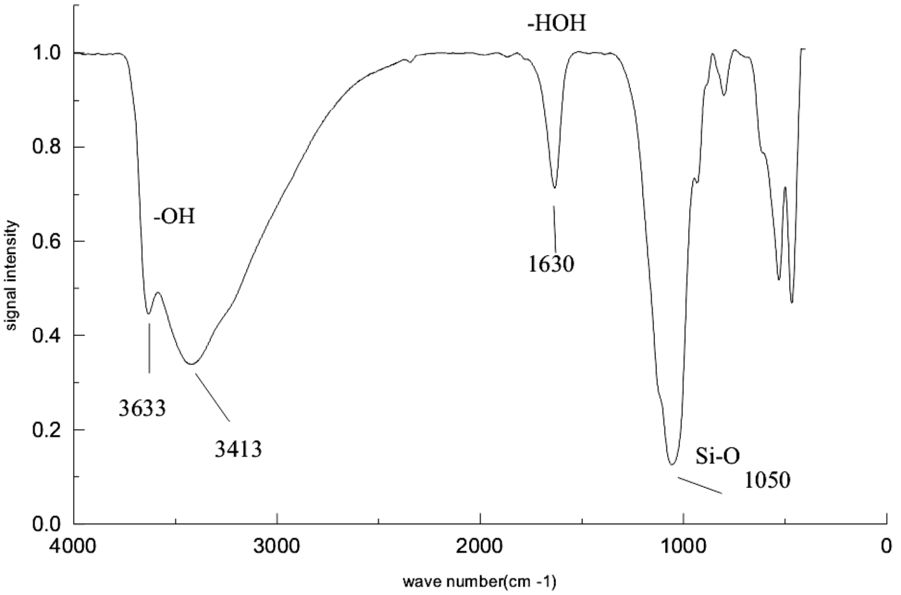
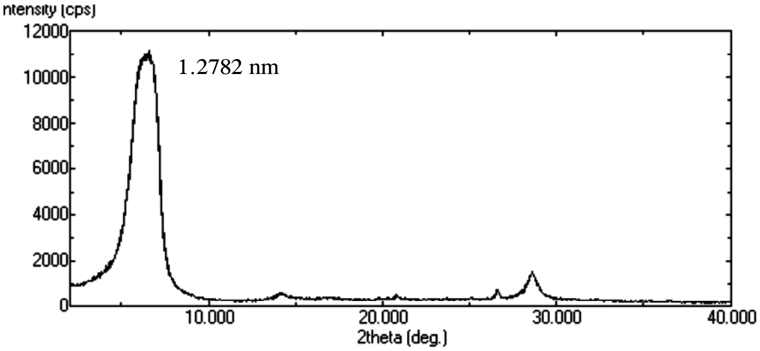
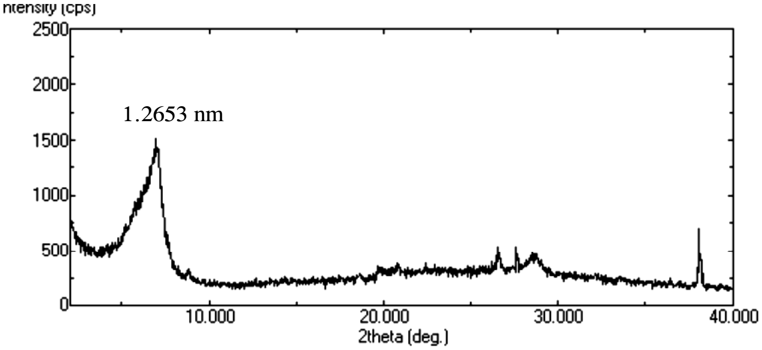


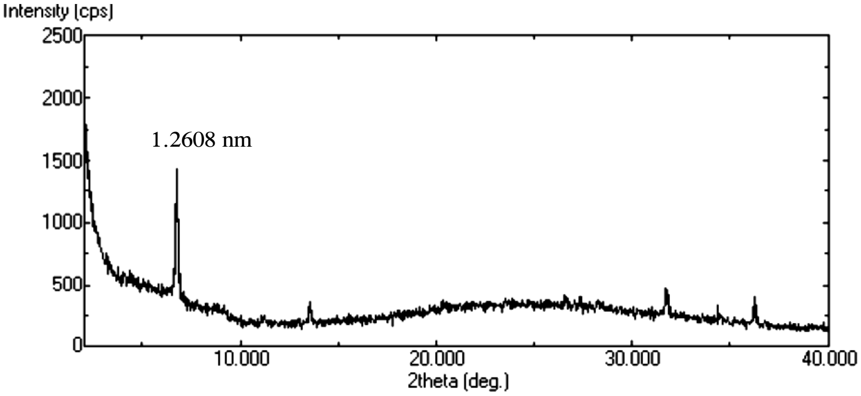
Fig. 4. FT-IR evaluation of Smectite-Ti.



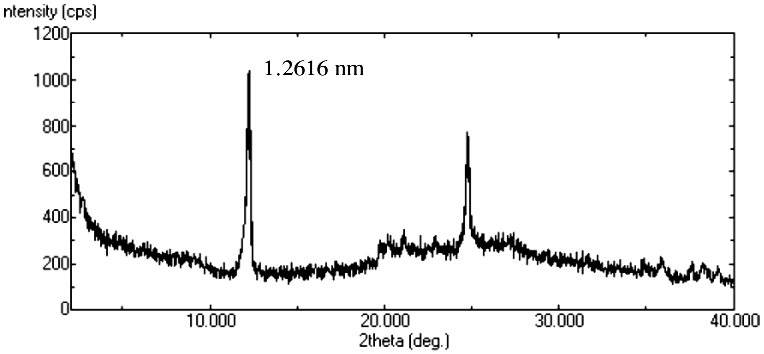
(a) Smectite (without grinding).



(b) Smectite-Ag (grinding at 350 ^{o}C).



(c) Smectite-Zn (grinding at 350 °C).



(d) Smectite-Ti (grinding at 350 °C).

Fig. 5. XRD analysis of smectite mineral and smectite catalysts.

Table 1. Specific surface area of catalyst carrier and clay catalysts

Catalysts	Specific surface area (m^2/g)
Smectite	536 ~ 552
Smectite-Ag	456 ~ 466
Smectite-Zn	493 ~ 508
Smectite-Ti	505 ~ 522

Table 2. Specific surface area of different clay minerals

Types	Researcher		
	Fripiat (1964) (m^2/g)	Greene-Kelly (1962) (m^2/g)	Kohnke (1968) (m^2/g)
Kaolinite	5 ~ 20	14.8 ~ 25	20 ~ 40
Illite	100 ~ 200	150 ~ 250	60 ~ 120
Vermiculite	300 ~ 500	–	–
Smectite	700 ~ 800	600 ~ 700	500 ~ 800

than that of the modified smectite catalysts. The specific surface area of the smectite mineral is 545 m^2/g, which is similar to the result in Table 2[26].

Background absorption experimental results of smectite catalysts :

Fig. 6 shows the background absorption experimental results of smectite catalysts for TCE without exposure to the sodium light source. As indicated in the figure, after an action time of 300 min, due to the lack of exposure to the light source, smectite catalysts are found with limited adhesive results of 4-CP and three types of smectite catalysts demonstrate 8.9 ~ 12.3% of TCE background absorption efficiency.

Photocatalytic efficiency with different percentages of catalysts :

During a photocatalytic reaction, the addition of a catalyst is a very important manipulator. Figs. 7 to 9 show the degradation of three types of smectite catalysts with the addition of different weight proportions after

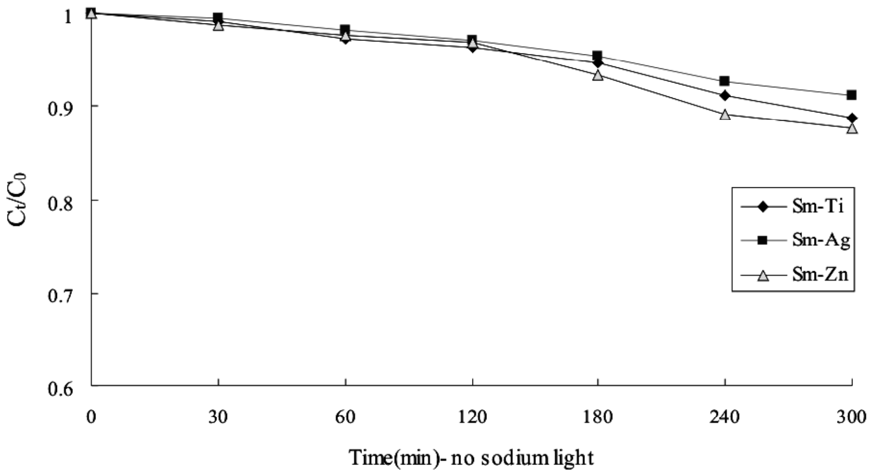


Fig. 6. TEC background absorption experiment of smectite catalysts.

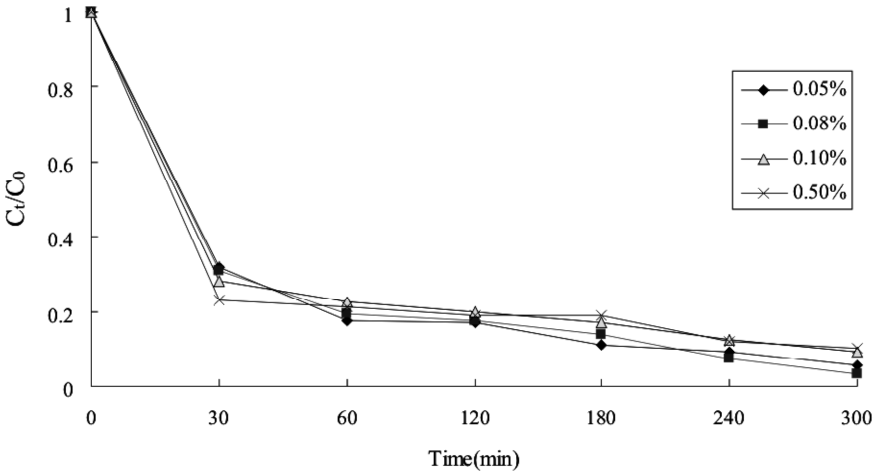


Fig. 7. Degradation efficiency and the best suitable mix proportion of Smectite-Ti to remove TCE.

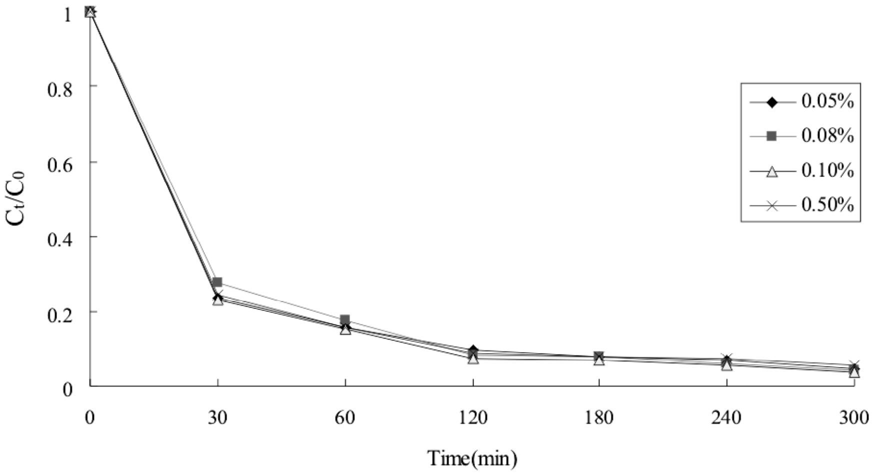


Fig. 8. Degradation efficiency and the best suitable mix proportion of Smectite-Ag to remove TCE.

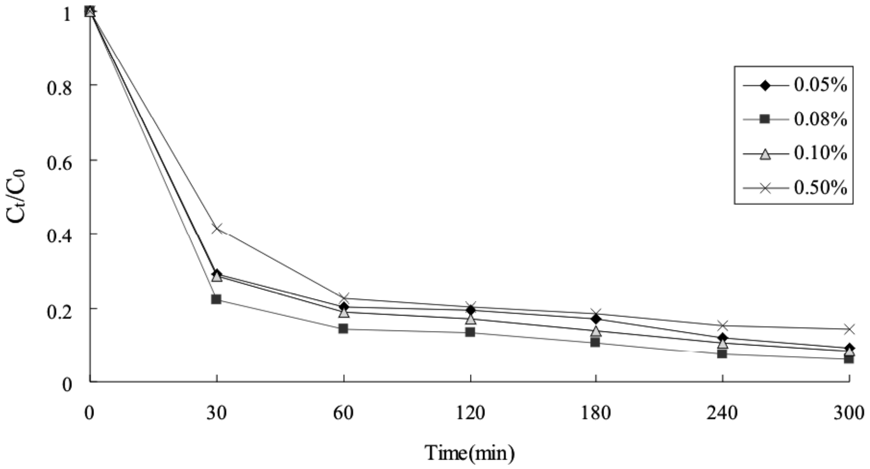


Fig. 9. Degradation efficiency and the best suitable mix proportion of Smectite-Zn to remove TCE.

exposure to light for 300 min. The results indicate that the best suitable mix proportion of Smectite-Ti and Smectite-Zn is 0.08% that can reach to 95% degradation after 300 min of exposure to light. Due to the characteristics of smectite with its large surface area and CEC value[27], the addition of ions such as Ti, Ag and Zn provides an ideal energy gap and conductivity to effectively play the role of a good electron catcher that delays the bonding of an electron-hole pair[28,14,29] and enhances the absorption of the light zone (400 ~ 800 nm)[30,31]. Smectite catalysts, thus, will have a better degradation result. These results also show better degradation for the treatment of chlorinated organic compounds. When the weight proportion of three types of smectite catalysts are higher than 0.1%, the degradation results are poorer indicating that the yield of the shielding effect is derived from additional amounts of smectite catalysts. This is consistent with the finding indicated in the literature review : when the addition of smectite catalysts exceeds 0.1%, a shielding effect will be generated[27]. There are more catalysts irradiated by sodium light, and therefore more catalysts occupy a number of positions that are irradiated by sodium light. This causes less quantity of sodium light to react with TCE. That is to say, theoretically, increasing the amount of smectite catalysts can produce more electrons and •OH free radicals with irradiation, but it also increases the opaqueness of the surface water, and fewer quantities of •OH free radicals will be produced in the surface water during the photocatalytic reaction[32]. In this case, the photocatalytic ability is reduced.

Table 3 shows the degradation constant, speed, and high-time period results. With the best suitable mix proportion of Smectite-Ti, Smectite-Ag, and Smectite-Zn, the half-time periods of TCE degradation efficiency are 0.95 h, 0.83 h and 1.12 h, respectively.

Table 3. Degradation constant, speed, and half-time period of TCE with the best suitable mix proportion of smectite catalysts

Smectite catalyst	Degradation constant	Degradation speed	Half-time period (h)
Smectite-Ti (0.08%)	0.6674	2.54	0.95
Smectite-Ag (0.1%)	0.8338	3.17	0.83
Smectite-Zn (0.08%)	0.6206	2.36	1.12

Mineralization of smectite catalysts with the best suitable mix proportion on TCE :

Under heterogeneous photocatalytic degradation, HPLC analysis is only able to show the initial concentration change of TCE. Therefore, mineralization and dechlorination is required to observe whether TCE can be converted into other compounds. Hydroxyl radicals can degrade pollutant compounds into toxin-free water and carbon dioxide and through TOC monitoring, we are able to understand the degradation of TCE. Fig. 10 shows the mineralization of the best suitable mix proportion of three types of smectite catalysts. The results indicate that mineralization decreased along with the degradation function of waste treatment and the transformation of organic compounds into inorganic compounds[7]. TCE mineralization, however, in the beginning shows a significant decreasing trend and after 180 min of degradation mineralization also grows slowly.

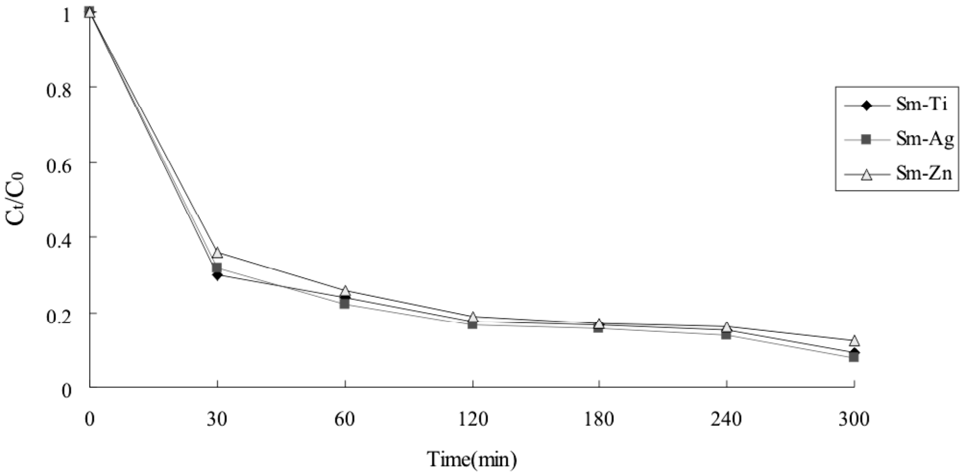


Fig. 10. Mineralization of TCE with smectite catalysts at the best suitable mix proportion.

Figs. 11 ~ 13 observe the existence type of TCE after being degraded with smectite catalysts and then compares the TCE concentration with the TOC. As indicated in the literature review, the bonding capacity of general compounds will impact the removal results. In terms of TCE bonding, the bond cleavage energy required for C-H, C-C, and C-Cl is 98.7, 82.6 and 81.0 Kcal/mol, respectively[33]. TCE during the degradation process forms the bond cleavage from C-Cl, C-C, and C-H to remove pollutant compounds gradually. Therefore, at the beginning, the degradation starts from where TCE exists. It is followed by the transformation from organic carbon into inorganic carbon, the existence area of TOC. This trend holds when TCE experiences a photocatalytic reaction with smectite catalysts such as Smectite-Ti and Smectite-Ag but poorer degradation results with Smectite-Zn. As a result, the residual TCE concentration is higher and the degradation concentration ratio is more likely to exist with TCE.

Degradation efficiency and mineralization of smectite catalyst immobilization :

Figs. 14 and 15 indicate initial testing results of the catalyst immobilization of Smectite-Ti and Smectite-Ag. An insignificant difference in degradation and batch degradation results is observed. After exposure to light after 300 min, the degradation rate is greater than 95% but TOC value first drops and then increases. It is assumed

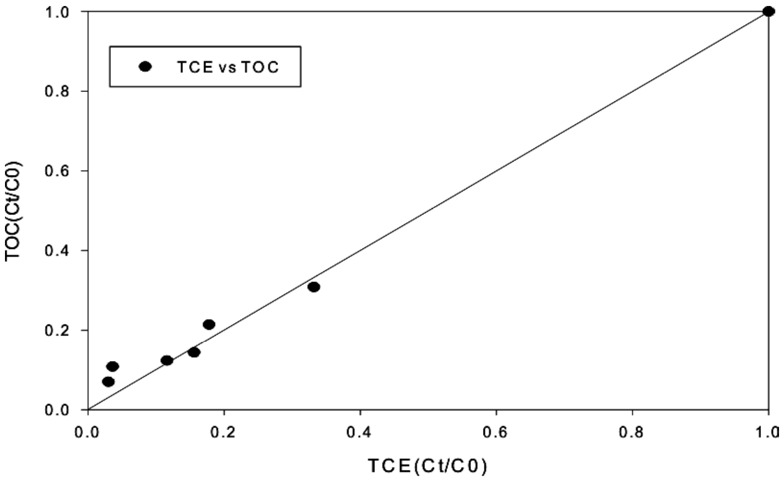


Fig. 11. The relevance of TCE and TOC after the Smectite-Ti photocatalytic reaction.

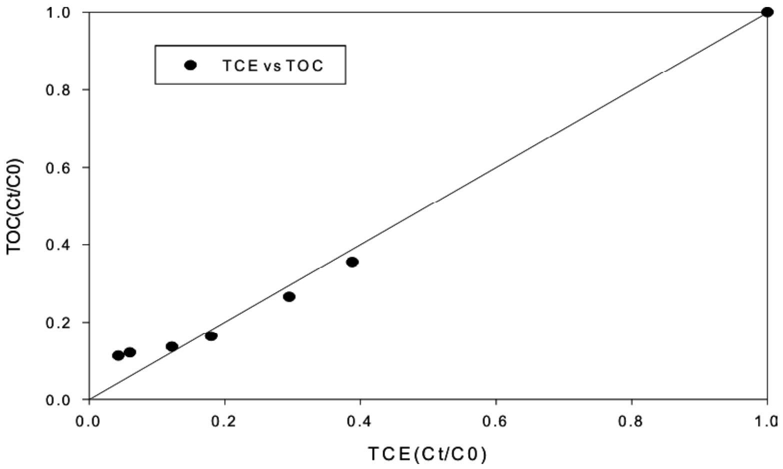


Fig. 12. The relevance of TCE and TOC after the Smectite-Ag photocatalytic reaction.

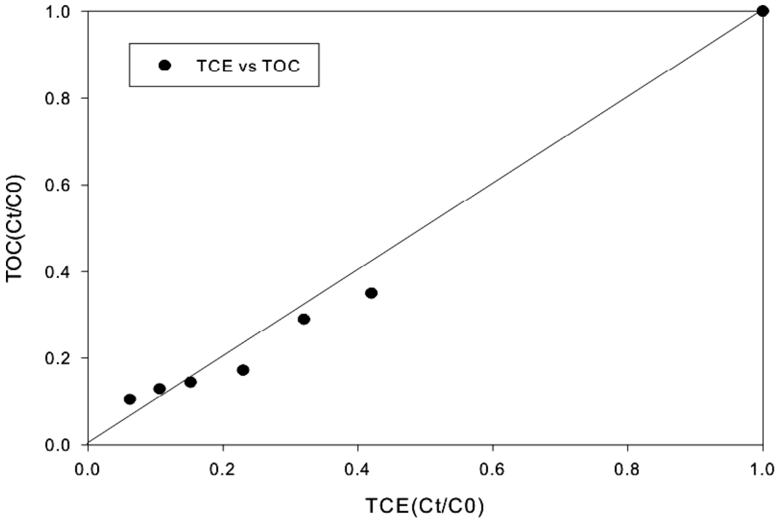


Fig. 13. The relevance of TCE and TOC after the Smectite-Zn photocatalytic reaction.

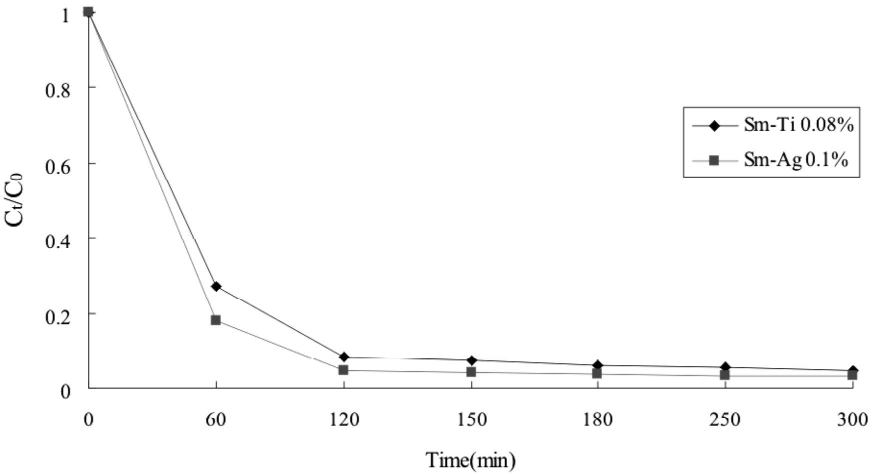


Fig. 14. Smectite catalyst immobilization on TCE degradation.

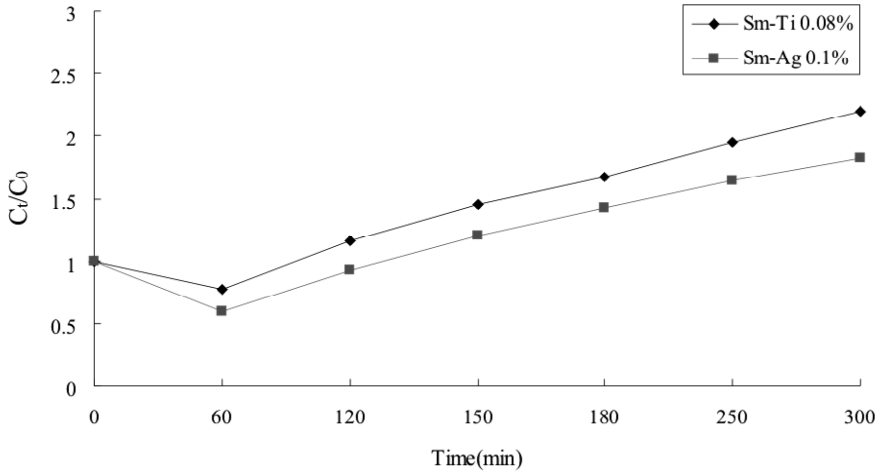


Fig. 15. Smectite catalyst immobilization on TCE mineralization.

that the adhesive (clear paint) is composed of solvent and diethyl malonate (DEM). Its decreasing TOC value reflects the degradation on TCE facilitated by smectite catalysts on a reaction board. However, on the surface, there is no clear paint, which proves that smectite catalysts not only degrade TCE but decompose the solvent and DEM of the adhesive. This results in an increasing TOC value.

Conclusion

This study analyzes modified smectite catalysts with FT-IR and the results indicate that the mineral structure of each clay catalyst remains intact and keeps the characteristic absorption function of clay mineral. Due to the semi-conducting properties of synthesized smectite catalysts, when exposed to sodium light, catalyst particles are excited for photocatalysis to achieve degradation purpose.

After exposure to a sodium lamp for 300 min, we observe that the best suitable mix proportion of Smectite-Ti and Smectite-Zn is 0.08% and after exposure to light after 300 min, their degradation reaches 95%. In this study, degradation efficiency is rendered by the shielding effect and it can be proved by poor degradation efficiency by adding 0.1 and 0.5% smectite catalysts than by adding 0.05%, or 0.08%. In the end, after 300 min of photocatalytic reaction, two types of smectite catalysts, Smectite-Ti and Smectite-Ag are fixed on the reaction board but there is no clear paint on the surface. It is estimated that smectite catalysts not only degrades TCE but decomposes the solvent and DEM of the adhesive. This results in an increasing TOC value. In this study, various smectite catalysts that have been modified provide semiconductor properties. The sodium lamp can stimulate the smectite catalyst particles to undertake photocatalysis and it can achieve the goal of degradation.

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