

The Photocatalytic Treatment of Trichloroethylene Using Self-Synthesis Soil Catalyst

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Abstract: Chlorinated organic compounds possess the following potential toxicity characteristics: carcinogenicity, mutagenicity, and teratogenicity. They are, therefore, classified as toxic pollutants in the environment. Among them, trichloroethylene (TCE) is a suspected carcinogen; it is an artificial synthetic substance with the following properties: carcinogenicity, high volatility, and low boiling point. Exposure to TCE will seriously affect the environment and damage human health. In light of the above information, this study used Taiwan's Ks series soil as a catalyst carrier and exchanged Ti^{4+} onto the carrier via ion exchange, whereby a soil catalyst at the nanolevel was formed. Photocatalysis was performed under visible light (sodium light) to degrade TCE in water, in order to explore the mechanism and effect of the soil catalyst on the degradation of TCE.

First, this study conducted an X-ray diffraction analysis (X-RD) on the synthesized soil catalyst. The results suggest that the Ks series soil contains vermiculite, a 2:1 clay mineral. Vermiculite has the following properties: a larger surface area, high cation exchange capacity (CEC), and high electrical charge, which make it suitable to use vermiculite as a carrier for the soil catalyst. Furthermore, the results of different percentages of added soil catalysts by weight (wt%) over the degradation of TCE in water suggest higher degradation efficiency when the 0.08 wt% Ks-Ti catalyst was added. As the experimental results show, only a small amount of sodium light could be transferred to the surface of TCE to induce a reaction when over 0.1 wt% soil catalyst was added due to the shielding effect, i.e. adding too much catalyst occupied more of TCE's light receiving area. As a result, the degradation level of TCE became lower.

Keywords: trichloroethylene, soil catalyst, photocatalysis, SEM-EDS, sodium light

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I. Introduction

TCE is a volatile hydrocarbon with the following properties: a low boiling point, high vapor pressure, chemical stability, low flammability and explosiveness, high dissolving capacity, and high-density vapor. Affected by photo-oxidation, TCE has a short half-life of approximately one day; in a body of water, its half-life can last 300 days. TCE is a nonflammable liquid with a sweet odor that most people can smell, even at concentrations as low as 1 ppm (parts per million). TCE is colorless at room temperature, less viscous than water (will sink in water), and a suspected carcinogen (Kuo and Wu, 2014). Based on animal testing, TCE may cause cancer, birth defects, and genetic damage. TCE can decompose at high temperatures forming toxic gases, such as hydrogen chloride, chlorine, and phosgene. Due to its high volatility, it evaporates quickly from surface waters-but not from the soil. TCE can percolate quickly through soil along with rainwater to the groundwater (Saha et al., 2013, Nam et al., 2015). Once it reaches the groundwater, it adsorbs onto the soil and may attach itself to water particles, and then it travels until it reaches an impermeable surface. When groundwater is drawn from this TCE-contaminated region, it poses serious health risks (Shi et al., 2015).

Heterogeneous catalysts have become a crucial part of many industrial activities, such as organic synthesis, oil refining, and pollution control (Liu et al., 2014; Leng et al., 2014). Modern heterogeneous catalysts consist of several elements in precise proportions (Liu et al., 2014). Currently, heterogeneous catalysts are optimized for the greatest reaction rate, which in turn results in optimal selectivity. It is possible to improve the heterogeneous catalyst activity over modifying the support by approaches such as nanotechnology and nanoscience or controlling the pore structure (Yamaguchi et al., 2005; Uysal and Oksal, 2013). For heterogeneous catalysis, the problem of catalyst separation and recovery from the reaction matrix are addressed by using various catalyst supports to immobilize the particle (Uysal and Oksal, 2013). This in turn provides a large enough surface area for the heterogeneous catalyst for it not to dissolve into the solution matrix (Yamaguchi et al., 2005). Therefore, the heterogeneous catalyst with broad supports such as Al_2O_3 , TiO_2 , ZrO_2 , ZnO , and others is applied based on its broad availability and cost-effective modes of synthesis.

In this study, Ti^{4+} was exchanged onto the carrier via ion exchange, whereby a soil catalyst at the

nanolevel was formed. The catalytic degradation of TCE was performed with different percentages of added soil catalysts by weight (wt%) to explore the catalytic mechanism and degradation efficiency of the soil catalyst over TCE. It is hoped that this study can provide fast effective ways to tackle TCE contamination, which can be used as a reference for water pollution control in the future.

II. Materials and methods

2.1 Sources of test soils

Rich in vermiculite, the Ks series soil is a typical red soil that mainly comes from Taitung County in Taiwan. Developed from dateless serpentinite, the red soil is a type of igneous rock in Taiwan spreading over foothills and plateaus on both ends of the East Rift Valley. Due to weathering over a longer period of time, it is a type of slightly acidic soil.

2.2 The purification and preparation of sodium saturated catalyst carrier

Put 60 g Ks series soil into a 2-liter beaker, and add 1.8 liters of deionized water to it. After stirring, soak it for days to fully expand it. After it is expanded, take 250 ml of the kaolinite suspension out of the beaker. Filter sand using the wet sieving method with a 300-mesh sieve. Transfer the filtrate to a 1-liter sedimentation cylinder, and add deionized water to make 1 liter. Leave it to naturally sediment after stirring it rigorously with a stirring rod. Siphon the suspension at the top of the sedimentation cylinder by 10 cm 8 hours later. Use an 18000 rpm high-speed centrifuge to have the suspension centrifuged. Perform sodium saturation of the kaolinite obtained after centrifugation with 1 M NaCl solution. Next, grind the saturated kaolinite into powder with an agate mortar after freeze drying it, and obtain the sodium saturated Ks series soil.

2.3 Preparation of Ks-Ti catalyst

After preparing the 0.1 N TiCl_4 solution, we add 2% sodium saturated Ks series soil. Water bath is also used to maintain the temperature at 40°C and stir evenly for 48 hours. Then stir evenly for 2 hours at the temperature of 80°C. Keep it still and remove the top layer, and 50% of ethanol is needed to remove chloride ions. The modified Ks series soil catalyst is dried by the freeze dry method and takes it out to grind. Then sinter them at the temperature of 350°C for 2 hours. Store the catalysts for use after they are cooled to room temperature.

2.4 X-ray Diffraction Analysis (XRD Analysis)

The X-ray Diffraction Analysis utilizes the X-ray Diffractometer coded with Rigaku RINT 200 to conduct the analysis. The $\text{CuK}\alpha$ is used as a photo source to separately analyze the crystalline forms of Ks-Ti catalyst after modifications in order to explore spacing of layers for these materials. The wavelength of the X-ray produced is 1.5418 \AA and 10 mA for testing operational current, 20kV for voltage, 5 deg/min for a scanning rate with a scanning angle of $2\theta=2\sim 40^\circ$.

2.5 Identification using a scanning electron microscope (SEM) and an energy dispersive spectrometer (EDS)

An SEM can be applied extensively. If used with an EDS, it can have the following functions: qualitative analysis, quantitative analysis, spot analysis, line analysis, and mapping. This experiment used an SEM to observe changes in the surface structures of the Ks series soil and a Ks-Ti catalyst. On the other hand, an EDS was mainly used to observe the distribution of elements in the structure of the Ks series soil, as well as the content and distribution of Ti in the structure of a Ks-Ti catalyst modified by Ti^{4+} .

III. Results and discussion

3.1 Results of Ks-Ti XRD analysis

Figure 1 shows the results of an XRD analysis on a Ks-Ti catalyst. As shown in the figure, the modified Ks-Ti catalyst has a peak at approximately 26° , meaning that the clay mineral, vermiculite, is its main component. Basically, the Ks series soil is a 2:1 expansion type clay mineral; water tends to exist in its layers if it is affected by humidity in the environment. After being modified by Ti^{4+} , shrinkage occurs in its layers due to water loss. However, there is still enough space between the layers to allow Ti^{4+} cations with a larger particle size to enter.

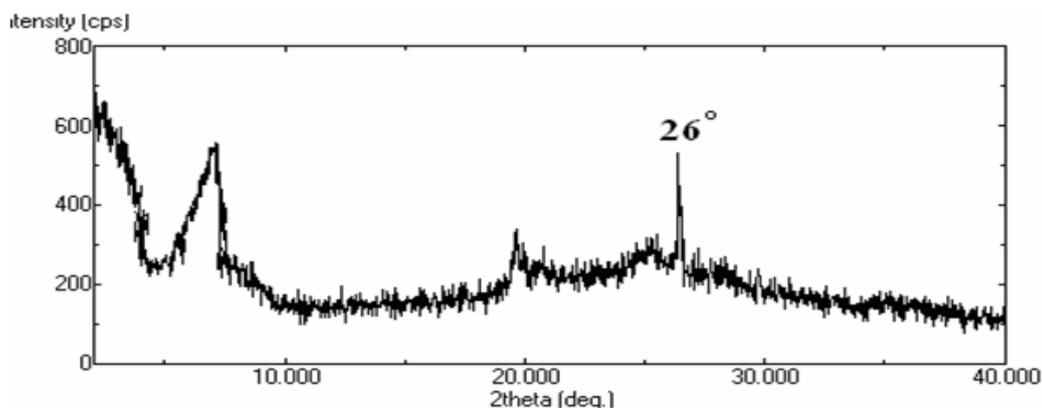


Figure 1. XRD analysis of Ks-Ti catalyst

3.2 Results of identification using an SEM and an EDS

3.2.1 Results of identification using an SEM

Figures 2-3 show the surface structures of the Ks series soil and a Ks-Ti catalyst identified using an SEM. Since the Ks series soil contains a large amount of vermiculite and is an expansion type clay mineral, its surface structure is loose, cotton-like, or layered, as shown in Figure 2. Furthermore, the Ks series soil also contains other mineral structures (e.g. kaolinite, vermiculite, chlorite, illite, etc.); its columnar surface structure is therefore more complicated and irregular. It can be observed from Figure 3 that after Ti^{4+} was exchanged onto the Ks series soil and the Ks series soil was sintered at $350^{\circ}C$, the surface of the Ks-Ti catalyst absorbed a considerable amount of Ti oxides in a crystalline state; it is therefore irregular (Doong et al., 2001).

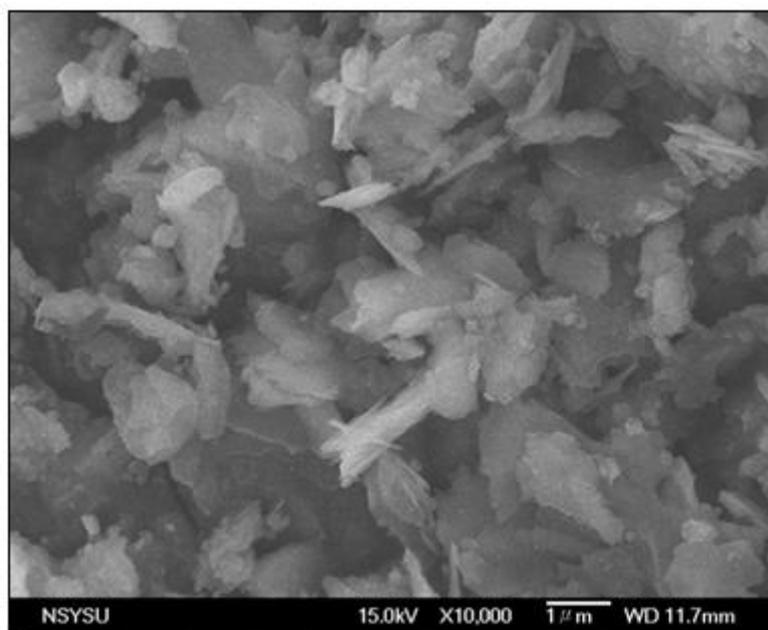


Figure 2. Results of surface identification of the Ks series soil using an SEM

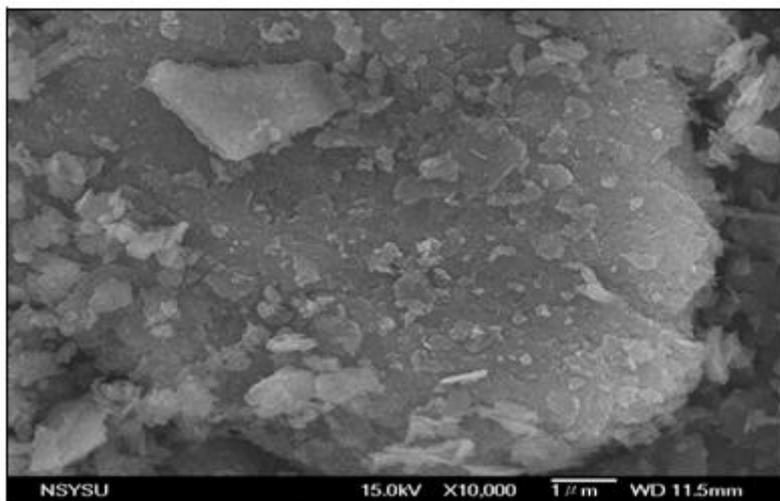


Figure 3. Results of surface identification of the Ks-Ti catalyst using an SEM

3.2.2 Results of identification using an EDS

Figures 4-5 show the results of mapping the Ks series soil and aKs-Ti catalyst using SEM-EDS, respectively. It can be observed from Figure 4 that the main component of the Ks series soil contains many oxides, such as Na_2O , MgO , Al_2O_3 , SiO_2 , CaO , Fe_2O_3 , etc. However, a few metal oxides, such as Ti, Ag, and Zn, are not found. Presumably, this is because a semi-quantitative analysis can only be conducted using an EDS in micro-areas, but the amounts of oxides: Ti, Ag, and Zn are minimal; therefore, an EDS cannot show the complete composition of a mineral. It can be observed from Figure 5 that there is a significant increase in the content of Ti in the Ks-Ti catalyst modified by Ti^{4+} ; as shown in the figure, the sparkling dots are at the nanolevel.

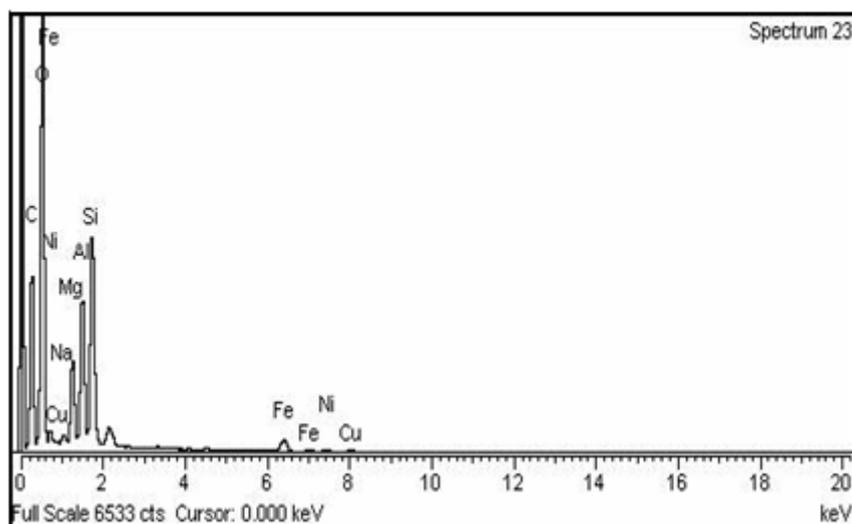


Figure 4. Results of the mapping analysis on the Ks series soil using SEM-EDS

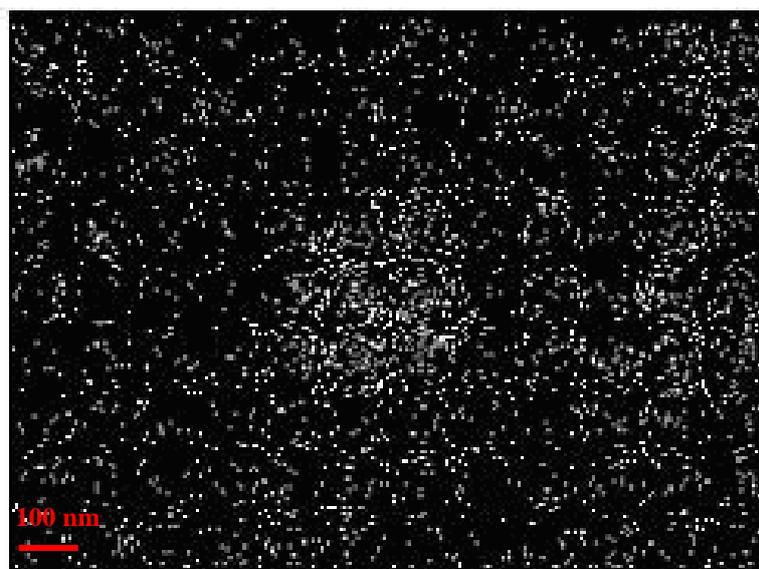


Figure 5. Results of the mapping analysis on the Ks-Ti catalyst using SEM-EDS

3.3 The catalytic degradation efficiency of a Ks-Ti catalyst over TCE

Figure 6 shows the degradation efficiency of different percentages of Ks-Ti catalysts by weight (0.05 wt%, 0.08 wt%, 0.1 wt% and 0.5 wt%) and sodium light over TCE. As shown in the figure, after catalyzing for 300 minutes, the 0.08 wt% Ks-Ti catalyst has higher degradation efficiency over TCE, which is approximately 97%. Since the Ks series soil carrier has the characteristic of a large specific surface area, it can absorb, while the added Ti^{4+} has the characteristics of an optimal band gap and good electrical conductivity, which can effectively play the role of an electron capturer to delay the recombination of electron hole pairs and increase the absorption rate in the visible light region (400~800 nm).

As mentioned in Section 3.1, after being modified by Ti^{4+} , shrinkage occurs in the layers of the Ks series soil due to water loss. However, there is still enough space between the layers to allow Ti^{4+} cations with a larger particle size to enter. Moreover, the Ti^{4+} used in this study is a strong oxide; when an exchange reaction is conducted, the spacing of layers of the Ks series soil can provide good reaction positions to boost -OH signals. A Ks-Ti catalyst has a positive effect of degradation on TCE because it has the following characteristics: (1) The surface of a Ti catalyst has super-hydrophilic properties (Almquist and Biswas, 2002); it has a specific water contact angle when it is in a dark environment. However, when a Ti catalyst receives light, the contact angle between it and the water becomes 0° , during which time it has super-hydrophilic properties. Thus, after receiving light, the surface of a Ti catalyst produces $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ with strong oxidation abilities. Meanwhile, water molecules on the surface of a Ti catalyst also form very strong hydrophilic groups. These mechanisms develop at the same time after the surface of a Ti catalyst receives light. As a result, after receiving sodium light for 300 minutes, the 0.08 wt% Ks-Ti catalyst has a degradation efficiency of approximately 97% over TCE. (2) During TCE degradation, the resulting Ti catalyst intermediates can continue to participate in the degradation reaction. As such, accumulation of toxic substances should not be a concern. Unlike a Zn catalyst, these intermediates will not compete with $\bullet\text{OH}$ for absorption positions (Liao and Kuo, 2008), whereby the degradation efficiency is higher and the photocatalytic efficiency is not affected. (3) Within a few hours of being involved in a photocatalytic reaction, a Ti catalyst can completely mineralize TCE to inorganic molecules. In other words, during photocatalysis, the properties of a Ti catalyst can facilitate the pyrolysis of TCE and therefore have a high level of TCE degradation. (4) As mentioned above, when a Ti catalyst receives light, it can produce $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ with high activity. To put it differently, electron transition occurs when electrons within a Ti catalyst receive light, whereby electrons jump up into the conduction band from the valence band, and Ti particles with electron holes are produced. This is called photosensitivity. Cho et al. (2001) and Xie et al. (2016) pointed out that when dye molecules are attached to the surface of TiO_2 , visible light is used to excite the dye; electrons excited via a photosensitive reaction are delivered to the conduction band of the semiconductor, whereby an oxidation-reduction reaction is conducted to destroy contaminants. TiO_2 itself is not excited, and no electron hole is produced throughout the whole process. Thus, the electron-hole recombination should not be a concern. (5) Chu and Choy (2002) and Yamada et al. (2013) indicated that when a Ti catalyst's particle sizes are 10-100 nm, the electron phase of the Ti catalyst particles transitions from the continuous energy band to the discrete band structure of the bulk phase materials, while the threshold value of the absorption light wave shifts to that of a shortwave, displaying the characteristics of size quantization. Moreover, a refined size also produces

a surface effect, quantum size effect, small size effect, and macroscopic quantum tunneling effect that bulk materials lack. On the other hand, when the particle size is reduced, the internal stresses in the particles increase, which leads to changes in the energy band structure; overlap of, and increase in, electron wave function; narrowing of the energy band gap; and the shifting of the absorption band to a long wave (visible light), which is called a red shift. In this study, the SEM analysis on aTi catalyst suggests thataKs-Ti catalyst's ion cluster sizes are 10-50 nm, a result which is equivalent to that of the study conducted by Almquist and Biswas (2002) and Xie et al. (2016), where organic matter can be oxidized in water or removed from water with a Ti catalyst withparticle sizes of 15-40 nm. It is evident that the microstructure can prove the occurrence of said effects and affect the process of catalytic activity.

Figure 6 shows that the 0.08 wt% Ks-Ti catalyst among different percentages of added Ks-Ti catalysts by weight (wt%) has higher degradation efficiency over TCE, whereas the 0.1 wt% and 0.5% wt% Ks-Ti catalysts have lower degradation efficiency than the 0.08 wt% Ks-Ti catalyst. It can thus be presumed that when higher percentages of Ks-Ti catalystsby weight are added, a shielding effect is more likely to occur. This result is the same as that of the study conducted byMcLoughlin et al. (2004) on killing E. coli K-12 in wastewater using UVs. In other words, although more light can be received when there is more Ks-Ti catalyst, too much catalyst will occupy more of TCE's light receiving area, while increasing its opaqueness. Consequently, a small amount of sodium light can be transferred to the surface of TCE for catalytic reaction. In this study, although a greater number of electrons and •OHwere generated when aKs-Ti catalyst wasinvolved in the catalytic reaction, the amount of •OHthatcould undergo a catalytic reaction with TCE was less and the photocatalytic capacity of the Ks-Ti catalyst was thus lowered. As such, the degradation efficiency of the Ks-Ti catalyst over TCE was lowered. On the other hand, although more electronhole pairs can be generated when higher percentages of Ks-Ti catalysts by weight are added, the number of photoelectrons they can excite are significantly more than that of the carriers in a semiconductor which receive electrons. As a result, superfluous electrons may be involved in a recombination reaction, whereby their photocatalytic capacity is lowered. Moreover, too much •OH is generated, which can easily lead to a decrease in the amount of •OHthat can react with TCE and the lowering of •OH's reaction capacity (Rincon and Pulgrain, 2004; Kushwaha et al., 2015). In this study, although a shielding effect was more likely to occur when adding the 0.08 wt% Ks-Ti catalyst than the 0.05 wt% Ks-Ti catalyst, the experimental results show that said effect is not significantwhenaddingthe0.08 wt% Ks-Ti catalyst. Rather, since there is more contact between the Ks-Ti catalyst and TCE, the photocatalyticcapacity of the 0.08 wt% Ks-Ti catalyst is obviously greater than the effect of the shielding effect.

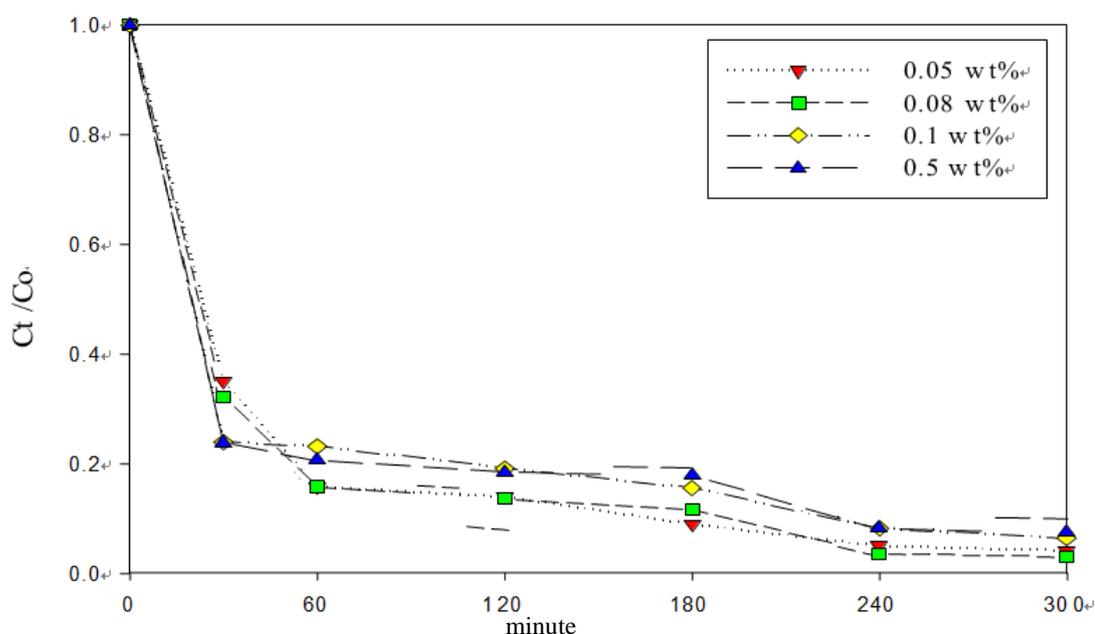


Figure 6. The degradation efficiency of four different wt% Ks-Ti catalysts over TCE

IV. Conclusion

In this study, Ti^{4+} was exchanged onto the soil carrier via ion exchange, whereby a soil catalyst at the nanolevel was formed. The catalytic degradation of TCE was performed with different percentages of added soil catalysts by weight (wt%) to explore the catalytic mechanism and degradation efficiency of the soil catalyst over TCE. The experimental results suggest that after receiving sodium light and catalyzing for 300 minutes, the 0.08 wt% Ks-Ti catalyst has higher degradation efficiency over TCE, which is approximately 97%. Since the Ti catalyst's particle size is at the nanolevel, it has many characteristics of a semiconductor and can therefore effectively degrade TCE concentrations in a very short period of time. Furthermore, it is found that when higher percentages of Ks-Ti catalysts by weight are added, a shielding effect is more likely to occur. In other words, although more light can be received when there is more Ks-Ti catalyst, too much catalyst will occupy more of TCE's light receiving area, while increasing its opaqueness. Consequently, a small amount of sodium light can be transferred to the surface of TCE for catalytic reaction, which leads to a decrease in the degradation efficiency of the Ks-Ti catalyst over TCE. With a synthesized soil catalyst that has good catalytic and degradation efficiency over organic contaminants, it is hoped that this study can provide fast effective ways to tackle TCE contamination, which can be used as a reference for water pollution control in the future.

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