

The effects of modified Zn-doped nano-clay minerals for TCE decomposition

Sol-A Bak^a, Myong-Shin Song^{a,*} and Seong-Kun Kim^{b,*}

^aResearch Center of Advanced Convergence Processing on Materials, Kangwon National University, Samcheok 25913, S.Korea

^bSchool of General Studies, Kangwon National University, Samcheok 25913, S. Korea

In this research, a Zn ion-doped laponite® photocatalyst material (ZnLP) is synthesized using ZnCl₂, which has a high solubility and fast ionization properties, and laponite®, which has a large specific surface area with a high light transparency and excellent ion exchangeability. Using this, we reviewed the photolysis efficiency of trichloroethylene (TCE), one of the main representative substances of recalcitrant (non-degradable) organic compounds. Laponite® (5, 10, and 15 wt%, respectively) and ZnCl₂ (30 wt%) are mixed in a 2 : 1 ratio and then filtered, dried, and pulverized (ZLC); this is followed by calcination in an electric furnace for 30 min at temperatures of 300, 500, and 600 °C, respectively. To verify the Zn compound crystal formation, X-ray diffraction (XRD) analysis is performed and the TCE optical resolution is reviewed using a gas chromatograph (GC). At XRD-result calcination temperatures of 500 and 600 °C degrees, respectively, ZnO and ZnMgSi₂O₆ crystals are formed, and through GC analysis, the ZnLP's TCE resolution is verified to be excellent. The resultant ZnLP, including the TCE, are determined to be applicable as new photocatalyst material with sufficient beneficial effects in the decomposition of recalcitrant organic compounds.

Key words: ZnO, Laponite®, TCE, Zn ion, Clay mineral, Organic pollutant.

Introduction

Owing to industrialization, groundwater contamination is increasingly deteriorating because of the considerable emission of recalcitrant organic compounds. Amongst these contaminations, chlorinated organic pollutants, in particular, are not only detected in industrial areas but also in certain residential areas. Trichloroethylene (TCE), a recalcitrant substance with a high water solubility and strong volatility, has the property to dissolve in organic solvents such as ether, chloroform, acetone, benzene, and alcohol. In order to process recalcitrant substances, an advanced oxidation process (AOP) is used; amongst the AOP methods, the photocatalytic oxidation process creates OH and O²⁻, irradiating them with ultraviolet rays on a semiconductor surface. This reaction decomposes the adsorbed material on the surface owing to a strong oxidizing power. Owing to the low efficiencies in pollution treatment and economic costs because of the unstable price markets of the existing photocatalyst material, the development of new material technology for domestic patents and photocatalytic technology is crucial. Extensive research is being done for applying and coating photocatalytic material such as montmorillonite and kaolinite, using titanium dioxide, silica, and charcoal. Meanwhile, it is possible to modify laponite® owing to

the exchangeability of its own cations as a clay mineral with a high light transmittance and specific surface area. This substance does not produce secondary pollution, rendering it safe for usage. Additionally, as a substance with a high solubility, ZnCl₂ is comparatively easier for ion replacement. Research on synthesizing photocatalyst material for ion replacement using this type of laponite® and ZnCl₂ [1-4] has not been reported; therefore, this research reviews the effectiveness of the photocatalytic decomposition of a representative recalcitrant organic compound, TCE, using ZnLP (synthesized according to requirement) and also creates variations in the calcination temperature and concentration conditions of laponite®, when synthesizing Zn-doped laponite®(ZnLP) in which the laponite® structure layer's Na ions are replaced by Zn ions. Nanoclay mineral laponite® is used owing to its high ion replacement and excellent light transmittance properties.

Materials and Experimental

Laponite® is composed of a 2 : 1 ratio of tetrahedral and octahedral sheets, with sodium plate-shaped clay between the tetrahedral silicate layers. Fig. 1 shows the particle size and structure of laponite®. The chemical formula for laponite® is Na_{0.7}[(Si₈Mg_{5.5}Li_{0.5}) O₂₀]_{0.7} and within its layers, it is possible to replace the existing Na ions with different ions [5, 6]. In this experiment, laponite® RD (Rockwood Additives Ltd. U.K) and ZnCl₂ (Gold Purification, 1st grade reagents) are used. When ZnCl₂ contacts with air, it becomes

*Corresponding author:
Tel : +82-33-570-6618
Fax : +82-33-570-6604
E-mail: kimseong@kangwon.ac, msong0422@kangwon.ac.kr

Table 1. Chemical composition and physical properties of ZnCl₂ and laponite®.

Laponite®		ZnCl ₂	
Chemical compositions (wt%)			
SiO ₂	59.5	Assay	≥ 98.0
MgO	57.5	Alkali salt(ZnO)	≤ 2.4
Li ₂ O	0.8	Nitrogen compounds (as N)	≤ 0.02
Na ₂ O	2.8	Sulfate	≤ 0.01
LOI ⁽¹⁾	15	Pb	≤ 0.003
		Fe	≤ 0.001
Physical properties			
Powder color	White	Appearance	White crystalline solid
Bulk density (kg/m ³)	1000	Density (g/cm ³)	2.91
Surface area (m ² /g)	370	Molecular weight	136.3
pH (2 wt.% suspension)	9.8	pH (2 wt% suspension)	4.6
		Melting point (°C)	293
		Boiling point (°C)	732

highly soluble in water and deliquescent, absorbing moisture; the aqueous solution appears to be a weak acid. The chemical composition and physical properties of laponite® and ZnCl₂ are presented in Table 1.

Methylene blue used in the preliminary experiments for verifying the resolution of TCE, has a chemical formula with organic dye molecules, C₁₆H₁₈N₃SCl·3H₂O. It is soluble in water, alcohol, and chloroform, but insoluble in ether. In this experiment, the concentration of methylene blue was adjusted to be 20 ppm using distilled water. The TCE used in the experiment is a Sigma-Aldrich product, with a molecular weight of 131.39 and a solution state of over 99.5% purity. The CAS No. is 79-01-6 and it is a substance with a strong volatile proportion of 1.465 g/cm³. The pollution concentration's reference value of the TCE is below 1 ppm. However, to verify the maximum degradation value of the synthetic material, the concentration of the TCE used throughout this study was modified to be 10 ppm.

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To synthesize ZnLP, an aqueous solution of laponite® (5, 10, 15 wt%), respectively and ZnCl₂ (30 wt%) were mixed. The solution was filtered after mixing at a 2:1 weight ratio, the maximum ratio for replacing Zn ions with laponite® Na ions. The maximum concentration was set to be 15 wt% because mixing of the solution is impossible at a higher value due to the swelling of laponite®. The minimum concentration was set to 5 wt% owing to the low absorbance of the aqueous solution below this value. The aqueous solution was

Table 2. Sample names and mixture proportions.

Sample	Laponite 5 wt%	Laponite 10 wt%	Laponite 15 wt%	ZnCl ₂ 30 wt%	Calcination temperature (°C)
ZCL5	2			1	Before calcination
ZCL10		2		1	
ZCL15			2	1	
ZnLP5	2			1	300, 500, 600
ZnLP10		2		1	
ZnLP15			2	1	

dried at 105 °C degrees for 24 hrs, after filtering. For this and for pulverization, a laboratory vibrating cup mill (Pulverisette 9, Fritsch, Germany) was used. Table 2 identifies the samples and their experimental formulations. After drying, the pulverized mixture (ZCL: before calcination) was calcined (ZnLP: after calcination) for 30 min at 300, 500, and 600 °C, respectively, in an electric furnace after reviewing its thermal properties to establish proper calcination temperature conditions through a thermogravimetric/differential thermal analyzer (TG-DTA). In the ZnLP, the Zn ions were replaced, forming the Zn mixture's crystal structure, which was verified through X-ray diffraction (XRD) analysis. The chemical bond structure was verified through Fourier transform-infrared spectroscopy (FT-IR) analysis.

25 ml of methylene blue with a concentration of 20 ppm and 10 g of synthetic ZnLP were placed in a clear glass vial and mixed for approximately 20 s. Depending on the time lapse after mixing, at 1, 3, 6, and 12 hrs, the color changes based on the absorption of methylene blue were visually verified; this was followed by imaging.

After filling a quartz tube (I. D. = 18 mm, O. D.=20.5 mm) with 30 g of ZnLP, 60 ml of TCE at a concentration of 10 ppm was poured inside, according to the experimental reactor size and capacity. Then, after blocking both sides of the quartz tube with

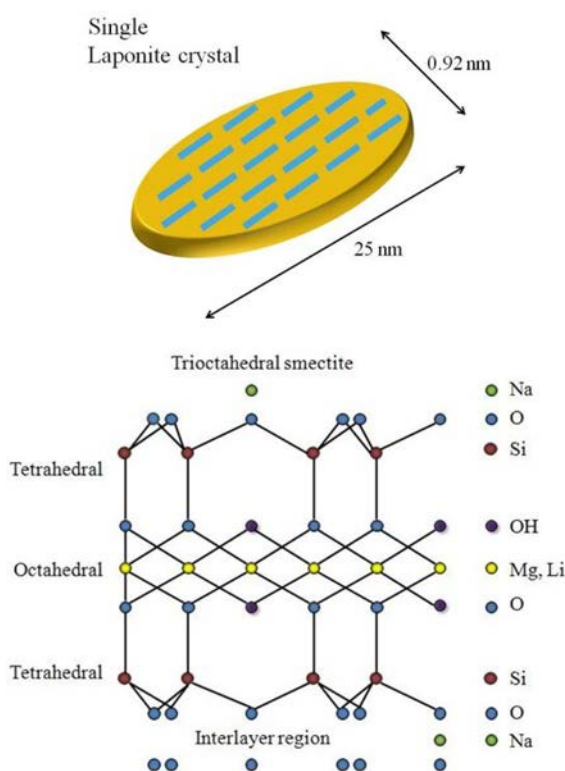


Fig. 1. Dimension and crystal structure of laponite®.

stoppers, it was used to secure the reactor. As per previous research, if the dosage of the photocatalyst used in the experiment is increased, the TCE removal rate will also increase. However, a continuous increase in dosage not only fails to constantly provide a favorable impact on the photolysis, but is also known to have economical and secondary environmental by-product effects that need to be considered [7]. Accordingly, considering the economic aspect as well as the optimal removal efficiency, the ZnLP dosage was set to 30 g. Further, it was irradiated with UV light by an ultraviolet-C (UVC) lamp. Samples were taken at 10, 20, 30, 40, 50, 60, 90, and 120 min after the initial UV radiation. The samples were prepared for use

by storing them in sealed sample bottles that prevented contact with sunlight. The shape and size of the reactor used in the experiment is shown in Fig. 2; the state of the reaction unit is identified by its setting. The reactor is made of acrylic and sealed from outside light contact. The interior light source is not emitted out but is reflected through a mirror such that it can be reused after irradiating the material with UV light. The wavelength of the UVC lamp used for the experiment is 254 nm with an intensity of 8.4 mW/cm^2 , at the surface of the quartz tube.

To establish the calcination temperature condition and the thermal properties of the sample before synthesizing ZnLP, TG-DTA (STA409PC Luxx, Netzsch, Germany) was performed. When the temperature was increased from 30–800 °C at 10 °C/min, N_2 was shed at a speed of 110 ml/min. After calcination, to verify the Zn mixture created from the ZnLP, XRD (D/Max-2500V, Rigaku, Japan) analysis was performed. The diffraction pattern was recorded between 2θ 5° and 80° with the diffractometer operated at a voltage of 40 kV and a current of 50 mA with Cu/K- α radiation. An FT-IR (Vertex70, Bruker, Germany) single reflection ATR unit was used and the frequency range was 600–4000 cm^{-1} ; the set number of scans and backgrounds scans were 64, each, as per requirement. To evaluate the TCE decomposition efficiency characteristics, a gas chromatograph (GC) (OP2010 Plus, Shimadzu, Japan) was used for analysis, as per the water pollution process tests [8]. N_2 gas was used as a carrying gas and the column temperature was held at 40 °C for 5 min; the heating rate speed was set to 10 °C/min at 260 °C. The capillary column used was GD624. The purge operating conditions of the purge and trap system were 40 °C for 30 min at 30 ml/min; the trap heating temperature was 280 °C and the heating time was set to 30 min.

Results and Discussion

To set the optimal temperature for synthesizing ZnLP, TG-DTA was used and the thermal properties of

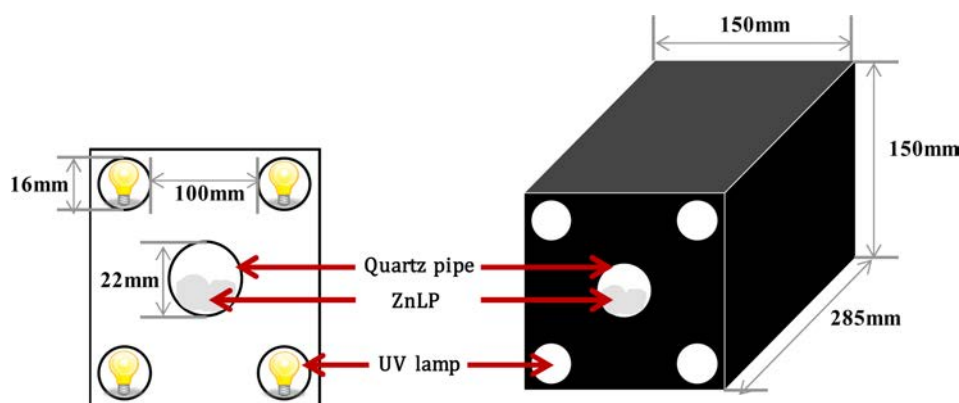


Fig. 2. Mimetic diagram and dimensions of the reactor.

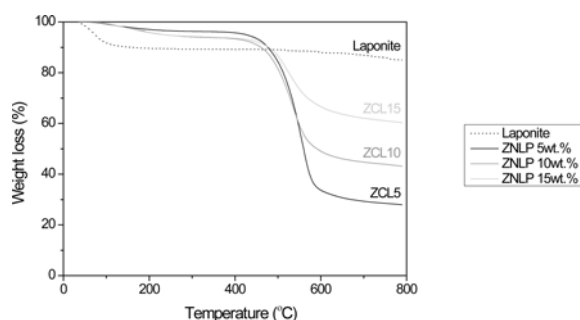


Fig. 3. TGA curves of (a) pure laponite®, (b) ZCL5, (c) ZCL10, and (d) ZCL15.

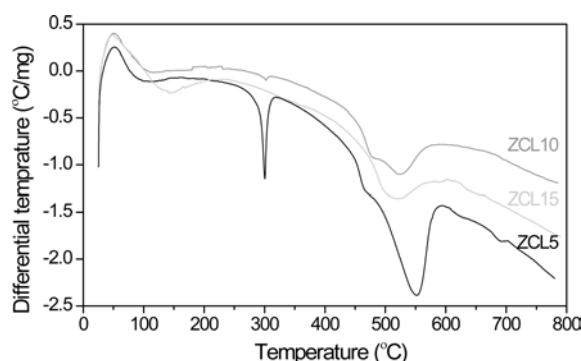


Fig. 4. DTA curves of (a) ZCL5, (b) ZCL10, and (c) ZCL15.

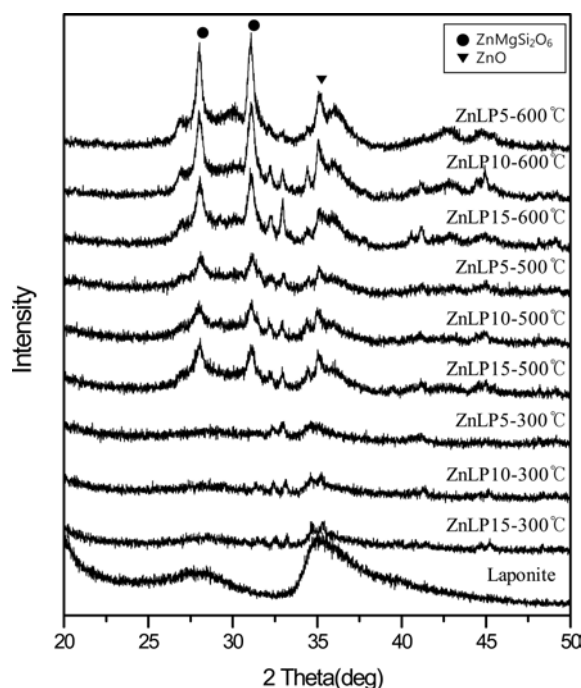


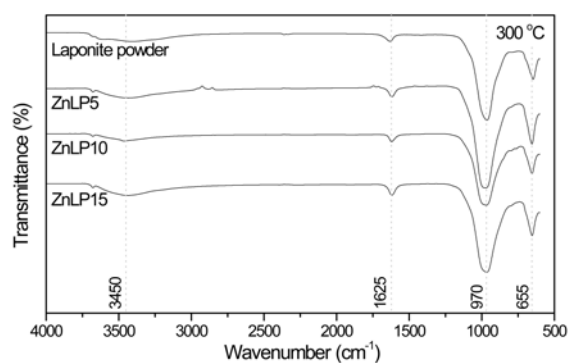
Fig. 5. XRD patterns of ZnLP calcined at various temperatures.

laponite, ZCL5, ZCL10, and ZCL15 were analyzed. From these results, the calcination temperature for synthesizing ZnLP was set. The laponite and ZCL TGA results are as shown in Fig. 3. The Laponite®'s total mass was reduced by approximately 10% at 100 °C; after this was judged to be due to combined decomposition,

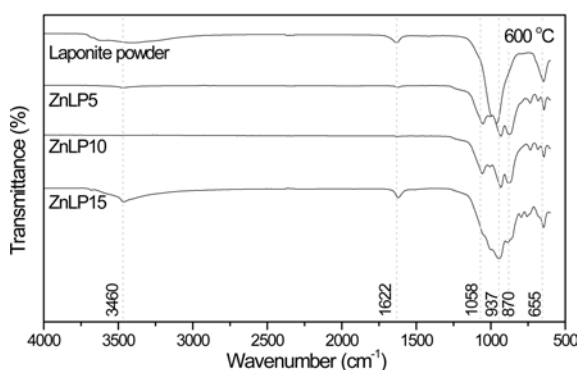
the total mass was reduced by approximately 15% at up to 800 °C. Additionally, before calcination and until the ZCL pyrolysis results presented themselves at 200–400 °C, the mass reduction was low. Further, a rapid loss in mass appeared at a temperature range of 450–600 °C. The corresponding weight losses were approximately 72% for ZCL5, 57% for ZCL10, and 40% for ZCL15. As the laponite® concentration increased in the ZCL, following the increase in the solid phase, the mass loss rate was reduced. An endothermic peak can be observed in the temperature range, 450–600 °C and a proximity temperature of 300 °C is shown in the DTA curve in Fig. 4. This was determined to be owing to the generation of a new compound and the ZCL compound's decomposition before calcination. Judging by these results, it was determined that a Zn-doped compound was generated by the Zn ion exchange with the laponite® Na ions. According to these DTA results, the ZCL calcination temperature for synthesizing ZnLP was set to 300, 500, and 600 °C, respectively.

The XRD analysis results with respect to the laponite® concentrations (5, 10, 15 wt%) and ZnLP calcination temperature are depicted in Fig. 5, with a peak in the temperature range, 2θ (20–50 °). The peak of the Zn compound, ZnMgSi₂O₆, at ZnLP calcination temperatures of 500 °C and 600 °C is 2θ, 28 ° and 31 °, respectively. It is important to note that the ZnO peak was observed at 2θ, 34 °. On the other hand, no ZnO and ZnMgSi₂O₆ peaks were observed at a ZnLP calcination temperature of 300 °C. Through these results, it was possible to verify the ZnO crystal and Zn compound generation, from calcination temperatures above 500 °C. Also, when calcined at 500 °C, it was seen that the ZnO and ZnMgSi₂O₆ peak intensities increased according to the laponite® concentration increase. When calcined at 600 °C, the ZnMgSi₂O₆ peak intensity was reduced according to the laponite® concentration increase, whereas the ZnO peak intensity showed a constant tendency. The reduction in the peak intensity of ZnMgSi₂O₆ at a 600 °C calcination temperature and the peaks at 2θ (33 ° and 34 °) that could be observed in the ZnLP5 XRD pattern were identifying points for the ZnLP10 and ZnLP15 samples, and were determined to be owing to decomposition of ZnMgSi₂O₆. Based on these results, a 600 °C calcination temperature was found to be more beneficial than calcination temperatures of 300 and 500 °C for the formation of the Zn compound. It was also verified that any change had a negligible effect on the generation of the Zn compound with respect to the increase in the laponite® concentration.

The ZnLP FT-IR spectrums of the ZCLs calcined at 300 and 600 °C, respectively, as per the laponite® concentration, are as depicted in Fig. 6. A peak of the Mg-O-bond in the vicinity of 655 cm⁻¹ and of the Si-O-bond in the vicinity of 970 cm⁻¹ can be seen in the laponite® powder IR spectrum; thus, the existence of a



(a) Calcined at 300 °C



(b) Calcined at 600 °C

Fig. 6. FT-IR spectra of ZnLP calcined at (a) 300 °C and (b) 600 °C.

silicate layer at 1630 cm^{-1} , as well as an OH-stretching peak was verified [9–11]. This type of peak appears due to the laponite®'s basic combined structure. As shown in Fig. 6(a), a similar basic laponite® peak pattern is seen in the IR spectrum of ZnLP calcined at 300 °C. This maintains its laponite® structure under the 300 °C temperature conditions and does not show structural variations according to the cation exchanges. The IR spectrum for ZnLP calcined at 600 °C can be seen in Fig. 6(b). Here, the complex and varied peaks differ from the previous peak patterns. The peaks at 870 cm^{-1}

appear by a combination of Si-O-Mg and the peaks verified at 1060 cm^{-1} appear owing to the presence of the Zn-O-Si bond. Generally, if the laponite® concentration increases for the M-O-Si (M = Si or Zn) peaks verified at $930\text{--}1110\text{ cm}^{-1}$, an increase in the peak intensity can be observed as the Zn ion replacement increases [12]. Therefore, the required optimal temperature for calcination to synthesize ZnLP as a photocatalytic material is determined to be 600 °C; it was also established that the laponite® concentration is to be increased for optimization or for increasing the generated quantity of the Zn ion-doped compound

Preliminary experiments were done with methylene blue to verify the decomposition property of the ZnLP organic substance. The results of applying methylene blue to the calcined ZnLP at 300, 500, and 600 °C, respectively, are as displayed in Fig. 7. With time, for the ZnLP calcined at 300 °C, the transparency of the methylene blue's coloring increases. On the other hand, the methylene blue's coloring presented almost no visible changes on the ZnLP calcined at 500 and 600 °C, respectively; this was determined to be due to the absorption of methylene blue in laponite® in an amorphous state, which does not generate crystal structures of ZnO and $\text{ZnMgSi}_2\text{O}_6$, as shown in the XRD results in Fig. 5 with respect to the ZnLP calcined at 300 °C. This can be verified through the blue color that visibly stands out in ZnLP calcined at 300 °C, as per the elapsed time periods. Meanwhile, because the ZnLP calcined at 500 and 600 °C, respectively, has ZnO and $\text{ZnMgSi}_2\text{O}_6$ in which the laponite® Na ions are replaced by the Zn ions, it can be determined that methylene blue is not absorbed, if it is not irradiated with UV. Therefore, it can be determined that ZnLP calcined at 300 °C can remove organic compounds by the adsorption of laponite®. ZnLP calcined at 500 and 600 °C, respectively, does not have simple adsorption properties; hence, it has to be irradiated with UV to confirm that it is a photocatalytic material.

ZnLP, produced by a replacement of the Zn ions, was

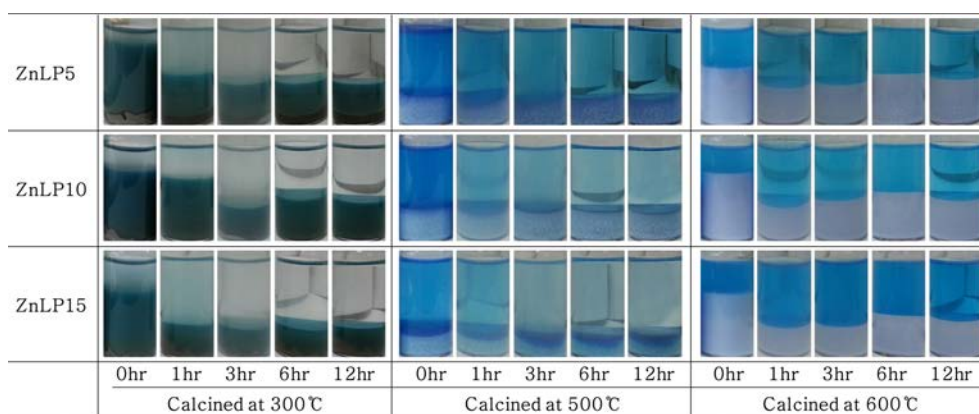


Fig. 7. Photographs of the decomposed methylene blue with the calcination temperatures and laponite® ratios.

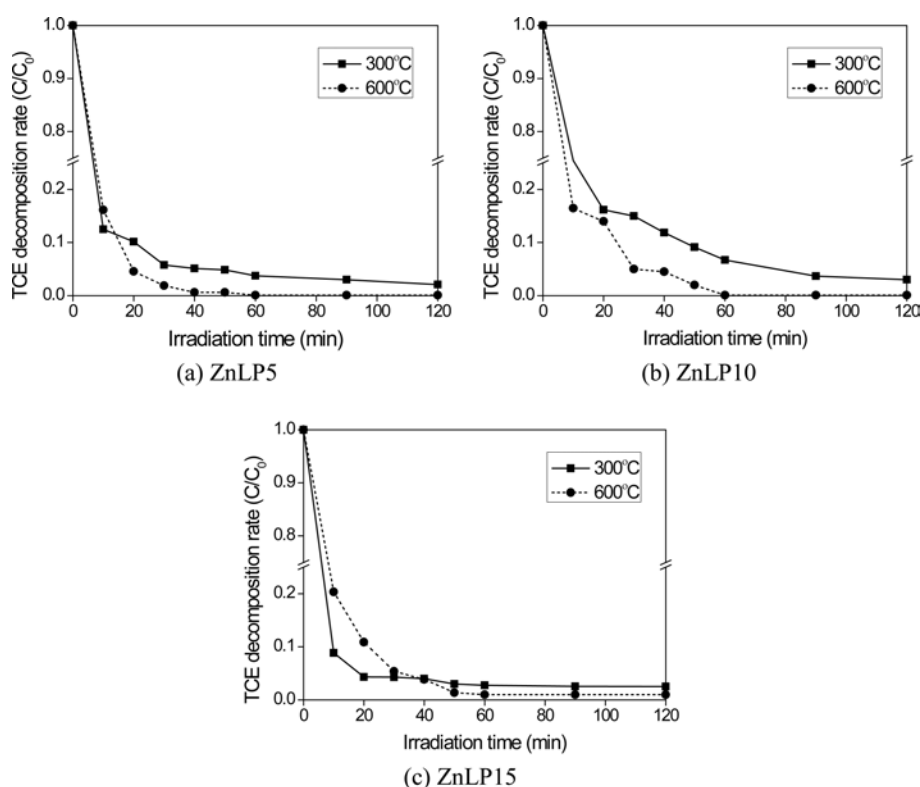


Fig. 8. TCE decomposition rates of ZnLP5, ZnLP10, and ZnLP15, respectively.

synthesized using ZnCl_2 and laponite® and was used to perform a TCE (a non-degradable organic material) decomposition test. The ZnLP calcined at 300 °C, exhibiting an adsorption reaction in the preliminary experimental results with methylene blue and the ZnLP calcined at 600 °C, not exhibiting adsorption, were selected for the TCE decomposition test. The effectiveness of the TCE decomposition performed using ZnLP was verified through the GC analyses of the samples collected during a 2-hour treatment. Fig. 8 shows the TCE's residual concentration versus the laponite® concentration using Eq. (1), after performing the TCE decomposition test on the ZnLP calcined at 300 and 600 °C, respectively.

$$\begin{aligned} \text{TCE decomposition rate} &= C/C_0 \\ C_0 &= \text{Initial TCE concentration} \\ C &= \text{TCE concentration after irradiation} \end{aligned} \quad (1)$$

The TCE decomposition test results showed that the TCE has an overall rapid removal rate in the initial stages regardless of the calcination temperature and laponite® concentration. ZnLP5 (calcined at 300 and 600 °C, respectively) presented a TCE decomposition of approximately 85% at 10 min. Particularly, ZnLP calcined at 600 °C presented a TCE decomposition of approximately 95% at 20 min. After 40 min, almost all the TCE had been decomposed. In comparison with the ZnLP5 calcined at 600 °C, the ZnLP5 calcined at 300 °C presented a relatively lower TCE decomposition

rate; however, after 120 min, it presented a high TCE decomposition rate of 97%. ZnLP10 calcined at 300 and 600 °C, respectively, demonstrated a TCE removal rate of 82% at 10 min and the ZnLP calcined at 600 °C had the TCE completely removed at 60 min. After 120 minutes, the ZnLP calcined at 300 °C presented a TCE removal rate of 95%. At 10 min, ZnLP10 exhibited a TCE decomposition rate of 82% and complete TCE decomposition, when calcined at 600 °C, at 60 minutes. ZnLP15 calcined at 300 °C presented at 10 min, a TCE decomposition rate higher than 90% and after 20 min, it steadily presented a TCE decomposition rate of 95%.

Conclusions

For developing new photocatalytic material to replace the existing ones, nanoclay minerals such as laponite® and ZnCl_2 with excellent light transmittance and ion exchange properties were used; ZnLP (which contains a Zn compound) was synthesized. In addition, the characteristics with respect to the concentration and calcination temperatures were reviewed. The absorption property of methylene blue was also verified using ZnLP. The conclusions derived from the results obtained in this research on the TCE photolysis efficiency are as follows:

1. Synthesis of ZnLP: It was generated in its amorphous form at calcination temperatures of up to 300 °C, and through ZnO and $\text{ZnMgSi}_2\text{O}_6$ at calcination temperatures of 500 and 600 °C, respectively.

2. Results of reviewing the absorption properties of ZnLP using methylene blue: Methylene blue presented excellent absorption capacities with the ZnLP calcined at 300 °C and had no absorption capacity with the ZnLP calcined at 500 and 600 °C, respectively.

3. Results of reviewing the TCE photolysis of ZnLP: The ZnLP calcined at 300 °C exhibited TCE removal by absorption and the ZnLP calcined at 600 °C demonstrated TCE decomposition by photolysis.

Therefore, ZnLP calcined at 600 °C has sufficient benefits in TCE decomposition and is a viable alternative for use as a new photocatalytic material.

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