

Evaluation of TCE degradation using newly-developed nano-ZnO/organic supports composites

Dae Gyu Jang · Chang Hyuk Ahn · Saeromi Lee · Hosang Ahn · Jin Chul Joo†

Abstract— The photocatalyst nano-ZnO powder was fixed on organic supports to overcome drawbacks of photocatalyst powder used in aqueous phase as difficulty of recovery and reutilization. Although photocatalyst surface area fixed on supports was resulted in decline of photocatalytic efficiency, sorption capacity of the organic supports (silicone, ABS, epoxy, polybutadiene) expected that photocatalytic efficiency was maximized through synergistic effect both the sorption capacity of organic support and photocatalytic mechanism of ZnO. The NZOC (Nano-ZnO/Organic Composites) was manufactured according to physical and chemical combination method. Before manufacturing NZOC, the raw organic supports were evaluated about sorption capacity of TCE, which is representative non-degradable organic material. Also, the developed NZOC was evaluated about 1) water resistance tests, and 2) photocatalytic removal efficiency tests of TCE. In the results of experiment, ABS resin was observed similarly with efficiency of blank (control). The polybutadiene showed the most excellent efficiency of about 30% among organic supports. The NZOCs which were each manufactured as a result of the water resistance of the experiment, it was determined to be suitable for use in aqueous phase. The photocatalytic removal were evaluated by utilizing the NZOC prepared, the result of experiments showed Nano-ZnO / polybutadiene composite was good removal efficiency better than others, it was superior sorption capacity of polybutadiene and photocatalytic mechanism of nano-ZnO through synergistic effect. Therefore, the most appropriate organic support was chosen of the polybutadiene in this research. Also, the experiments are required such as initial concentration of TCE, loading amount of nano-ZnO/polybutadiene, intensity of light source, pH to verify effects of factor.

Keywords—organic supports, silicone, epoxy, ABS, polybutadiene, ZnO, photocatalyst

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I. Introduction

Over traditional water treatment processes, heterogeneous photocatalytic oxidation processes using semiconductor particles such as TiO₂-based materials and other oxides (e.g., ZnO, Cu₂O, WO₃, V₂O₅, α -Fe₂O₃, Bi₂O₃ etc.) have been found to be a promising solution to remediate the water resources contaminated by chlorinated hydrocarbons (Di Paola et al. 2012). Although most studies dealt with photocatalytic oxidation of chlorinated hydrocarbons using bare TiO₂ powder (e.g., Degussa P25) or modified TiO₂ (i.e., doping, loading and sensitization) (Yang et al. 2008, 2010; Yokosuka et al. 2009), several drawbacks (i.e., high recombination rate, difficulty to support powered TiO₂ on supporting media, filtration and recovery processes etc.) using bare TiO₂ powder or modified TiO₂ have also been reported (Di Paola et al. 2012).

Therefore, in this study, as a valid alternative to bare TiO₂ powder, nanoscale (nano-) ZnO was considered due to its good catalytic and photochemical properties along with its low cost. Also, various organic supports (e.g., silicone, epoxy, ABS resin, polybutadiene) were considered as supporting media due to both high sorption capacity and great water resistance. Thus, innovative nano-ZnO/organic supports composites (NZOC) to degrade chlorinated hydrocarbons were developed to overcome drawbacks using bare TiO₂ powder.

The purpose of this study was to evaluate the feasibility of NZOC as a valid alternative to TiO₂ powder to mineralize chlorinated hydrocarbons without difficulties for filtration and recovery of photocatalysts.

II. Materials and Methods

A. Development of NZOCs

Nano-ZnO powder (purity 99%) with average particle size of 20 nm and specific surface area greater than 90 m²/g was purchased from Nabond Technologies Co. (KL, Hong Kong). Based on the high sorption capacity and greater water resistance, several selected organic supports such as silicone, epoxy, ABS resin, and polybutadiene were purchased from local manufacturer. For silicone and epoxy, the nano-ZnO/organic supports composites (NZOC) were prepared by mixing 100 g of ZnO powder and 100 g of respective organic supports. Then, ball type of NZOC was produced manually with certain pressure. For ABS resin, the ABS resin was mixed in petri dish on 30 rpm rotated reactor with 3 g of ZnO powder for 10 min. The ZnO-coated ABS resin was heated at furnace at 300 °C for 3 min. As the ABS resin surface was

melt and became sticky, ZnO powder was attached on the surface of ABS resin. For polybutadiene, the polybutadiene was soaked into the tetrahydrofuran (THF), and was melted on the surface. Then, 100 g of polybutadiene were mixed with 30 g of ZnO, and the ZnO-coated polybutadiene was heated at 130 °C for 1 hr. After heating, ZnO-coated polybutadiene was sonicated for 30 min, and dried at 100 °C. The pictorial views of NZOC developed in this study are shown in Figure 1.

Generally, produced NZOC were small white balls with the size of 4-6 mm in diameter. Both surface morphology and microchemical analyses of NZOC were performed using Field Emission Scanning Electron Microscopy (FE-SEM, HITACHI, S-4700) and SEM with energy-dispersive X-ray spectrometer (EDS-EMAX, Horiba), respectively. The concentration of TCE was measured using gas chromatography (Varian CP-3800, Varina, Inc) with electron capture detector (GC-ECD) and an autosampler with a 10 µL syringe. The TCE was separated on a 30 m x 0.53 mm x 3 m 624 CB column (Varina, Inc., Palo Alto, CA).

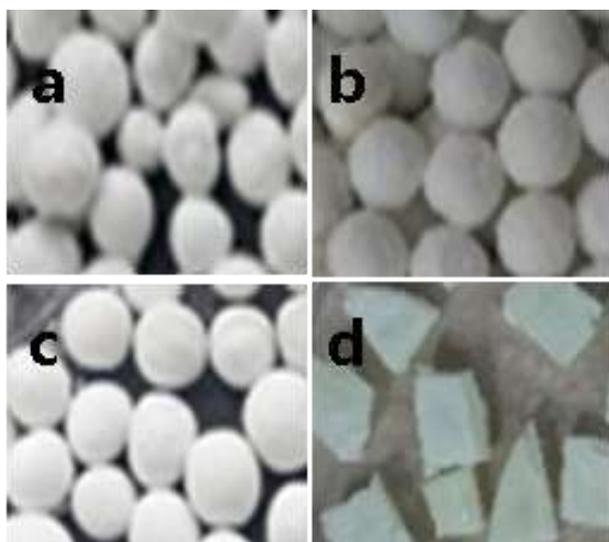


Figure 1. Pictorial view of the nano-ZnO/organic supports composites developed in this study: (a) nano-ZnO/silicone, (b) nano-ZnO/Epoxy, (c) nano-ZnO/ABS, and (d) nano-ZnO/polybutadiene

B. Investigation of Water Resistance

In order to investigate water resistance (insolubility) of NZOC in aqueous phase, 5g of each NZOC was weighted, soaked into the distilled water in 25 mL vial, and left for 7 days. After, prepared under same condition each vial was sonicated for 30 minutes, the gathered each composite from vial was dried in the oven at 100 °C. Finally, each NZOC was weighted again, and comparison of weight before soaking and after soaking was performed. This water resistance experiments were performed five times.

C. Batch Photocatalytic Reactor and Experimental Design

As shown in Figure 2, a batch photocatalytic reactor (BPR) consisted of a rectangular mirror-coated PVC plastic, 4 UV-C lamps (8 W, 254 nm in wavelength), 75-mL quartz reactor with mininert valve at one end, temperature sensor and controller. All experiments were performed in triplicate using TCE solution with identical initial concentrations (i.e., 10 mg/L) and different types of NZOC with identical amounts (i.e., 10 g/L) during a reaction period of 60 min. Detail experimental conditions are summarized in Table 1.



Figure 2. Pictorial view of a batch photocatalytic reactor (BPR)

TABLE. 1 Detail experimental conditions for TCE degradation using different types of NZOC

#quartz cell	#1	#2	#3	# 4
Sorption	silicone (10g)	ABS resin (10g)	epoxy (10g)	Poly-butadiene (10g)
Photo-catalyst	UVC (8w*4ea) nano-ZnO/silicone (10g)	UVC (8w*4ea) nano-ZnO/ABS (10g)	UVC (8w*4ea) nano-ZnO/epoxy (10g)	UVC (8w*4ea) nano-ZnO/polybutadiene (10g)

III. Results and discussion

A. Investigation of Water Resistance

The differences of weight before and after water resistance are summarized in Table 2. The weight differences before and after water soaking for 7 days were found to be negligible. However, after the sonication, the weight differences of both nano-ZnO/ABS resin and nano-ZnO/epoxy were greater than those of both nano-ZnO/silicone and nano-ZnO/polybutadiene, indicating that nano-ZnO/silicone and nano-ZnO/polybutadiene were more insoluble and stable composites against water solution. Thus, nano-ZnO/silicone and nano-ZnO/polybutadiene were more feasible NZOC to degrade TCE.

TABLE. 2 The differences of weight for each composite before/after in water soaking for 7 days and before/after sonication for 30 min

Types of composites	before/after in aqueous weight difference	Ultrasonic cleaning before/after weight difference
nano-ZnO/silicone	0.0014 g	0.007 g
nano-ZnO/ABS resin	0.003 g	0.0247 g
nano-ZnO/epoxy	0.0046 g	0.0544 g
nano-ZnO/polybutadiene	0.002 g	0.0112 g

B. Sorption of TCE to different types of organic supports

Sorption of TCE to different types of organic supports (i.e., silicone, ABS resin, epoxy, and polybutadiene) was investigated, and presented in Figure 3. The concentration changes of TCE in control test were insignificant [i.e., $C/C_0 = 0.92\sim 1.04$], indicating that both sorption of TCE to quartz reactor with Teflon®-lined septa and partitioning of TCE to headspace were found to be negligible in this study. After 60 min of reaction time elapsed, sorption of TCE to polybutadiene was greater than that to other organic supports. This result can be attributed to the different permeability flux of TCE to various organic supports. Since the mass transfer of organic compounds through organic supports involves the partition of an organic compound between the surface of the organic supports and the medium and the diffusion of an organic compound through the organic supports, the physicochemical and structural properties of organic supports are significant factors (Joo et al. 2004). In this study, the structure of polybutadiene is amorphous whereas the structures of other organic supports are condensed, where greater degree of crystallinity may decrease the partition coefficient and diffusion coefficient, resulting in low amount of TCE sorption.

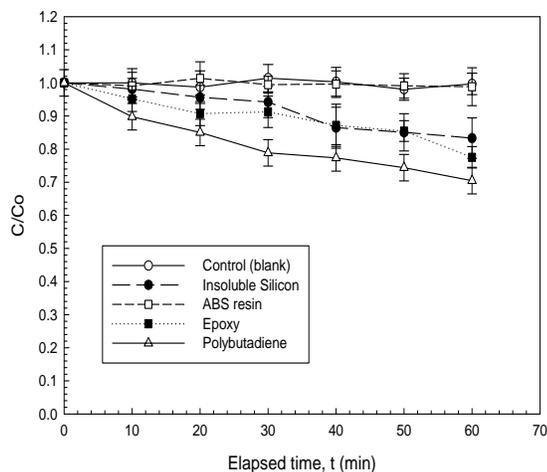


Figure 3. Sorption of TCE to different types of organic supports

C. Degradation of TCE using different types of Nano-ZnO/organic supports composites

As shown in Figure 5, the degradation efficiency of TCE at 1 hr decreased in the order of nano-ZnO/polybutadiene (99%) > nano-ZnO/ABS (55%) > UV (50%) > nano-ZnO/epoxy (50%) > nano-ZnO/silicone (30%). For nano-ZnO/polybutadiene, the sharp decrease in the initial period of reaction (i.e., 10 ~ 20 min) was observed and greater removal efficiency was also observed. Since the polybutadiene has greater sorption capacity and photoactivities due to greater light transparency, photocatalytic degradation of TCE mostly occurred on the surface of ZnO by photogenerated holes and $\cdot OH$ radicals along with other oxidants. As a result, the multiple reaction processes (i.e., sorption, photolysis, and photocatalysis) synergistically occurred on the surface of nano-ZnO/polybutadiene.

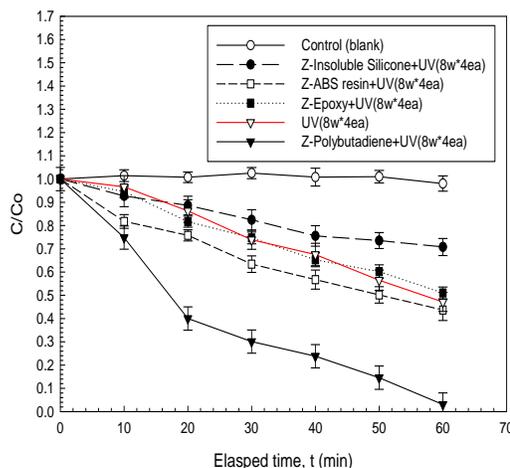


Figure 4. Degradation of TCE using different types of Nano-ZnO/organic supports composites

IV. Conclusions

The photocatalyst composites was made to overcome drawbacks of reuse and recovery used in aqueous phase. Also, when photocatalyst was fixed on supports, the photocatalytic removal efficiency was declined due to decreasing surface area compare with power type. Then, using organic supports with high sorption capacity was expected to overcome efficiency decrease through synergistic effect both photocatalytic mechanism and sorption. The organic supports was chosen of silicone, ABS resin, epoxy and polybutadiene. Among organic supports, the polybutadiene was superior sorption capacity of TCE. The manufactured NZOCs (nano-ZnO/Organic Composites) were considered as use capable in aqueous phase through water resistance test. The Nano-ZnO / polybutadiene composite was due to the synergistic effect of sorption and photocatalytic mechanism to show the most

excellent efficiency more than 99% TCE removal efficiency. Therefore, it was to confirm that the polybutadiene was suited as a support.

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References

- [1] Di Paola, E. Garcia-Lopez, G. Marci, L. Palmisano, “A survey of photocatalytic materials for environmental remediation”, Journal of Hazardous Materials (2012)211–212,3–29.
- [2] L. Yang, L.E. Yu, M.B. Ray, “Degradation of paracetamol in aqueous solutions by TiO₂ photocatalysis”, Water Research 42 (2008) 3480,3488.
- [3] H. Yang, G. Li, T. An, Y. Gao, J. Fu, “Photocatalytic degradation kinetics and mechanism of environmental pharmaceuticals in aqueous suspension of TiO₂”: a case of sulfa drugs, Catalysis Today 153 (2010) 200,207.
- [4] Y. Yokosuka., K. Oki., Y. Tatsumi., N. Tanaka., T. Fujii., “Photocatalytic degradation of trichloroethylene using N-doped TiO₂ prepared by a simple sol–gel process”, Res Chem Intermed (2009) 35:43-53.
- [5] J. C. Joo., J. Y. Kim., A. M.ASCE., K. P. Nam., “Mass Transfer of Organic Compounds in Dilute Aqueous Solutions into High Density Polyethylene Geomembranes”, Journal of Environmental Engineering, 130(2), 175-183.

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