EVALUATION OF TCE DEGRADATION USING NEWLY-DEVELOPED NANO-ZNO/ORGANIC SUPPORT PHOTOCATALYST

Jang DG[1]*, Ahn HS[2], Lee SRM[2], Kim JY[2], Joo JC[2 †]

1 Korea University Science Technology, Department of Construction & Environment Engineering, Republic of Korea

2 Korea Institute of Construction Technology, Water Resource & Environment Research Department, Republic of Korea

1. Introduction

Over traditional water treatment processes, heterogeneous photocatalytic oxidation processes using semiconductor particles such as TiO_2-based materials and other oxides (e.g., ZnO, Cu_2O, WO_3, V_2O_5, α-Fe_2O_3, Bi_2O_3 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 TiO_2 powder (e.g., Degussa P25) or modified TiO_2 (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 TiO_2 on supporting media, filtration and recovery processes etc.) using bare TiO_2 powder or modified TiO_2 have also been reported (Di Paola et al. 2012).

Therefore, in this study, as a valid alternative to bare TiO_2 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 TiO_2 powder.

The purpose of this study was to evaluate the feasibility of NZOC as a valid alternative to TiO_2 powder to mineralize chlorinated hydrocarbons without difficulties for filtration and recovery of photocatalysts.

2. Material and method

2.1 Development of Nano-ZnO/organic supports composites

Nano-ZnO powder (purity 99%) with average particle size of 20 nm and specific surface area greater than 90 m^2/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).

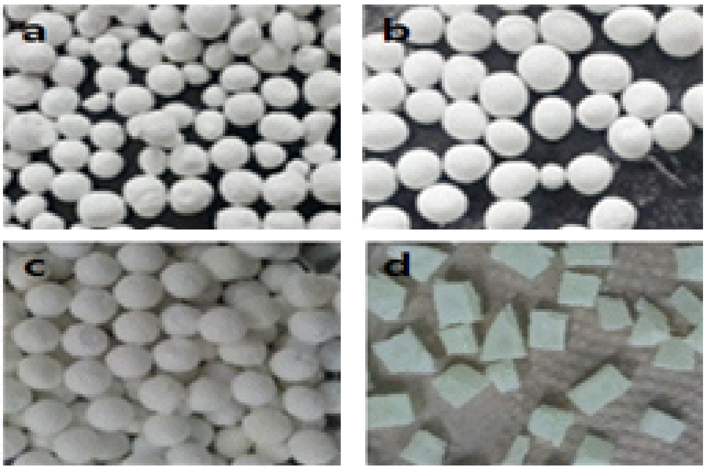

Figure 1. Pictorial view of the nano-ZnO/organic supports composites developed in this study: (a) nano-ZnO/silicone, (b) nano-ZnO/Epoxy, (c) nano-ZnO/ABS, and (d) nano-ZnO/polybutadiene

2.2 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 ℃. 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.

2.3 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)	polybutadiene (10g)
Photocatalytst	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)

3. Result and discussion

3.1 Water Resistance Results

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 mins

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

3.2 TCE degradation experiment result

3.2.1 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 = 0.92~1.04], 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; 2005). 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.

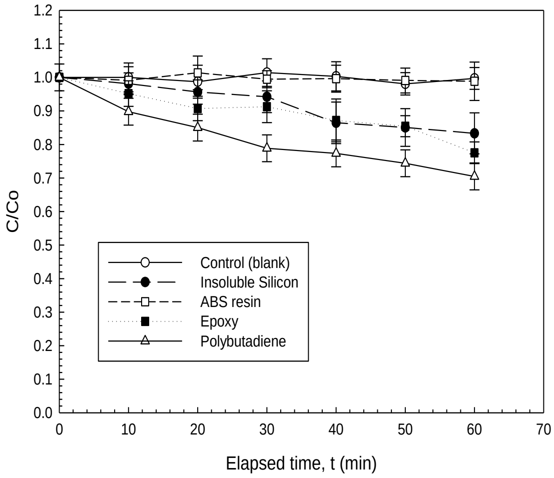

Figure 3. Sorption of TCE to different types of organic supports

3.2.2 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 $^{\bullet}OH$ 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.

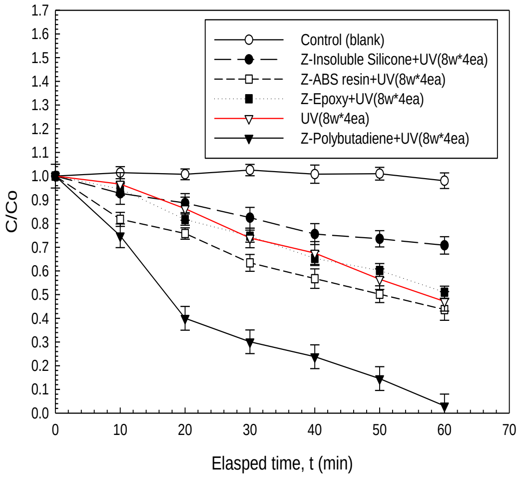

Figure 4. Degradation of TCE using different types of Nano-ZnO/organic supports composites

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