

# Photocatalytic degradation of trichloroethylene in water using nano-ZnO/butadiene composites

Jin Chul Joo, Dae Gyu Jang, Chang Hyuk Ahn, Saeromi Lee, Jong Kyu Kim

**Abstract**—According to the FE-SEM, EDX, and imaging analysis, nano-ZnO/butadiene rubber composites (NZBC) with various sizes and types of porosity and crack was measured to be coated with relatively homogeneous-distributed nano-ZnO particles. The sorption capacity of NZBC for trichloroethylene (TCE) was close to 60% relative to the initial concentration, and this result was mainly attributed to the amorphous structure of NZBC, hence the hydrophobic partitioning of TCE to the amorphous structure of NZBC intensively occurred. The removal efficiency of TCE in aqueous phase using NZBC was superior to close to 99% relative to the initial concentration, and the removal efficiency of TCE was improved as the amount of NZBC increased. These results stemmed from the synergistic mechanisms with great sorption capability of butadiene rubber and superior photocatalytic activities of nano-ZnO. Finally, the removal efficiency of TCE in aqueous phase using NZBC was well represented by linear model ( $R^2 \geq 0.936$ ), and the  $K_{app}$  values of NZBC were from 2.64 to 3.85 times greater than those of  $K_{photolysis}$  with UV only, indicating that butadiene rubber was found to the suitable organic support materials with enhanced sorption capacity and without inhibition of photocatalytic activities of nano-ZnO.

**Keywords**— butadiene rubber, nano-ZnO/ butadiene rubber composites (NZBC), photocatalytic activity, sorption

## I. Introduction

Although most studies dealt with photocatalytic oxidation of chlorinated hydrocarbons using bare TiO<sub>2</sub> powder (e.g., Degussa P25) or modified TiO<sub>2</sub> (i.e., doping, loading and sensitization with rare earth metal species or metal-free phthalocyanines) (Yang et al. 2010), several drawbacks using bare TiO<sub>2</sub> powder or modified TiO<sub>2</sub> have also been reported as follows: (1) small amount of absorbed photon in the visible light region, (2) high recombination rate for electron-hole pairs, (3) difficulty to support powered TiO<sub>2</sub> on supporting media, and (4) difficulty to extend the lifetime without substantial loss of photocatalytic activity (Di Paola et al. 2012).

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In this study, as a valid alternative to bare TiO<sub>2</sub> powder or modified TiO<sub>2</sub>, nanoscale (nano-) ZnO was considered due to its good optoelectronic, catalytic and photochemical properties along with its low cost. Also, commercial butadiene rubber (LG, KO) was considered as a supporting medium due to both high sorption capacities and amorphous structure. Finally, innovative nano-ZnO/butadiene rubber composites (NZBC) were developed to overcome drawbacks using bare TiO<sub>2</sub> powder or modified TiO<sub>2</sub>.

In accordance with the aforementioned considerations, the purpose of this study was to evaluate the feasibility of NZBC as a valid alternative to TiO<sub>2</sub> to mineralize chlorinated hydrocarbons without difficulties for filtration and recovery of photocatalysts. The specific objectives of this study were (1) to investigate the photocatalytic degradation of TCE in aqueous phase using NZBC, and (2) to evaluate the effects of initial concentration of TCE, loading amount of NZBC, intensity of light, and initial solution pH on photocatalytic degradation of TCE in aqueous phase.

## II. Materials and Methods

### Preparation of nano-ZnO/butadiene composites

Crosslinked butadiene rubber (LG, KO) with excellent abrasion resistance and elasticity was prepared as 5–7 mm size specimens. Then, 30 g of crosslinked butadiene rubber were immersed in 300 mL of tetrahydrofuran (Daejung Chemical & Metals Co., Ltd.) for more than 2 h. After the immersion of crosslinked butadiene rubber, the swelled butadiene rubber specimens were placed on the patch of nano-ZnO powder to physically attach nano-ZnO powder on the surface of the butadiene rubber specimens. Finally, the nano-ZnO powder-coated butadiene rubber specimens were dried in an electric furnace at 130 °C for 5 min.

### Batch Photocatalytic Reactor & Experimental Design

A batch photolysis reactor applied in Joo et al. (2013) was used in this study. All experiments were carried out in triplicate during a reaction period of 60 min. To compare the photocatalytic activities of NZBC (10 g) and nano-ZnO powder (0.05 g) was inserted in a quartz reactor before the experiments. To evaluate the effect of the initial concentration, TCE solutions were prepared with different concentrations (1, 5, 10, and 20 mg/L). The effects of the loading amount of NZBC, the intensity of light, and the initial solution pH on

photocatalytic degradation of TCE in water were also evaluated.

### III. Results and Discussion

#### Physicochemical properties of NZBC

As shown in Figure 1, the FE-SEM, EDX, and imaging analysis of NZBC indicated that various sizes and types of porosity and cracks were developed on the surface of NZBC. Also, NZBC was found to be coated with relatively homogeneous-distributed nano-ZnO particles.

#### Degradation of TCE Using NZBC

Removal of TCE in water under the various conditions [i.e., only TCE solution (control), TCE solution with UV (photolysis), TCE solution with NZBC (sorption), and TCE solution with both NZBC and UV (sorption + photocatalysis)] was displayed in Figure 2. The control test was nearly changed (i.e.,  $C/C_0 = 0.96-1.03$ ), suggesting that negligible experimental errors caused by sorption with Teflon®-lined septa and partitioning of TCE to the headspace.

The TCE removal efficiencies of NZBC via sorption to NZBC were close to about 60%. The sorption mechanism of TCE to NZBC was mainly due to the partitioning of TCE at the interface. Considering the non-crystalline and flexible butadiene polymer, the partitioning and diffusion of TCE to NZBC are non-specific and favorable in thermodynamics.

Based on comparison of degradation efficiency between photolysis and photocatalysis, the degradation efficiency can be significantly improved using NZBC under UV irradiation, indicating that ZnO-mediated heterogeneous photocatalytic degradation occurred, and surface reactions in heterogeneous photocatalysis were more dominant than photo-induced radical reactions in aqueous solutions. Thus, ZnO complexed with butadiene rubber was found to be an effective photocatalyst for photodegradation of TCE in aqueous solutions.

As also shown in Figure 2, the photocatalytic activities of nano-ZnO as powder type were lower than those of NZBC although the surface area of powder nano-ZnO exposed to UV irradiation was expected to be greater. This result may be due to the fact that the surface of nano-ZnO was covered with preferential adsorption of physisorbed water molecules, and TCE molecules cannot effectively compete against physisorbed water molecules, resulting in lower removal efficiency of TCE by powder nano-ZnO. Also, nano-ZnO used in this study was found to be clustered into larger agglomerates, and those agglomerates were deposited at the bottom of the quartz reactor. These agglomeration and deposition of nano-ZnO may reduce UV radiant flux and block the available ZnO surface for photon absorption.

While the NZBC were used as balls instead of powder, the removal efficiency of NZBC balls was greater since the multiple reaction processes (i.e., sorption, photolysis, and photocatalysis) synergistically occurred at the same time. Therefore, innovative NZBC with the crosslinked butadiene are expected to overcome drawbacks (e.g., filtration and

recovery of catalysts, and dispersion issues) associated with application of nano-TiO<sub>2</sub> and ZnO powder in degradation of chlorinated hydrocarbons for various water resources.

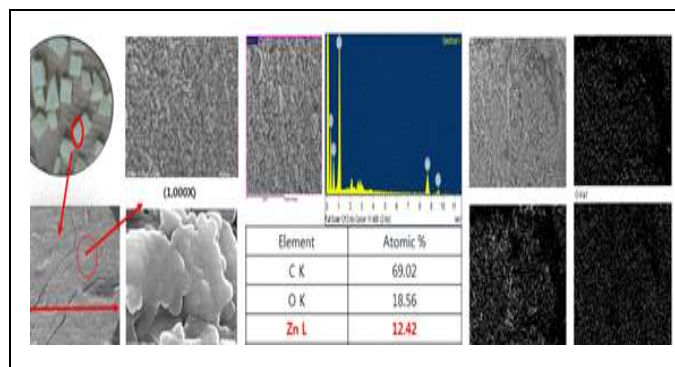


Figure 1. FE-SEM, SEM/EDX, imaging results of various Nano-ZnO/Butadiene Composites (NZBC)

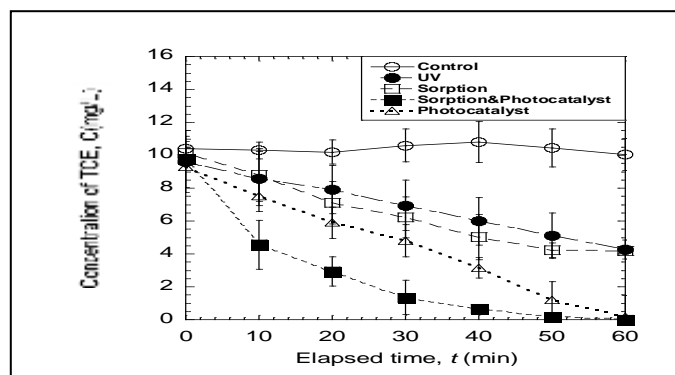


Figure 2. Removal of TCE in water under the various conditions at pH of  $7.0 \pm 0.2$  [only TCE solution (control test), TCE solution with 10 g/L-NZBC (sorption), TCE solution with UVC intensity of  $8.4 \text{ mW/cm}^2$  (photolysis), TCE solution with both 10g/L-NZBC and UVC intensity of  $8.4 \text{ mW/cm}^2$  (sorption+photocatalysis), and TCE solution with both 0.05 g/L-nano ZnO powder and UVC intensity of  $8.4 \text{ mW/cm}^2$  (sorption+photocatalysis)]

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