

Impacts of environmental conditions on the sorption of volatile organic compounds onto tire powder

Dong I. Oh^a, Kyongphile Nam^b, Jae W. Park^c, Jee H. Khim^d,
Yong K. Kim^b, Jae Y. Kim^{b,*}

^a Division of R&D Planning and Management, Korea Institute of Environmental Science and Technology, Seoul, Republic of Korea

^b School of Civil, Urban & Geosystem Engineering, College of Engineering, Seoul National University, Gwanak-Ku, 151-742 Seoul, Republic of Korea

^c Department of Civil Engineering, Hanyang University, Seoul, Republic of Korea

^d Department of Civil & Environmental Engineering, Korea University, Seoul, Republic of Korea

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Abstract

A series of batch tests were performed and the impacts of environmental conditions and phase change on the sorption of volatile organic compounds (VOCs) were investigated. Benzene, trichloroethylene, tetrachloroethylene, and ethylbenzene were selected as target VOCs. Sorption of VOCs onto tire powder was well demonstrated by a linear-partitioning model. Water–tire partition coefficients of VOCs (not tested in this study) could be estimated using a logarithmic relationship between observed water–tire partition coefficients and octanol–water partition coefficients of the VOCs tested. The target VOCs did not seem to compete with other VOCs significantly when sorbed onto the tire powder for the range of concentrations tested. The influence of environmental conditions, such as pH and ionic strength also did not seem to be significant. Water–tire partition coefficients of benzene, trichloroethylene, tetrachloroethylene, and ethylbenzene decreased as the sorbent dosage increased. However, they showed stable values when the sorbent dosage was greater than 10 g/L. Air–tire partition coefficient could be extrapolated from Henry's law constants and water–tire partition coefficient of VOCs.

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1. Introduction

In the Republic of Korea, it was reported that 699,214 t of volatile organic compounds (VOCs) were emitted to the atmosphere from oil stations and industries such as printing and coating facilities in 2001 [1]. Due to the problems caused by the presence of VOCs, there is an increasing interest in developing new methods to decrease the cost of VOC removal.

The disposal of scrap tires also poses a serious environmental problem in Korea. Over 23.2 million tires were discarded in 2003 [2]. Scrap tires cannot be easily disposed of due to their poor compressibility, potential combustibility, and associated toxic fumes [3]. For these reasons, application technologies to recycle and reuse large volumes of scrap tires are required. Since the main constituents of tire materials were synthetic rubber, natural

rubber, and carbon black [4], scrap tires can sorb significant amounts of VOCs in the aqueous phase [5]. Tire powder may be a possible candidate for both a sorption medium in the permeable reactive barrier and a supplemental aggregate in the slurry cutoff wall for the treatment of the VOC-contaminated groundwater [6–8]. Also, scrap tires can be used for gaseous VOC removal as a filter medium [9,10].

The objectives of this study were (1) to examine the sorption behavior of VOCs onto tire powder in the aqueous and gaseous phase, and (2) to evaluate the impacts of environmental conditions (i.e., pH, ionic strength, and tire powder/solution ratio).

2. Materials and methods

2.1. Sorbates and sorbents

Benzene (BZ), ethylbenzene (EB), tetrachloroethylene (PCE), and trichloroethylene (TCE) were selected for testing

* Corresponding author. Tel.: +82 2 880 8364; fax: +82 2 889 0032.
E-mail address: jaeykim@snu.ac.kr (J.Y. Kim).

Table 1
Properties of volatile organic compounds tested at 20 °C [11]

Compound	Molecular weight (g/mol)	Specific gravity (dimensionless)	Aqueous solubility (mg/L)	log K_{ow} ^a
Benzene	78.11	0.789	1780	2.13
Trichloroethylene	131.50	1.460	1100 ^b	2.42
Tetrachloroethylene	165.83	1.626	150 ^b	2.60
Ethylbenzene	106.17	0.867	152	3.15

^a The octanol–water partition coefficient.

^b At 25 °C.

and their properties were summarized in Table 1. The liquid sorbates were obtained from Sigma–Aldrich, and the purity of these sorbates was 99% or higher. Target VOCs were analyzed using a gas chromatograph (600D; Young Lin Instrument Co., Korea) equipped with an HP-FFAP capillary column (50 m × 0.25 mm × 0.17 μm) and a flame ionization detector (FID). An aliquot of 1.0 μL liquid sample was directly injected into the column using a 10 μL gas-tight syringe. Nitrogen gas was used as a carrier with a flow rate of 2.0 mL/min. The gas flow to the FID was combined with make-up gas (N₂ at 26 mL/min), hydrogen (30 mL/min), and air (300 mL/min). The oven temperature was held at 65 °C. The injection port and the detector temperatures were held at 280 and 300 °C, respectively. The relative standard deviations of the sample analyses ranged from 3.8% for benzene and 12.5% for PCE.

Tire powder was obtained from the Korea Environment & Resources Corporation (Incheon, Korea). Tire powder was sieved to obtain uniform particles using two sieves with openings measuring 0.6 and 1.18 mm and was air-dried without any pretreatment. The tire powder was then stored in a desiccator. The particle size of tire powder was estimated to be 0.84 mm, obtained by taking the geometric mean of the sieve openings.

2.2. Batch test in aqueous phase

Batch tests were conducted using 40 mL screw-capped glass vials with Teflon-lined septa. VOC-containing solutions were added to the glass vial with tire powder. The volume of solution and amount of the tire powder applied were all measured by a weight scale. A VOC-containing solution was prepared by combining a few microliters of pure VOC liquid to 1 L of deionized water and stirring overnight. These tests were conducted in a constant temperature room (20 ± 1 °C) using 10–100 mg/L of the initial concentrations of the VOC solution. Sodium azide (NaN₃), with a concentration of 0.05% (by weight), was added in order to inhibit microbial activity in the VOC-containing solution. The vials were capped immediately after adding the VOC-containing solution and then tumbled end-to-end at 10 rpm to achieve equilibrium.

A preliminary test was conducted to determine the loss of vaporized VOCs during the batch test and to estimate the time required for the sorption equilibrium of the VOCs onto the tire powder. The overall loss of the VOCs by experimental apparatus and procedures was less than 5% after 7 days. Control vials without sorbents were used to account for any loss of VOCs and the corrected concentrations were used as initial VOC concentrations.

The change in VOC concentration in the aqueous phase was monitored to estimate the required time for VOC sorption equilibrium onto tire powder. After 24 h, there was no significant change (less than 5%) in the VOC concentration, indicating that a contact time of 24 h was sufficient enough for reaching equilibrium. In this study, a 72-h contact time was adopted to ensure sorption equilibrium. At the end of tumbling, 1 mL of supernatant was sampled and analyzed by GC/FID.

Sorption isotherms were developed with the following equation:

$$C_s = \frac{(C_i - C_e)V_1}{M_s} \quad (1)$$

where C_s is the sorbed concentration of a VOC (mg/kg); V_1 the added VOC solution volume (mL); M_s the dry weight of tire powder (g); C_i the initial VOC concentration from control vials (mg/L); and C_e is the equilibrium concentration of the VOC (mg/L).

The water–tire partition coefficient, K_1 , was calculated from linear regression of sorbed concentration versus aqueous equilibrium concentration:

$$C_s = K_1 C_e \quad (2)$$

VOC sorption onto tire powder was also examined using Freundlich relationship:

$$C_s = K_F C_e^N \quad (3)$$

where K_F is the Freundlich adsorption coefficient and N is the Freundlich exponent.

2.3. Influence of environmental conditions

In order to evaluate the effect of the presence of other VOCs on the sorption of a single VOC onto tire powder, the partition coefficients obtained from the single-solute batch tests were compared with those from the multi-solute batch tests. The values of the water–tire partition coefficient observed at three different levels of pHs (5, 7, and 9) and two levels of ionic strengths (0 and 100 mM) were compared with each other. The initial pH was adjusted with 0.1 M sulfuric acid and 0.1 M sodium hydroxide solutions. Another series of batch tests were performed to evaluate the effect of sorbent concentration on measured partition coefficients from approximately 0.5 to 60 g/L sorbent dosages.

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