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Immobilization of MTBE using cyclodextrins

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Abstract

Immobilization behavior of methyl tert-butyl ether (MTBE) by various cyclodextrins(CDs) was studied to investigate the feasibilityof MTBE removal using cyclodexrins. Even though MTBE has relatively low hydrophobicity and higher polarity compared to other organics, it was effectively immobilized by CDs. The immobilization isotherms was shown as a type of Freundlich isotherms, and the immobilization capacity of -CDs was the largest among natural CDs. The initial apparent association constant for MTBE-CD complex follows the order : gamma = beta > methyl-beta > hydroxypropyl beta > alpha. These differences of the constants are related to the size of MTBE and CDs. The size of beta-CD and gamma-CD is large to encapsulate MTBE molecule into the cavity, which that of alpha-CD is too small to encapsulate MTBE.

key word : MTBE, Cyclodextrin, Immobilization, Inclusion

1. Introduction

The presence of methyl *tert*-butyl ether (MTBE) in groundwater and drinking water has become a significant environmental issue due to its taste and toxicity MTBE was compounded by its relatively recent but widespread introduction into the environment as a gasoline additive. Because MTBE is highly soluble in waterand seldom adsorbs onto the soil particle due to its low hydrophobicity, it is readily transported into groundwater and surface water systems. It also has a low taste and odor threshold and is tentatively classified by the U.S. EPA as a possible human carcinogen [1]. Conventionaltreatment methods such as air stripping, carbon adsorption, and aerobic biodegradation do not remove MTBE from water as effectively as they do for other volatile organic compound (VOC) contaminants [2].

Cyclodextrins (CDs) have a low-polarity cavity in which organic compounds of appropriate shape and size can form inclusion complexes. This unique property provides CDs with a capacity to significantly increase the apparent solubilities of low polarity organic contaminants such as polyaromatic hydrocarbons, herbicides, pesticides, iodine, and various organics [3-4]. For VOCs with relative high water solubility such as benzene and MTBE, however, CDs can immobilize the VOCs into the cavity in aqueous phase.

In this study, the feasibility of natural and chemically modified CDs for the immobilization of MTBE from water into CD cavity was investigated, which has not yet been examined elsewhere in detail.

2.Materials and Methods

Analytical grade MTBE was purchased from Aldrich chemical Co. Three different types of natural CDs (alpha-CD, beta-CD, gamma-CD) and chemically modified CDs (hydroxypropyl beta-CD and methyl beta-CD) were purchased from TCI chemical (Japan). The characteristics of alpha-CD, beta-CD and gamma-CD were summarized in Table 1. Headspace analysis using solid phase microextraction (SPME) is a useful tool to detect the concentration of MTBE in aqueous phase [5-6]. SPME holder and firber coated with polydimethylsiloxane (PDMS) and Carboxen (30 m film thickness) were purchased from Supelco (Bellefonte, USA). MTBE analysis was performed with a Hewlett Packard (Sunnyvale, USA) GC 6890 series II coupled with a FID.

The extraction was performed in an open-top screw cap vial (20ml) equipped with a teflon-coated silicon septum. A sample of 10 ml containing the desired amount of CDs and MTBE was stirred for 2 hours at 25°C in order to achieve a phase equilibrium. After the headspace extraction during 10 min, the SPME fiber was removed from the vial and immediately inserted into the GC injector. Desorption of MTBE from SPME fibre was executed during 3 min at 250C (GC injector temperature).

The chromatographic capillary column was a HP1 (30 m0.25 mm) with 0.2m film thickness. The injector program was as follows: injector temperature, 250°C, from 40°C to 130°C at a rate of 10°C/min, and the detector temperature, 250°C.

3.Results and Disccusions

The immobilization of MTBE in various CDs solutions can be regarded as a measure of their MTBE-binding capacity under the present experimental conditions. Figure 1, 2, and 3 shows the immobilization of MTBE in alpha-CD, beta-CD, and gamma-CD, respectively. The immobilization behavior of MTBE into CD is similar to the sorption phenomenon of MTBE into CD, as a result, the immobilization isotherms is similar to sorption isotherms. As shown in Fig 1, 2, and 3, the data have been plotted according to the Freundlich isotherm. The immobilization capacity was observed to increase remarkably with increasing equilibrium concentration of MTBE, and the relationship between the sorption capacity and the equilibrium concentration could be expressed with the Freundlich equation described according to

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where q_e is the adsorption capacity (moles / moles) and C_e is the equilibrium concentration (mM).

Based on the result of immobilization isotherms, beta-CD showed highest immobilization capacity, however, the solubility of beta-CD is too low (16.3 mM). To study immobilization isotherms of MTBE according to the concentration of beta-CD, two different types of chemically modified beta-CD, methyl beta-CD and hydroxypropyl beta-CD, were investigated (Fig. 4). The association constants, K_{ass}, calculated from the initial slope (to 0.5 wt% concentration of each CD), because the constant was variable in this study. The initial association constant for CD-MTBE system is too low compared to other organics such as benzene, toluene, xyelene and iodine because the hydrophobicity of MTBE was lower than other organics and polarity of MTBE was greater than other organics. The highest constant was obtained from the beta and gamma-CD, and about three times higher than that obtained for alpha-CD. This order of association constant can be explained by the size of MTBE and CDs.

3.Conclusions

The immobilization isotherms of MTBE into CDs closely followed the Freundlich sorption isotherms. Immobilization capacity for MTBE was lower than other hydrophobic organics due to the lower hydrophobicity of MTBE. Among other CDs tested in this study, beta-CD showed the highest immobilization capacity. The association constant of MTBE-CD complex was calculated assuming 1 : 1 stoichiometry. beta-CD and gamma-CD showed similar values of association constant because of the comparable size for immobilzation of MTBE. Cyclodexrins can be used for the removal of MTBE from subsurface water or groundwater.

4. Acknowledgement

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5. References

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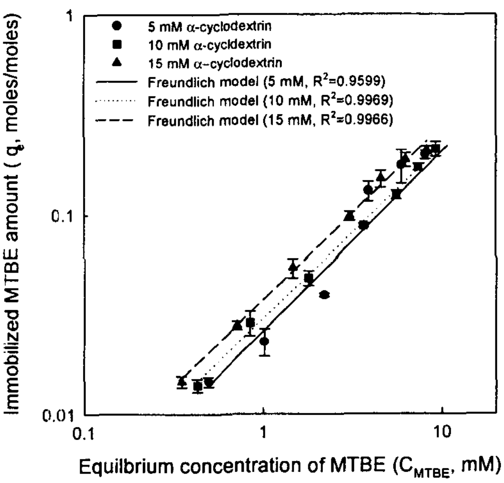

Figure 1

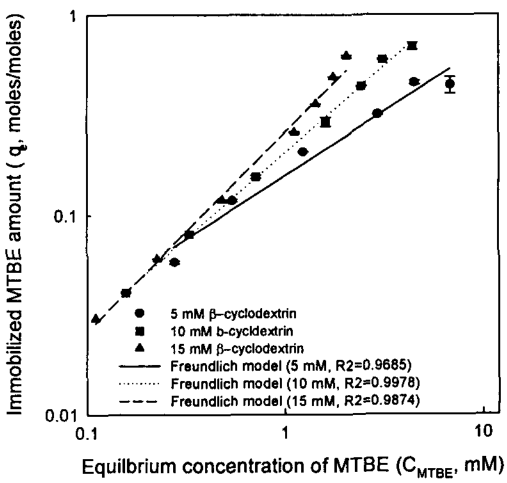

Figure 2

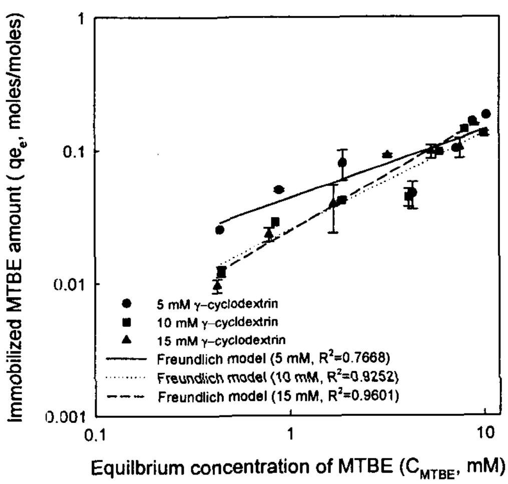

Figure 3

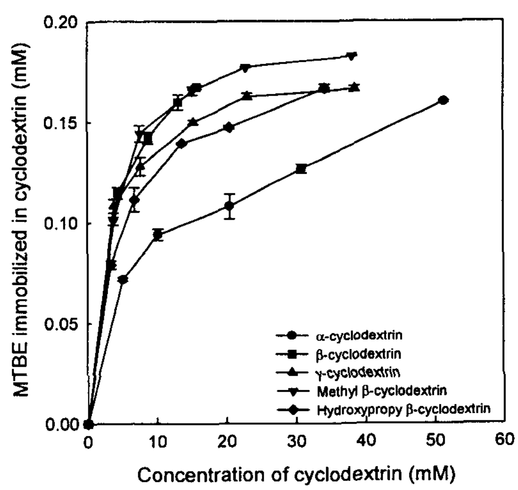

Figure 4