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Adsorption behavior of some aromatic compounds on hydrophobic magnetite for magnetic separation

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ABSTRACT

In this study, a hydrophobic magnetite coated with an alkyl chain or a phenyl group on the surface was prepared and used as an adsorbent to investigate the adsorption behavior of aromatic compounds having various values of $\log P_{ow}$ (phenol 1.46, benzonitrile 1.56, nitrobenzene 1.86, benzene 2.13, toluene 2.73, chlorobenzene 2.84 and *o*-dichlorobenzene 3.38) onto hydrophobic magnetite. The hydrophobic magnetites were modified with stearic acid and phenyltrimethoxysilane, and the modification amounts were 9.84×10^{-3} and 4.17×10^{-2} mmol/g, respectively. The aromatic compounds used in this study were divided into 3 groups depending on the $\log P_{ow}$: $1 < \log P_{ow} < 2$, $2 < \log P_{ow} < 3$ and $3 < \log P_{ow}$. The adsorption amounts of above each group on the magnetite at an initial concentration of 100 ppm were 3.62×10^{-3} (nitrobenzene), 1.92×10^{-2} (phenol), 1.13×10^{-1} (chlorobenzene), 2.42×10^{-1} (benzene), and 3.10×10^{-1} mmol/g (dichlorobenzene), respectively. This indicates that the adsorption behaviors depend on the strength of hydrophobicity of aromatic compounds. The adsorption mechanism for $2 < \log P_{ow} < 3$ and $3 < \log P_{ow}$ is hydrophobic interaction and that for $1 < \log P_{ow} < 2$ is π-electron interaction. The quantitative relationship between the amount of adsorbed compounds and modified functional groups and the fitting for adsorption isotherm models suggested that this adsorption might form a multi-layer adsorption in the most cases.

1. Introduction

Global attention to water pollution from harmful chemicals has increased in recent decades. Many kinds of pollutants have been discovered in aquatic environments such as rivers, ponds and seas. These contaminants originated from industrial and domestic wastewater, sometimes from accidental spills. Various mono and polycyclic aromatic compounds have been found in aquatic environments. These aromatic compounds must be removed before the water is discharged or consumed.

In order to treat harmful organic compounds in effluent, two types of technology are currently available. The first is a decomposition technology where hazardous organic compounds are converted to more environmentally friendly compounds. Technologies such as chemical oxidation [1], electrolysis [2], photo oxidation [3], and ozonation [4] are included in this category. The second type is a separating technology, where harmful organic pollutants are separated from the effluent by various methods. Technologies such as membrane separation [5], adsorption [6], and solvent extraction [7] belong to the second category.

Among these types of technologies, adsorption is one of the simplest and most effective processes. Adsorption is fast, economic and widely applicable techniques. Using adsorption is applicable for various pollutants such as organic compounds and heavy metals by selecting the type of adsorbent and adsorption conditions. In addition, recently treatment methods for wastewater using low-cost adsorbents such as by-products or waste materials have been reported [8,9]. Gupta and co-workers have reviewed the details of treatment methods for various pollutants in water using low-cost adsorbents [10,11].

Activated carbon is the most widely used adsorbent in various cases because of a large capacity and a wide variety of adsorbates. However, there are some limitations, particularly in regeneration [12]. There is poor mechanical rigidity and low selectivity when activated carbon is applied to real environmental pollution. Furthermore, it is difficult to collect activated carbon powder that has been widely diffused into the environment. If it is not collected, the adsorbent that is used to adsorb harmful pollution could become a secondary source of pollution.

Magnetic separation has been applied recently in various fields such as analytical biochemistry [13], medical science [14] and biotechnology [15]. From an environmental point of view, magnetic separation offers advantages due to the easy recovery of the

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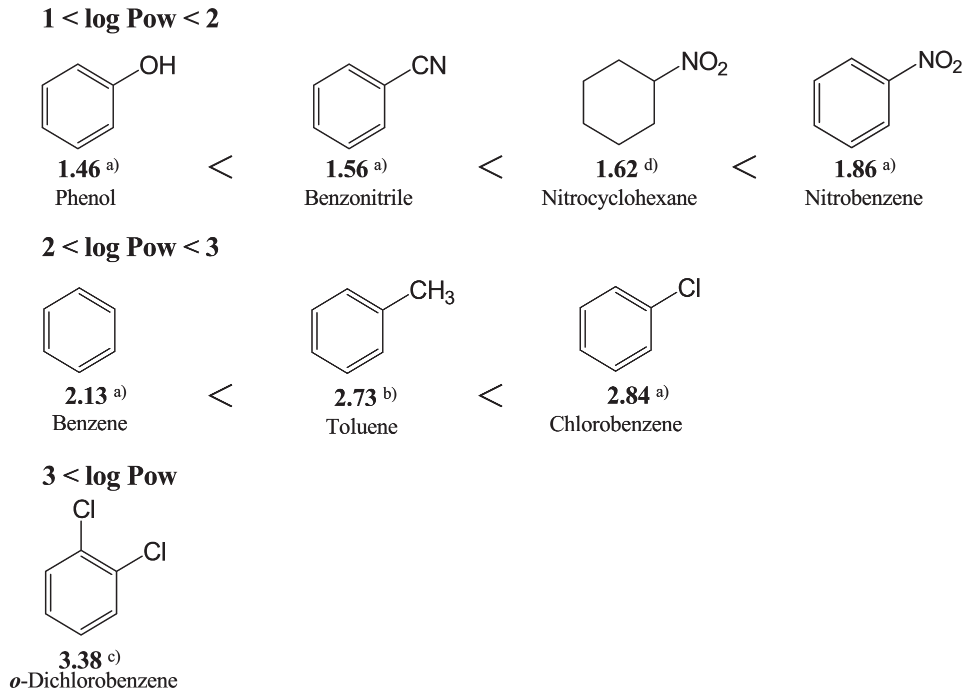

Fig. 1. Structures and $\log P_{ow}$s of aromatic compounds and nitrocyclohexane. a) the values of $\log P_{ow}$ was referred to Ref. [25] b) the values of $\log P_{ow}$ was referred to Ref. [26] c) the values of $\log P_{ow}$ was referred to Ref. [27] d) the values of $\log P_{ow}$ was referred to Ref. [28].

adsorbent without filtration or centrifugation. Several studies have reported magnetic separation using modified magnetite (Fe_3O_4) as an environmentally friendly approach to remove heavy metal ions [16,17] and organic pollutants [18,19].

The removal of harmful organic compounds with adsorbents is in most cases based on the hydrophobic interaction between an adsorbent and its target compounds. This hydrophobic interaction has been applied to not only the removal of harmful substances by adsorbents but also to the preconcentration of analytes by using solvents [7] and solid extraction [20]. A hydrophobic adsorbent can be prepared by using a hydrophobizing agent on the surface of materials such as magnetite and silica beads [18,21]. One of the most popular techniques for hydrophobizing involves the use of silane coupling agents. Silane coupling agents are known as surface modifiers that can add an organic property to the surface of an inorganic material [22,23]. Therefore, a silane coupling agent is important when forming a hybrid inorganic-organic material. Another technique is the use of an ionic surfactant. An ionic group of the surfactant will turn toward the surface of mineral oxides such as alumina, silica, titanium dioxide and ferric oxide, and then the alkyl chain, the hydrophobic group of the surfactant, will orient to the outside. As a result, the surface of the material becomes hydrophobic [24].

The strength of the hydrophobic interaction depends on the degree of hydrophobicity of both the adsorbent and the adsorbate. The hydrophobicity of an organic compound can be varied by the structure and functional group of the compound. The octanol–water partition coefficient (P_{ow}) is a well-known indicator of the hydrophobicity of an organic compound. A higher hydrophobicity compound will have a larger P_{ow}. Therefore, the hydrophobicity, or P_{ow}, of an organic compound is very important in the prediction of the adsorptive behavior of some organic compounds in water.

The aim of the present study was to clarify the adsorption behaviors of organic compounds on hydrophobic magnetite and to evaluate the possibility of magnetic separation for the removal of organic compounds dissolved in water. Organic compounds with low P_{ow}s, or relatively weak hydrophobicities, were used in this study. These organic compounds were selected on the basis of the value of $\log P_{ow}$. The selected compounds were divided into 3 groups according to $\log P_{ow}$: $1 < \log P_{ow} < 2$, $2 < \log P_{ow} < 3$, and $3 < \log P_{ow}$. The P_{ow}s of phenol, benzonitrile and nitrobenzene fell into the $1 < \log P_{ow} < 2$ group. Those of benzene, toluene and chlorobenzene were in the $2 < \log P_{ow} < 3$ group. *o*-Dichlorobenzene was in the $3 < \log P_{ow}$ group [25–29]. The individual values of $\log P_{ow}$s of aromatic compounds used in the adsorption experiments are summarized in Fig. 1. The hydrophobic magnetite was prepared by hydrophobizing the surface of a magnetite particle. Stearic acid and phenyltrimethoxysilane were used to hydrophobize the surface of magnetite. By using two different types of hydrophobic magnetite, the difference in adsorption behaviors of the various aromatic compounds was investigated.

2. Experiments

2.1. Materials

Magnetite where average size was 0.3 μm (the data was provided from Kishida Chemical.), was purchased from Kishida Chemical Co., Ltd. (Osaka, Japan) and used as the adsorbent carrier. The modifying reagents, stearic acid and phenyltrimethoxysilane were purchased from MP biomedicals Japan K. K. (Tokyo, Japan) and Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), respectively. The organic compounds used as adsorbates, phenol, nitrobenzene and benzene were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Toluene, chlorobenzene and *o*-dichlorobenzene were purchased from Nacalai Tesque, Inc. (Kyoto, Japan). Benzonitrile was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Nitrocyclohexane was purchased from Tokyo Chemical Industry Co., Ltd. In analysis for fatty acid, a boron trifluoride solution was used as an esterification agent, anhydrous sodium sulfate was used as a dehydration agent, and methylene chloride was used as a solvent, and all were purchased from Wako Pure Chemical Industries, Ltd. The reagents used in Si analysis, (hydrochloric acid, nitric acid,