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.

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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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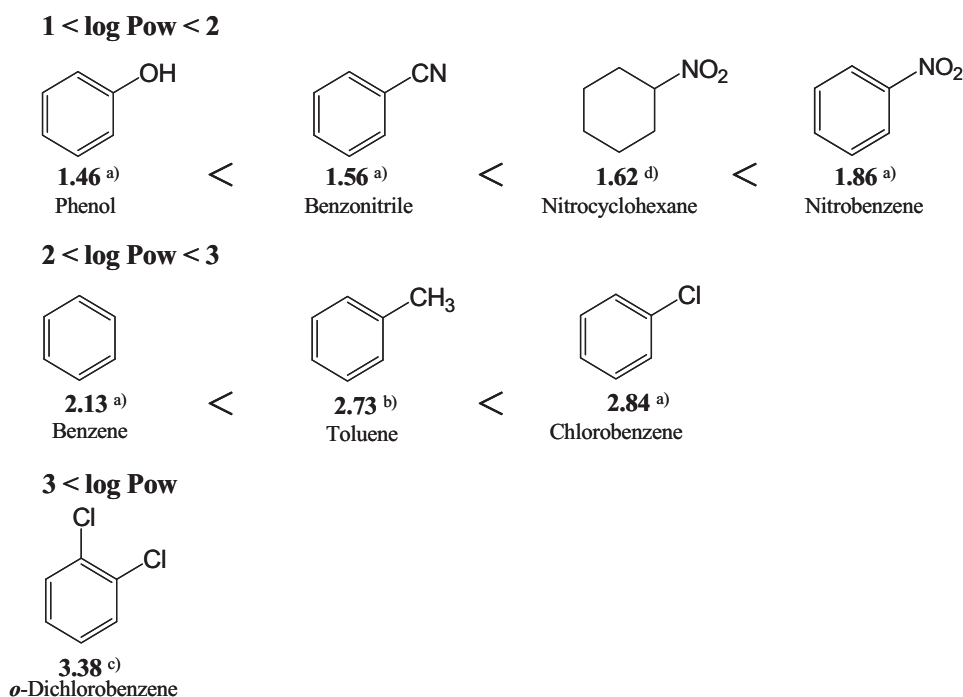
1 < log Pow < 2

1.46 [a]	**1.56** [a]	**1.62** [d]	**1.86** [a]
Phenol	Benzonitrile	Nitrocyclohexane	Nitrobenzene

2 < log Pow < 3

2.13 [a]	**2.73** [b]	**2.84** [a]
Benzene	Toluene	Chlorobenzene

3 < log Pow

3.38 [c]
o-Dichlorobenzene

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,

sulfuric acid, hydrofluoric acid, boric acid, hexaammonium hep-tamolybdate tetrahydrate and sodium chloride) were purchased from Wako Pure Chemical Industries, Ltd. All regents were of ana-lytical grade and used without further purification.

2.2. Preparation of hydrophobic magnetite

Two kinds of hydrophobic adsorbents were prepared: stearic acid modified magnetite (SA-mag) and phenyl group modified mag-netite (Ph-mag) [29,30]. SA-mag was prepared in the following way. 1.0 g of magnetite was added in 50 ml of methanol for distribution. Then 10 mg of stearic acid was added to the suspension with stir-ring to dry out the methanol. The residue was washed twice with methanol and dried in an oven at 50 °C. Ph-mag was prepared in the following way. 1.0 g of magnetite was added in 40 ml of ethanol and distributed with stirring. Then, 0.1 ml of phenyltrimethoxysilane was added to the suspension. After phenyltrimethoxysilane was sufficiently dissolved in the solvent, 0.058 ml of H_2O and 0.025 ml of 1 M HCl were added to the suspension. The suspension was then heated at 50 °C with continuous stirring until the solvent was dry. The obtained magnetite was heated in a muffle furnace at 120 °C for 1 h. After heating, the modified magnetite was washed twice with ethanol and dried in an oven at 50 °C.

2.3. Characterization of hydrophobic magnetite

2.3.1. Surface areas of hydrophobic magnetite
The surface areas of SA-mag and Ph-mag were determined using a N_2 BET analysis (AutoSorb6 YUASA, Japan). The samples were pretreated by degassing at 80 °C for 6 h.

2.3.2. Amount of modified stearic acid on magnetite
For desorption of modified stearic acid from SA-mag, 30 mg of SA-mag was washed with 20 ml of ethanol for 1 h with sonica-tion. The washing procedure was repeated 3 times. And then, the collected ethanol solution that included stearic acid was evapo-rated under vacuum. The obtained sample was dissolved in 3 ml of methanol and 1 ml of methanolic solution containing lauric acid (1 mg/l) as the surrogate standard. The mixture was transferred to a test tube and 2 ml of 14% BF_3 methanolic solution was added. The sample was placed in a water bath at 80 °C for 3 min and then 1 ml of water was added to stop the reaction. The fatty acid esters were extracted twice by 1 ml of methylene chloride each time. The collected organic phase was dehydrated with anhydrous sodium sulfate and placed in a 10 ml volumetric flask after filtration. The adjusted 10 ml of sample solution was measured using a GC-17A (Shimadzu, Japan) equipped with a GCMS-QP5050A (Shimadzu, Japan). A DB-5 ms (30 m × 0.25 mm × 0.25 μm) column (Agilent, USA) was used. 1 μl of sample solution was injected. The injections were performed in splitless mode. The carrier gass was helium (Air Water, Japan) at a constant flow of 1.5 ml/min. The injection port was heated to 200 °C. The oven temperature was set at 75 °C for 2 min, then increased 30 °C/min to 270 °C, and the final temperature was held for 1 min. The temperature at the detector was 280 °C. All mass spectra were acquired in the electron impact (EI) mode as the ionization source with a quadrupole mass filter. The analysis was carried out in SIM mode, and the selected ions of the compound were m/z 55, 74 and 87. The concentrations of the fatty acids were calculated using the internal standard method [31].

2.3.3. Amount of modified phenyl group on magnetite
The amount of modified phenyltrimethoxysilane on the mag-netite surface was determined from the measurement of silica dioxide as a decomposition component of Ph-mag in the follow-ing way [32]. First, 1 g of Ph-mag was decomposed using 40 ml of the mixed acid contained 6 M hydrochloric acid and 6 M nitric acid

covering a watch glass with heating at 80 °C until the black precip-itate disappeared. The obtained precipitated silicate was filtrated by a membrane filter and washed with water several times. Sec-ond, the filter paper carrying the precipitation was moved into a PTFE beaker and then 5 ml of 4% (w/v) NaCl solution and 3 ml of 60% hydrofluoric acid were added to the beaker. The mixture was heated until dry here in a water bath. After dissolving the obtained residue with 15 ml of water, 10 ml of saturated boric acid solution was added to the mixture and then was heated almost to the boiling point (<100 °C). Finally, 2 ml of 5N sulfuric acid was added to the obtained mixture followed by cooling to about 40 °C to an acidic condition. After filtration of the obtained mixture, the filtrate and the hot water used for washing were collected in 50 ml of vol-umetric flask and cooled to room temperature. Then, 5 ml of 2% (w/v) ammonium molybdate solution was added to the solution and the volume was adjusted to 50 ml with water. After 10 min, the absorbance of the mixed solution was measured by UV–vis at 425 nm.

2.4. Adsorption experiments

All adsorption experiments were carried out by the follow-ing batch test. To 10 ml of organic compound solution was added 20 mg of adsorbent that was mixed with a shaker (V BR-36 TAITEC Co., Ltd., Saitama, Japan). After adsorption, the mag-netite was separated from the solution using a Nd–Fe–B magnet (50 mm × 10 mm × 5 mm, 0.4 T). Then, the supernatant was mea-sured by UV–vis (V-550 Jasco Co., Tokyo, Japan). Nitrocyclohexane measurement was performed by HPLC (Waters 2695 separation module and 2487 dual λ absorbance detector Waters, Milford, MA) with a C_{18} ODS column (CAPCELL PAK C18 MG II S5 (5 μm, 4.6 mm id × 150 mm length) Shiseido Oo., Ltd. Tokyo, Japan). The mobile phase was acetonitrile–water (80:20), the flow rate was 1 ml/min and the wavelength was 210 nm.

3. Resuts and discussion

3.1. Preparation of hydrophobic magnetite

The modification processes of the surface modifiers on the mag-netite surface are shown in Fig. 2. Stearic acid had a carboxyl group. However, the magnetite had a hydroxyl group on the surface. Therefore, the carboxyl group of the stearic acid and the hydroxyl group on the magnetite interacted by hydrogen bond. As a result, the carboxyl group of the stearic acid faced inward to contact the magnetite, and the alkyl chain of the stearic acid was oriented toward the outside (Fig. 2A) [24].
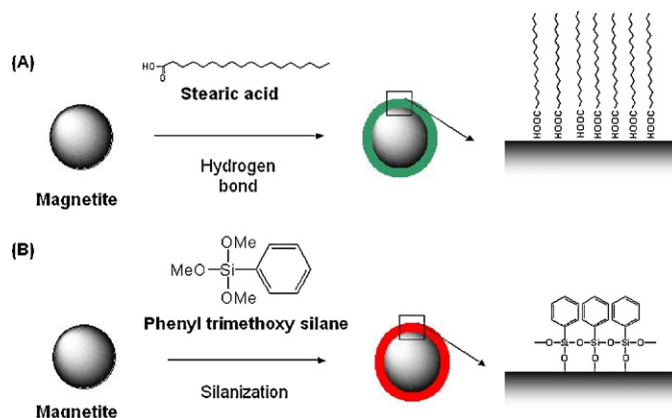

Fig. 2. Hydrophobization of magnetite surface (A) is modification with stearic acid and (B) is with phenyl group on magnetite surface.
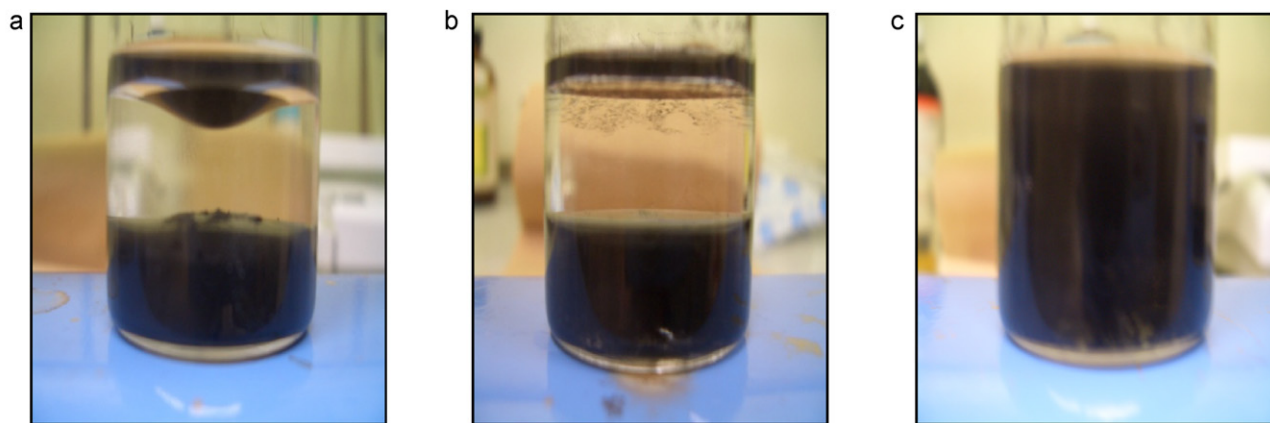
Fig. 3. Photographs of the distribution behaviors of (A) SA-mag, (B) Ph-mag and (C) plane-mag in two-phase system. The upper phase was water and the bottom phase was chloroform.

Phenyltrimethoxysilane had 3 methoxyl groups in its structure. These methoxy groups were substituted for hydroxyl groups in a solution of HCl. The hydroxyl groups interacted with a hydroxyl group on the magnetite surface through a hydrogen bond, then a covalent bond was formed by dehydration and condensation followed by heating for 1 h at 120 °C (Fig. 2B) [30]. This produced magnetite with a modified phenyl group. To confirm that the prepared modified magnetite had a hydrophobic surface, the powder of the modified magnetite was added and shuffled into a two-phase system composed of water in a neutral pH and chloroform. As a comparative control, plane magnetite was also added to the same system. Fig. 3 shows the distribution behaviors of 3 types of magnetite in a two-phase system. SA-mag and Ph-mag were selectively dispersed in the chloroform phase at the bottom of a vial container. These results showed that the surfaces of magnetite modified with stearic acid and phenyltrimethoxysilane were hydrophobic. However, the plane magnetite was dispersed in both phases. This result indicated that the plane magnetite had a middle property between hydrophilic and hydrophobic.

3.2. Characterization of hydrophobic magnetite

3.2.1. Surface areas of hydrophobic magnetite

The N_2 adsorption/desorption isotherms of the SA-mag and Ph-mag are shown in Fig. 4. Both isotherms scarcely revealed a hysteresis loop, therefore, SA-mag and Ph-mag were nonporous

Fig. 4. N_2 adsorption/desorption isotherm of SA-mag and Ph-mag.

materials. The surface areas of SA-mag and Ph-mag were 3.65 m^2/g and 4.88 m^2/g, respectively.

3.2.2. Amount of modified stearic acid on magnetite

Ethanol was used in the extraction of fatty acid because of a higher dissolving ability for stearic acid and a lower volatility than other organic solvents.

A high sensitivity with no interference was obtained in the SIM analysis. The retention times of the peaks of lauric acid methyl ester and stearic acid methyl ester were about 7 and 9.5 min, respectively. A calculation result showed that the modified amount of stearic acid on the magnetite was 9.84×10^{-3} mmol/g. After the extraction of stearic acid, a hydrophobic property on the magnetite surface could not be observed.

3.2.3. Amount of modified phenyl group on magnetite

The amount of the modified phenyl group on the magnetite surface was determined by measurement of the silicate included in the modified phenyltrimethoxysilane. The first treatment using hydrochloric acid and nitric acid with heating was performed for the decomposition of magnetite. Simultaneously, the modified silane coupling agent, an organosilicon compound, was oxidized with nitric acid and precipitated as an insoluble inorganic silicate. Next, the treatment by hydrofluoric acid can dissolve the insoluble silicate by formation of sodium hexafluorosilicate with sodium ion and hydrofluoric acid. The excess hydrofluoric acid after the above reaction was removed from the mixture with further heating. The dissolved mixture of boric acid solution was heated almost to the boiling point, which led to the release of soluble silicic acid with a reaction between the fluoric ion in the hexafluoric silicate and boric acid. Molybdosilicate acid, which is measurable by UV–vis, was formed with a reaction between the obtained soluble silicic acid and ammonium molybdate in an acidic condition. According to the analysis results of the molybdosilicate acid, the amount of modified phenyl group on the magnetite surface was 4.17×10^{-2} mmol/g. These results of modifier amounts on magnetite were used in the following discussion about the adsorption behaviors of aromatic compounds.

3.3. Adsorption experiments for aromatic compounds

The adsorption behaviors of several aromatic compounds were examined using two kinds of hydrophobic magnetite. Fig. 5 shows the results of adsorption experiments in various initial concentrations (10–100 ppm of these compounds). The large slope of adsorption isotherms in Fig. 5 represents a high adsorption ability. Both SA-mag and Ph-mag showed a higher ability for
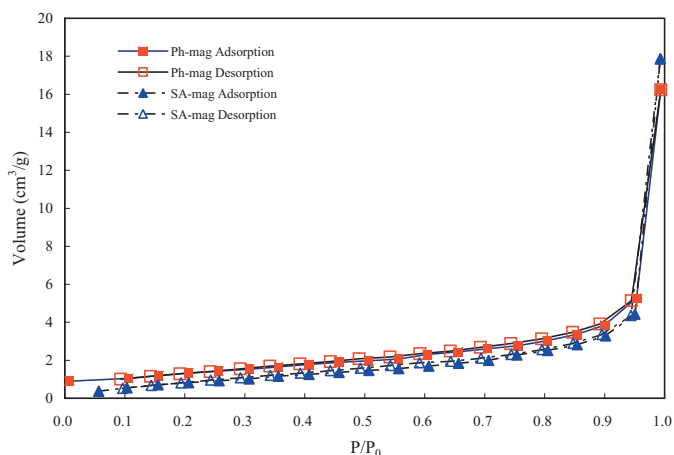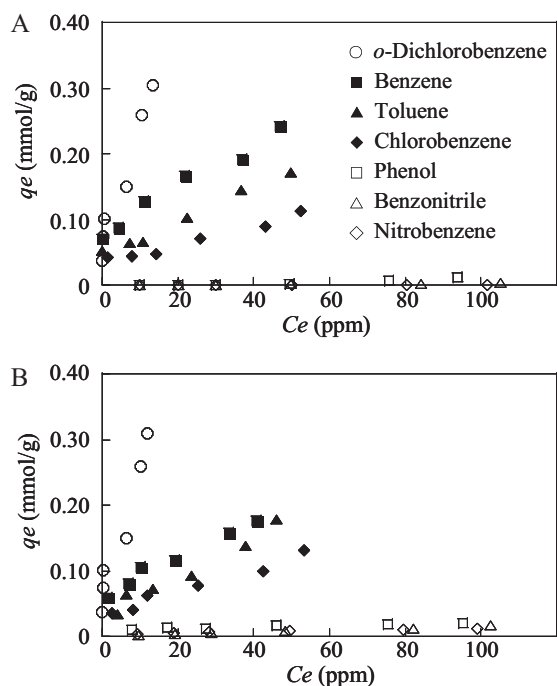
Fig. 5. The adsorption amounts of aromatic compounds onto (A) SA-mag and (B) Ph-mag in various initial concentrations (10–100 ppm).

o-dichlorobenzene compared with the other compounds. The slopes for benzene, toluene and chlorobenzene were almost equal, and were lower than that of *o*-dichlorobenzene. The slopes for phenol, benzonitrile and nitrobenzene were the smallest of the compounds tested here. These results show that the adsorption ability of the modified magnetite seemed to depend on the values of $\log P_{ow}$ for these compounds. The adsorption behaviors could be divided into 3 groups according to the following P_{ow} order: $1 < \log P_{ow} < 2$, $2 < \log P_{ow} < 3$, and $3 < \log P_{ow}$.

3.3.1. $3 < \log P_{ow}$

o-Dichlorobenzene has the highest hydrophobicity among the compounds used in this study. The results by adsorption experiments with SA-mag and Ph-mag are represented in Fig. 6. Fig. 6 shows that the adsorption amount of *o*-dichlorobenzene continued to increase as the concentration increased. When the initial concentration of *o*-dichlorobenzene was 100 ppm, the adsorption ratio (C/C_0) of *o*-dichlorobenzene on both SA-mag and Ph-mag reached about 90%. If this adsorption was due to the mono-layer adsorption, the adsorption amount of adsorbate would be expected to level off. However, a leveling off was not observed in this
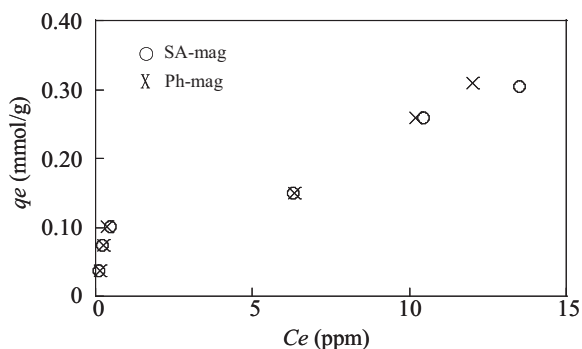
case. In addition, Fig. 6 shows that the adsorption amounts of *o*-dichlorobenzene onto SA-mag or Ph-mag under all initial concentration were larger than the modified amounts of stearic acid and phenyl groups on the magnetite surface. Thus, the adsorption behavior of *o*-dichlorobenzene was multi-layer adsorption rather than mono-layer adsorption for an adsorption site. The adsorption behavior of *o*-dichlorobenzene did not depend on the type of modifiers (SA-mag and Ph-mag). The hydrophobic interaction between the modified surface of magnetite and *o*-dichlorobenzene may be too strong to determine the dependency of the adsorption amount on the functional group on the surface.

3.3.2. $2 < \log P_{ow} < 3$

Benzene, toluene and chlorobenzene had medium hydrophobicity ($2 < \log P_{ow} < 3$) in this study. The results of adsorption experiments using these compounds with hydrophobic magnetite are shown in Fig. 7. The adsorption ratios of all compounds were about 50% of the initial concentration of 100 ppm. In this group, the dependency of the adsorption behavior on the type of the modifiers could not be confirmed, because of the relatively high hydrophobicity of these compounds. As shown in Fig. 7, the adsorption amounts of all compounds under most conditions were larger than the modified amounts of stearic acid and phenyl groups, so the adsorption behavior of this group also seemed to be that of multi-layer adsorption. The order of the adsorbed amounts was as follows: benzene > toluene > chlorobenzene. This result was not consistent with the order of $\log P_{ow}$. That is, the order of the adsorption ability did not always depend on the $\log P_{ow}$ of the compounds in this group. The adsorption mechanism in this group was also that of multi-layer adsorption based on the hydrophobic interaction. Therefore, the adsorption amount depended on the strength of the interaction and the size of the molecule forming the multi-layer. Benzene was adsorbed most because there was no substituent group and it had the smallest molecular size [33]. On the other hand, toluene and chlorobenzene are more bulky than benzene because of a substituent group. The methyl group, a substituent group of toluene, supplies electrons to the benzene ring because
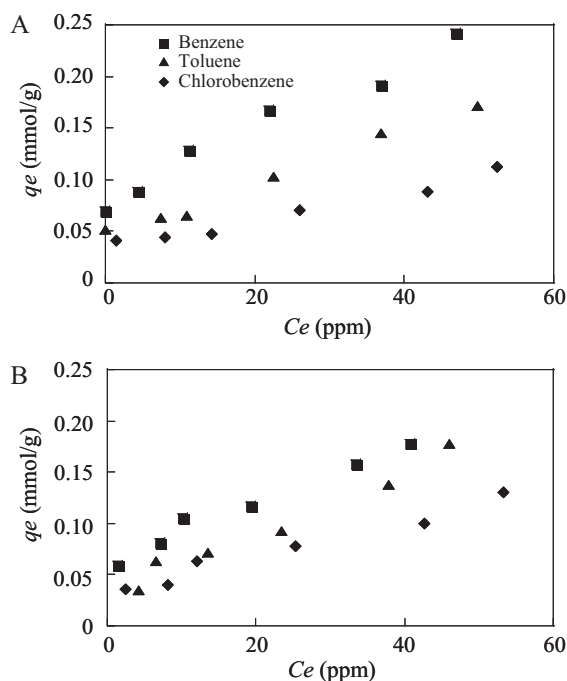

Fig. 6. The adsorption amounts of *o*-dichlorobenzene onto SA-mag and Ph-mag in various initial concentrations (10–100 ppm).

Fig. 7. The adsorption amounts of aromatic compounds in $2 < \log P_{ow} < 3$ onto (A) SA-mag and (B) Ph-mag in various initial concentrations (10–100 ppm).

the functional group is the electron-donating group. By contrast, chlorine, a substituent group of chlorobenzene, is an electron-withdrawing group and withdraws electrons from the benzene ring. The strength of the π-electron interaction depends on the richness of the π-electron in the benzene ring, that is, the interaction works well in a π-electron-rich state. The π-electron interaction between aromatic compounds seems to be important for the formation of a multi-layer in these cases. Thus, toluene adsorbed more than chlorobenzene.

3.3.3. 1 < log P_ow < 2

Phenol, benzonitrile, nitrobenzene and nitrocyclohexane had the lowest hydrophobicity ($1 < \log P_{ow} < 2$) in this study. Fig. 8 shows the results of these adsorption experiments. The adsorption amounts of these compounds in this group were small by comparison with other groups. This happened because these compounds have strong polar groups such as hydroxyl, cyano and nitro groups and can be hydrated with water molecules around their polar groups. Therefore, the hydrophobic interaction between these compounds and the modified magnetite becomes weak. In the same way, the interaction between their compounds also becomes weak. According to Fig. 8, phenol, benzonitrile and nitrobenzene were more selectively adsorbed onto Ph-mag than onto SA-mag. These results indicate that the functional group on the magnetite surface significantly affects adsorption behavior and π-electron interactions between the compounds and the phenyl group on Ph-mag works stronger rather than hydrophobic interaction in these cases. When nitrocyclohexane, having no aromatic ring, was scarcely adsorbed onto Ph-mag, this suggested that the adsorption mechanism of this group was based on π-electron interaction. The order of the adsorption amount of these aromatic compounds was as follows: phenol > benzonitrile > nitrobenzene. These results did not agree with the order of log P_ow (phenol 1.46, benzonitrile 1.56, nitrobenzene 1.86). Phenol has a hydroxyl group, an electron-donating group, and the π-electron interaction between phenol

and Ph-mag was strongest among them. However, the substituent groups of benzonitrile and nitrobenzene are electron-withdrawing groups that make their aromatic rings relatively electron-poor. The electron-withdrawing property of benzonitrile might be weaker than that of nitrobenzene because the dipole moment of benzonitrile, 4.05, is smaller than that of nitrobenzene, 4.22–4.91 [34,35]. The aromatic ring of benzonitrile is more electron-rich than that of nitrobenzene. The π-electron interaction between the compound and the phenyl group on the magnetite surface was dominant in this adsorption mechanism and so the adsorption amount of benzonitrile on Ph-mag was more than that of nitrobenzene. According to Fig. 8A, phenol was adsorbed on SA-mag, and the amount of adsorbed phenol was close to the modified amount of stearic acid on magnetite. However, this does not mean that adsorption is a one-to-one relationship between phenol and stearic acid like a mono-layer adsorption because of the shape of the adsorption isotherm. A feature of the adsorption isotherm is that the adsorption amount immediately increases with a high concentration of adsorbate during multi-layer adsorption. Moreover, the dipole moment of phenol, 1.53 [36], was the lowest and hydration for phenol was the weakest. Thus, a small amount of phenol could be adsorbed onto SA-mag by hydrophobic interaction. However, the adsorption behaviors of this group were not clear in the initial concentration range (10–100 ppm). Fig. 8 shows that the adsorption amounts of the compounds are smaller compared with the amounts of the modified functional groups, particularly in the case of a phenyl group with an initial concentration of 100 ppm. Therefore, the adsorption experiment for this group should be carried out with a higher initial concentration.

3.4. Adsorption isotherm models

This section describes an investigation into the adsorption isotherms of these aromatic compounds onto two adsorbents (in Fig. 5) by application of the adsorption isotherm models. The multi-layer adsorption model in the gas phase is known as the BET model. Many researchers have reported the use of the-multi layer adsorption model in the liquid phase based on the BET model, but this model has not yet been established [37]. Thus, in this study, adsorption behaviors were studied by fitting these adsorption data into the Langmuir and Freundlich models.

The Langmuir and Freundlich models are as follows:

$$\frac{1}{q_e} = \frac{1}{K_L\, q_m\, C_e} + \frac{1}{q_m} \tag{1}$$

$$q_e = K_f\, C_e^{1/n} \tag{2}$$

where q_e is the equilibrium adsorption capacity, C_e represents the solute concentration in equilibrium, q_m (mg/g) is the maximal sorption capacity, K_L (L/g) is a binding constant, and K_f and n are the Freundlich constants to be determined. Table 1 shows the fitting results for the Langmuir and Freundlich models.

When applying the Langmuir model, most correlation coefficients are not improved. The Langmuir model is well known as a mono-layer adsorption model and most of the adsorption behaviors seem not to be of the mono-layer adsorption type, because of the low correlation coefficients. On the other hand, when applying the Freundlich model, most correlation coefficients are better than that of the Langmuir model. However, most of the correlation coefficients for the Freundlich model were not so good. The Freundlich model does not provide insight into adsorption behavior, because of an empirical formula. However, the Freundlich model is well known to be a better fit for adsorption into a porous material such as activated carbon. Thus, these adsorption behaviors seemed not to be porous adsorption. This result also agrees with Fig. 4. These fitting results for the models were not definitive as to whether the
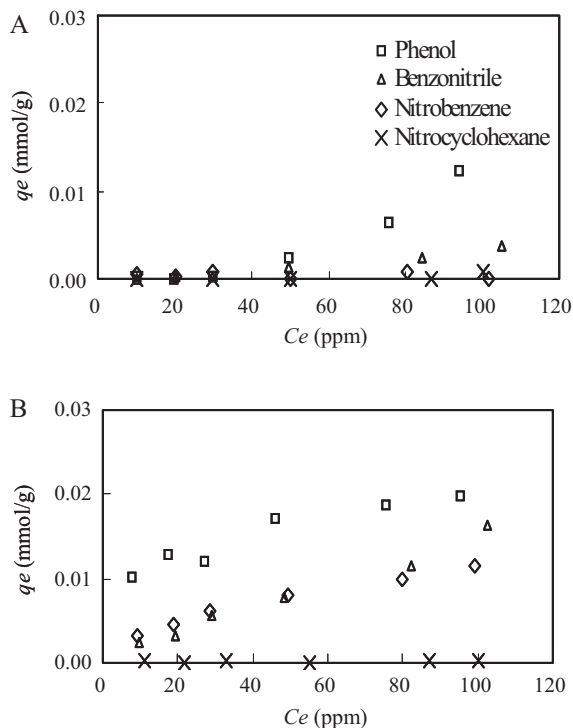

Fig. 8. The adsorption amounts of aromatic compounds and nitrocyclohexane in $1 < \log P_{ow} < 2$ onto (A) SA-mag and (B) Ph-mag in various initial concentrations (10–100 ppm).

Table 1
Isotherm parameters of aromatic compounds onto SA-mag and Ph-mag.

Adsorbent	Adsorbate	Freundlich model			Langmuir model		
		K_f	n	R^2	q_m (mmol/L)	K_L (L/mg)	R^2
SA-mag	Phenol	3.46e−5	0.453	0.807	1.17e−3	0.0101	0.213
	Benzonitrile	2.70e−4	0.647	0.988	9.52e−4	9.86e−3	0.991
	Nitrobenzene	–	–	–	–	–	–
	Benzene	3.83	2.52	0.984	0.234	0.135	0.960
	Toluene	1.76	1.80	0.962	0.203	0.0543	0.911
	Chlorobenzene	2.80	1.45	0.930	0.0690	0.933	0.423
	o-Dichlorobenzene	16.4	2.97	0.883	0.248	1.90	0.979
Ph-mag	Phenol	0.528	3.63	0.932	0.0189	0.135	0.819
	Benzonitrile	0.0383	1.26	0.978	0.0185	0.0151	0.937
	Nitrobenzene	0.115	1.83	0.995	0.0134	0.0310	0.908
	Benzene	3.78	3.07	0.951	0.135	0.508	0.812
	Toluene	1.53	1.70	0.935	0.199	0.0534	0.927
	Chlorobenzene	1.56	0.885	0.986	0.0907	0.224	0.724
	o-Dichlorobenzene	16.1	2.82	0.853	0.292	1.19	0.944
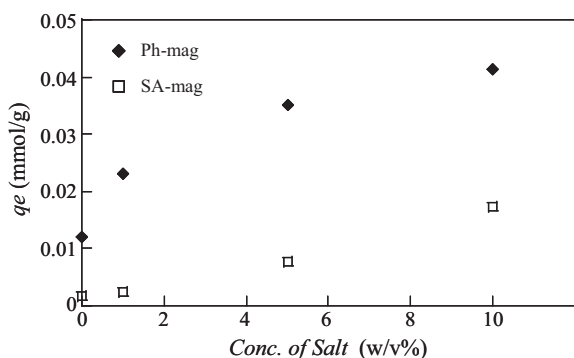
Fig. 9. Influence of salt in adsorption of nitrobenzene onto SA-mag and Ph-mag.

adsorption behaviors in $1 < \log P_{ow} < 2$ were mono or multi-layer adsorption.

3.5. Nitrobenzene adsorption in various salt concentrations

Shown in Fig. 9 are nitrobenzene adsorption isotherms for various concentrations of salt on SA-mag and Ph-mag. This experiment was performed to validate whether hydration with water inhibits the adsorption of aromatic compounds in $1 < \log P_{ow} < 2$ on hydrophobic magnetite. The dehydration effects of the addition of salt were investigated. The addition of salt deprives hydrated adsorbate of water molecules. If the adsorption amount of nitrobenzene is increased when the adsorption experiment is carried out under dehydration conditions, then hydration would be an inhibiting factor in its adsorption onto hydrophobic magnetite. As shown in Fig. 9, the adsorption amounts of nitrobenzene on SA-mag and Ph-mag increased with increasing salt concentration. Furthermore, nitrobenzene was hardly adsorbed onto SA-mag without the addition of salt, but was adsorbed onto SA-mag in the presence of salt. The nitrobenzene adsorption onto SA-mag was by hydrophobic interaction, which seems to indicate that the hydrophobicity of nitrobenzene was enhanced by dehydration. This result indicates that hydration is one of the inhibitors of the adsorption of nitrobenzene onto hydrophobic magnetite.

4. Conclusion

Aromatic compounds with various $\log P_{ow}$s were investigated for adsorption onto hydrophobic magnetite coated alkyl chains and phenyl groups. The adsorption behaviors of each compound 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 generally increased as the $\log P_{ow}$ of each group increased. However, the adsorption amounts for the compounds in each group did not depend on the values of $\log P_{ow}$. In the $2 < \log P_{ow} < 3$ and $3 < \log P_{ow}$ groups, the adsorption mechanism was mainly a hydrophobic interaction between aromatic compounds and the surface of hydrophobic magnetite. The adsorption behaviors did not depend on the difference in modified functional groups on the magnetite surface. The adsorption behavior of hydrophobic magnetite in these groups seemed to form a multi-layer on the hydrophobic magnetite because of the quantitative relationship between the amount of adsorbed aromatic compound and the amount of modified functional groups on the magnetite, and there was a poor fitting for the adsorption isotherm models. However, the adsorption behavior of the $1 < \log P_{ow} < 2$ group was sensitive to the modified functional group on the hydrophobic magnetite. The main adsorption mechanism for this group was the π-electron interaction between the compounds and the phenyl group on Ph-mag rather than the hydrophobic interaction. The adsorption behavior of this group could not be demonstrated for either mono or multi-layer adsorption under these adsorption conditions. The results of adsorption experiments under dehydration conditions indicated that an inhibiting factor for nitrobenzene adsorption is hydration from water molecules.

The simple system of the present study, which used magnetite without porosity, enabled clarification of the factors that determine adsorption behavior. Thus, the results were significant with regard to the selection of an optimal surface modifier for adsorption or solid-phase extraction as well as magnetite separation, which could be valuable in the design of a novel high-performance adsorbent.

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