Effect of surface functional group on adsorption of organic pollutants on hexagonal mesoporous silicate

P. Patiparn* and S. Takizawa**

*Department of Environmental Engineering, Chulalongkorn University, Bangkok, 10330, Thailand
(E-mail: patiparn.p@eng.chula.ac.th)

**Department of Urban Engineering, University of Tokyo, Tokyo, 113-8656, Japan
(E-mail: takizawa@env.t.u-tokyo.ac.jp)

Abstract
Hexagonal mesoporous silicates (HMSs) are synthetic silicate materials that have uniform mesopores, comparatively large surface areas, and uniform surface functional groups, which lead to higher adsorption selectivity. Selective adsorption characteristics of HMSs for six types of organic pollutants (2,4-D, mecoprop, 4-chlorophenol, toluene, dichloroacetic acid, and thioflavin T) from synthetic wastewater were investigated. Five different types of HMSs were synthesized by surfactant-templating methods, and three of them were subsequently grafted with organic surface functional groups, i.e. n-octyldimethyl-, 3-aminopropyltriethoxy-, and 3-mercaptopropyl-groups. Titanium-substituted HMS was also made in the same way as pristine HMS. Increasing hydrophobicity of HMSs did not always enhance adsorption of hydrophobic adsorbates, such as toluene. Grafted organic functional groups changed surface charge, which enhanced electrostatic force between HMSs and ionic pollutants. Negatively charged contaminants, i.e. 2,4-D, mecoprop and dichloroacetic acid, were more readily adsorbed on positively charged AM-HMS by electrostatic interaction. Hydrogen bonding and van der Waals interaction between adsorbents and adsorbates, as well as combination of these forces, also enhanced the adsorption capacities of HMSs. In addition to the electrostatic interaction, a cationic dye, thioflavin T, was adsorbed on the surfaces due to hydrogen bonding and van der Waals interaction for hydrophilic surfaces and hydrophobic surfaces, respectively.

Keywords Adsorption; hexagonal mesoporous silicate (HMS); organic pollutants; selective adsorption; surface functional groups

Introduction
Increasing public concern about water contamination and the effects of organic micro pollutants has led to tighter controls on the level of organic pollutants in water and wastewater treatment. Among the methods currently employed to remove recalcitrant organic compounds are adsorption by activated carbon and destructive oxidation process, often assisted by light or adsorption onto porous solids. Activated carbon is one of the most effective adsorbents possessing high surface areas, and granular activated carbon can be regenerated by thermal desorption or combustion of toxicants in air. However, a substantial amount of the carbon is lost during each regeneration cycle. Moreover, for the removal of a pollutant in very low concentration range by adsorption, the adsorbent should have a very high molecular selectivity; otherwise, many coexisting compounds with higher concentrations would saturate the capacity of the adsorbent. This has aroused an increasing interest in the development of recyclable inorganic sorbents, also with high molecular selectivity, for the efficient removal of organic pollutants from aqueous solutions.

Recently, inorganic porous solids have been used technically as adsorbents, catalysts, and catalyst supports owing to their high surface areas. Inorganic porous materials are divided into three classes: microporous (<2 nm), mesoporous (2–50 nm), and
macroporous materials (>50 nm). However, two classes of materials that are used extensively as heterogeneous catalyst and adsorption media are microporous (e.g. as zeolite) and mesoporous (e.g. MCM-41 and HMS) inorganic materials. The utility of these materials is enhanced by their meso-structures, which allow molecules to reach large internal surfaces and cavities that enhance catalytic activity and adsorptive capacity. The presence of large pore size may enhance the adsorption of macromolecular pollutants (Mercier and Pinnavaia, 1997; Inumaru et al., 2000; Lee et al., 2001).

Hexagonal mesoporous silicate (HMS) has meso-scale pores and uniform surface functional groups. HMS surface can be modified by various methods, e.g. organic ligand modification and metal substitution in crystalline structure, to give it specific characteristics. HMSs are expected to be highly selective adsorbents because of uniform surface functional groups. However, selective adsorption characteristics of organic pollutants affected by surface functional groups have not yet been studied.

The objective of this research was to investigate the effect of surface functional groups on selective adsorption of organic pollutants on HMSs from synthetic wastewaters. In this study, five different types of HMSs were synthesized by surfactant-templating methods, and three of them were subsequently grafted with organic surface functional groups, i.e. n-octyldimethyl-, 3-aminopropyltriethoxy-, and 3-mercaptopropyl-groups (OD-HMS, MP-HMS, and AM-HMS, respectively). Titanium-substituted HMS (Ti-HMS) was also made in the same way as HMS. Adsorption capacities of these HMSs for six types of organic pollutants (2,4-D, mecoprop, 4-chlorophenol, toluene, dichloroacetic acid, and thioflavin T) were investigated in batch adsorption experiments in single-solute solutions. Obtained adsorption data were comparatively analysed based on physico-chemical characteristics of both adsorbents and adsorbates.

Materials and methods

Adsorbent syntheses

HMS was prepared by the following method: tetraethoxysilane (TEOS) (Wako Pure Chemical Industries, Japan) 1.0 mole was dissolved into a mixture of water 29.6 mole, dodecylamine (Chameleon Reagent, Japan) 0.27 mole, and ethanol (Chameleon Reagent, Japan) 9.09 mole under vigorous stirring. The reaction mixture was aged at ambient temperature for 18 h, and the resulting mixture was filtered and air-dried on a glass plate. The product was calcined in air under static conditions at 923 K for 4 h to remove organic template (Tanev and Pinnavaia, 1995).

Grafting of organic functional groups on HMS

Silanization of HMS with n-octyldimethylchlorosilane, denoted as OD-HMS, was carried out as follows: after drying 5 g of HMS at 423 K under vacuum for 24 h, the sample was put into a 250 mL, three-neck round flask under N₂ flow. 140 mL of dichloromethane (Aldrich, Germany) and a magnetic stirrer were added into the flask and stirred. 1.8 g of 1-methyl-2-pyrrolidinone (Sigma, Germany) and 3.6 g of n-octyldimethylchlorosilane (TCI-EP, Japan) were added under N₂ flow. The mixture reacted under reflux at 333 K for 4 h. After that, the mixture was filtered and washed twice with 50 mL of chloroform (Sigma-Aldrich, Germany) and 50 mL of ethanol. The sample was then dried at 313 K in vacuum for 4 h. Hydrophobicity of HMS was increased by grafted ligands.

Silanized HMS with 3-aminopropyltriethoxysilane, denoted as AM-HMS, was prepared by drying 8 g of HMS at 423 K under vacuum for 18–20 h under vacuum. Then the sample was put into a 250 mL three-neck round flask under N₂ flow. 115 mL of toluene (Aldrich, Germany), 5.2 g of 3-aminopropyltriethoxysilane (Fluka), and glass beads were added to the flask under N₂ flow. The mixture was kept stirring at room temperature for 4 h, then...
filtered and washed well with toluene (50 mL for each rinsing). After that, the harvested AM-HMS was dried at 423 K for 4 h under vacuum. Grafted amino functional groups retained the hydrophilic characteristic of HMS.

Silanization of HMS with 3-mercaptopropyltrimethoxysilane, denoted as MP-HMS, was carried out as follows: 1 g of HMS was dried at 383 K, refluxed with 1 g of 3-mercaptopropyltrimethoxysilane (Chisso Corp., Japan) in 50 mL of toluene for 48 h. Then the product was filtered, washed several times with toluene, followed by ethanol. The material was subjected to Soxhlet extraction by ethanol for 18 h in order to remove ungrafted organosilane. Mercapto functional groups increase hydrophobicity of obtained adsorbent.

Titanium-substituted HMS

Titanium-substituted HMS, denoted as Ti-HMS, was prepared following the same protocol as that of HMS, except that 0.01 mol of tetraisopropyl orthotitanate (TIPOT) (TCI-EP, Japan) was added at the same time as TEOS (Tanev et al., 1994).

Characterization of HMSs

Powder X-ray diffraction (XRD) patterns of synthesized adsorbents were recorded on a MX Labo powder diffractometer equipped with Cu Kα radiation (MAC Science Inc., Japan). Surface areas and pore sizes of HMS, modified HMS, and PAC were calculated from nitrogen adsorption isotherms measured at 77 K by a Belsorp 28SA sorptometer (Bel Japan Inc., Japan). BET specific surface area was calculated using nitrogen adsorption isotherm at relative pressure between 0.04 and 0.20. Pore diameter and mesopore volume were calculated from the isotherm by D-H method (Dollimore and Heal, 1964). External area was calculated from the isotherm by t-plot method. Surface functional groups of prepared adsorbents were investigated by Fourier Transform Infrared (FT-IR) spectroscopy (Jasco FT-IR-610, Japan) with JASCO DR-81 Diffuse Reflectance Attachment at a spectral resolution of 4 cm⁻¹ after drying at 105°C for 4 h in order to reduce interference on monitored peaks caused by hydroxyl group. The presence of Ti(IV) and Ti(VI) in Ti-HMS was confirmed by UV-VIS spectroscopy (Varian DMS 300 UV-VIS) and ICP-AES (Perkin Elmer Optima 3000DV).

Surface charge measurement

Surface charge of synthesized HMSs and PAC was measured by the acid/base titration method using 10 mL of adsorbents mixture (1 g/L) mixed with a predetermined amount of NaCl for adjustment of initial ionic strength at 1 mM when diluted to 25 mL. Different amounts of 0.025 M HCl or 0.025 M NaOH were added to HMS or PAC solutions in order to vary pH. Intrinsic pH was also measured for each of HMSs or PAC solutions without adding acid or base. Each sample was then diluted to a final volume of 25 mL with deionized Mili-Q water, and shaken overnight at ambient temperature (25 ± 2°C). After equilibration, the supernatant pH of each sample was measured and the pH data of the entire batch of experiments were plotted against surface charge data that were calculated from the principle of electroneutrality shown in the following equation:

Surface charge density (C/m²) = \{[HCl]_{add} - [NaOH]_{add} - [H^+] + [OH^-]\} \times F/S \quad (1)

where F is the Faraday’s constant (96 500 C/mol) and S (m²/g) is the BET surface area of adsorbents.
Organic pollutants

Table 1 shows physico-chemical characteristics of applied organic pollutants (2,4-D, Fluka; mecoprop, Kanto chemical; 4-chlorophenol, TCI; toluene, Aldrich; dichloroacetic acid, Chameleon Reagent; and thioflavin T, Aldrich). Molecular size (weight and length) of each organic pollutant was calculated by ACD Labs Chemsketch program version 5.

Adsorption experiment

Each synthesized adsorbent was transferred to a 50 mL volumetric flask with a stopper, and 25 mL of each organic pollutant dissolved in Mili-Q water with known concentrations was added. After stirring overnight in a water bath at 25°C, the mixture was filtered through a Dismic filter (pore size 0.2 µm). The first 10 mL of filtrate was discarded and the rest was harvested for analysis by a UV spectrophotometer (Hitachi U2000 with 5 cm quartz cell) at 275 nm for 2,4-D, mecoprop, 4-chlorophenol, toluene, and 412 nm for thioflavin T, respectively, or by HPLC-MS (Agilent 1100 with LCQ Finnigan Mat) for dichloroacetic acid analysis. The adsorption capacity was calculated from the difference between the initial and equilibrium concentrations divided by the amount of adsorbents.

The experimental results were fitted to Langmuir and Freundlich equations.

Results and discussion

Physical characteristics of HMSs

As shown in Table 2, nitrogen adsorption isotherms also showed smaller pore size and BET surface areas of HMSs modified with organic-functional groups (MP-HMS, OD-HMS, and AM-HMS) than non-grafted HMS. Grafted organic functional groups on HMS surface were detected by FT-IR, and the valence of titanium detected by UV-Visible spectrophotometer and FT-IR was predominant Ti(IV). The amount of titanium incorporated into one gram of HMS was quantified as 10 mg (i.e. 1.0 per cent) by ICP-AES. Ti-HMS had a larger surface area and also higher uniformity of pore size than pure HMS. XRD patterns proved crystalline structure of synthesized adsorbents, Ti-HMS having the highest quality of hexagonal crystalline structure. These observations proved the presence of grafted species and titanium attached to the framework walls of HMS, causing constriction of the channels, but mesoporosity and pore structure were still conserved, even after ligand-grafting.

Surface charge

Figure 1 shows the surface charge density of HMS and modified HMSs as a function of pH. The pH value that gives zero surface charge is defined as the zero point of charge (pH_{zpc}). At this pH value, the positive charge of cationic surface groups and the negative charge of anionic surface groups are balanced. The zero points of charge of HMS and Ti-HMS were pH 5.0 and 5.5, respectively. As for organic-grafted HMS (OD-HMS, MP-HMS, and AM-HMS), the zero points of charge were pH 4, 6.8, and 8.2, respectively.

Table 1 Physico-chemical characteristics of studied organic pollutants

<table>
<thead>
<tr>
<th>Pollutants</th>
<th>MW</th>
<th>Water solubility (g/L)</th>
<th>Width (nm)*</th>
<th>Length (nm)*</th>
<th>Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-D</td>
<td>221.0</td>
<td>0.89</td>
<td>0.54</td>
<td>0.96</td>
<td>Negative</td>
</tr>
<tr>
<td>Mecoprop</td>
<td>214.6</td>
<td>0.734–0.895</td>
<td>0.64</td>
<td>0.89</td>
<td>Negative</td>
</tr>
<tr>
<td>4-Chlorophenol</td>
<td>128.56</td>
<td>27</td>
<td>0.48</td>
<td>0.65</td>
<td>None</td>
</tr>
<tr>
<td>Toluene</td>
<td>92</td>
<td>0.515</td>
<td>0.48</td>
<td>0.57</td>
<td>None</td>
</tr>
<tr>
<td>Dichloroacetic acid</td>
<td>128.94</td>
<td>100</td>
<td>0.69</td>
<td>0.46</td>
<td>Negative</td>
</tr>
<tr>
<td>Thioflavin T</td>
<td>318.86</td>
<td>easily soluble</td>
<td>0.64</td>
<td>1.44</td>
<td>Positive</td>
</tr>
</tbody>
</table>

*ACD Labs Chemsketch program version 5
As shown in Figure 3, the surface charge density decreased as pH increased from acidic region to neutral pH. At low pH, surface sites of HMSs are protonated and the surfaces become positively charged; whereas at high pH, the surface functional group lose their protons, and the surface becomes negatively charged.

Grafted organic moieties affect the surface charge of HMSs. Grafting 3-aminopropyltriethoxy-group shifts up the surface charge of HMS because of amino functional groups, which gain protons in the acid to neutral pH. On the contrary, surface modification with n-octyldimethyl-group brings the surface charge down to the negative region in the pH range higher than 4. The 3-mercaptopropyl-groups on the surface altered the surface charge of HMS only slightly; hence, the effect of this functional group on adsorption capacity is considered to be due mainly to reduced surface areas and the number of silanol groups replaced by this functional group.

### Adsorption isotherm of 2,4-D and mecoprop

2,4-Dichlorophenoxy acetic acid (2,4-D) adsorption isotherms of HMS and modified HMSs, and Freundlich equation parameters are shown in Figure 2a and Table 3, respectively. Adsorption of 2,4-D on silanol group (Si-OH) of pristine HMS was not significantly different from 2,4-D adsorption on n-octyldimethyl-group of OD-HMS. 2,4-D adsorption capacity on Ti-HMS was the lowest. In the pH range of 4 to 6, surface charge of these adsorbents (HMS, Ti-HMS, OD-HMS) was nearly zero or negative. In this pH range, carboxyl groups of 2,4-D are ionized. Hence, 2,4-D was rejected from negatively charged adsorbents by charge repulsion. In contrast, adsorption capacity of 2,4-D by 3-mercaptopropyl-group on MP-HMS was not different from pristine HMS and OD-HMS, although its surface charge is slightly positive. The obtained

### Table 2 Physical characteristics of HMS, modified HMS, and PAC

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Pore size Ø (nm)</th>
<th>BET surface area (m²/g)</th>
<th>Pore volume (mm³/g)</th>
<th>pHZPC</th>
<th>Particle sizes (µm)</th>
<th>Surface functional groups</th>
<th>Surface characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMS</td>
<td>3.00</td>
<td>668</td>
<td>1078</td>
<td>5.0</td>
<td>0.46</td>
<td>Silanol</td>
<td>Hydrophilic</td>
</tr>
<tr>
<td>Ti-HMS</td>
<td>3.18</td>
<td>767</td>
<td>1276</td>
<td>5.5</td>
<td>0.50</td>
<td>Silanol</td>
<td>Hydrophilic</td>
</tr>
<tr>
<td>MP-HMS</td>
<td>3.00</td>
<td>567</td>
<td>883</td>
<td>6.8</td>
<td>0.49</td>
<td>Mercapto</td>
<td>Hydrophobic</td>
</tr>
<tr>
<td>OD-HMS</td>
<td>2.36</td>
<td>477</td>
<td>499</td>
<td>4</td>
<td>0.61</td>
<td>Octyl</td>
<td>Hydrophobic</td>
</tr>
<tr>
<td>AM-HMS</td>
<td>2.32</td>
<td>533</td>
<td>592</td>
<td>8.2</td>
<td>0.50</td>
<td>Amino</td>
<td>Hydrophilic</td>
</tr>
</tbody>
</table>

As shown in Figure 3, the surface charge density decreased as pH increased from acidic region to neutral pH. At low pH, surface sites of HMSs are protonated and the surfaces become positively charged; whereas at high pH, the surface functional group lose their protons, and the surface becomes negatively charged.

Grafted organic moieties affect the surface charge of HMSs. Grafting 3-aminopropyltriethoxy-group shifts up the surface charge of HMS because of amino functional groups, which gain protons in the acid to neutral pH. On the contrary, surface modification with n-octyldimethyl-group brings the surface charge down to the negative region in the pH range higher than 4. The 3-mercaptopropyl-groups on the surface altered the surface charge of HMS only slightly; hence, the effect of this functional group on adsorption capacity is considered to be due mainly to reduced surface areas and the number of silanol groups replaced by this functional group.

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2,4-Dichlorophenoxy acetic acid (2,4-D) adsorption isotherms of HMS and modified HMSs, and Freundlich equation parameters are shown in Figure 2a and Table 3, respectively. Adsorption of 2,4-D on silanol group (Si-OH) of pristine HMS was not significantly different from 2,4-D adsorption on n-octyldimethyl-group of OD-HMS. 2,4-D adsorption capacity on Ti-HMS was the lowest. In the pH range of 4 to 6, surface charge of these adsorbents (HMS, Ti-HMS, OD-HMS) was nearly zero or negative. In this pH range, carboxyl groups of 2,4-D are ionized. Hence, 2,4-D was rejected from negatively charged adsorbents by charge repulsion. In contrast, adsorption capacity of 2,4-D by 3-mercaptopropyl-group on MP-HMS was not different from pristine HMS and OD-HMS, although its surface charge is slightly positive. The obtained
result of MP-HMS was consistent with literature that, when pores are significantly larger than the adsorbate (2,4-D), they do not contribute to adsorbate retention in the pores (Goyne et al., 2004). AM-HMS had the highest adsorption capacity because adsorption to positively-charged 3-aminopropyltriethoxy-groups by 2,4-D was done via electrostatic interaction: 

\[
\text{Si-R-NH}^+3 \quad \text{---} \quad 2\text{OOC–R}.
\]

In the case of mecoprop, adsorption mechanisms on the surfaces are considered to be the same as 2,4-D mechanisms. However, hydrophobic surface caused by \( n \)-octyldimethyl group on OD-HMS slightly enhanced the adsorption capacity of mecoprop on OD-HMS. While hydrophobic pores are likely important for adsorption of hydrophobic organic pollutants, hydrophilic porous surfaces may also affect adsorption capacity by way of steric effects, slow diffusion, and tortuosity that may inhibit desorption.

**Adsorption isotherm of 4-chlorophenol and toluene**

Figure 3a and b show 4-chlorophenol and toluene adsorption isotherms on HMS and modified HMSs. The order of 4-chlorophenol affinity shown in Figure 3a is: OD-HMS > Ti-HMS > MP-HMS > HMS. Although HMS had low adsorption capacity, organic-chain-grafted HMSs (OD-HMS and MP-HMS) have higher adsorption capacities, especially OD-HMS, which possesses the highest hydrophobicity. Moreover, Ti-HMS also possesses high adsorption capacity, compared with pristine HMS. As reported by Tanev et al. (1994), titanium silicate is an effective molecular-sieve catalyst for the hydroxylation of phenol. Surface charges of applied adsorbents are suggested not to be an important factor on 4-chlorophenol adsorption because of the nonionic characteristic of 4-chlorophenol. Hydrogen bonding between the hydroxyl part of 4-chlorophenol and silanol groups on HMS and Ti-HMS is expected to play an important role in the adsorption phenomenon. However, hydrophobic surfaces had stronger affinity to the hydrophobic molecule of 4-chlorophenol adsorption than hydrophilic surfaces. Table 3 reports Freundlich equation parameters of 4-chlorophenol adsorption on HMS, modified HMSs.

The order of toluene affinity shown in Figure 3b is: OD-HMS > HMS > AM-HMS > Ti-HMS > MP-HMS. The results were different from 4-chlorophenol results because the pristine HMS preformed a higher adsorption capacity than 4-chlorophenol. OD-HMS had the highest adsorption capacity in synthesized HMSs, which might be caused by hydrophobicity, but Ti-HMS had the lowest adsorption capacity. With regard to the 4-chlorophenol adsorption isotherm of Ti-HMS, OH group part of the 4-chlorophenol molecule...
caused the higher affinity to Ti-substituted surface, causing higher adsorption capacity than toluene. MP-HMS, grafted with (-HS) long chain hydrocarbon, has the lowest adsorption capacity of toluene, although it is hydrophobic adsorbent. Concerning the water solubility of 4-chlorophenol and toluene (27.1 g/L and 0.5 g/L, respectively), toluene, which is more hydrophobic, should have a higher adsorption capacity compared with 4-chlorophenol, especially for hydrophobic adsorbents (OD-HMS and MP-HMS), but the obtained results were different. Moreover, AM-HMS, a hydrophilic adsorbent, had a higher adsorption capacity of toluene than MP-HMS and Ti-HMS.

Based on these results with 4-chlorophenol and toluene, it is estimated that interaction between the modified part (organic moiety and Ti-substitution) and the organic adsorbate molecule causes molecular selectivity for adsorption reaction. Increasing hydrophobicity of silicate adsorbents cannot always ensure a higher adsorption capacity for hydrophobic organic compound.

### Adsorption isotherm of dichloroacetic acid (DCAA) and thioflavin T (BY)

DCAA adsorption experiments were conducted at pH 3.5–6. The results shown in Figure 4a demonstrate that DCAA was barely adsorbed on HMS and Ti-HMS. Similarly, hydrophobic HMSs (OD-HMS and MP-HMS) did not adsorb DCAA. Surface hydrophobicity, coupled with nearly neutral electric charge of MP-HMS and negative surface charge of OD-HMS, resulted in little adsorption of hydrophilic, negatively charged DCAA. On the contrary, AM-HMS that has a strong positive charge can adsorb DCAA to a significant extent. In the case of AM-HMS, the combined effects of hydrophilicity and coulombic interactions play a significant role in the adsorption of DCAA.

![Figure 4a](https://iwaponline.com/ws/article-pdf/6/3/17/418205/17.pdf)

**Figure 3** Adsorption isotherms of 4-chlorophenol and toluene on HMS and modified HMSs at pH 4–6: ▲, HMS; ◆, Ti-HMS; ○, OD-HMS; ×, MP-HMS; □, AM-HMS

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>2,4-D</th>
<th>Mecoprop</th>
<th>4-chlorophenol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K/n$</td>
<td>$R^2$</td>
<td>$K/n$</td>
</tr>
<tr>
<td>HMS</td>
<td>0.1292</td>
<td>0.753</td>
<td>0.8904</td>
</tr>
<tr>
<td>Ti-HMS</td>
<td>0.2160</td>
<td>0.565</td>
<td>0.7253</td>
</tr>
<tr>
<td>OD-HMS</td>
<td>0.0450</td>
<td>1.15</td>
<td>0.9631</td>
</tr>
<tr>
<td>MP-HMS</td>
<td>0.1603</td>
<td>0.869</td>
<td>0.8571</td>
</tr>
<tr>
<td>AM-HMS</td>
<td>0.0473</td>
<td>1.6257</td>
<td>0.9585</td>
</tr>
</tbody>
</table>

Table 3: Freundlich equation parameters from adsorption isotherms of 2,4-D and mecoprop on HMSs.
interaction force between the amino functional group of AM-HMS and DCAA are suggested to work for DCAA adsorption.

The molecular size of DCAA was calculated as 0.69 nm and 0.46 nm in width and length, respectively, by ACD Labs Chemsketch program version 5. Hence, it is clear that the effect of pore blocking of AM-HMS can be neglected. In addition, the area per one adsorbed DCAA molecule on AM-HMS (approximately 6.34 nm²) was much higher than the molecular size of DCAA (0.32 nm²), which indicated that the surface area was not the limiting factor for DCAA adsorption.

Figure 4b shows the adsorption isotherm of thioflavin T (BY) on HMSs (see also Table 4). L-shape isotherms were detected, which are consistent with other research works (Espantaleon et al., 2003; Janos et al., 2003; Mohamed, 2004). Coulomb interaction, which is caused by electrostatic force, was suggested to be an important factor for adsorption of ionic dyes. BY is a cationic dye that is positively charged in water; hence, negatively charged HMSs have a higher affinity with BY than positively charged HMS.

The order of this affinity, shown in Figure 4b, is OD–HMS > HMS > Ti–HMS > MP–HMS > AM–HMS. This order is in agreement with the strength of negative surface charge of HMSs, as shown in Figure 1. In addition to electrostatic force, van der Waals force between hydrophobic surfaces (OD-HMS and MP-HMS) and BY molecule promotes adsorption of BY. The combined effects of van der Waals force and electrostatic force produced the highest BY adsorption capacity of OD-HMS.

Hydrogen bonding between hydroxyl groups (HMS and Ti-HMS) or amino groups (AM-HMS) on hydrophilic surface and nitrogen atoms of BY molecule can also contribute to adsorption of BY on HMSs. Since HMS and Ti-HMS had a weakly negative

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Freundlich</th>
<th>Langmuir</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(K)</td>
<td>(1/n)</td>
</tr>
<tr>
<td>HMS</td>
<td>11.4</td>
<td>0.14</td>
</tr>
<tr>
<td>Ti-HMS</td>
<td>7.70</td>
<td>0.23</td>
</tr>
<tr>
<td>OD-HMS</td>
<td>9.08</td>
<td>0.25</td>
</tr>
<tr>
<td>MP-HMS</td>
<td>7.78</td>
<td>0.19</td>
</tr>
<tr>
<td>AM-HMS</td>
<td>0.14</td>
<td>0.80</td>
</tr>
</tbody>
</table>

**Figure 4** Adsorption isotherms of dichloroacetic acid (pH 3.5–6) and thioflavin T (pH 5–7) on HMS and modified HMSs: •, HMS; ●, Ti-HMS; ○, OD-HMS; ×, MP-HMS; □, AM-HMS
charge at pH 5–7, the effect of an electric charge is less significant, and hydrogen bonding may be the only attractive force that facilitates adsorption of BY on HMS and Ti-HMS. Hence, adsorption capacities of HMS and Ti-HMS for BY were not high compared with OD-HMS. MP-HMS and AM-HMS, which had a weak and strong positive charge, respectively, had low adsorption capacities for BY because of the repulsive force of electrostatic charges that offsets hydrogen bonding (AM-HMS) or van der Waals force (MP-HMS). Although it was reported that hydrogen bonding is the major attractive force for adsorption of BY (Al-Ghouti et al., 2003), hydrogen bonding between the amino-group of AM-HMS and BY did not increase the adsorption capacity significantly.

Conclusions
Increasing hydrophobicity was not always found to bring about higher adsorption capacities of HMSs for hydrophobic adsorbates, such as toluene. The effects of other physico-chemical interactions between surface functional groups and adsorbate molecules played more important roles in determining adsorption capacities. Grafted organic functional groups changed surface charge, which enhanced the electrostatic force between HMSs and ionic pollutants. Negatively charged contaminants, i.e. 2,4-D, mecoprop and dichloroacetic acid, were adsorbed more readily on positively charged AM-HMS by electrostatic interaction. Hydrogen bonding and van der Waals interaction between adsorbents and adsorbates, as well as a combination of these forces, also enhanced the adsorption capacities of HMSs. In addition to the electrostatic interaction, a cationic dye, thioflavin T, was adsorbed on the surfaces due to hydrogen bonding and van der Waals interaction for hydrophilic surfaces and hydrophobic surfaces, respectively.

References