(28) Effect of Organic Grafting Modification of Hexagonal Mesoporous Silicate on Haloacetic Acid Removal

メソポーラスシリカ表面の有機修飾によるハロ酢酸除去への影響

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ABSTRACT; Batch adsorption experiments were carried out using Hexagonal Mesoporous Silicates (HMSs) and dichloroacetic acid (DCAA) as a model Haloacetic acids (HAAs). The three types of grafted organic functional were n-octyldimethyl-, 3-aminopropyltriethoxy-, and 3-mercaptopropyl-groups. Titanium substituted HMS was also applied. Bi-functional grafted HMSs, which have both amino and mercapto functional groups, were synthesized to evaluate the effects of combined functional groups on adsorption capacities. Physical characteristic of synthesized HMSs didn't affect DCAA adsorption capacity; but grafted functional groups changed the surface charge of HMSs. Negatively charged DCAA was adsorbed only by positively charged HMS. A higher amount of surface amino-functional groups on HMS gave a higher positive surface charge and exhibited a higher adsorption capacity of DCAA. Combination of amino and mercapto-functional groups gave higher adsorption capacities in high DCAA concentration range despite lower surface charge than the amino-grafted HMS. Adsorption of DCAA decreased positive surface charge of HMSs due to neutralization of surface charge. At a low DCAA concentration range, adsorption capacities were strongly dependent on surface charge, and hence adsorbents with high positive charge densities, i.e. AM-HMS and A-HMS, had very high adsorption capacities for DCAA.

KEYWORDS; Hexagonal Mesoporous Silicate (HMS); Organic grafting modification; Haloacetic acids (HAAs); Adsorption.

1. INTRODUCTION

Haloacetic acids (HAAs) are common disinfection by-products (DBPs) usually found in chlorinated drinking water. Oxidative reactions involving free chlorine, bromide, and natural organic matter (NOM) may form nine common species of HAAs. The kinds and amount of compounds formed depend mainly on the composition of the water and on the dose of halogenic chemical oxidants. Several researchers have suggested an association between HAAs and incidence of cancers, including bladder, rectal and colon cancer. Moreover, some of HAAs (Mono-, Dichloroacetic acid), are not only used as intermediates for the manufacture of drugs, dyes and chemicals, but also as herbicides. Awarness that HAAs present serious human healthy hazards has increased. The US Environmental Protection Agency (USEPA) has classified dichloroacetic acid as a groups B2 human cacinogen and trichloroacetic acid as group C human cancinogen (Sarrion *et al.*, 2000; Nissinen *et al.*, 2002).

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UPEPA has promulgated regulations to control disinfection by-products. The largest group of compounds formed during this process are trihalomethanes(THMs), followed by HAAs. The EPA has proposed the disinfectants/disinfection by-products (D/DBPs) rule, the first stage of which establishes maximum contaminant levels (MCLs) of 60 μg/L for the sum of the five regulated HAAs. The HAAs selected for control include monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), dibromoacetic acid (BCAA) and trichloroacetic acid (TCAA) (Xie *et al.*, 2002; Zhou *et al.*, 2002).

The control of HAAs is a challenge and a necessity because of the uncertainty of mechanisms of their generation upon halogenation of NOM in drinking water, high hydrophilicity, high yield at $pH<7$ and health effects putatively associated with them. Because accepted treatment technologies (e.g. adsorption on granular activated carbon or biologically activated carbon) may not perform well with HAAs due to their very high hydrophilicity (Spenth *et al.*, 1998; Tung *et al.*, 2002; Xie *et al.*, 2002; Zhou *et al.*, 2002; Korshin *et al.*, 2001), it is relevant to evaluate alternative adsorbents which to decrease the concentration of these compounds in drinking water.

Hexagonal mesoporous silicate (HMS), which has been studied extensively in chemical reaction fields, has mesoscale pore and a uniform surface functional group was expected to have high surface accessibility and molecular selectivity than powder activated carbon (PAC). Silanol group on HMS surface is expected to have high affinity to high hydrophilic molecules such as HAAs. HMS surface can be modified by various methods to enhance specific characteristics, e.g., organic ligand modification and metal substitution in crystalline structure. However, removal of HAAs from aqueous phase by adsorption to HMS and modified HMSs has not yet been studied.

The objective of this study is to evaluate the effect of surface modification and surface charge of HMSs on adsorption capacity for dichloroacetic acid (DCAA). Batch adsorption experiments were carried out with three types of HMSs grafted with different single ligands (SL-HMSs), and one of titanium substituted HMS (Ti-HMS) to investigate effects of surface functional groups. Surface areas, pore size distribution, surface charges of these materials were measured and their effects on adsorption mechanisms were discussed. In addition, effects of bi-functional organic grafting and their ratios on adsorption capacity of DCAA were investigated. We employed the information from adsorption isotherm together with a theoretical evaluation of the surface properties of adsorbent and adsorbate to elucidate adsorption capacities and mechanisms of HMSs and PAC.

2. MATERIALS AND METHODS

2.1 Adsorbent synthesis

HMS was prepared by the following method: tetraethoxysilane (TEOS) (Wako, Osaka, Japan) 1.0 mole to a mixture of water 29.6 mol, dodecylamine (Chameleon Reagent, Osaka, Japan) 0.27 mol and ethanol (Chameleon Reagent, Osaka, Japan) 9.09 mol were mixed under vigorous stirring. The reaction mixture was aged at an 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 condition at 923 K for 4 h, to remove organic template (Tanev *et al.*, 1995).

2.2 Grafting of Organic functional group on HMS

Silanization with n-octyldimethlchlorosilane, denoted as OD-HMS, was prepared by drying 5 g of HMS at 423 K under vacuum for 24 h. Then the sample was put into a 250 mL, three-neck round flask under N_2 flow. 140 mL of dichloromethane (Aldrich, Germany) and stirrer bead 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, Tokyo, Japan) was added under N_2 flow. The mixture reacted under reflux at 333 K for 4 h. After that, the mixture was filtered and washed with 50 mL chloroform (Sigma-Aldrich) 2 times and 50 mL of ethanol. Then, sample was dried at 313 K under vacuum for 4 h. Hydrophobicity of HMS was increased by grafted ligands.

Silanization with 3-aminopropyltriethoxysilane, denoted as Am-HMS, was prepared by drying 8 g of HMS at 423 K for 18-20 h under vacuum. Then the sample was put into a 250-mL three-neck round flask under N_2 flow. 115 mL of toluene (Aldrich, Germany), 5.2 g of 3-aminopropyltriethoxysilane (Fluka) and glass beads were added into the flask under N_2 flow. The mixture was kept stirring at a room temperature for 4 hours, 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 cause hydrophilic characteristic of the adsorbent.

Silanization of HMS with 3-mercaptopropyltrimethoxy, denoted as MP-HMS, was carried out as follows: 1 g of HMS was dried at 383 K, refluxed with 1 g of 3-mercaptopropyltrimethoxy (Chisso) 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 over ethanol for 18 h in order to remove ungrafted organosilane. Mercapto functional groups increase hydrophobicity of obtained adsorbent.

2.3 Synthesis of bi-functional HMSs (BF-HMSs)

Bi-functional HMS was prepared by pre-functional groups grafting procedure following method of Lee *et al.* (2001): tetraethoxysilane (TEOS) (Wako, Osaka, Japan) 1.0 mol to a mixture of water 50 mol, dodecylamine (Chameleon Reagent, Osaka, Japan) 0.25 mol and ethanol (Chameleon Reagent, Osaka, Japan) 10.25 mol under vigorous stirring. The stirring was continued for 30 min, then 3-aminopropyltriethoxysilane (APTES) and 3-mercaptopropyltrimethoxysilane (MPTMS) were added. The molar ratios of the reactants are listed in Table 1. The reaction mixtures were vigorously stirred for 20 h at ambient temperature, and the resulting mixtures were filtered and air-dried on a glass plate for 24 h. Residual organosilanes and surfactant were removed by Soxhlet extraction for 72 h with ethanol.

Table 1. Molar ratio of APTES and MPTMS

Reactants	AM-HMS	A7M3-HMS	A5M5-HMS	A3M7-HMS	M-HMS
APTES	0.25	0.175	0.125	0.075	-
MPTMS	-	0.075	0.125	0.175	0.25

2.4 Titanium substitution modification of 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, Tokyo, Japan) was added at the same time as TEOS (Tanev *et al.*, 1994).

2.5 Characterization of HMSs

HMS, Ti-HMS, single functional grafted HMSs and PAC were characterized physical properties by the following methods. Powder X-ray diffraction (XRD) patterns of synthesized adsorbents were recorded on a MX Labo Powder Diffractometer equipped with Cu Kα radiation (MAC science, Japan). Nitrogen adsorption isotherms were measured at 77 K on a Belsorp 28SA Sorptometer. Surface functional groups of prepared adsorbents were investigated by Fourier Transform Infrared (FT-IR) spectroscopy (Jasco FT-IR-610) with JASCO DR-81 Diffuse Reflectance Attachment, and a spectral resolution of 4 cm^{-1}. The presence of Ti^{+4} and Ti^{+6} in crystalline of Ti-HMS samples was confirmed by UV-VIS spectroscopy (Varian DMS 300 UV-VIS) and ICP-AES (Perkin Elmer Optima 3000DV).

2.6 Surface charge

Acid/base titration of synthesized HMSs and PAC was carried out using 10 mL of adsorbents mixture (1 g/L). Varying amounts of 0.025 M HCl or 0.025 M NaOH solutions were added to a maximum of 13 samples to vary pH of each sample. There was also one sample with no acid or base addition. Each sample was then diluted to a final volume of 25 mL with Milli Q water. The ionic strength was adjusted with NaCl at 0.001 M when diluted in 25 mL. Then the samples were shaken overnight at room temperature. After equilibrating, the suspension pH of each sample was measured and the pH data of entire batch were plotted against surface charges that were calculated from the principle of electroneutrality as follows:

$$\text{Surface charge (C/g)} = [\, (\text{HCl})_{add} - (\text{NaOH})_{add} - (H^+) + (OH^-) \,] \times 96500 / \text{weight}$$

2.7 Adsorption Experiments

Synthesized adsorbents were transferred to a 50-mL volumetric flask with a stopper, and 25 mL of DCAA (Chameleon Reagent) solution with known concentrations was added. After stirring overnight in a water bath at 298 K, the mixture was filtered through Dismic filter (pore diameter 0.2 μm). The first 10 mL of filtrate was discarded and the rest was harvested for analysis by either a UV-spectrophotometer at 200 nm (Hitachi U2000 with 1-cm quartz cell) or LC-MS for DCAA depending on DCAA concentration. The analytical conditions of HPLC-MS were listed on Table 2. Adsorption capacity was calculated from the difference between initial and equilibrium concentrations divided by amount of adsorbents.

3. RESULTS AND DISCUSSION

3.1 Physical characteristic of HMSs

Surface areas and pore sizes of HMS, modified HMS and PAC were calculated using nitrogen adsorption isotherms (Table 3). The results revealed that synthesized HMS had larger pore sizes than PAC, but surface areas of synthesized adsorbents were less than PAC. N_2 adsorption isotherms also showed a decrease in BET

Table 2. Analytical conditions of LC-MS for DCAA analysis

HPLC	MS
Instrument : Agilent 1100	Instrument : LCQ Finnigan Mat
Column : Inertsil ODS 3 (150mm,2.1mm,5μm)	Mass range : m/z 90-500
Mobile phase A : CH_3CN	Ionization : Electrospray
Mobile phase B : 5mM Dibutylamine acetate A/B = 10/90 to 50/50 in 20 min	Fragmentor : 40 V
Flow rate : 0.20 mL/min	Nebulizer : N_2 (50 psi)
Oven Temp. : 313 K	Drying gas : N_2 (10L/min, 623 K)
Injection vol. : 100 μL	Mode : Negative

(up to a maximum concentration at 1 mg/L)

surface area of HMSs modified with organic-functional groups (MP-HMS, OD-HMS and Am-HMS). Grafted organic functional groups on HMS surface were detected by FT-IR pattern, and presence of Ti^{4+} was confirmed by UV-Visible spectrophotometer and FT-IR. The amount of titanium incorporated into a gram of HMS was quantified by ICP-AES. Ti-HMS had a larger surface area than pristine HMS and also higher uniformity of pore size. Hexagonal crystalline structures of synthesized adsorbents were proved by X-ray diffraction pattern (XRD). XRD patterns proved crystalline structure of synthesized adsorbents, with Ti-HMS having the highest quality of hexagonal crystalline structure. These observations proved the presence of significant amount of grafted functional groups and titanium incorporated in the framework of HMS, causing constriction of the channels. Mesoporosity and pore structure, however, were well conserved even after applied modification.

Table 3. Physical characteristics of HMS, modified HMS and PAC

Adsorbents	**Pore diameter (nm)**	**Surface area (m^2/g)**		**Pore volume (mm^3/g)**	**Surface functional groups**	**Surface characteristic**
		BET surface area	**External area**			
HMS	3.00	667.75	85.32	1078	Silanol	Hydrophilic
Ti-HMS	3.18	766.51	99.35	1276	Silanol	Hydrophilic
MP-HMS	3.00	567.31	74.96	883	Mercapto	Hydrophobic
OD-HMS	2.36	476.56	58.78	499	Octyl	Hydrophobic
AM-HMS	2.32	533.41	44.31	592	Amino	Hydrophilic
PAC	1.9	980.46	59.41	276	Carboxyl Phenyl others	Hydrophobic

From obtained physical characteristics of synthesized HMSs and PAC comparing with molecular structure of DCAA, it might be concluded that pore size of these adsorbents will not interfere with accessibility of DCAA to active surface sites of these materials.

3.2 Surface charge

Figure 1 show the surface charge density of HMS, Ti-HMS, SF-HMSs and PAC as function of pH. Such pH value that give zero surface charge is called the zero point of charge (pH_{zpc}). At this pH cationic surface groups and anionic surface groups posses equal amount of electric charge. Pristine HMS and Ti-HMS have the zero point of charge at pH values between 4-6.5. Organic grafted HMS (OD-HMS, MP-HMS and AM-HMS) have

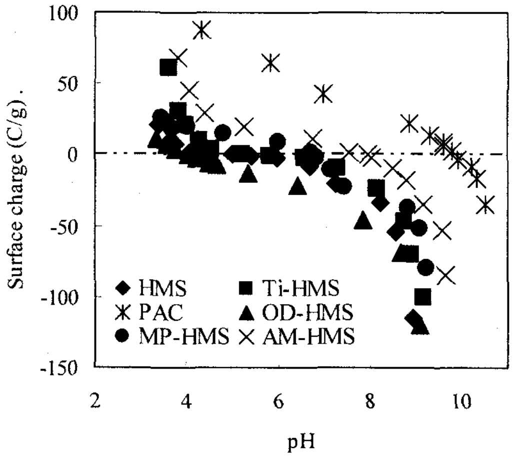

Figure 1. Surface charge of HMS, Ti-HMS, single-functional grafted HMSs and PAC as a function of pH.

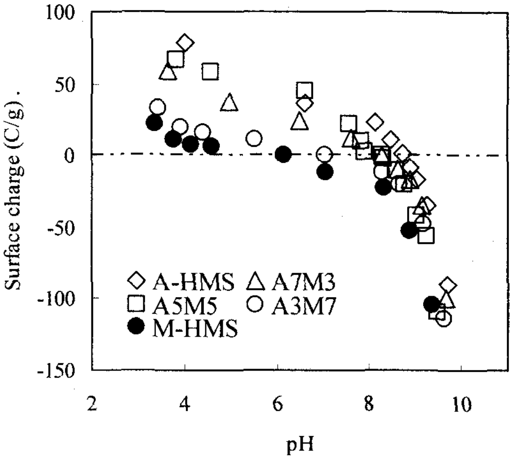

Figure 2. Surface charge of bi-functional grafted HMSs, comparing with AM-HMS and PAC as a function of pH.

values of 4, 6.8 and 8.2, respectively. pH_{zpc} of PAC is the highest about 9.8. As shown in Figure 1, the surface charge density decrease as the pH increases. The functional groups present on the surface of HMSs can gain or lose protons, which varies the surface charge with changing pH. At low pH, most of the surface sites are protonated and the surface becomes positively charged, while at high pH, the surface functional groups lose protons, and the surface becomes anionic. At pH 4-7 surface charge of HMSs didn't change significantly, suggesting that adsorption capacity should be nearly constant in a pH range of 4 to 7.

As shown in Figure 2, pH_{zpc} of bi-functional grafted HMS really depend on ratios of amino and mecapto functional groups. A-HMS, A7M3-HMS, A5M5-HMS, A3M7-HMS and M-HMS have pH_{zpc} at 9, 8.3, 7.9, 7, and 6, respectively.

3.3 The adsorption of DCAA on HMS, Ti-HMS, single functional grafted HMSs and PAC

Adsorption experiments were conducted at pH between 3.4-6.2 and 3.5-9.4 for HMSs and PAC respectively. From the data in Figure 1, the surface charges of HMS and Ti-HMS in this pH range are nearly zero, which implies that effect of electrostatic interaction between their surfaces and negative charge of DCAA molecule can be neglected. The surface charge of MP-HMS is weakly positive, while those of AM-HMS and PAC were strongly positive. But the surface of OD-HMS has strong negative charge in the pH range between 3.4 and 6.2. All of BF-HMSs have positive surface charges in the same pH range.

It was expected that hydrophilic surface of HMS and Ti-HMS, which have silanol groups as main functional group on surface, would enhance adsorption capacity for DCAA. But the results shown in Figure 3 demonstrate that DCAA was barely adsorbed on HMS and Ti-HMS. Similarly hydrophobic SF-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 and PAC that have strong positive charge can adsorb DCAA to a significant extent. In the case of AM-HMS combined effects of hydrophilicity and coulomb interaction force

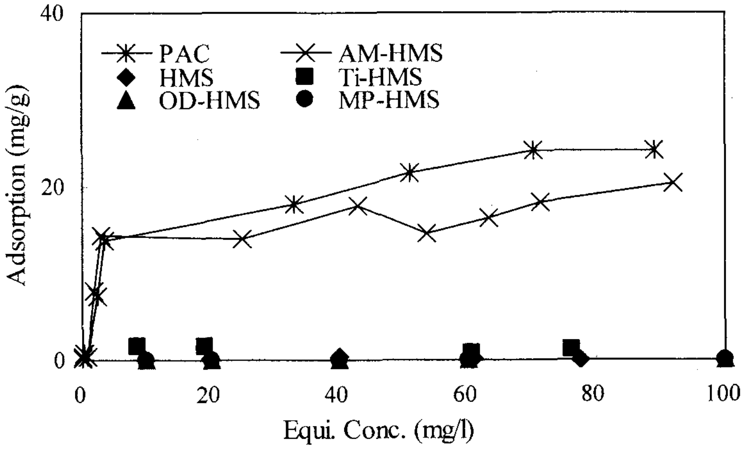

Figure 3: Adsorption isotherms of DCAA on HMS, Ti-HMS, single organic-grafted HMSs and PAC at high concentrations.

between amino functional group of AM-HMS and DCAA are suggested to work for DCAA adsorption. Although PAC is a hydrophobic adsorbent, the strongest active surface sites as well as the strongest positive charge of the surface gave a high adsorption capacity for DCAA. Among five HMSs shown in Figure 3, only AM-HMS had comparable adsorption capacity as PAC, which indicates that increasing the number of surface amino-group may lead to a higher adsorption of DCAA than PAC.

Moreover, 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. It is clear that effect of pore blocking of AM-HMS and PAC can be neglected. In addition, areas per one adsorbed DCAA molecule on PAC and AM-HMS (approximately 10.45 and 6.34 nm^2, respectively) were much higher than the molecular size of DCAA (0.32 nm), which indicated that the surface area was not the limiting factor for DCAA adsorption. Adsorption also depends on other factors such as electrostatic force, hydrophilicity and stability in bulk solution of DCAA. Studies of Tung *et al.* (2002) and Spent *et al.* (1998) indicated that adsorption capacities of granular activated carbon (GAC) for HAAs decreased as the level of halogen substitution increased; in addition, adsorption capacities of bromine species were found to be higher than chlorine species. However, confirmation of these effects on HAAs adsorption by HMSs is needed.

3.4 The adsorption of DCAA on BF-HMSs

From the results of DCAA adsorption on single-functional group adsorbents, it was revealed that amino-functional groups have high affinity with DCAA. The effects of the amount of amino-functional groups on adsorption capacity were then investigated. AM-HMS studied in the previous experiment was synthesized by the post-grafting procedure, which might lead to a lower efficiency of grafting functional groups on silanol groups than pre-grafting procedure. These two modification methods were compared to evaluate their DCAA adsorption capacities. The amounts of amino-functional groups and mercapto-functional groups, which have no affinity to DCAA adsorption, were varied according to the ratio shown in Table 1. After synthesis, the amount of amino-functional groups and mercapto-functional groups were analyzed and represented by percent of N and S, respectively (Figure 4). Grafted amino-functional groups on post-grafted adsorbent (AM-HMS) are less than pre-grafted synthesized adsorbents (A-HMS). The amount of each functional group of bi-functionally grafted adsorbents can be reconfirmed and were as same as the ratios that were shown in table 1.

Figure 5 shows adsorption isotherms of BF-HMSs, in comparison with PAC and AM-HMS at high concentration. Isotherm data on PAC and AM-HMS are the same as those plotted in Figure 3. A-HMS, AM-HMS and PAC had the highest surface amino-functional groups; hence they had the highest DCAA adsorption capacity in the low concentration (<10mg/L). But A-HMS unexpectedly had less adsorption capacity in the high DCAA concentration range (> 20mg/L) than A5M5 and A7M3. Surprisingly, A5M5 and A7M3 had the highest adsorption capacity for DCAA in the high concentration range, followed by A3M7, A-HMS, PAC and AM-HMS. M-HMS has no adsorption capacity for DCAA as shown in Figure 6, but when mercapto-group is grafted together with amino-group they had the highest adsorption capacity than HMS grafted with only amino-group.

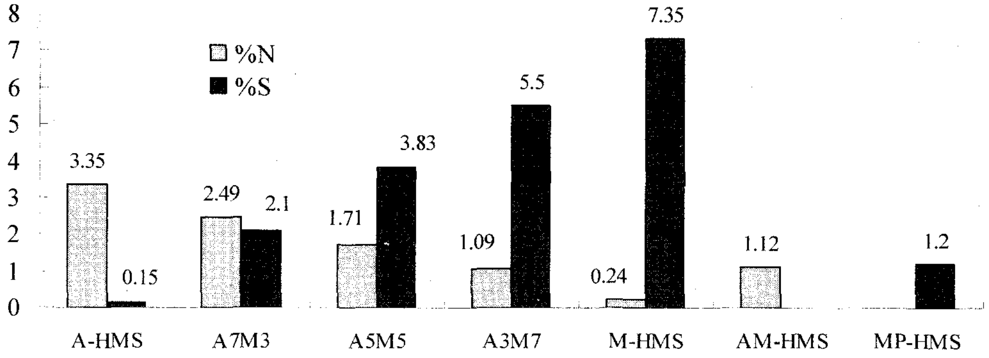

Figure 4: Amount of N and S on BF-HMSs, AM-HMS and MP-HMS

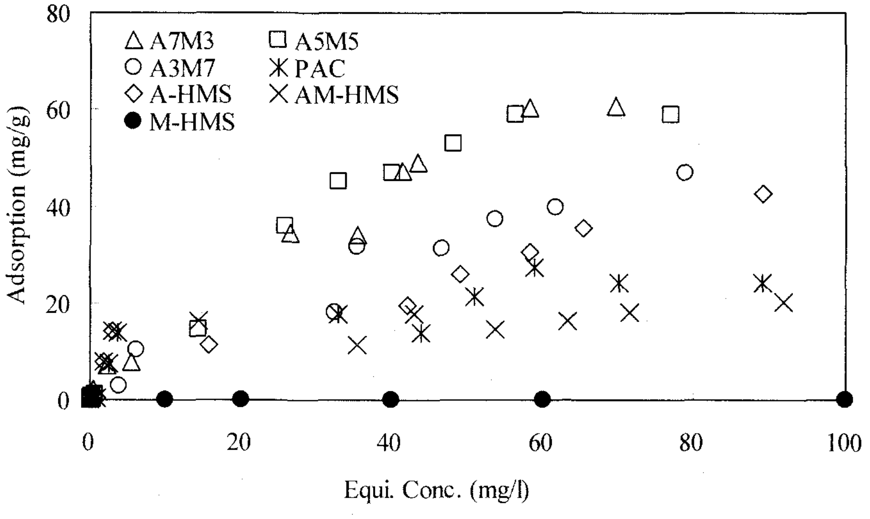

Figure 5: Adsorption isotherm of DCAA on BF-HMSs, AM-HMS and PAC.

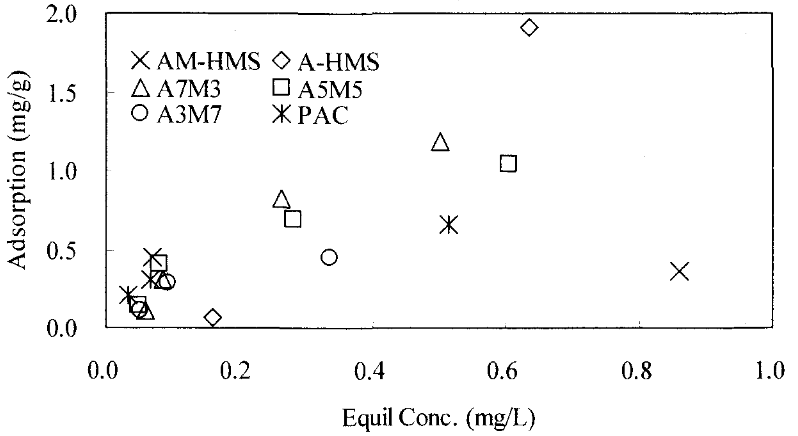

Figure 6: Adsorption isotherm of DCAA on BF-HMSs, AM-HMS and PAC at lower concentration than 1 mg/L.

Figure 6 shows adsorption isotherms of BF-HMSs, PAC and AM-HMS in lower equilibrium than 1 mg/L. Adsorption capacities of BF-HMSs relates with ratios of amino functional groups, resulting different of surface charges. Comparison between the isotherms of AM-HMS and A-HMS might be indicated effect of amount of grafted amino-functional groups. Increasing of amino-functional groups can increase adsorption capacity of DCAA. However, because of hydrophilicity of DCAA, adsorption capacity of hydrophobic PAC at such low concentration is lower than hydrophilic AM-HMS and A-HMS and hydrophilic increased BF-HMSs. Increasing surface charge by grafting more amino-functional groups and increasing hydrophilicity of surfaces were suggested to improve DCAA adsorption efficiency at low concentration of HMSs.

For bi-functionally grafted adsorbents, the presence of mecapto functional group significantly enhances adsorption capacity of A-HMS for DCAA. Ratio of amino and mercapto functional groups at 5:5 and 7:3 gave the highest adsorption capacity of DCAA. Surface charges of all BF-HMSs are clearly related with the ratio of grafted functional groups; however, adsorption capacity in this case was not consistent with the surface charge density. Different adsorption capacity of HMSs and PAC for DCAA at different DCAA concentration can be explained as follows. At low DCAA concentrations the surface charge plays an important role for DCAA adsorption. However, at higher DCAA concentration a high amount of DCAA is adsorbed and neutralizes the surface charge, which makes the surface charge less important than other factors. Combination of mercapto and amino functional groups causes a higher surface complexity and produces more active surface sites for adsorption of DCAA. AM-HMS and PAC had L shape isotherms, whereas BF-HMSs had S shape isotherms. The difference of these adsorption isotherms were caused by increased adsorption capacities of BF-HMSs due to surface complexity. AM-HMS and PAC had lower adsorption capacities that were caused by electrostatic force only. This finding suggests that further exploration of combined effects of different surface functional groups may lead to discovery of better adsorbents.

4. CONCLUSIONS

The effect of surface functional groups and surface charge of five types of Hexagonal Mesoporous Silicates (HMSs) on dichloroacetic acid (DCAA) adsorption capacity were investigated by batch adsorption experiments.

The pore size and BET surface area of synthesized HMS had little effect on DCAA adsorption, but surface charge and amino-functional group had a strong influence on DCAA adsorption. HMS grafted with amino group had a comparable DCAA adsorption capacity as powdered activated carbon, but HMS with neutral or negative surface charge had no adsorption capacity for DCAA.

The amount of amino-functional groups grafted on AM-HMS affected directly on positive surface charge of HMSs. Higher amount of amino-functional grafted HMS cause higher positive surface charge and gives a higher adsorption capacity of DCAA. Three types of bi-functionally grafted HMS were applied to DCAA adsorption experiments to studying the effect amino-functional groups. DCAA adsorption capacities of all bi-functional by grafted HMSs were higher than AM-HMS at higher DCAA concentration range despite the fact that some of them had lower positive charge than AM-HMS. This result suggests that surface charges of HMSs and PAC were neutralized at high concentration of DCAA, and hence plays less important role in determining the adsorption capacity of HMSs for DCAA. At high concentration of DCAA, grafting mercapto groups together with amino groups improved the adsorption capacity significantly. The adsorption capacity for DCAA was maximized at ratios of amino and mercapto groups between 5:5 to 7:3. Further exploration of these unique effects of different functional groups may lead to a discovery of better adsorbents. At low DCAA concentration range, adsorption capacities are strongly dependent on surface charge, and hence adsorbents with high positive charge density, i.e. AM-HMS, A-HMS, had very high adsorption capacities for DCAA.

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