

Adsorption of MX (3-chloro-4 (dichloromethyl)-5-hydroxy-2-(5H)-furanone) on amphiphilic mesoporous silica in aqueous solution

Eun-Ah Yoo* and Kang-Sup Chung¹

Department of Chemistry, Sungshin Women's University, Seoul, 136-742, Korea
¹Korea Institute of Geoscience and Mineral Resources(KIGAM), 30 Gajeong-dong,
Yuseong-gu, Daejeon 305-350, Korea

(Received February 11, 2011; Accepted March 21, 2011)

양쪽성 메조 포러스 실리카에 의한 수용액 속의 MX의 흡착

유은아* · 정강섭

성신여자대학교 화학과, ¹한국지질자원연구원

(2011. 2. 11. 접수, 2011. 3. 21. 승인)

Abstract: Mesoporous silica was synthesized in a water solvent and in an ethanol solvent with the non and cationic cetyltrimethyl ammonium chloride (CTAC) by varying the amount of the amphiphilic acrylic urethane oligomer (AAU) and the pH of the solution. The adsorption of the MX (3-chloro-4 (dichloromethyl)-5-hydroxy-2-(5H)-furanone) in drinking water was studied using the synthesized mesoporous silica as an adsorbent. The most appropriate silica was synthesized in acidic conditions in the water solvent and in alkali conditions in the ethanol solvent. The average pore sizes of the synthesized mesosilica were 3 nm and more. The mesoporous silica synthesized by the addition of the AAU oligomer showed excellent adsorption characteristics. With respect to the co-surfactant, the best adsorption characteristics were obtained when the P64, a non-ionic surfactant with a high molecular weight, was used to synthesize the silica than when other co-surfactants were used. The adsorption rate decreased as the MX concentration in the water increased. Different adsorption equilibrium conditions were reached depending on the adsorbate MX concentration in the adsorbent and the solution. It was seen that perfect adsorption does not occur due to such equilibrium conditions.

요 약: 본 연구에서는 양쪽성 메조 다공성 실리카를 다양한 조건(용매, 계면활성제와 올리고머의 량, 용액의 pH)에서 합성하였다. 메조 다공성 실리카를 사용하여 염소 소독으로 인해 음용수 중에 미량 존재하는 변이원성 물질인 MX (3-chloro-4-(dichloromethyl)-5-hydroxy-2-(5H)-furanone)의 흡착에 관한 특성을 연구하였다. 소수성과 친수성의 양쪽성 폴리우레탄 올리고머를 사용하여 합성된 메조다공성 실리카의 경우 뛰어난 흡착특성을 나타내었다. 그리고 보조 계면 활성제의 경우에는 비이온성이며 분자량이 큰 폴리에틸렌 프로필렌 옥사이드(PEO-PPO)를 사용하여 합성된 메조 다공성 실리카가 가장 좋은 흡착 특성을 보였다.

Key words: amphiphilic mesoporous silica, 3-chloro-4(dichloromethyl)-5-hydroxy-2-(5H)-furanone, mutasenic-Halogen

★ Corresponding author

Phone : +82-(0)2-920-7168 Fax : +82-(0)2-920-7168

E-mail : eayoo@sungshin.ac.kr

1. Introduction

Since the synthesis of mesoporous molecular materials by the researchers in Mobil in the early 19th century, extensive researches have been conducted on the synthesis and applicability of the mesoporous materials in various fields.¹⁻⁵ Due to the characteristic of mesoporous materials that their surface area, pore volume, pore size distribution and pore structure can be controlled, they are receiving attention as a critical compound delivery system, a catalyst, and an adsorbent.⁶⁻⁸ Recent studies released on mesoporous silica include a study on the selective adsorption and reaction of a gas compound in the mesoporous silica MCM 41 family by adding a metal element, and a study on the selective adsorption of metal ions dissolved in an aqueous solution by grafting a silane compound with an amine functional group on the surface of mesoporous silica.^{9,10} A study on the application of mesoporous silica to the adsorption of a gaseous light hydrocarbon has also been released.¹¹

Using mesoporous silica as an adsorbent for a hydrocarbon dissolved in waste water, the following must be considered: 1) the interaction between the hydrocarbon and the surfactant in the mesopores, 2) the interaction between the silica's surface and the hydrocarbon, and 3) the wetting characteristics of the water based on the silica surface's hydrophobic/hydrophilic characteristics. In the case of adsorption by the interaction between the hydrocarbon and the surfactant contained in the mesopores, significant adsorption such as capillary condensation does not occur since the surfactant is contained in the pores and its interaction with the hydrocarbon is not significant, and thus, the adsorption rate is also very low. Results of a study on the adsorption of organic pollutants dissolved in water using fluoride-modified hydrophobic mesoporous silica and with a TiO₂ photocatalyst have been reported by H. Yanashita *et al.* When mesoporous silica is used as an adsorbent in a water solvent, it has problems in its applicability as an adsorbent since its adsorption characteristic differs and the wetting characteristics of water and

silica tend to decrease depending on the hydrophilic/hydrophobic degree of the organics dissolved in the water.¹² Based on the results of a study conducted by Y. X. Zaho *et al.* on the adsorption characteristics of an organic compound dissolved in water using exchanged mesoporous silica that was dissolved and that substituted the surfactant in the mesoporous silica pores into ammonium nitrate, and using silica that had a surfactant in its pores, the silica with the surfactant had better adsorption characteristics than the exchanged or calcined mesoporous silica.¹³

Based on the results of a study on the oil-contaminated soil-washing process using an aqueous solution with dispersed amphiphilic polyurethane particles by J.Y. Kim *et al.*, it is more effective to wash off soil using an aqueous solution with polyurethane particles than a surfactant of over CMC concentration.¹⁴ To be able to use amphiphilic polyurethane as an adsorbent, however, the adsorbent must be solid and the amphiphilic polyurethane medium must be chemically or physically stable. In this study, mesoporous silica impregnated with an amphiphilic acrylic urethane (AAU) oligomer was synthesized and used as an adsorbent.

In this study, the amphiphilic acrylic urethane oligomer, which has appropriate hydrophobic and hydrophilic characteristics, was synthesized, and mesoporous silica that has proper wetting characteristics and large adsorption characteristics for organic pollutants was synthesized using non-ionic and cationic surfactants as co-surfactants. Using this synthesized mesoporous silica, the adsorption characteristics of polychlorinated polycyclic hydrocarbons (PAHs) dissolved in drinking water were studied. Among the polychlorinated polycyclic hydrocarbons, MX (3-chloro-4-(dichloromethyl)-5-hydroxy-2-(5H)-furanone) is created as trace impurities from chlorination and dissolved in drinking water. MX has both aromatic and aliphatic functional groups and is especially effective in studying the adsorption characteristics of the mesoporous silica surface in a water solvent, and is important due to its applicability.

2. Experiment

2.1. Reagents and materials

As a standard solution, 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX) (Aldrich) was diluted to 1,000 ppm with ethylacetate and stored in a dark place at -20 °C. As a derivatization reagent, a 2 (v/v)% sulfuric acid solution was prepared with an isopropanol (Aldrich) solvent. For the ethylacetate, hexane, sulfuric acid, and methanol, commercial products (Aldrich) were used, as they needed no purification.

A 500 mg/3 mL silica column (SI-1 silica, 50 μ m, 70 Å) Phenomenex was used in the analysis. As an internal standard, mucobromic acid (MBA) (Aldrich) was diluted to 500 ng/mL with ethylacetate.

Commercial products of (15 w/w% aqueous solution of cetyltrimethylammonium chloride) CTAC (Miwon Co., Korea) (tetraethyl orthosilicate, Degusa) TEOS, the copolymer surfactant poly(oxyethylene-oxypropylene) block copolymer, PEO-PPO (P64 and P61), and the polyoxyethylene alkylamine ether series LM5 and LM20 (Green Softchem Co., Korea) were also used. Hydrochloric acid, ammonia water, trimethylamine, and ethanol (J. T. Baker) were also used, as they needed no purification.

2.2. Preparation

2.2.1. Synthesis of amphiphilic oligomer

The amphiphilic polymer oligomer (amphiphilic acrylic urethane (AAU) oligomer), which was added for the synthesis of mesoporous silica, was synthesized according to the method reported by J. Y. Kim *et al.* (14) Polypropylene glycol (130.19 g GP1000, Koreapolyol Co.) and isophorone diisocyanate (130.19 g) (Degusa) were added, and dibutyl tin dilaurylate (0.02 g Air products) was added as a catalyst at 45-50 °C, after which they were stirred for two hours while a 65 °C temperature was maintained. Under this temperature, 45.34 g of 2-hydroxyethyl acrylate (2-HEA), (Mitsubishi Rayon) and 0.02 g of the alkyl tin catalyst were further added and stirred for two hours, after which 128.84 g of polyethylene glycol (PEG 600, Sanyo Chemical) and 0.02 g of a catalyst were

added and stirred for three hours to react. The reaction was terminated after it was confirmed that no residual -NCO (isocyanate) existed, using an IR spectroscopy. The molecular weight of the synthesized AAU that was measured using GPC in this study was in the range of 5,000-3,000, and the average molecular weight was about 4,500.

2.2.2. Synthesis of mesoporous silica

The mesoporous silica was synthesized by varying the solvent type, the pH, the surfactant type, and the surfactant amount. The synthesis conditions are shown in *Table 1*.

1) Synthesis of mesoporous silica using oligomer and CTAC

CTAC (20 g) and oligomer (0, 1, 2 and 3 g, respectively) were added to the 200 mL of water, a solvent, and stirred thoroughly for 30 minutes at 45 °C to obtain a homogeneous micelle solution. TEOS (20 mL) was added to this solution, followed by hydrochloric acid and trimethylamine to produce pH 1 and pH 10 solutions, respectively. They were then stirred for five hours at 45 °C and for 12 hours at room temperature. After filtering, they were rinsed with water and ethanol. Then white powder was dried at 70 °C in the oven and heat-treated for two hours at 150 °C in air. The same procedures were applied for the synthesis of the ethanol-based mesoporous silica.

2) Synthesis of mesoporous silica using oligomer, P64 and P61

P61 and P64 (2 g each) and AAU (0, 1 and 2 g) were added to the 200 mL of water and ethanol, respectively, and stirred for 30 minutes at 45 °C. In the case of the water-based solution, CTAC (1 g, 15 w/w%) was added to ensure perfect dispersion of AAU. TEOS (50 mL) was added to this solution and ethylacetate (10 mL) was also added as a catalyst. Finally, hydrochloric acid and triethylamine were added, respectively, to produce two different solutions, one with pH 1 and the other with pH 10, respectively, to determine the pH dependency of the mesoporous

Table 1. Synthetic Conditions of mesoporous silicas.

Solvent	Amphiphilic Oligome(g)	Surfactant(g)					TEOS (mL)	Catalyst	
		P64	P61	LM5	LM20	CTAC		Acid	Base
Water (200 mL)	0.5	-	-	-	-	20	20	0	-
	1	-	-	-	-	20	20	0	-
	2	-	-	-	-	20	20	0	-
	2	2	-	-	-	-	50	0	-
	2	-	2	-	-	-	50	0	-
	2	-	-	2	-	-	50	0	-
	2	-	-	-	2	-	50	0	-
	0.5	2	-	-	-	-	50	0	-
	1	2	-	-	-	-	50	0	-
	3	2	-	-	-	-	50	0	-
	1	-	2	-	-	-	50	0	-
	3	-	2	-	-	-	50	0	-
	5	-	2	-	-	-	50	0	-
	10	-	2	-	-	-	50	0	-
	Ethanol (200 mL)	0.5	-	-	-	-	20	20	-
1		-	-	-	-	20	20	-	0
2		-	-	-	-	20	20	-	0
3		-	-	-	-	20	20	-	0
0.5		2	-	-	-	-	50	-	0
1		2	-	-	-	-	50	-	0
2		2	-	-	-	-	50	-	0
3		2	-	-	-	-	50	-	0
1		-	2	-	-	-	50	-	0
3		-	2	-	-	-	50	-	0

silica. These two solutions were stirred for 12 hours, and their sediment was filtered and rinsed with water and ethanol. They were dried at 70 °C in the oven and heat-treated at 150 °C. The mesoporous silica's synthesis procedures as described above are shown in Table 1.

2.3. Characterization

The synthesized mesoporous silica was dried at room temperature, after which its thermal stability was measured using TG/DSC (Thermal Instruments, SDT 2950 TA 4000). The measurement was performed in the temperature range of 25-800 °C with a 2 °C/min heating rate in the air. The structural characteristics of the mesoporous silica were identified using SAXRD (RigaKu, D/MAX 2200 Ultima). The XRD measurement conditions were a 0.1 °C/min scanning

rate and a 2 θ range of 1-7 °C, and the x-ray source was CuK α , with 1.45 Å λ . The synthesized mesoporous silica was hardened for three hours at 550 °C, and its surface area and pore size distribution were determined from the isothermal adsorption/desorption results of the nitrous gas using the BET device. The structural characteristics of the oligomer were determined using an IR spectroscope (Thermal-Nicolet, Waltham).

2.4. Adsorption of MX

The adsorption experiments were performed as the following. Mesoporous silicas (0.5-3 g) synthesized by various condition were added into 5 mL of ethylacetate aqueous solution of MX (1, 2.5, 5, 10, 60, 100 ppm). The mixture was stirred for 3 h in the dark at room temperature. Then, the mixture was centrifuged and the solvent of the supernatant was

evaporated under the stream of N_2 gas to dryness. The residue was dried for 24 h in the vacuum desiccator. To elaborate the procedure of analysis, MX was isopropylated with an isopropanol- H_2SO_4 mixture.

The reaction mixture was neutralized with 2% $NaHCO_3$ extracted four times with 1 mL n-hexane. The extracts were blended together, Then the remaining water in blended extracts was eliminated using anhydrous sodium sulfate.

The contents of MX that remained in the supernatants were determined by gas chromatography (HP 6890)/mass spectrometry (HP 5973) at the electron impact mode and scan mode. 3,4-dibromo-5-hydroxy-2(5H) furanone (mucobromic acid) was used as the internal standard.

3. Results and Discussion

3.1. Morphologies of synthesized mesoporous silicas

The adsorption capacity of mesoporous silica is significantly dependent on the hydrophobic/hydrophilic characteristics of the silica's surface. The mesoporous silica adsorbent was synthesized in the alcohol solvent and in the water solvent, respectively, because the mesoporous silica that was synthesized in the water solvent was generally hydrophilic and the mesoporous silica that was synthesized in the alcohol solvent was generally hydrophobic.

The surfactant micelle's stability and the alkoxide's hydrolysis rate are largely dependent on the pH; and thus, according to such characteristics, the morphology of mesoporous silica is dependent. In this study, mesoporous silicas were synthesized in a water solvent and an ethanol solvent using HCl and trimethylamine, respectively, to produce pH 1 and pH 10 conditions. In the sol-gel reaction, acid and alkali react as catalysts in the hydrolysis reaction and also affect particle formation due to the dispersion effect by the surface charge of the synthesized silica. When mesoporous silica was synthesized in the AAU/surfactant/ H_2O system, the silica particle was not grown and dispersed in gel conditions under alkali

conditions. Thus, it was more effective to synthesize the mesoporous silica under acidic conditions. In addition, when the mesoporous silica was synthesized in the AAU/surfactant/ethanol system, the silica particle was better formed and had better filtration under alkali conditions than under acidic conditions; and thus, the adsorbent was synthesized and used under alkali conditions in the alcohol solvent. Compared with existing studies, studies on the characteristics of

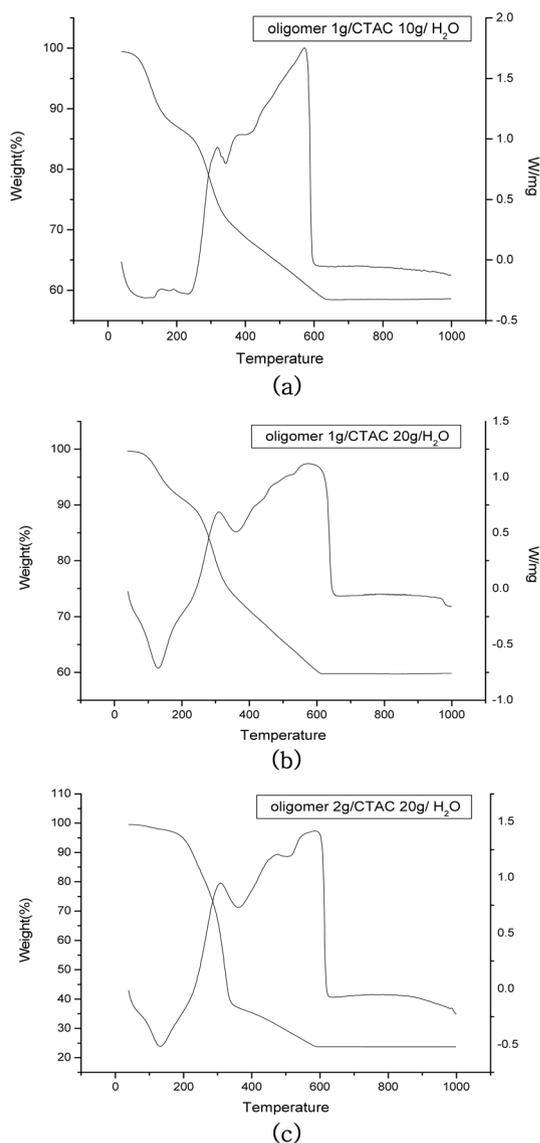


Fig. 1. TG/DSC curves of the mesoporous SiO_2 powder synthesized varying amount of CTAC and oligomer.

mesoporous silica that are dependent on the pH were carried out by L. Pasqua *et al.* and L. Sierra *et al.*, but sodium silicate and silicic acid were used as alkoxides, respectively, in their study.¹⁵⁻¹⁶ In this study, tetraethoxysilane was used as an alkoxide, and the shape and size of the pores were also largely dependent on the hydrolysis rate of the alkoxide.

Fig. 1 shows the results of the measurement of mesoporous silica synthesized in the oligomer/CTAC/HCl/H₂O system. As shown in *Fig. 1* (a) and (b), the weight loss of the mesoporous silica was about 40%, which is quite high, when it was synthesized by adding to it 1 g of AAU regardless of the CTAC amount. When 2 g of AAU was added to it, the weight loss of the mesoporous silica was about 80%, which is higher, as shown in (c). From this result, it was identified that AAU is contained in the mesoporous silica proportional to the AAU amount added. The weight loss in the temperature range of 100-200 °C was due to the evaporation of water, which partially remained, and of the hydrated H₂O, and the weight loss in the range of 300-400 °C was due to the combustion of CTAC in the air and the partial decomposition of the oligomer. At a temperature of over 400 °C, the oligomer was combusted, which resulted in a strong exothermal reaction; and at 500 °C, an almost perfect combustion occurred.

Fig. 2 shows the results of the TG/DSC measurement of the mesoporous silica synthesized in the AAU/P64/H₂O system. Very good dispersion occurred when AAU was used even under room temperature when the cationic surfactant CTAC was added to the water solvent. When P64 and P61, which are poly(oxypropylene-oxyethylene) block copolymers, were added, however, their dispersion was low in room temperature and they dispersed properly only when heated up to 50 °C or higher. Therefore, in the AAU/CTAC/H₂O system, AAU was almost uniformly deposited on the mesoporous silica. When p64 was used, the resulting combustion in the temperature ranges and the resulting weight loss were similar to those in the cases using CTAC. In the case of P64, however, complete combustion into dust occurred at 700°C when the amount of AAU was increased.

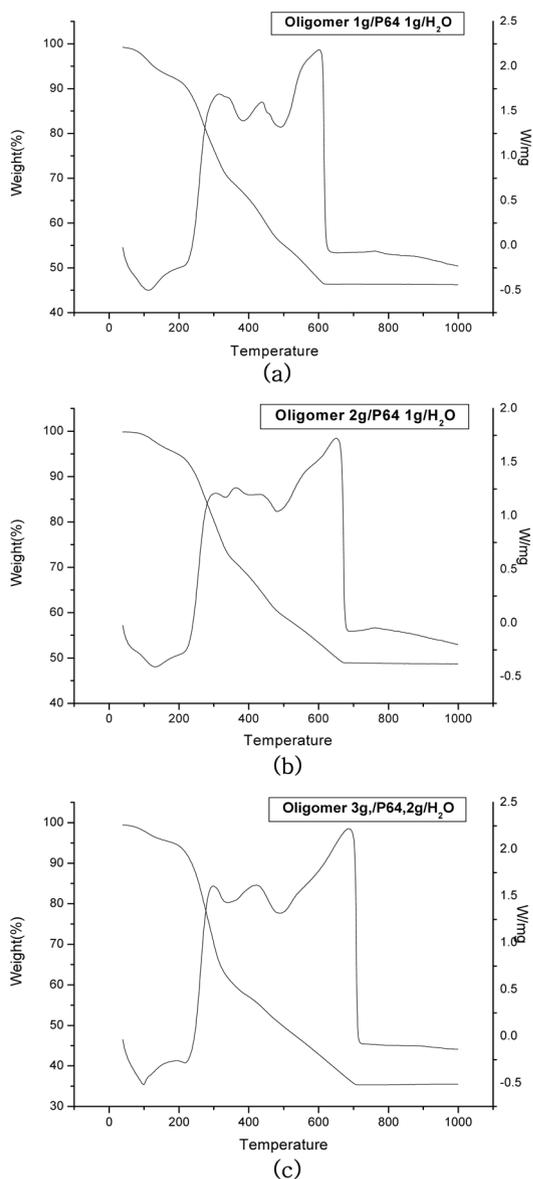


Fig. 2. TG/DSC curves of the mesoporous SiO₂ powder varying amount of oligomer and P64.

This is thought to be because the combustion of P64, which has a higher molecular weight than CTAC, and AAU occurred at the same temperature. It is well known that the pore characteristics of mesoporous silica are dependent on the hydrophobic/hydrophilic characteristics and the pH of the solvent and the type of surfactant, which is a structure direction agent.

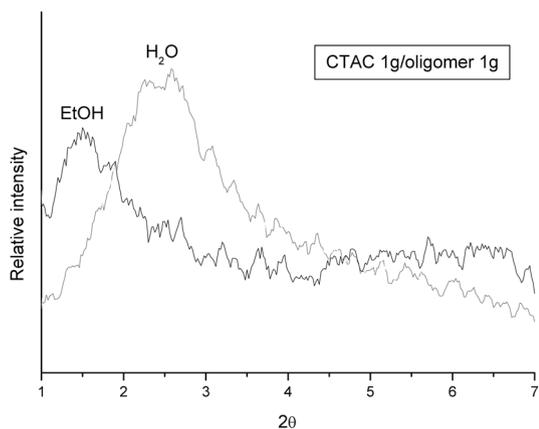


Fig. 3. XRD results of mesoporous silicas synthesized in water and ethanol solvent.

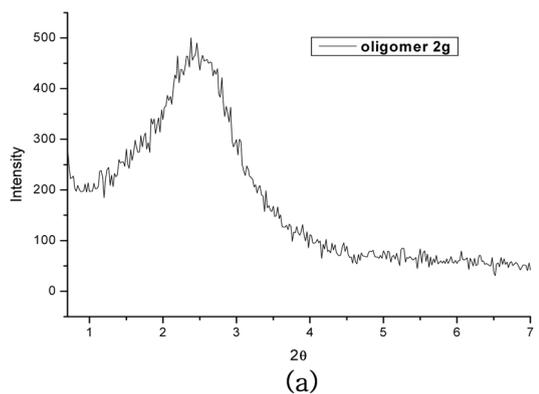


Fig. 4. XRD result of the mesoporous silica samples synthesized in the CTAC/H₂O/oligomer a) 2 g and b) 3 g system.

The results of the XRD measurement of the mesoporous silica that was synthesized in a water solvent and an ethanol solvent using AAU and CTAC are shown in

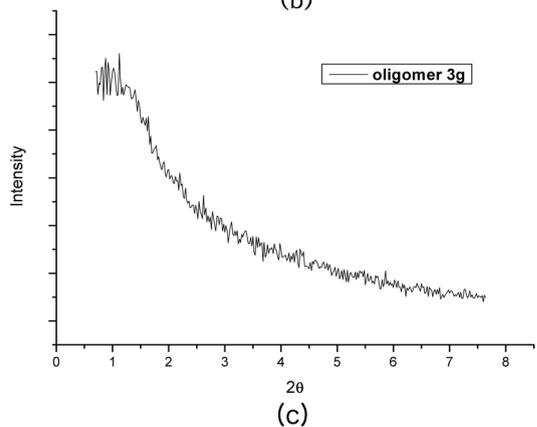
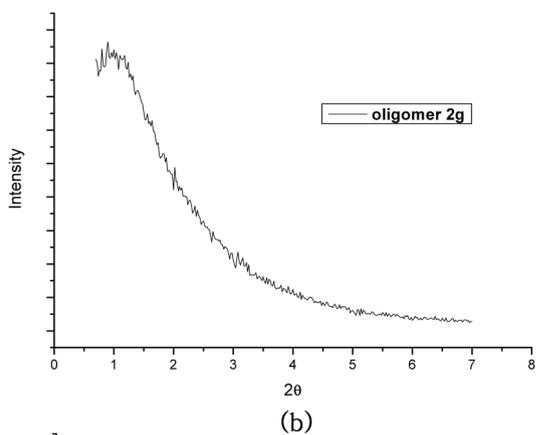
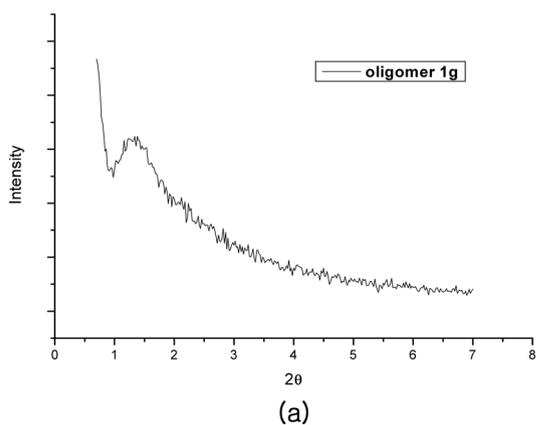


Fig. 5. XRD results of the mesoporous silica samples synthesized in the P64/ethanol/oligomer 3 g system.

Fig. 3. The pore size was bigger when the ethanol solvent was used, but the pore distribution was more uniform when the water solvent was used.

Fig. 4 shows the results of the XRD measurement

of the mesoporous silica that was synthesized under acidic conditions in the AAU/P64/H₂O system by varying the amount of AAU. There was no significant difference in the pore size when the amount of AAU was increased. *Fig. 5* shows the results of the XRD measurement of the mesoporous silica that was synthesized under alkali conditions in the AAU/P64/ethanol system by varying the amount of AAU. According to this result, however, the pore size was relatively larger when CTAC was used than when P64 was used, and was slightly larger depending on the amount of the oligomer.

The perfect combustion temperature of the AAU-added mesoporous silica was very high, about 600 °C, according to the result of the TG/DSC measurement. In this study, the BET was measured by perfectly

sintering the synthesized mesoporous silica, but the result of the BET measurement was not obtained due to the structural deformation of the mesoporous structure through the sintering of the sample under a high temperature for many hours. In this study, the result of the BET measurement was obtained only for the mesoporous silica synthesized in the CTAC/HCl/H₂O system without adding AAU, and for the mesoporous silica to which 1 g AAU was added. The result of the BET measurement and the pore size distribution are shown in *Fig. 6*. The average pore size of the mesoporous silica synthesized with the addition of only CTAC was about 2 nm, and that of the mesoporous silica synthesized with the addition of 1 g AAU was about 3 nm, which shows that the pore size of silica increases when AAU is added.

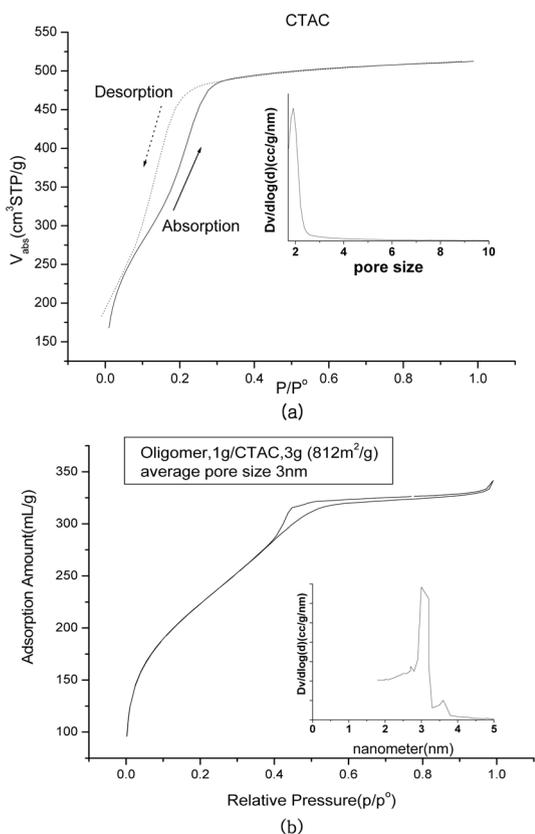


Fig. 6. Adsorption/desorption isotherms and pore size distribution of the mesoporous silica synthesized in the CTAC/H₂O system (a) and the CTAC/H₂O/AAU 1 g system (b).

3.2. Adsorption of MX based on the surfactant type

To compare the adsorption characteristics of MX depending on the surfactant type, an adsorption test was carried out with a 1 ppm MX concentration using mesoporous silica that was synthesized under alkali conditions in AAU (2 g)/CTAC (20 g)/ethanol, and the result is shown in *Fig. 7*. P64, which has a higher surfactant molecular weight, had the highest adsorption rate, followed by P61 and CTAC. This shows that MX is not an ionic hydrocarbon compound; and thus, the contribution of the dipole-dipole interaction is larger than of the ion-ion

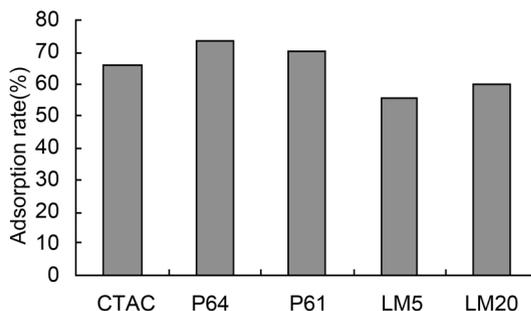


Fig. 7. Adsorption ratio of MX on the mesoporous silicas synthesized with variable surfactant (surfactant 2 g/AAU 2 g/ethanol system).

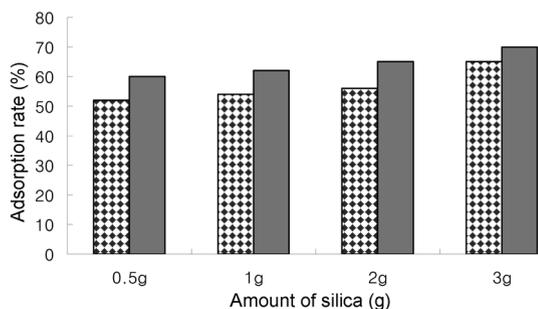


Fig. 8. Adsorption ratio of MX on the mesoporous silicas synthesized by AAU 2 g/CTAC 20 g/H₂O/HCl (left) and AAU 2 g/CTAC 20 g/ethanol/TEA (right) system.

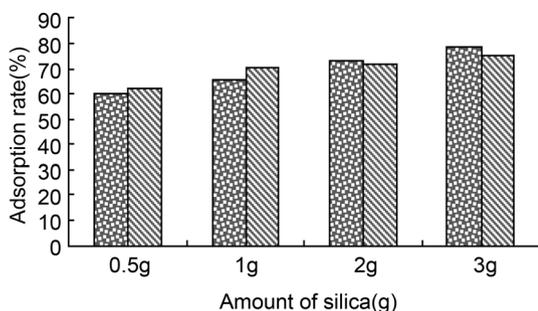


Fig. 9. Adsorption ratio of MX on the mesoporous silicas synthesized by AAU 2 g/p64 2 g/H₂O/HCl (left) and AAU 2 g/p64 2 g/ethanol/TEA (right) system.

interaction.

3.3. Adsorption of MX based on the solvent

Mesoporous silica has different hydrophobic/hydrophilic characteristics depending on the solvent. Therefore, in this study, mesoporous silica was synthesized in a water solvent and an ethanol solvent, respectively, and the adsorption rate of each per 1 g of mesoporous silica was compared. The comparison of MX's rate of adsorption of the mesoporous silicas synthesized in the AAU (2 g)/CTAC (20 g)/H₂O/HCl system and in the AAU (2 g)/CTAC (20 g)/ethanol/TEA system are shown in Fig. 8. In Fig. 9, the MX's rates of adsorption of the mesoporous silicas synthesized in the water solvent and the ethanol solvent using P64 were compared. The silica adsorbent synthesized using P64 showed almost the same adsorption rate in both the water solvent and the ethanol solvent, but the adsorption

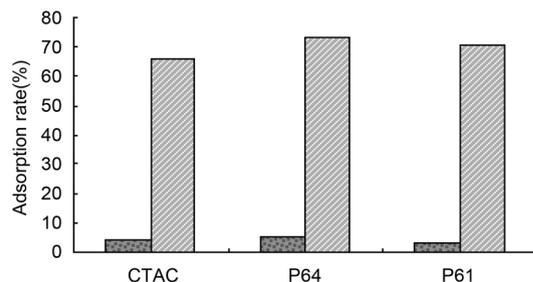


Fig. 10. Adsorption ratio of MX on the mesoporous silicas synthesized by surfactant 2 g/ethanol(left) and surfactant 2 g/AAU 2 g/ethanol(right) systems.

rate of the silica adsorbent synthesized using CTAC was higher in the ethanol solvent than in the water solvent. This shows that the silica adsorbent's surface is more hydrophobic when an ethanol solvent is used. Fig. 10 shows a comparison of the MX adsorption rate of the mesoporous silica that was synthesized without adding the AAU oligomer. When the AAU oligomer was not impregnated, almost no MX was adsorbed in the mesoporous silica.

3.4. Adsorption of MX with variation of MX concentration

The MX concentration was varied from 1 ppm to 100 ppm to determine the adsorption characteristics of mesoporous silica depending on the MX concentration, and the MX adsorption rate and the amount per 1 g of the silica adsorbent are shown in Fig. 11. There was no significant difference in the MX adsorption rate depending on the concentration when the MX concentration was 10 ppm or more. This result shows that perfect adsorption does not occur due to the MX equilibrium between the solution and the adsorbent, and that MX remains in the solution. When the adsorbate was a hydrophobic hydrocarbon, which is totally insoluble in water, almost no adsorption occurred; but when the adsorbent that had a partially polarized structure and that could be dispersed in water was used, a state of equilibrium was maintained and perfect adsorption did not occur.

The adsorption amount based on the temperature was measured to calculate the MX adsorption activation energy of the mesoporous silica adsorbent,

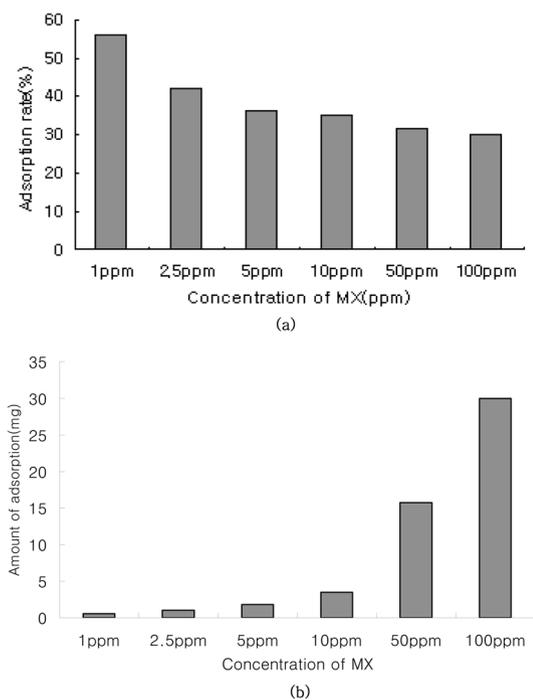


Fig. 11. Adsorption ratio (a) and amounts (b) with variation of the MX concentration on the mesoporous silicas 1g synthesized by AAU 1 g/CTAC 20 g/H₂O/HCl.

but the measurement result was not obtained because the MX was unstable in air when the temperature increased. It is thought that the adsorption mechanism of a hydrocarbon in a water solution can be identified if the proper hydrocarbon compound is selected considering its hydrophobic and hydrophilic characteristics, and if further study is carried out on mesoporous silica synthesized with the addition of an AAU oligomer.

4. Conclusions

Based on the result of the adsorption of MX on the mesoporous silica adsorbent that was synthesized with the addition of the amphiphilic acrylic urethane oligomer (AAU) together with the non-ionic surfactant poly(oxyethylene-oxypropylene) block copolymer, PEO-PPO (P64 and P61), and cationic cetyltrimethyl ammonium chloride (CTAC), the mesoporous silica that was synthesized with the addition of the AAU

oligomer showed excellent adsorption characteristics compared to that synthesized without the addition of the AAU oligomer. Also, the mesoporous silica that was synthesized in the water solvent showed better adsorption characteristics than that synthesized in the alcohol solvent. With respect to the co-surfactant, the best adsorption characteristics were obtained when P64, which is a non-ionic surfactant with a high molecular weight, was used to synthesize the silica compared to when other co-surfactants were used. The adsorption rate decreased as the MX concentration in the water increased. Different adsorption equilibrium conditions were reached depending on the adsorbate MX concentration in the adsorbent and the solution. The adsorption did not occur perfectly due to such equilibrium conditions, and only the amount of MX that corresponded to the equilibrium concentration dissolved in the solution.

Acknowledgement

This study was conducted by Sungshin univ. project fund.

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