

CHAPTER IV

RESULTS AND DISCUSSION

4.1. Synthesis of HPMSP doped mesoporous silica

4.1.1. Effect of catalyst concentration

The synthesis of HPMSP doped mesoporous silica was performed using the following reaction composition: 1 TEOS : 140 H₂O : 13 CH₃OH : 0.18 CTAB : 0.06 HPMSP, where H₂O was the aqueous solution of NaOH. The concentration of NaOH solution varied as 0.01, 0.05, 0.075, and 0.1 M in the experiments.

During the synthesis, it was found that a slower dissolving of HPMSP was observed when the NaOH concentration was decreased. HPMSP did not completely dissolve with the solution of 0.01 M NaOH, even 4 hours and passed by. In addition, the silica precipitation was observed in a few minutes after the addition of TEOS when 0.1 M NaOH was used in the synthesis. As the NaOH concentration was decreased, the precipitation of silica was slower. Furthermore, when the 0.075, 0.05, and 0.1 M NaOH were used, the HPMSP doped mesoporous silica obtained from the synthesis was about 3 g, whereas the HPMSP doped mesoporous silica obtained from the synthesis was about 2 g when 0.01 M NaOH was used.

A UV spectrum, carried out on the filtrate and washing solutions has shown that the mentioned solutions did not contain HPMSP. This result indicated that the HPMSP molecules were completely incorporated into doped mesoporous silica.

4.1.1.1. Characterization of materials

Organic matter contents

The organic matter contents in HPMSP doped mesoporous silica determined by calcination method are shown in Table 4.1. The results show that the HPMSP doped mesoporous silica prepared with 0.01 M NaOH solution has the lowest organic matter contents. The organic matter contents in HPMSP doped mesoporous silica determined by calculation from the starting materials and that determined by calcination are compared in Table 4.2.

Table 4.1 Organic matter contents in HPMSp doped mesoporous silica determined by calcination.

[NaOH] (M)	Weight of silica (g)		Organic matter contents	
	Before calcination (SiO ₂ + organic matters)	After calcinations (SiO ₂)	(g)	(%)
0.010	1.3717	0.8121	0.5596	40.80
0.050	1.5612	0.6863	0.8749	56.04
0.075	0.6766	0.2858	0.3908	57.76
0.100	1.5977	0.6476	0.5901	59.47

Table 4.2 Organic matter contents in HPMSp doped mesoporous silica determined by calcination and calculation.

[NaOH] (M)	Organic matter contents (%)	
	By calcination	By calculation ^a
0.010	40.80	56.37
0.050	56.04	56.45
0.075	57.76	56.48
0.100	59.47	56.27

^a Calculation method of organic matter content in doped mesoporous silica is given in Appendix B.

As shown in Table 4.2, when the 0.075 and 0.1 M NaOH are used, the organic matter contents in HPMSp doped mesoporous silica determined by calcination is slightly higher than those determined by calculation (1-3%). This finding may be explained by water adsorption on doped silica. The adsorbed water molecules were removed by heating at temperature above 150°C [14, 15]. These results indicated that the HPMSp molecules were completely incorporated into HPMSp doped mesoporous silica. For HPMSp doped mesoporous silica synthesized with 0.01 and 0.05 M NaOH, the organic matter contents determined by calcination was less than that determined by calculation. It was probably due to lower incorporated CTAB into these silicas.

Accessible HPMSP

Accessible HPMSP contents in HPMSP doped mesoporous silica determined by UV-visible spectrophotometry after extractions with a solvent mixture of heptane/ethanol (1:1) are shown in Table 4.3.

Table 4.3 Accessible HPMSP contents in doped mesoporous silica.

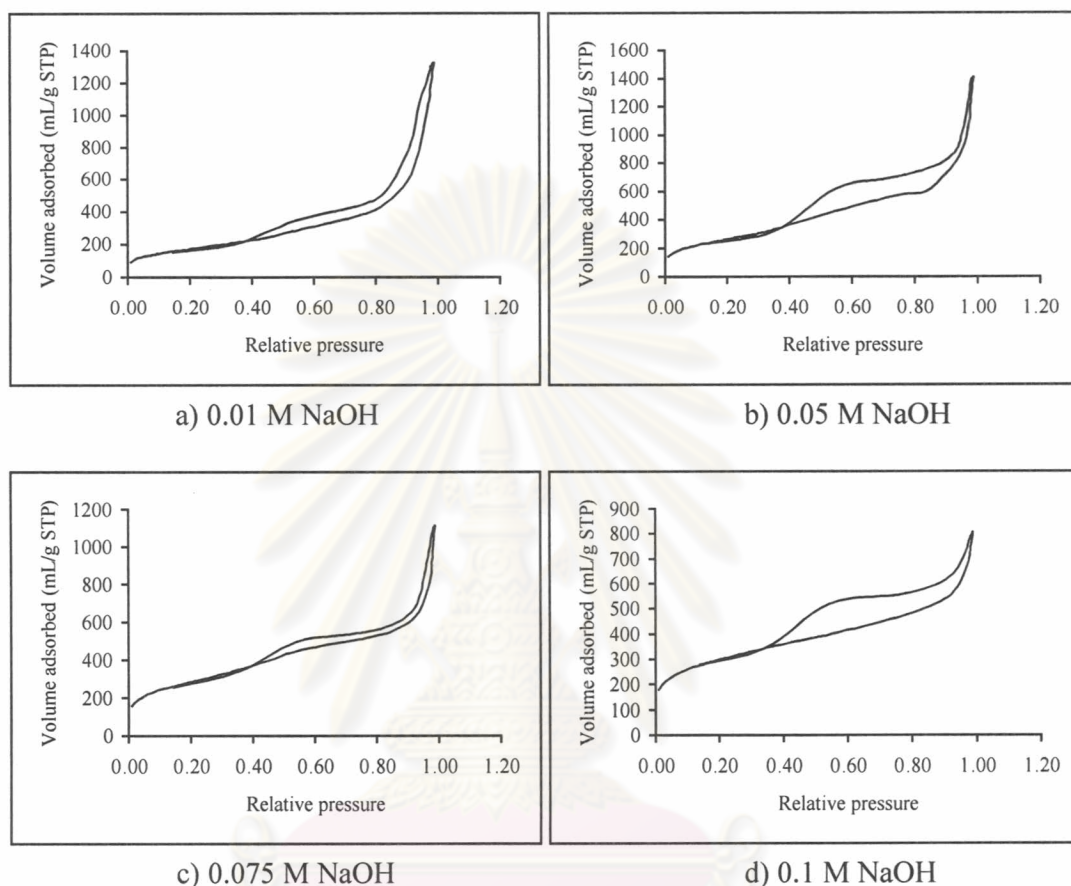
[NaOH] (M)	HPMSP contents		
	Incorporated HPMSP (μmole)	Accessible HPMSP	
		(μmole)	(%)
0.010	21.6	28.0	129.63
0.050	21.7	23.6	108.76
0.075	21.8	22.1	101.38
0.100	22.0	23.0	104.55

As shown in Table 4.3, the contents of HPMSP obtained in this way are slightly higher than those introduced into doped mesoporous silica. This finding shows that the ligand is quantitatively extracted with a solvent mixture of heptane/ethanol and so the accessibility of the HPMSP molecules to the liquid is excellent.

Mesoporosity, surface area, and pore size of materials

The mesostructure of material was confirmed by nitrogen adsorption-desorption isotherms (Figure 4.1). The adsorption isotherms obtained from the calcined materials synthesized with different concentrations of NaOH are all of type IV in IUPAC system. The isotherms show an important H4 hysteresis, indicating the characteristic of slit-shaped pore of material [28]. In addition, the nitrogen adsorption-desorption isotherms and application of the BET equation yielded the surface area. The average pore size of material was also calculated from nitrogen adsorption experiment. The specific surface area and average pore size of the prepared doped mesoporous silica are summarized in Table 4.4. All HPMSP doped mesoporous silicas have pore size between 38-116 Å. The values of pore size indicate that these sol-gel materials are mesoporous silica. In addition, the pore size of material increases with decreasing concentration of NaOH solution. This increase in pore size value

would result from slower silica precipitation when the concentration of NaOH was decreased. However, the relation between specific surface area of HPMSP doped mesoporous silica and concentration of NaOH solution was not significant difference.



a) 0.01 M NaOH

b) 0.05 M NaOH

c) 0.075 M NaOH

d) 0.1 M NaOH

Figure 4.1 Nitrogen adsorption-desorption isotherms of calcined HPMSP doped mesoporous silica.

Table 4.4 The specific surface area and pore size of calcined HPMSP doped mesoporous silica.

[NaOH] (M)	Specific surface area (m ² /g)	Pore size (Å)
0.010	603	115.65
0.050	898	78.65
0.075	989	55.11
0.100	867	38.53

Specific surface area: BET equation; average pore size: $4V_p/a$, by BET.

Particle size of materials

The particle size of materials was measured by Malvern laser diffraction technique. The particle sizes of as-synthesized HPMSp doped mesoporous silica prepared with different concentrations of NaOH solution are not significant difference as shown in Table 4.5.

Table 4.5 Particle size of as-synthesized HPMSp doped mesoporous silica.

[NaOH] (M)	Particle size (μm)
0.010	108.18
0.050	176.78
0.075	31.30
0.100	65.70

For HPMSp doped mesoporous silica prepared with 0.1 M NaOH, the particle sizes of as-synthesized and calcined silica are 65.70 and 30.38 μm , respectively. This decrease in particle size value can be explained by the removal of organic species after calcination process.

4.1.1.2. Copper extraction property

As Na^+ and NO_3^- are ubiquitous in natural water samples [38-39] and A. Boos and co-workers reported that addition of 0.1 M NaNO_3 into copper solution increase the copper extraction capacity of HPMSp doped mesoporous silica [6], so the 200 ppm $\text{Cu}(\text{NO}_3)_2$ in 0.01 M HNO_3 containing 0.1 M NaNO_3 was chosen for extraction experiment. The extraction of copper on non-doped mesoporous silica was measured to be used as a blank. It was shown that the non-doped mesoporous silica did not extract copper from these mediums. The copper extraction capacity of HPMSp doped mesoporous silica is shown in Figure 4.2. The results show that the amounts of copper extracted on HPMSp doped mesoporous silica prepared with different NaOH concentrations are comparable. However, the maximum copper extraction capacity was observed for the HPMSp doped mesoporous silica synthesized with 0.01 M NaOH. This result was probably due to the largest pore size of doped mesoporous silica, which increases the facility of surfactant to leach out from the material.

Therefore, higher mole ratio of HPMSP/surfactant in doped mesoporous silica was obtained when 0.01 M NaOH was used in the synthesis.

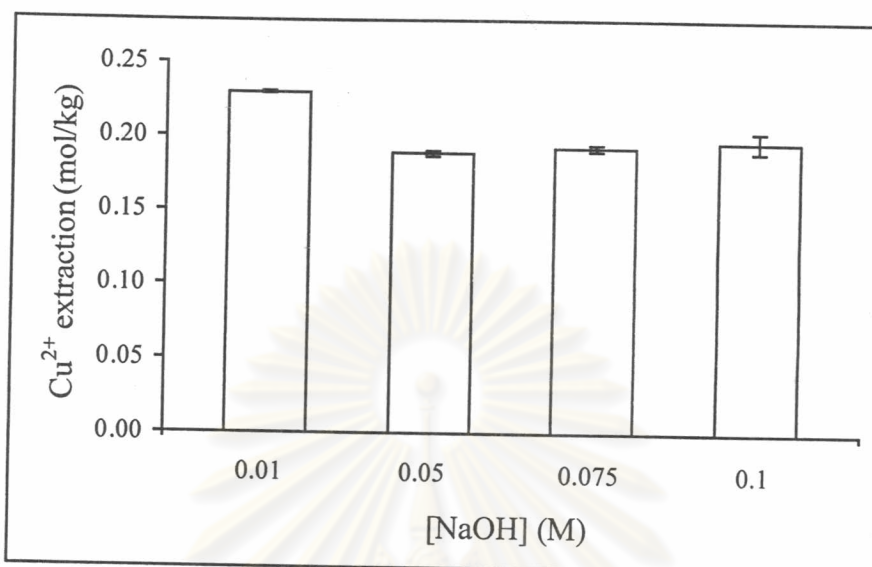


Figure 4.2 Amount of copper extracted on HPMSP doped mesoporous silica synthesized using various NaOH concentrations.

4.1.2. Effect of doping molecule

To delineate the effect of doping molecule quantity on the synthesis of HPMSP doped mesoporous silica, the mole ratio of HPMSP, x , was varied as 0, 0.04, 0.05, 0.06, 0.075 and 0.09 mole in the reaction composition: 1 TEOS : 140 H₂O : 13 CH₃OH : 0.18 CTAB : x HPMSP. When 0.1 M NaOH was used as catalyst in the synthesis, the HPMSP was easily dissolved and the silica precipitation was rapidly occurred.

During the synthesis, it was found that dissolving of higher HPMSP content in 0.1 M NaOH required longer time. The use of 0.075 HPMSP/TEOS required about 4 hours to dissolve completely. All obtained materials were easy to filter using Whatmann no. 42 filter paper. In addition, the filtrate and washing solution from the synthesis did not contain the HPMSP molecules. This result indicated that HPMSP molecules were completely incorporated into HPMSP doped mesoporous silica in all cases. This route of synthesis was capable of incorporating HPMSP into doped mesoporous silica at the maximum 0.09 mole.

4.1.2.1. Characterization of materials

Organic matter contents

The organic matter contents in HPMSF doped mesoporous silica determined by calcination method are shown in Table 4.6.

Table 4.6 Organic matter contents in HPMSF doped mesoporous silica determined by calcination.

HPMSF/TEOS	Weight of silica (g)		Organic matter content	
	Before calcination (SiO ₂ + organic matters)	After calcination (SiO ₂)	(g)	(%)
0	1.0047	0.5333	0.4714	46.92
0.04	1.3143	0.5742	0.7404	56.31
0.05	0.6717	0.2877	0.3840	57.17
0.06	1.5977	0.6476	0.9501	59.47
0.075	1.5858	0.6103	0.9755	61.51
0.09	1.5569	0.5899	0.9670	62.11

As shown in Table 4.6, the contents of organic matter in the materials increase with increasing amount of HPMSF used in synthesis. The organic matter contents in HPMSF doped mesoporous silica determined by calculation from the starting materials and that determined by calcination are compared in Table 4.7.

Table 4.7 Organic matter contents in HPMSF doped mesoporous silica determined by calcination and calculation.

HPMSF/TEOS	Organic matter contents (%)	
	By calcination	By calculation
0	46.92	45.80
0.04	56.31	53.49
0.05	57.17	55.04
0.06	59.47	56.27
0.075	61.51	58.46
0.09	62.11	59.89

As shown in Table 4.7, the loss of mass on materials from different syntheses using various amounts of HPMSP shows that the organic matter contents in HPMSP doped mesoporous silica is scarcely higher than those which are incorporated during syntheses. These results of higher organic matter contents may be explained by water adsorption on doped silica. The result of the experiment can be concluded that the organic molecules were completely incorporated into HPMSP doped mesoporous silica in all cases.

Thermogravimetric analysis (TGA) was used to confirm the water and organic matter contents in mesoporous silica. Figure 4.3 shows TGA profile and the corresponding differential thermogravimetry (DTG) profile for the non-doped mesoporous silica (HPMSP/TEOS = 0). The sample lost 3.6% of its original mass at about 95.9 °C; this loss is associated with the desorption of water. A sharp weight loss took place at 241.3 °C and 289.9 °C, indicating the decomposition of organic molecules. When the temperature was increased to 289.9 °C, the rate of weight loss decreased. At about 584.9 °C, the organic molecules in non-doped mesoporous silica were completely decomposed. The total weight loss was about 45.9% at this temperature. If the adsorbed water is excluded from the total weight, the organic loading is calculated to be about 42.3% by weight. This value is consistent with the incorporated organic matter contents in non-doped mesoporous silica. This result indicated that there was no organic matter loss during the synthesis of non-doped mesoporous silica.

Figure 4.4 shows TGA profile and the corresponding differential thermogravimetry (DTG) profile for the HPMSP doped mesoporous silica prepared with 0.1 M NaOH and 0.06 mole HPMSP/mole TEOS. The thermogram is similar to that of non-doped mesoporous silica. According to Figure 4.4, the sample lost 2.3% of its original mass at 75 °C due to the desorption of water. The total weight loss was about 59.9% at 588.3 °C. If the adsorbed water is excluded from the total weight, the organic loading was calculated to be about 57.6%. This value is not different from that incorporated in HPMSP doped mesoporous silica (Table 4.7).

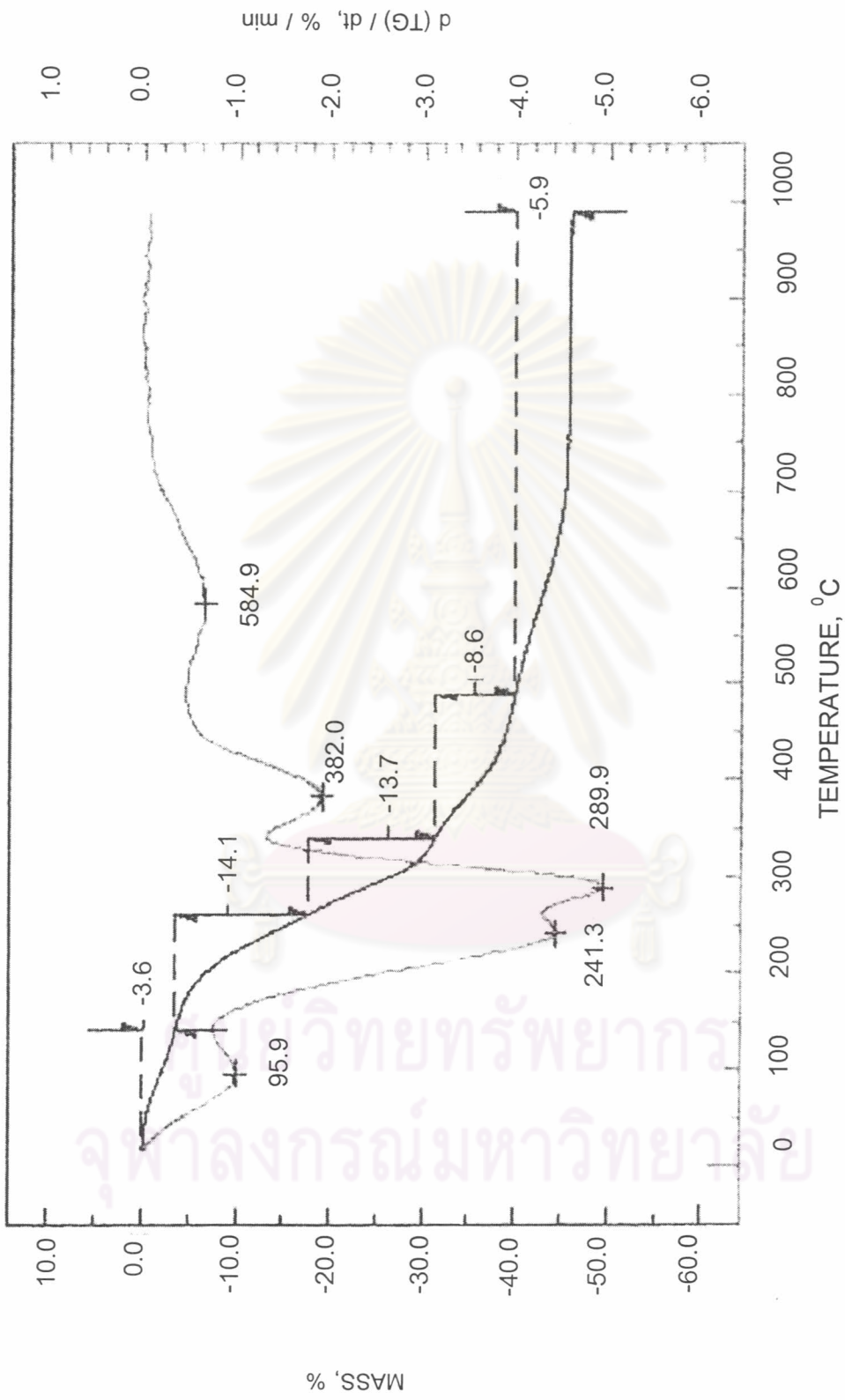


Figure 4.3 TGA profile and the corresponding differential thermogravimetry (DTG) profile for non-doped mesoporous silica prepared with 0.1 M NaOH.

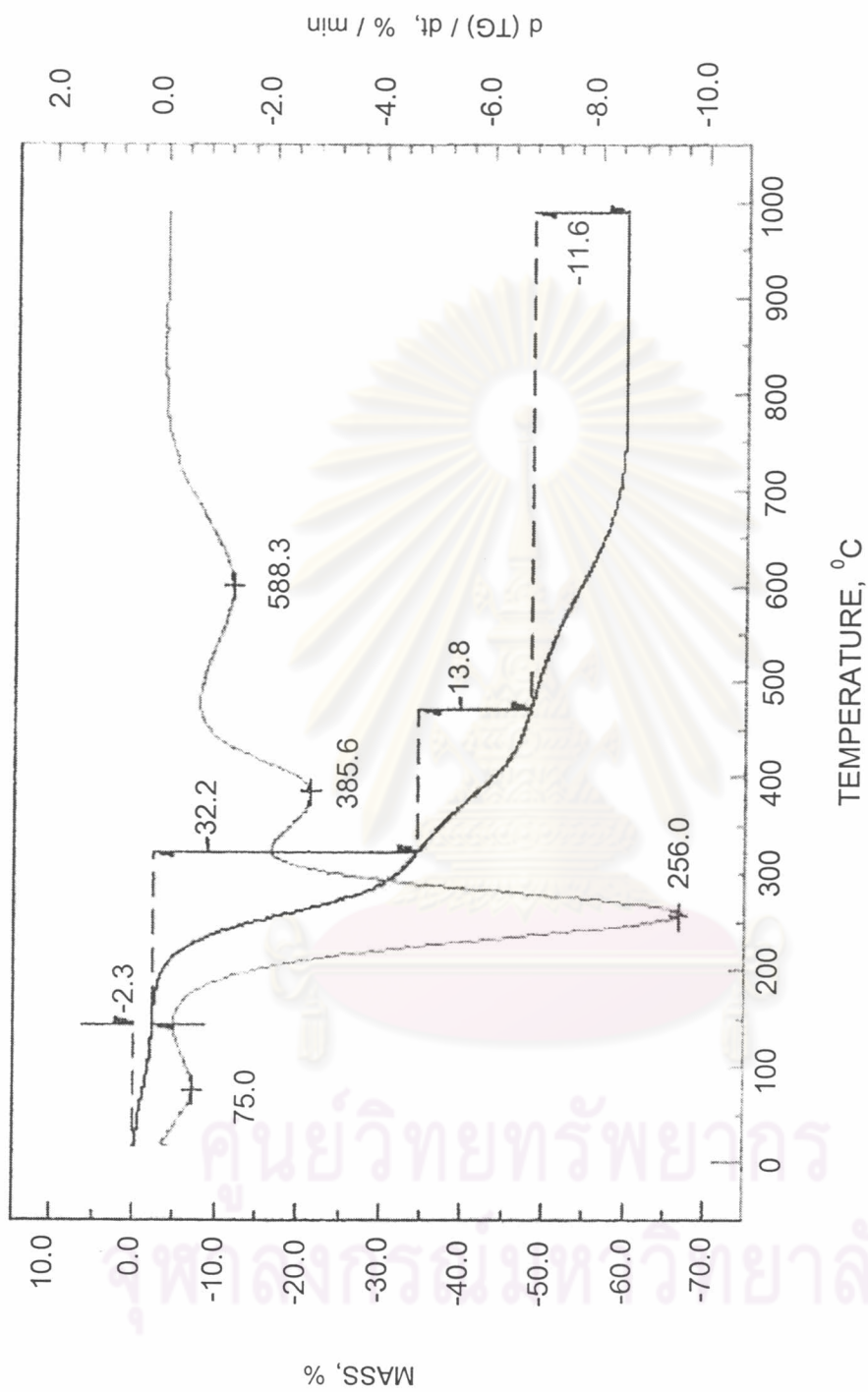


Figure 4.4 TGA profile and the corresponding differential thermogravimetry (DTG) profile for HPMSP doped mesoporous silica prepared with 0.1 M NaOH and 0.06 mole HPMSP/TEOS.

Accessible HPMSP

Accessible HPMSP contents in HPMSP doped mesoporous silica were determined by UV-visible spectrophotometry after extraction with a solvent mixture of heptane/ethanol (1:1) (Table 4.8).

Table 4.8 Accessible HPMSP contents in doped mesoporous silica.

HPMSP/TEOS	HPMSP contents		
	Incorporated HPMSP (μmole)	Accessible HPMSP	
		(μmole)	(%)
0.04	15.4	16.8	109.09
0.05	19.1	21.7	113.61
0.06	22.0	23.0	104.55
0.075	26.0	29.3	112.69
0.09	30.0	33.9	113.00

As shown in Table 4.8, the contents of HPMSP obtained are slightly higher than that actually introduced into HPMSP doped mesoporous silica. The results indicate that the complete accessibility of the HPMSP molecule to the liquid is excellent in all cases.

Mesoporosity, surface area, and pore-size of materials

The nitrogen adsorption-desorption isotherms of different HPMSP doped mesoporous silica are shown in Figure 4.5. The adsorption isotherms of every synthetic material using various amounts of HPMSP are type IV in IUPAC system, indicating the mesostructure of doped silica. In addition, the isotherms present an important H4 hysteresis, showing the characteristic of slit-shaped pore of material [28]. The pore size of calcined HPMSP doped mesoporous silica seems to increase with increasing amount of HPMSP (Table 4.9). However, the relation between the specific surface area and pore size of HPMSP doped mesoporous silica is not significantly different. Similarly, the particle size of HPMSP doped mesoporous silica is not related to the amount of HPMSP used in the synthesis.

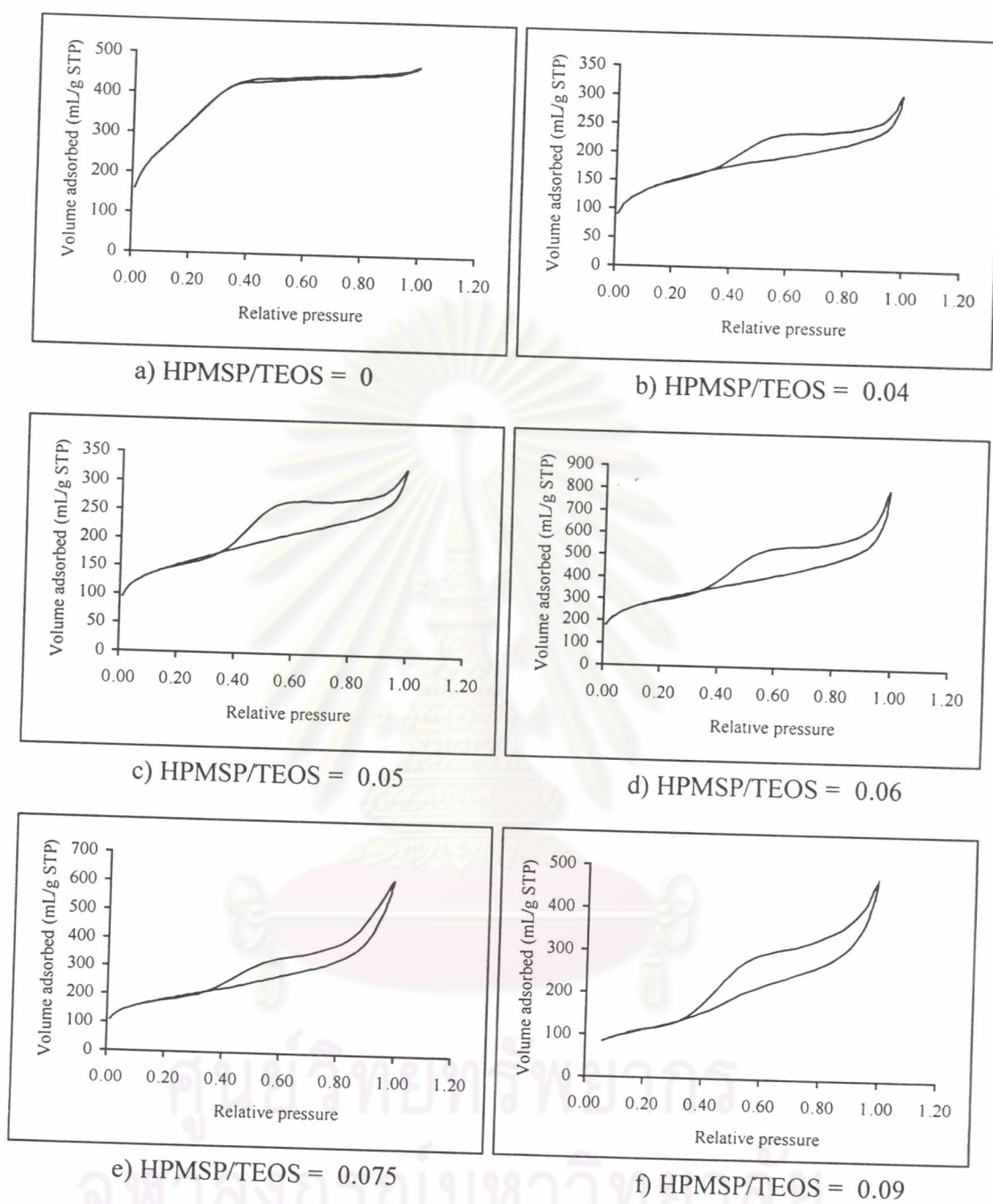


Figure 4.5 Nitrogen adsorption-desorption isotherms of calcined HPMSiP doped mesoporous silica prepared using different HPMSiP/TEOS mole ratios.

Table 4.9 The specific surface area, pore size and particle size of calcined HPMSM doped mesoporous silica.

HPMSM/TEOS	Specific surface area (m ² /g)	Pore size (Å)	Particle size (μm)
0	1059	27.35	77.86
0.04	535	33.11	30.60
0.05	544	35.15	66.08
0.06	867	38.53	65.70
0.075	650	55.19	27.40
0.09	416	64.09	65.62

Specific surface area: BET equation; average pore size: $4V_p/a$, by BET.

XRD patterns

Normally, the intensity, broadness, and position of peak in the X-ray diffraction patterns indicate the crystallinity of the solid. As shown in Figure 4.6, the XRD patterns of as-synthesized doped mesoporous silica present the diffraction peak, which exhibit the crystalline solid structure. The XRD characteristics of as-synthesized HPMSM doped mesoporous silica are reported in Table 4.10. The results show that the interplanar distance of HPMSM doped mesoporous silica tends to increase with increasing amount of HPMSM used in the preparation.

Table 4.10 The XRD characteristics of as-synthesized HPSMP doped mesoporous silica.

HPMSM/TEOS	2θ (degree)	interplanar distance (Å)
0	2.18	40.00
0.04	2.36	37.40
0.05	2.20	40.12
0.06	2.06	42.85
0.075	2.02	43.70
0.09	2.00	44.14

Table 4.9 The specific surface area, pore size and particle size of calcined HPMSP doped mesoporous silica.

HPMSP/TEOS	Specific surface area (m ² /g)	Pore size (Å)	Particle size (μm)
0	1059	27.35	77.86
0.04	535	33.11	30.60
0.05	544	35.15	66.08
0.06	867	38.53	65.70
0.075	650	55.19	27.40
0.09	416	64.09	65.62

Specific surface area: BET equation; average pore size: $4V_p/a$, by BET.

XRD patterns

Normally, the intensity, broadness, and position of peak in the X-ray diffraction patterns indicate the crystallinity of the solid. As shown in Figure 4.6, the XRD patterns of as-synthesized doped mesoporous silica present the diffraction peak, which exhibit the crystalline solid structure. The XRD characteristics of as-synthesized HPMSP doped mesoporous silica are reported in Table 4.10. The results show that the interplanar distance of HPMSP doped mesoporous silica tends to increase with increasing amount of HPMSP used in the preparation.

Table 4.10 The XRD characteristics of as-synthesized HPSMP doped mesoporous silica.

HPMSP/TEOS	2θ (degree)	interplanar distance (Å)
0	2.18	40.00
0.04	2.36	37.40
0.05	2.20	40.12
0.06	2.06	42.85
0.075	2.02	43.70
0.09	2.00	44.14

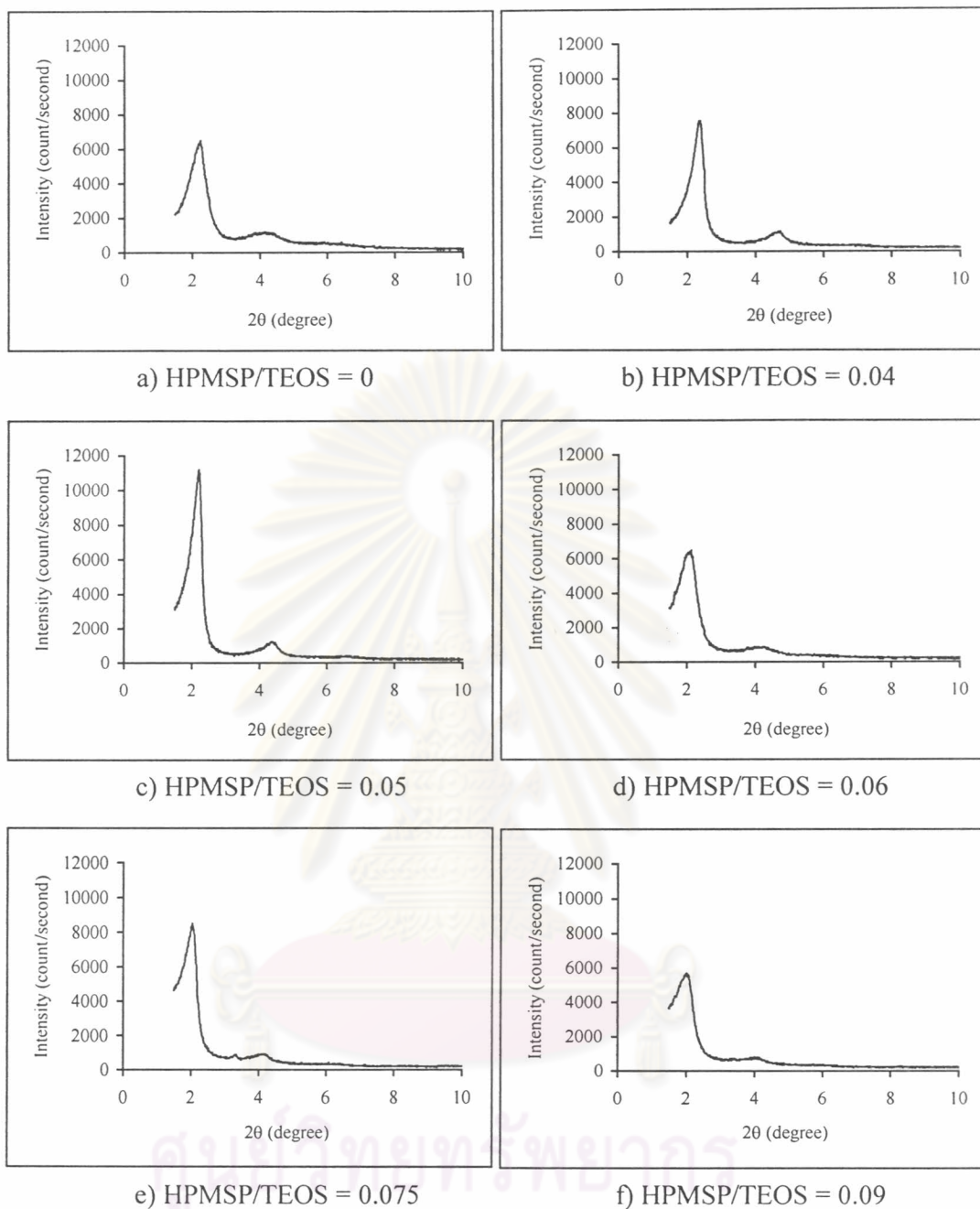


Figure 4.6 X-ray diffraction patterns of as-synthesized HPMSP doped mesoporous silica.

Figure 4.7 shows X-ray diffraction patterns of non-doped mesoporous silica before and after calcination at 540 °C for 10 hours, the XRD pattern of non-doped mesoporous silica before calcination exhibits a high intensity peak at

$2\theta = 2.18^\circ$ corresponding to an interplanar distance of approximately 40 Å. After removal of the organic by calcination, the peak broadened and shifted to 2.56° , relating to an interplanar distance of approximately 34.48 Å. The results show that the crystallinity of non-doped mesoporous silica was preserved after calcination process. In contrary, the diffraction peaks in XRD pattern of calcined HPMSP doped mesoporous silica were disappeared. This observation suggested that the amorphous solid structure of these doped mesoporous silicas were obtained after calcination process.

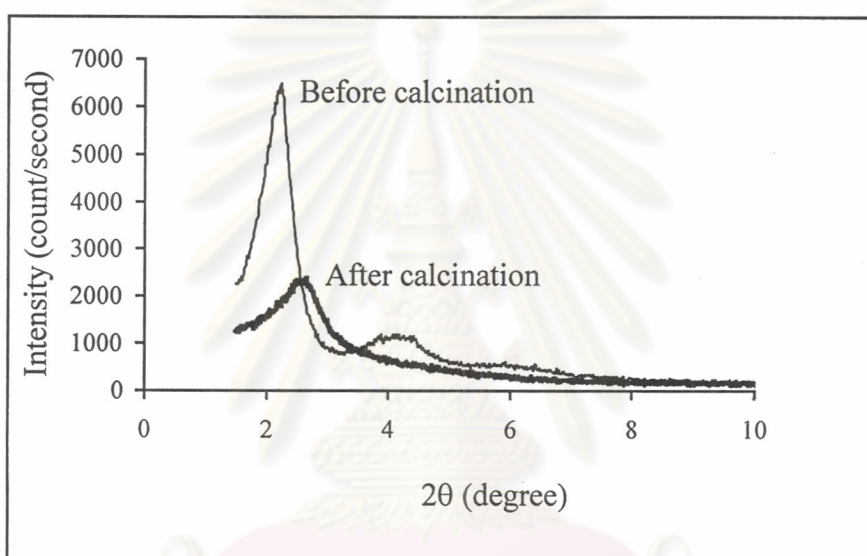


Figure 4.7 X-ray diffraction patterns of non-doped mesoporous silica before and after calcination at 540 °C (10 hours).

4.1.2.2. Copper extraction property

The 200 ppm $\text{Cu}(\text{NO}_3)_2$ in 0.01 M HNO_3 containing 0.1 M NaNO_3 medium was used in the copper extraction experiment. The extraction results are shown in Figure 4.8. The amount of copper extracted on the HPMSP doped mesoporous silica increases with increasing amount of HPMSP in doped mesoporous silica. However, the amount of copper extraction per mole of HPMSP in doped mesoporous silica is almost constant, 0.5 mol Cu^{2+} /mol HPMSP, indicating the 1:2 stoichiometry of the complex formed between copper and HPMSP.

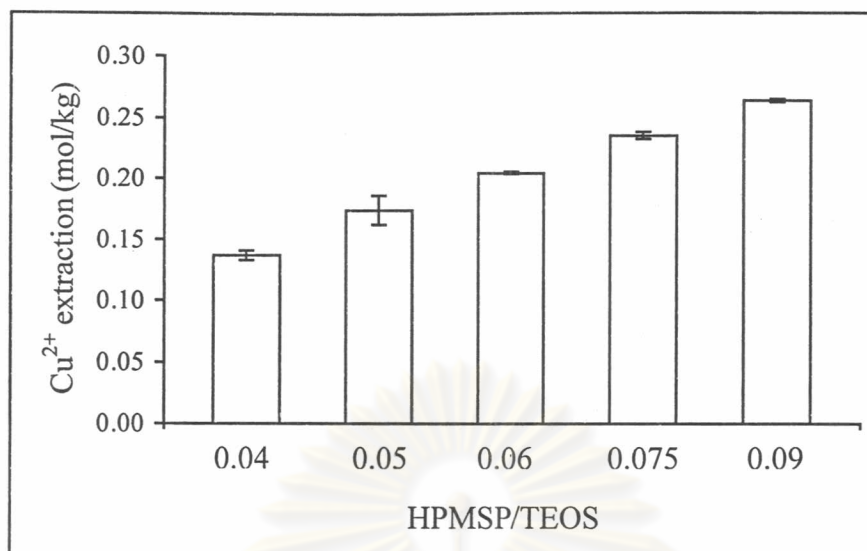


Figure 4.8 Amount of copper extracted on HPMSp doped mesoporous silica synthesized using different HPMSp/TEOS mole ratios

4.2. Extraction behaviors of HPMSp doped mesoporous silica

The HPMSp doped mesoporous silica synthesized with 0.1 M NaOH and 0.06 mole HPMSp was used in the experiment. Copper, cobalt and nickel were used in the study of the parameters influencing the extraction process. These parameters include effect of medium, concentration and pH of metal solution, and extraction time. Especially for the copper extraction, effect of amount of HPMSp doped mesoporous silica, and foreign metal ions present in solution were also studied. Finally, HNO₃ and HCl were tested as desorption agents. Each extraction and desorption experiments were done in duplicate.

4.2.1. Effect of medium

The metal extraction capacity of HPMSp doped mesoporous silica in various mediums was studied. The 200 ppm metal solution used in the experiment was prepared in aqueous, 0.01 M HNO₃, 0.1 M NaNO₃, and 0.01 M HNO₃ containing 0.1 M NaNO₃, respectively. Especially for the copper extraction, effect of concentration of NaNO₃ in 0.01 M HNO₃ was also investigated. The non-doped mesoporous silica was used as a blank in extraction experiment.

4.2.1.1. Copper extraction

At first, the copper extraction of HPMSP doped mesoporous silica from 200 ppm $\text{Cu}(\text{NO}_3)_2$ solution in 0.01 M HNO_3 and 200 ppm $\text{Cu}(\text{NO}_3)_2$ solution in 0.01 M HNO_3 containing 0.1 M NaNO_3 were investigated according to the experiment of A. Boos and co-worker [6]. When the 200 ppm copper solution prepared in 0.01 M HNO_3 was added into the HPMSP doped mesoporous silica, the color of silica was immediately changed to green. After the mixture was stirred for 24 hours, the solution was separated from the solid. The solution obtained after extraction was turbid and the pH of solution was about 2.4. In this condition, the copper extraction capacity of HPMSP doped mesoporous silica reached 0.17 mol/kg. Addition of 0.1 M NaNO_3 increased the copper extraction capacity to 0.21 mol/kg. This observation was in accord with the previous work of Boos and co-workers [6].

The effect of concentration of NaNO_3 on copper extraction was also studied. When the concentration of NaNO_3 in the solution was increased, the solution obtained after the extraction was less turbid, and became clear if using more than 0.1 M NaNO_3 . Influence of the NaNO_3 concentration on the copper extraction capacity is shown in Figure 4.9.

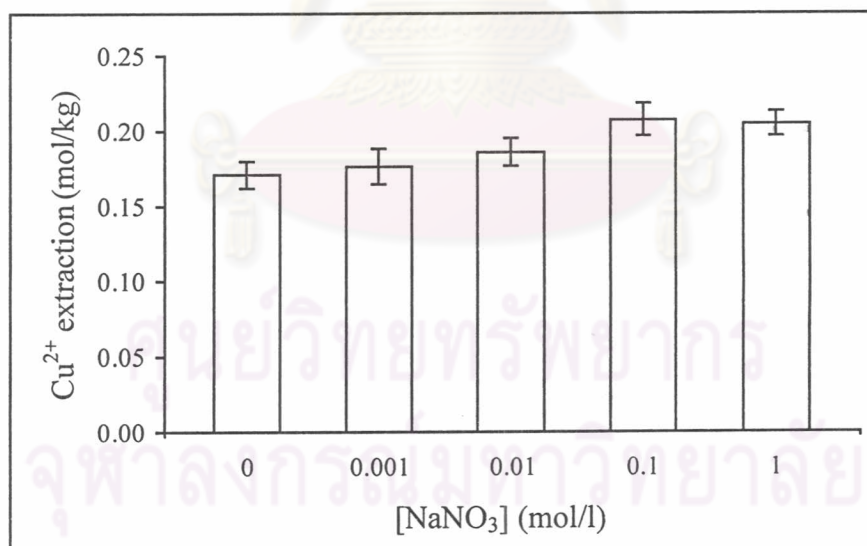


Figure 4.9 Influence of the NaNO_3 concentration on copper extraction.

According to Figure 4.9, the capacity of copper extraction tends to increase with the increase of NaNO_3 concentration. A. Boos and co-workers [6] suggested that Na^+ could be substituted quaternary ammonium, which adsorbed at the surface of silica, and decreased repulsion of solid particles. So the increasing of copper

extraction at the surface of HPMSP doped mesoporous silica was observed when the concentration of NaNO_3 in copper solution was increased. The repeatability of the copper extraction is quite good since the standard deviation measured for the amount of extracted copper in seven experiments is 1.26% (Table 4.11). The results indicated that the homogeneity of the synthesized HPMSP doped mesoporous silica is obtained in each synthesis.

Table 4.11 The amount of copper extracted by HPMSP doped mesoporous silica resulting from the same synthesis.

Number of extraction	Amount of Cu^{2+} extracted (mol/kg)
1	0.2152
2	0.2181
3	0.2212
4	0.2210
5	0.2221
6	0.2223
7	0.2229
Average	0.2204
SD	0.0028
%RSD	1.27

Copper extraction of sixteen doped mesoporous silica resulting from different synthesis was also studied. The reproducibility of the copper extraction, and as a consequence the reproducibility of the synthesis, is quite good since the standard deviation measured for the amount of extracted copper in the sixteen materials is 4.11% (Table 4.12). The result showed that the reproducibility of HPMSP doped mesoporous silica was excellent. Copper extraction capacity of non-doped mesoporous silica was also studied in 0.01 M HNO_3 medium and 0.01 M HNO_3 containing 0.1 M NaNO_3 medium. It was found that this type of silica did not extract any copper from such mediums.

Table 4.12 The amount of copper extracted by HPMSp doped mesoporous silica resulting from different synthesis.

Number of synthesis	Cu ²⁺ extracted (mol/kg)	Number of synthesis	Cu ²⁺ extracted (mol/kg)
1	0.2128	9	0.2022
2	0.2000	10	0.2018
3	0.2133	11	0.1951
4	0.2152	12	0.1965
5	0.2110	13	0.2057
6	0.2079	14	0.1955
7	0.2212	15	0.1968
8	0.2154	16	0.1977
		Average	0.2055
		SD	0.0084
		%RSD	4.09

4.2.1.2. Cobalt extraction

The 200 ppm Co(NO₃)₂ solution in 0.01 M HNO₃ was used in the cobalt extraction experiment of non-doped mesoporous silica and HPMSp doped mesoporous silica. The results showed that both materials did not extract cobalt, even 0.1 M NaNO₃ was added. When the aqueous solution of cobalt was added into non-doped mesoporous silica, it was found that the pink color of cobalt solution was faded, while the color of silica was not changed. The equilibrium pH of solution was about 6.8, while Co(OH)₂ precipitation occurred above pH 7.5. So the cobalt did not precipitate at this condition. The results showed that the cobalt extraction capacity of non-doped mesoporous silica reached 0.09 mol/kg (Figure 4.10). When the same cobalt solution was added into HPMSp doped mesoporous silicas, the color of the sorbents changed into darker orange-brown and the cobalt extraction capacity of these materials was about 0.13 mol/kg. Addition of 0.1 M NaNO₃ made the capacity of non-doped mesoporous silica increase to 0.19 mol/kg, whereas that of HPMSp doped

mesoporous silica increase to 0.30 mol/kg (Figure 4.10). So the next experiments concerning cobalt extraction will be carried out in 0.1 M NaNO_3 medium.

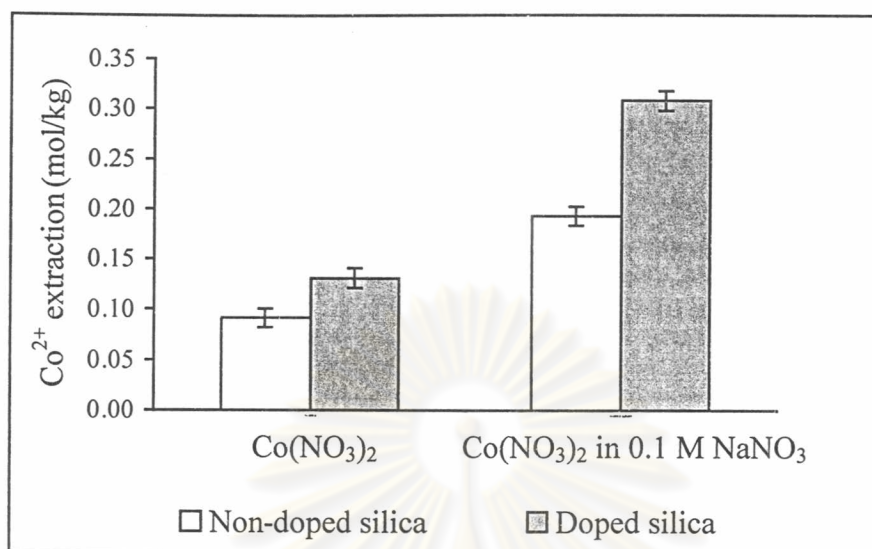


Figure 4.10 Influence of medium on cobalt extraction.

4.2.1.3. Nickel extraction

The results of nickel extraction are similar to those of cobalt extraction. The non-doped mesoporous silica and HPMSF doped mesoporous silica have no capacity to extract nickel in both 0.01 M HNO_3 medium and 0.01 M HNO_3 containing 0.1 M NaNO_3 medium. In contrary, the extraction capacity of HPMSF doped mesoporous silica for nickel was about 0.17 mol/kg when the 200 ppm $\text{Ni}(\text{NO}_3)_2$ in aqueous solution was used in the extraction experiment. By using the same condition, the nickel extraction capacity of non-doped mesoporous silica was about 0.11 mol/kg. This decrease in extraction is probably due to the ionization of silanol in silica surface. In addition, when the concentration of NaNO_3 in 200 ppm $\text{Ni}(\text{NO}_3)_2$ solution increased to 0.1 M, both non-doped and HPMSF doped mesoporous silica exhibited maximum extraction capacities at 0.28 and 0.32 mol/kg, respectively (Figure 4.11).

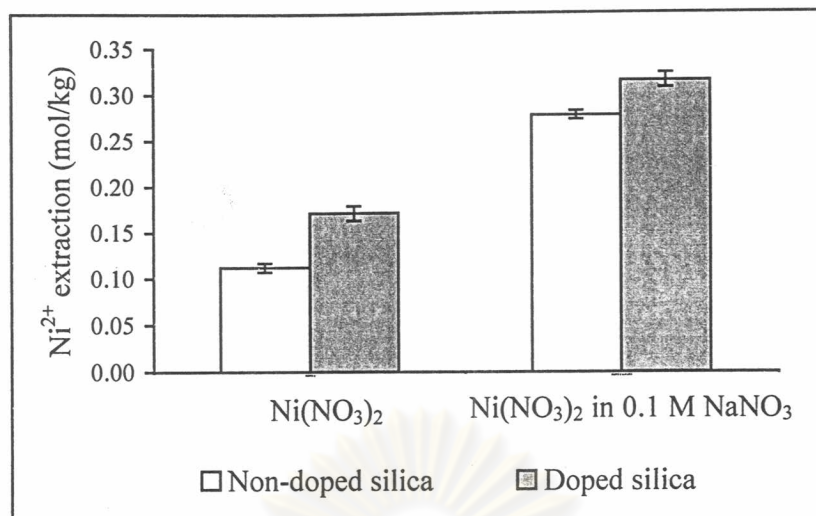


Figure 4.11 Influence of medium on nickel extraction.

4.2.2. Effect of concentration of metals solution

To verify the effect of copper concentration on the copper extraction capacity of HPMSP doped mesoporous silica, the copper concentration varied from 200 to 400 ppm and 0.01 M HNO₃ containing 0.1 M NaNO₃ medium were used in the extraction experiments. For determination the cobalt and nickel extraction capacities of HPMSP doped mesoporous silica, the metal concentration varied from 200 to 600 ppm and 0.1 M NaNO₃ medium were used. The results showed that the amount of metal extracted by HPMSP doped mesoporous silica was constant for each metal, even though there was an increase of metal concentration (Figure 4.12).

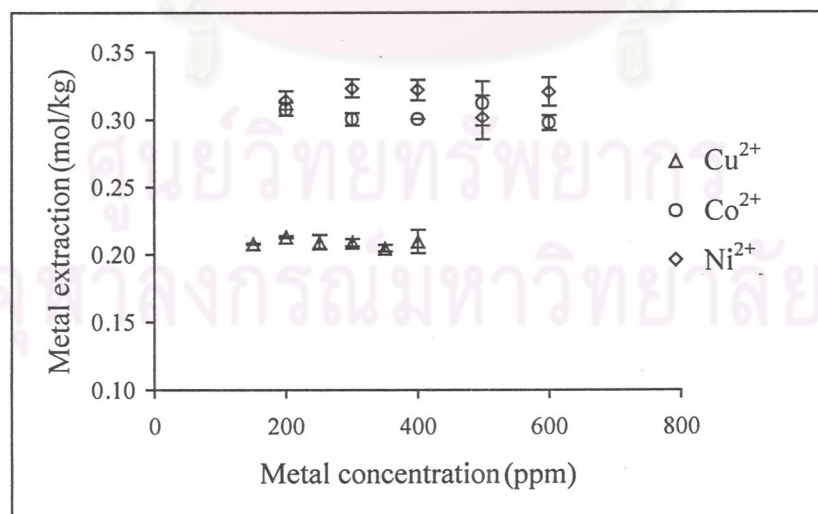


Figure 4.12 Influence of metals concentration on extraction property.

4.2.3. Effect of pH

The extraction of copper, cobalt and nickel by HPMSD doped mesoporous silica at various initial pH values were investigated by batch extraction. The 200 ppm metal solution in 0.1 M NaNO₃ at various initial pH values was used in this study. The pH values of the metal solution were adjusted using 1 M HNO₃ solution. After extraction experiments, the pH values of metal solution were higher than the initial pH values. The plots of amount of metal extracted by HPMSD doped mesoporous silica versus the pH values of metal solution after extraction experiments are shown in Figure 4.13.

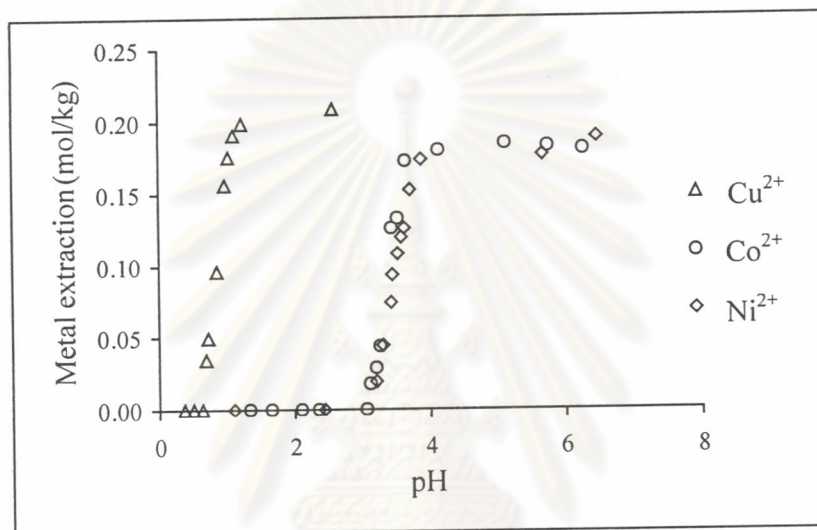


Figure 4.13 Influence of pH on metals extraction.

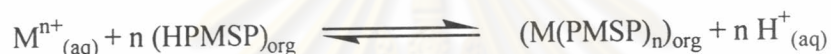
The results shown in Figure 4.13 indicated that the HPMSD doped mesoporous silica was not able to extract copper at pH < 0.6. Then the copper extraction increased rapidly with increasing pH. The maximum copper extraction capacity was observed in the pH range of 1.7-2.5. The copper extraction capacity of non-doped mesoporous silica at pH 2.5 was also measured. The results showed that these non-doped mesoporous silica was not able to extract copper at this pH value.

Extraction of cobalt and nickel as a function of pH had similar trend as copper extraction. The extraction of cobalt and nickel increased with increasing pH, from its minimum at pH 3 to its maximum at pH 4. The extraction of cobalt and nickel was constant in the pH range of 4-6.5. The cobalt and nickel extraction capacity of non-doped mesoporous silica in the pH range of 4-6.5 was also measured. The results

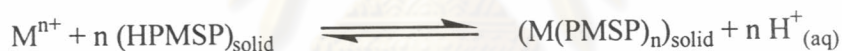
showed that these non-doped mesoporous silica was not able to extract both metals in this pH region.

Determination of equilibrium constant for copper extraction of HPMSp doped mesoporous silica

As a result shown in Figure 4.13, the HPMSp doped mesoporous silica is able to extract copper in the pH range of 0.6-2.5. In addition, non-doped mesoporous silica is not able to extract copper in this pH range. So the extraction of copper on doped mesoporous silica in this pH range is due to HPMSp molecules incorporated in the doped silica. It is generally assumed that the mechanism of copper extraction on HPMSp doped mesoporous silica is similar to those of liquid-liquid extraction. For liquid-liquid extraction, the extraction of metal with HPMSp is described by following equilibrium [40]:



Therefore, the reaction between metal ions and HPMSp in the solid can be written as shown below:



$$K = \frac{[(M(HPMSp)_n)_{solid}] [H^+]^n}{[M^{n+}][HPMSp_{solid}]^n}$$

Where K is an equilibrium constant

$$\text{From } D = \frac{[(M(HPMSp)_n)_{solid}]}{[M^{n+}]}$$

$$\text{It will be } K = \frac{D[H^+]^n}{[HPMSp_{solid}]^n}$$

$$D = \frac{K[HPMSp_{solid}]^n}{[H^+]^n}$$

And when take log, it will be

$$\log D = \log K + n \text{pH} + n \log [(\text{HPMSP})_{\text{solid}}]$$

The linear relation between $\log D$ and pH provides the amount of H^+ of ligand that exchanges with copper ion in the complex formation (n value). From n values, the equilibrium constant (K value) for copper extraction was calculated.

Figure 4.14 shows the relation between $\log D$ and pH of copper extraction by HPMSP doped mesoporous silica, HPMSP doped microporous silica [6], and liquid-liquid extraction of copper by HPMSP solution in toluene [6]. The HPMSP doped mesoporous silica and HPMSP doped microporous silica could extract copper in lower pH region than that of the case of liquid-liquid extraction. This low pH value is less than the pK_a value of HPMSP (pK_a 4.1). This is the advantage of the use of solid-phase extraction. The K value obtained from copper extraction experiments of HPMSP doped mesoporous silica was 4.20 ± 0.60 kg/L. Similar to the complex formed between copper and HPMSP in liquid-liquid extraction, the complex formed between copper and HPMSP in the HPMSP doped mesoporous silica and the HPMSP doped microporous silica has also 2:1 stoichiometry. Nevertheless, the extraction capacity of HPMSP doped mesoporous silica is higher than that of HPMSP doped microporous silica (the copper extraction capacity of HPMSP doped microporous silica was about 0.04 mol/kg).

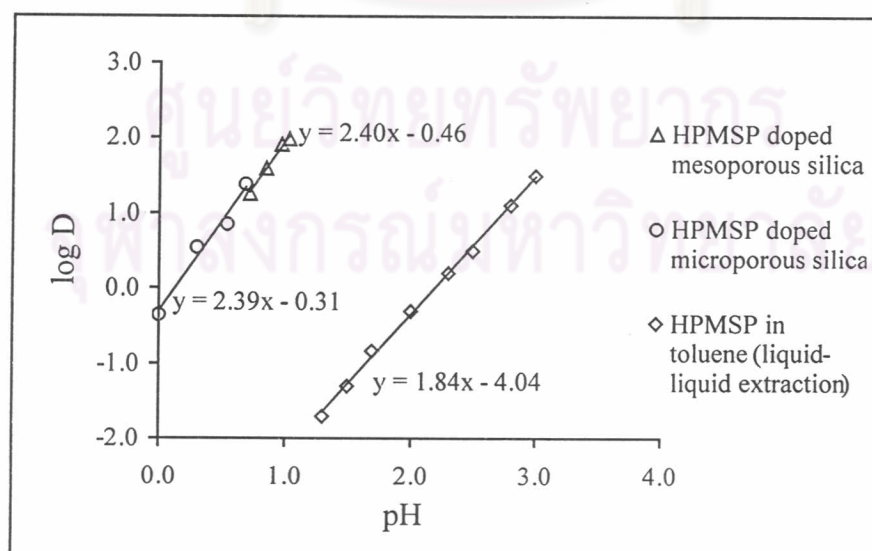


Figure 4.14 Relation between $\log D$ and pH of copper extraction.

4.2.4 Extraction time

To study the effect of time for copper extraction by HPMSD doped mesoporous silica, a 200 ppm $\text{Cu}(\text{NO}_3)_2$ in 0.01 M HNO_3 containing 0.1 M NaNO_3 medium was used, whereas the conditions for cobalt and nickel were 200 ppm $\text{Co}(\text{NO}_3)_2$ and 200 ppm $\text{Ni}(\text{NO}_3)_2$ in 0.1 M NaNO_3 medium, respectively. The relation between extraction time and the ratio of metal extraction in each time (q_t) per metal extraction at equilibrium (q_e) are shown in Figure 4.15. The results show that the rate of metal extraction is extremely rapid in the first 12 minutes, which is the first measurement. Therefore, the investigation of the kinetic order of each metal extraction cannot be accomplished since the metal extraction by HPMSD doped mesoporous silica has already approached equilibrium at the first measurement.

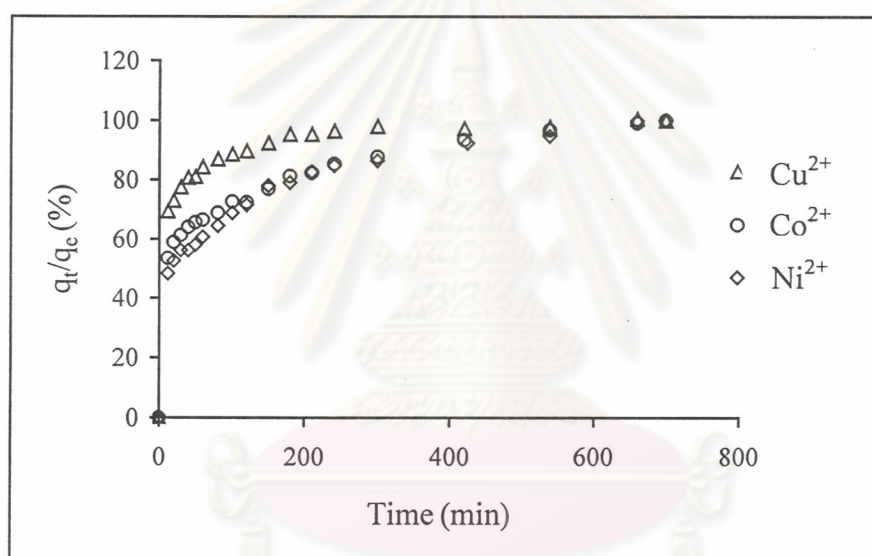


Figure 4.15 The effect of extraction time on metal extraction.

4.2.5. Effect of amount of material

The various amounts of HPMSD doped mesoporous silica in the range of 0.1-0.5 g and 200 ppm $\text{Cu}(\text{NO}_3)_2$ in 0.01 M HNO_3 containing 0.1 M NaNO_3 were used in the copper extraction experiment. The relation between the amount of HPMSD doped mesoporous silica and amount of the copper extracted on the materials is shown in Figure 4.16. When the amount of doped mesoporous silica used in extraction experiment was less than 0.35 g, the amount of copper extraction was linearly increased with increasing amount of doped mesoporous silica. However, the extraction capacity of copper on doped mesoporous silica was maximum at about 0.21 mol/kg. Furthermore, the results showed that the complex formed between

HPMSP and copper had a 2:1 stoichiometry. Copper was completely extracted when more than 0.4 g of doped mesoporous silica was used.

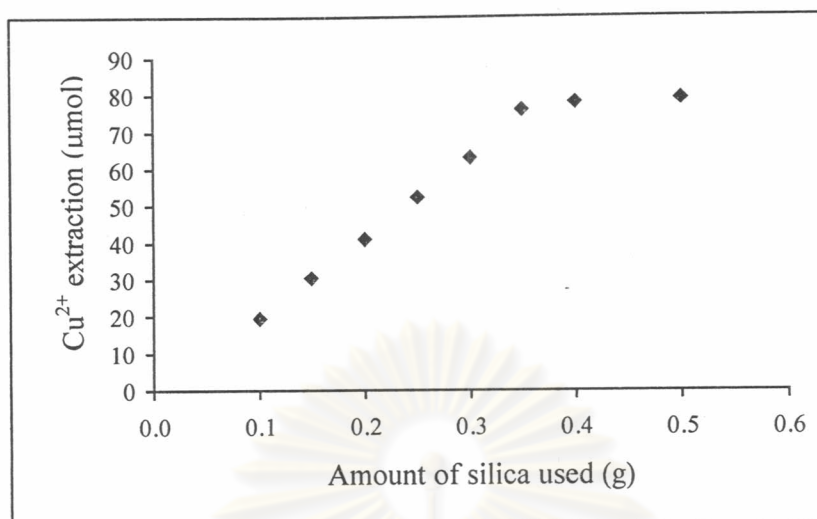


Figure 4.16 Influence of amount of HPMSP doped mesoporous silica used on copper extraction.

4.2.6. Effect of foreign metal ions present in solution

Several ions such as K^+ and Ca^{2+} are also presented in natural water [38]. The influence of these ions on copper extraction capacity of HPMSP doped mesoporous silica was determined.

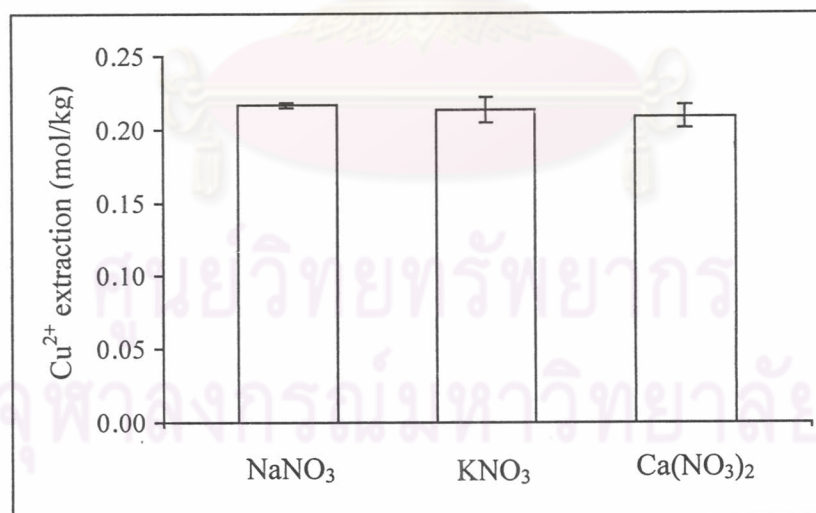


Figure 4.17 Influence of $NaNO_3$, KNO_3 and $Ca(NO_3)_2$ on copper extraction.

According to Figure 4.17, the addition of 0.1 M $\text{Ca}(\text{NO}_3)_2$ or 0.1 M KNO_3 in 200 ppm copper solution prepared in 0.01 M HNO_3 did not interfere the copper extraction behavior of HPMSP doped mesoporous silica. This observation suggested that the materials can be applied to ion separation of metal from a charged matrix.

4.2.7. Metal desorption study

4.2.7.1. Copper desorption

The possibility of copper desorption was studied using 1 M HNO_3 and 1 M HCl as desorption agents (Figure 4.18). The results show that 1 M HNO_3 can desorb copper from the doped silica up to 80%, whereas 1 M HCl can desorb copper maximum at 50%. The effect of time on copper desorption with 1 M HNO_3 and 1 M HCl were also studied. The copper desorption using 1 M HNO_3 was completed within 4 hours. Moreover, effect of HNO_3 concentration on copper desorption was also studied using 0.5, 1.0, 1.5, and 2.0 M HNO_3 solutions as eluents. The results show that the copper desorption was completely achieved using 1 M HNO_3 (Figure 4.19).

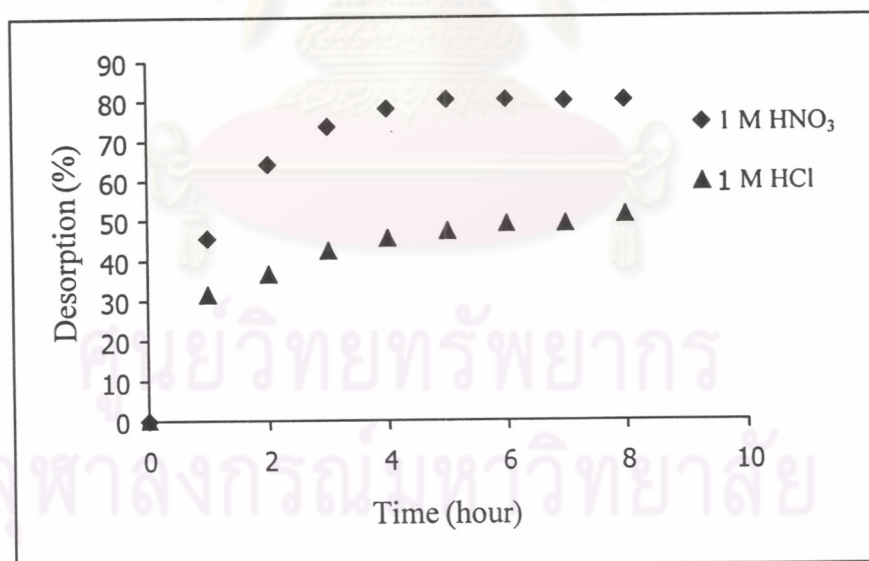


Figure 4.18 Effect of time on copper desorption.

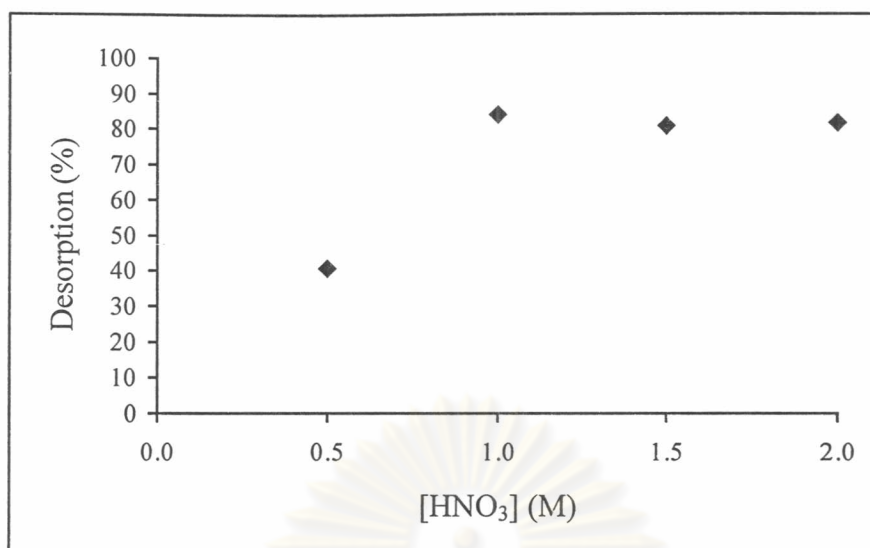


Figure 4.19 Influence of HNO₃ concentration on copper desorption.

4.2.7.2. Cobalt desorption

Cobalt can be desorbed completely from non-doped mesoporous silica and HPMSD doped mesoporous silica using 1 M HNO₃ within 8 hours.

4.2.7.3. Nickel desorption

The amount of 10% of nickel was desorbed from non-doped mesoporous silica using 1 M HNO₃ within 8 hours. And only 20% of nickel was desorbed from non-doped mesoporous silica using 1 M HNO₃ containing 0.1 M NaNO₃ within 24 hours. Considering the desorption of nickel from HPMSD doped mesoporous silica, nickel can be desorbed up to 70% using 1 M HNO₃ within 8 hours.

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