CHAPTER IV

POROUS CLAY HETEROSTRUCTURE FOR WASTEWATER TREATMENT : A DEVELOPMENT FROM BENTONITE CLAY IN THAILAND

4.1 ABSTRACT

A wide variety of toxic metals and organic chemicals are discharged to the environment as industrial or laboratory wastes, causing serious water, air, and soil pollution. One of the interesting materials for using as the adsorbents to adsorb these pollutants in wastewater treatment is porous clay heterostructures (PCHs). These porous materials are obtained by the surfactant-directed assembly of mesostructured silica within clay layers. In the present work, the PCHs were synthesized within the galleries of Na-bentonite clay by the polymerization of tetraethoxysilane (TEOS) in cetyltrimethylammonium ion and dodecylamine templates. These PCHs were functionalized with 3-mercaptopropyltrimethoxysilane (MPTMS) and *N,N*-dimethyldecylamine to obtain the MP-PCH and DM-PCH for utilizing as heavy metal and organic pollutant adsorbent, respectively. According to N_2 adsorption-desorption data, the results show that PCH, MP-PCH and DM-PCH had surface areas of 549.7, 488.7 and 459.9 m^2/g, average pore diameter in the supermicropore to small mesopore range of 3.16 , 3.28 and 3.31 nm and pore volume of 0.45, 0.48 and 0.56 cc/g, respectively. Moreover, these adsorbents were investigated the adsorption properties which concerned with their function as adsorbents for aqueous solution. The results show that the adsorption capacity of MP-PCH was 0.50, 0.48, 0.24 , 0.22 and 0.11 mmol/g for Mn, Ni, Cu, Cd and Pb, respectively and the adsorption capacity of DM-PCH was 3.6 and 1.4 mM/g for 4-chloroguiacal or 2,6-dinitrophenol, respectively. They point out the potential of these PCHs for utilizing as the heavy metal and organic pollutant adsorbents in wastewater treatment.

keywords : porous clay heterostructures, bentonite, heavy metal, organic pollutant, adsorption.

4.2 INTRODUCTION

The presence of heavy metals and organic pollutants in various surface water or ground water as industrial or laboratory wastes has been of great concern because of their toxic effect on plants, animals and human beings [1]. Therefore, effective removal of heavy metals from water or various industrial effluents is very important and has attracted considerable research and practical interest. There are several methods including chemical precipitation, ion exchange, electrodeposition, reverse osmosis and adsorption, etc., have been used to remove heavy metal ions from various aqueous solutions. Among these methods, adsorption process has increasingly received more attention in recent years because the method is simple, relatively low cost and effective in removing heavy metal ions, especially at medium to low metal ion concentrations and form wastewaters.

One of the interesting materials for using in wastewater treatment is porous clay heterostructures (PCH) due to their large surface area, unique combined micro- and mesoporosity, and well-modified surface properties [2]. These porous materials which are obtained by combining the pillaring and template approaches, are form by the surfactant-directed assembly of mesostructured silica within the two-dimensional galleries of a 2:1 phyllosilicate host such as fluolohectorite, vermiculite, and mont-morillonite [3]. In the first step, cationic surfactant templates and neutral amine co-surfactant are intercalated between the sheets of the clay plates forming micelle templates. Subsequently, the silica sources are formed by polymerization around the micelle structures. Finally the surfactant templates are removed from the as-synthesized PCH either by calcinations or chemical extraction to obtained the mesoporous materials.

Mesoporous materials of interest for the removal of toxic heavy metals, such as mercury, cadmium, zinc, chromium, and lead, are based mostly on mesoporous silicates functionalized with mercaptopropyl surface groups [4]. The thiol functionalities, which exhibit a high affinity for these metals, have been incorporated with mesoporous materials either by grafting (also known as post-synthesis) or by co-condensation (also known as direct synthesis) techniques [5]. Furthermore the functionalization of mesoporous silica with *N,N* – dimethyldecylamine has also been prepared to use as the organic pollutants adsorbents [1].

This research work focused on the synthesis of mesoporous materials from Na-bentonite clay, which is the available local clay minerals. These mesoporous materials were functionalized with 3-mercaptopropyltrimethoxysilane (MPTMS) and *N,N*-dimethyldecylamine (DMDA) for utilizing as heavy metals and organic pollutant adsorbents for wastewater treatment, respectively. Subsequently, the functionalized PCHs was investigated the adsorption properties which concerned with their function as adsorbents for aqueous solution.

4.3 EXPERIMENTAL

Materials

Na-Bentonite (BTN), (Mac-Gel® GRADE SAC), was obtained from Thai Nippon Chemical Industry Co., Ltd. The cation exchange capacity (CEC) of BTN is 43.5 mmol/100g of clay.

Cetyltrimethylammonium [$C_{16}H_{33}N^+(CH_3)_3$] bromide (CTAB) was supplied by Fluka. Dodecylamine, $C_{12}H_{27}N$, (98% purified) was supplied by Aldrich. Tetraehtyl orthosilicate (TEOS), $Si(OC_2H_5)_3$ and Methyltriethyl orthosilicate (MTS), $CH_3Si(OC_2H_5)_3$, were purchased from Fluka. Methanol (CH_3OH) was supplied by Lab Scan and Hydrochoric acid (HCl) was supplied by Carlo Erba, *N,N* - Dimethyldecylamine (DMDA), $CH_3(CH_2)_8CH_2N(CH_3)_2$ was supplied by Aldrich, ICP Muti Element Standard Solution (1000 ppm) was supplied by Merck, 2,6-Dinitrophenol, $C_6H_4N_2O_5$, (95% purified) was supplied by Aldrich and 4-Chloro-2-methoxyphenol, $C_7H_7ClO_2$, (99% purified) was supplied by Acros Organics.

Purification of Bentonite Clay

Bentonite was pulverized and sieved through 325 mesh. The passing part were purified by centrifugation and then washed with distilled water. The samples were air-dried overnight and pulverized in a mortar.

Synthesis of Porous Clay Heterostructures (PCH)

The purified bentonite was stirred with cetyltrimethylammonium bromide at 50°C for 24 h. After the reaction time, the intercalated clay was filtered out, washed with a mixture of methanol and water and then air-dried. The 2 g of obtained organoclay was stirred in dodecylamine for 30 min at 50°C following which TEOS was added at molar ratio of organoclay:dodecylamine:TEOS was 1:20:150. The mixture was allowed to stir for further 4 h at room temperature. The modified clay was separated from solution by filtration and air-dried overnight at room temperature to form the as-synthesized PCH. The surfactant was removed from the as-synthesized PCH by solvent extraction using a mixture of methanol and HCl. Typically, 1 g of the as-synthesized PCH has been added to 45 mL of methanol and 5 mL of HCl and refluxed for 2 h. The surfactanted-extracted PCH was filtrated and washed with a mixture of methanol and water and air-dried at room temperature overnight.

Synthesis of Functionalized PCH for Utilizing as Heavy Metal Adsorbent

The purified bentonite was stirred with cetyltrimethylammonium bromide at 50°C for 24 h. After the reaction time, the intercalated clay was filtered out, washed with a mixture of methanol and water and then air-dried. The 2 g of obtained organoclay was stirred in dodecylamine for 30 min at 50°C Then a mixture of TEOS and MPTMS in a mole fraction of 1:1 or 4:1 was added under N_2 atmosphere for further 24 h at room temperature. The modified clay was separated from solution by filtration and air-dried overnight at room temperature to form the as-synthesized PCH. The surfactant was removed from the as-syn-thesized PCH by solvent extraction using a mixture of methanol and HCl. Typically, 1 g of the as-synthesized PCH has been added to 45 mL of methanol and 5 mL of HCl and refluxed for 2 h. The surfactanted-extracted PCH was filtrated and washed with a mixture of methanol and water and air-dried at room temperature overnight. The mercaptopropyl-functionalized PCH was denoted MP-PCH.

Synthesis of Functionalized PCH for Utilizing as Organic Pollutant Adsorbent

The purified bentonite was stirred with cetyltrimethylammonium bromide at 50°C for 24 h. After the reaction time, the intercalated clay was filtered out, washed with a mixture of methanol and water and then air-dried. The 2 g of obtained organoclay was stirred in dodecylamine for 30 min at 50°C. Then a mixture of TEOS and DMDA in a mole fraction of 1:1 or 4:1 was added under N_2 atmosphere for further 24 h at room temperature. The modified clay was separated from solution by filtration and air-dried overnight at room temperature to form the as-synthesized PCH. The surfactant was removed from the as-synthesized PCH by solvent extraction using a mixture of methanol and HCl. Typically, 1 g of the as-synthesized PCH has been added to 45 mL of methanol and 5 mL of HCl and refluxed for 2 h. The surfactant-extracted PCH was filtrated and washed with a mixture of methanol and water and air-dried at room temperature overnight. The DMDA- functionalized PCH was denoted DM-PCH.

Adsorption properties of functionalized-PCH

The 0.05 g of MP-PCH or DM-PCH was stirred in 100 mL of heavy metal standard in the concentration range 0-10 ppm or organic pollutant standard solutions in the concentration range 0.2-0.4 m molar. The stirring continued for 24 h before the slurries were filtered, and obtained solution was analyzed by Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) for heavy metals standard solution and High Performance Liquid Chromatography (HPLC) for organics pollutant standard solution.

The adsorption capacity of MP-PCH were obtained from ICP-OES data. The 0.05 g of the adsorbent was srirred in the 100 mL of standard heavy metal solution at room temperature which varied pH of standard solution and contact time. The initial and final concentration of the standard heavy metal solution was measured by using ICP-OES. The adsorption capacity of each element was calculated from this equation.

Adsorption Capacity (q)

$$q = \frac{(Ci - Ce)V}{W}$$

where:

C_i = initial concentration of standard heavy metal solution

C_e = final or equilibrium concentration of standard heavy metal solution

V = volumn of solution

W = weight of the adsorbent

For the adsorption capacity of DM-PCH, High Performance Liquid Chromatography (HPLC) with UV-Visible detector was utilized to investigate adsorption capacity of DM-PCH. The adsorbent was stirred with organic solutions which varied concentration and contact time and then the concentration of organic solutions was measured by HPLC. The adsorption capacities of DM-PCH was calculated by taking the same equation with MP-PCH. Figure 4.1 and 4.2 shows the calibration curve of 4-chloroguaiacol and 2,6-dinitrophenol for calculation of adsorption capacity.

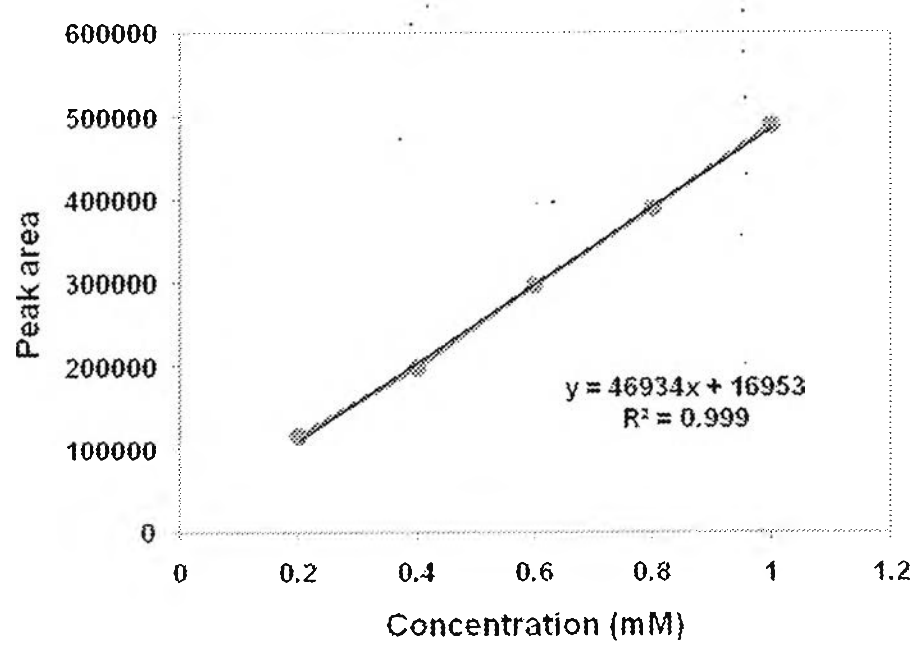


Figure 4.1 The calibration curve of 4-chloroguaiacol.

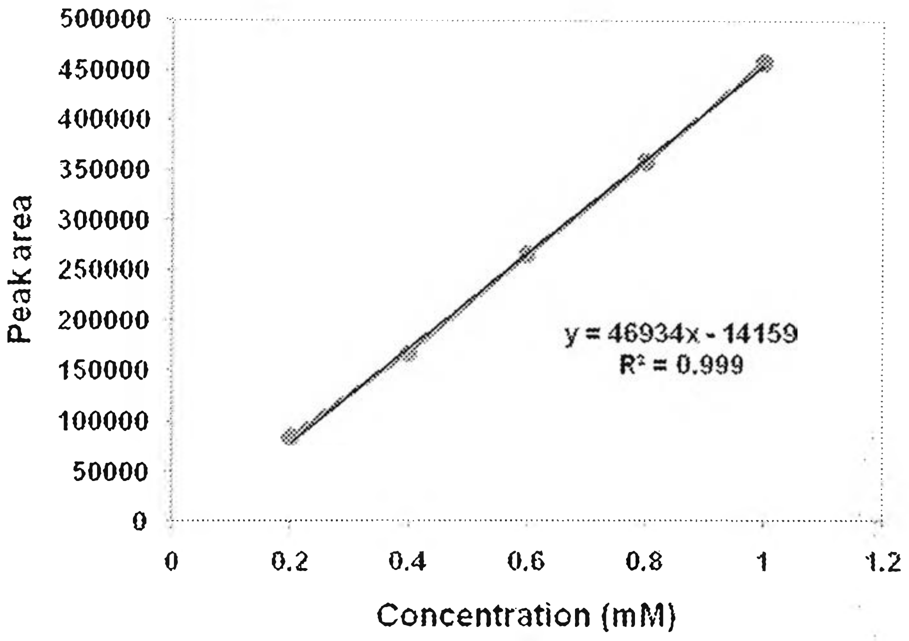


Figure 4.2 The calibration curve of 2,6-dinitrophenol.

Physical Measurements

Powder X-ray diffraction patterns were measured on a Rigaku Model Dmax 2002 diffractometer with Ni-filtered Cu K_α radiation operated at 40 kV and 30 mA. The powder samples were observed on the 2θ range of 2-20 degree with a scan speed of 2 degree/min and a scan step of 0.02 degree.

N_2 adsorption-desorption isotherms were obtained at -196°C on a Sorptomatic. Powder samples were degassed at 150°C during 12 h under vacuum prior to analysis. Surface areas were calculated using the BET equation. The pore size distributions were constructed based on Barrett, Joyner and Halenda (BJH) method using the adsorption branch of the nitrogen isotherm.

Scanning electron microscopy was performed on JSM-6400 Model. The specimens were coated with gold under vacuum to make them electrically conductive.

Transmission electron microscopy was performed on JEOL JEM-2100 model and an accelerating voltage of 150 kV. TEM samples were prepared by embedding the powder in resin and sectioning on an ultramicrotome.

Chemical Analysis

FT-IR spectra of organoclays, PCHs, and HPCHs were obtained using a Nicolet Nexus 670 FT-IR spectrometer in the frequency range of 4000-400 cm^{-1} with 32 scans at a resolution of 2 cm^{-1}. KBr pellet technique was applied in the preparation of powder samples. The incorporation of organic group into silicate network is investigated by using FTIR technique.

X-ray Fluorescence spectrometer was used to identify the presence of an element in the BTN, PCH, MP-PCH and DM-PCH and to confirm the functionalization of PCH. X-ray Fluorescence was measured on a PHILIPS Model PW-2400 of wavelength dispersive type (WDS) with Rh target X-ray tube excited source operated at 3 kw power. The powder samples were observed with the tube current 438 μA for the acquisition livetime 30.0s.

Inductively Coupled Plasma-Optical Emission Spectrometry was performed on PerkinElmer Optima 4300 DV to measure concentration of heavy metal in sample. The pre-optical system was purged with Argon gas for 4h, operated with an axial view of 5 KVA. The concentration of metal was detected by using UV-Vis detector at appropriate wavelength of each element. The sample was prepared by dissolution with 1 M HNO_3 to obtain the required concentration before analyze.

High Performance Liquid Chromatography (HPLC) was performed on Perkin Elmer 200LC to determine quanlitatively of organic pollutant solution. The concentration of pollutants was measured by HPLC using UV-Visible detector and C18 column. The mobile phase was 85:15 v/v methanol/water for 4-Chloro-2-methoxyphenol and 59:40:1 methanol/water/acetic acid for 2,6-dinitrophenol. The detector was set at 254 and 270 nm for 2,6-dinitrophenol and 4-Chloro-2-methoxyphenol, respectively.

4.4 RESULTS AND DISCUSSION

Characterization of Bentonite and Organo Bentonite

Bentonite (BTN) which has a cationic exchange capacity (CEC) of 43.5 mmol/100g clay was intercalated with cetyltrimethylammonium bromide. A corresponding XRD pattern show the presence of the (001) reflection peak. As seen from

Figure 4.3, the basal spacing of BTN was 1.15 nm (Figure 4.1(a)). For the organoclay (Figure 4.1(b)), the d_{001} peak were observed at lower angle than the pristine BTN and the basal spacing was 1.96 and 3.94 nm. This result reveals that the interlayer distance of BTN is expanded when long chain ammonium salt is added.

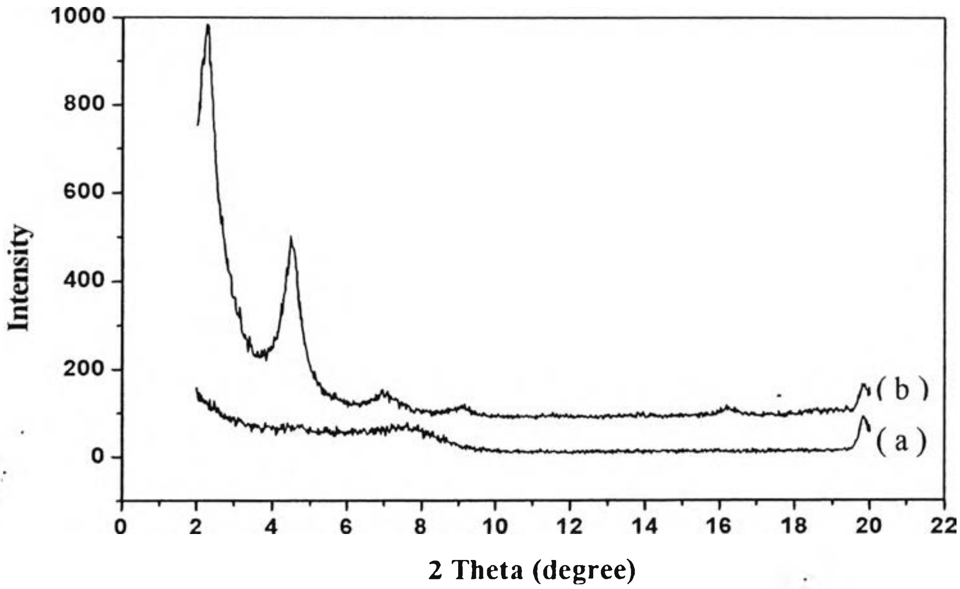


Figure 4.3 XRD pattern of (a) bentonite and (b) organoclay

Formation of Porous Clay Heterostructures (PCH) and Functionalization of Porous Clay Heterostructures (PCH)

After the purification of bentonite clay, the clay galleries were first opened up by the intercalation of the surfactant cetyltrimethylammonium cation. Subsequently, neutral amine co-surfactant was then intercalated between clay layers to form micelle templates. Then silica sources (TEOS, TEOS/MPTMS and TEOS/DMDA for PCH, MP-PCH and DM-PCH respectively) were introduced to polymerize surrounding the surfactant micelles in the galleries of clay. By solvent extraction method, the surfactant templates were removed from as-synthesized PCHs and MP-PCHs, resulting in the formation of porous structures.

After the intercalation of co-surfactant and silica sources, as-synthesize PCH, MP-PCH and DM-PCH are obtained. XRD patterns of these samples are illustrated in Figure 4.4. There is no obvious peak observed in the XRD patterns of these as-synthesized products. A possible reason due to disordered structure of silica framework which is formed in the galleries of clay shields a highly regular interstratification of the clay layers.

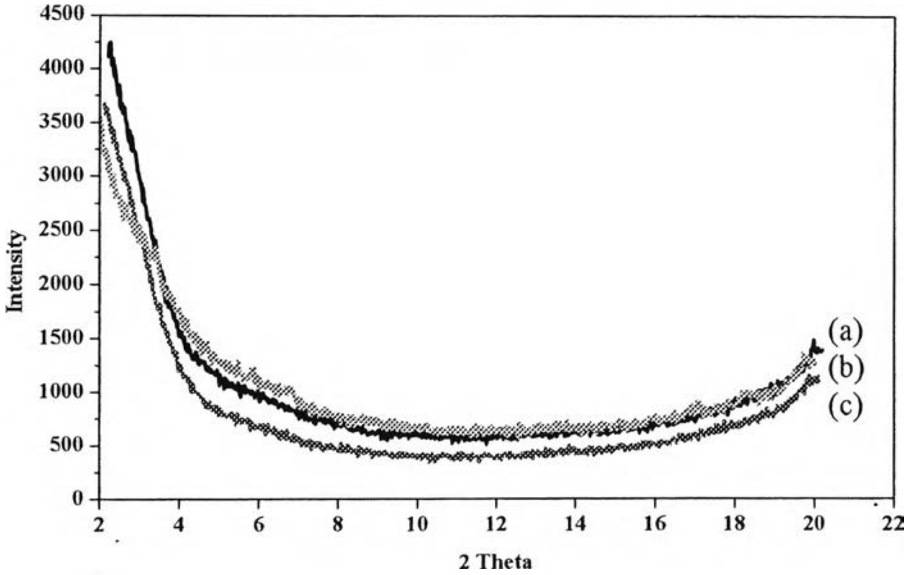
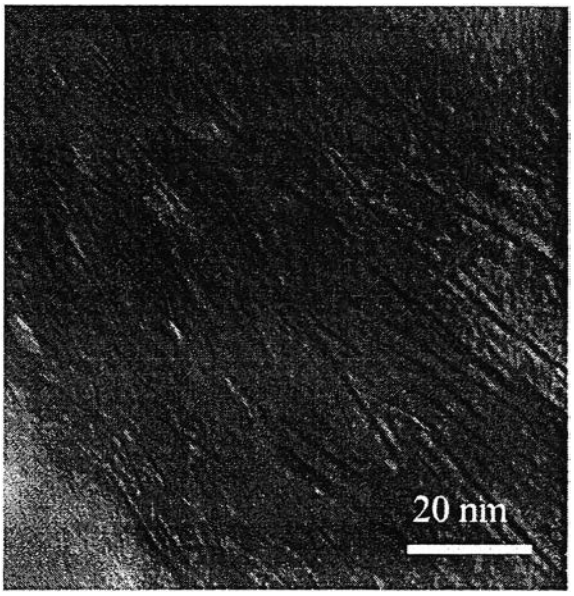
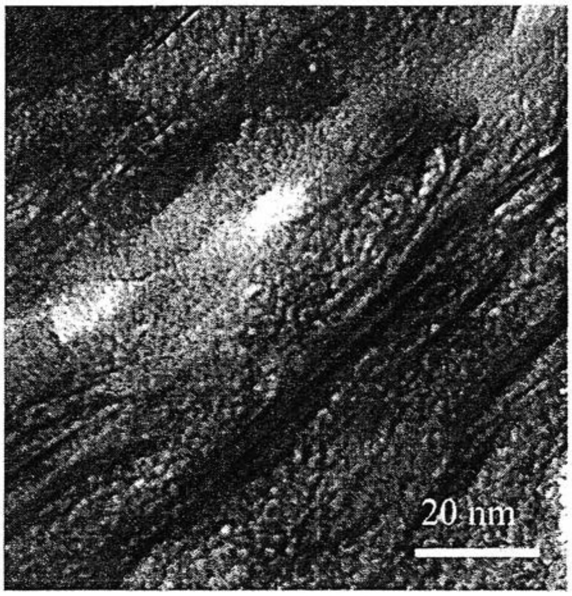


Figure 4.4 XRD patterns of (a) PCH, (b) MP-PCH and (c) DM-PCH.

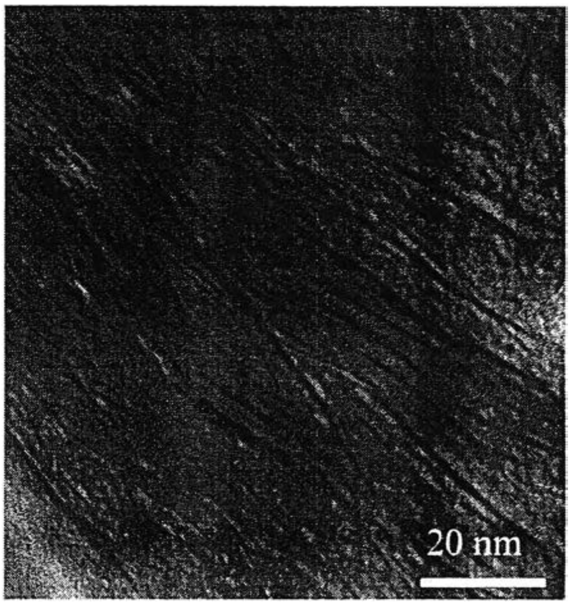
However, the presence of the clay layers can be confirmed by TEM images of representatives of both PCH and MP-PCH and DM-PCH (Fig. 4.5(a) ,(b) and (c)). From the TEM images, the clay layers are discernible as solid dark lines and reveal aggregated domains of several layers. Although the clay layers are easily observed, pore structure in the galleries of clay is more difficult to notice due to the nature of these materials. However, the white spots observed in Fig 4.5(b) might represent the characteristic of pore structure.



(a)



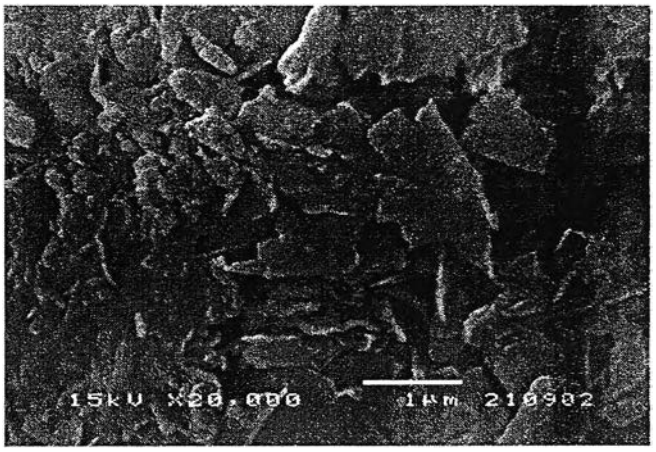
(b)



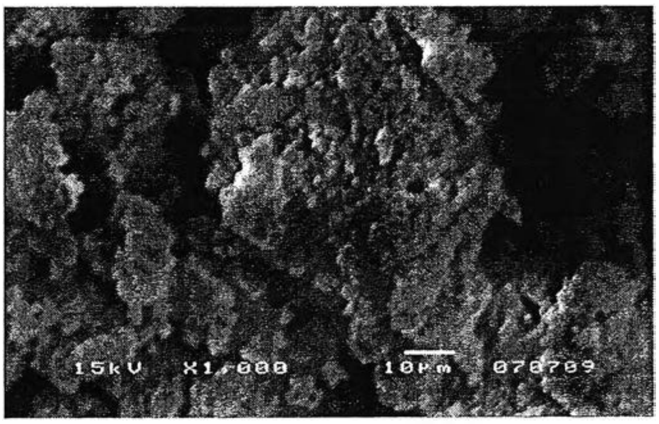
(c)

Figure 4.5 TEM images of (a) PCH, (b) MP-PCH and (c) DM-PCH.

Moreover, the BTN exhibits a layered or plate-like structure in SEM image (Figure. 4.6(a)). According to N_2 adsorption-desorption results in Figure. 4.7 and Table 4.1., the isotherm of BTN shown a characteristic of non-porous solid indicating low adsorption amount of nitrogen and present a plateau exactly parallel to the pressure axis. In addition, the BET surface area of BTN was 31.4 m^2/g. After modification, the SEM images of PCH, MP-PCH and DM-PCH (Figure 4.6(b)-(d)) revealed a roughness and a porosity on the surface of clay layers comparing to the pristine clay. Furthermore, the surface areas of PCH, MP-PCH and DM-PCH increase significantly from that of pristine clay. The results shown that PCH, MP-PCH and DM-PCH had surface areas of 549.7, 488.7 and 459.9 m^2/g, average pore diameter in the supermicropore to small mesopore range of 3.16 , 3.28 and 3.31 nm and pore volume of 0.45, 0.48 and 0.56 cc/g, respectively. The isotherms of PCH, MP-PCH and DM-PCH were abruptly increased in nitrogen adsorption at low partial pressure and gradually increased to medium partial pressure (P/P_0:0.05-0.3) suggesting that these materials possess supermicropore to small mesopore region.


15kV X20,000
1µm 210902

(a)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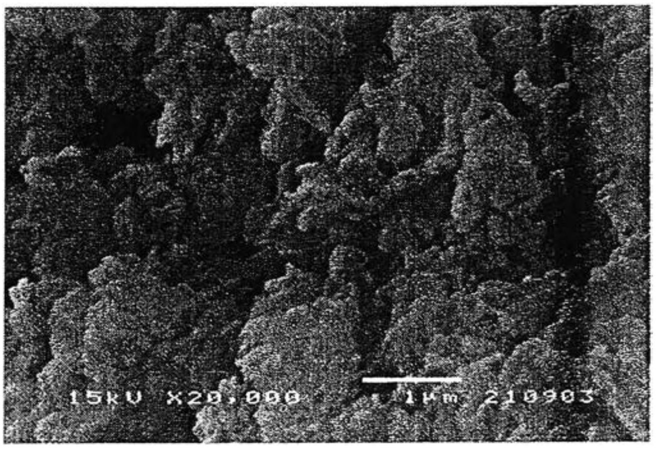
(b)


15kV X20,000
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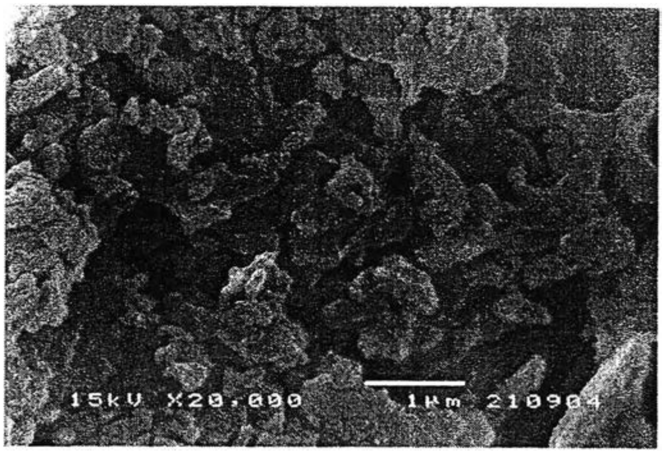
(c)



(d)

Figure 4.6 The SEM images of (a) bentonite, (b) PCH (c) MP-PCH and (d) DM-PCH.

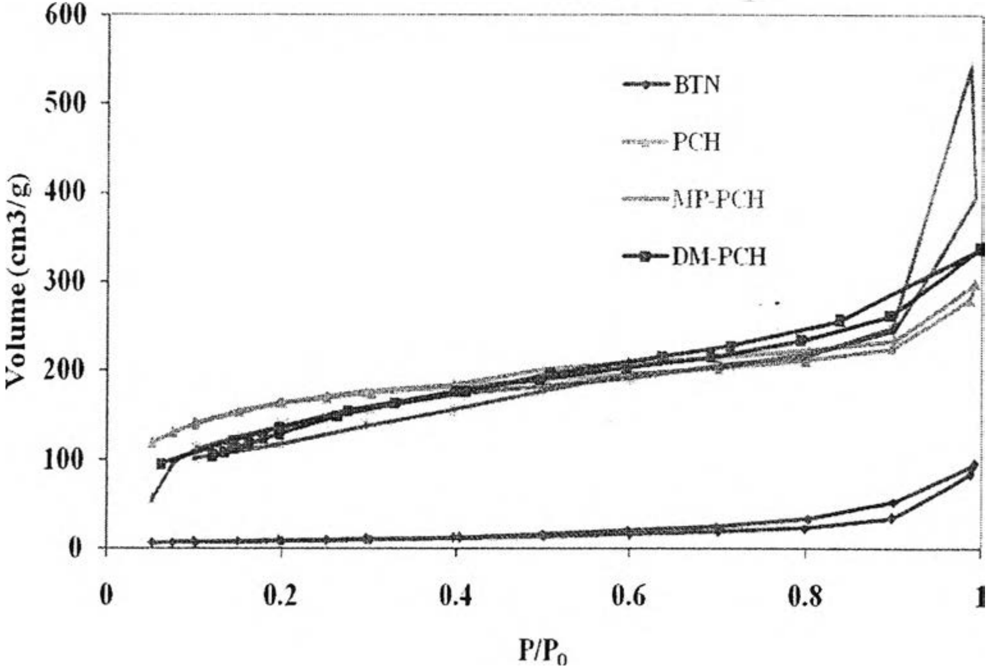


Figure 4.7 N_2 adsorption-desorption isotherms of BTN, PCH, MP-PCH and DM-PCH

Table 4.1 Porosity characteristics of bentonite, PCH , DM-PCH and MP-PCH

Sample	Multipoint BET surface area (m^2/g)	Average pore diameter (nm)	BJH pore volume (cc/g)
Bentonite	31.4	16.45(depth of clay)	0.15
PCH	549.7	3.16	0.45
MP-PCH	488.7	3.28	0.48
DM-PCH	459.9	3.31	0.56

The FTIR spectrum of BTN is given in Fig. 4.8(a). The broad peak around 3500 cm^{-1} can be assigned to the stretching vibration of the silanol associated with the silica structure. The peak at 1000, 1100 and 800 cm^{-1} can be assigned to the stretching vibration of the SiO_4 units, the asymmetric and symmetric stretching vibrations of the Si-O-Si linkage, respectively. The presence of surfactant is evidenced by FTIR spectra of organobentonite (Fig.4.8(b)) indicating the asymmetric and symmetric vibrations of methyl and methylene groups of cetyltrimethyl ammonium ion at 2920 and 2800 cm^{-1}, respectively. For clarity, only the spectrum of as-synthesized PCH (Fig. 4.8(c)), which has surfactant templates, and spectra of solvent-extracted PCH (Fig. 4.8(d)) were selected to confirm that removal of surfactant in as-synthesized PCH by solvent extraction in methanol and hydrochloric system is an effective method to eliminate the surfactant templates due to the absence of peak at 2920 and 2985 cm^{-1} in solvent-extracted samples. The FTIR spectra of PCH are different from starting BTN indicated by the absence of peak at 1000 cm^{-1}. So it roughly infer that the structure of starting clay are changed after the modification.

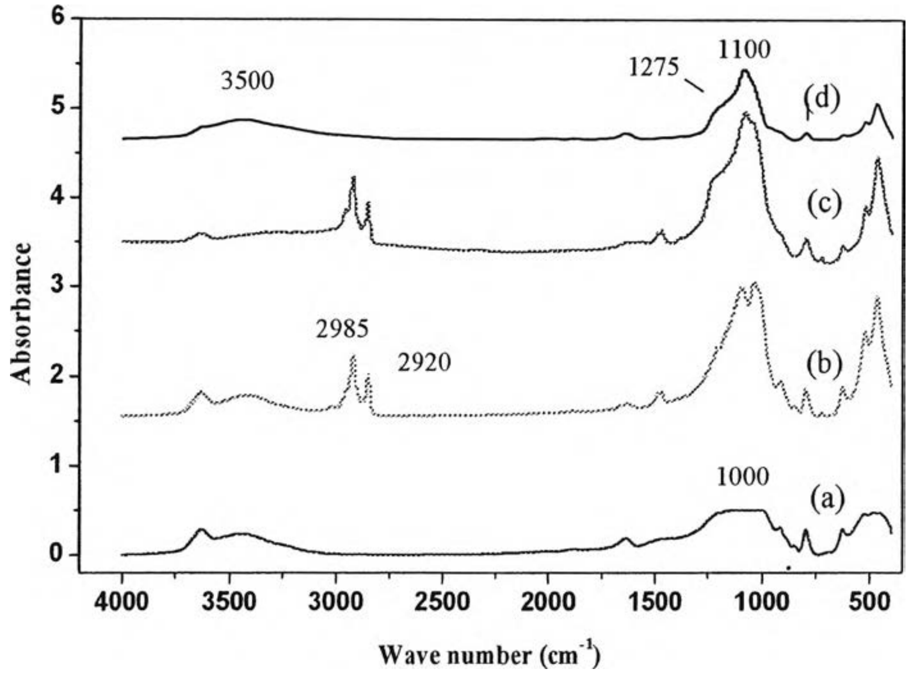


Figure 4.8 FTIR spectra of (a) BTN, (b) organobentonite, (c) as-synthesized PCH, (d) PCH .

In order to confirm the incorporation of the functional group in PCH, the XRF technique are required. From XRF results, the percentage of sulfur in MP-PCH(1) was increased to 4.32 while the percentage of sulfur was absence in case of bentonite clay. It can conclude that the functionalization of thiol groups (-SH) into PCH is successfully incorporated.

Table 4.2 % element of bentonite , MP-PCH(1) and MP-PCH(2).

Sample	% element											
	O	Na	Mg	Al	Si	K	Ca	Ti	Fe	Cu	S	Total
BTN	49.4	2.38	1.72	7.04	34.6	1.08	2.10	0.22	1.09	0.14	-	100
MP-PCH (1)	53.0	-	0.55	2.04	38.5	0.24	0.56	0.08	0.36	0.18	4.32	
MP-PCH (2)	54.5	-	0.34	1.50	29.9	0.27	0.50	0.09	0.27	0.13	12.5	

In the case of DM-PCH, the incorporation of the functional group in PCH was performed by the FTIR spectrum in Fig. 4.9. From the spectrum of DM-PCH, the peak at 1130 indicating the N-H bending vibrations of NH- group in N,N-dimethyldecylamine and the peak at 1621 can be assigned to the C-NH-C bending vibration. These peak were selected to confirm that the functionalization of DMDA into PCH is successfully incorporated.

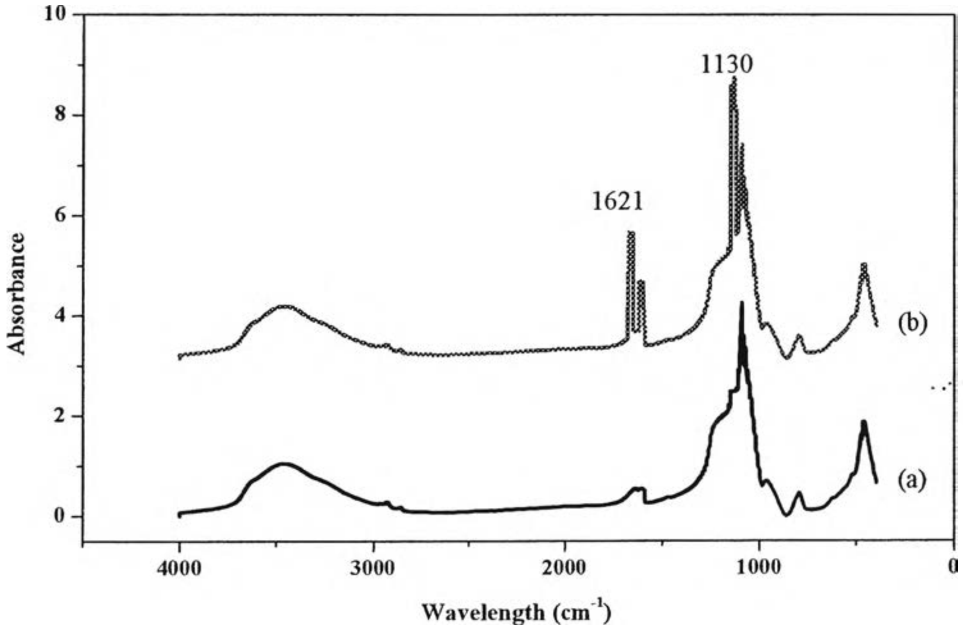


Figure 4.9 FTIR spectra of (a) PCH and (b) DM-PCH.

Adsorption properties of PCH

The 0.05 g of PCH and MP-PCH(2) were used to adsorb each standard heavy metal solution at pH 7 for 24 hr. The adsorption capacity of these adsorbents showed in Figure 4.10

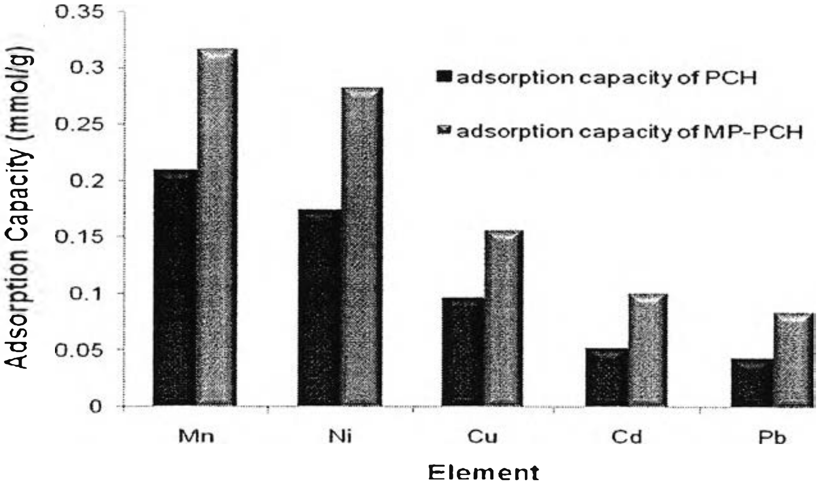


Figure 4.10 Adsorption Capacity for each heavy metal by 0.05 g of PCH and MP-PCH(2) at pH 7 for 24 hr.

From the results, MP-PCH can adsorb each heavy metal more than PCH even surface area of MP-PCH less than PCH. It is due to the functionalization of thiol group which has the ability to adsorb heavy metal in the porous structure.

Adsorption properties of MP-PCH(2)

Effect of pH

The pH of the aqueous solution is an important controlling parameter in the adsorption process. Therefore, the effect of hydrogen ion concentration was examined from the solutions at pH ranging from 3 to 9. Figure 4.11 summarizes the adsorption capacity of adsorbents to remove Cd, Cu, Mn, Ni and Pb at various pH values.

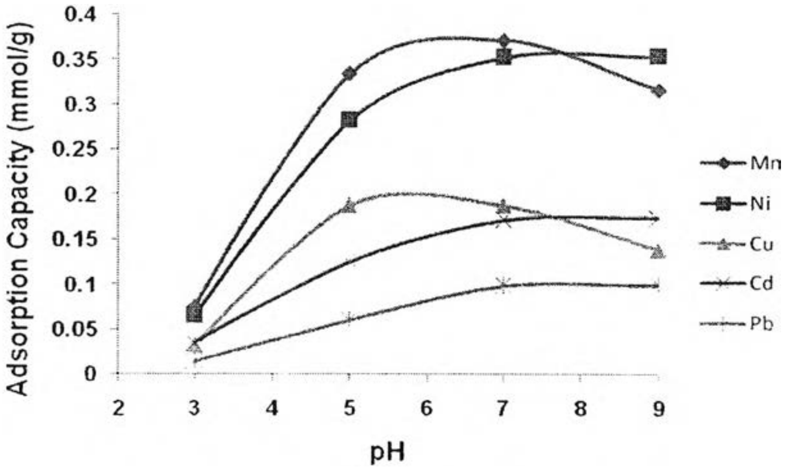


Figure 4.11 Effect of pH on the adsorption of heavy metal by 0.05 g of MP-PCH(2)

The suitable pH values to adsorption is pH 7 for all heavy metals. At lower pH values, the H_30^+ ions compete with the metal ions for the exchange sites in the adsorbent so the adsorption at low pH is low. An increase in metal ion uptake was observed as the pH value increases from 3 to 7 because the amount of H_30^+ ions decrease. After that, the decrease of heavy metals adsorption is due to the beginning of precipitation of metalhydroxide.

Effect of Contact Time

For study on the effect of contact time, the experiments were carried out at 25 °C and using the suitable pH value 7 when the contact time was varied at 4, 12, 24 and 48 hr. The dependence of adsorption of heavy metal with time was presented in Figure 4.12. The adsorption increased with increasing contact time, and the equilibrium was attained after shaking for 24 h.

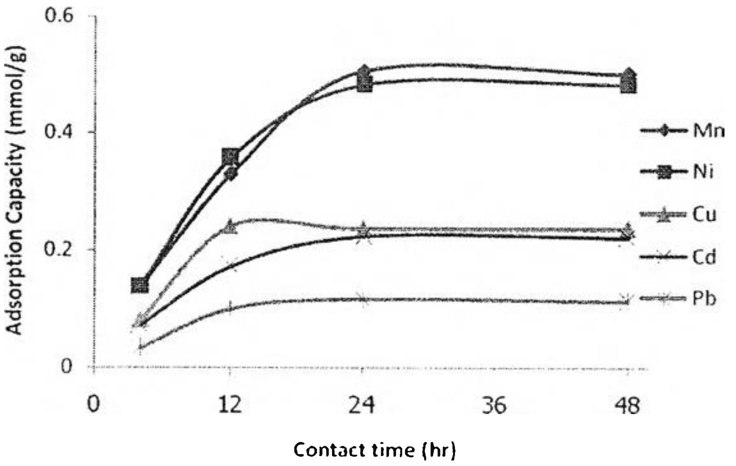


Figure 4.12 Effect of contact time on the adsorption of heavy metal at pH 7 of MP-PCH (2).

At suitable condition, pH 7 and contact time for 24 hr, the adsorption capacity of MP-PCH was concluded in Table 4.3.

Table 4.3. Adsorption capacity of heavy metal on MP-PCH(2) in pH 7 for contact time 24 hr. (Testing condition 0.05 g MP-PCH(2) in 100 mL of 10 ppm metal ion)

Element	**Adsorption Capacity of MP-PCH(2) (mmol/g)**
Mn	0.50
Ni	0.48 ± 0.001
Cu	0.24 ± 0.003
Cd	0.22 ± 0.001
Pb	0.11

Adsorption Properties of PCH and MP-PCH for wastewater sample

Purified bentonite, PCH, MP-PCH(1) which prepared at mol ratio of MPTMS:TEOS was 1:4 and MP-PCH(2) which prepared at mol ratio of

MPTMS:TEOS was 1:1 were used as the adsorbents to adsorb metals in standard metal solution and wastewater samples collected from a natural pond near laboratory. The XRF results in Table 4.3 shows the content of each element in bentonite clay, PCH, MP-PCH(1) and MP-PCH(2). The percentage of sulfur represents the content of thiol group which incorporated in PCH. From the data, bentonite and PCH were not shown the percentage element of sulfur but after functionalization with MPTMS, the percentage of sulfur was increased to 4.32 for MP-PCH (1) and increased to 12.5 for MP-PCH(2) , they were used to confirm the incorporation of thiol group into PCH when more content of MPTMS was added. The adsorption properties of 4 adsorbents were investigated by ICP-OES. The results of wastewater were shown in Figure 4.13.

Table 4.4 % element of MP-PCH(1) and MP-PCH(2)

Sample	% element											
	O	Na	Mg	Al	Si	K	Ca	Ti	Fe	Cu	S	Total
BTN	49.4	2.38	1.72	7.04	34.6	1.08	2.10	0.22	1.09	0.14	-	100
PCH	51.7	-	0.51	1.98	43.4	0.23	0.51	0.13	0.36	1.18	-	
MP-PCH (1)	53.0	-	0.55	2.04	38.5	0.24	0.56	0.08	0.36	0.18	4.32	
MP-PCH (2)	54.5	-	0.34	1.50	29.9	0.27	0.50	0.09	0.27	0.13	12.5	

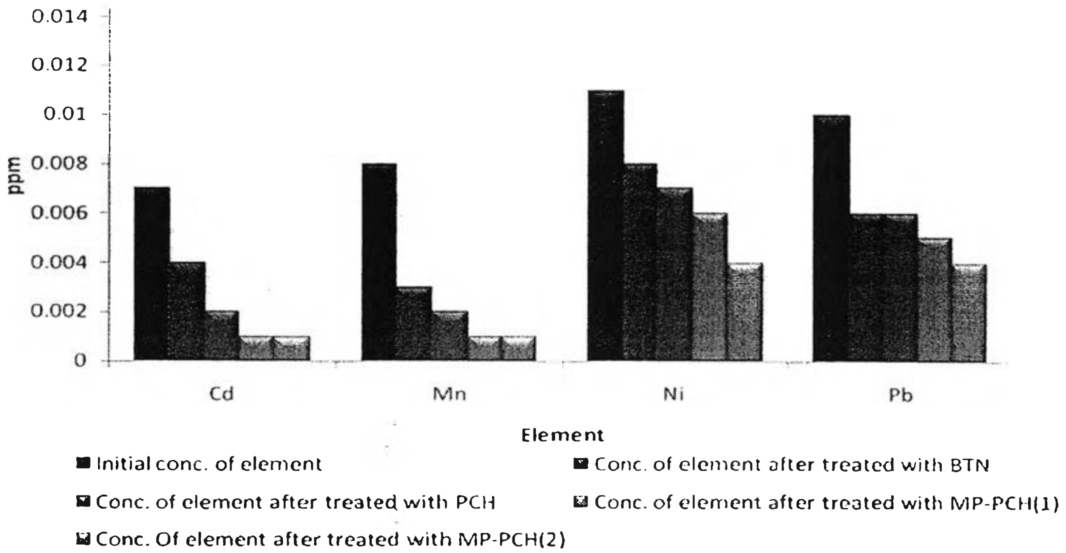


Figure 4.13 Bar graph results of heavy metal absorbent derived from PCHs

Adsorption Properties of DM-PCH

The 0.05 g of PCH and DM-PCH were used to adsorb 4-chloroguiacol and 2,6-dinitrophenol at concentration 0.2 mM for 24 hr. The adsorption capacity of these adsorbents showed in Figure 4.14. DM-PCH which prepare from functionalization of PCH with *N,N*-dimethyldecylamine can adsorb both organic pollutants greater than PCH.

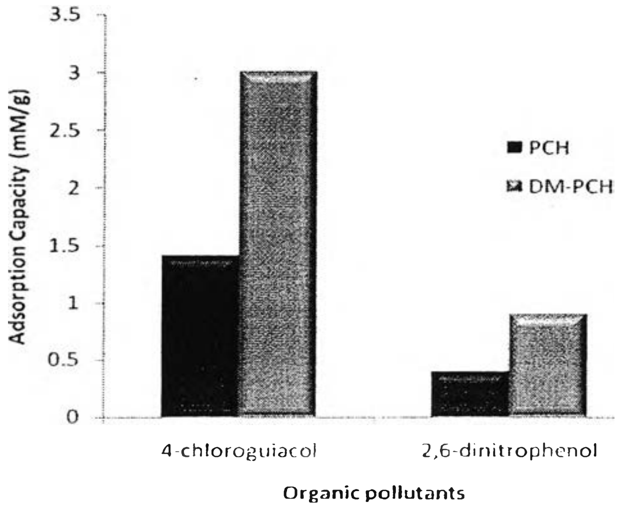


Figure 4.14 Adsorption Capacity for organics pollutants by 0.05 g of PCH and DM-PCH at concentration 0.2 mM for 24 hr.

Effect of Concentration

The adsorption properties are influented by the concentration of organic solution so the adsorption dependent the concentration should be investigated. Using DM-PCH with different initial concentrations of 4-chloroguiacal or 2,6-dinitrophenol, the adsorption properties was performed in Fig. 4.15. The capacity was high at 0.4 mM for both organics solution.

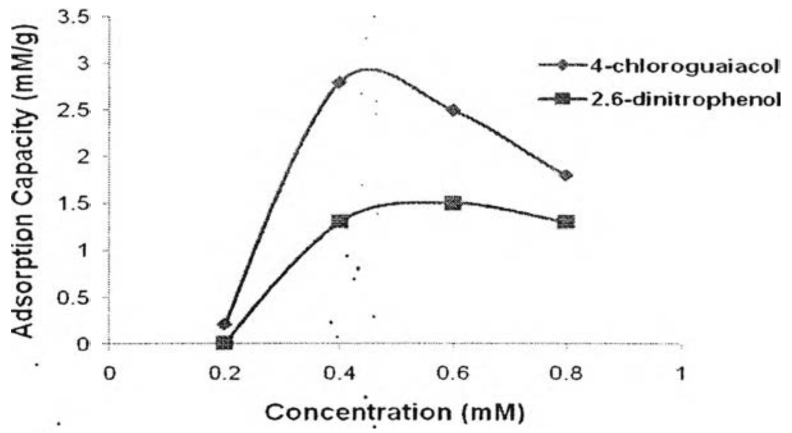


Figure 4.15 Effect of concentration on the adsorption of organics pollutant by DM-PCH 0.05 g for 24 hr treatment time.

Effect of Contact Time

Using DM-PCH and solutions of 4-chloroguiacal or 2,6-dinitrophenol, the experiments were carried out at 25 °C when the contact time was varied at 4, 12, 24 and 48 hr. The adsorption data of 4-chloroguiacal or 2,6-dinitrophenol was shown in Fig. 4.16.

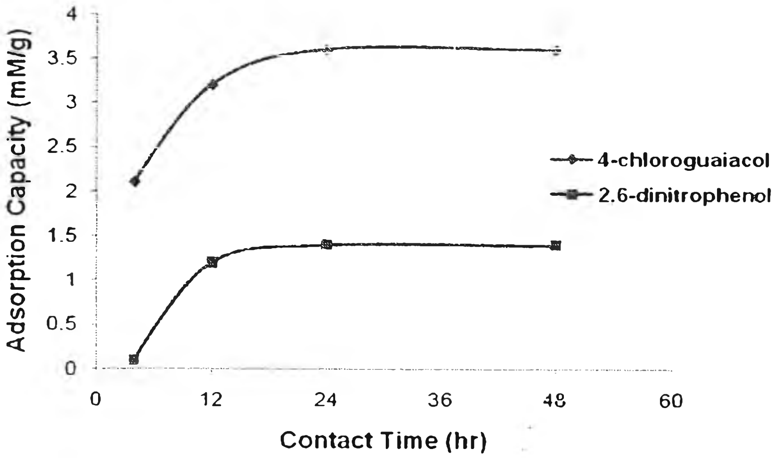


Figure 4.16 Effect of contact time on the adsorption of organics pollutant at concentration 0.4 mMolar by using DM-PCH 0.05 g.

The adsorption capacity of 4-chloroguiacal or 2,6-dinitrophenol was high after stirring for 24 hr, the adsorption capacity of DM-PCH was 3.6 and 1.4 mM/g for 4-chloroguiacal or 2,6-dinitrophenol, respectively.

Many materials can act as the adsorbent for remove heavy metal or organics substance. These materials and their adsorption capacity were shown in table 4.5.

Table 4.5 Reported adsorption capacities (mmol/g) for various materials

adsorbents	Source	Cd	Cr	Hg	Pb
Bark	Randall *et al.*, 1974 [6]	0.28	0.37	2	0.88
Chitosan	Masri *et al.*, 1974 [7]	4.98	1.77	5.615	3.84
Coffee bean	Katsuya *et al.*,2006 [8]	0.06			
Fungi biomass:					
Mucor rouxii	Yan and Viravaghavan, 2003 [9]	0.06			0.082
Lignin	Srivastava *et al.*, 1994 [10]			0.75	7.67
Seaweed	Leush *et al.*, 1995 [11]	1.92			1.52
Zeolite	Santiago *et al.*, 1992 [12]		0.013		0.75

The adsorption capacity of MP-PCH which synthesized in this research has the ability to adsorb heavy metal more than several adsorbents such as bark, coffee bean, fungi biomass while chitosan, seaweed and zeolite can adsorb heavy metal greater than MP-PCH and this research did not examined about the Hg adsorption. However, the adsorption capacity of this adsorbent has ability more to used as the adsorbent for wastewater treatment.

4.5 CONCLUSIONS

PCH and MP-PCH derived from Na-bentonite clay have been synthesized by a surfactant directed assembly of silica species within the clay galleries. MP-PCH and DM-PCH have been functionalized through co-condensation reaction for finding a new application of these porous clays in wastewater treatment. From the N_2 adsorption-desorption data, The surface areas of PCH and MP-PCH increase significantly from pristine clay. From the study of adsorption properties of MP-PCH, the suitable pH values to adsorption Cd, Cu, Mn, Ni and Pb is pH 7 and the adsorption increased with increasing contact time. The adsorption capacity to adsorp heavy metals of MP-PCHs is 0.22, 0.24, 0.50 , 0.48 and 0.11mmol/g for Cd, Cu, Mn, Ni and Pb, respectively. Moreover, the increasing of MPTMS content in PCH can improve the ability of the MP-PCH. In the case of organics pollutant, the adsorption capacity of DM-PCH was 3.6 and 1.4 mM/g for 4-chloroguiacal or 2,6-dinitrophenol, respectively. They point out the potential of these PCHs for utilizing as the heavy metal and organic pollutant adsorbents in wastewater treatment.

4.6 ACKNOWLEDGEMENTS

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