



## COVER SHEET

---

This is the author-version of article published as:

**Frost, Ray and Zhou, Qin and He, Hongping and Xi, Yunfei (2007)  
Changes in the surfaces of adsorbed parnitrophenol on HDTMA  
organoclay -an XRD and TG study . *Journal of colloid and Interface  
Science*. 307(1):pp. 50-55.**

Accessed from <http://eprints.qut.edu.au>

© 2007 Elsevier B.V.

## Changes in the surfaces of adsorbed paranitrophenol on HDTMA organoclay -an XRD and TG study

Qin ZHOU<sup>1,2,3</sup>, Ray L. FROST<sup>2\*</sup>, Hongping HE<sup>1,2</sup>, Yunfei Xi<sup>2,4</sup>

<sup>1</sup> Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

<sup>2</sup> Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane, QLD 4001, Australia

<sup>3</sup> Graduate University of Chinese Academy of Sciences, Beijing 100039, China

<sup>4</sup> Centre for Environmental Risk Assessment & Remediation, University of South Australia, Mawson Lakes, SA, 5095, Australia

### Abstract

Surfactant modified montmorillonitic clays synthesised by the ion exchange using the hydrothermal reaction method have been compared using XRD and thermal analysis. X-ray diffraction (XRD) shows the changes in the surface properties of organo-clays through expansion with surfactant loading. A polynomial relationship exists between the basal spacing and the CEC loading described by the equation  $y = 0.3232x^2 + 0.2052x + 1.2834$  with an  $R^2 = 0.9955$ . Different arrangements of the surfactant molecules in the organo-clays are inferred from the changes in basal spacings. Paranitrophenol also causes the expansion of the montmorillonite clay and effects the arrangements of the surfactant molecules within the clay layers. Changes in the surfactant molecular arrangements were analysed by thermogravimetry. Additional thermal decomposition steps were observed when paranitrophenol is adsorbed on the organoclay.

**Key words:** montmorillonite, organo-clay, surfactant, high resolution thermogravimetric analysis, X-ray diffraction

### Introduction:

Smectites are widely used in a wide range of applications as a result of their high cation exchange capacity, swelling capacity, high surface areas and consequential strong adsorption capacities [1-5]. Among the swelling clays, the most common dioctahedral smectite is montmorillonite, which has two siloxane tetrahedral sheets sandwiching an aluminium octahedral sheet. Due to an isomorphic substitution within the layers (for example,  $Al^{3+}$  replaced by  $Mg^{2+}$  or  $Fe^{2+}$  in the octahedral sheet;  $Si^{4+}$  replaced by  $Al^{3+}$  in the tetrahedral sheet), the clay layer is negatively charged, which is counterbalanced by the exchangeable cations such as  $Na^+$ ,  $Ca^{2+}$  in the interlayer. The hydration of inorganic cations on the exchange sites causes the clay mineral surfaces to be hydrophilic. Thus natural clays are ineffective sorbents for organic compounds [6-8]. However such a difficulty can be overcome by ion exchange of the inorganic cations with organic cations.

Organo-montmorillonites are synthesized by intercalating cationic surfactants such as quaternary ammonium compounds into the interlayer space through ion exchange [9-11]. When using long-chain alkyl ammonium cations, hydrophobic partition medium within the clay interlayer can form and function analogously to a bulk organic phase. The interlayer height of clay before modification is relatively small and the intergallery environment is then hydrophilic. Intercalation of cationic surfactant not only changes the surface properties from hydrophilic to hydrophobic, but also greatly increases the basal spacing of the layers. Such surface property changes effect the applications of the organoclay. In particular the hydrophobic nature of the organoclay implies the material can be used as a filter material for water purification.

The objective of this research is to use organoclays to adsorb paranitrophenol (pnp) from an aqueous solution. We wish to use pnp as a test molecule to see if the organoclay will be effective in removing the pnp from water. This study seeks to show the changes in surface properties of the organoclay with and without the adsorption of pnp.

## **Experimental:**

### *1.1. Materials*

Montmorillonite ( $\text{Na}_{0.053}\text{Ca}_{0.176}\text{Mg}_{0.1}\cdot n\text{H}_2\text{O}$ )[ $\text{Al}_{1.58}\text{Fe}_{0.03}\text{Mg}_{0.39}$ ][ $\text{Si}_{3.77}\text{Al}_{0.23}$ ] $\text{O}_{10}(\text{OH})_2$  used was primarily Ca-Mt from Neimeng, China. The montmorillonite was cation exchanged with sodium ions by repeated reaction with sodium carbonate. Its cation exchange capacity (CEC) is 90.8meq/100g. The p-nitrophenol and HDTMAB used were of analytical grade chemical reagents. The aqueous solubility of p-nitrophenol is  $1.6\times 10^4$  mg/L. The surfactant used was hexadecyltrimethylammonium bromide labeled HDTMAB ( $\text{CH}_3(\text{CH}_2)_{15}(\text{CH}_3)_3\text{N}^+\text{Br}^-$ ).

### *1.2. Preparation of the organoclay*

The syntheses of surfactant-clay hybrids were undertaken by each of the following procedure: The pure Ca-Mt was added into  $\text{Na}_2\text{CO}_3$  solution, stirred for 3h with 800rpm and drops of HCl were added into the suspension to dissolve the  $\text{CO}_3^{2-}$ . Then the suspension was washed several times with deionized water until it was chloride free and dried at  $108^\circ\text{C}$ . Such a treated montmorillonite is designated as Na-Mt. There is much advancement comparing to the previous method about preparing the HDTMAB pillared montmorillonites [12, 13]. The clarifying surfactant solution was obtained when certain amounts HDTMAB were added into hot distilled water. Then certain amounts Na-Mt were added into the above mentioned solution and the mixtures were stirred slightly in order to provide the yield of spume in an  $80^\circ\text{C}$  water bath for 2h. The water/ Na-Mt mass ratio is 10. Then the suspension was subsequently washed with distilled water for 4 times. The moist solid material was dried at  $60^\circ\text{C}$  and ground with a mortar. The different amounts of  $[\text{HDTMA}]^+$  pillared montmorillonites were identified by 0.5CEC-Mt, 0.7CEC-Mt, 1.5CEC-Mt, 2.5CEC-Mt.

### *1.3. Adsorption of the paranitrophenol on the organoclay*

A total of 0.2g of different type montmorillonites were combined with 30mL of a range of concentrations of p-nitrophenol solution whose initial pH value is about 5.0 in 50mL Erlenmeyer flasks with glass caps. A range of concentrations from 100 mg/l to 8000 mg/l were used for the adsorption of paranitrophenol. The flasks were shaken for different time intervals at specific temperatures at 150rpm. After being centrifuged at 3500rpm for 10 minutes, the p-nitrophenol concentration in the aqueous phase was determined by a UV-260 spectrophotometer at 317nm, the detection limits being 0.05mg/L. The p-nitrophenol uptake on the montmorillonite was calculated by the following equation:  $Q = (C_0 - C_t) V / m$ , Q is the p-nitrophenol uptake,  $C_0$  is the initial concentration,  $C_t$  is the equilibrium concentration, V is the column of p-nitrophenol solution and m is the quality of sorbents. In order to get the optimum sorption of p-nitrophenol from aqueous solutions, conditions were modified according to specific parameters. The losses of the p-nitrophenol by both photochemical decomposition and volatilization were found to be negligible during adsorption [14].

#### **1.4. Characterization methods**

##### *1.4.1. Thermogravimetric analysis*

Thermogravimetric analyses of the surfactant modified montmorillonite hybrids were obtained using a TA Instruments Inc. Q500 high-resolution TGA operating at ramp 10 °C /min with resolution 6.0 °C from room temperature to 1000 °C in a high-purity flowing nitrogen atmosphere (60 cm<sup>3</sup>/min). Approximately 50 mg of finely ground sample was heated in an open platinum crucible. For the thermogravimetric analyses 4000 mg/l of paranitrophenol was used for the adsorption prior to TG analysis. This concentration was chosen as it is in the mid range of the concentrations used.

##### *1.4.2. X-ray diffraction*

The Neimeng montmorillonite and surfactant montmorillonite hybrids were pressed in stainless steel sample holders. X-ray diffraction (XRD) patterns were recorded using CuK $\alpha$  radiation ( $n = 1.5418\text{\AA}$ ) on a Philips PANalytical X' Pert PRO diffractometer operating at 40 kV and 40 mA with 0.25° divergence slit, 0.5° anti-scatter slit, between 3 and 15° (2 $\theta$ ) at a step size of 0.0167°. For XRD at low angle section, it was between 1 and 5° (2 $\theta$ ) at a step size of 0.0167° with variable divergence slit and 0.5° anti-scatter slit. For the XRD analyses 4000 mg/l of paranitrophenol was used for the adsorption on the organoclays prior to powder XRD analysis.

##### *1.4.3. Electron Microscopy*

A FEI QUANTA 200 scanning electron microscopy (SEM) is used for morphological studies. Neimeng montmorillonite and HDTMAB ( $\text{CH}_3(\text{CH}_2)_{15}(\text{CH}_3)_3\text{N}^+\text{Br}^-$ ) are dried at room temperature and coated with gold under vacuum conditions in an ionization chamber in an argon atmosphere for the SEM studies.

A Philips CM 200 transmission electron microscopy (TEM) at 200KV is used to investigate the microstructural of organo-clays. All samples were dispersed in 50% ethanol solution and then dropped on carbon coated films, dried in an oven at 50°C for 10 mins for TEM studies without using any resin.

## 2.0 Results and Discussion

### 2.0 Powder X-ray diffraction Analysis

With the cation exchange of the sodium ion for the cationic surfactant, expansion of the montmorillonite layers occurs. This expansion is readily measured by X-ray diffraction. Fig. 1a shows the XRD patterns of montmorillonite and surfactant intercalated montmorillonite hybrids and at different surfactant concentrations (0.5, 0.7, 1.5 and 2.5CEC). Fig. 1b shows the XRD patterns of montmorillonite and surfactant intercalated montmorillonite hybrids with adsorbed paranitrophenol and at different surfactant concentrations (0.5, 0.7, 1.5 and 2.5CEC). The basal spacing for the untreated calcium montmorillonite is 1.24 nm. This figure clearly shows the increase in the basal spacing from 1.24 nm for montmorillonite to 3.84 nm for 2.5CEC-mont as concentration of the surfactant used is increased. The graph also shows that for 1.5CEC-mont, there are two peaks for each samples, at around 1.71 and 2.71 nm. For the 2.5 CEC-mont there are multiple peaks at 3.84, 1.94, 1.21 and 0.94 nm. Figure 2 shows the relationship between the interlayer space and the CEC. It is clear that a polynomial relationship exists between these parameters which may be described by the equation  $y = 0.3232x^2 + 0.2052x + 1.2834$  with an  $R^2 = 0.9955$ .

The basal spacing for paranitrophenol (pnp) adsorbed on montmorillonitic clay is 1.49 nm compared with 1.24 nm for the non expanded clay. These numbers support the proposition that the paranitrophenol has penetrated the clay layers and expanded the clay by an additional 0.25 nm which is close to the size of the pnp molecule. The basal spacing for the 0.5 CEC-mont and 0.5 CEC-mont-4000 both have spacings of ~1.48 nm. However the basal spacing for 0.7 CECmont4000 (1.49 nm) is less than that for 0.7 CECmont of 1.78 nm. This suggests that the pnp has replaced some of the surfactant within the clay layers. For the 1.5 CECmont-4000 there are three distinct basal spacings of 1.06, 1.56 and 3.11 nm. The first two basal spacings may be attributed to the arrangement of the pnp molecules within the clay layers perpendicular to the clay siloxane surface or as molecules parallel to each other and at an angle to the siloxane surface. The 3.11 nm basal spacing is ascribed to the surfactant expanded montmorillonite. For the 2.5 CECmont-4000 four basal spacings of 0.91, 1.21, 1.77 and 3.48 nm are found. The first two values are quite comparable with 0.94 and 1.21 nm for the unabsorbed organoclay at 2.5 CEC. The two expansions of 1.77 and 3.48 nm are less than the values for the organoclay of 1.94 and 3.84 nm. These values suggest that the pnp molecules are effecting the arrangement of the surfactant molecules in the clay layers.

In the 0 to 0.5 CEC-mont it is suggested that monolayer structures of the

surfactant exist in the interlayer gallery. At higher CEC values it is concluded that for 1.5CEC-mont, both monolayer and bilayer structures of surfactant exist. For 2.5CEC-mont it is proposed that pseudotrimolecular layer arrangements exist as well as the monolayer and bilayer structures. This data shows that the basal spacings of organo-clay are not uniform, some bigger and some smaller. It is because when intercalating into the layer of montmorillonite, some layers are easier for surfactant to intercalate and some layers, on the contrary, are difficult for them to intercalate, so different basal spacings are formed. Such variation in the interlayer gallery space can be checked by TEM.

## 2.1 Thermogravimetric Analysis

The high resolution thermogravimetric analysis (HRTG) of the synthesised organo-clays is shown in Figure 3 (derivative weight %/°C versus temperature). Our previous studies have shown that the decomposition of organo-clay takes place in 4 steps: (1) water-desorption, (2) dehydration, (3) de-surfactant and (4) dehydroxylation of clay OH units. The results of the analysis of the DTG curves are reported in Table 1. In addition, from the XRD results there are three different structural arrangements of the surfactant. When the concentration of the surfactant is relatively low, the organic cations ion exchange with the Na<sup>+</sup> ions and mainly adhere to surface sites via electrostatic interactions. With the increase in concentration of surfactant, some of surfactant molecules attach to the surface of montmorillonite. If the concentration increases further, the concentration of the surfactant exceeds the CEC of clay. Surfactant molecules then adhere to the surface of other adsorbed surfactant cations by van der Waals forces.

The DTG curve of the non-intercalated montmorillonite shows two peaks at 485 and 617 °C. Both these DTG peaks are assigned to the dehydroxylation of the montmorillonite. The mass loss for these two steps is 3.9 and 2.1 %. The first dehydroxylation peak is assigned to hydroxyl units found at the ends of the clay layers whereas the second peak is ascribed to hydroxyl units within the clay structure. The HDTMAB (CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>(CH<sub>3</sub>)<sub>3</sub>N<sup>+</sup>Br<sup>-</sup>) decomposes or is combusted at 202 °C. For the 0.5 CEC-mont a DTG peak is observed at 85 °C attributed to the loss of adsorbed water. A second peak is observed at 117 °C and is assigned to the loss of bound water. Two DTG peaks are observed at 317 and 365 °C and are attributed to the combustion and loss of the surfactant molecule from between the clay sheets. It is proposed that the reason for the two peaks is due to different structural arrangements of the surfactant molecules in the interlayer gallery. The two peaks for 0.5 CEC-mont at 483 and 602 °C are as before assigned to the dehydroxylation of the montmorillonite. It is noted that there is a significant shift to lower temperatures of the dehydroxylation of the organoclay. This shift is attributed to the penetration of the methyl groups of the surfactant into the siloxane layer. This may provide a mechanism for the removal of the OH units as water vapour.

The DTG of the 0.7CEC-mont displays two peaks at ~85 and 116 °C which are as before attributed to adsorbed water and chemically bonded water. A thermal decomposition step additional to that for the 0.5 CEC is observed at 254 °C and is attributed to surfactant molecules adsorbed on the external surfaces of the organoclay. Two peaks at 317 and 368 °C with 5.4 and 8.76 % mass loss are assigned to the mass

loss of surfactant molecules in the interlayer gallery. The fact that the surfactant molecules are not lost until 368 °C compared with the loss of the pure surfactant at 202 °C shows how strongly the surfactant molecules are bonded in the interlayer of the montmorillonite. Further the second dehydroxylation temperature of the montmorillonite for the 0.7 CEC-mont is at 595 °C and is significantly lower than for the pure montmorillonite. This shows that the surfactant molecule is bonding to the siloxane surface. For the 1.5 CEC-mont an additional peak is observed at 218 °C with a 12.3 % mass loss attributed to surfactant molecules adsorbed on the external surfaces of the organoclay. For the 2.5 CEC-mont four decomposition steps are observed at 205, 278, 380 and 607 °C with mass losses of 29.0, 6.7, 7.5 and 3.32 %. The last thermal decomposition step is attributed to the dehydroxylation of the montmorillonite. It is noted that for the 1.5 CEC-mont and 2.5 CEC-mont that one of the thermal decomposition steps occurs at 218 °C (1.5 CEC) and 205 °C (2.5 CEC) which corresponds to the thermal decomposition of pure HDTMA. Such a thermal decomposition is not observed for montmorillonites loaded with surfactant at concentrations less than 1.0 CEC. This observation is evidence for the adsorption of the surfactant molecules on the external clay surfaces.

The DTG patterns for paranitrophenol adsorbed on the organoclays are shown in Figure 4. Paranitrophenol sublimes to a vapour at 131 °C. When adsorbed on the untreated montmorillonite 3.85 % is lost at 179 °C and 2.0 % mass loss is found at 285 °C. This mass loss is attributed to some paranitrophenol being intercalated between the clay layers. The dehydroxylation of the montmorillonite now occurs at the higher temperature of 625 °C. This provides evidence for the chemical reaction of the paranitrophenol and the siloxane surfaces of the montmorillonite. It is noted that a thermal decomposition at 797 °C is observed but it is not known what is the reason for this higher temperature decomposition. The thermal decomposition of 0.5CEC-mont with adsorbed paranitrophenol is very different to that of the organoclay. Two thermal decomposition steps not observed in the decomposition of the 0.5CEC-mont are found at 192 and 278 °C with mass losses of 4.45 % and 4.1 %. These mass loss steps are ascribed to paranitrophenol adsorbed on the organoclay. The reason for two mass loss steps is attributed to the desorption of paranitrophenol and the removal of paranitrophenol from between the clay layers. The mass loss at 368 °C of 2.66 % is the loss of the surfactant. Two additional mass loss steps at 417 and 466 °C are observed for the 0.5CEC-mont with adsorbed paranitrophenol. The observation of these two mass loss steps confirms changes in the structure of the surfactant within the clay layers and the paranitrophenol is reacting with the clay surfaces.

A similar DTG pattern is observed for 0.7CEC-mont. Two thermal decomposition steps are observed at 188 and 268 °C. These are attributed to the loss of adsorbed paranitrophenol. The thermal decomposition step at 370 °C is the same as for 0.5 CEC-mont. Two additional thermal decomposition steps are observed at 408 and 455 °C and are attributed to the loss of surfactant molecules and paranitrophenol. It is proposed that the paranitrophenol causes the structural rearrangement of the surfactant molecules with the clay layers. When the surfactant loading is increased above 1.0 CEC the thermal decomposition patterns resemble that of the organoclay without paranitrophenol adsorption. The 1.5 CEC-mont with adsorbed paranitrophenol shows three decomposition steps at 187, 222 and 227 °C. The dehydroxylation of the organoclay occurs at 387 °C. In Figure 4, the higher temperature steps at around 607 °C are not shown in the 1.5 and 2.5 CEC DTG curves.

The reason for this is that these DTG peaks are hidden in the background. The intense DTG peaks at 222 °C (1.5 CEC) and 191 °C (2.5 CEC) are so large that smaller peaks are buried in the background. The temperatures for the loss of paranitrophenol are significantly greater than that of pure paranitrophenol. This shows that the paranitrophenol is strongly bonded to the organoclay.

## **Conclusions:**

Water purification is of extreme importance in many parts of the world, including Australia and China. Many of the world's water ways and water sources are polluted or contaminated with a range of chemicals including pesticides and herbicides. In this work, we have used paranitrophenol as a test chemical to design and test an organoclay for the removal of pnp from an aqueous medium. This work has shown that the pnp intercalates the organoclay and displaces the surfactant molecules or rearranges the structure of the surfactant molecule within the organoclay interlayer. Future work will test the use of this organoclay and other di and trialkyl clays for the removal of herbicides and pesticides from water. Further work will need to test the efficiency of the pnp adsorption.

HDTMA<sup>+</sup> pillared montmorillonites were obtained by pillaring different amounts of the surfactant hexadecyltrimethylammonium bromide (HDTMAB) into sodium montmorillonite in an aqueous solution. The optimum conditions and batch kinetics of sorption of p-nitrophenol from aqueous solutions need to be studied. Contact time and pH value will affect the sorption of p-nitrophenol. The maximum p-nitrophenol absorption/adsorption is thought to occur when solution pH is approximately equal to the pK<sub>a</sub> of the p-nitrophenol ion deprotonation reaction (pH = 7.15~7.35). X-ray diffraction analysis showed that surfactant cations had been pillared into the interlayer and the p-nitrophenol affected the arrangement of surfactant. With the increased concentration of surfactant cations, the arrangement of HDTMA<sup>+</sup> within the clay interlayer changes and adsorption of p-nitrophenol increases.

## **Acknowledgements**

This work was funded by National Natural Science Foundation of China (Grant No. 40372029) and Natural Science Foundation of Guangdong Province (Grant No. 030471 and 05103410). The Inorganic Materials Research Program, Queensland University of Technology, is gratefully acknowledged for infra-structural support.

## References

1. G. R. Alther, *Contaminated Soils* 8 (2003) 189.
2. G. R. Alther, *Special Publication - Royal Society of Chemistry* 259 (2000) 277.
3. C. Breen, R. Watson, J. Madejova, P. Komadel and Z. Klapyta, *Langmuir* 13 (1997) 6473.
4. S. K. Dentel, J. Y. Bottero, K. Khatib, H. Demougeot, J. P. Duguet and C. Anselme, *Water Research* 29 (1995) 1273.
5. H. P. He, J. G. Guo, X. D. Xie and J. L. Peng, *Environment International* 26 (2001) 347.
6. J. H. Kim, W. S. Shin, Y. H. Kim, S. J. Choi, Y. W. Jeon and D. I. Song, *Water science and technology : a journal of the International Association on Water Pollution Research* 47 (2003) 59.
7. R. Prost and B. Yaron, *Soil Science* 166 (2001) 880.
8. D. Chaiko, (University of Chicago, USA). Application: WO WO, 2002, p. 24 pp.
9. H. He, R. L. Frost, F. Deng, J. Zhu, X. Wen and P. Yuan, *Clays and Clay Minerals* 52 (2004) 350.
10. N. M. Soule and S. E. Burns, *Journal of Geotechnical and Geoenvironmental Engineering* 127 (2001) 363.
11. M. M. Mortland, S. Shaobai and S. A. Boyd, *Clays and Clay Minerals* 34 (1986) 581.
12. J. Zhu, H. He, J. Guo, D. Yang and X. Xie, *Kuangwu Yanshi* 23 (2003) 1.
13. J. Zhu, H. He, J. Guo, D. Yang and X. Xie, *Chinese Science Bulletin* 48 (2003) 368.
14. L. Zhu and B. Chen, *Environmental Science and Technology* 34 (2000) 2997.

## **List of Tables**

Table 1 Thermal decomposition steps for organoclay at a range of CEC compositions and for paranitrophenol adsorbed on the organoclay.

## **List of Figures**

Figure 1a X-ray diffraction patterns of sodium montmorillonite, 0.5, 0.7, 1.5 and 2.5 CEC organoclay

Figure 1b X-ray diffraction patterns of sodium montmorillonite, 0.5, 0.7, 1.5 and 2.5 CEC organoclay with adsorbed paranitrophenol

Figure 2 Variation of interlayer distance with CEC value

Figure 3 Thermal decomposition patterns of sodium montmorillonite, 0.5, 0.7, 1.5 and 2.5 CEC organoclay

Figure 4 Thermal decomposition patterns of sodium montmorillonite, 0.5, 0.7, 1.5 and 2.5 CEC organoclay with adsorbed paranitrophenol



<i>Sample name</i>	<i>First Decomposition step</i>	<i>Second Decomposition step</i>	<i>Third Decomposition step</i>	<i>Fourth Decomposition step</i>	<i>Fifth Decomposition step</i>
Na-Mt				485°C 3.29%	617°C 2.11%
HDTMA B	202°C 99.77%				
p-nitrophenol	131°C 99.2%				
0.5CEC			365°C 8.98%		602°C 5.29%
0.7CEC	254°C, 1.4%	317°C 5.4%	368°C 8.76%		595°C 5.13%
1.5CEC	218°C 12.32%	281°C 5.92%	380°C 7.82%		607°C 3.86%
2.5CEC	205°C 29.04%	278°C, 6.7%	380°C 7.52%		607°C 3.32%
Na-4000	179°C 3.85%	285°C 2.01%			625°C 2.61%
0.5CEC-4000	192°C 4.45%	278°C 4.1%	368°C 2.62%	417°C 6.45%	466°C 5.13%
0.7CEC-4000	188°C, 8.74%	268°C 3.07%	370°C 2.04%	408°C 9.44%	455°C 3.79%
1.5CEC-4000	187°C 8.53%	222°C 14.63%	277°C 8.51%	387°C 8.73%	515 3.81%
2.5CEC-4000	191°C 43.66%	227°C 4.02%	389°C 8.31%		

**Table 1 Thermal decomposition steps for organoclay at a range of CEC compositions and for paranitrophenol adsorbed on the organoclay.**

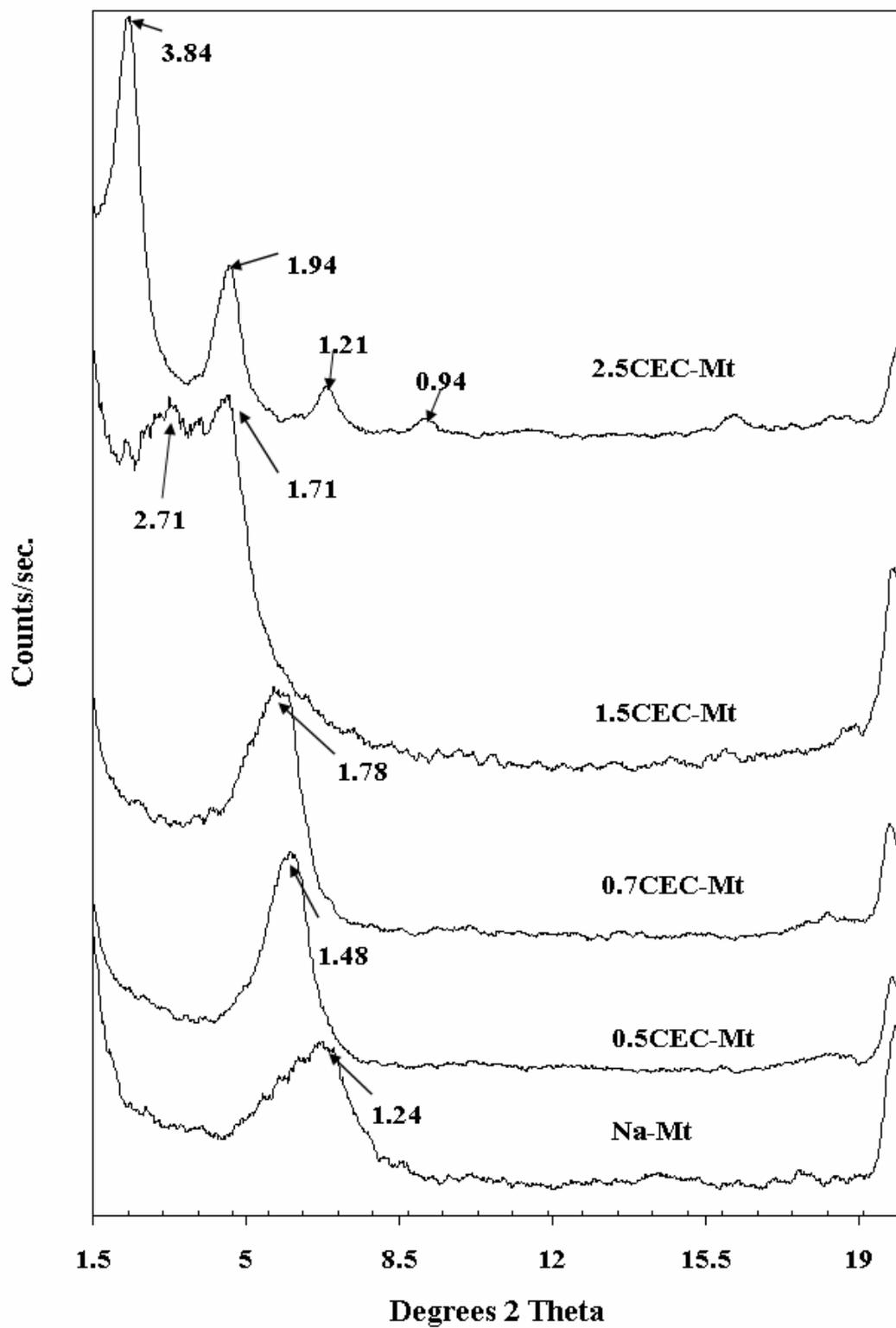


Figure 1a

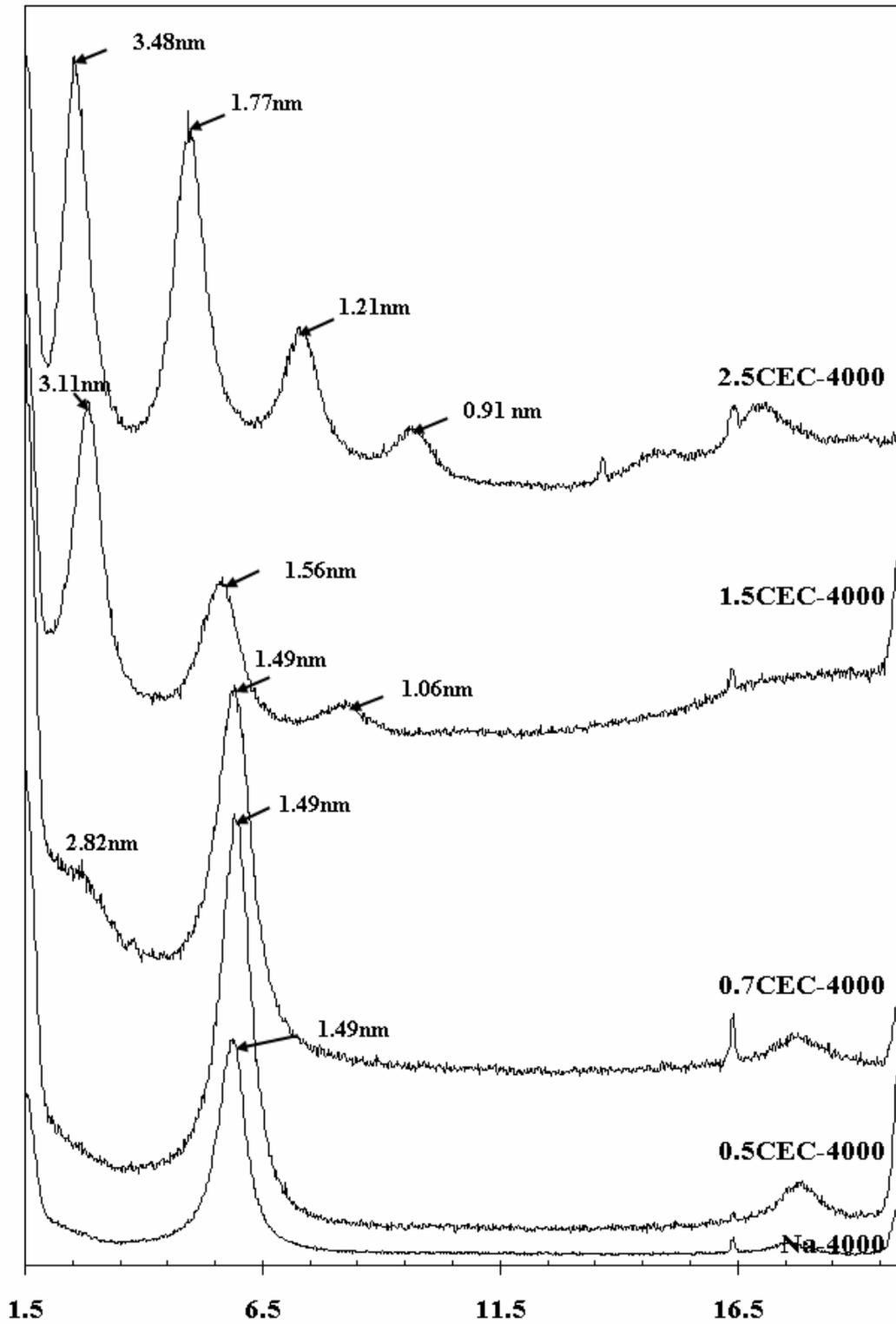
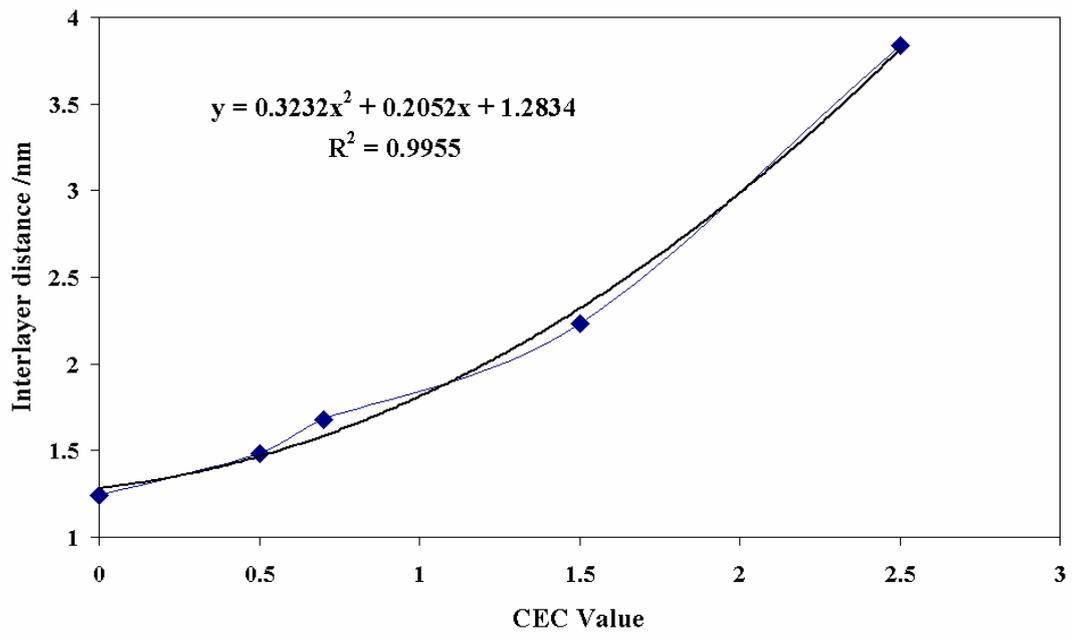


Figure 1b



**Figure 2**

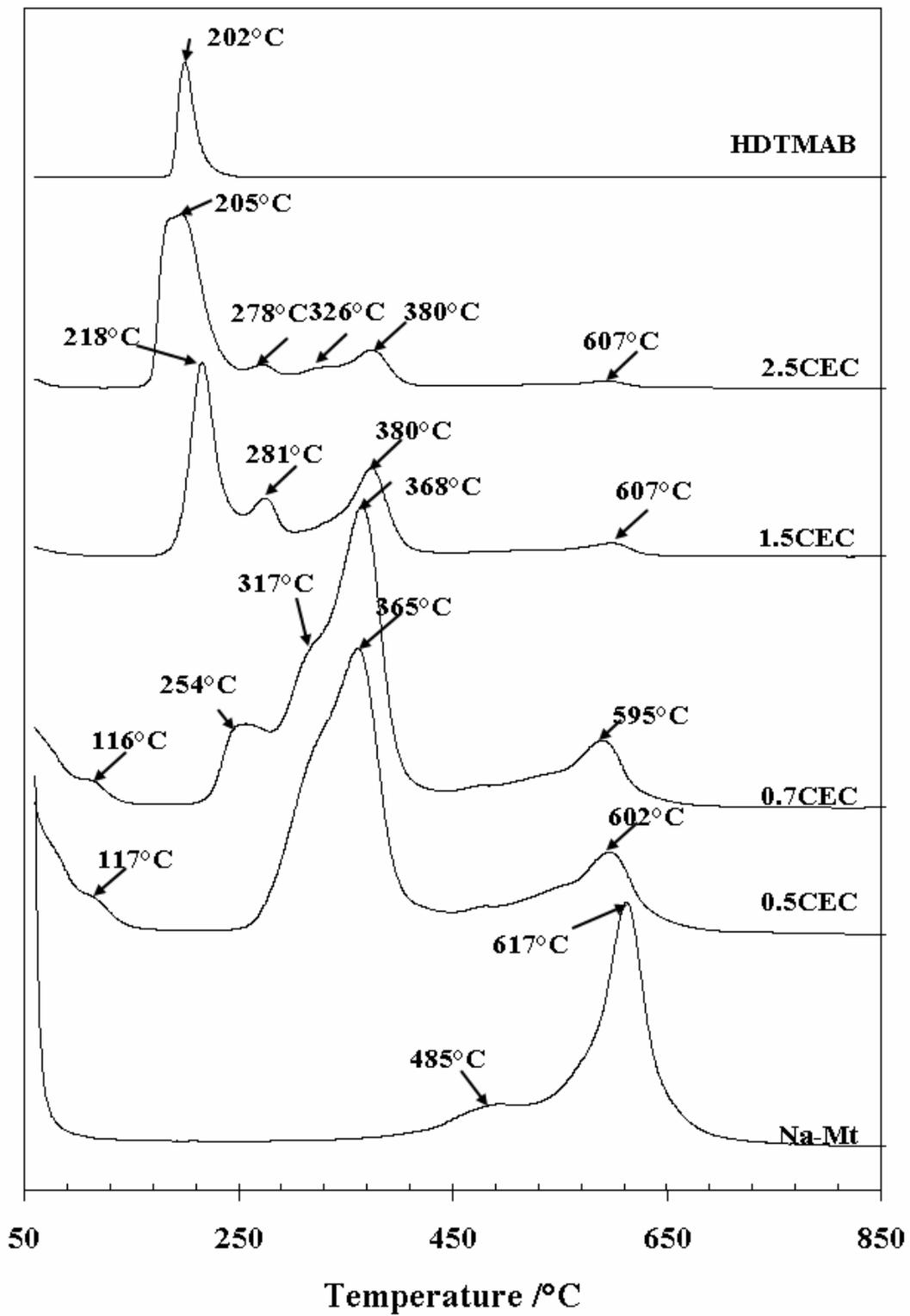


Figure 3

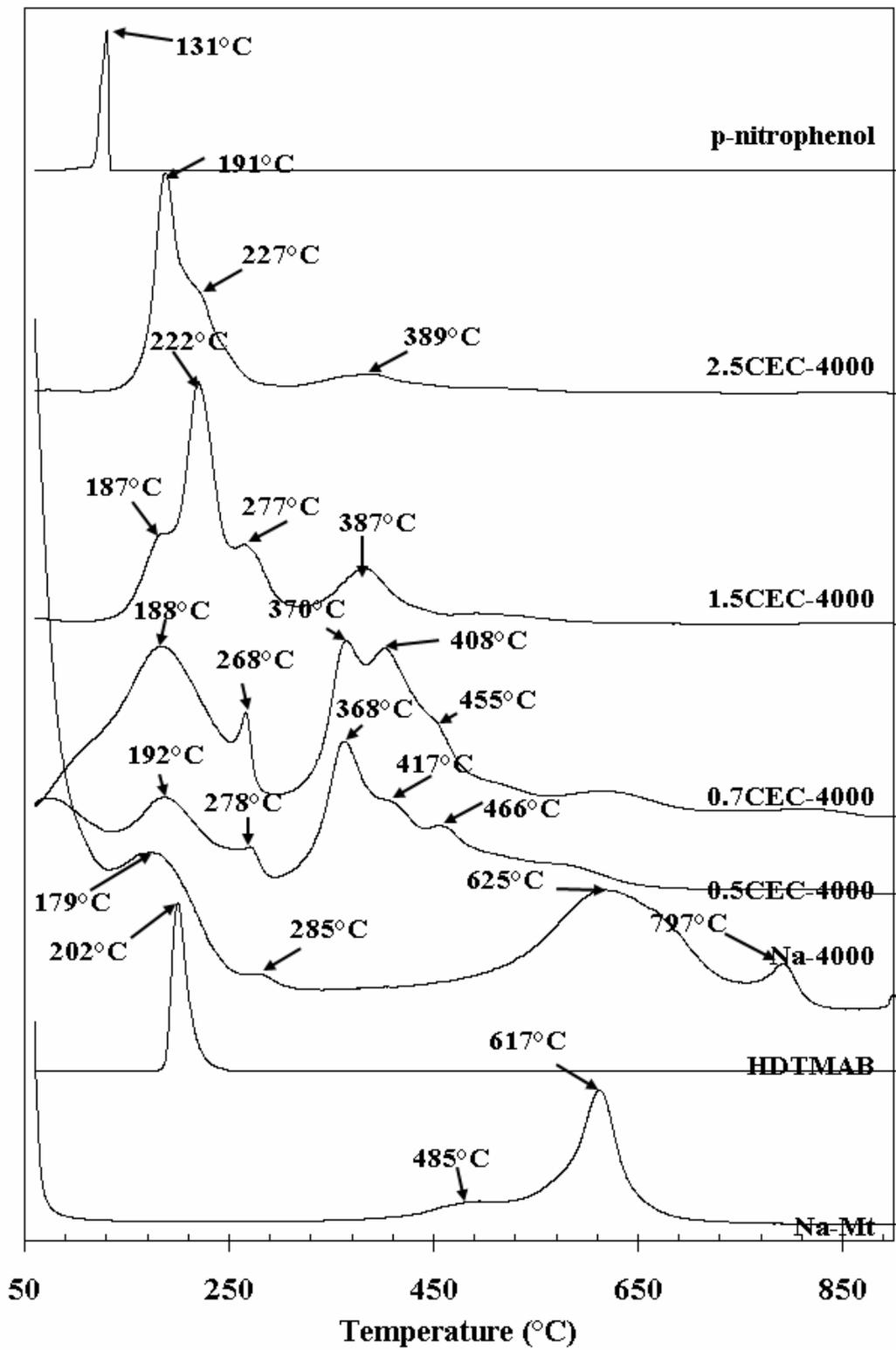


Figure 4