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Pore structure of surfactant modified montmorillonites

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Abstract - A series of organoclays with different surfactant arrangements were prepared by ion exchange. The resulting organoclays were investigated using a combination of characterization techniques, including XRD, FTIR, TG and N₂ adsorption-desorption. In the present study, the pores within the organoclays were discussed on the basis of the microstructural parameters, including BET-N₂ surface area, pore volume, pore size, surfactant loading and distribution. The results show that both BET-N₂ surface area and pore volume decrease from low to high packing density of the surfactant as the average pore size increases. Two basic organoclay models were proposed for hexadecyltrimethylammonium bromide (HDTMAB) modified montmorillonites: 1) the surfactant mainly occupied the clay interlayer and 2) both the clay interlayer space and external surface were modified by surfactant. This study demonstrates that the pore structure of the resulting organoclays has a significant influence on the sorption efficiency and mechanism of p-nitrophenol onto the organoclays.

Keywords - Organoclay, BET-N₂ surface area, Pore size and volume, Sorption efficiency and mechanism.

INTRODUCTION

Organoclays represent a family of materials with hydrophobic surfaces, resulting from modifying swelling clays with various surfactants. During the last two decades, organoclays have attracted great interest in various applications, including adsorbents for organic contaminants (Stackmeyer, 1991; Zhu and Chen, 2000; Zhu et al., 2000) and clay-based nanocomposites (Ray and Okamoto, 2003; Herrera et al., 2004).

Montmorillonite is hydrophilic in nature due to the cations within interlayer region, making natural clays ineffective sorbents for organic compounds. Modifying clay mineral surfaces with surfactants to convert the hydrophilic silicate surface to an organophilic surface is a strategic step in the preparation of clay-based sorbents for organic pollutants (Bergaya and Lagaly, 2001). Various organoclays have been synthesized and demonstrated to be effective as sorbents for organic contaminants in water (Smith and Galan, 1995; Zhu et al., 1998; Shen, 2001; Wang et al., 2004; Yilmaz and Yapar, 2004). Meanwhile, different sorption mechanisms are proposed, depending on the characteristics of the used surfactants and organic pollutants (Boyd et al., 1988a; Lee et al., 1990; Jaynes and Boyd, 1991; Smith and Galan, 1995; Zhu and Chen, 2000; Yilmaz and Yapar, 2004). Wang et al. (2004) suggested that the sorption capacity of organoclays strongly depends on the surfactant loadings within the clay interlayer and others proposed that the characteristics of the surfactants and the organic contaminants significantly affected the sorption mechanism and capacity.

Previous study showed that “house of cards” structure is extensively existed in clays and clay-based materials (Yuan et al., 2006). Also, the arrangements of surfac-

tants within the clay interlayer spaces have been demonstrated from monolayer, to bilayer, then to paraffin-type monolayer and finally to paraffin-type bilayer with the increase of the surfactant loading via various techniques, including X-ray diffraction (XRD) (Lagaly, 1981; Zhu et al., 2003), Fourier transform infrared spectroscopy (FTIR) (Vaia et al., 1994; He et al., 2004a), Raman spectroscopy (He et al., 2004b), thermogravimetric measurement (TG) (Xie et al., 2002; Yariv, 2004; He et al., 2005), nuclear-magnetic-resonance (NMR) (He et al., 2004c) and transmission electron microscopy (TEM)) (Lee and Kim, 2002; Yaron-Marcovich et al., 2005; He et al., 2006). Here, an interesting question arises, i.e., what happens for the “house of cards” structure during the modification of clays with surfactants?

To the best of our knowledge, only a few studies have tried to elucidate the pore structure of the organoclays, and correlate the microstructure and sorption characteristics of organoclays. (Wang et al., 2004; Mandalia and Bergaya, 2006). This is of high importance for well understanding the sorption mechanism and the selection of organoclays for wastewater treatment and contaminated soil and groundwater remediation. Hence, the main aim of this study is to investigate the pore structure of surfactant modified montmorillonites and their consequent influence on the sorption mechanism. The compound p-nitrophenol was chosen as model contaminant. This study provides new insights of the pore structure of organoclays and its effects on the sorption mechanism.

MATERIALS AND METHODS

Ca-montmorillonite (Ca-Mt) was obtained from Hebei, China. The sample was purified by sedimentation and the montmorillonite with a particle size less than 2 μm was collected for use. Its cation exchange capacity (CEC) is 90.8 meq/100g, determined by NH_4^+ method as described in the literature (He et al., 2001). The surfactant used in this study is hexadecyltrimethylammonium bromide (HDTMAB) with a purity of 99%, provided by YuanJu Chem. Co. Ltd., China. Analytical grade p-nitrophenol with a water solubility of 1.6×10^4 mg/L was used.

Synthesis and Characterization of Organoclay

The synthesis of HDTMAB modified montmorillonites followed the method as described in the literature (He et al., 2004a). Before the investigation of N_2 adsorption-desorption to determine the pore structure parameters, the organoclays were characterized using XRD, FTIR, TG and ^{13}C MAS NMR. The interlayer structure of the organoclays and conformations of the loaded surfactants have been determined.

N_2 adsorption-desorption isotherms were gained at liquid nitrogen temperature with a Micromeritics ASAP 2010 gas sorption analyzer (Quantachrome Co., USA). Before measurement, the samples were pre-heated at 80 $^\circ\text{C}$ under N_2 for ca. 24 h. The specific surface area was calculated by the BET equation and the total pore volumes were evaluated from nitrogen uptake at relative pressure of ca. 0.99. The Barrett-Joyner-Halenda (BJH) method was used to evaluate the average pore diameter (APD) (Barrett et al., 1951).

p-nitrophenol sorption

The Na-Mt or organoclay samples (0.1 g) were combined with 15 mL of p-nitrophenol solution (5-60 mg/L) in 50-ml Erlenmeyer flasks with glass caps. The flasks were shaken for 1 h at 25 °C on a shaker at 200 rpm. The solution pH value is 8.0. After centrifugation, the p-nitrophenol concentration in the aqueous phase was determined by a UV-260 spectrophotometer (Shimadzu Co., Kyoto, Japan) at 317 nm with a detection limit of 0.05 mg/L. The p-nitrophenol uptake on Na-Mt or organoclays was calculated by the following equation:

$$Q = (C_0 - C_e) V / m$$

In this equation, Q is the p-nitrophenol uptake, C_0 is the initial concentration, C_e is the equilibrium concentration, V is the volume of p-nitrophenol solution and m is the quantity of the adsorbent. The loss of p-nitrophenol by photochemical decomposition, sorption to Erlenmeyer flask and volatilization were found to be negligible (Zhu et al., 2000).

RESULTS AND DISCUSSION

The pore characteristics of the organoclays

The structure parameters of Na-Mt and the organoclays, including basal spacings, specific surface area (S_{BET}), total pore volume (V_p), average pore diameter (APD), pore diameter with highest concentration (APD_{HC}) and surfactant loading (SL), are summarized in Table 1. On the basis of the configuration of $HDTMA^+$ and the inter-layer distances of montmorillonite and the organoclays, different $HDTMA^+$ arrange-

ment models within the montmorillonite interlayer space are proposed, i.e., monolayer in 0.5CEC-Mt, bilayer in 0.7CEC-Mt, pseudotrilayer in 1.0CEC-Mt, paraffin monolayer in 1.5CEC-Mt and paraffin bilayer in 2.0CEC-Mt and 2.5CEC-Mt, respectively, in agreement with previous experimental and molecular modeling reports (Lagaly, 1981; Yui et al., 2002; Zhu et al., 2003; Zeng et al., 2004; He et al., 2006).

As shown in Figure 1, the BET surface areas of the clay/organoclays decrease in the order Na-Mt \gg 0.5CEC-Mt > 0.7CEC-Mt > 1.0CEC-Mt > 1.5CEC-Mt > 2.0CEC-Mt > 2.5CEC-Mt. A dramatic decrease of the BET-N₂ surface area was observed from Na-Mt to 0.5CEC-Mt. A similar trend is also found for the pore volumes of Na-Mt and the resulting organoclays as shown in Figure 1.

The nitrogen adsorption-desorption isotherms of Na-Mt and organoclays are shown in Figure 2. The adsorption isotherms are of Type II in the Brunauer, Demming, Demming and Teller (BDDT) classification (Brunauer et al., 1940). A large uptake of nitrogen was observed close to saturation pressure, exhibiting multilayer adsorption and implying the presence of mesopores (Wang et al., 2004). This is in agreement with the pore diameter calculated from Barrett-Joyner-Halenda (BJH) desorption isotherm as shown in Table 1. Meanwhile, it could be observed that the pore volume decreases dramatically with the loading of surfactants. The decrease of pore volume obviously relates with the amount of the loaded surfactants, suggesting that the surfactants are loaded into the pores. This suggestion is supported by the HRTG results, i.e., the surfactant within the pores show similar thermal stability to those adsorbed on the clay surface (He et al., 2005). The hysteresis loops of the isotherms of Na-Mt and the

organoclays resemble H5 in the IUPAC classification (Gregg and Sing, 1982), indicating “ink-bottle” like pores in the related clays. These pores could be described as a “house of cards” structure (Lagaly and Ziesmer, 2003). However, with the increase of the loaded surfactant, the sudden release of nitrogen gas at $P/P_0 \approx 0.5$ becomes less and less prominent, implying that most spaces of the interparticle pores are occupied by the loaded surfactants. This is in agreement with the pore size distribution as shown in Figure 3, calculated from BJH desorption isotherm. The inserted diagrams (pore diameter distribution between 3 – 10 nm) clearly show that the dominant pores within Na-Mt have a diameter about 4.0 nm while those for organoclays about 3.3 nm. For Na-Mt and the organoclays prepared at low concentration of surfactant (< 1 CEC), the pore size distribution has only a small range between 3 - 4 nm. However, when the loaded surfactant is more than 1 CEC (for 1.5CEC-Mt, 2.0CEC-Mt and 2.5CEC-Mt), there is a prominent distribution of pore sizes besides the range of 3 – 4 nm. This is due to the loading of surfactants into the interparticle pores resulting in an enlargement of the corresponding pore size. Accordingly, an obvious increase of APD was observed from Na-Mt to organoclays with low surfactant loadings, and then to organoclays with high surfactant loadings.

As shown in Figure 1, the organoclays can be divided into two groups on the basis of their BET-N₂ surface area and pore volume. Group I includes 0.5CEC-Mt, 0.7CEC-Mt and 1.0CEC-Mt, with similar BET-N₂ surface area of 9.07 – 11.89 m²/g and pore volume of 0.06 cm³/g. Group II is 1.5CEC-Mt, 2.0CEC-Mt and 2.5CEC-Mt, with similar BET-N₂ surface area of 0.82 – 4.31 m²/g and pore volume of 0.01-0.04

cm³/g. Our previous studies have shown that the intercalated HDTMA⁺ cations in 0.5CEC-Mt, 0.7CEC-Mt and 1.0CEC-Mt lie flat on clay surface while a paraffin arrangement in 1.5CEC-Mt, 2.0CEC-Mt and 2.5CEC-Mt (Zhu et al., 2003). This suggests that the BET-N₂ surface area and pore volume of the organoclays relate with the surfactant arrangement models.

As is well known, montmorillonite is capable of interlamellar expansion with the intercalation of surfactants. The large intercalated HDTMA⁺ cations may result in serious blocking of the interlamellar space that inhibits the passage of nitrogen molecules, leading to a decrease of BET surface area and pore volume of the resultant organoclays. In the other hand, previous studies (Juang et al., 2002; He et al., 2005) showed that the surfactants not only enter into the interlayer spaces but also locate outside the clay. In the latter case, the loaded surfactant occupies the interparticle pores with a “house of cards” structure, resulting in a decrease of BET surface area and macro-pore volume. The amounts of the loaded surfactant in the resulting organoclays are shown in Table 1, calculated from high-resolution thermogravimetric analysis. Our calculation shows that more than 1 CEC of surfactant can be loaded into the resulting organoclays, i.e., 1.19 CEC in 1.5CEC-Mt, 1.9 CEC in 2.0CEC-Mt and 2.4 CEC in 2.5CEC-Mt. The excess part of surfactant occupies the interparticle pores and results in a decrease of pore volume and BET surface area.

Combining of the pore structure, the arrangement models of the intercalated surfactants within the interlayer spaces and surfactant distribution, two basic schematics of organoclays are proposed (Figure 4): 1) the surfactant mainly occupies the clay in-

terlayer spaces and 2) both the clay interlayer space and external surface are modified by surfactant. The schematic is helpful to well understand the sorption mechanism of organic contaminants onto organoclays.

Sorption mechanism of p-nitrophenol onto organoclays

Sorption curves for p-nitrophenol at pH = 8 and 25 °C on Na-Mt and the corresponding organoclays are shown in Figure 5. Obviously, it can be seen that the sorption mechanism of p-nitrophenol onto organoclays strongly depends on the pore characteristics of the used organoclays.

For Na-Mt, the sorption isotherm display S-type and the interaction between clay and p-nitrophenol has been demonstrated to be surface adsorption (Banat et al., 2000; Al-Asheh et al., 2003; Yilmaz and Yapar, 2004). For the organoclays in group I (e.g. 0.5CEC-Mt, 0.7CEC-Mt and 1.0CEC-Mt), the sorption curves are very similar to S-type isotherms and those for 0.5CEC-Mt and 0.7CEC-Mt almost overlap each other. This suggests a similar sorption mechanism involved. As indicated by a number of previous studies, the sorption mechanisms for montmorillonite modified by HDTMAB below 1.0 CEC concentration contains both adsorption and partition (Zhu et al., 2000; Al-Asheh et al., 2003; Cruz-Guzmán et al., 2004). However, for 1.5CEC-Mt, 2.0CEC-Mt and 2.5CEC-Mt in group II, the sorption curves are definitely linear, reflecting a partition process and the highest sorption efficiency (Boyd et al., 1988b; Chun et al., 2003). Our analysis demonstrates that Na-Mt has the largest BET-N₂ surface area and pore volume whereas organoclays in group II have the lowest BET-N₂ surface area and pore volume. This reflects that BET-N₂ surface area and pore volume are not the key factors that control the affinity between clay/organoclay and organic pollutants. However, our study suggests that the distribution of the loaded surfactants has a prominent influence on the sorption of p-nitrophenol onto organoclays. As shown in Figure 4, when the surfactant loading is more than 1 CEC (samples

in group II), the excess surfactant probably occupies interparticle pores with a “house of cards” structure. Meanwhile, the intercalated surfactant within the clay interlayer adopts a paraffin arrangement model. In this case, the clay layers are almost completely enclosed by surfactant and an organic medium can be visualized as formed within the clay layer space and in the interparticle pores. This organic medium is of high importance for the excellent sorption capacity of organoclay to organic contaminants, and is available as a partition medium for contaminant sorption (Boyd et al., 1988b; Chun et al., 2003).

For organoclays with a surfactant loading less than 1 CEC (group I), the surfactant mainly occupies the clay interlayer spaces rather than the interparticle pores. In this case, the clay interlayer is organophilic whereas the external clay surface is hydrophilic. The organophilic clay interlayer is available as a partition medium for contaminant sorption whereas the external clay surface is available for surface adsorption (Lee et al., 1990; Jaynes and Boyd, 1991; Celis et al., 2000; Cruz-Guzmán et al., 2004). Accordingly, both adsorption and partition are involved in the sorption mechanism.

CONCLUSIONS

Our study indicates that both the BET-N₂ surface area and pore volume of the organoclays decreased as the increase of surfactant loading. Combining of the pore structure and the distribution of the loaded surfactants, two basic schematics of organoclays are proposed, i.e., 1) the surfactant mainly occupies the clay interlayer spaces and 2) both the clay interlayer space and external surface are modified by surfactant. The distribution and arrangement of surfactant in the organoclays have a more prominent influence on the sorption efficiency and mechanism than BET-N₂ surface area, pore volume, or pore diameter. When the loaded surfactant is less than 1

CEC, the sorption of p-nitrophenol onto organoclays involves both surface adsorption and partition. However, when the loaded surfactant is more than 1 CEC, the sorption mechanism mainly involves partition.

Acknowledgements

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Table 1 Structural parameters and surfactant loadings of Na-Mt and the HDTMA organoclays.

Sample	d_{001} (nm)	S_{BET} (m^2/g)	V_p (cm^3/g)	APD_{HC} (nm)	APD	SL (%)	SL (vs CEC)
Na-Mt	1.24	54.97	0.107	4.0	6.82	-	-
0.5CEC-Mt	1.48	11.89	0.061	3.3	7.49	9.73	0.33
0.7CEC-Mt	1.78	10.06	0.060	3.3	8.73	16.73	0.61
1.0CEC-Mt	1.95	9.07	0.056	3.3	9.11	22.13	0.86
1.5CEC-Mt	2.23	4.31	0.037	3.3	12.69	28.19	1.19
2.0CEC-Mt	3.61	1.19	0.011	3.3	14.14	38.73	1.9
2.5CEC-Mt	3.84	0.82	0.007	3.3	16.28	44.17	2.4

S_{BET} : specific surface area.

V_p : pore volume determined by BJH method from N_2 desorption isotherm.

APD_{HC} : pore diameter with the highest concentration, determined by the curve of BJH desorption dV/dD pore volume.

APD: average pore diameter determined by the curve of BJH desorption dV/dD pore volume.

SL: surfactant loading within the corresponding organoclay, evaluated from high-resolution thermogravimetric analysis.

SL(vs CEC): surfactant loading expressed in CEC of montmorillonite (100 g).

Figure Captions

Figure 1 BET-N₂ surface area and pore volume of Na-Mt and organoclays.

Figure 2 Nitrogen adsorption-desorption isotherms of Na-Mt and organoclays.

Figure 3 The pore size distribution curves of Na-Mt and organoclays.

Figure 4 The schematics of Na-Mt and organoclays.

Figure 5 Sorption curves of p-nitrophenol in Na-Mt and organoclays (pH=8.0, T=25 °C).

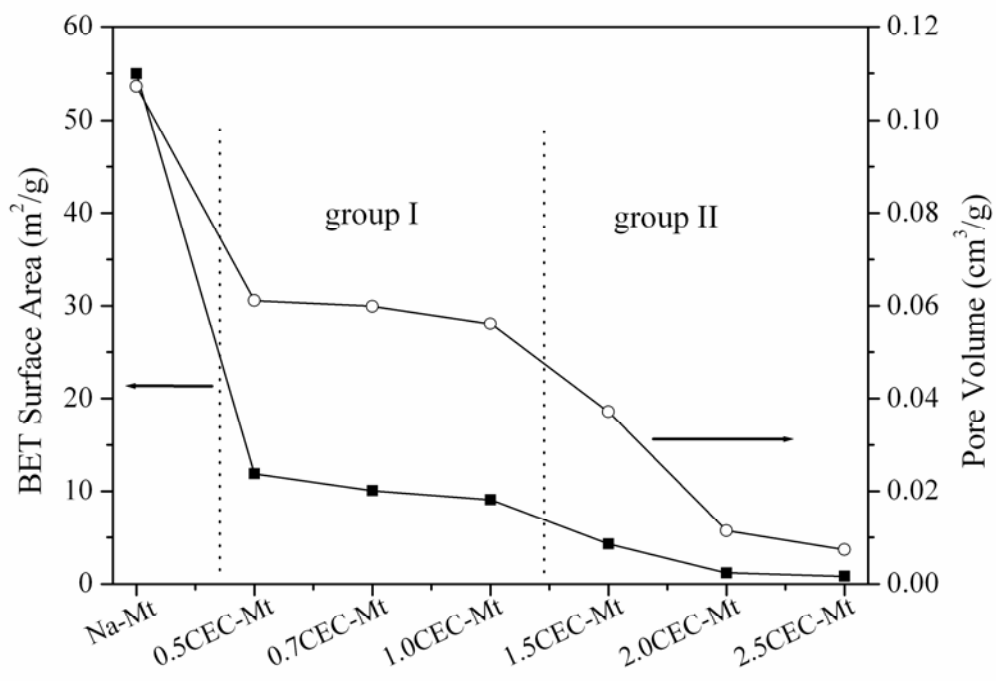


Figure 1

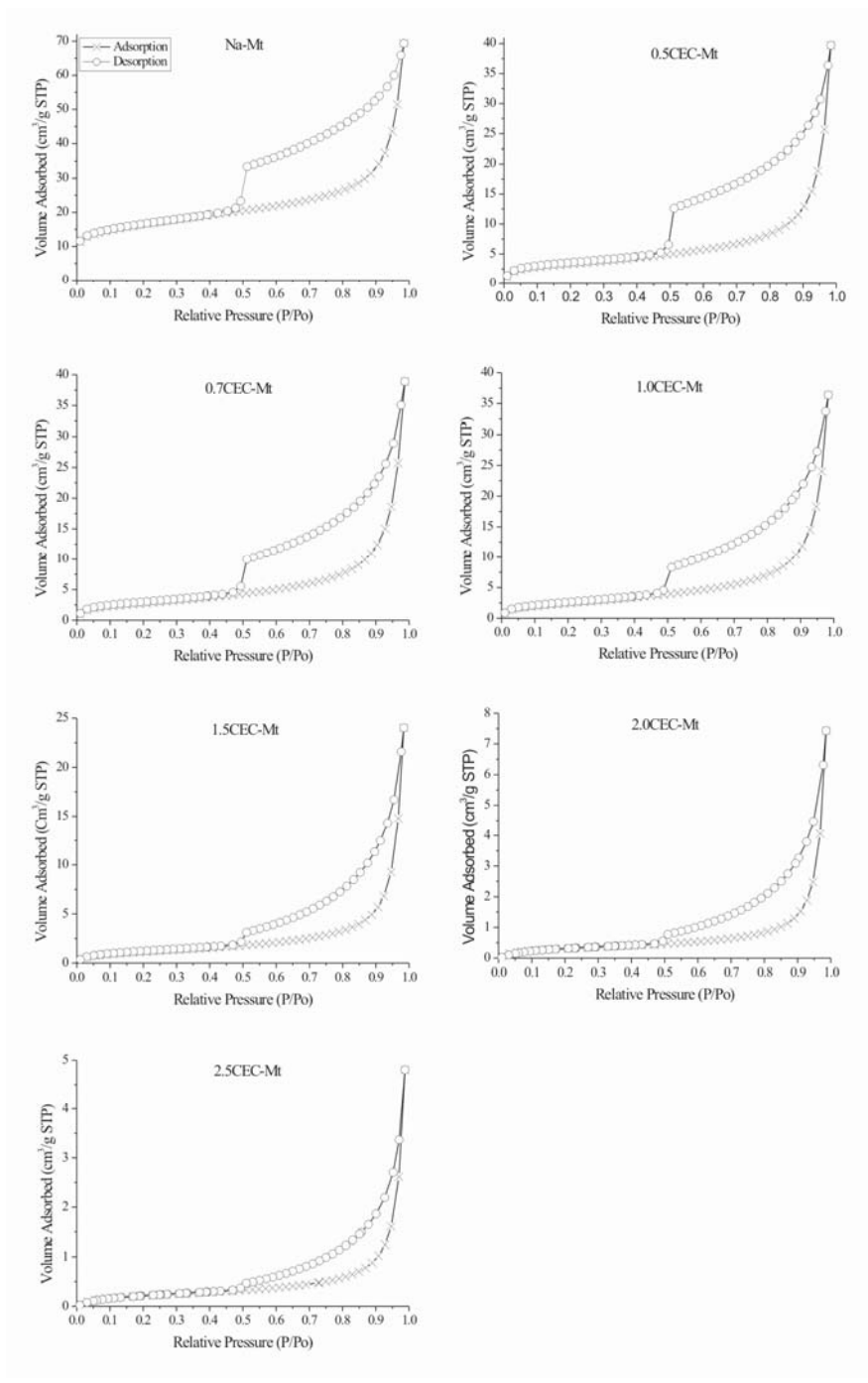


Figure 2

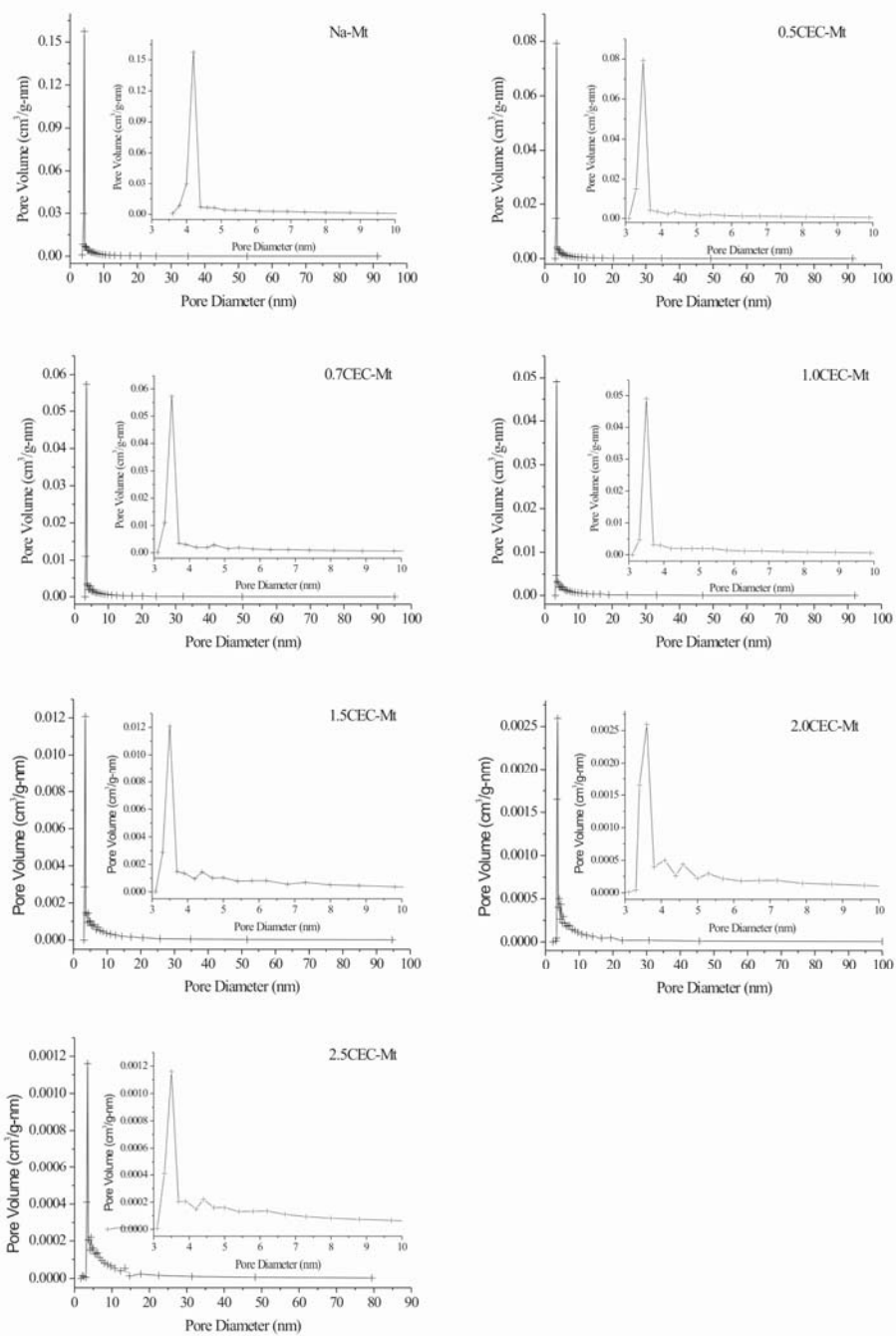


Figure 3

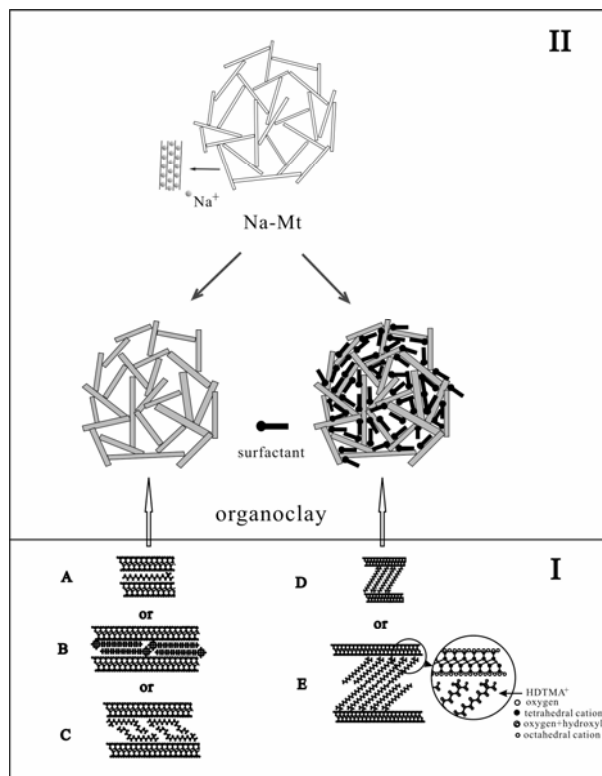


Figure 4

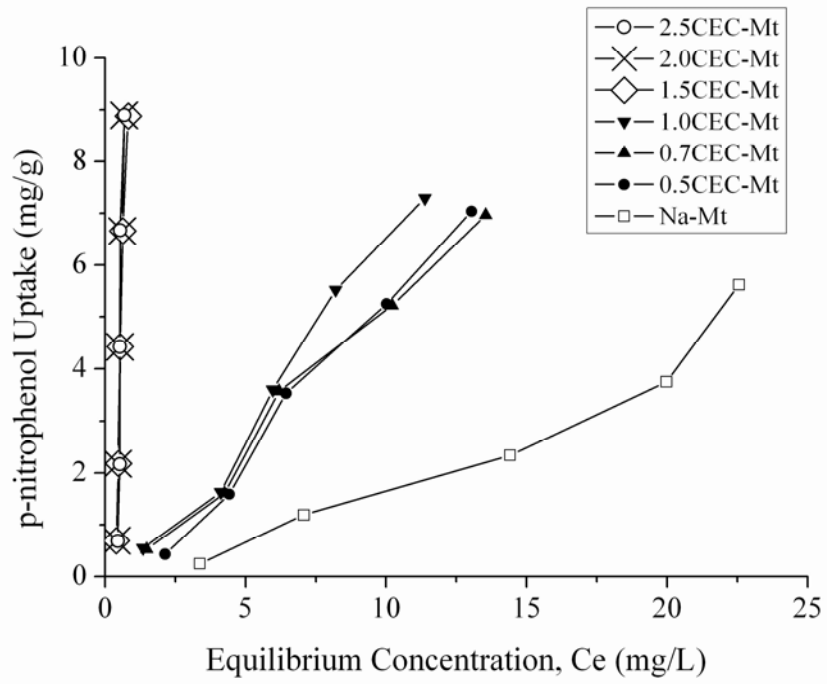


Figure 5