RSC Advances

Enhanced adsorption of inorganic and organic pollutants by amine modified sodium montmorillonite nanosheets

Munusamy Thirumavalavan, Ya-Ting Jhuang and Jiunn-Fwu Lee[*]

Graduate Institute of Environmental Engineering,

National Central University,

Chung-Li, Taoyuan County, 320, Taiwan

[*]Corresponding author

E-mail: jflee@ncuen.ncu.edu.tw

Phone: +886-3-4227151-34658

Fax: +886-3-4226742

ABSTRACT

This article highlighted the preparation of viable and eco-friendly adsorbents for both organic and inorganic pollutants by modifying sodium montmorillonite using three different modifiers viz. N,N,N,N′,N′,N′-hexamethylhexamethylenediammonium dibromide (HM), N,N,N,N',N',N'-hexabutylhexamethylenediammonium dihydroxide solution (HDS) and N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA). X-ray diffraction (XRD) results indicated that the interlayer spacing was increased upon modification process. The successful grafting of modifiers onto interlayer was confirmed by ^{29}Si magic-angel spinning nuclear magnetic resonance (^{29}Si MAS NMR) spectral analysis. The adsorption of inorganic pollutants (Cu^{2+} and Zn^{2+}) and organic pollutants [(benzene, toluene, ethylbenzene and p-xylene (BTEX)] was discussed based on different properties. Based on the experimental results, in the case of HM, 100% modification was achieved and HM-modified montmorillonite possessed larger surface area. But contrarily HDS-modified montmorillonite with lower surface area showed enhanced adsorption capacity towards inorganic pollutants. Adsorption was 6 to 8 times greater in the modified montmorillonite compared to that of unmodified one. Adsorption carried out in the mixed pollutants showed that there is no interaction between these pollutants and the presence of one did not retard the adsorption of another one. Adsorption phenomenon was very complex and influenced by various combined factors. However, adsorption was mainly controlled not only by surface area and also by nature and surface charge of the modifiers.

Key words

Modifiers; modified sodium montmorillonite; adsorption; metal ions; BTEX

1. INTRODUCTION

A variety of toxic chemicals such as organic chemicals (polycyclic aromatic hydrocarbons, dyes, solvents) and heavy metals have been discharged to the environment, causing serious water, air and soil pollutions and they daunt the human health also.[1] Also simultaneous contamination of soil with both organic and inorganic pollutants has become a serious environmental problem and the discharge of these toxic chemicals into water bodies causes detrimental effects to the environment and health.[1-3] The removal of these pollutants cannot be attained entirely by using traditional methods. It is now extensively recognized that adsorption is feasible and efficient for the removal of pollutants from waste water[2,3] and the use of sediment (soil) has also become a feasible alternative being cheap, naturally abundant and easily sourced.[1] The adsorption of these pollutants by soil or clay can diminish their risky effects by restricting their movement in the soil and thus reducing their potential for groundwater contamination.[4,5] As a result of their high chemical and mechanical stability and a variety of surface and structural properties, the application of these soils has been and also being explored by various researchers.[6-10] Generally, the pore structure and chemical properties determine the adsorption ability of the soils.[11] In cases of contaminated soils, metals and organic pollutants often coexist. However, soil does carry negative charge in general and thus it has profound affinity for metal ions only and not for organic pollutants. It is apparent that low organic matter soils, and clays, have little adsorption capacity for removing these pollutants from water and are therefore ineffective. However, this limited adsorption capacity of low organic matter clays and soils can be greatly improved by modification process. A number of studies[12-15] systematically investigated that surface modification of soils by surfactants definitely affected the adsorption ability of soils. In the case of modified montmorillonite using surfactants, the affinity of the mineral toward organic matter is enhanced and thus the surface properties would be transformed from hydrophilic to hydrophobic. As a result, the adsorption of organic contaminants onto montmorillonite can be considerably improved.[16-19] Zhu *et al*.,[16,17] have reported the structure and adsorption capacity of montmorillonite modified by zwitterionic surfactants. They have reported that the chain length, loading and concentration of surfactants mainly affected the structure and properties of modified montmorillonite. The basal spacing was mainly increased if the chain length and concentration of surfactants were increased. On the basis of nitrobenzene and p-nitrophenol adsorption studies, they have concluded that the adsorption coefficients, normalized with organic carbon content were highly affected by surfactant loading levels.[16,17]

Thus so far, majority of studies reported only on adsorption of organic pollutants. If a special surface modifier, which has both negative charges that could adsorb heavy metal ions and hydrophobicity that could adsorb organic pollutants, is used, the adsorption ability of the soil would be achieved for both organic pollutants and heavy metals. There have been few reports[4,20,21] on the adsorption of both organic pollutants and heavy metals on an amphoteric soil surface modified with amphoteric surface modifying agent (ASMA) and such adsorption probably be achieved due to special molecular structure of amphoteric modifier.

In this work, we investigated the adsorption of inorganic and organic pollutants by montmorillonite modified with the modifiers that are neither amphoteric nor contain carboxyl functional groups which is the novelty of this study. Thus, the significant of this work is that we have used modifiers such as quaternary amines and neutral amines that do not contain COOH group which are also not amphoteric modifiers as reported in earlier studies.[4,20,21] In this study, adsorption characteristics of modified montmorillonites for both organic and inorganic pollutants were investigated using three modifiers such as HM, HDS, and PMDETA. The modifiers consist of both hydrophobic and hydrophilic groups.[4,20,21] The modified montmorillonite is formed, when the positively charged groups of the modifiers are adsorbed to the negatively charged sites on the surface of montmorillonite. The modifiers reported in earlier studies[4,20,21] mainly contained nitrogen ($^{+}$N or NR) and carboxyl (COO^{-}) functional group and according to our knowledge, for the first time we have explored the possibility of using the above said quaternary and neutral amine compounds as effective modifiers in this study. The modifier's hydrophobic carbon chain forms an organic phase on the surface of montmorillonite that increases the adsorption of organic pollutants. At the same time, the adsorption of heavy metal ions is also increased because the nitrogen atom in the modifier increases adsorption through coordination bonds with heavy metal ions. The results provided evidence that the adsorption was mainly controlled by various factors. Adsorption of inorganic pollutants was influenced by surface area and nature of the modifiers. Adsorption of organic pollutants was greatly affected by solubility and organic matter content. However, the adsorption was not clearly explained based on single factor only. A deep insight is yet to be focused into this. Most of the literature reports just discussed the adsorption phenomenon,[4,22,23] but detailed information was not obtained. Thus, the main purpose of this study is to investigate the surface modification of Na-montmorillonite with a series of differently structured surfactants which are definitely not amphoteric modifiers and to examine the efficacy of modified Na-montmorillonites as dual functional adsorbents for effective adsorption of both inorganic and organic pollutants. We have also tried to test if the removal extent of organic pollutants is further increased along with photo catalytic decomposition in the organic pollutants and binary mixtures. But however, there is no change in the extent of removal of organic pollutants and the removal of organic pollutants is almost same as the adsorption by modified Na-montmorillonites. But, interestingly in the case of photocatalytic binary mixture systems, the presence of Cu^{2+} comparatively enhanced the removal extent of benzene than that of Zn^{2+}. Thus, in order to explain the significance of adsorption over the photochemical decomposition, the photocatalytic test was also performed in the organic pollutants and binary mixtures along with adsorption and the photochemical decomposition and volatilization of organic pollutants are negligible during adsorption. It was also explored by carrying out the adsorption in the presence of photocatalyst under UV light and compared in order to emphasize the ability of these modified adsorbents. Adsorption studies carried out in mixed pollutants clearly conveyed that there is no interaction between inorganic and organic pollutants and they both did not retard the adsorption of each other. But so far in the literatures[4] a decrease in the adsorption of metal ions due to the presence of organic pollutants was only reported, but in this present work interestingly the combined adsorption was enhanced in the presence of each other.

2. EXPERIMENTAL SECTION

2.1. Chemicals

The montmorillonite used in this study was supplied by the Clay Minerals Society as SWy-2-Na-montmorillonite (Wyoming). It is referred as Na-montmorillonite in this study and the chemical formula of the Na-montmorillonite is expressed as $Na_{0.73}[Si_{7.66}Al_{0.34}][Al_{3.07}Fe_{0.44}Mg_{0.56}]O_{20}(OH)_4$. The mineralogical contents[24,25] identified as quartz, feldspar, gypsum, mica, illite in the SWy-2 sample represent 8% purification. The proportion of various mineralogical contents is: SiO_2 62.9%, Al_2O_3 19.6%, Fe_2O_3 3.35%, MgO 3.05%, CaO 1.68% and Na_2O 1.53%. The surface area is 34.03 m^2/g and the cation exchange capacity (CEC) is 78 meq/100g. The montmorillonite was used without further purification. High purity of laboratory grade copper and zinc standard solutions (1000 ppm) were purchased from J. T. Baker. All the reagents were of analytical grade and used without further purification. Deionized water was used in all experiments.

2.2. Modifiers

The modifiers used in this experiment were N,N,N,N′,N′,N′-hexamethylhexamethylenediammonium dibromide (HM) (Alfa Aesar, >98%, molecular weight = 362.19), N,N,N,N',N',N'-hexabutylhexamethylenediammonium dihydroxide solution (HDS) (Alfa Aesar, 20% w/w aqueous solution, molecular weight = 488.87), and N,N,N′,N″,N″-pentamethyldiethylenetriamine (Alfa Aesar, >99%, PMDETA) (molecular weight = 173.30). The molecular structures and chemical formulae of these modifiers are shown in Fig. 1.

2.3. Preparation of modified Wyoming (SWy-2-Na-montmorillonite)

The schematic representation of preparation of modified montmorillonite is shown in Fig. S1 (See figure S1). A suspended solution containing Na-montmorillonite was prepared by dispersing 10 g of Na-montmorillonite in 1 L deionized water. The solution was stirred for 2 h and then it was allowed to stand for 1 h. Then, the clay fraction was separated by sedimentation of the clay suspension. The supernatant clay fraction was then removed and put aside.

Then 20 ml of appropriate amount of respective modifiers (usually double or more than double CEC dissolved in 1 L deionized water) were added to the supernatant clay fraction (20 ml) and the reaction mixture was stirred for 2 h. The modifiers loaded were determined[4] by an equation as follows;

W_{soil} x soil's CEC x modification ratio x molecular weight of modifiers x 10^{-2}, where W_{soil} is weight of the soil modified.

Then all the products were washed free of anions (determined by the use of $AgNO_3$) and separated from water. The resulting modified Na-montmorillonites were filtered and lyophilized (freeze-dried). Finally, they were ground in an agate mortar and stored in a vacuum desiccator. The HM, HDS and PMDETA modified montmorillonites were denoted as HM-M, HDS-M and PMDETA-M respectively.

2.4. *Batch adsorption studies*

The batch adsorption experiment included three pollutant treatments: (1) organic pollutants (benzene; >99%, toluene; >99.9%, ethylbenzene; >99.6% and xylene; > 99.5%, in brief BTEX) only, (2) inorganic pollutants (Cu^{2+} and Zn^{2+}) only and (3) mixture of both inorganic and organic pollutants. The adsorption experiments were carried out as depicted in Fig. S2 (See figure S2). Stock solutions (5, 10, 20, 50, 100, 200, 300, 400 and 500 mg/L) of various pollutants were prepared using the standard solutions in deionized water.

2.4.1. *Adsorption of inorganic pollutants (Cu^{2+} and Zn^{2+})*

The adsorption experiments were performed at 28 °C in glass centrifuge tubes containing different heavy metal ion solutions (20 mL) and the modified montmorillonites (2 g), shaken at pH 5 (measured by pH meter) for 24 h at 130 rpm in a Lab-line orbit environ shaker. The reaction mixture was centrifuged at 8000 rpm for 10 min to precipitate the soil samples. Finally, the supernatant liquid was drawn and analyzed using a Varian AA280Fs atomic absorption spectrophotometer (AAS) (<2% error-no more dilution errors) to determine the concentration of metal ions in the solution.

2.4.2. Adsorption of organic pollutants (BTEX)

The adsorption experiments were performed at 28 °C in glass centrifuge tubes containing different organic pollutant solutions (20 mL) and the modified montmorillonites (2 g), shaken for 24 h at 130 rpm in a Lab-line orbit environ shaker. The reaction mixture was centrifuged at 8000 rpm for 10 min to precipitate the soil samples. Then the supernatant liquid was extracted with carbon disulfide (1:4) and drawn into brown bottle and the bottle was covered immediately. In general liquid-liquid micro-extraction was used for analysis of volatile compounds and in such extraction, the hydrophobic solutes become enriched in the extraction solvent and then it is dispersed throughout the bulk solution.[26] Due to increased enrichment factor, low standard deviation and better repeatability of the volume of settled phase, carbon disulfide was selected as extraction solvent.[26] Thus, the phases were separated and finally the sample was analyzed using a Hewlett Packard (GC, Model: HP-6890) gas chromatograph) (≈7% analytical error) equipped with a flame ionization detector (GC-FID) in 5 mL aliquot samples to determine the concentration of organic pollutant in the solution. Analysis was performed using DBWAX column (1 μm thickness, 30 m length, 0.53 mm internal diameter) using He as carrier gas. In all cases, control experiments were carried out to ensure any possible degradation or leaks.

2.4.3. Adsorption of both organic and inorganic pollutants

The adsorption experiments were performed at 28 °C in glass centrifuge tubes containing mixture of inorganic pollutant (metal ion) solution (20 mL) and organic pollutant (20 mL) and the modified montmorillonites (2 g), shaken at pH 5 (measured by pH meter) for 24 h at 130 rpm in a Lab-line orbit environ shaker. The reaction mixture was centrifuged at 8000 rpm for 10 min to precipitate the soil samples. Then the supernatant liquid was extracted with carbon disulfide (1:4) and drawn into brown bottle and the bottle was covered immediately. Thus, the phases were separated and finally both the extracted sample and the supernatant sample were analyzed to determine quantitatively the organic pollutants and inorganic pollutants respectively.

2.4.4. Photocatalytic degradation studies

The photocatalytic degradation experiments were carried out using H_2O_2 under UV light (λ_{max} = 365 nm, purchased from the Black-Ray) in the organic pollutants as well as in the binary mixtures in order to emphasize the significance of adsorption by modified montmorillonite. An appropriate amount (20 mL) of organic and inorganic pollutants was added to the suspension of modified montmorillonite (2 g) in deionized water in a catalytic reactor and stirred under UV light at 28 °C. Then 100 mM of H_2O_2 was added into the reaction mixture and the reactor was covered with black cloth. The stirring under UV light was continued and the resulting suspensions were collected at regular time interval (0, 5, 10, 20, 30, 40, 50, 60, 90, 120, 150 and 180 min), centrifuged (8000 rpm) for 10 min and the supernatant liquid was collected. Then the supernatant liquid was extracted with carbon disulfide (1:4) and drawn into brown bottle and the bottle was covered immediately. Finally, both the extracted sample and the supernatant sample were analyzed by GC-FID to determine quantitatively the organic pollutants.

2.5. Determination by analytical procedure

The equilibrium adsorption of various pollutants was calculated using the following equation;

$q_e = [(C_0\text{-}C_e)V]/M$

where q_e is the amount of pollutants adsorbed per unit amount of the adsorbent (mg/g); C_0 and C_e are the concentrations of the pollutants in the initial solution (mg/L) and at equilibrium respectively; V is the volume of the adsorption medium (L); and M is the amount of the adsorbent (g). The value of q_{max} was calculated from q_e using the Langmuir isotherms and the corresponding q_{max} values were obtained using a linear method.

2.6. Characterization techniques

The Brunauer-Emmett-Teller (BET) specific surface area and average pore diameter were measured by degassing the samples at 368 K and measured at 77 K on a Quantochrome NOVA 1000 using standard continuous adsorption/desorption procedure (Analytical error <2%). Scanning electron microscopy (SEM) images of samples were obtained by mounting on 0.5 cm diameter stubs coated with a layer of gold membrane, and then analyzed with a JOEL JAM-6700F cold cathode and HITACHI S-800 scanning electron microspectrometer operated at 5-20 kV. Fourier transform infrared spectra (FT-IR) of samples were obtained using a Neclit 6700 model spectrometer by mixing the sample with KBr in a ratio of 1:100 and press to a disc. X-ray diffraction (XRD) patterns were obtained on a Siemans X-ray diffractometer D-5000 equipped with a Cu Kα radiation source operating at 40 kV and 30 mA. ^{29}Si magic-angel spinning nuclear magnetic resonance spectra (^{29}Si MAS NMR) were recorded using a Bruker DRX400 spectrometer equipped with a multinuclear probe.

3. RESULTS AND DISCUSSIONS

3.1. FT-IR, SEM, BET, elemental analyses, XRD and ^{29}Si NMR

SWy-2-Na-montmorillonite was characterized using FT-IR technique before and after modification as shown in Fig. 2. In the case of pristine SWy-2-Na-montmorillonite, the broad peak around 3400-3900 cm^{-1} is due to ν(O-H) and ν(H_2O), the peak around 1100 cm^{-1} is due toν(Si-O) and the peak around 1600 cm^{-1} is due to interlayer water deformation vibrations. The appearance of new peaks in the modified montmorillonite (double CEC) around 2800-2900 cm^{-1} due to $\nu_{\mathrm{stretching}}$($CH_3$ and CH_2), around 1800 cm^{-1} due to ν_{bending}(CH_3) and around 1400 cm^{-1} due to ν_{bending}(CH_2)[27] clearly evidenced the successful modification using different modifiers. But, however invariably in all cases, the position of Na-montmorillonite peaks was almost remained unaltered after modification also. Also upon modification, the extent of broadening of water peak decreases and the peak around 3400-3900 cm^{-1} became sharp due to the hydrophobic nature of modified montmorillonite, i.e., the water content in the interlayer decreases during modification. However, the remaining water molecules in the modified adsorbents are considered to be due to the release of the residual free water retained in particle pores after drying.[18] Upon modification, variation of relative peak intensities occurred as a result of the change of relative concentrations. But however, we have tried to correlate such significant variation based on the structural differences also. In the case of HDS-M, sharp and strong peaks are observed comparatively than that of HM-M and PMDETA-M and this is due to the fact that the difference in structural formula. The modifier HDS contains more CH_2 and CH_3 groups than that of remaining two and thus causing for sharp and intense CH_2 and CH_3 peaks. The definite changes in the structural properties of modified montmorillonites were clearly witnessed from SEM analysis as shown in Fig. 3. From Fig. 3 it is observed that SWy-2-Na-montmorillonite before modification possessed an indefinite layered structure due to hydration and swelling phenomenon. But after modification the soil structure was greatly enhanced and the modified soils possessed a definite uniform sheet like structure. Upon modification, the modifiers are presumed to be penetrated into interlamellar region of the clay by the expansion of clay sheets in the *c*-axis.[28] Expansion occurs due to the grafting of modifiers to silanol groups within the interlayer where the silica framework is in contact with the clay layers.[28] Thus, in the presence of modifiers, the swelling or hydration is eliminated (the water is removed due to lyophilization) and the interstitial layer of the surface morphology is easily stretched. Thus, the gap between surface layer and modifier is condensed and due to this narrow gap between the layer structure and the organic soil modifier, masking of porous layer structured is also observed in the case of modified soils. At the same time, from Fig. 3, it is obvious that in the presence of HDS, still small amount of swelling is retained, i.e., the distance between layers is somewhat retained because of the factor that, the extent of modification by HDS is lower than that of both HM and PMDETA. Thus, in the case of HDS-modified soil, still some layer structure is retained like pristine SWy-2-Na-montmorillonite. In the case of HM-modified soil, due to the enhanced modification, the organic soil modifier is pulled towards the surface layer of the soil and thus, the gap between layer and modifier is condensed due to which size was reduced and area was increased. Thus, it easily attained the sheet like structure. In the case of PMDETA, though the extent of functionalization is lower than that of HM, still a well defined three dimensional sheet like structure is observed suggesting that the structure of modifier itself can act as a modifier. In the case of both HM and HDS, the modification was achieved through ion-exchange between Na and cationic nitrogen ions, but in the case of PMDETA it is entirely different and ion-exchange is completely ignored due to the presence of non-ionic nitrogen atoms. Thus in the case of PMDETA, the structure is relatively strong due to the presence of three non-ionic nitrogen atoms and this can be easily compressed, tangled or stretched into the soil resulting into the well defined sheet like structure with masked porous structure. Thus among three modifiers, PMDETA produced well defined significant structural morphology on the soil surface. As the extent of functionalization increased, the structural improvement from layer to sheet like structure also significantly increased because of the stretching of interstitial layer of soils due to the removal of swelling or hydration. Thus, this clearly conveyed that the extent of functionalization greatly influenced the structural characteristics of modified soil.[24] The elemental analysis data, extent of functionalization, BET surface area and pore size of both pristine and modified soils are shown in Table 1. From both SEM analysis results as well as from Table 1, we can easily understand that the extent of functionalization in the case of HDS is comparatively lower than that of others due to the steric hindrance of longer carbon chain. From Table 1, it is seen that the weight percentage of C, H and N was significantly increased upon modification of soils which confirmed the effective modification of soil. The value of functional group content explained the modification ability of different modifiers. As it is already known, during the ion-exchange process the cations form an inner sphere complex.[18] By using HM modifier, the soil was efficiently modified (82.8 meq/100g), almost the Na ion (78 meq/100 g) was completely replaced by cationic nitrogen ions. However, by using HDS modifier, the calculated functional group content is only 39.2 meq/100g, which clearly revealed that only 50% of the Na ion was replaced due to the steric hindrance caused by the long carbon chain. Thus, it is clear that in the case of HM-M, the CEC (functional group content) is considerably higher due to the ease in the formation of inner sphere complex by linear HM modifier which is free from the steric hindrance. As discussed in earlier, in the case of PMDETA the modification did not occur through ion-exchange mechanism and the calculated functional group content is 63 meq/100 g. Thus the modification ability of modifier could be arranged in the order as HM>PMDETA>HDS. But the BET surface area of the modified soils decreased in the following order as HM-M>HDS-M>PMDETA-M and accordingly the pore size also increased in the order as HM-M<HDS-M<PMDETA-M. Thus, from Table 1, it is witnessed that modification of soils significantly enhanced the surface area of the soils except in the case of PMDETA-M. Among the modified soils, HM-M possessed larger surface area (99.69 m^2/g) and smaller pore size (4.02 nm), and PMDETA-M possessed smaller surface area (8.86 m^2/g) and larger pore size (12.79 nm). HDS-M possessed intermediate surface area (39.31 m^2g) and pore size (7.98 nm) between HM-M and PMDETA-M. The BET surface area of the modified montmorillonites is much larger than that of unmodified montmorillonite. However, the result is opposite to PMDETA-M where the surface area became small after modification. Such a difference is likely due to the comparatively larger particle size of the clay.[28] Thus, based on this, interlayer expansion and cation exchange mechanisms were assumed and

discussed. From Table 1, it is also seen that the pore volume of modified soils decreases even though pore size increases which is due to the pore blocking by modifiers upon modification. This pore blocking is depending upon the nature of modifiers and has no significant correlation with pore size of the modified soils. Based on the above results, it is confirmed that both nature and structure of the modifier played a significant role on the structural characteristics of modified soils. In overall, based on BET and SEM analysis, it is concluded that the specific surface area, pore size and structural properties of modified montmorillonites are significantly influenced by various combine factors and very complicated to interpret also. Thus, deep and more careful insights are still needed.

The XRD patterns of montmorillonites were obtained before and after modification as shown in Fig. 4. The peak around $2\theta = 5.7°$ was slightly shifted to lower 2θ values ($2\theta \approx 5.1$ to $5.2°$) after modification. Compared with Na-montmorillonite (corresponding to a basal plane spacing [d_{001}] of 1.41 nm), modified montmorillonites have a larger basal spacing. Based on basal spacing, the modified montmorillonites can be arranged in the order as HDS-M (1.83 nm) > PMDETA-M (1.79 nm) > HM-M (1.74 nm). It is thus witnessed that the interlayer spacing of the montmorillonite is significantly increased by the modifiers.[18,19] The ^{29}Si MAS NMR spectra of montmorillonite show two peaks around the range between δ = -91 and -108 ppm. In the case of modified montmorillonites, the peaks are slightly shifted towards lower frequencies due to the grafting of modifiers into the interlayer framework.[18]

3.2. N_2 adsorption isotherms

The obtained nitrogen adsorption isotherms as shown in Fig. 5a obviously conveyed that all the samples exhibited typical type II S-type curves. The hysteresis was not obvious initially (it may occur only in the high relative pressure range). At low relative pressure ($P/P_0 < 0.1$) the adsorbed volume increased linearly upon increasing the pressure. This region corresponds to a monolayer-multilayer adsorption on the pore walls. Increasing the value of P/P_0 from 0.1 to 0.5, we observed a sharp increase in the adsorbed volume, which we attribute to capillary condensation of multilayer adsorption. At this stage, the changes in nitrogen adsorption can be used as a measure of uniform pore size distribution. If greater is the adsorption, larger will be the uniform size distribution. At higher relative pressures ($P/P_0 > 0.5$-0.8), multilayer adsorption occurred on the external surface and larger hole appeared, thus resulting into a dramatic increase in the adsorbed volume. At a value of P/P_0 of 1, saturation was reached indicating that all of the pores were filled with the condensed adsorbents. The isotherm for the modified soils exhibited sharp inflection characteristic of capillary condensation within a narrow pore size distribution,[29] where the value of P/P_o of the inflection point is related to the average diameter of the pores. These N_2 adsorption data confirmed the uniformity of the pore size distribution of the soils. The pore size distribution is shown in Fig. 5b. In the case of HM-M and HDS-M, the observed hysteresis was narrow and less obvious, whereas PMDETA modified soil showed obviously widespread hysteresis loop. These nitrogen adsorption curves clearly revealed that the different modifiers could affect the pore size and its distribution. Thus uniform and narrow pore size distribution was accumulated in the case of HM-M and HDS-M whereas in the case of PMDETA-M, the broader pore size distribution was observed. Thus Fig. 5b and Table 1 are in good agreement conveying the smaller pore size of HDS-M. This study vividly revealed that the modifiers with quaternary nitrogen atoms resulted into modified soils with a larger surface area and smaller pore size compared to that of modifiers with neutral nitrogen atoms which resulted into modified soils with a lower surface area but relatively larger pore size. Thus, it could be concluded that HM is the most effective modifier among all the modifiers used in this study.

3.3. Adsorption of inorganic pollutants

The effect of modifier on adsorption of heavy metal ions such as Cu^{2+} and Zn^{2+} was explored in this study. The Langmuir adsorption isotherms of metal ions onto modified soils are shown in Fig. 6 and Langmuir parameters are shown in Table 2. The calculated R^2 value is found to be 0.9 indicating that the Langmuir isotherm model fitted well in all cases. The results, suggested that the adsorption process involved a chemical adsorption with the adsorption capacity not only depending upon the surface area but also depended upon nature (surface charge) and structure of the modifiers too. From Fig. 6, and Table 2, it is witnessed that even though, HDS-M and PMDETA-M possessed lower surface area than that of HM-M, interestingly they showed enhanced adsorption for both Cu^{2+} and Zn^{2+} than that of HM-M and the order of adsorption ability of modified soils for metal ions could be arranged as HDS-M>PMDETA-M>HM-M. Thus, despite of larger surface area, HM-M still showed lower adsorption capacity for metal ions. This discrepancy in behavior can be explained based on the structure of the modified soils due to the structure of modifiers. Being a divalent cation, heavy metal ions can exit as a free ion or ion pairs in a mixture of soil and the aqueous phase. Though, these cations could provide some extent of electrostatic repulsion with quaternary nitrogen, adsorption does occur due to the enhanced distribution ratio of modified soils in aqueous phases.[30] The basic mechanism of adsorption was based on the complexation of nitrogen atom with metal ions or hole-filling (adsorption by ion-exchange).[30] In addition, the surface charges covered by the modifiers could also contribute for the effective adsorption of pollutants, since the modification has little effect on surface charge of the montmorillonite. From Table 1, the observed surface coverage based on functional group content, did not provide any direct correlation between adsorption and surface coverage. Thus, the adsorption phenomenon is combined factor of both surface charge, surface area of adsorbents and structure of modifiers. However, HM was capable of modifying soils completely, HM-M showed decreased adsorption tendency towards metals ions than that of others. This is due to the fact that the formation of quaternary amine structure in the modified soils. In the case of HM-M, even though almost 100% of sodium atom was replaced by modifier, the electrons on quaternary amine was almost utilized by counter ions and it became neutral and hence it can not provide electrons for metal ions. However, in the case of HDS-M, the quaternary amine can not share its electrons completely with methyl groups only and thus partial electrons are utilized for metal binding. Thus, due to poor coordination behavior (protonation), the complexation ability of HM-M for metal ions is comparatively lower than that of HDS-M. This is the reason why HDS-M showed enhanced adsorption than that of HM-M. But in the case of PMDETA-M, the adsorption capacity lies between HDS-M and HM-M. This is because of the structural stabilization of modifier even though it contains non-ionic nitrogen atoms with unshared electrons. Thus, based on the combined effect it was concluded that HDS-M showed enhanced adsorption tendency towards metal ions in this study. Based on the experimental results it was observed that among all heavy metal ions, the adsorption behavior of Cu^{2+} was appreciably higher than that Zn^{2+}.[28,31,32] This may be because of the fact that the ionic radii[33] of Cu^{2+} is slightly lower than that of Zn^{2+} and also due to the higher electronegativity[34] of Cu^{2+} than that of Zn^{2+}. Thus the nitrogen atoms in the modified soils showed higher affinity for Cu^{2+} than that of Zn^{2+}.

3.4. Adsorption of organic pollutants (BTEX)

These modified soils were also utilized as adsorbents for organic pollutants such as BTEX in order to explore their adsorption capacity. Due to high volatile nature of BTEX, calibration for recovery of BTEX was done in order to avoid any error by covering the adsorbent and adsorbate mixture and almost about 95% of BTEX was recovered in all cases. Langmuir adsorption isotherms for adsorption of BTEX are shown in Fig. 7. Langmuir constants (R^2) are shown in Table 2 and distribution constants (k_d) are displayed in Table 3. For benzene and ethylbenzene, the order of k_d is as follows; HM-M>HDS-M>PMDETA-M, for toluene, the order of k_d is as follows; PMDETA-M>HM-M>HDS-M and for p-xylene the order of k_d is as follows; PMDETA-M>HDS-M>HM-M. The nature of organic modifiers played a vital role both on adsorption of organic and inorganic pollutants. The adsorption results indicated that the solubility of BTEX in water and organic matter content may affect the adsorption of BTEX[12], but however the adsorption phenomenon did not show any significant correlation with single parameter. Thus, it was quite complex and the adsorption ability of modified soils was different for different systems. This adsorption mainly occurred on organic carbon matters and thus the determination organic content (OC) was done and the total percentage of organic content (OC %) is reported in Table 3. However, this total organic content reported in Table 3 is slightly different from the C% reported in Table 1. This difference in C% perhaps may be due to the presence of small amount of inorganic carbonates in the modified soils. Thus both organic content (OC%), water solubility (S_w) and distribution constant (k_d)[24,35-38] mainly influenced the adsorption of BTEX onto modified soils.

Due to higher water solubility, the organic adsorbate molecules tend to form an aqueous solution, while the lower water soluble adsorbate molecules are easily distributed in the organic phase of the hydrophobic adsorbent. Thus for higher water solubility cases, k_d is always smaller than that of lower water solubility cases, i.e. S_w and k_d are inversely proportional to each other. However, due to this distribution of non-ionic organic pollutant into organic phase of the adsorbent, again the total organic content and constant of organic compound (OC) have to be corrected as shown in Table 4. In this case OC is actual organic content before addition of organic pollutants and OM is the total organic content after addition of organic pollutants. Thus, this study provided more insight into the investigation of distribution constant (k_d), organic content (OC and OM), corrected constant value (K_{OC} and K_{OM}) and water solubility (S_w). This is very significant work as it explored the effect of different organic modifier composition of soil on K_{OC} or K_{OM} value of the BTEX as shown in Table 4. From Table 4, several observations could be derived. K_{OC} is widely used to predict the value of the non-ionic organic pollutants present in the soil.[37-39]

The water solubility (S_w) of BTEX was found to be in the order as benzene>tolune>p-xylene>ethylbenzene (1780>515>197>152). For all cases, K_{OC} is always higher than that of K_{OM} and the order of both K_{OC} and K_{OM} for BTEX was observed to be ethylbenzene>p-xylene>toluene>benzene. Thus, it is very clear that as the water solubility increased, both K_{OC} and K_{OM} decreased.

The irregularities in adsorption mechanisms as shown in Fig. 6 and Fig. 7 could be perhaps either due to surface irregularity of the adsorbents or due to the attraction or repulsion of different speciation at different reaction conditions.[4] The different speciation of inorganic pollutants (M^{2+}, $M(OH)^+$, $M_2(OH)_2^{2-}$, $M(OH)_3^-$, $M(OH)_2$; M= metal), organic pollutants (intermediate complexes) and modifiers (ionic, neutral or quaternary nitrogens) as a function of pH is apparently important to be considered. On a comparison in overall, regardless of the pollutants, the adsorption ability of modified montmorillonite is 6 to 8 times greater than that of unmodified montmorillonite.

The results obtained in this study were compared with reported studies[4,18,19] and this comparative study revealed that the adsorption of metal ions by modified soil was enhanced by 1-2 times and the adsorption of organic pollutants was increased by 2-3 times when compared with unmodified soil. But in this study, the adsorption after modification was significantly enhanced by 6-8 times which clearly emphasized the superior behavior of modified montmorillonite as adsorbents for both inorganic and organic pollutants.

3.5. Adsorption of binary systems (both inorganic and organic pollutants)

In order to evaluate the interaction between inorganic and organic pollutants, adsorption of binary system was also carried out. For this purpose, HDS was selected as adsorbent as it showed increased affinity towards metal ions than other adsorbents. Also benzene was mainly selected as organic pollutant simply to avoid error as it has higher water solubility. In the case of binary mixture, total adsorption was greatly enhanced, but however, no competitive adsorption phenomenon could be witnessed due to the different mechanism involved in both inorganic and organic pollutant adsorption as shown in

Fig. 8. From Table 1, HM-M is presumed to possess inter-functional linear structure due to which the soil layer distance resulting into larger surface area, whereas in the case of HDS and PMDDETA, the phenomenon of bending within the structure of the soil may restrict the increase of the surface area. But, however in all cases both nitrogen atoms are expected to be interacting with pollutants. Thus, as a comparative study with literature reports,[4] in this study total adsorption was greatly increased and this clearly indicated that there is no interaction between cations and BTEX. But in reported studies,[4,22,23] the presence of organic pollutant could cause crowding and thereby decrease the amount of metal that could adsorb due to steric hindrance. Thus, our present work is considered to be more significant when compared with literature reports.

3.6. Photocatalytic degradation in binary systems

In order to confirm the significance of adsorption, to compare the adsorption phenomenon with the photocatalytic decomposition, to emphasize the adsorption efficacy of modified montmorillonites over the photocatalytic degradation and also to confirm the presence of metal ions does not retard the removal of organic pollutants, we have also performed photocatalytic degradation of benzene using H_2O_2 catalyst under UV light along with modified adsorbents. Since no competitive adsorption phenomenon in binary mixture was witnessed, it was carried out in the binary mixtures also. The experimental results clearly explained that up to 52% of benzene was removed within 180 min in the presence of Zn^{2+} and HDS-M. But the extent of removal was still increased to 65% in the presence of Cu^{2+} and HDS-M. Thus, it is confirmed that the presence of Cu^{2+} enhanced the removal of benzene during adsorption combined with photocatalytic decomposition. However, there is no significant variation in the removal of BTEX along with photocatalytic decomposition and thus modified montmorillonites are able to act as efficient adsorbents even in the absence of any catalyst. Thus, based on the above experimental results, it is confirmed that HDS-M was found to be efficient adsorbent among all modified soils and it showed enhanced affinity towards Cu^{2+} ion. Also benzene was considered to be convenient adsorbent among BTEX. In overall, the organic composition of adsorbent played a major role in controlling the both adsorption studies.

4. CONCLUSIONS

Adsorption of both organic and inorganic pollutants using modified eco-friendly sodium montmorillonite was reported in this study. The role of different composition of modifiers on structural and adsorption characteristics was mainly discussed. This study provided detailed insight in to the effect of organic content, solubility of pollutant and distribution constant on the adsorption mechanisms. Upon modification, the structural morphology was significantly improved along with surface area. Both XRD and ^{29}Si MAS NMR results confirmed the successful formation of modified montmorillonites. A shift in the peak position was observed in both XRD and ^{29}Si MAS NMR spectra of modified montmorillonites. An increase in the basal spacing was also witnessed from the XRD results of modified montmorillonites. The adsorption mechanism was correlated with various properties and the various factors controlling the adsorption isotherms were better explained. Based on the above results, regardless of the surface are, the surface charge and organic matter significantly affected the adsorption of pollutants. Thus, HDS-M was concluded to be an efficient adsorbent among all modified soils and Cu^{2+} was observed to adsorb effectively. In the binary mixture no competitive adsorption was observed due to different adsorption mechanisms in the case of both organic and inorganic pollutants. The removal of benzene using H_2O_2 under UV light in the presence of HDS-M conveyed that the extent of removal of benzene is unaltered by photocatalytic decomposition. However, the removal of benzene carried out in binary mixture using H_2O_2 under UV light in the presence of HDS-M revealed that 65% of benzene removal was attained in the case of Cu^{2+} binary system which is greater than that of Zn^{2+} binary system (52%). The result of this study indicated that the modified adsorbents used in this present study are better than that of unmodified one and also cost-wise more economic.

SUPPORTING INFORMATION

Supplementary figures (Fig. S1 to S2) are produced as supporting information. This material is available free of charge via the Internet at.

ACKNOWLEDGMENT

We thank the National Central University and National Science Council (NSC, (Grant No.: NSC99-2221-E-008-025-MY3), Taiwan, Republic of China (ROC), for financial support.

Notes and References

1. C. N. Owabor, U. M. Ono, A. Isuekevbo, A. *Adv. Chem. Eng. Sci.*, **2012**, *2*, 330.

2. A. M. Mastral, T. Garcia, R. Murillo, M. S. Callen, M. V. Narvarro, J. Galban, *Energy Fuels*, **2001**, *15*, 1.

3. O. Gök, S. A. Özcan, A. Özcan, *Desalination*, **2008**, *220*, 96.

4. Z. -F. Meng, Y. -P. Zhang, Z. -Q. Zhang, *J. Hazard. Mater.*, **2008**, *159*, 492.

5 O. Abollino, M. Aceto, M. Malandrino, C. Sarzanini, E. Mentasti, *Water Res.*, **2003**, *37*, 1619.

6 J. P. Chen, S. Wu, K. H. Chong, *Carbon,* **2003**, *41*, 1979.

7. M. Khalid, G. Joly, A. Renaud, P. Magnoux, *Ind. Eng. Chem. Res.*, **2004**, *43*, 5275.

8. A. S. Özcan, A. Özcan, *J. Colloid Interface Sci.*, **2004**, *276*, 39.

9 A. Özcan, A. S. Özcan, *J. Hazard. Mater.*, **2005**, *125*, 252.

10. W. T. Tsai, C. W. Lai, T. Y. Su, *J. Hazard. Mater.*, **2006**, *134*, 169.

11. R. S Juang, S. H. Lin, K. H.; Tsao, *J. Colloid Interface Sci.*, **2002**, *254*, 234.

12. S. A. Boyd, J. -F. Lee, M. M. Mortland, *NatureI,* **1998**, *333*, 345.

13. H. Chen, R. Q. Yang, *J. Hazard. Mater.*, **2002**, *94*, 191.

14. A. Z. Redding, S. E. Burns, *J. Colloid Interface Sci.*, **2002**, *250*, 261.

15. R. T. Upson, S. E. Burns, *J. Colloid Interface Sci.*, **2006**, *297*, 70.

16. J. Zhu, Y. Qing, T. Wang,, R. Zhu, J. Wei, Q.Tao, P. Yuan, H. He, *J. Colloid Interface Sci.*, **2011**, *360*, 386.

17. J. Zhu, Y. Qing, L. Ma, R. Zhu, H. He, *Miner. Petrol.*, DOI 10.1007/s00710-014-0339-1.

18. M. C. Pazos, M. A. Castro, M. M. Orta, E. Pavón, J. S. V. Rios, M. D. Alba, *Langmuir*, **2012**, *28*, 7325.

19. L. H. -Bin, X. H. -Ning, *J. Inorg. Mater.*, **2012**, *27*, 780.

20. Z. -F. Meng, Y. -P. Zhang, G. -D. Wang, *Pedosphere*, **2007**, *17*, 235.

21. G. Y. Sheng, S. H. Xu, S. A. Boyd, *Soil Sci. Soc. Am. J.*, **1999**, *63*, 73.

22. S. Andini, R. Cioffi, F. Montagnaro, F. Pisciotta, L. Santoro, *Appl. Clay Sci.*, **2006**, *31*, 126.

23. J. Y. Yoo, J. Choi, T. Lee, J. W. Park, *Water Air Soil Pollut.*, **2004**, *154*, 225.

24. Y. Xi, R. L. Frost, H. He, *J. Coll. Interface Sci.*, **2007**, *305*, 150.

25. L. Le Forestier, F. Muller, F. Villieras, M. Pelletier, *Appl. Clay Sci.*, **2010**, *48*, 18.

26. Y. Assadi, F. Ahmadi, M. R. M. Hossieni, *Chromatographia*, **2010**, *71*, 1137.

27. R. C. Weast, M. J. Astle, W. H. Bayer, "*CRC Handbook of CHEMISTRY and PHYSICS*", 68th Ed., CRC Press Inc., Boca Raton, Florida, **1988**.

28. S. -H. Lin, R. -S. Juang, *J. Hazard. Mater B*, **2002**, *92*, 315.

29. S. J. Gregg, K. S. W. Sing, "*Adsorption, Surface Area, and Porosity*"**,** 2nd Ed., Academic Press, London, Inc.: **1982**.

30. W. Zhou, K. Zhu, H. Zhan, M. Jiang, H. Chen, *J. Hazard. Mater. B*, **2003**, *100*, 209.

31. T. Vengiris, R. Binkiene, A. Sveikauskaite, *Appl. Clay Sci.*, **2001**, *18*, 183.

32. M. P. F. Fontes, P. C. Gomes, *Appl. Geochem.*, **2003**, *18*, 795.

33. P. Trivedi, L. Axe, J. Dyer, *Colloids and Surf. A: Physicochem. Eng. Aspects*, **2001**, *191*, 107.

34. M. B. McBride, "*Environmental Chemistry of Soils*", Oxford University Press, New York, **1994**.

35. W. Huang, M. A. Schlautman, W. J. Weber. JR, *Environ. Sci. Technol.*,**1996**, *30*, 2993.

36. B. T. Mader, K. U. Goss, S. J. Eisenreich, *Environ. Sci. Technol.*, **1997**, *31*, 1079.

37. J. -F. Lee, Y. -T. Chang, H. -P. Chao, H. -C. Huang, M. -H. Hsu, *J. Hazard. Mater.*, **2006**, *129*, 282.

38. C. T. Chiou, J. P. Louis, H. F. Virgil, *Science,* **1979**, *206*, 831.

39. C. T. Chiou, P. E. Porter, D. W. Schmedding, *Environ. Sci. Technol.*, **1983**, *17*, 227.

Table 1: Surface area, pore size, elemental analysis and functional group content of modified and pristine Na-montmorillonite

Soils	BET surface area (m^2/g)	Pore size (nm)	Pore volume (cm^2/g)	Element Weight (%)			Functional group	
				C	H	N	mmol /100g	meq/ 100g
Na-montmorillonite	34.03	5.67	0.027	0.00	1.98	0.05	-	-
HM-M	99.69	4.02	0.100	6.21	2.85	1.21	41.4	82.8
HDS-M	39.31	7.98	0.078	7.88	2.68	0.60	19.6	39.2
PMDETA-M	8.86	12.79	0.028	7.38	2.59	2.71	63	63

Table 2: Adsorption of inorganic and organic pollutants by modified soils and Langmuir isotherms parameter

Adsorbates	HM-M		HDS-M		PMDETA-M		Unmodified Na-montmorillonite	
	q_{max} (mg/g)	R^2	q_{max} (mg/g)	R^2	q_{max} (mg/g)	R^2	q_{max} (mg/g)	R^2
Cu^{2+}	2.000	0.9585	3.333	0.9884	2.500	0.9146	0.658	0.9253
Zn^{2+}	1.111	0.9710	2.500	0.9759	2.000	0.9688	0.432	0.9724
Benzene	100000	0.9497	75008	0.9509	87506	0.8901	12600	0.9002
Toluene	37502	0.9577	31258	0.8589	43754	0.8959	4786	0.9244
Ethylbenzene	17503	0.9277	12507	0.9559	15303	0.9199	2603	0.9201
p-Xylene	17520	0.9297	18759	0.9376	25004	0.9458	2436	0.9542

Table 3: Organic carbon content and distribution constants values for different systems

Adsorbates		HM	HDS	PMDETA
	OC %	4.15 ± 0.02	8.30 ± 0.03	9.12 ± 0.02
Benzene	K_d	59.76 ± 0.03	44.55 ± 0.04	36.86 ± 0.04
Toluene		124.18 ± 0.02	101.38 ± 0.02	130.56 ± 0.03
Ethylbenzene		180.46 ± 0.04	120.23 ± 0.03	116.68 ± 0.04
p-Xylene		162.58 ± 0.02	253.7 ± 0.04	293.78 ± 0.04

Table 4: Corrected organic carbon content and constant (K_{OC} and K_{OM}) values for different systems

Adsorbates		HM	HDS	PMDETA
	OM%	8.30 ± 0.05	16.60 ± 0.07	18.24 ± 0.04
Benzene	K_{OC}	1440.02 ± 0.05	536.76 ± 0.02	404.14 ± 0.02
	K_{OM}	720.01 ± 0.06	268.38 ± 0.04	202.27 ± 0.06
Toluene	K_{OC}	2992.29 ± 0.07	1221.45 ± 0.03	1431.58 ± 0.03
	K_{OM}	1496.14 ± 0.03	610.72 ± 0.03	715.79 ± 0.02
Ethylbenzene	K_{OC}	4348.67 ± 0.04	1448.55 ± 0.02	1279.50 ± 0.04
	K_{OM}	2174.34 ± 0.02	724.28 ± 0.01	639.75 ± 0.05
p-Xylene	K_{OC}	3917.59 ± 0.05	3056.27 ± 0.06	3221.27 ± 0.02
	K_{OM}	1958.80 ± 0.02	1528.13 ± 0.02	1610.64 ± 0.04

Figure captions

Fig. 1: Molecular structure and chemical formulae of modifiers

Fig. 2: FT-IR of unmodified and modified (double CEC) Na-montmorillonite

Fig. 3: SEM images of (a) Na-montmorillonite; (b) HM-M; (c) HDS-M; (d) PMDETA-M

Fig. 4: XRD of (a) Na-montmorillonite; (b) HM-M; (c) HDS-M; (d) PMDETA-M

Fig. 5: (a) N_2 adsorption isotherms of unmodified and modified soils; (b) BJH pore distribution diagram

Fig. 6: Adsorption of Cu^{2+} and Zn^{2+} ions by modified soils

Fig. 7: Adsorption of BTEX

Fig. 8: Adsorption mechanisms for inorganic and organic pollutants

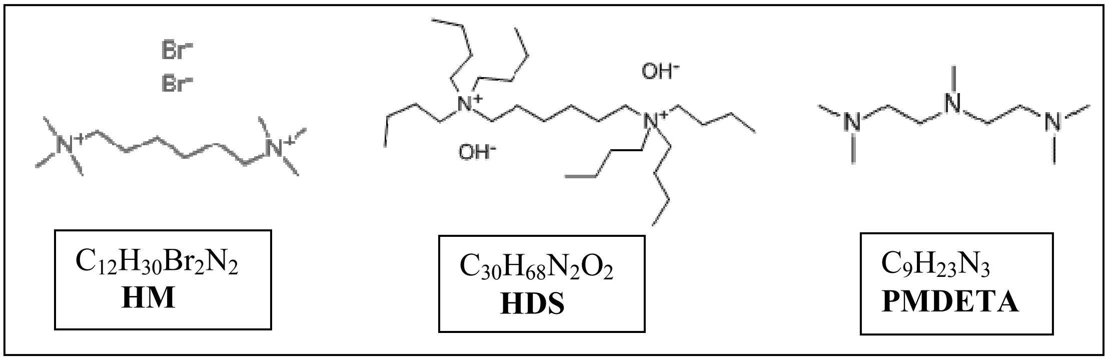

Br⁻
Br⁻
N⁺
N⁺
$C_{12}H_{30}Br_2N_2$
HM
OH⁻
OH⁻
N⁺
N⁺
$C_{30}H_{68}N_2O_2$
HDS
N
N
N
$C_9H_{23}N_3$
PMDETA

Fig. 1

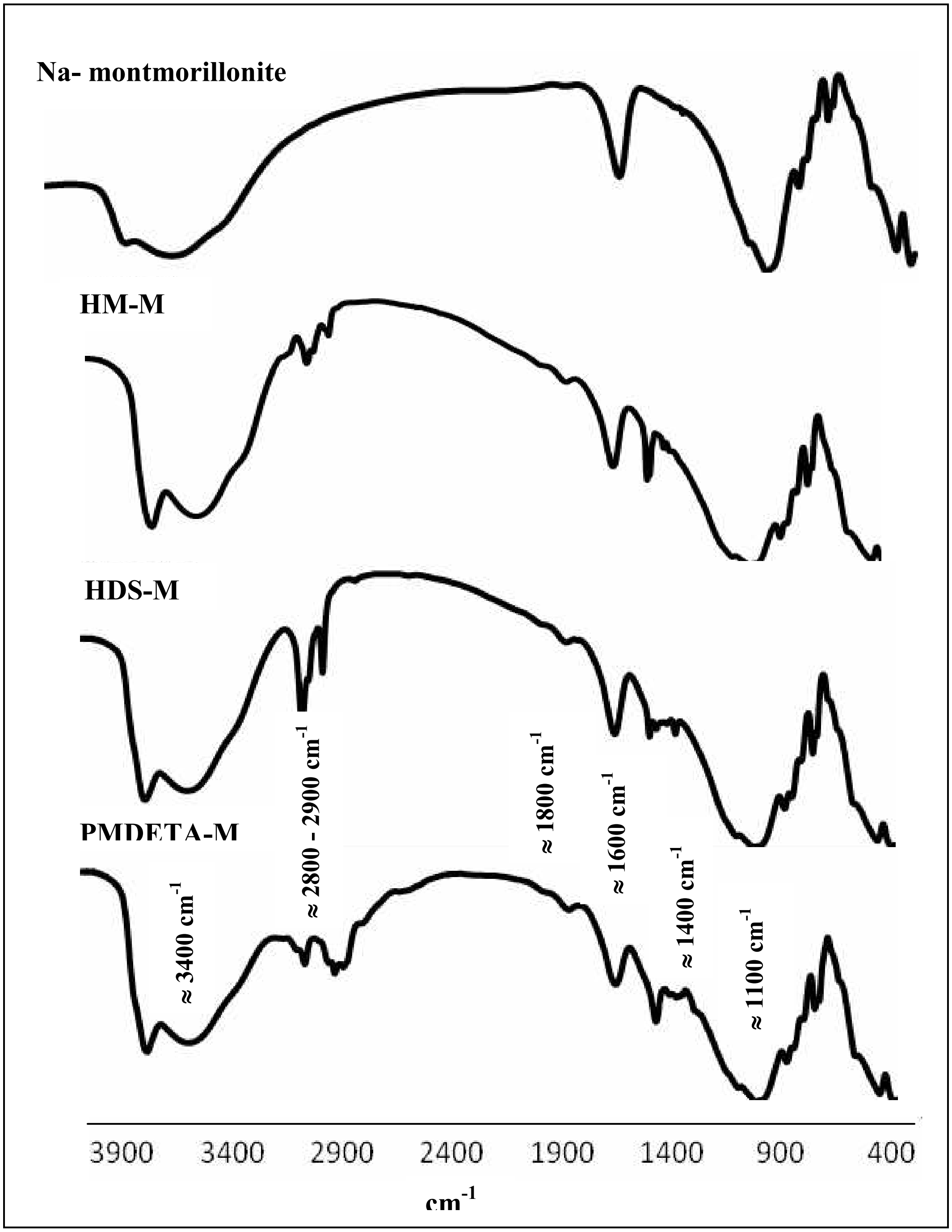

Na- montmorillonite
HM-M
HDS-M
PMDETA-M
≈ 3400 cm^{-1}
≈ 2800 - 2900 cm^{-1}
≈ 1800 cm^{-1}
≈ 1600 cm^{-1}
≈ 1400 cm^{-1}
≈ 1100 cm^{-1}
3900
3400
2900
2400
1900
1400
900
400
cm^{-1}

Fig. 2

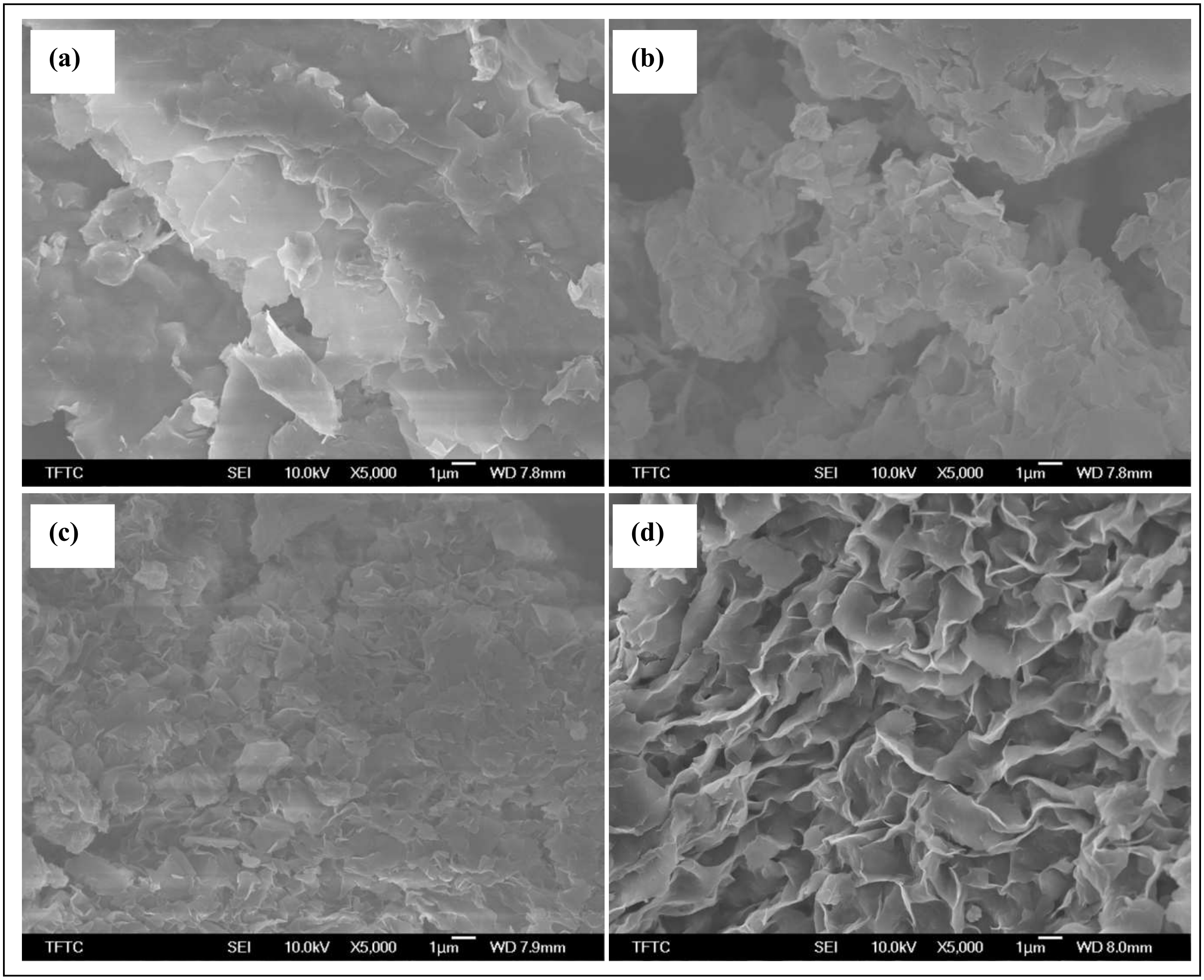

(a)
(b)
(c)
(d)
TFTC SEI 10.0kV X5,000 1µm WD 7.8mm
TFTC SEI 10.0kV X5,000 1µm WD 7.8mm
TFTC SEI 10.0kV X5,000 1µm WD 7.9mm
TFTC SEI 10.0kV X5,000 1µm WD 8.0mm

Fig. 3

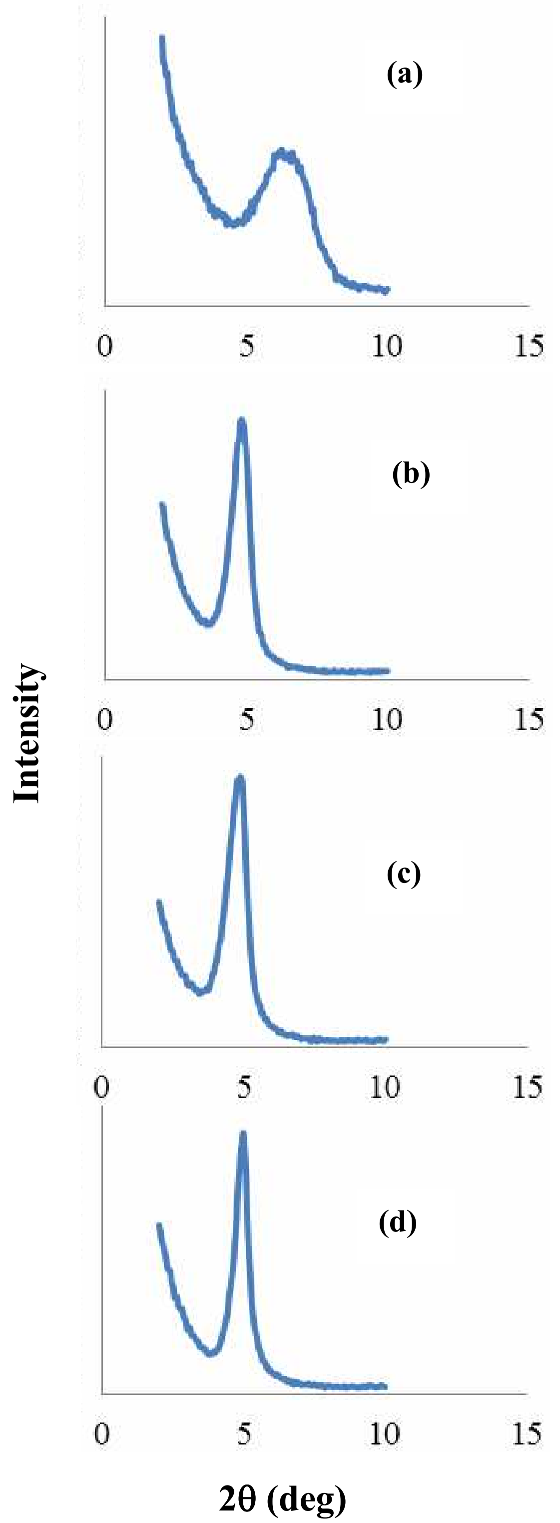
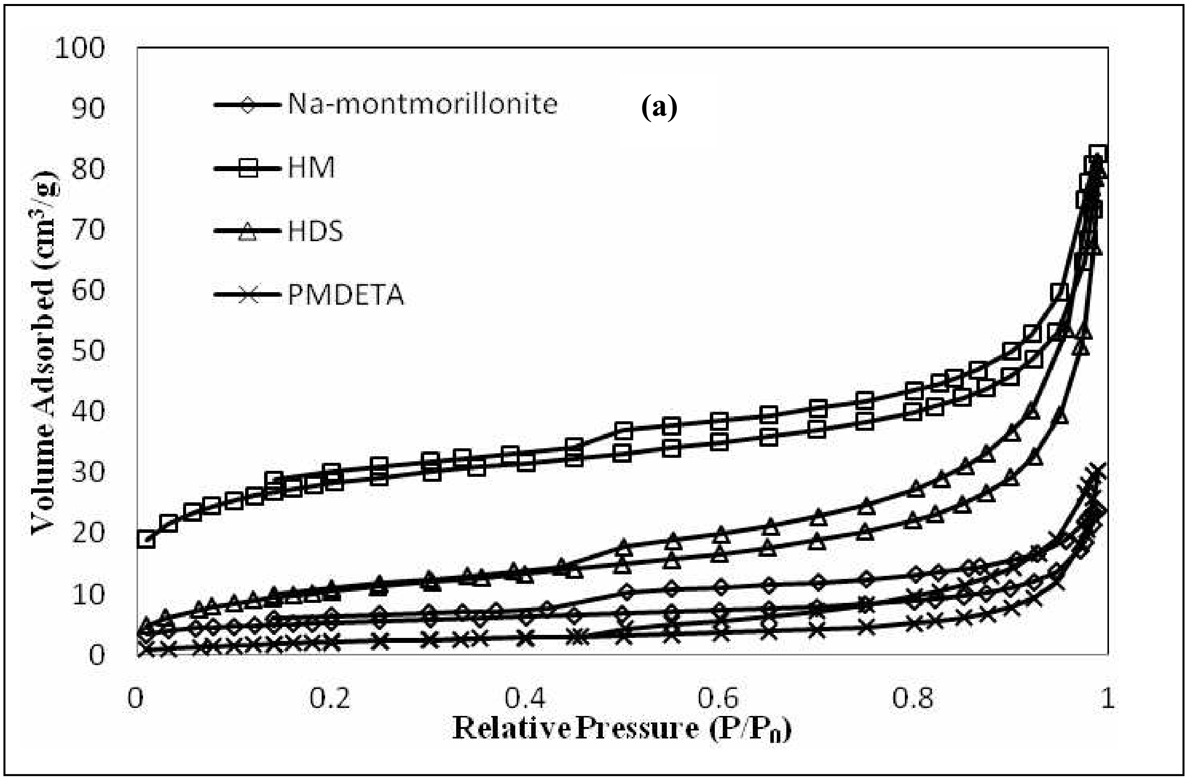


Fig. 4


(a)
Na-montmorillonite
HM
HDS
PMDETA
Volume Adsorbed (cm³/g)
Relative Pressure (P/P0)
0
10
20
30
40
50
60
70
80
90
100
0
0.2
0.4
0.6
0.8
1

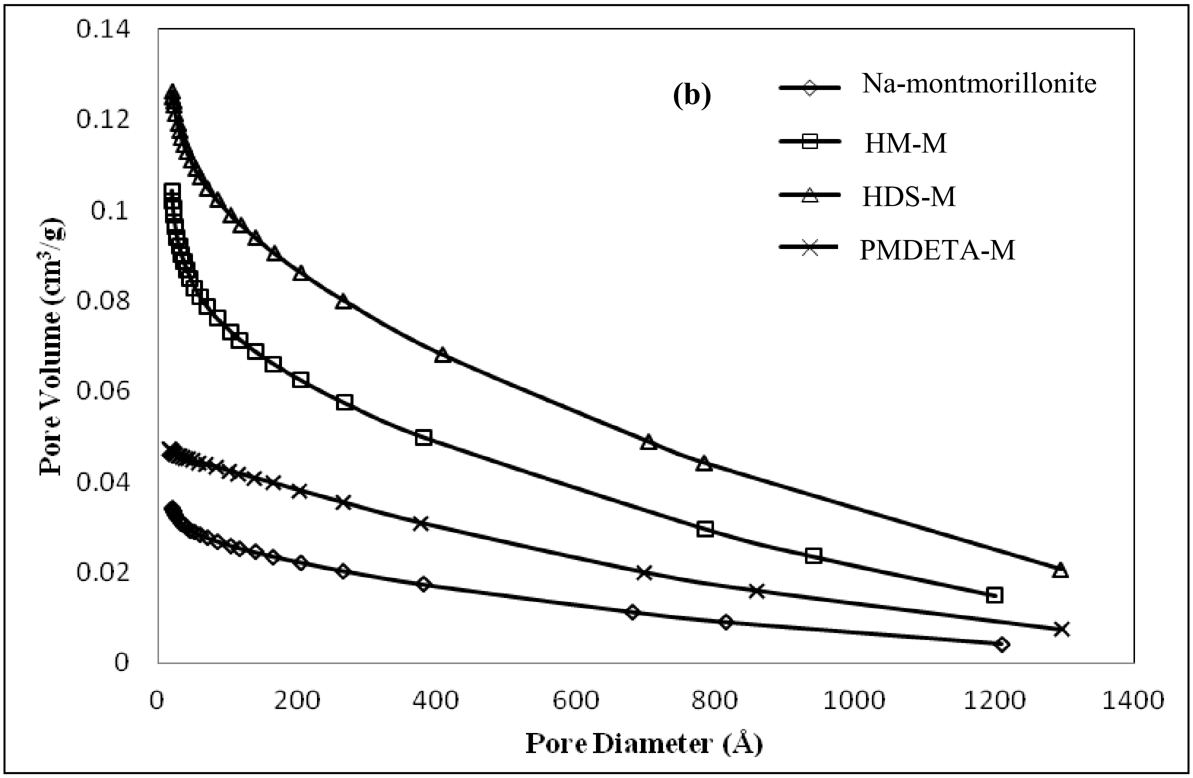

(b)
Na-montmorillonite
HM-M
HDS-M
PMDETA-M
Pore Volume (cm³/g)
Pore Diameter (Å)
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0
200
400
600
800
1000
1200
1400

Fig. 5

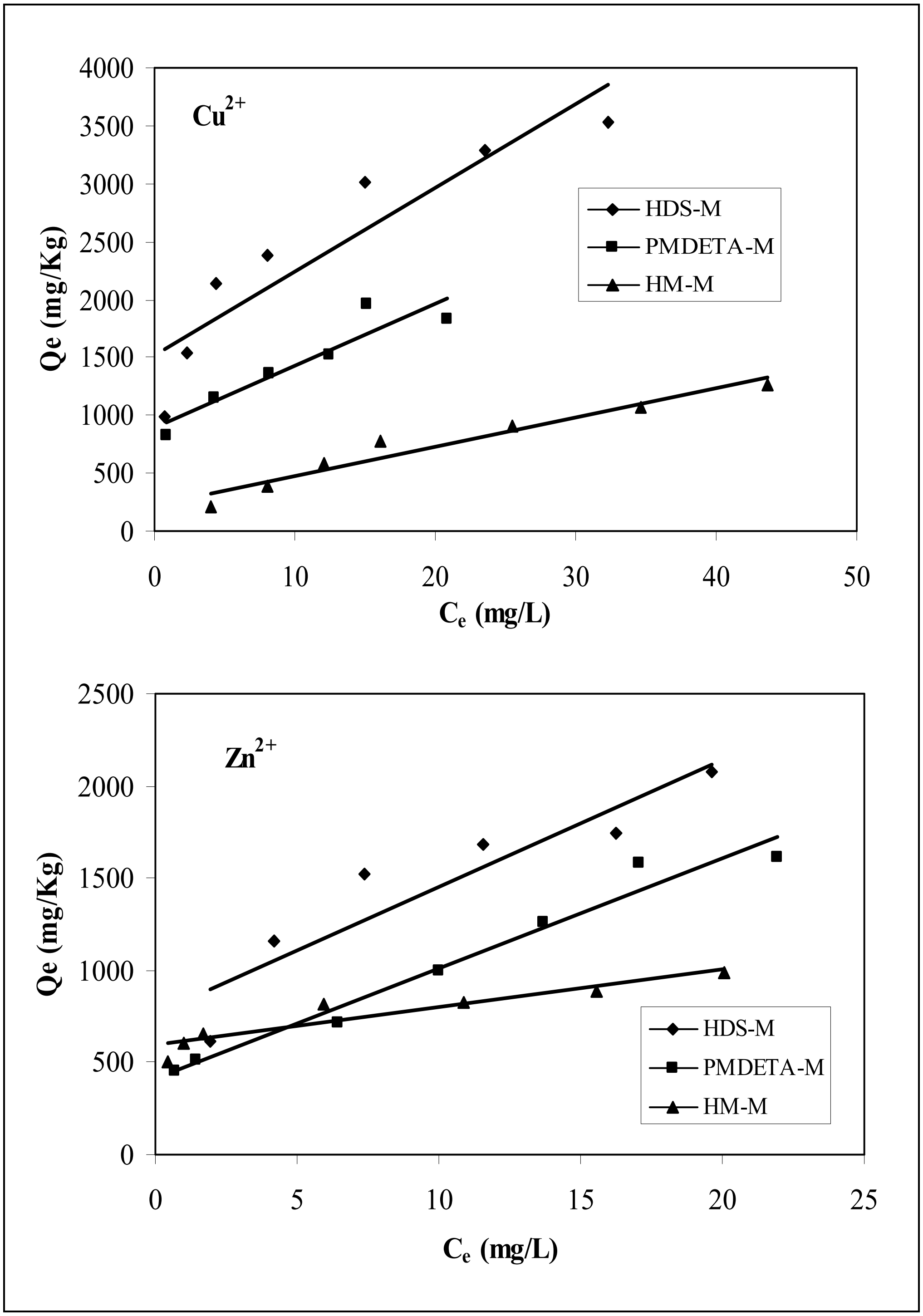

Cu^{2+}
Qe (mg/Kg)
4000
3500
3000
2500
2000
1500
1000
500
0
0
10
20
30
40
50
C$_e$ (mg/L)
HDS-M
PMDETA-M
HM-M
Zn^{2+}
Qe (mg/Kg)
2500
2000
1500
1000
500
0
0
5
10
15
20
25
C$_e$ (mg/L)
HDS-M
PMDETA-M
HM-M

Fig. 6

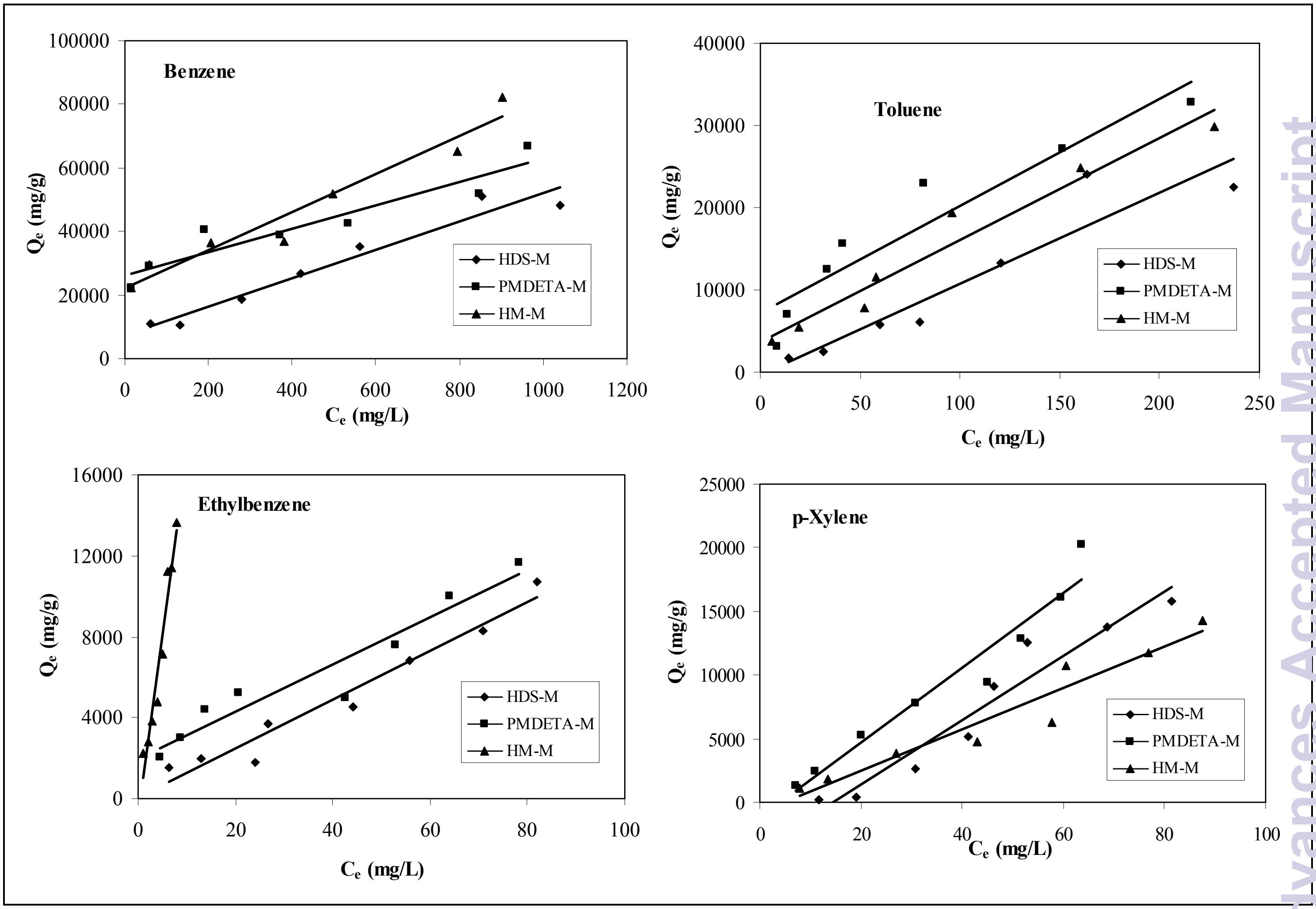

Benzene
Toluene
Ethylbenzene
p-Xylene
Q_e (mg/g)
C_e (mg/L)
HDS-M
PMDETA-M
HM-M
100000
80000
60000
40000
20000
0
200
400
600
800
1000
1200
40000
30000
20000
10000
50
100
150
200
250
16000
12000
8000
4000
20
40
60
80
100
25000
20000
15000
10000
5000

Fig. 7

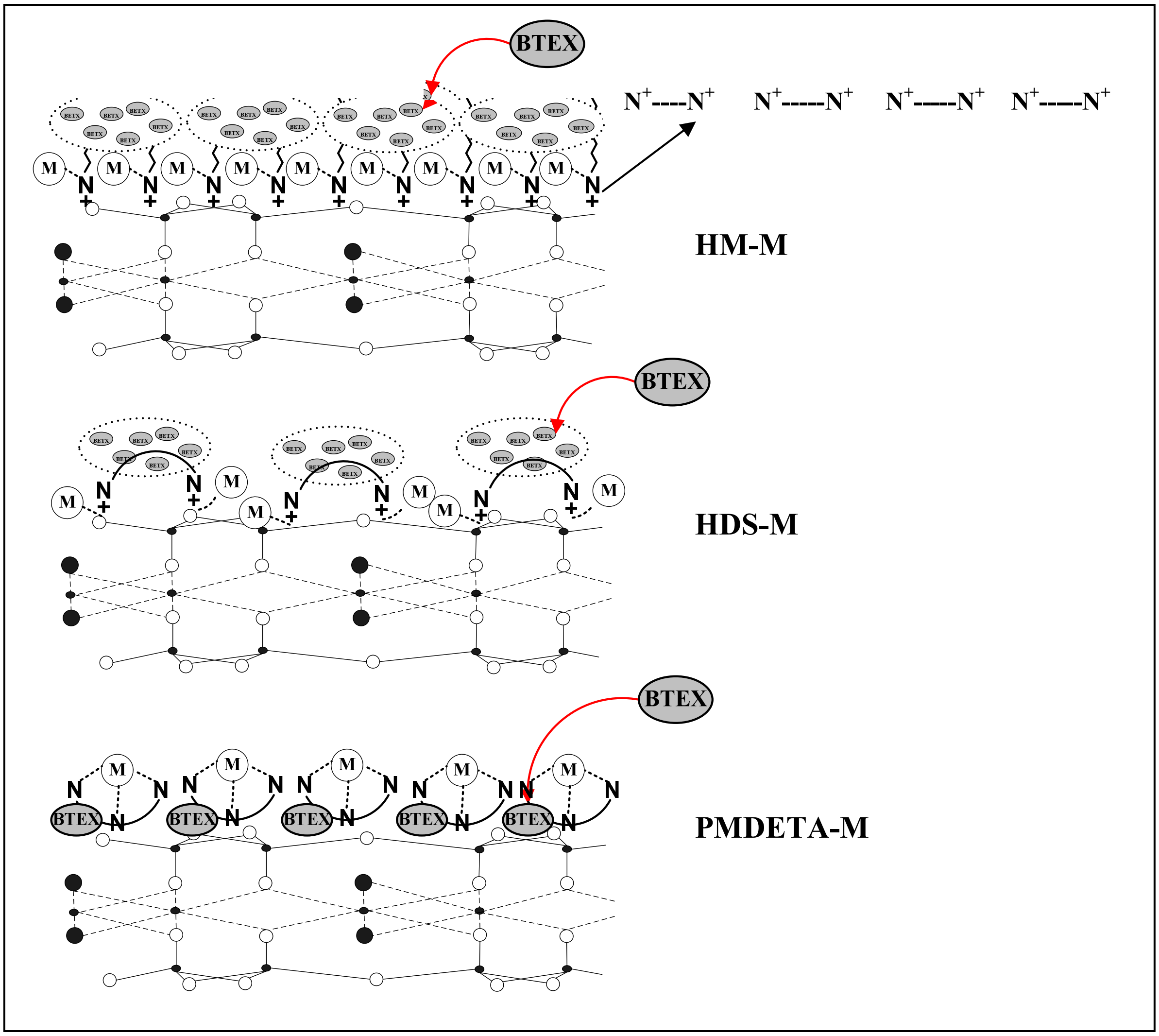


Fig. 8