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A facile approach for effective dual sorption ability of Si/SH/S grafted sodium montmorillonite

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ABSTRACT

In this study sodium montmorillonite was grafted with SH, S and Si functional groups using four different soil modifiers such as 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane [BAT], 3,3'-tetrathiobis(propyl-triethoxysilane) [TP], thiodiglycol bis(3-aminocrotonate) [TDBA] and (3-mercaptopropyl)trimethoxysilane [MPTMS] for effective uptake of both organic and inorganic pollutants. The uptake of inorganic (Cu^{2+}, Zn^{2+}) and organic [(benzene, toluene, ethylbenzene and p-xylene (BTEX)] pollutants was studied in individual as well as binary mixtures. Based on the experimental results, the soil modifier MPTMS favored the sorption characteristics and among two metal ions, Cu^{2+} showed enhanced adsorption. Sorption of BTEX was not correlated with single parameter and hence it differed for different cases based on organic matter content. The obtained log K_{OC} and log K_{OM} values of BTEX in this study for modified montmorillonite are comparatively larger than that of unmodified montmorillonite or natural soil. Sorption carried out in the binary mixtures showed that there is no interaction between these pollutants and the presence of one did not retard the adsorption of another one. Uptake phenomenon was influenced by various combined factors such as nature, surface charge and surface area of modified soils.

Key words

Modified sodium montmorillonite; grafting; modifiers; metal ions; BTEX

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1. INTRODUCTION

In general pollutants are introduced into the environment through natural phenomenon and human activities.[1] Although certain organic and inorganic materials are necessary in small amounts for the usual development of the biological cycles, most of them become toxic at high concentration which is extremely risk also.[1] Thus, preserving soils from dilapidation and particularly from pollution is of more and more concern. The concentration and mobility of such pollutants in soils and clays have been extensively studied in recent decades since these soils or clays are used as barriers in landfills to avoid contamination of subsoil and groundwater.[2] These linings are mainly constituted of bentonite (montmorillonite), which can uptake both organic and inorganic pollutants by different mechanisms.[3] In order to predict the nature of these pollutants in soil or clay, it is important to know the behavior of such soil or clay systems.[4] Variety of surface and structural properties determine the uptake ability of clay or soil which can be desirably altered by various modification processes.[5] Clay and other layered silicate clays are naturally hydrophilic and the natural form of soil or clay is considered to be ineffective adsorbent for neutral organic contaminants such as polycyclic aromatic hydrocarbons. This limitation of adsorption capacity of clays and soils can be overcome by modification process. Thus, the uptake properties of clay or soil for neutral polycyclic aromatic hydrocarbons can be significantly improved by replacing the neutral interlayer cations with large organic cations.[6,7] These modified organo-clays have been effective in the removal of various neutral organic contaminants.[8-10] Handling and modification of the adsorbents are easily possible[11] and such modification processes are really rapid and particle size controlled. Surface modified soils or clays by means of cationic surfactants

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are successfully proven to be suitable adsorbents for inorganic and organic contaminants.[12] During modification process, the structure and properties, in particular the basal spacing of modified soil or clay is significantly affected. However, the treatment with a cationic surfactant is not effective in the case of simultaneous pollution with both organic and heavy metal pollutants because cationic heavy metals are weakly adsorbed, due to hydrophobic nature of modified adsorbents. Thus, the results reported by other researchers[13,14] clearly indicated that cationic surfactant modified adsorbents favored only the uptake of organic pollutants, but simultaneously decreased the adsorption of inorganic pollutants. In the case of thiol grafted montmorillonite, a problem of accessibility of grafted sites was witnessed.[15] Thus, a special surface modifier, amphoteric modifier which has both negative and positive charges that could adsorb cationic and anionic pollutants, came into use.[16] But it is obvious as amphoteric modifier has both negative and positive charges, there is no any significant or surprise to act as dual adsorbent for both organic and inorganic pollutants. Also, so far majority of soil or clay system have been focused on organic pollutants only and adsorption of dual pollutants are limited. The main restrictions of these above said techniques are found either in their selectivity or in the extent of their effects. Thus, it is important to go for some alternative approaches which are promising, effective and interesting for the removal of both organic and inorganic pollutants. We believed that introduction of either S or thiol (SH) groups into montmorillonite would definitely lead to improved affinity of modified montmorillonite in terms of improvement of the sorption capacity for certain metal ions such as Cu^{2+}, Pb^{2+} and Zn^{2+} which are classified as *chalcophiles*. In the case of S or SH grafted soils, the electron pair of the functional group is not shared after it is

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bonded to the soil due to their special structures which is the advantage of this method. By this grafting, the surface energy of montmorillonite would decrease and the interlayer spacing is expected to expand. Thus, the basal spacing of the resulting modified montmorillonite depends on the chemical structure of the modifier, the degree of ion exchange, and silicate layer thickness. So, we have chosen these different modifiers and studied how these different modifiers affect the above said properties of montmorillonite. Thus, these modifiers are considered to be more significant as they can hold the physiochemical properties for simultaneous adsorption of both organic and inorganic pollutants. Hence, enhanced sorption properties are expected in this study. The main objective of this study was to increase the organic content of montmorillonite by different soil modifiers with special structures such as 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane [BAT], 3,3'-tetrathiobis(propyl-triethoxysilane) [TP], thiodiglycol bis(3-aminocrotonate) [TDBA] and (3-mercaptopropyl)trimethoxysilane [MPTMS] and also to obtain simultaneous uptake of both organic and inorganic pollutants.

Thus we attempted to graft either S or SH groups in the interlayer space of montmorillonite soil, in order to obtain modified soils which are accessible to both inorganic and organic pollutants and compared their activities. Thus, these modified soils behave as a dual sorbent rather than a single or mixed adsorbent. Such modification treatments markedly modify surface area, adsorption energy, porosities of typical montmorillonite soil and checking this hypothesis on soils was also the aim of this paper. A practical importance of such studies is that the above soil properties control soil water retention, hydraulic conductivity, solute transport, and sorption of pollutants, which can modify the efficiency of remediation processes. According to our knowledge, there have

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been only few studies on surfactant modified, and SH grafted montmorillonite, but so far no reports on S grafted montmorillonite. In these cases, possible covalent bonds formation between the S or SH atoms of the respective modifier molecules and the montmorillonite surface may occur, leading to their high density and fixation of grafting. Simultaneously the total Si contents were also greatly enhanced in Si grafted soil due to their molecular structures. In this study, the influence of presence of Si, SH and S groups on structural properties was also explained. The results indicated that the uptake of pollutants was mainly influenced by various factors. Uptake of inorganic pollutants was altered by surface area and structure of the modifiers and uptake of organic pollutants was controlled by solubility and organic matter content. The observed log K_{OC} and log K_{OM} values of BTEX in this study for modified soils are comparatively greater than that of natural soils. However, the uptake was not dependent on single factor and deep insight is yet to be focused into this. The previous reports just discussed the adsorption phenomenon[16-18], but detailed information was not explained properly. Thus, the present methodology is very significant and novel in its approach.

2. EXPERIMENTAL SECTION

2.1. Chemicals

The montmorillonite used in this study was obtained from the Clay Minerals Society as SWy-2-Na-montmorillonite (Wyoming) 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 surface area is 28.02 m^2/g and the cation exchange capacity (CEC) is 78 meq/100g. The montmorillonite was used without further purification. High purity laboratory grade copper and zinc standard solutions (1000 ppm) were purchased from J. T. Baker. All the

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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 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane [BAT] (Sigma-aldrich, molecular weight = 248.51), 3,3'-tetrathiobis(propyl-triethoxysilane) [TP] (Sigma-aldrich, molecular weight = 538.95), thiodiglycol bis(3-aminocrotonate) [TDBA] (Sigma-aldrich, molecular weight = 288.36) and (3-mercaptopropyl)trimethoxysilane [MPTMS] (Sigma-aldrich, molecular weight = 196.34). The molecular structures and chemical formulae of these four modifiers are shown in Fig. 1.

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

In this study modified Na-montmorillonite was obtained by two different methods using different modifiers. One is by simple mixing in water and another is by refluxion in toluene.

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 CEC) was added to the supernatant clay fraction (20 ml) and the reaction mixture was stirred for 2 h. Then all the products were washed and 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 BAT, TP, TDBA and MPTMS

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modified montmorillonites obtained by simple mixing in water method were denoted as BAT-M, TP-M, TDBA-M and MPTMS-M respectively.

For refluxion method in toluene, two modifiers TP and MPTMS were chosen. 5 g of Na-montmorillonite was added into 200 mL of anhydrous toluene and stirred for 5 min. To this appropriate amount of respective modifiers (usually double CEC) was added and stirred for 5 min. Then the reaction mixture was refluxed at 110 °C for 24 h. After cooling to room temperature, toluene was removed and the samples were collected, rinsed with toluene to remove any unreacted modifier and vacuum dried for 12 h. Finally, they were ground in an agate mortar and stored in a vacuum desiccator. The TP and MPTMS modified montmorillonites obtained by refluxion grafting method were denoted as TPG-M and MPTMSG-M respectively.

2.4. Batch sorption studies

To test the efficiency of modified montmorillonites as adsorbents, we used three methods. The batch sorption experiment included three pollutant type treatments: (1) inorganic pollutants (Cu^{2+} and Zn^{2+}) only, (2) organic pollutants (benzene; >99%, toluene; >99.9%, ethylbenzene; >99.6% and xylene; > 99.5%, in brief BTEX) only, and (3) mixture of both inorganic and organic pollutants. 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 uptake experiments were performed at 25 °C in glass centrifuge tubes containing different heavy metal ion solutions (20 mL) and the modified montmorillonites (2 g), shaken at pH 2 for 24 h at 130 rpm in a Lab-line orbit environ

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shaker. The reaction mixture was centrifuged at 6000 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. Uptake of organic pollutants (BTEX)

The experiments were performed at 25 °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 6000 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 the sample was analyzed using a Hewlett Packard (GC, Model: HP-6890) gas chromatograph) equipped with a flame ionization detector (GC-FID) in 5 mL aliquot samples to determine the concentration of organic pollutant in the solution.

2.4.3. Uptake of both organic and inorganic pollutants

The experiments were performed at 25 °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 2 for 24 h at 130 rpm in a Lab-line orbit environ shaker. The reaction mixture was centrifuged at 6000 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

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sample were analyzed to determine quantitatively the organic pollutants (GC) and inorganic pollutants (AAS) respectively.

2.5. *Determination by analytical procedure*

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

$q_e = [(C_0 - C_e)V]/M$

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. 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. Elemental analysis was carried out by CE EA-1110 elemental analyzer.

3. RESULTS AND DISCUSSIONS

3.1. *FT-IR, BET, elemental analyses, XRD*

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In this work SWy-2-Na-montmorillonite was modified using four different modifiers by two different grafting methods both in water and toluene. The grafting mechanism may be possibly explained based on the covalent bond formation between the grafting groups of (Si, S or SH) of the modifiers and montmorillonite surface. There may be single, double or multiple covalent bond formation depending upon the nature and affinity of Si, S or SH groups present in the modifiers towards the surface of montmorillonite soil. Accordingly different modified montmorillonites with varying physico-chemical properties were obtained and characterized using various techniques. Upon grafting of modifiers onto montmorillonite surface, the organosilanes of BAT, TP and MPTMS modifiers undergo self assembly as shown in Fig. 2. However, in the case of TDBA, it contains organosuphur and this organosulphur will undergo self assembly in this case. Thus, molecular-self assembly of organosilanes or organosulphur groups of modifiers has been proven to be a powerful technique for grafting of montmorillonite surface.[19] In this process, organisilanes or organosulphur groups of modifiers are hydrolyzed in the presence of SiO_2 group of montmorillonite to create corresponding hydroxysilane or hydroxysulphur. Then, these are hydrogen bound to SiO_2 group of montmorillonite. Eventually aggregation of these hydrogen bound species resulted into condensation between hydroxysilanes/sulphur and SiO_2 group of montmorillonite.[19] The modified and unmodified montmorillonites were subjected to FT-IR analysis as shown in Fig. 3, in order to confirm the presence of functional groups. In the case of unmodified Na-montmorillonite, the broad peak around 3400-3900 cm^{-1} is assigned to to ν(O-H) and $\nu(H_2O)$, the peak around 1050 cm^{-1} is assigned to ν(Si-O-Si), and the peak around 1600 cm^{-1} is assigned to interlayer water deformation vibrations. The appearance of new

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peaks[20] apart from original peaks in the modified montmorillonites confirmed the successful modification using different modifiers. In the modified montmorillonites, the peak around 2800-2900 cm^{-1} is due to $\nu_{stretching}$(CH_3 and CH_2), the peak around 1595 cm^{-1} is due to $\nu_{stretching}$(NH_2) and the peaks around 1040 cm^{-1} and 800 cm^{-1} are due to $\nu_{stretching}$(Si-O-Si) and $\nu_{bending}$(Si-O-Si) is observed around 450 cm^{-1}. In the case of TP-M and TPG-M, the peak around 620 cm^{-1} is assigned to $\nu_{stretching}$(S-S). However in the case of MPTMS-M and MPTMSG-M the peaks due to ν(SH) and ν(OCH_3) are not clearly distinguished due to of peak merging. Invariably in all cases, the position of Na-montmorillonite peaks was almost remained unaltered after modification also. Upon modification, the broadening of water peak decreases and the peak around 3400-3900 cm^{-1} became sharp due to the hydrophobic nature of modified montmorillonites. The elemental analysis data, extent of functionalization, BET surface area and pore size of both unmodified and modified montmorillonites are shown in Table 1. From Table 1, we can easily understand that the extent of functionalization determined by potassium dichromate method varied for different modifiers and in the case of MPTMS, functionalization is comparatively larger than that of others due to its simple shorter chain length. The functional group content values explained the modification ability of different modifiers. Thus, it is obvious that the functionalization of linear longer carbon chain is less effective due to the steric hindrance. Thus, the molecular structure of modifiers played a significant role in controlling the functionalization process. Thus the ability of modifier could be arranged in the order as MPTMS>TP>TDBA>BAT. From Table 1, it is seen that the weight percentage of C, H and N was significantly increased for modified soils which also confirmed the effective

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modification of soil. The BET surface area of montmorillonite was significantly decreased after modification, but however the pore size was drastically increased. But the BET surface area of the modified soils is not dependent on functionalization. Based on BET surface area the modified soils could be arranged in the following order as TPG-M>MPTMSG-M>BAT-M>TDBA-M>MPTMS-M>TP-M. But the pore size of the modified soils did not show any direct correlation with surface area and according to pore size the modified soils could be arranged in the following order as TDBA-M>MPTMS-M>MPTMSG-M>BAT-M>TPG-M>TP-M. Among modifiers, TP which contains both Si and S groups favorably increased extent of functioanlization, surface area. However, BAT with Si groups moderately increased the surface area. However, TDBA with sulphur group and MPTMS with SH group resulted into soils with smaller surface area. Thus the Si groups present in the modifier structure significantly favored the structural properties of modified soils. Thus, from Table 1, it is witnessed that modification of soils significantly enhanced the pore size of the soils but decreased the surface area. It is also seen that in all cases, the pore volume of modified soils decreased significantly 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. The basal spacing in the modified montmorillonites was expected to be significantly increased due to the grafting of such modifiers into the interlayer framework.[8,21,22] This is confirmed by the obtained XRD patterns of montmorillonites before and after modification as shown in Fig. 4. The XRD patterns consisted of three peaks corresponding to [001], [002] and [004] reflections along with quartz peaks as shown in Fig. 4. The XRD also revealed a shift in the peak position corresponding to (001)

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reflection around $2\theta = 6.7°$ to lower 2θ values ($2\theta \approx 6.7$ to $4.1°$) after modification, indicating relatively a larger increase in the basal distance of these planes from 1.32 nm to 2.20 nm. This increase clearly confirmed the occurrence of intercalation of modifiers between montmorillonite clay layers. Thus, compared with Na-montmorillonite (corresponding to a basal plane spacing [d_{001}] of 1.32 nm), modified montmorillonites have a larger basal spacing. Based on basal spacing, the modified montmorillonites can be arranged in the order as BAT-M (2.20 nm) > TPG-M (2.10 nm) > TDBA-M (2.01 nm) > TP-M (1.75 nm) > MPTMS-M (1.52 nm) MPTMSG-M (1.42 nm). However basal distance of the planes corresponding to [002] and [004] reflections were not significantly altered and this highlights the successful intercalation of [001] planes of montmorillonite. It is thus confirmed that the interlayer spacing of the montmorillonite is significantly increased by the modifiers. 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.

3.2. N_2 adsorption isotherms

The specific surface area and pore size distribution are important indicators of adsorbent's adsorption capacity. The obtained nitrogen adsorption isotherms before and after modification as shown in Fig. S1 (See Fig. S1) obviously conveyed that all the samples exhibited typical type II S-type curves. The hysteresis was not seen obviously and at low relative pressure ($P/P_0 < 0.01$) the adsorption is low. The adsorbed volume increased linearly upon increasing the pressure in the range of P/P_0 from 0.1 to 0.5. This region corresponds to a monolayer-multilayer adsorption on the pore walls. Beyond $P/P_0 = 0.5$, a sharp increase in the adsorbed volume was observed, which could be

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attributed 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 a drastic increase in the adsorbed volume was resulted. 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,[23] 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. Thus, it is clear that the structural property of soil was not altered upon soil modification. The pore size distribution is shown in Fig. 5, and it is observed that in the range between 2 to 40 nm particles with smaller pore sizes are distributed, and in the range between 70 to 150 nm, particles with larger pore sizes are distributed. A uniform and narrow pore size distribution was accumulated in the case of MPTMS-M, TP-M and TDBA-M whereas in the case of TPG-M, BAT-M and MPTMSG-M, the pore size distribution was broadened and less accumulated. These nitrogen adsorption and pore size distribution curves clearly revealed that the different modifiers could affect the pore size and its distribution. This study vividly revealed that the modifiers with siloxane or thiol groups resulted into modified soils with a larger surface area and smaller pore size compared to that of modifiers with sulphur atom which resulted into modified soils with a lower surface area but relatively larger pore size.

3.3. Adsorption of inorganic pollutants (heavy metal ions)

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In this study, adsorption of heavy metal ions such as Cu^{2+} and Zn^{2+} by both modified and unmodified montmorillonite soils was explored. The adsorption of both Cu^{2+} and Zn^{2+} by unmodified montmorillonite soil is shown in Fig. 6. It was found that as the initial concentration of unmodified soil increased, the adsorption capacity also increased. When the initial concentration reached about 15 mg/L, the equilibrium was attained and beyond which the adsorption became almost unaltered. At this saturated point, the availability of active sites of adsorbent for further adsorption is limited and thus further increase in initial concentration caused no more increase in the adsorption of metal ions. The adsorption of Cu^{2+} and Zn+ by modified soils is given in Fig. 7. For modified soils, the adsorption of inorganic pollutants was drastically increased compared to that of unmodified soil. This is due to the fact that the shrinkage of water in interlayer of the modified soils. During modification, the modifiers are assumed to penetrate into interlamellar region of the soil/clay by the expansion of clay sheets. Such 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. Thus, in the presence of modifiers, the water is removed and the interstitial layer of the surface morphology is easily stretched. On comparison between Langmuir and Freundlich adsorption isotherms of modified soils, the calculated R^2 value of Langmuir adsorption model is found to be 0.9 as shown in Table 2, indicating that the Langmuir isotherm model fitted well in all cases. It can be also seen that for unmodified soil, the adsorption capacity of Cu^{2+} was comparatively larger than that of Zn^{2+}. This is because of the reason that the difference in electronegativity of metal ions. Thus, it is very clear that, the adsorption of heavy metals is not dependent on surface area but it is dependent on the coordinating properties

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(affinity) of metal ions towards the adsorbents. For modified soils, the adsorption of Zn^{2+} was also significantly increased which is due to the presence of S or SH functional groups in the modifier structures. These functional groups are capable of forming strong coordination bonds with Zn metal ions also and thus in the case of modified soils, both the adsorption of Cu^{2+} and Zn^{2+} were significantly enhanced. This suggested that the adsorption process involved a chemical adsorption with the adsorption capacity not only depending upon the surface area of adsorbents but also depended upon nature (surface charge) and structure of the modifiers and the affinity of metal ions. From Fig. 7, and Table 2, it is witnessed that even though, MPTMS-M and TP-M possessed lower surface area than that of BAT-M and TDBA-M, interestingly they showed enhanced adsorption for both Cu^{2+} and Zn^{2+} and the order of adsorption ability of modified soils for metal ions could be arranged as MPTMS-M>TP-M>TDBA-M>BAT-M. Thus, despite of larger surface area, BAT-M still showed lower adsorption capacity for metal ions. This is because of the reason that MPTMS-M and TP-M contained more unshared electron pairs and thus forming strong coordination bonds with metal ions causing for enhanced adsorption. Thus, this discrepancy in behavior can be explained based on the structure and nature of the modifiers used in modified soils. The basic mechanism of adsorption was based on the complexation of functional groups present in modified soils (nitrogen, sulphur or SH groups) with metal ions or hole-filling (adsorption by ion-exchange). In addition, the surface charges due to modifiers could also contribute for the adsorption of pollutants. Thus, the adsorption phenomenon is dependent on various combined factors such as surface charge, surface area and structure of adsorbents and also electronegativity of metal ions. Thus, based on the combined effect it was concluded that MPTMS-M

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showed enhanced adsorption tendency towards metal ions in this study. Based on the experimental results it was observed that among two metal ions, the adsorption behavior of Cu^{2+} was significantly greater than that Zn^{2+}.[5,24,25] This is due to comparatively smaller ionic radii and higher electronegativity of Cu^{2+} than that of Zn^{2+}.

As it is already discussed, two different modification methods were adapted in this study. Thus in order to obtain a better understanding of both methodologies, a comparative study was carried out as shown in Table 2. Under the same conditions, the adsorption of metal ions by modified soils obtained by simple mixing in water (TP-M and MPTMS-M) was greater than that of modifiers obtained by refluxion in toluene (TPG-M and MPTMSG-M). This can be explained based on different adsorption mechanisms. In the case of modifiers by simple mixing in water, the modifiers can be attached to the soils in the upper surface of interlayer and thus the resulting physical adsorption may be a multilayer adsorption. Where as in the case of modifiers by refluxion in toluene, the modifiers can be attached to the soils into the lower surface of interstitial layer and thus the resulting chemical adsorption may be a monolayer adsorption. Thus due to the structural behavior of MPTMS and TP modifiers, the grafting of modifiers by refluxion in toluene is less effective due to bending of structure during refluxion which caused steric hindrance. Thus expansion of interstitial layer is limited and grafting of modifiers is less efficient in refluxion in toluene than that of simple mixing in water. Thus, it is suggested that compared to MPTMSG-M and TPG-M, MPTMS-M and TP-M were considered to be effective adsorbents for metal ions.

3.4. Uptake of organic pollutants (BTEX)

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In this study, as already discussed montmorillonite soil was modified using special modifiers which contain specific functional groups that have greater affinity for metal ions (inorganic pollutants) and long carbon chains due to which the organic carbon content of modified soil also greatly improved. Thus, these modified soils could also function as partition media for nonionic organic pollutants such as BTEX in order to explore their uptake capacity for organic pollutants. This section will explore the role of distribution coefficient (partition coefficient, k_d), the role of soil-water saturated systems, the nature of soil and organic pollutant and the equilibrium concentration (C_e) of organic pollutants. Calibration for recovery of BTEX was done in order to avoid if any error due to high volatile nature of BTEX by covering the batch adsorption mixture and about 95% of BTEX was recovered. The distribution coefficients (k_d) of organic compounds between the solid and the solution may be calculated by a linear relationship as follows;

$$x/m = k_\mathrm{d}C$$

where x is the compound uptake on the solid (mg), m the weight of the solid (kg) and C is the equilibrium compound concentration in the solution (mg/L).

The uptake of BTEX by modified montmorillonites is shown in Fig. 8 and distribution constants (k_d) are displayed in Table 3. From Table 3, it is clear that the distribution of BTEX in soil-water systems is not similar to metal ion adsorption and it is mainly dependent on organic matter content of modified soils. Differences in water solubility of BTEX will definitely affect both the distribution constant (k_d) and equilibrium concentration (C_e) values. From Table 3, it was also observed that invariably the modifiers TP and MPTMS caused for significant increase in k_d values than that of BAT and TDAB modifiers due to their functional group structures and organic content

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matter. In general both BAT and TDBA, contain more polar functional groups (oxygen or nitrogen), more planar structure and limited distribution environment and thus due to this hydrophobic nature, the distribution of organic pollutants is also limited. The uptake results also indicated that the solubility of BTEX in water and organic matter content may affect the partitioning of BTEX,[26] but at the same time the uptake phenomenon did not show any significant correlation with single parameter only. Thus, it was quite complex and the uptake of organic pollutants by modified soils was different for different systems. As it is known, the uptake mainly occurred on organic carbon matters, the determination of 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)[27,28] mainly influenced the uptake of BTEX onto modified soils.

It is very important to understand the water solubility of adsorbate molecules in soil-water systems. In general adsorbate molecules with higher water solubility, tend to form an aqueous solution easily, where as the adsorbate molecules with lower water solubility, are easily distributed in the organic phase of the hydrophobic adsorbent rather than dissolving in the medium. Thus for higher water solubility adsorbate molecules, k_d is always smaller than that of lower water soluble adsorbate molecules, 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 in soil-water system, again the total organic content has to be corrected as shown in Table 4. i.e. total mass transfer of

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contaminant which is dependent of solubility has to be considered significantly. Thus both equilibrium constants K_{OC} and K_{OM} could provide an indication of constituent sorption onto soil or organic matter respectively and K_{OC} is always greater than that of K_{OM}. Hence, there is s a gap between K_{OC} and K_{OM} values in natural soil systems which is a limiting factor that has to be considered seriously. Thus, larger values of both constants indicate the preference of the constituent to be sorbed onto soil or organic matter. Thus, the significance of both K_{OC} and K_{OM} values can be understood in terms of their respective log K_{OC} and log K_{OM} values. 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 significant insights 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). Invariably in all cases, the value of K_{OC} is greater than that of K_{OM}. From Table 4, several observations could be derived and both K_{OC} and K_{OM} are mainly used to predict the value of the non-ionic organic pollutants present in the soil.[28,29] Though K_{OC} seems to be greater than that of K_{OM}, the difference in log K_{OC} and log K_{OM} values are very less, i.e. they are almost identical to each other. Thus, this study successfully eliminated the gap between K_{OC} and K_{OM} values and both obtained log K_{OC} and log K_{OM} values in this study are significantly greater than that of natural soil system as well literature values[28,30] reported so far as shown in Table 5. Thus, from Table 5, it is confirmed that modified soils obtained in this study enhanced the effective uptake of organic pollutants in overall.

The water solubility (S_w) of BTEX was found to be in the order as benzene>tolune>p-xylene>ethylbenzene (1780>515>197>152). However the order of k_d

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varied for different systems. The irregularities in sorption mechanisms as shown in Fig. 5 and Fig. 6 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.[16] The different speciation of inorganic pollutants, organic pollutants and modifiers as a function of pH is apparently important parameters to be taken into the account. Again due to the difference in the structural properties of modified soils obtained by two different methods in this study, the k_d values in toluene refluxion system are relatively found to be smaller than that of simple mixing in water due to steric hindrance by structural bending and also less availability of distribution environment. Thus k_d values of TP-M and MPTMS-M are always greater than that of TPG-M and MPTMSG-M. Thus the nature of organic modifiers played a vital role both on adsorption of organic and inorganic pollutants.

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

In order to evaluate the interaction between inorganic and organic pollutants, adsorption of binary system using both inorganic and organic pollutants was also carried out and discussed in this study. For this purpose, both MPTMS-M and MPTMSG-M were selected as adsorbent as modifier MPTMS showed increased affinity towards metal ions than the others. Also benzene was mainly selected as organic pollutant simply to avoid error as it has higher water solubility. In the case of binary mixture, the 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. The results obtained in this are compared with literature reports[16] and the total adsorption was greatly increased in this study. This clearly indicated that there is no interaction between cations and BTEX. But in most of the

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reported studies[16-18] the presence of organic pollutant caused crowding and thereby decreased the adsorption of metal that ions due to steric hindrance.

The significant effect of soil modifiers used in this study on the adsorption of heavy metal ions can be better explained by comparing with few reported reports[1,5] as well as commercially available granular activated carbon (GAC)[31] and zeolite[32] as shown in Table 6. From Table 6, it is very clear that the adsorption capacities reported in this study by MPTMS-M and other modified montmorillonite soils are definitely greater than that of others and thus the importance, significance and capability of modifiers with special Si, S or SH groups used in this study were witnessed and they are considered to be superior to that of so far reported modifiers. In overall, our present work is considered to be more significant to obtain different versatile modified montmorillonite soils for enhanced adsorption of both organic and inorganic pollutants.

4. CONCLUSIONS

In this study, modified sodium montmorillonite soils were prepared using four different soil modifiers by two different methods. The modified soils take advantage of uptake of both organic and inorganic pollutants due to the special structures provided by different soil modifiers. Thus uptake of both organic and inorganic pollutants was reported in this study as both single and binary mixtures in order to investigate the feasibility of sorption ability of obtained modified soils. The role of different parameters on uptake characteristics was mainly discussed. Upon modification, the structural morphology was significantly altered. This study provided detailed insight in to the effect of organic matter content, solubility and distribution constant of pollutants on the uptake mechanisms. Regardless of the surface are, nature the surface charge and organic matter

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content of soils significantly affected the uptake phenomenon. Among different modifiers used in this study, the modified soil obtained using MPTMS modifier was concluded to be an efficient adsorbent. Also modified soils obtained by simple mixing in water method (MPTMS-M and TP-M) act as better adsorbents than that of corresponding adsorbents obtained by refluxion in toluene (MPTMSG-M and TPG-M). This is due to the fact that two different mechanisms were operated during grafting of modifiers in these two methods. Metal ions Cu^{2+} showed enhanced adsorption than that of Zn^{2+} ions. The uptake of organic pollutants was significantly affected by both solubility and k_d values. Uptake of BTEX was different for different cases and the observed log K_{OC} and log K_{OC} values of BTEX was invariably enhanced in this study. In the case of binary mixture no competitive adsorption was observed due to different adsorption mechanisms operated both in organic and inorganic pollutants. The result of this study suggested the superior adsorption ability of modified soils over unmodified soil and the methodology used in this study is cost-wise more economic also.

SUPPORTING INFORMATION

Supplementary figure (Fig. S1) is 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.: NSC102-2221-E-008-002-MY3), Taiwan, Republic of China (ROC), for financial support.

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

Soils	BET surface area (m^2/g)	Pore size (nm)	Element Weight (%)				Functional group (mmol/100g)
			C	H	N	S	
Na-montmorillonite	28.02	9.45	0.41	1.41	0.12	--	--
BAT-M	6.91	15.55	6.49	2.65	1.15	--	40.89
TP-M	0.22	12.00	8.52	--	--	8.04	62.81
TDBA-M	1.81	51.77	11.82	2.72	1.34	--	47.68
MPTMS-M	1.52	38.67	8.33	--	--	3.71	115.94
TPG-M	12.99	15.19	4.92	--	--	2.89	22.54
MPTMSG-M	7.87	17.98	4.46	--	--	1.95	60.94

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Table 2: Adsorption of inorganic pollutants by modified soils and Langmuir isotherm parameters

Adsorbents	Cu^{2+}		Zn^{2+}	
	q_{max} (mg/Kg)	R^2	q_{max} (mg/Kg)	R^2
Na-montmorillonite	2987	0.9677	2948	0.9129
BAT-M	2967	0.9718	5789	0.9490
TP-M	9061	0.9801	8019	0.9891
TDBA-M	4324	0.9658	4088	0.9259
MPTMS-M	24803	0.9977	8750	0.9765
TPG-M	4103	0.9234	7753	0.9811
MPTMSG-M	14180	0.9964	4626	0.9690

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

Adsorbates		BAT-M	TP-M	TDBA-M	MPTMS-M	TPG-M	MPTMSG-M
	OC %	6.7	8.8	12.21	8.61	5.08	4.61
Benzene	K_d	302.79	564.65	552.2	409.84	445.91	500.55
Toluene		317.34	648.32	414.62	1691.2	966.95	241.36
Ethylbenzene		--	1702.4	--	5194.5	5648.9	307.26
p-Xylene		441.44	2253.1		103.17	524.78	529.41

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

Adsorbates		BAT-M	TP-M	TDBA-M	MPTMS-M	TPG-M	MPTMSG-M
	OM%	26.62	17.6	24.42	17.22	10.16	9.22
Benzene	K_{OC}	2274.91	6416.48	4522.52	4760.05	8777.76	10857.92
	log K_{OC}	3.36	3.81	3.66	3.88	3.94	4.04
	K_{OM}	1137.45	3208.24	2261.26	2380.02	4388.88	5428.96
	log K_{OM}	3.06	3.51	3.35	3.38	3.64	3.73
Toluene	K_{OC}	2992.29	2384.22	7367.27	3395.74	19034.45	5235.57
	log K_{OC}	3.38	3.87	3.53	4.29	4.28	3.72
	K_{OM}	1496.14	1192.11	3683.64	1697.87	9517.22	2617.79
	log K_{OM}	3.08	3.57	3.23	3.99	3.98	3.42
Ethylbenzene	K_{OC}	--	19345.45	--	60331.01	111198.82	6665.08
	log K_{OC}	--	4.29	--	4.78	5.05	3.82
	K_{OM}	--	9672.73	--	30165.51	55599.41	3332.54
	log K_{OM}	--	3.99	--	4.48	4.75	3.52
p-Xylene	K_{OC}	3316.60	25603.41	--	1198.26	10330.31	11483.95
	log K_{OC}	3.52	4.41	--	3.08	4.01	4.06
	K_{OM}	1658.30	12801.70	--	599.13	5165.16	5741.97
	Log K_{OM}	3.22	4.11	--	2.78	3.71	3.76

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Table 5: Comparison of logK_{OC} and logK_{OM} values of BTEX obtained in this study with natural soil system as well as literature reports

Values	Benzene		Toluene		Ethylbenzene		p-Xylene	
	log K_{OC}	log K_{OM}	log K_{OC}	log K_{OM}	log K_{OC}	log K_{OM}	log K_{OC}	log K_{OM}
Estimated values	2.09	1.21	2.85	1.65	3.59	2.08	3.48	2.02
In references [28,30]	2.24	1.30	2.06	1.19	2.32	1.35	2.52	1.46
In this study	3.36 to 4.04	3.06 to 3.73	3.38 to 4.29	3.08 to 3.99	3.82 to 5.05	3.49 to 4.48	3.08 to 4.41	2.78 to 4.11

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Table 6: Comparison of adsorption capacity of modified Na-montmorillonite soils obtained in this study with literature reports

Adsorbents	Modifiers	Reference	Cu^{2+}		Zn^{2+}	
			q_{max} (mg/Kg)	R^2	q_{max} (mg/Kg)	R^2
Na-montmorillonite	SDS	[1]	5275	--	2086	--
Na-montmorillonite	HDS	[5]	3333	--	2500	--
GAC	--	[31]	5845	0.9900	--	--
Zeolite	--	[32]	8968	0.9775	--	--
Na-montmorillonite	TDBA	[In this study]	4324	0.9658	4088	0.9259
Na-montmorillonite	BAT	[In this study]	2967	0.9718	5789	0.9490
Na-montmorillonite	TP	[In this study]	9061	0.9801	8019	0.9891
Na-montmorillonite	MPTMS	[In this study]	24803	0.9977	8750	0.9765

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Figure captions

Fig. 1: Molecular structure and chemical formulae of four different modifiers

Fig. 2: Schematic representation of grafting of modifiers onto montmorillonite

Fig. 3: FT-IR spectra of (a) unmodified montmorillonite; (b) BAT-M; (c) TP-M; (d) MPTMS-M

Fig. 4: XRD patterns of unmodified and modified montmorillonites

Fig. 5: BJH pore distribution diagram of modified soils

Fig. 6: Adsorption isotherms of Cu^{2+} and Zn^{2+} ions by unmodified montmorillonite

Fig. 7: Adsorption isotherms of (a) Zn^{2+}; (b) Cu^{2+} by modified montmorillonites

Fig. 8: Adsorption isotherms for uptake of BTEX by modified montmorillonites

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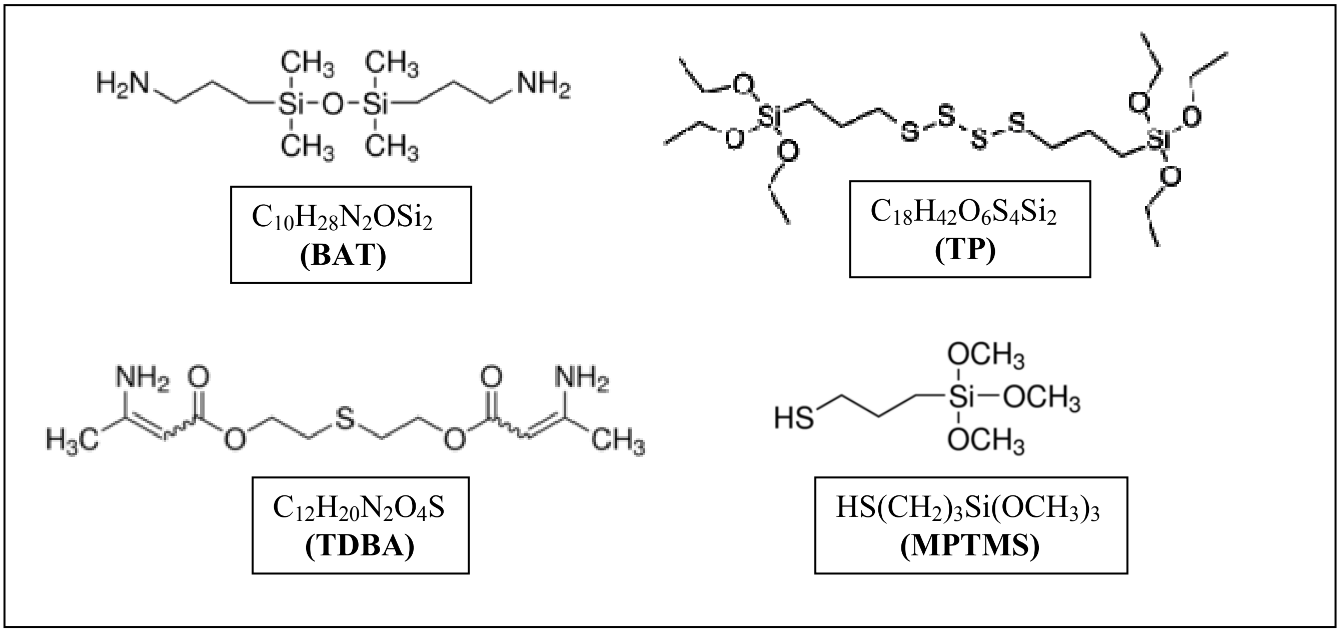

Fig. 1

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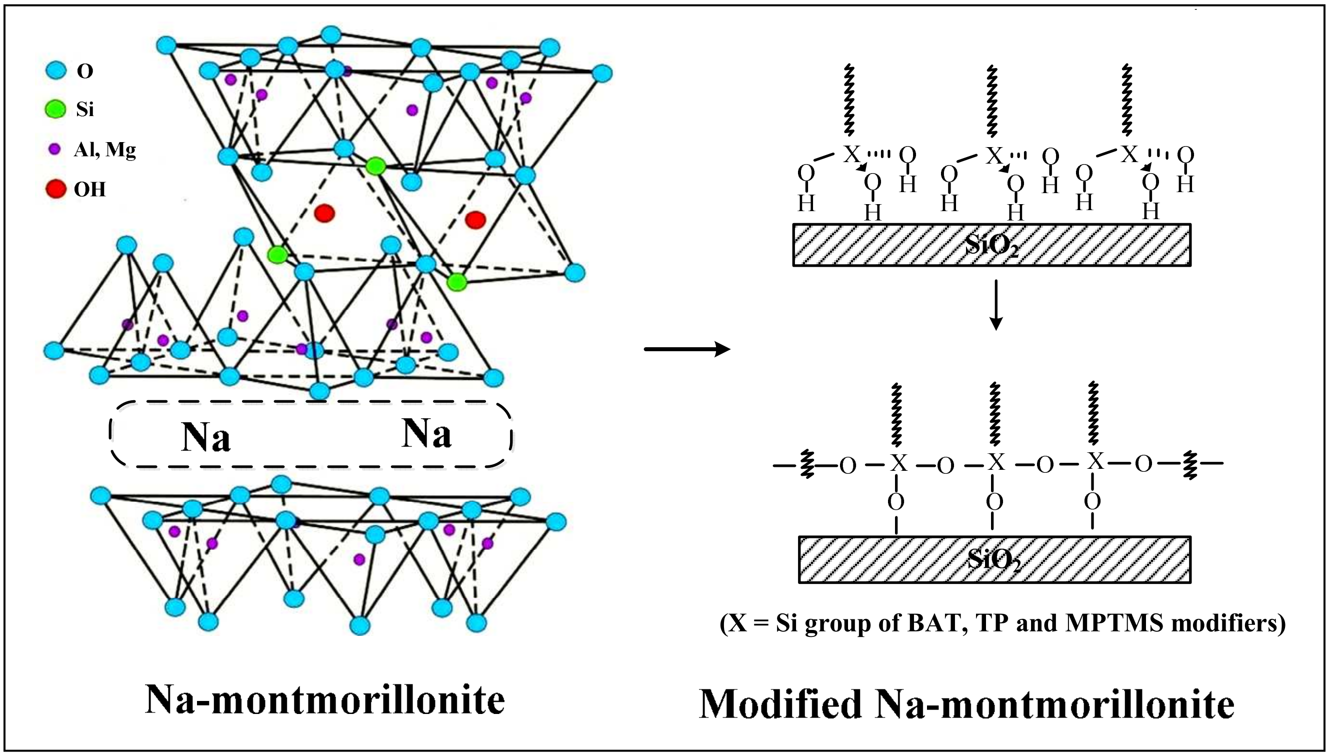

Fig. 2

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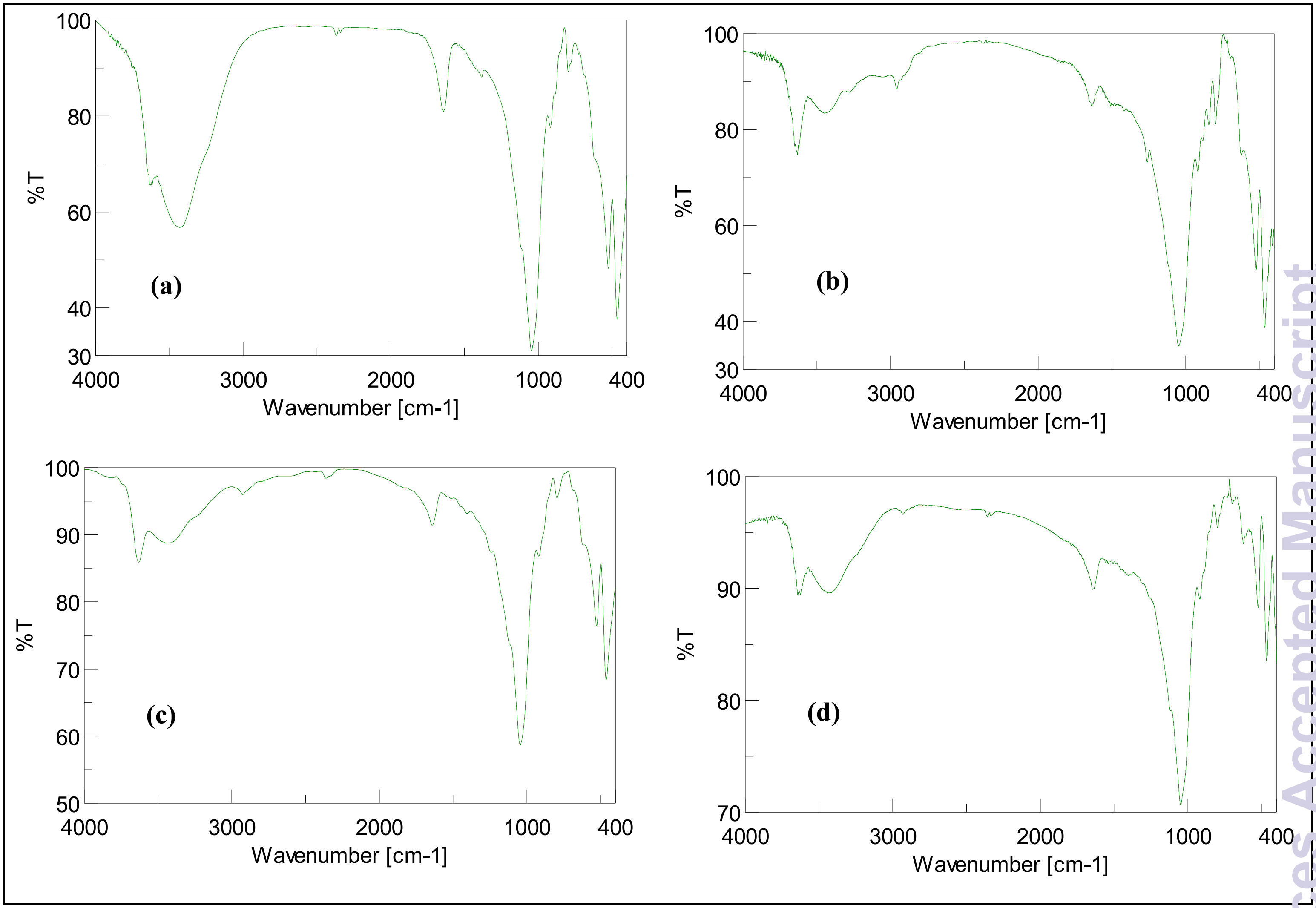

Fig. 3

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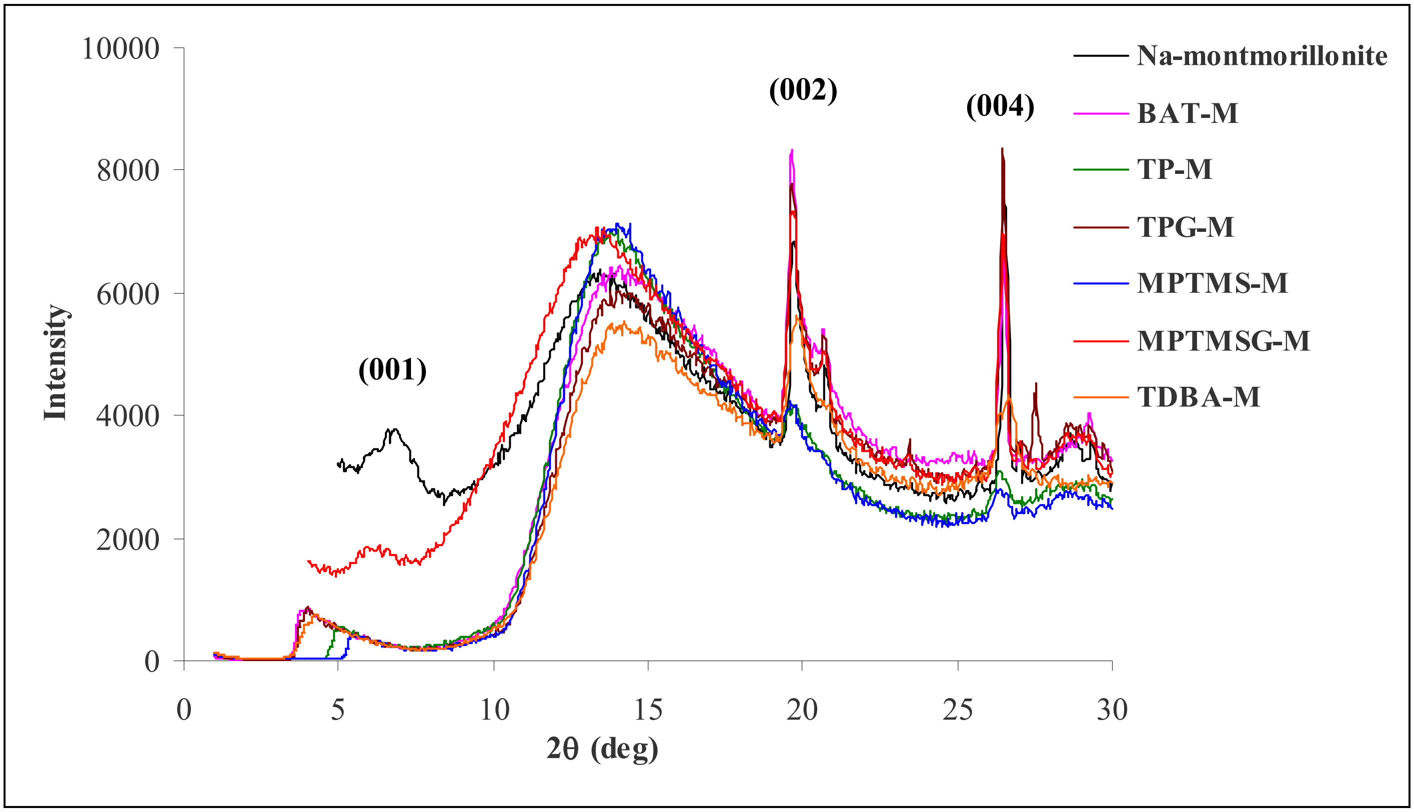

Fig. 4

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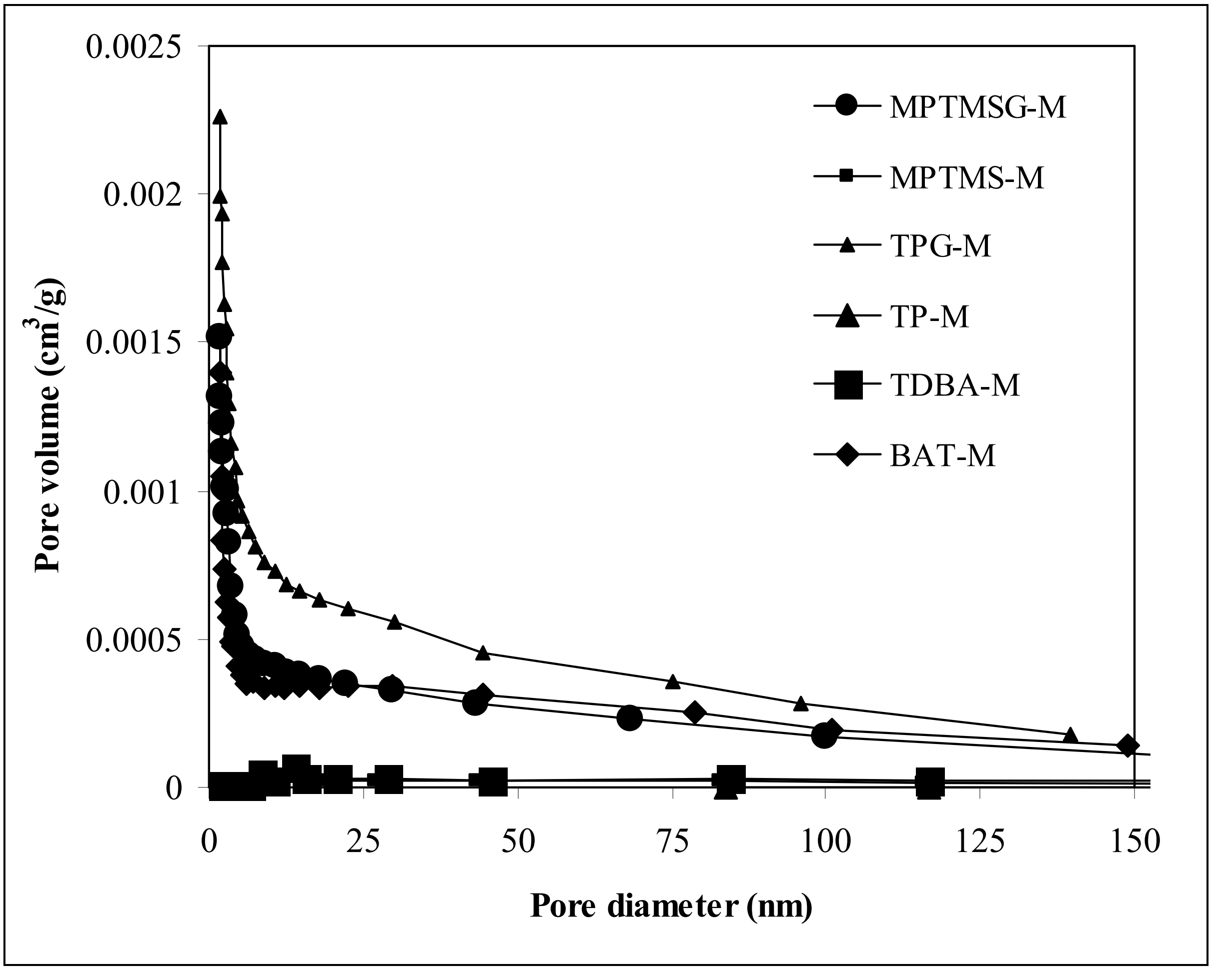

Fig. 5

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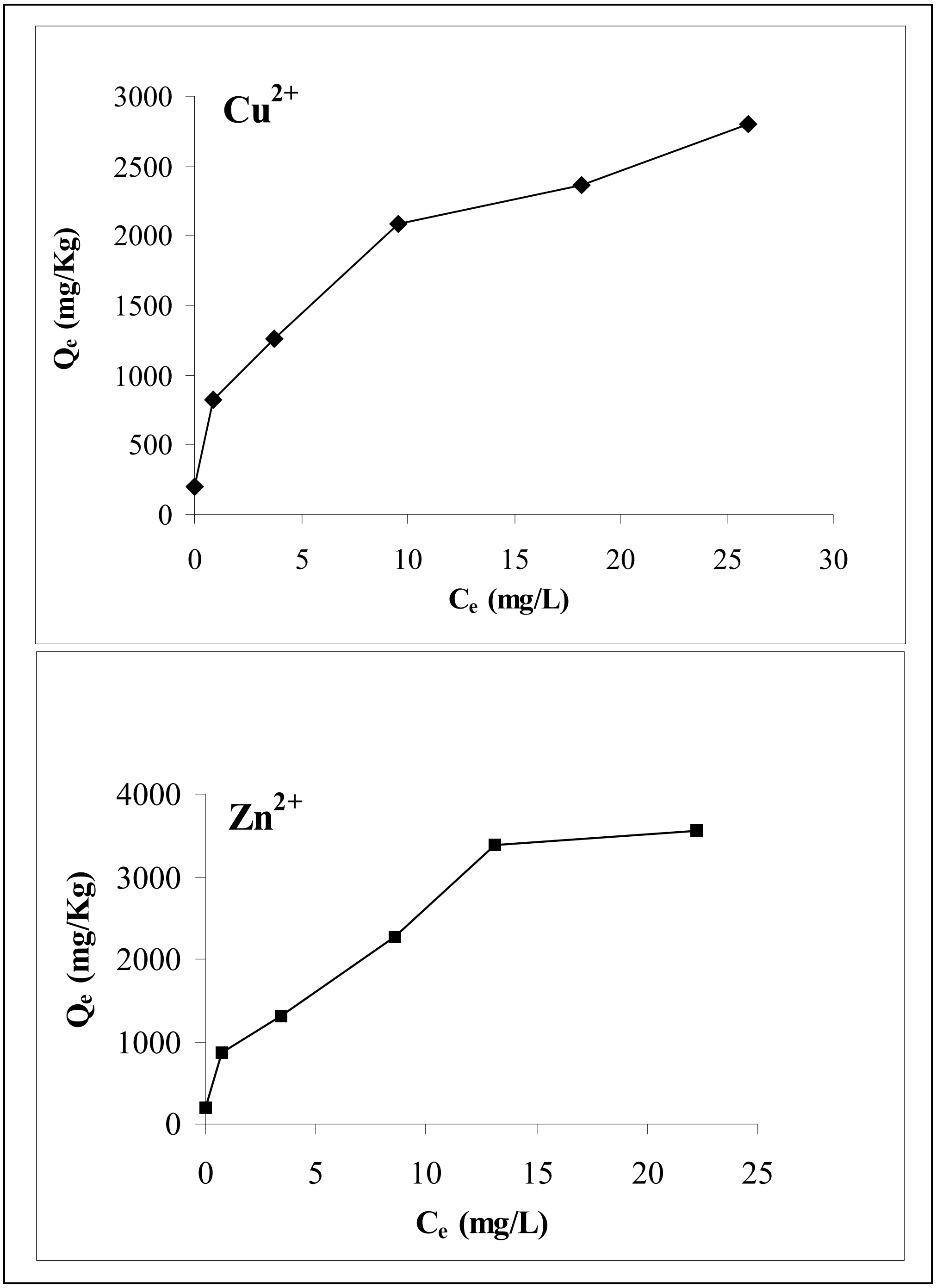

Fig. 6

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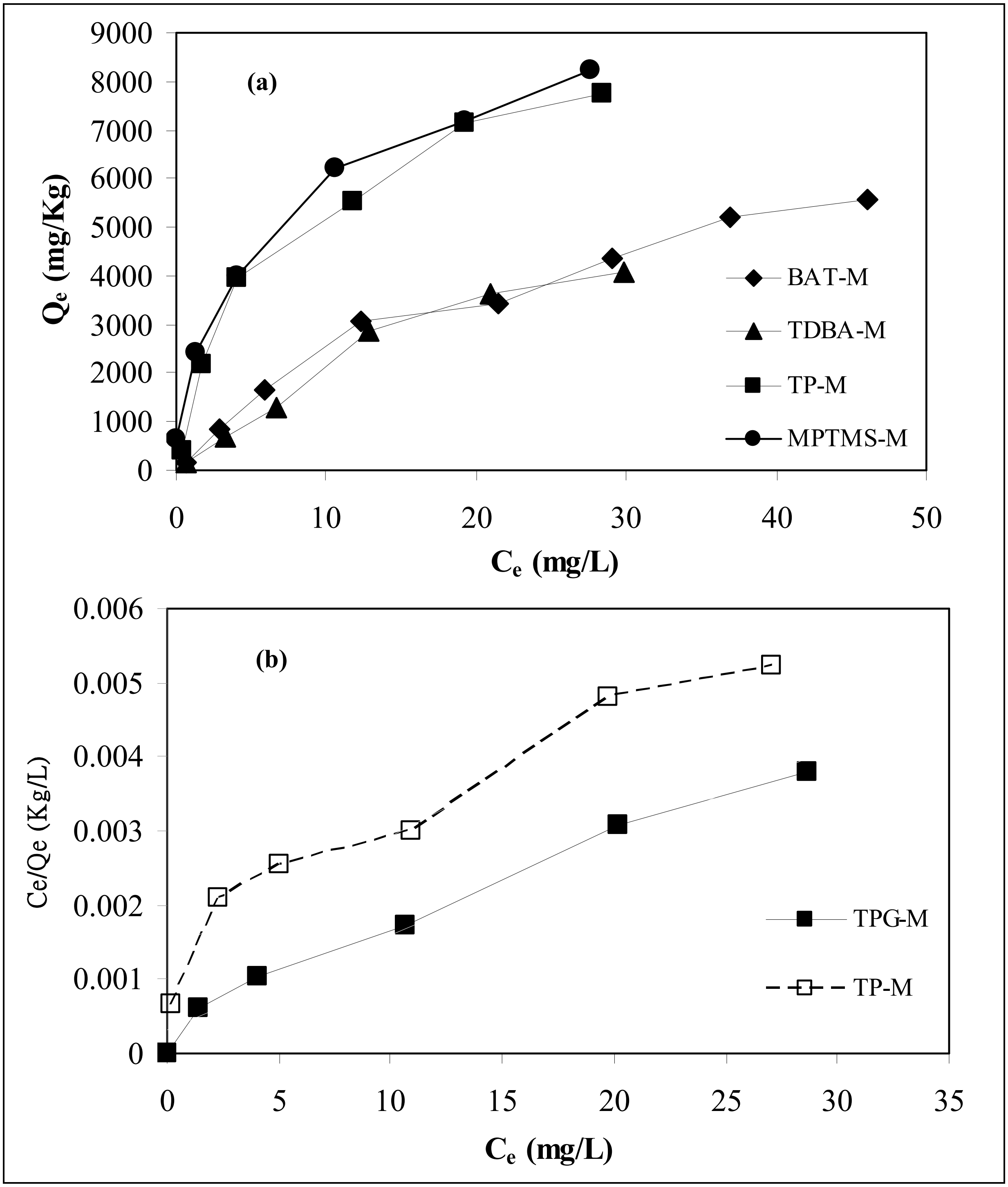

Fig. 7

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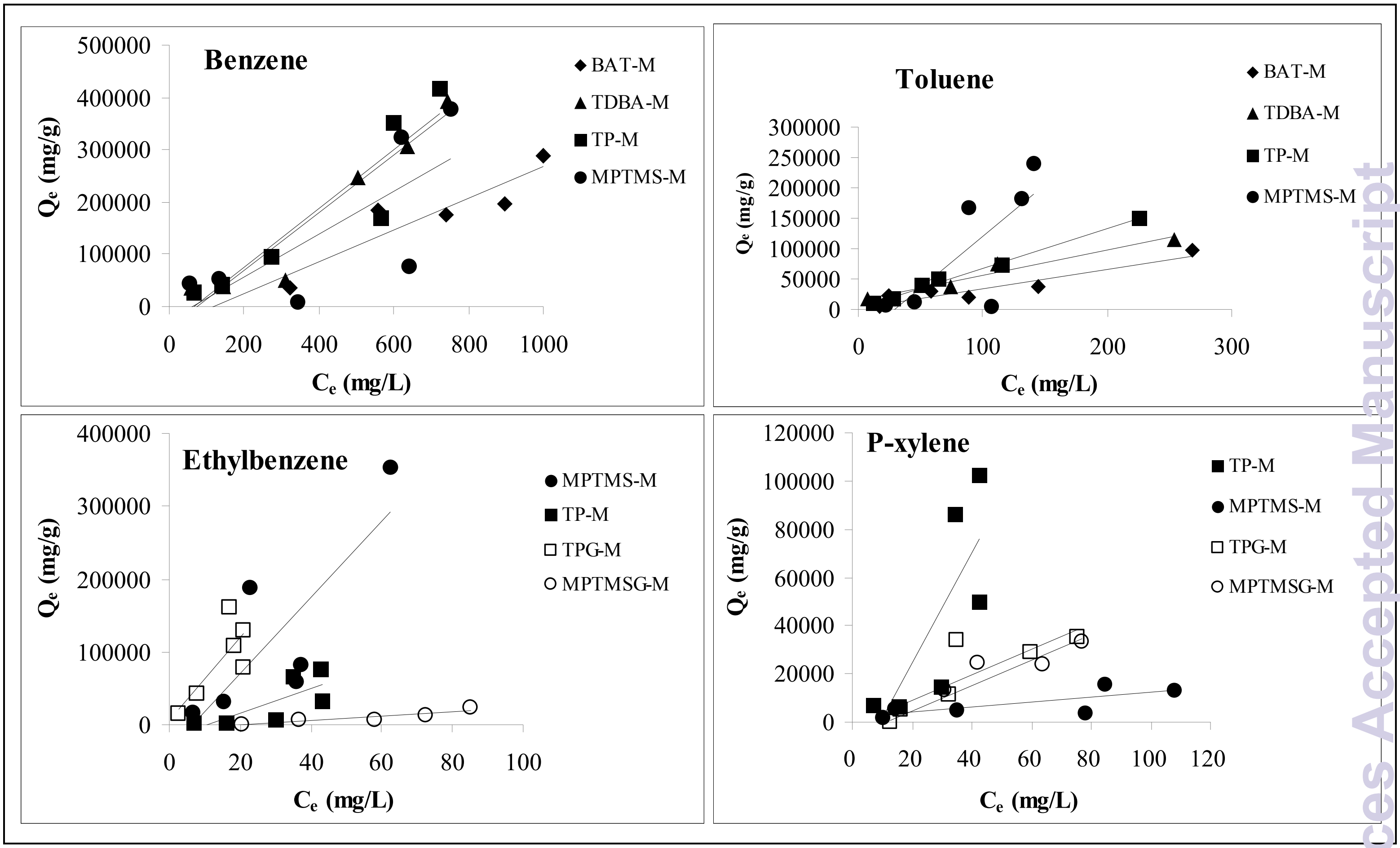

Fig. 8

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