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The influence of structural and processing parameters of modifiers on interlayer structure of modified montmorillonite

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ABSTRACT

This study mainly focused on exploring the influence of different processing methods on structure, physical and chemical characteristics and adsorption ability of modified montmorillonites. The effect of three different modifiers with different chain length such as 12-aminododecanoic acid (ADA), 1,12-diaminododecane (DDC) and octadecylamine (ODC) on *d*-spacing of montmorillonite was studied in details. FT-IR spectra and N₂ adsorption isotherms were used to confirm the formation of modified montmorillonites. XRD experiments were carried out and the influence of structural and processing parameters of modifiers on the interlamellar spacing of modified montmorillonites was studied. It was found that ODC modifier with longer carbon chain comparatively enhanced the interlamellar spacing than that of other modifiers. The influence of HCl, amount of modifiers and temperature on interlayer structure was also discussed. Upon modification, the peak around $2\theta = 6.8^\circ$ due to [001] plan was shifted to lower 2θ values and the corresponding interlamellar spacing was increased from 1.39 nm to 2.97 nm. The adsorption behavior of modified montmorillonites for both inorganic and organic pollutants was also discussed based on structural and surface properties. The observed $\log K_{OM}$ values for the distribution of organic pollutants onto modified montmorillonites are comparatively larger in this study indicating that these modified montmorillonites are superior to both natural soil system as well as literature studies reported so far.

Key words

Montmorillonite; modifiers; interlamellar spacing, adsorption

1. INTRODUCTION

The layered silicates due to their unique structure are considered to be more significance in the production of materials/nanocomposites with improved applications.^{1,2} Montmorillonite (MMT) is one of the layered silicates currently most widely employed in the production of clay materials/nanocomposites. The presence of net charges confers to the pristine structure of MMT a highly polar nature, and this, in turn, renders this silicate quite incompatible with the vast majority of organic molecules. Thus, there are some possible problems associated with the presence of small charged inorganic cations such as Na^+ , K^+ or Ca^{2+} within the interlayer of clay due to which the extent of application of clay materials is hindered. These inorganic cations and their associated hydration spheres generate a hydrophilic environment which is unfavorable to the sorption of organic molecules. If the water of hydration is removed, the interlamellar spacing is simultaneously collapsed and preventing the exfoliation of the clay sheets.³ Therefore, chemical modification of MMT is required which plays a crucial role in the formation of modified materials. A technique often used to overcome this problem is surface modification of clay by intercalation or exfoliation. The improved thermo-chemical and mechanical properties of modified clay platelets have resulted in these materials receiving much attention from researchers.³ In general, these clay minerals are layered aluminosilicates consisting of stacks of negatively charged two-dimensional sheets and the combined width of the interlayer space and sheet lying in the nanometer range, so that the modifier molecules intercalated between these sheets is scaled within a nanosized domain. Several efforts have been made in order to reduce the hydrophilicity of the MMT and in particular the cation exchange reaction with a quaternary ammonium salt stands

for the most commonly used method to modify clay surface. Such modification processes render organophilic nature to the clay interlayer region via exchange of the hydrated cations with hydrophobic organoammonium cations^{3,4} and thereby facilitating the sorption of organic molecules. Thus clay minerals, due to their large surface area and high cation exchange capacity^{5,6} have been studied for removal of inorganic and organic contaminants from water, particularly after modification with organic compounds. Hence, there is a necessary for surface modification of clay using modifiers to enhance their adsorption ability during which a significant increase in interlayer space should be observed. Normally such exchange reaction is carried out using long hydrocarbon chain surfactant molecules.⁷ This modification increases the interlamellar spacing and creates a more favorable organophilic environment. However, the water solubility of surfactants and the thermal instability of conventional ammonium ion-modified clay is a strong drawback and thus, recently there has been an increased concern for the amine modified clay where both adsorption and structural properties are highly altered.⁷⁻¹⁰

In the preparation of modified montmorillonites using modifiers, depending upon the method of synthesis the clay sheets are almost separated and also it is desirable to be able to control the extent of separation to produce modified materials with different properties. Interestingly, modifiers containing amine (NH₂) group with a hydrophobic backbone have a tendency to self-assemble within the clay interlayer,¹¹⁻¹³ conferring well defined and controlled interlamellar spacing (basal d-spacing). It is also believed that depending upon the molecular structure and molecular weight of the amine, the interlayer separation can be altered. Additionally, the use of different carbon chain length and

composition of modifiers will definitely also affect the amphiphilic properties of the modified montmorillonites.

Thus, the purpose of the present study was to report the preparation of modified montmorillonites using three different modifiers bearing amine group such as 12-aminododecanoic acid (ADA), 1,12-diaminododecane (DDC) and octadecylamine (ODC) in order to increase the organic matter content, the basal spacing, and furthermore to increase the sorption ability of montmorillonite. The modifiers are successfully intercalated in the clay and they significantly increased the basal spacing also. Depending upon the type and nature of different modifiers, the modified montmorillonites obtained in this study possess dual functional behavior, i.e., as adsorbents for both organic and inorganic pollutants. The influence of the structural and processing parameters of modifiers on interlamellar spacing and adsorption ability of modified montmorillonite were explored. Some physicochemical properties of montmorillonite were definitely expected to considerably change with acid treatment. For this purpose, modification of montmorillonite was carried out in the presence of hydrochloric acid (HCl). The HCl treatment can produce alterations in the structure of montmorillonites such as the removal of most of the octahedral Al^{3+} cations, and the formation of an amorphous silica phase, producing a high development of both the internal and the external surface of the solids. Thus, the acid treatment of montmorillonite has been accounted to protonate the amine group which further can be used as exchangeable cation¹⁴ and such acid treatment of montmorillonite in our study also generated a significant increase both in surface area and porosity of modified montmorillonites. The novelty and highlights of the present work are that this study deals with the different modifiers with amine groups in different

chemical environments. Thus, the effect of both nature and carbon chain length of the modifiers on interlamellar spacing, the inherent properties caused by organic moieties in such materials and effects of various parameters were investigated in a single work. Modifiers with longer carbon chain could obviously increase basal spacing to larger extent. Adsorption of inorganic (Cu^{2+}) and organic pollutants (benzene; toluene; ethylbenzene; and xylene; in brief BTEX) were discussed in this study based on various factors. The results of larger $\log K_{OM}$ values clearly showed that the modified montmorillonites obtained in this study are well-partitioning media indicating that these modified montmorillonites are superior to natural soil system as well as literature studies reported so far. Thus, the present methodology is very simple and significant. The advantages of these modified montmorillonites over the natural ones are that they have special properties such as homogeneity, controlled porosity and controlled surface area which are indeed desirable properties for new applications.

2. EXPERIMENTAL SECTION

2.1. Chemicals

The chemical formula of SWy-2-Na-montmorillonite (Wyoming) obtained from the Clay Minerals Society is expressed as $\text{Na}_{0.73}[\text{Si}_{7.66}\text{Al}_{0.34}][\text{Al}_{3.07}\text{Fe}_{0.44}\text{Mg}_{0.56}]\text{O}_{20}(\text{OH})_4$ [Na-MMT] and it was used without further purification. The calculated surface area is $28.02 \text{ m}^2/\text{g}$ and the cation exchange capacity (CEC) is 78 meq/100g. High purity laboratory grade copper standard solution (1000 ppm) was 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

Three different modifiers such as 12-aminododecanoic acid (ADA) [Sigma-aldrich, molecular weight = 215.33], 1,12-diaminododecane (DDC) [Sigma-aldrich, molecular weight = 200.36] and octadecylamine (ODC) [Sigma-aldrich, molecular weight = 269.51] were used in this experiment in order to study the influence of structural parameters of modifiers. The molecular structures and chemical formulae of these modifiers are shown in Fig. 1.

2.3. *Preparation of modified montmorillonites*

A suspension containing Na-montmorillonite was prepared by dispersing 10 g of Na-montmorillonite in 1 L deionized water. The suspension was stirred for 2 h and then it was allowed to stand for 1 h. The clay fraction was separated by sedimentation and the supernatant clay fraction was then put aside. Then 20 ml of appropriate amount of respective modifiers (usually double to triple CEC) was added to the supernatant clay fraction (20 ml) and the reaction mixture was stirred at room temperature (25 °C) for 2 h. The resulting modified Na-montmorillonites were filtered, collected in a dialysis bag, sealed and then immersed in deionized water for 8 h. Thus, all the products were washed free of anions (determined by the use of AgNO_3), separated from deionized water and lyophilized (freeze-dried). Finally, they were dried, ground and stored. The ADA, DDC and ODC modified montmorillonites were represented as ADA-M, DDC-M and ODC-M respectively. The schematic representation of formation and possible arrangements of modified montmorillonites is shown in Fig. 2.

In order to study the influence of processing parameters, modification of montmorillonite was also carried out using different dosages of modifiers in the presence of different amount of 12 M HCl at different temperatures and times as shown in Table 1.

2.4. *Adsorption of inorganic and organic pollutants*

The experiments for adsorption of inorganic pollutants were performed at 25 °C in glass centrifuge tubes containing Cu²⁺ ion solution (20 mL) and the modified montmorillonites (2 g), shaken at pH 5 for 24 h at 130 rpm in a shaker. The reaction mixture was centrifuged to precipitate the clay samples. Finally, the supernatant liquid was drawn and analyzed using a Varian AA280Fs atomic absorption spectrophotometer (AAS) to determine the concentration of metal ions in the solution.

The experiments for uptake of organic pollutants were performed at 25 °C in glass centrifuge tubes containing different organic pollutant (benzene; toluene; ethylbenzene; and xylene; in brief BTEX) solutions (20 mL) and the modified montmorillonites (2 g), shaken for 24 h at 130 rpm in a shaker. The reaction mixture was centrifuged to precipitate the clay 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.

2.5. *Characterization techniques*

The Brunauer-Emmett-Teller (BET) specific surface area and average pore diameter were measured on a Quantochrome NOVA 1000. Fourier transform infrared spectra (FT-IR) of samples were obtained using a Neclit 6700 model spectrometer. X-ray diffraction (XRD) patterns were obtained on a Siemens X-ray diffractometer D-5000 equipped with a Cu K α radiation source operating at 40 kV and 30 mA.

3. RESULTS AND DISCUSSIONS

3.1. FT-IR and N_2 adsorption isotherms

The FT-IR spectra of montmorillonite before and after modification are shown in Fig. 3. For unmodified montmorillonite, the peak around 3625 cm^{-1} is assigned to the stretching vibration due to aluminium and/or silicon bonded OH groups. The broad peak around 3445 cm^{-1} due to stretching vibration of OH groups (H_2O) and a peak around 1650 cm^{-1} due to H-O-H bending vibration vividly showed the presence of some moisture in the samples. Besides, the peaks in the range $1100\text{-}500\text{ cm}^{-1}$ are assigned to stretching and bending vibrations due to Si-O-Al and Si-O-Si groups of the samples.¹⁵ The peak around 2350 cm^{-1} is due to instrumental peak caused by adsorption of air during operation. But after modification the peak due to OH stretching at 3625 cm^{-1} was slightly shifted towards lower frequency (3615 cm^{-1}) and this implied that the removal of some structural bonded OH groups from the Si-OH or Al-OH sites. The broad peak due to water OH group around 3445 cm^{-1} was also slightly shifted to lower frequency and became less intense upon modification due to removal of some water molecules. The new peaks appeared for modified montmorillonites around 2925 and 2855 cm^{-1} are attributed to asymmetric and symmetric vibrations of respective CH_3 and CH_2 groups of modifier molecules used for modification of montmorillonite. The corresponding peaks due to both N-H stretching and bending vibrations for modified montmorillonites are observed around 3200 cm^{-1} and 1470 cm^{-1} respectively. For ADA-M, the peak around 1715 cm^{-1} is assigned to C=O stretching vibration. Upon modification, the corresponding Si-O-Al and Si-O-Si peaks in the range $1100\text{-}500\text{ cm}^{-1}$ are almost unchanged which clearly depicted that the main bones of montmorillonite before and after modification are similar. Thus,

the results obtained from FT-IR analysis confirmed the successful modification of montmorillonite to increase its organic matter content.

The specific surface area and pore size are important factors that control the ability of the adsorbents. Thus in order to determine the surface area and pore size, nitrogen adsorption/desorption analyses were carried out for montmorillonite before and after modification. The nitrogen adsorption/desorption isotherms of montmorillonite as shown in Fig. 4a exhibited S-shaped typical type II curves, i.e., the porosity is located over a pore range. The hysteresis was not observed initially and it occurred only in the high relative pressure range. At low relative pressure ($P/P_0 < 0.1$) a monolayer adsorption was formed on the surface of the adsorbents. In the range of P/P_0 from 0.1 to 0.5, multilayer adsorption was observed due to which there was a sharp increase in the adsorbed volume also. 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. Thus, these nitrogen adsorption curves as shown in Fig. 4a clearly revealed that the different modifiers could affect the pore size and its distribution. BET surface area and pore size of montmorillonite before and after modification are shown in Table 2. From adsorption isotherms, the monolayer adsorption of nitrogen by modified montmorillonites increased in the order as follows; DDC-M>ADA-M>ODC-M. Accordingly from Table 2 also, this showed good agreement with specific surface area increasing in the same order as DDC-M>ADA-M>ODC-M. In all cases, a significant decrease in the pore volume of modified montmorillonites was observed due to the pore blocking by modifiers upon modification.

This pore blocking was entirely depending upon the nature of modifiers. Thus, it is obvious that both the nature and structure of modifier molecules significantly influenced the surface areas and porosity of modified montmorillonites. In this study, three types of organic modifiers were used and among which octadecylamine (ODC) modifier though it possessed comparatively smaller surface area, due to its longer carbon chain has the opportunity to dramatically change the hydrophobic properties of montmorillonite. Thus, ODC was selected to study the influence of dosage of modifiers and for this purpose various amount (8, 16 and 24 mmol) of ODC was used and corresponding N₂ adsorption isotherms were obtained as shown in Fig. 4b. Actually it was noticed that the adsorption isotherms for different dosage systems are completely overlapped (are almost same), suggesting that the change in dosage of the modifier produced only limited changes in the adsorption isotherms and thus the adsorption mechanism is almost close to each other. In order to study the influence of processing parameters, various amount of HCl (0.66 to 9 ml) was added to the system and corresponding N₂ adsorption isotherms were analyzed. From Table 2, it was clearly understood that addition of HCl (9 ml) to the system favorably enhanced the adsorption capacity, surface area and porosity of ODC-M. With increasing the concentration of both ODC and HCl, higher surface areas and larger pore sizes were observed. Thus, addition of HCl definitely caused a significant increase in the adsorption ability of modified montmorillonites in this study. This is due to the fact that in the presence of acid, the activation force and number of acidic sites increase.¹⁶

3.2. *XRD analysis*

As already discussed, due to small interlamellar spacing of the hydrophilic layered silicate surface of montmorillonite, it was modified using three different modifier

molecules in order to increase the interlayer gap spacing. The extent of influence of modifier on interlayer structure was mainly studied by XRD analysis. The XRD patterns of montmorillonite before and after modification were obtained and analyzed as shown in Fig. 5a. It is well known if CEC of modifier is increased, both the interlayer space and organic matter content of modified montmorillonite will also obviously increase. Thus, in order to explain the influence of processing parameters, different dosages (double to triple CEC) of modifiers were used at different temperatures using different amount of HCl and corresponding XRD patterns were obtained and analyzed. The influence of processing parameters on interlayer structure is clearly shown in Table 1. The XRD patterns of unmodified montmorillonite displayed a peak around $2\theta = 6.8^\circ$ which is assigned to [001] reflection and the corresponding basal plane spacing, d_{001} is 1.39 nm. From both Fig. 5 and Table 1, the distinguished variation in both XRD peak position and interlayer distance is clearly evident for modified montmorillonites. Upon modification of montmorillonite using three different amine modifiers, the corresponding peak around $2\theta = 6.8^\circ$ displayed a shift towards lower 2θ values.¹⁵ But relatively a larger increase in the interlayer space was observed for modified montmorillonites. However, in the case of DDC-M, the peak position and interlayer gap spacing was not altered significantly. Based on increasing order of interlayer spacing, the modified montmorillonites could be arranged as follows; ODC-M>ADA-M>DDC-M. From Table 1, among three modifier molecules, long carbon chain ODC displayed comparatively larger increase (2.97 nm) in the interlayer space than that of other two modifiers and thus it was considered to be effective modifier in this study. A careful evaluation on different dosage of ODC during modification of montmorillonite clearly indicated that upon increasing dosage of ODC

from 8 mmol to 16 mmol, the interlayer space also gradually increased. A further increase in ODC dosage to 24 mmol, did not produce any significant change in the interlayer distance. Thus, larger CEC of modifier makes the layered silicate structure stretched to the maximum distance and thus facilitates the embedding of modifiers between the layers. Thus, presence of more quantity of modifiers in the interlayer space will obviously increase the organic matter content of modified montmorillonites. However with increasing interlamellar spacing, layered silicate density will decrease^{17,18} and thus reforming the distribution of modifier tendency in the clay surface to lateral conformations. Due to this, a further increase in ODC dosage causes for softening of silicate stretching¹⁹ and thus obviously there is no significant increase in interlamellar spacing. It is thus, concluded that the interlamellar spacing of montmorillonite is greatly extended in this study by modification with different modifiers. From Table 1, it was noted that the structure of modifiers mainly functional group and carbon chain length have significantly affected the layered silicate arrangement and interlayer gap spacing in the modified montmorillonites. A difference in carbon chain length produced slight variation in hydrophobic nature of modifiers and thus longer carbon chain length increased the hydrophobic nature of the modifiers. Thus, when modifier with longer carbon chain is used, the organic molecules in the interlayer layers have the opportunity to possess paraffin structure arrangement due to hydrophobic interaction. Modifiers with shorter carbon chain length will be arranged as monolayer where as modifiers with longer carbon chain length will be arranged in multi-layers in the interstitial layer and thus increases the layer gap spacing. The influence of HCl on interlayer spacing was also studied as shown in Fig. 5b and the observed results indicated that as the amount of HCl

increased, it induced a gradual increase in the interlamellar spacing also. However if excess HCl is used, the increase in interlamellar spacing is limited. In such cases, perhaps the exchangeable Na^+ ions could be replaced by H^+ ions instead of amine molecules and thus increase in interlayer distance is hindered. The effect of temperature was studied by varying the temperature from 25 °C to 80 °C and the obtained results showed that the interlayer spacing is only slightly altered by varying temperature. Even at high temperature (80 °C), no drastic change in interlamellar spacing was observed. This perhaps due to the reason that the solubility and energy of modifiers are almost same (not altered significantly) in the studied range of temperatures. However, when the reaction temperature is high (80 °C), comparatively larger interlamellar spacing was obtained in this study. Thus the effect of dosage of modifier and acid is obviously significant whereas the impact of temperature is less obvious in this study. The observed difference in the interlayer spacing of modified montmorillonites could be correlated with different possible arrangements of modifier molecules due to their self assembly nature during the process¹⁵ as shown in Fig. 2. Such arrangement due to self assembly was also influenced by α -methyl orientation of modifier molecules onto montmorillonite surface. Thus for DDC, due to symmetric linear structure, α -methyl orientation relative to that of both amine groups resulted into rigid planarity due to which extent of modification (cation exchange by DDC) may be limited and hence, the peak position and interlamellar spacing of DDC-M is almost unaltered (same as unmodified montmorillonite) as shown in Fig. 5a. Hence, it is very clear that the difference in backbone chain and functional head group of modifiers must have a determining influence on interlayer arrangements.^{3,20} Thus XRD

analysis clearly explained the influence of various processing parameters on the interlayer structure of modified montmorillonites.

3.3. Adsorption study

In order to evaluate the adsorptive properties of both modified and unmodified montmorillonite, the adsorption studies of inorganic (Cu^{2+}) and organic (BTEX) pollutants were carried out in this study. The adsorption isotherms for Cu^{2+} as shown in Fig. 6 indicated that modified montmorillonites showed enhanced adsorption than that of unmodified montmorillonite. In this study both Langmuir and Freundlich adsorption isotherms were studied and among which Langmuir adsorption fitted well. It was observed that among modified montmorillonites, ADA-M displayed increased adsorption of Cu^{2+} which is probably due to the presence of both amino and carboxyl functional groups in ADA molecule that favored the adsorption of metal ions by chemisorption. In the case of ODC-M and DDC-M, the amine groups are protonated and hence hindered the adsorption of metal ions, where as in the case of ADA-M, the presence of COO^- ion accelerated the affinity for metal ions.

The uptake of organic pollutants (BTEX) was studied as shown in Fig. 7. The distribution of BTEX on montmorillonite was mainly controlled by water solubility (S_w), organic carbon (OC%) content and distribution constant (K_d).^{21,22} The k_d values of BTEX and organic matter content of modified montmorillonites are given in Table 3. From Table 3, the modified montmorillonites based on organic carbon content (OC%) can be arranged as ODC-M>ADA-M>DDC-M. However, invariably in all cases, the uptake of BTEX by ODC-M is larger than that of others and the order of uptake of BTEX is as follows; ODC-M>DDC-M>ADA-M. Among all ADA-M, due to the presence of highly

polar carboxyl functional group showed weak affinity for non polar organic pollutants (BTEX). Thus in the case of BTEX, both water solubility and organic carbon content of modified montmorillonites together controlled the distribution and uptake of BTEX. The value of k_d is affected by total organic carbon content (OC%) and during distribution of BTEX onto modified montmorillonites, there will be a difference in total organic carbon content and hence it has to be considered seriously. Thus the corrected organic matter (OM%) has also been taken into consideration as shown in Table 3. The equilibrium constants K_{OC} and K_{OM} as shown in Table 3, could also provide an indication of constituent sorption onto montmorillonite (clay or organic matter) respectively. Larger values of both constants show the preference of BTEX to be sorbed onto modified montmorillonites and these values can be understood in terms of their respective $\log K_{OC}$ and $\log K_{OM}$ values as shown in Table 3. The difference in $\log K_{OC}$ and $\log K_{OM}$ values are very less (they are almost equal) and these values are compared with literature values reported so far. Thus, the obtained $\log K_{OM}$ values for different systems as shown in Table 4, are comparatively larger than that of literature values^{22,23} reported so far and this clearly explains the significance of the present study, i.e, the modified montmorillonites obtained in this study are considered to be superior to natural soil system as well as so far reported studies.^{2,17,24-26} Thus different mechanisms were operated simultaneously for sorption of inorganic and organic pollutants by modified montmorillonites. Also, the adsorption ability was dependent on surface and structural characteristics of modified montmorillonites exerted by structural and processing parameters of modifiers during modification process.

4. CONCLUSIONS

In this study, montmorillonite was successfully modified using three different modifiers and both the structural and surface characteristics were significantly altered upon modification. The influence of structural and processing parameters of modifiers on interlamellar spacing was mainly studied and based on the experimental results, among three modifiers used in this study ODC exerted an increase in interlamellar spacing in modified montmorillonites. The processing parameters such as dosage of modifiers, temperature and amount of HCl were varied and the optimum parameters were fixed. Based on XRD results, it was observed that the XRD peak was shifted to lower 2θ values and interlayer distance was relatively increased. These observations confirmed the successful modification of montmorillonite. The adsorption ability of modified montmorillonites was evaluated by studying the adsorption of both organic (BTEX) and inorganic (Cu^{2+}) pollutants. The adsorption of inorganic pollutants was explained based on chemisorption which was mainly influenced by surface area and functional groups of modified montmorillonites. The uptake of organic pollutants was significantly affected by partitioning of BTEX onto modified montmorillonites depending on organic matter content of montmorillonite. The partitioning of BTEX was mainly controlled by water solubility and K_d values. The observed $\log K_{OC}$ and $\log K_{OM}$ values of BTEX were significantly enhanced in this study. Thus, the result of this study suggested that the modified montmorillonites obtained in this study are more significant to achieve enhanced adsorption of both organic and inorganic pollutants.

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Table 1: Various processing parameters and observed interlamellar spacing from XRD

Montmorillonites	Amount of modifiers (mmol)	Amount of HCl (ml)	Temperature (° C), time (h)	Interlayer gap spacing (nm)
Unmodified montmorillonite	--	--	--	1.39
	8	0.66	80, 2	1.79
	8	1	80, 2	1.78
	8	3	80, 2	1.83
	8	9	80, 2	1.82
	16	2	80, 2	2.97
ODC-M	24	3	80, 2	2.17
	8	0.66	80, 3	1.77
	8	0.66	80, 1	1.78
	8	0.66	60, 2	1.81
	8	0.66	40, 2	1.78
	8	0.66	25, 2	1.79
	8	0.66	80, 2	1.35
DDC-M	8	1	80, 2	1.33
	8	1.33	80, 2	1.34
ADA-M	8	0.66	80, 2	1.72

Table 2: Surface area and pore size of modified and unmodified montmorillonite

Samples	BET surface area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)
Unmodified montmorillonite	28	9.45	0.593
Modified montmorillonites obtained under various parameters			
DDC (8 mmol)	57	12.44	0.172
ADA (8 mmol)	34	17.55	0.152
ODC (8 mmol)	22	16.70	0.092
ODC (16 mmol)	20	18.90	0.100
ODC (24 mmol)	23	20.26	0.110
ODC (8 mmol) + HCl (9 ml)	24	21.85	0.140

Table 3: Organic carbon content, corrected organic matter content, distribution constant, K_{OC} , K_{OM} , $\log K_{OC}$ and $\log K_{OM}$ values for different systems

Adsorbates		ODC-M	ADA-M	DDC-M
		OC %	26.60	15.90
	OM %	53.20	31.80	18.66
Benzene	K_d	114.29	48.28	36
	K_{OC}	429.66	303.62	385.84
	K_{OM}	214.83	151.81	192.92
	$\log K_{OC}$	2.63	2.48	2.59
	$\log K_{OM}$	2.33	2.18	2.29
Toluene	K_d	139.15	66.24	32.15
	K_{OC}	523.12	416.62	344.53
	K_{OM}	261.56	208.31	172.27
	$\log K_{OC}$	2.72	2.62	2.54
	$\log K_{OM}$	2.42	2.32	2.24
Ethylbenzene	K_d	111.84	45.55	64.6
	K_{OC}	420.45	286.47	692.34
	K_{OM}	210.23	143.24	346.17
	$\log K_{OC}$	2.62	2.46	2.84
	$\log K_{OM}$	2.32	2.16	2.54
<i>p</i> -Xylene	K_d	142.76	123.58	84.76
	K_{OC}	536.69	777.23	908.45
	K_{OM}	268.35	388.62	454.23
	$\log K_{OC}$	2.73	2.89	2.96
	$\log K_{OM}$	2.43	2.59	2.66

Table 4: Comparison of $\log K_{OC}$ and $\log K_{OM}$ 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	2.83	1.64	3.59	2.08	3.48	2.02
In references [22,23]	2.24	1.30	2.06	1.19	2.32	1.35	2.52	1.46
In this study	2.48 to 2.63	2.18 to 2.33	2.54 to 2.72	2.24 to 2.42	2.46 to 2.84	2.16 to 2.54	2.73 to 2.96	2.43 to 2.66

Figure captions

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

Fig. 2: Schematic representation of formation and possible arrangements of modified montmorillonites

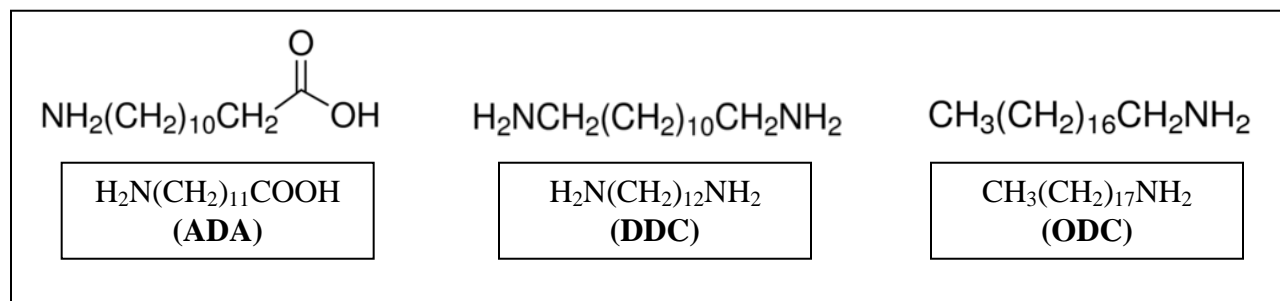
Fig. 3: FT-IR spectra of unmodified and modified montmorillonites

Fig. 4: N₂ adsorption/desorption isotherms of unmodified and modified montmorillonites

Fig. 5: (a) XRD patterns of unmodified and modified montmorillonites (0.66 ml HCl, 2h at 80 °C); (b) Effect of HCl on XRD patterns of modified montmorillonites obtained from ODC

Fig. 6: Adsorption isotherms of Cu²⁺ by unmodified and modified montmorillonites

Fig. 7: Sorption of BTEX by modified montmorillonites

**Fig. 1**

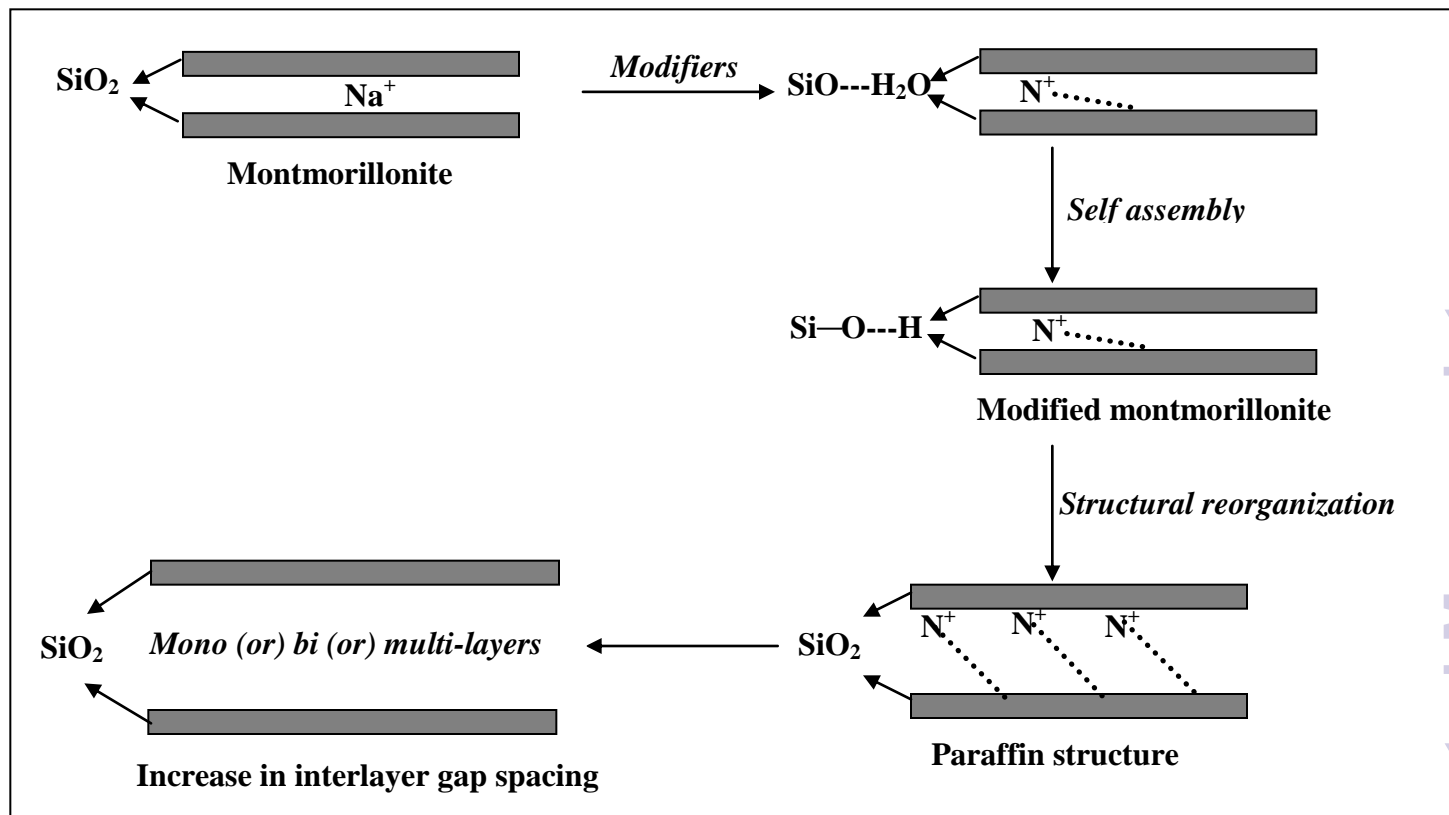
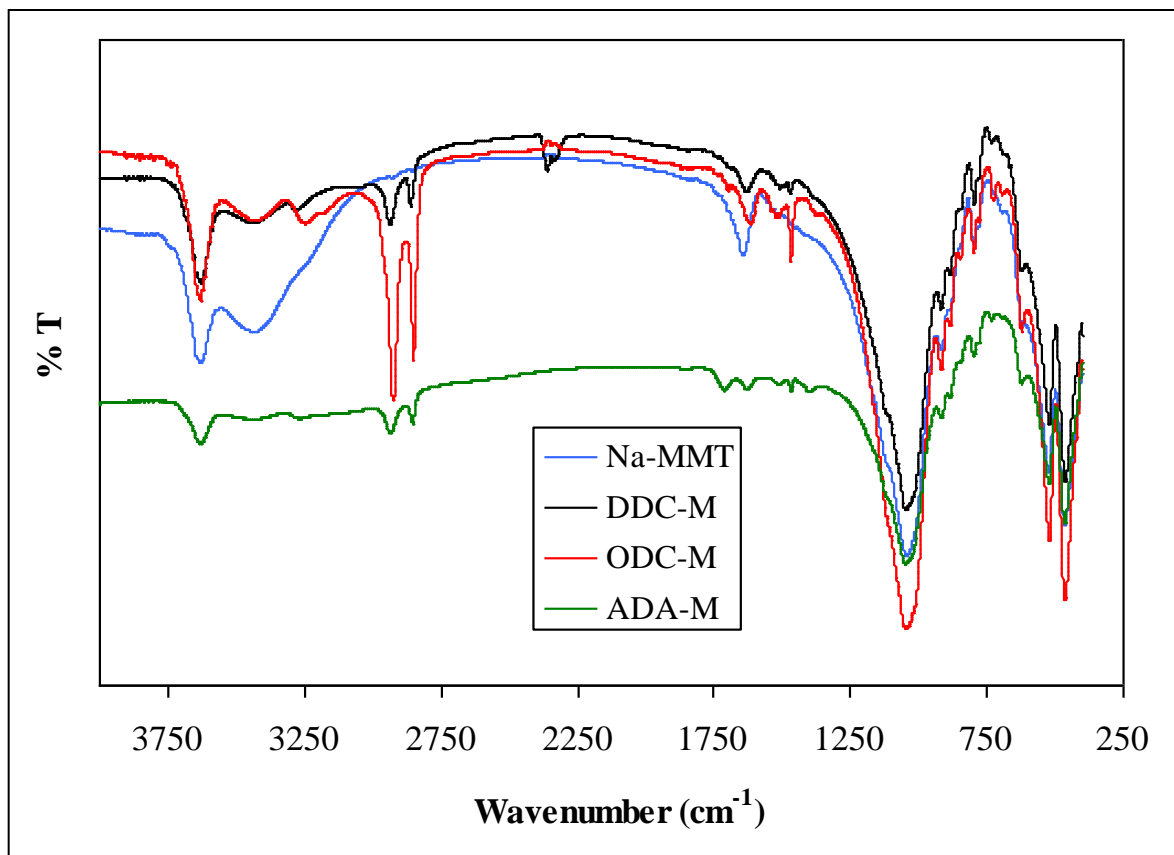


Fig. 2

**Fig. 3**

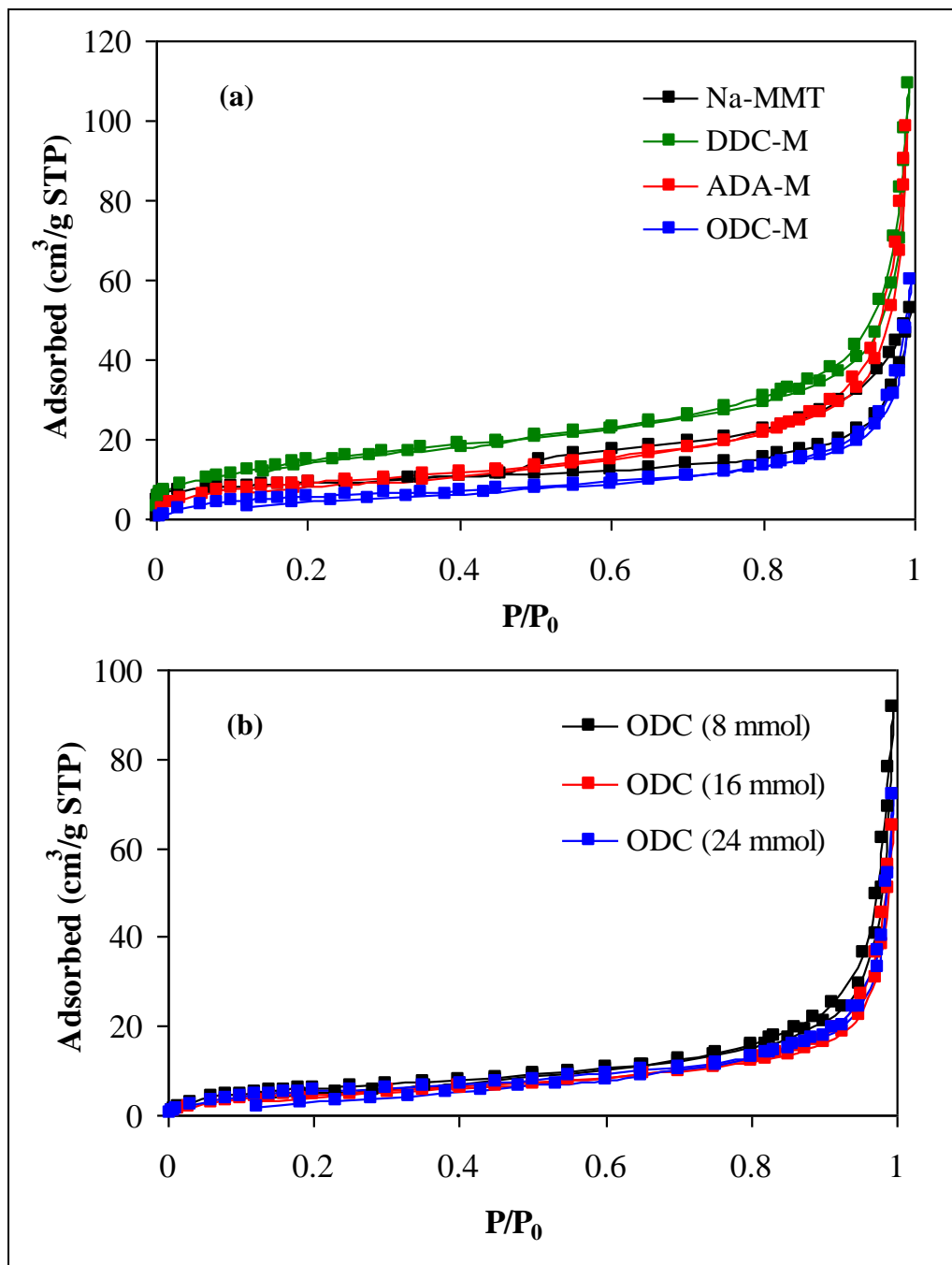


Fig. 4

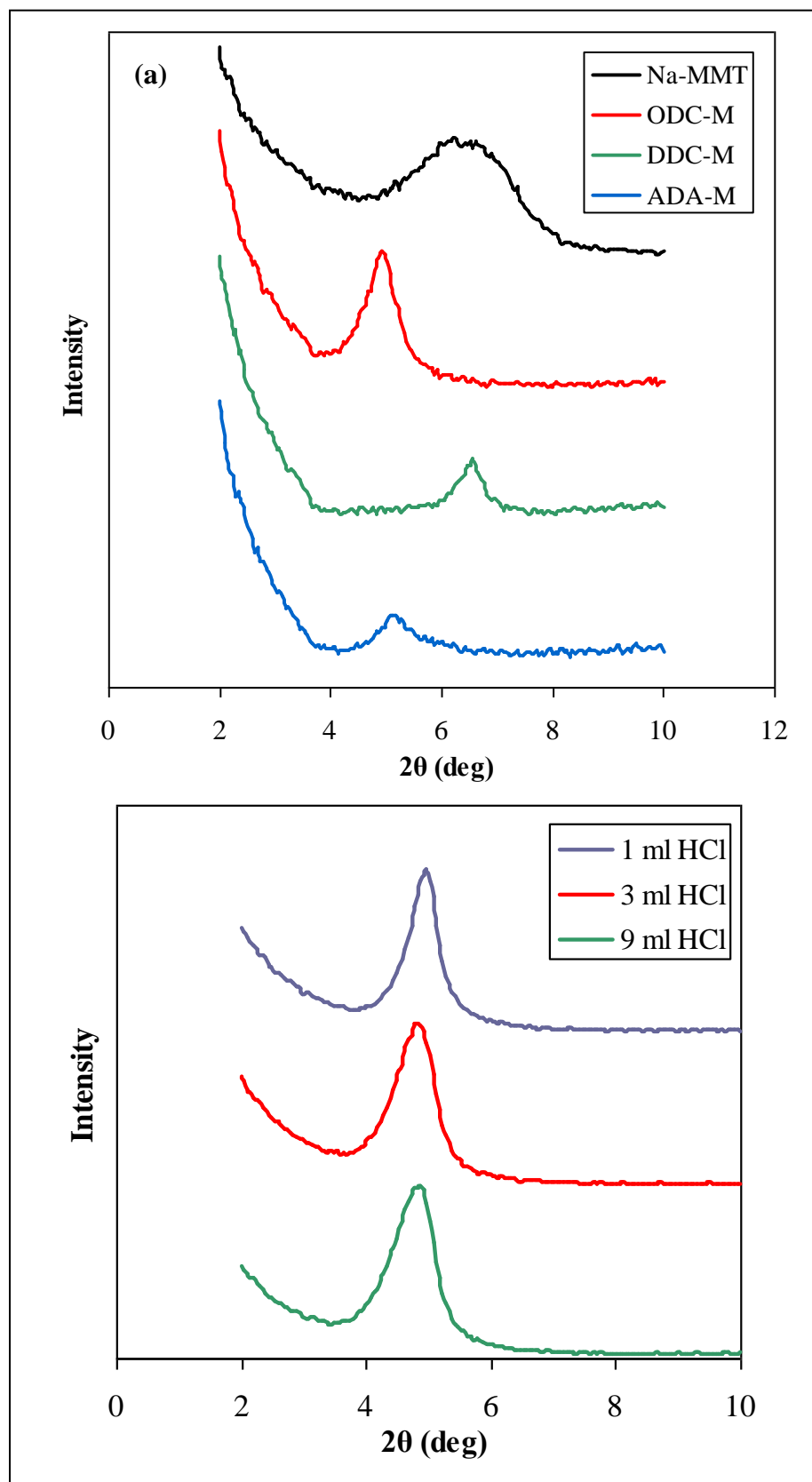


Fig. 5

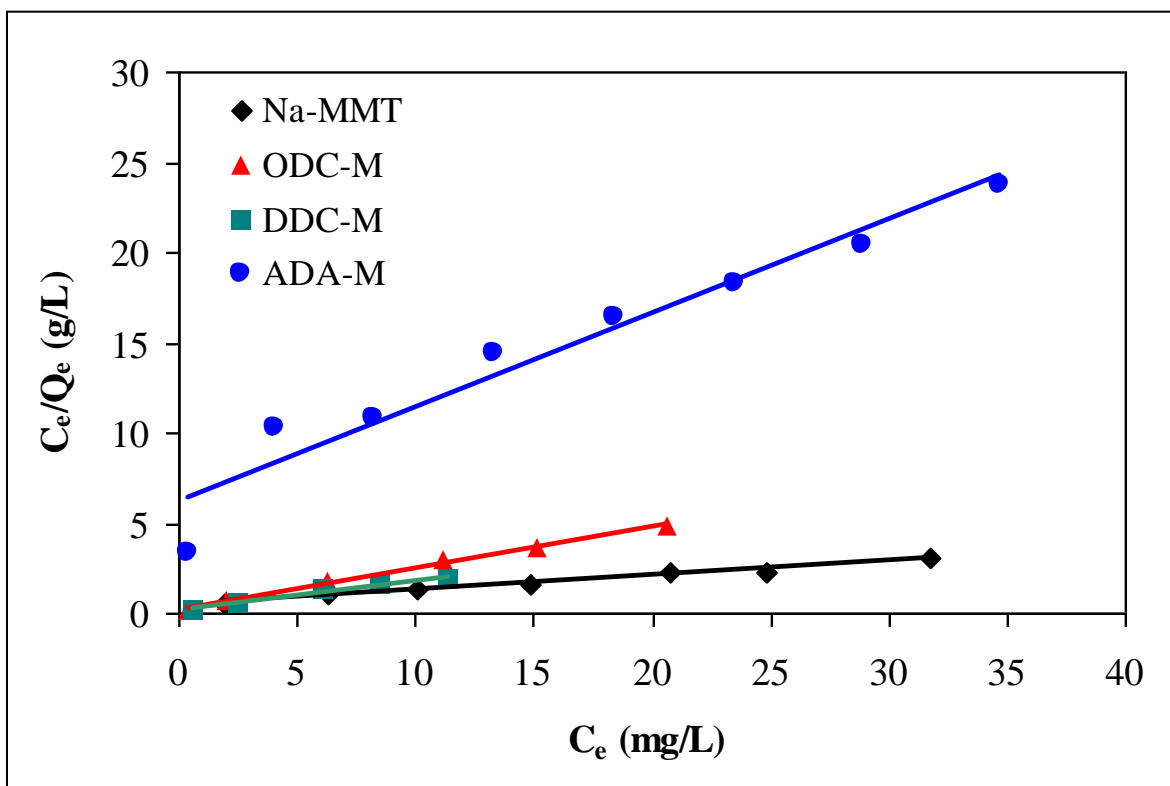


Fig. 6

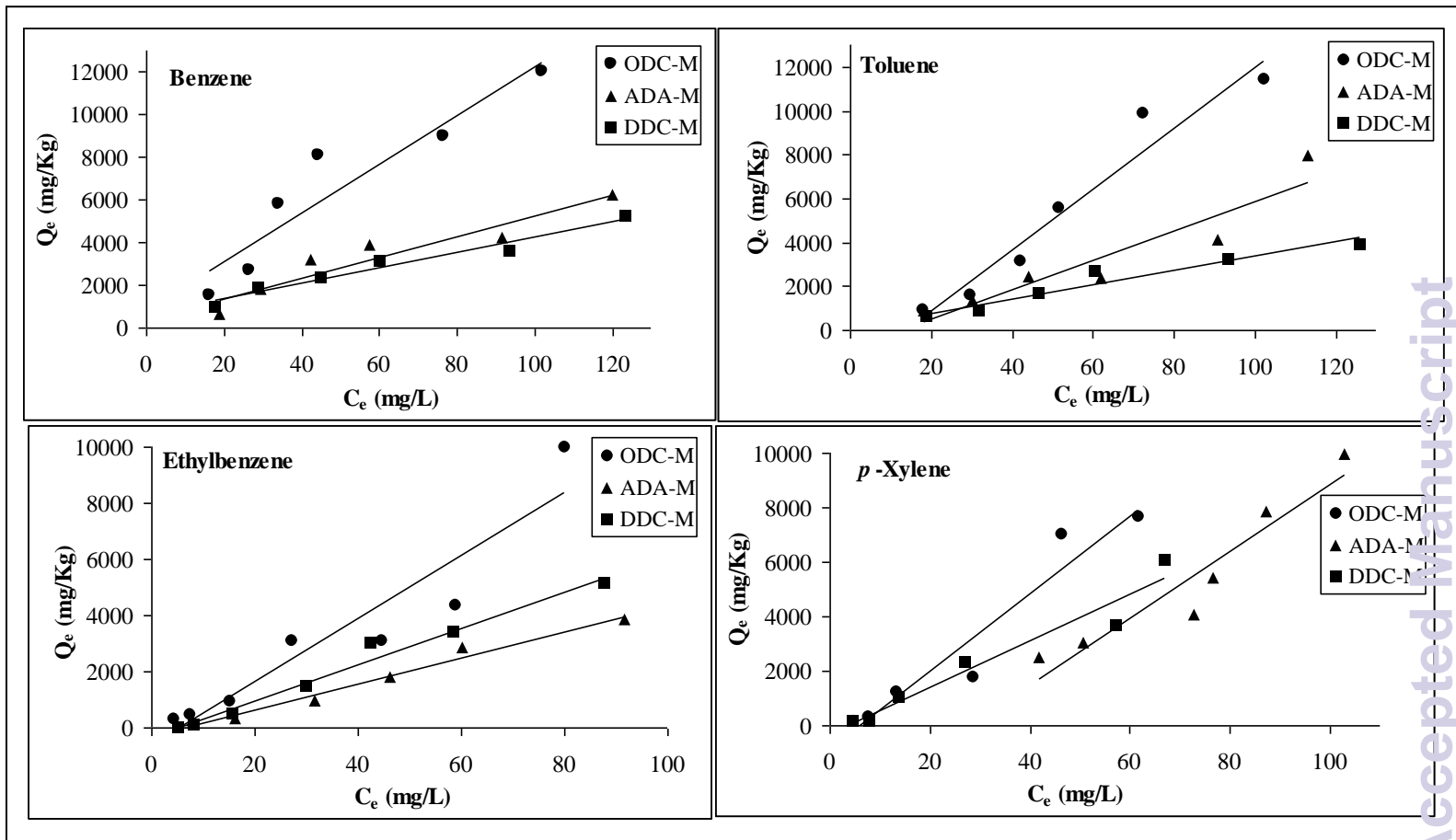


Fig. 7