Feasibility study of utilising Montmorillonite clay as an adsorbent for removing organic toxicants from water

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ABSTRACT

The aim of this study is to investigate the feasibility of utilizing Montmorillonite and various of its modified forms as an adsorbent for the removal of organic waste from aqueous media. Montmorillonite is a smectite clay mineral based on bidimensional lamellar alumino-silicate structure leading to a natually high surface area/volume ratio. Due to this reason, like zeolite, Montmorillonite has been proposed as an adsorbent in water treatment applications. Moreover, Montmorillonite is relatively abundant in certain parts of the world and thus it is inexpensive. Chemical and physical property modifications of Montmorillonite are important in order to improve the adsorption affinity of the clay towards different adsorbate species. Two main types of modified Montmorillonite, named as Al-PILCs (alumina-pillared clay) and surfactant-modified clays respectively, were synthesized in this work. Hexadecyltrimethylammonium bromide (HDTMA), a long chain quaternary ammonium cation, was the surfactant used in the preparation of surfactant-modified clays. The clays produced were characterized using the physical nitrogen adsorption Micromeritics ASAP 2000, X-ray diffraction and ICPAES techniques. Adsorption of 6 different organic toxicants; humic acid, two types of dyes (methylene blue and dichoro(R)fluorescein) and three phenolic compounds (phenol, 3-monochlorophenol and 3,5 dichlorophenol), were explored. Most of the adsorbates studied are classified as polluting elements, which cause problem to the environment. A series of batch adsorption experiments has been carried out. Comparative experiments were also conducted using Montmorillonite, the starting clay, as a reference material. The batch adsorption processes are well described by Langmuir isotherm with a very good correlation coefficient and the adsorption capacity of each adsorbent clay towards the particular organic waste was also calculated. The adsorption results demonstrate an interesting ability of surfactant-modified Montmorillonite in separating organic compounds from water. It is because the surfactant molecules alter the hydrophilic surface property of Montmorillonite into the organophilic surface property of the modified clays. These effects enhance the adsorption capacity of the clay towards the organic compounds. It is seen that the preparative route of the clays influences their adsorption properties as compared with the precursor Montmorillonite. Selection of an appropriate combination of the modified clay and the organic adsorbate can optimize the adsorption process. It is, therefore, shown by these experiments that Montmorillonite and its modified forms may be alternative adsorbents in some specific water treatment processes.

INTRODUCTION

Montmorillonite, the clay of alumino-silicate layer structures, is a member of smectite group of mineral. It has attracted increasing interest in adsorption applications due to its ability to swell and undergo pillaring [Wibulswas *et al* 1998]. However the Montmorillonite has a high negatively charge surface that is compensated by inorganic cations, generally Ca+ and Na+, situated between their layer structures. The water molecules present in the hydration sphere of these solvated cations confer a hydrophilic(organophobic) nature upon such surface. Accordingly this kind of mineral may not be a good adsorbent for hydrosoluble organic compounds, which are unable to compete with the highly polar water molecules. There has been an attempt to replace the inorganic cations of Montmorillonite by quaternary ammonium cations (QACs) of the form $[(CH_3)_3NR]^+$ in order to alter the organophobic surface of this mineral into an organophilic one [Hsu *et al.* 2000 and Sarkar *et al.* 2000]. The organophilic properties of the modified clay result in part from the reduced degree of hydration of the organic cations as compared to natural inorganic exchangeable cations like Ca+ and Na+ [Lawrence M.A.M. *et al.* 1998 and Kukkadapu *et al.* 1995].

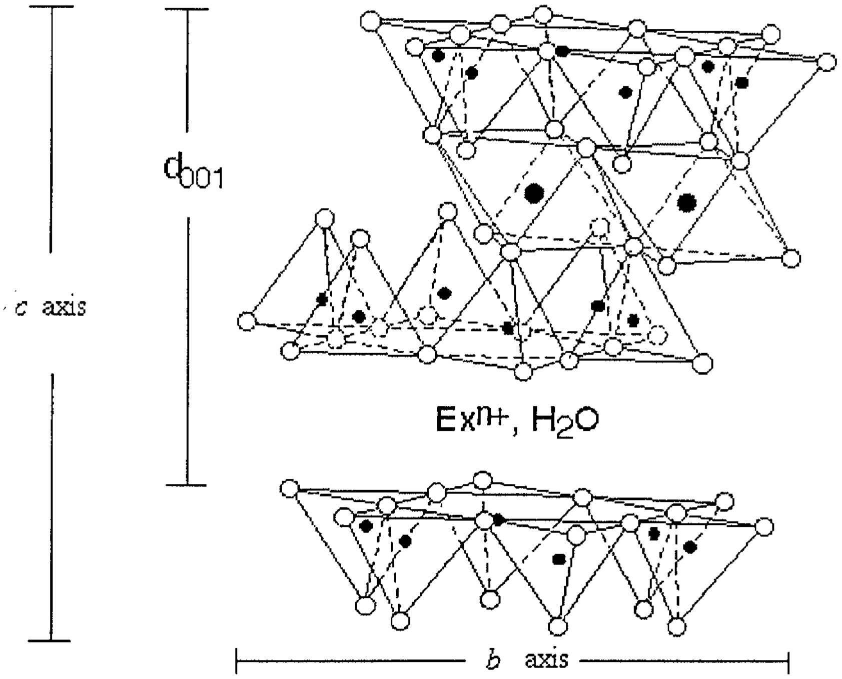


Figure 1 Structure of Montmorillonite. Small dark circles are Si^{4+},big dark circles are Al^{3+}, open circles oxygen atoms. Exchange cations andwater occupy the interlayer region.

The aim of this work was to study the adsorption isotherms of Montmorillonite and its modified forms toward various organic pollutants in aqueous system. Adsorption experiments were carried out with 6 organic molecules; humic acid, two types of dyes (methylene blue and 2,7-dichoro(R)fluorescein) and three phenolic compounds (phenol, 3-monochlorophenol and 3,5 dichlorophenol). The choice of these molecules was justified by their properties, for example, methylene blue is a cationic dye while 2,7-dichoro(R)fluorescein is an anionic dye. Two types of modified Montmorillonite were prepared. They were the conventional alumina-pillared clay (Al-PILC) and HDTMA-modified clay. Hexadecyltrimethylammonium (HDTMA) is a QACs.

MATERIALS

1. Precursor clay

The starting clay used was Montmorillonite from Aldrich Co.Ltd. This commercial product was available with a particle size of less than 1 μm. The chemical composition of Montmorillonite was analysed by ICPAES technique as shown in Table 1. The cation exchange capacity (CEC) of the Montmorillonite clays was calculated from the chemical compositions because only Na^+, Ca^{2+} and K^+ can be exchanged [Yang R.T. and Cheng L.S. 1995]. The calculated CEC of Montmorillonite is 58.86 meq per 100 grams of Montmorillonite. Prior to use, Montmorillonite was converted into the Na-exchanged form by contact with NaCl. Excess salts were removed by resuspension in distilled water until the conductivity of the surrounding water was less than 1.5 μS [Gil A. and Montes M. 1994]. The resulting product is Na-saturated Montmorillonite.

Table 1 Chemical compositions per 100 grams of Montmorillonite

SiO_2	70.55	**Na_2O**	0.53
Al_2O_3	14.18	**K_2O**	1.56
Fe_2O_3	3.09	**P_2O_5**	0.07
MgO	1.44	**TiO_2**	0.52
CaO	0.24	**MnO**	< 0.05

2. Alumina hydroxypolycation solution

The alumina hydroxypolycation solution, sometimes known as Al-pillaring agent, was a solution of hydrolyzed aluminium polycations. It was prepared by hydrolyzing 0.5 M $AlCl_3$ in 1.0 M HCl with 1.0 M NaOH added dropwise under vigorous stirring at 343 K with the initial OH/Al ratio of 2.4 [Bottero J.Y. *et al.* 1987]. This pillaring agent, in the form of a white gel, was aged for a week at room temperature.

3.Hexadecyltrimethylammonium (HDTMA) solution

HDTMA $[CH_3(CH_2)_{15}(CH_3)_3NBr]$ solution was prepared by dissolution of the appropriate amount of HDTMA in distilled water. The purity of HDTMA, supplied by BDH Chemicals Ltd., was ≥ 98% and it was used without further purification.

EXPERIMENTAL MEHODS

1.Synthesis of alumina pillared clay (Al-PILC)

Al-PILC were obtained by slowly adding Na-Montmorillonite suspension into the alumina pillaring solution at 343K. The slurry was stirred for 2 hours [Selvaraj S. *et al.* 1996] and for 3 days. During ageing, it was washed in distilled water until the water conductivity was under 1.5 μS. They were, then, separated from water and air dried overnight. Subsequently, a thin bed of air-dried sample was put in a furnace and the desired temperature, 673 K, was maintained for 48 hours.

2.Synthesis of HDTMA-modified clay (HDTMA-clay)

HDTMA solution was added to a stirred Na-Montmorillonite suspension. The concentration of HDTMA was desired to saturate the CEC of Montmorillonite. After mixing, the suspension was aged overnight and washed until the water conductivity was under 1.5 μS. The solid was separated from water by vacuum filtration and dried under air flow.

3.Batch adsorption studies

The adsorption isotherms were carried out using a batch equilibration technique in a 250 mL conical flask. Each flask was filled with a specific type and a fixed amount of adsorbent and adsorbate, at a known concentration, depending on each experiment. A control sample with no adsorbent was also prepared. Besides, comparative adsorption experiments were conducted with the untreated Montmorillonite as a reference material. The flask was then closed and shaken overnight at 16 °C to allow equilibrium to be achieved. The following day, the sample was centrifuged at 3500 rpm for 30 minutes to separate the adsorbent clays from the slurry. The supernatant was analyzed for adsorbate concentration.

RESULTS AND DISCUSSION

1.Characterization

BET surface area and pore size of adsorbent were measured using nitrogen physical adsorption by Micromeritics ASAP 2000. X-Ray diffraction (XRD) was used to determine the interlayer d_{001}-spacing which is the degree of pillaring of the modified products and, for comparison, the starting Montmorillonite. XRD analysis was carried out using CuKα radiation. The results are in Table 2. It is seen that the synthesis conditions of adsorbent effect their physical properties.

Table 2: Surface area, pore diameter and d_{001}-spacing of the starting and modified clays

Adsorbent	*d*-spacing (nm.)	BET surface area (m^2g^{-1})	Pore diameter (nm.)
Montmorillonite	1.57	245.9	5.49
Al-PILC	1.71	170.4	6.48
HDTMA-clay	1.81	34.3	11.16

From N_2 adsorption-desorption isotherm, Al-PILC and HDTMA-clay exhibited lower nitrogen adsorption capacity indicating that the modified agents, either HDTMA or alumina complex cations, were adsorbed into the interlayer space of the Montmorillonite and had occupied most of the micropore volume resulting to the lower BET surface area. On the contrary, the average pore diameter of the modified products is higher than the precursor clays.

From XRD result, the interlayer distance d_{001} varies with the nature of the pillars. The XRD patterns were a shift of d_{001} peak of most of the modified samples to lower diffraction angle, lower 2θ value, than that of Montlorillonite. It is corresponding to the expansion of the basal spacing, for example from 1.57 nm.of Montmorillonite to 1.81 nm. of HDTMA-clay, due to the exchange of the interlayer Na^+ of the raw Montmorillonite by the HDTMA species. The differences in the surface area and XRD interlayer spacing between the HDTMA-clays and the Al-PILC is due to the different sizes of the modified agents, either HDTMA or alumina complex cations. These results indicated the intercalation process was successful.

2. Adsorption isotherm

The amount of adsorbate in solution before and after adsorption can be analyzed by UV spectrophotometer. The concentration of adsorbate on adsorbent can be calculated from a simple mass balance by the assumption that the decrease from the initial concentration was due to adsorption by the adsorbent. It was noticed that phenolic compounds and 2,7 dichloro (R)fluorescein, which is an anionic dye, were uptaken only by the HDTMA-clay. They were not adsorbed on the starting Montmorillonite and the Al-PILC to any measurable degree. Moreover, adsorption of humic acid and methylene blue by HDTMA-clay showed more uptake than those by Montmorillonite and Al-PILC even HDTMA-clay has a lower BET surface area than the Montmorillonite and the Al-PILC. These behaviors reveal that the adsorption efficiency was not singularly dependent on surface area. It could be said that the surface of HDTMA-clay has an affinity for hydrophobic organic compounds. One of the adsorption isotherms is shown in the following diagrams.

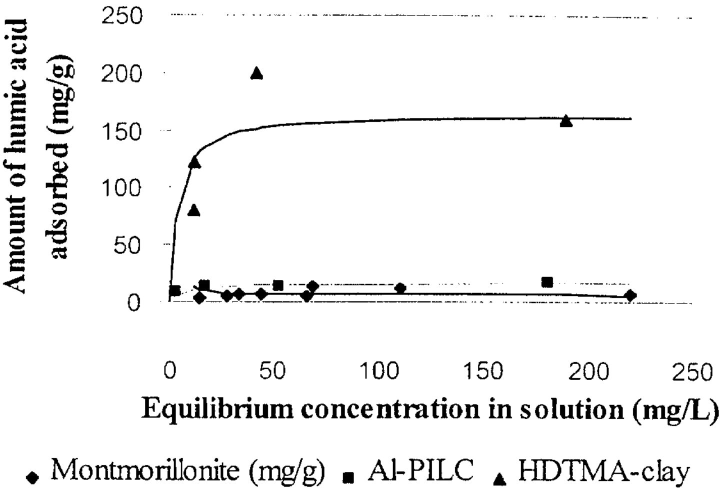


Figure 1Adsorption isotherm of humic acid on Montmorillonite and its modified forms.

The adsorption isotherm is non-linear indicating the sorption occurred by a physical adsorption mechanism [Lee J.H. *et al.* 1997]. Since the amount of adsorbate adsorbed seems to have a limiting value when the concentration in the solution tended to infinity as seen in Figure 1, Langmuir model was used to analyze the adsorption behavior. For a single solute system, Langmuir isotherm may be expressed as [Seader *et al* 1998]:-

$$y = \frac{ax}{1+bx} \qquad (1)$$

where y = the concentration of adsorbate on adsorbent (mg g^{-1} of adsorbent)
x = the equlibrium concentration of adsorbate in solution (mg L^{-1})
a and b = Langmuir constants.

The above equation can be modified to give:-

$$\frac{x}{y} = \frac{1}{a} + \frac{bx}{a} \qquad (2)$$

A plot of x/y against x will give a straight line for the isotherm if the Langmuir relationship can be applied. It is common to describe the fit of linear regression in term of R^2, which is the square of correlation coefficient. If the $R^2 = 1$, then the fit is perfect, but R^2 is always less than unity [Altin O. *et al.* 1998]. As shown Table 3, the straight line fit to the transformed data with R^2 approach to one. It is clear from these data that a Langmuir isotherm does satisfactorily describe the adsorption behaviour of the studied organic toxicants on Montmorillonite and its modified forms. The monolayer adsorption capacity, amount of adsorbate adsorbed per unit weight of adsorbent, was calculated for each adsorbent-adsorbate system from its Langmuir constants and shown in Table 4.

Table 3: Correlation coefficient, R^2, for each adsorbent-adsorbate system

Adsorbent	Humic acid	Methylene blue	Dichloro(R) fluorescein	Phenol	3-chloro phenol	3,5-dichloro phenol
Montmorillonite	0.886	0.994	-	-	-	-
Al-PILC	0.997	0.993	-	-	-	-
HDTMA-clay	0.992	0.995	0.999	0.918	0.991	0.998

Table 4: Adsorption capacity (mg of adsorbate per g of adsorbent).

Adsorbent	Humic acid	Methylene blue	Dichloro(R) fluorescein	Phenol	3-chloro phenol	3,5-dichloro phenol
Montmorillonite	6.6	357	0	0	0	0
Al-PILC	16.6	128	0	0	0	0
HDTMA-clay	163.9	417	66	16.9	130	115

As the results indicate, the HDTMA-clay showed a significantly affinity in removing organic molecules from water. The quaternary ammonium cations (QACs), HDTMA, seem to have a dual effect on Montmorillonite. Firstly, HDTMA changed the clay structure not only by decreasing its BET surface area but also by increasing its pore diameter and d_{001}-spacing. The higher d_{001}-spacing and lower BET surface area of HDTMA-clay indicate that the pores of the modified clay were occupied mainly by HDTMA molecules. Second, HDTMA molecules change the hydrophilic surface property of Montmorillonite into organophilic surface. This effect enhances the adsorption capacity of the clay for organic molecules.

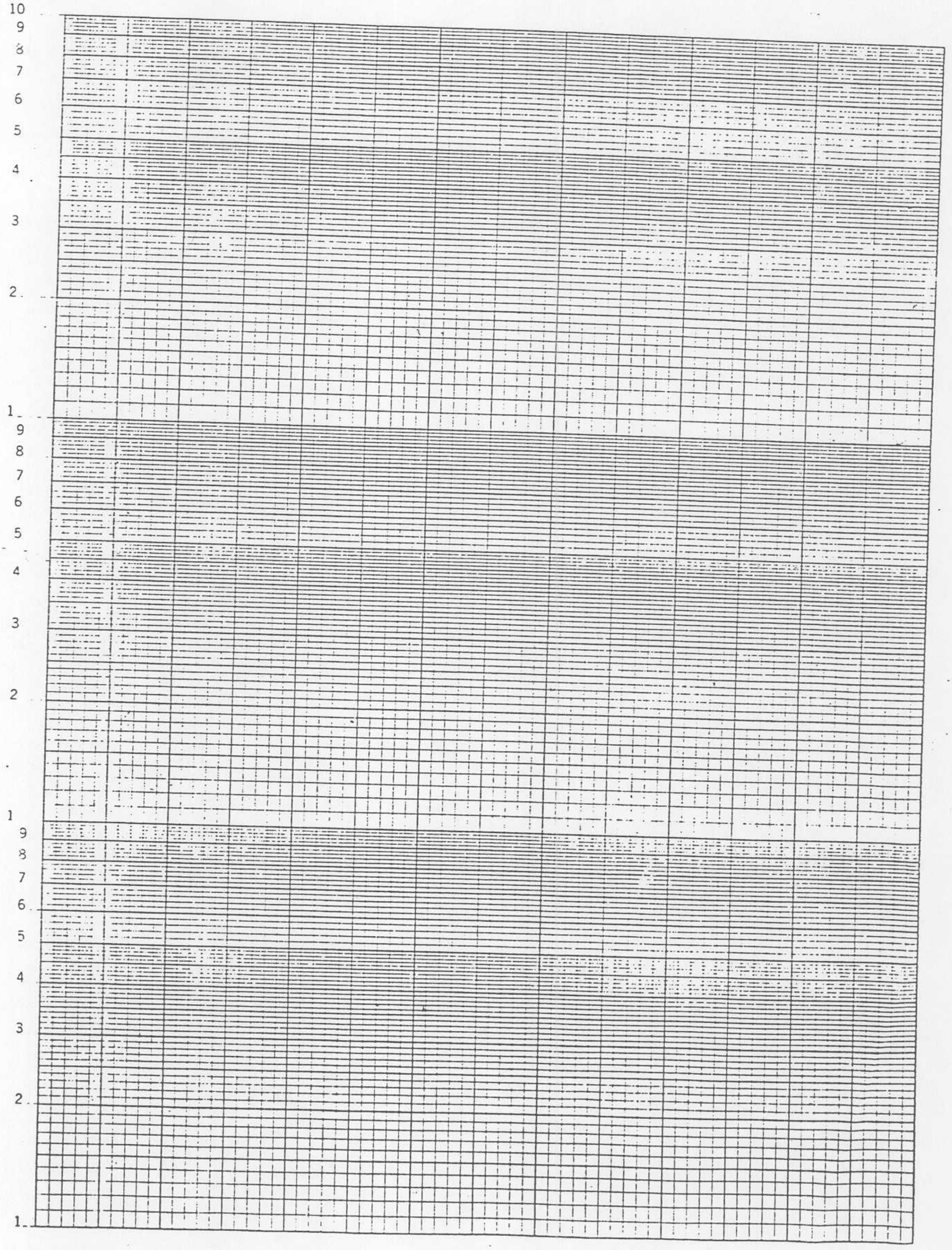
It appears from the experimental results that even phenol is a smaller molecule than chlorinated phenols, the uptake of phenol by HDTMA-clay was less than that of chlorinated phenols. Phenol has higher water solubility than chlorinated phenols as shown in Table 5, hence, its interaction with organophilic surface of HDTMA-clay was weaker and resulting in lower adsorption.

Table 5 Physicochemical properties of the phenolic compounds

Compounds	UV maxima wavelength (nm)	MW.	pKa (at 20°c)	Water solubility (g kg^{-1} at 20°c)
Phenol	269	100.16	9.98	77.5
3-chlorophenol	274	128.56	9.08	25.0
3,5-dichlorophenol	277	163.00	8.15	4.5

CONCLUSION

The comparative studies of the adsorption of organic contaminants by Montmorillonite, Al-PILC and HDTMA-clay suggest that HDTMA-clay was a better adsorbent than Montmorillonite and Al-PILC. The higher degree of hydration of the Na+, Ca+ and/or alumina complex cations in Montmorillonite and Al-PILC renders them unable to accommodate any of the phenols and anionic dye studied into their interlayer region. The properties of Motmorillonite were affected significantly by replacing its native interlayer cations like Na+ and Ca+ with HDTMA+, which are quaternary ammonium cations (QACs). Montmorillonite modified by HDTMA+, namely organo-clay, can be used as an adsorbent of various organic contaminants from water. The non-linear adsorption isotherms were obtained and well described by Langmuir adsorption theory.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