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ADSORPTION OF THE CATIONIC SURFACTANTS ON MONTMORILLONITE

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Abstract

Adsorption of cetyltrimethylammonium (CTA) and cetylpyridinium (CP) on Na-rich montmorillonite (MMT) was studied. For this purpose, the adsorption isotherms of CTA and CP along with desorption curves of metal cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) were constructed. The adsorption of CP is well described by the Langmuir isotherm. In the case of CTA, the best fitting Langmuir- Freundlich model with the power constant $r<1$ was found. It can be explained by the CTA higher degree of intercalation into the MMT interlayer space. Infrared, X-ray diffraction patterns, specific surface area, porosity, and moisture adsorption measurements of montmorillonite also revealed that both the surfactants were adsorbed in a monolayer arrangements but CP in a higher amount than CTA.

The results of molecular modelling showed that interaction energies between CTA and the external MMT surface have lower energy values than in the case of CP. This supports an idea that CTA keeps more strongly near the MMT layer and also restrict interaction of another CTA cations with the layer. This finding agrees with the experimental determination of higher amount of CP bound to the MMT face.

Introduction

Phyllosilicates are layered silicates in which the SiO_4 tetrahedra are linked together in infinite two-dimensional sheets and are condensed with the layers of AlO_6 or MgO octahedra in the ratio 2:1 or 1:1. The negatively charged layers attract positive cations (e.g., Na^+, K^+, Ca^{2+}, Mg^{2+}) which hold the layers together. Their large cation exchange capacities enable them to adsorb heavy metals and to be modified with quaternary salts [1] including cationic surfactants [2]. One of the exceptional properties of such prepared organo-phyllosilicates is their ability to sorb hydrophobic organic contaminants, such as chlorinated phenols [3, 4], perchlorethylene, naphtalene and phenanthrene [5–7], aniline [8] or phenol [9] etc. The retention of inorganic oxyanions, such as chromate, nitrate, and arsenate, on organo-kaolinite [10] and organo- clinoptilolite [11] have been studied, as well.

The aim of this work was to understand the cationic surfactants (CSs) sorption on phyllosilicates in order to prepare efficient and selective organo-phyllosilicate adsorbents. For this study Na-rich montmorillonite was used along with the typical cationic surfactants, such as cetyltrimethylammonium and cetylpyridinium.

Materials and methods

Adsorption procedure

Na^+-rich montmorillonite type Wyoming $(Al_{2.90}Mg_{0.59}Fe^{3+}_{0.49}Ti_{0.01})_{3.99}$ $(Si_{7.92}Al_{0.08})_{8.0}$ $O_{20}(OH)_4$ with a cation exchanged capacity (CEC) about 0.9 meq/g was used as the host structure for the absorption of CTA and CP. The cationic surfactants were dissolved in a mixture of water and ethanol (50:50, v/v), a portion of MMT was added and this suspension was shaken vigorously for 2 hours. The suspension was centrifuged for 20 minutes and a supernatant was analysed by a capillary isotachophoresis and the atomic absorption spectrometry. The organo-montmorillonite samples intended for spectral and surface analyses were filtered out on 1.2 m glass fibre filters (Whatman) and washed several times with water until a reaction with a 1 % $AgNO_3$ solution was negative. The laboratory temperature varied from 20 to 24 °C.

Analytical and testing methods

The amounts of cationic surfactants adsorbed and metal cations desorbed were determined by the method of capillary isotachophoresis (EA 102, Villa-Labeco, Slovakia) developed for this purpose [12]. Only potassium was determined by the atomic absorption spectrometry (Spectra AA30, Varian Inc., USA) using a conventional method. The IR spectra were obtained by the KBr method using Fourier transform (FTIR) spectrometer (NEXUS 470, Thermo Nicolet, USA).

The surface areas of the MMT samples were measured (Sorptomatic 1990, Thermo Electron Corporation, USA) using nitrogen as an adsorbing gas and calculated by Advance Data Processing software according to the BET isotherm within the range p/p^0=0 to 0.3 at a temperature of 77.31 K. Moisture adsorption on the MMT samples was studied by using a dynamic vapour sorption (DVS) system. The adsorption isotherms were measured by weighting of samples under static humidity conditions at 297 K.

Analysis of equilibrium data

Adsorption data were fitted using several adsorption isotherms describing the monolayer adsorption: Langmuir, Freundlich, and Langmuir-Freundlich (Sips). Non-linear regressions was performed by the Gauss-Newton method. The best fitting model was chosen according to the statistical regression criteria: Regression coefficient (R), Akaike information criterion (AIC), and mean error of prediction (MEP).

Molecular modelling

The montmorillonite surface was based on the structure data published by Tsipursky and Drits [13], space group C2/m. The unit cell parameters according to Méring and Oberlin [14] have been used to define the planar unit cell dimensions: $a = 5.208$ Å; $b = 9.020$ Å. To create a suitable supercell for calculation, we used the following layer composition: $(Al_{3.25}Mg_{0.75})Si_8O_{20}(OH)_4$. The crystal supercell $2a$ $2b$ $1c$ with the composition $(Al_{13}Mg_3)Si_{32}O_{80}(OH)_{16}$ was build with the corresponding layer charge (-3) per one supercell. After that one montmorillonite layer was cleaved in Surface builder module to create a platform for solving molecules arrangement above the layer surface. The layer was built as a periodically repeated supercell in 2 dimensions. Under the basic layer unit there was 1 Na^+ cation and above the layer there were 2 cations (CP or CTA) which compensate there the negative layer charge. Gasteiger method was used for charge estimation.

Data processing

Isotachopherograms and electropherograms were recorded and evaluated by using the programme ITPPro32 (KasComp, Ltd., Slovakia). The non-linear regression (the Gauss-Newton iteration method) and all statistical calculations made at the = 0.05 significance level were performed by the program QC.Expert 2.5 (Trilobyte Statistical Software, Czech Republic).

Molecular mechanics and classical molecular dynamics were carried out in a *Cerius*^{2} modeling environment [15]. The strategy of energy minimization was based on the following estimations: The montmorillonite layer and the Na^+ cations were fixed with respect to the Cartesian coordinates (atom moves are not possible) and all cations or molecules above the layer were without any restriction in positions and rotations. Energy was calculated on the universal force field parameters base [16].

Results and discussion

Adsorption isotherms of cationic surfactants

All adsorption (batch) experiments were performed in water-methanol (50:50, v/v) solutions to avoid micellization of the cationic surfactants [17]. The cationic surfactants adsorbed and metal cations desorbed were analysed by the capillary isotachophoresis and the atomic adsorption spectrometry, respectively. In order to understand adsorption mechanisms, the adsorption isotherms were constructed (Fig. 1). These equilibrium data were analysed by their fitting with the monolayer isotherm models: Langmuir, Freundlich, and Langmuir-Freundlich. The non-linear regression results are given in Table 1.

According to the R and AI criteria, Langmuir-Freundlich isotherm is the most suitable model characterizing the adsorption of CTA on MMT (Fig. 1). In the case of CP, all regression criteria show that both Langmuir and Langmuir-Freundlich models are potential for the experi-

Table 1. Results of the adsorption isotherms fitting

	Adsorption models – adsorption of CTA (n=11)		
Param.	**Langmuir**	**Freundlich**	**Langmuir-Freundlich**
a_m	0.5288 ± 0.0251	0.5514 ± 0.0462	0.5564 ± 0.0452
k	100.5 ± 46.3	—	100.1 ± 47.1
p/r	—	9.326 ± 4.253	0.7008 ± 0.2680
R	0.9579	0.8824	0.9769
MEP	0.0021	0.0034	0.0118
AIC	-76.68	-65.80	-81.16
	Adsorption models – adsorption of CP (n=12)		
Param.	**Langmuir**	**Freundlich**	**Langmuir-Freundlich**
a_m	0.6408 ± 0.0231	0.6769 ± 0.0608	0.6574 ± 0.0372
k	139.6 ± 33.1	—	131.5 ± 37.6
p/r	—	7.866 ± 2.652	0.8137 ± 0.2503
R	0.9842	0.9147	0.9868
MEP	0.0011	0.0054	0.0014
AIC	-90.6	-69.1	-90.9

mental data smoothing. In addition, the power constant *r* is statistically equal to 1 (see the *r* confidence interval), which means that the Langmuir-Freundlich can be replaced by the simpler Langmuir one. The evaluation of the best fitting isotherms could elucidate how the cationic surfactants are adsorbed on the montmorillonite surface.

CP was adsorbed in agreement with the Langmuir model which was theoretically derived supposing no interactions between the compounds forming monolayers on solids. On the other hand, the adsorption of CTA is better described by the Langmuir-Freundlich isotherm with $r < 1$ which indicates that an another significant type of the CTA interaction with MMT exists. It is likely its intercalation into the MMT interlayer space which was recognized by measurements of the MMT basal spacings d_{001}. It was found that MMT saturated with CTA exhibited a higher basal spacing (d_{001} = 1.75) than in the case of CP (d_{001} = 1.66) [17] which can indicate that CTA was intercalated in a higher amount than CP. That is why CTA is supposed to be bound to the MMT face by stronger forces than CP. It agrees with the recent findings of molecular dynamic simulations [18, 19]. Both CTA and CP were suggested to be arranged within the interlamellar space in a liquid like disordered monolayer. Besides, the lower CP d_{001} values also indicate that CP has to be predominantly located on the external MMT surface.

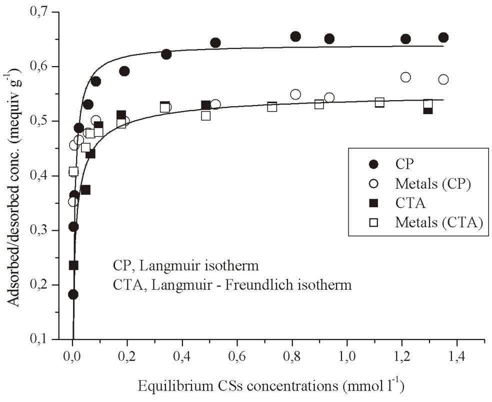

Figure 1. Adsorption data fitting with the Langmuir and Langmuir-Freundlich isotherms.

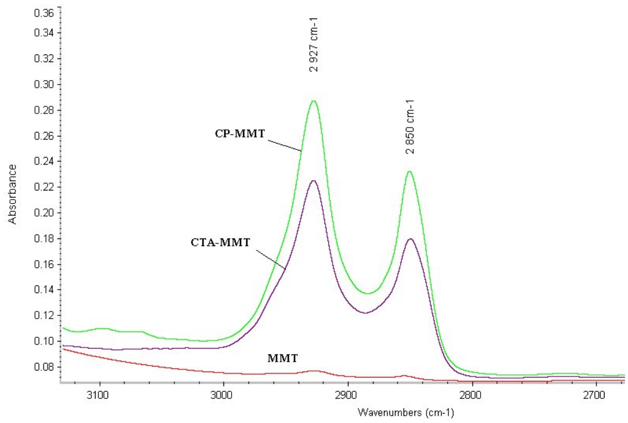

Figure 2. FTIR spectra of MMT-CTA and MMT-CP.

It is also obvious from Fig. 1 that CP is sorbed in significantly higher amounts than CTA. The FTIR spectra of the saturated MMT samples demonstrated in Figure 2 show a higher portion of sorbed CP, as well. Generally, there are the two most important mechanisms of the cationic surfactant sorption on solids: i) ion exchange and ii) the hydrophobic chain-chain interactions [20]. Some CSs adsorption arrangements are illustrated in Figure 3 showing the CSs adsorption on the external phyllosilicate surface. If the monolayer governed by ion exchange reactions is created, a ratio *f* between the amount of a cationic surfactant (meq/g) adsorbed and metals desorbed (meq/g) should be *f* = 1 in agreement with this ion exchange reaction:

$$\text{MMT-M}^+ + \text{CS}^+ = \text{MMT-CS} + \text{M}^+ \qquad (1)$$

A bilayer arrangement formed on the basis of hydrophobic interactions should be completed if *f* = 2. When 1< *f* <2 an incomplete bilayer is being formed. Accordingly, the CTA monolayer (*f* = 0.992±0.028, *n* = 6) and the CP incomplete bilayer (*f* = 1,159±0.029, *n* = 6) formation on the MMT external surface should be expected. However, the CP monolayer arrangement was confirmed by fitting the sorption equilibrium data with the Langmuir curve.

Montmorillonite surface analysis

From the facts given above it follows that the excessive non-stoichiometric amount of CP is likely arranged in the dense monolayer located on the external MMT face. To prove this idea, a sorption of water on the samples of natural MMT and MMT covered by CP (MMT-CP) and CTA (MMT-CTA) was examined [17]. Supposing the CP bilayer formation according to Figure 3c, the positively charged CP headgroups should enhanced the water adsorp-

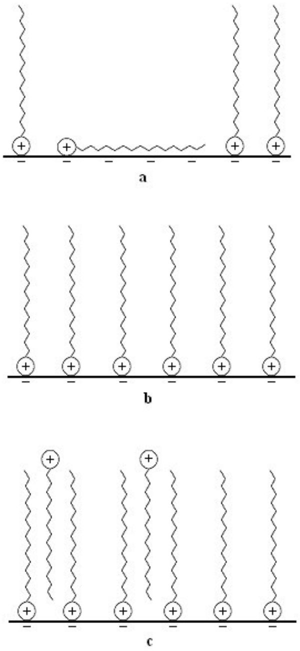

Figure 3. Arrangements of alkylammonium cationic surfactants adsorbed on phyllosilicates. a) incomplete monolayer (*f* < 1), b) monolayer (*f* = 1), c) incomplete bilayer (1 < *f* < 2).

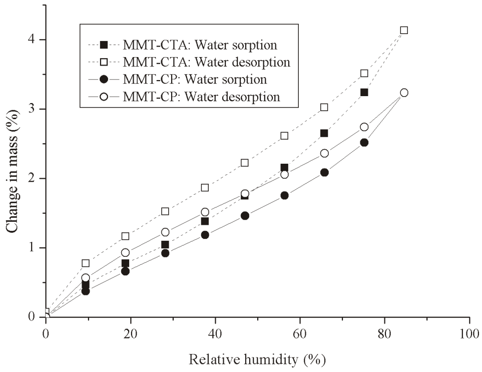

Figure 4. Water adsorption and desorption isotherm plots.

tion in comparison with MMT-CTA. But from Fig. 4 it is clear that the lowest adsorption of water occurred on MMT-CP. These results well agree with the high amount of CP fixed on MMT which makes its surface more hydrophobic in comparison with MMT as well as with MMT-CTA.

The adsorption of the cationic surfactants on MMT modifies its surface so that it becomes hydrophobic and its porosity and specific surface area are changed. The total specific surface areas of MMT, MMT-CTA, and MMT-CP were determined using the BET method (Table 2). The 5 50 nm and 50 1000 nm pores areas were estimated by means of the Dallimotre Heal isotherm. The area of the pores with r < 0.5 nm was calculated as a difference between the total surface area and a sum of the 5 50 and 50 1000 nm pores areas. The area of 0 to 50 nm pores significantly decreased by the surfactant adsorption. Even in the case of MMT-CTA, the nearly zero area of the pores with $r < 0.5$ nm was found because of their total blinding by this surfactant. On the contrary, the 50 1000 nm pores of the both modified MMTs enlarged.

Table 2. Pores areas of the natural and modified montmorillonite.

	MMT	MMT-CTA	MMT-CP
Total surface area (m^2/g)	28.5	4.4	8.8
< 0.5 nm pore area (m^2/g)	21.8	0.4	2.6
5-50 nm pore area (m^2/g)	6.4	2.8	4.4
50-1000 nm pore area (m^2/g)	0.3	1.2	1.8

Mathematical modelling of the cationic surfactants adsorption

Intercalation of phyllosilicates with alkylamonium cations was firstly described by Lagaly [21 23]. His suggestions have been confirmed by many experimental works and also by using computer simulations [15, 18, 19]. In this work, the molecular modelling describing the cationic surfactant adsorption on the external MMT surface are presented.

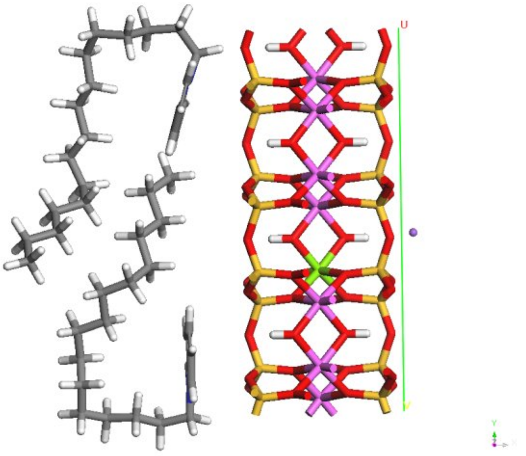

Figure 5. Optimized structure with minimum total crystal energy CP without water and ethanol.

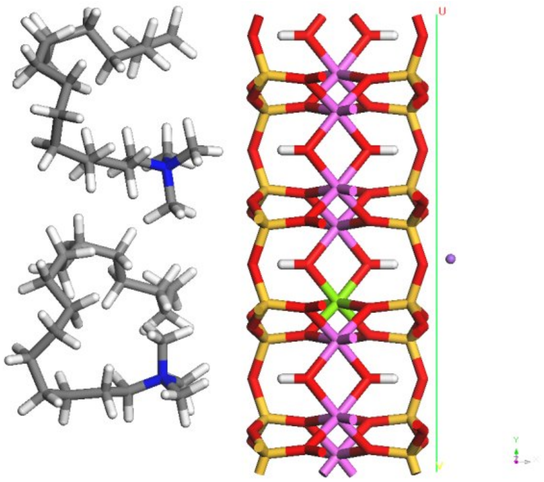

Figure 6. Optimized structure with minimum total crystal energy CTA without water and ethanol.

The first set of initial models was built above the basic surface unit with two CP cations which were placed randomly above the basic layer. The initial models were created with alkyl chains laying (i) parallel with the MMT layer, (ii) perpendicular to the MMT layer and head groups of CP adjacent to the silicate layer or in an opposite position, (iii) under different angles between the alkyl chain and the layer. The initial models were optimized and minimized under the conditions mentioned above and the model with minimum energy was selected for subsequent calculations. This calculated minimized surface structure has CP head-groups near the silicate layer (Fig. 5). The same procedure was done for the MMT surface with the CTA cations. The model with minimum energy has the head-groups adjacent to the silicate layer and also the second part of the alkyl chains is adjacent to the silicate layer. It looks like letter u with upper part turning to the layer (Fig. 6). Both the minimized and optimized models were used as the initial models for subsequent calculations with

Table 3. Total crystal energy and its components [kcal/mol] for MMT surface with CP and CTA cations immersed into 55 water and 17 ethanol molecules.

Model	Bond	Angle	Torsion	Inversion	v dWaals	Coulomb	Total
CP1	10.2	23.1	13.7	0.0	-195.3	-431.5	-579.3
CP2	9.2	21.2	13.8	0.0	-208.5	-535.0	-698.7
CP3	8.0	19.6	12.9	0.0	-209.1	-525.8	-693.9
CP4	7.8	23.3	18.8	0.0	-166.7	-602.0	-718.6
CP5	8.8	25.6	19.6	0.1	-153.9	-610.8	-710.6
CTA1	13.9	29.8	11.7	0.0	-201.0	-585.0	-730.6
CTA2	13.7	32.3	15.1	0.0	-211.1	-646.4	-796.3
CTA3	13.6	36.6	17.2	0.0	-174.0	-622.7	-729.4
CTA4	12.2	38.0	19.9	0.0	-152.7	-587.2	-669.9
CTA5	12.0	37.2	19.3	0.0	-175.9	-580.8	-688.1

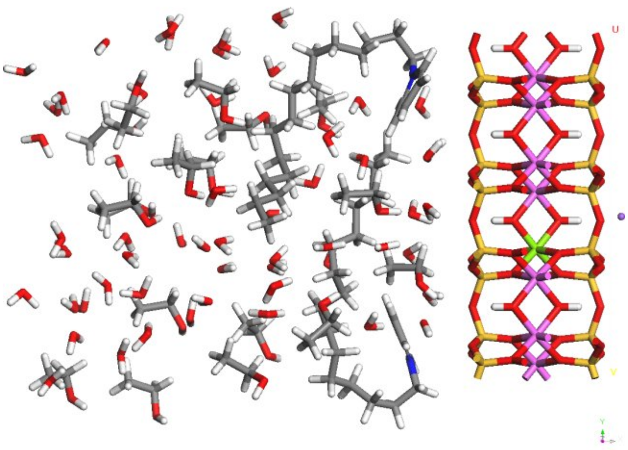

Figure 7. Optimized structure with minimum total crystal energy CP in the presence of water and ethanol.

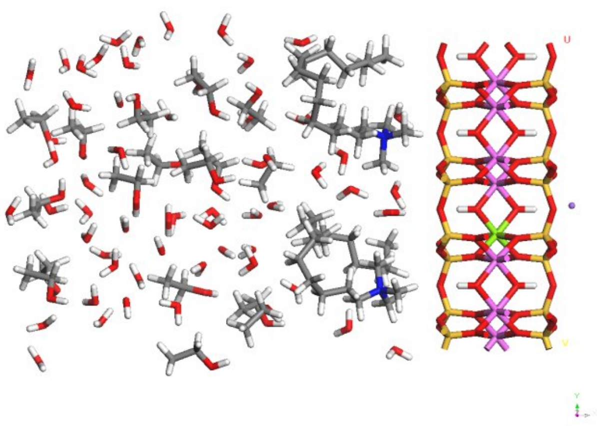

Figure 8. Optimized structure with minimum total crystal energy CTA in the presence of water and ethanol.

55 water and 17 ethanol molecules which corresponds to the composition of the water-ethanol mixtures (50 %, v/v).

The series of new initial models were built with the water and ethanol molecules placed above the CP cations, which were adjacent to the MMT layer. It relates to the model (marked as CP1) with the highest distance of the water and ethanol molecules bulk from the MMT layer. This distance was gradually decreased in the models CP2, CP3, CP4 and CP5, where the CP cations (Fig. 5) were completely immersed in the water and ethanol molecules bulk. The same procedure was done for the CTA cations. The series of the initial models were subsequently minimized and optimized and the influence of the water and ethanol molecules on the CP or CTA adsorption was investigated.

The resultant values of crystal energy and its components are presented in Table 3. The total crystal energy consists of valence (bond, angle, torsion, inversion terms) and non-bond (van der Waals, Coulomb) components. The energy values in Table 3 show a very interesting contrast between the CP and CTA models. Water and ethanol molecules immersion is available for the CP cations because of the energy values are lower for the models with surroundings cations. On the contrary, from the energy values of CTA models we can derive that a gradual immersion is stopped and the special positions of the CTA cations successfully inhibit the subsequent water or ethanol immersion.

On the basis of these results as well as the value of total crystal energy we can derived that the CTA cations have the stronger interactions with the MMT layer than the CP cations. Moreover the CTA cations probably inhibit not only the water and ethanol immersion but likely also subsequent adsorption of another CTA cations. The optimized structure with the minimum total crystal energy is shown in Figure 7 and 8 for models CP4 and CTA2, respectively.

This idea was confirmed by the models with addition of higher amount of the CP and CTA cations on the MMT surface. From the sublimation energy values in Table 4 it follows that by an addition of another cationic surfactnats the

Table 4. Sublimation non-bond energy [kcal/mol] for the MMT surface covered with different numbers of CP and CTA.

Model	v dWaals	Coulomb	Total	Decrease
2xCP	-236,9	-645,9	-882,9	0
3xCP	-285,3	-863,5	-1148,8	265,9
4xCP	-321,7	-1097,2	-1418,9	270,1
2xCTA	-267,2	-733,0	-1000,3	0
3xCTA	-285,9	-864,0	-1149,9	149,6
4xCTA	-266,8	-998,6	-1265,5	115,6

Note: Decrease – A decrease of the total sublimation energy connected with addition of another molecule.

total sublimation energy values of these models decreased. In addition in the case of CP, the energy decreased steeply than for CTA. It confirms the easier adsorption of the higher amount of CP molecules on the MMT surface. It was also observed experimentally.

Conclusion

The experimental results of this adsorption study revealed the monolayer arrangement of both surfactants on the MMT external surface. In addition, CP was found to be bound in the higher amount than CTA which was adsorbed according to the ion exchange stoichiometry. The CTA stronger interactions with the MMT layers were also confirmed by the outputs of the molecular modelling and indicate that CP could form the dense monolayer in which its molecules can be easily re-arranged.

By the surfactants coverage the montmorillonite surface was significantly modified. It became very hydrophobic and its porosity was substantially changed so that micro- and mesopore were completely disappeared or diminished, respectively. Such prepared MMT surface is potential for the adsorption of various toxic compounds as we intend to investigate in future.

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