

ADSORPTION OF PHENOL AND ANILINE BY ORIGINAL AND QUATERNARY AMMONIUM SALTS-MODIFIED MONTMORILLONITE

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ABSTRACT

Adsorption of phenol and aniline onto original and with quaternary ammonium salts (QASS)-modified montmorillonite was described by sorption isotherms of type III and II, respectively. For the montmorillonite (MMT) modification - hydrophobisation, cetyltrimethyl- ammonium (CTMA) and tetramethylammonium (TMA) cations were used. In comparison with phenol, aniline was adsorbed largely on original MMT but less on modified one. XRD patterns indicated that both aromatic compounds were intercalated in the MMT interlayer being perpendicularly oriented to silicate sheets. Alkyl chains of CTMA and TMA probably act as organic "pillars" stabilising the MMT tabular structure against exfoliation due to the intercalation with phenol and aniline of high concentrations.

KEYWORDS: adsorption, intercalation, montmorillonite, quaternary ammonium salts, phenol, aniline

INTRODUCTION

Montmorillonite is a representative of 2:1 layered phyllosilicates. The MMT layers are built from two tetrahedral silicate SiO₄ sheets and an octahedral sheet of AlO₆. Tetrahedral and octahedral cations can be replaced by lower valence cations, such as Al³⁺ and Fe²⁺ or Mg²⁺, respectively. The excessive negative charge of these layers is compensated by metal cations (Na⁺, K⁺, Ca²⁺ and Mg²⁺) in the interlayer space, which can be exchanged with various cations, such as quaternary ammonium salts forming the organically modified phyllosilicates (organo-phyllosilicates) with hydrophobic properties (Jaynes and Boyd, 1991).

Nowadays organo-phyllosilicates attract increasing attention as sorbents, catalysts, molecular sieves, ion conductors, non-linear optical materials etc. Our core interest is the preparation of the effective sorbents for removal of toxic organic compounds from environment. Therefore, the aim of this work was to investigate adsorption of phenol and aniline on original and organically modified montmorillonite. For the modification two different quaternary ammonium salts, such as cetyltrimethylammonium and tetramethylammonium, were used.

EXPERIMENTAL

REAGENTS

The used chemicals were of the analytical reagent grade: Phenol, aniline (both from Merck,

Germany), cetyltrimethylammonium bromide and tetramethylammonium chloride (all from Sigma, USA). Na⁺-rich montmorillonite Wyoming (Source Clays Depository, Purdue University, USA). Twice distilled and deionised water by a mixed-bed ion-exchanger (Watek, Czech Republic) was used for preparation of all solutions.

THE ADSORPTION PROCEDURE

Adsorption of phenol and aniline was tested on original and organically modified montmorillonite. Na⁺-rich montmorillonite Wyoming was used for all intercalation and adsorption experiments. Its ion-exchanged capacity of 121 cmol kg⁻¹ was determined by saturations with NH₄⁺ (Madejová et al., 1999) and by analyses of released metals (Na⁺, K⁺, Ca²⁺, Mg²⁺) by atomic absorption spectrometry. The structural MMT formula of Na_{0.38}K_{0.04}(Ca_{0.12} Mg_{0.50} Fe³⁺_{0.41} Al_{2.90} Ti_{0.01} Mn_{0.01}) (Si₈) O₂₀(OH)₄ was calculated from results of X-ray fluorescence analyses of powdered montmorillonite. Fraction of MMT with particle size < 5 μm separated by sedimentation was used for all experiments.

CTMA was intercalated into MMT by shaking of its suspension in a 50:50 (v/v) water-ethanol mixture for 2 hours (Praus et al., 2006; Praus and Turicová, 2007). TMA was intercalated by shaking of the water suspensions for 24 hours (Kurková et al., 2000). MMT suspensions were centrifuged for 20 minutes, filtered, and dried at 105 °C. All experiments were

performed at the laboratory temperature of 22 ± 2 °C. In this paper, montmorillonite intercalated (modified) with QASs was denoted as QAS-MMT and by analogy CTMA-MMT and TMA-MMT when modified with CTMA and TMA, respectively.

The adsorption of phenol and aniline onto MMT and QAS-MMT was carried out by shaking the aqueous suspensions of phenol and aniline for 24 hours. Then, the suspensions were centrifuged (4500 min^{-1}) for 20 minutes and supernatants were analysed. The pH values of phenol and aniline equilibrium solutions were of about 6.0-7.5. In order to understand adsorption mechanisms, adsorption isotherms were constructed. The adsorbed amounts of both compounds a (mol kg^{-1}) were calculated as follows:

$$a = \frac{(c_B - c_e)V}{w} \quad (1)$$

where c_B and c_e are blank and equilibrium concentrations (mmol l^{-1}), respectively, V is volume of phenol and aniline solutions and w is mass of MMT. The equilibrium concentrations of phenol and aniline were determined directly in the supernatants by UV spectrometry. In order to correct turbidity of the suspensions, the concentrations of both compounds were calculated from differences of absorbances measured at 262 nm and 257 nm for phenol and 295 nm and 290 nm for aniline. The blank concentrations were analysed in blank solutions, which were handled as other samples to correct the adsorption of phenol and aniline on laboratory vessels.

ANALYSIS OF EQUILIBRIUM DATA

The adsorption isotherms of aniline were determined by fitting experimental data with Langmuir and Freundlich adsorption isotherms. Non-linear regression was performed by Gauss-Newton iteration method. The best fitting model was chosen according to statistical criteria: Regression coefficient (R), Akaike information criterion (AIC), and mean error of prediction (MEP).

LANGMUIR ISOTHERM

Langmuir isotherm was theoretically derived supposing that the adsorption takes place on fixed homogenous adsorption sites of equal energy, forming a monolayer surface coverage. Langmuir model can be described by the equation

$$a = a_m \frac{bc_e}{1 + bc_e} \quad (2)$$

where a (mol kg^{-1}) and c_e (mmol l^{-1}) are equilibrium concentrations of adsorbate on adsorbent surface and adsorbate concentration in a solution, respectively. The constant b is related to the equilibrium constant, which represents the affinity between adsorbate and

adsorbent and a_m (mol kg^{-1}) is the maximum amount adsorbed on the surface.

FREUNDLICH ISOTHERM

Freundlich isotherm is strictly an empirical model. The adsorbent concentration is a power function of the adsorbate concentration as follows:

$$a = Kc_e^{1/p} \quad (3)$$

Unlike Langmuir model, it does not manifest saturation of adsorbent surface. The sorbed amount increases indefinitely with the concentration in the solution. It was found that Freundlich isotherm holds for the heterogenous surface when adsorption energy is reciprocal to $\log \Theta$, where Θ is a/a_m (a degree of surface coverage).

X-RAY POWDER DIFFRACTION

The X-ray powder diffraction (XRD) study was performed using a powder diffractometer (INEL, France) equipped with a curved position-sensitive detector PSD 120 MB/11 (reflection mode, Gemonochromatized, $\text{CuK}\alpha_1$ radiation). Diffraction patterns were taken in ambient atmosphere under constant conditions (2000 s, 35 kV, 20 mA).

RESULTS AND DISCUSSION

MONTMORILLONITE MODIFICATION WITH QASS

In general, during the hydration of phyllosilicates their layered structures expand and/or exfoliate. QASs can be adsorbed on the outer and/or exfoliated silicate sheets of montmorillonites. By the adsorption of QASs, the exfoliated sheets can be spontaneously rearranged in the layered structure again (Jesenák, 2007).

Original montmorillonite was saturated with CTMA and TMA as described above. For characterisation of prepared materials the XRD analysis was used. Table I demonstrates the calculated montmorillonite basal spacings d_{001} , which well agree with the literature data: For instance, $d_{001}=1.431$ nm for TMA-MMT (Janeba et al., 1998) and $d_{001}=1.80$ nm for CTMA-MMT (Pospíšil et al., 2001). Increase of the d_{001} values is caused by the intercalation of QASs into the MMT interlayer space. According to these values, CTMA was intercalated forming bilayers (Lagaly, 1986) or disordered monolayers, as found by molecular modelling (Pospíšil et al., 2001), and TMA was arranged in monolayers (Lagaly, 1986; Janeba et al., 1998).

ADSORPTION OF PHENOL

The adsorption of phenol on MMT and QAS-MMTs can be recognised in Figure 1. The curves can be classified as the adsorption isotherms of type III (IUPAC Recommendation, 1994), which generally indicate that adsorbate-adsorbate interactions are

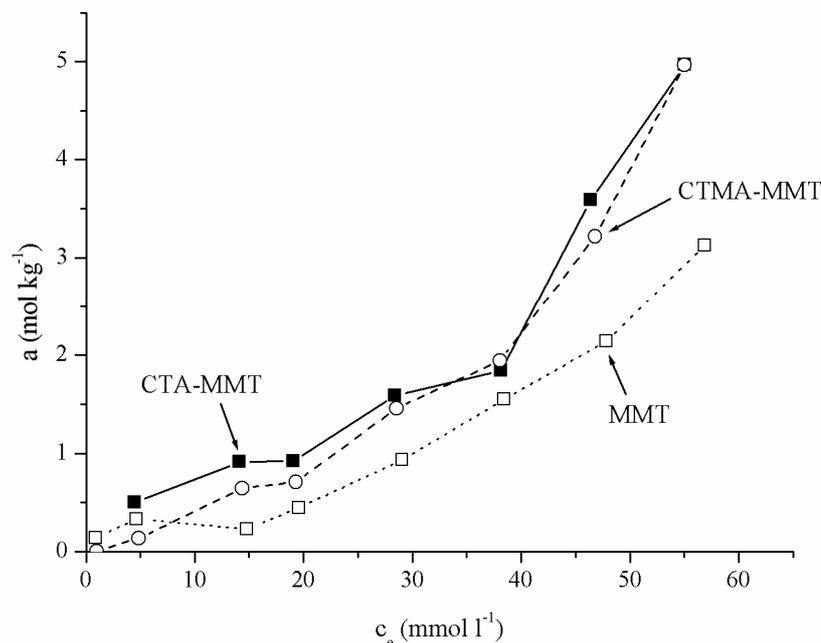


Fig. 1 Adsorption of phenol on original and modified montmorillonite.

Table 1 Observed basal spacings d_{001} of original and intercalated montmorillonites.

	$d_{001}(\text{nm})$	$d_{001}(\text{nm}) / a(\text{phenol})$	$d_{001}(\text{nm}) / a(\text{aniline})$
MMT	1.26	1.43 / (1.55 mmol g ⁻¹)	1.48 / 11.7 (mmol g ⁻¹)
CTMA-MMT	1.80	1.82 / (1.95 mmol g ⁻¹)	1.84 / 1.67 (mmol g ⁻¹)
TMA-MMT	1.42	1.46 / (1.84 mmol g ⁻¹)	1.49 / 2.03 (mmol g ⁻¹)

Note: $a(\text{phenol})$ and $a(\text{aniline})$ stand for the intercalated amounts of phenol and aniline, respectively.

stronger than adsorbate-adsorbent ones, and multilayers are created on separated islands. At pHs of the used adsorption solutions, phenol (a weak acid, $pK_a \approx 10$) exists as a neutral molecule dissolved in water. The value $d_{001} = 1.43 \text{ nm}$ (Table I) of MMT intercalated with phenol is in consistency with the perpendicular orientation of the benzene ring to the silicate layers.

When the MMT surface was modified with QASs, the water molecules were removed from the silicate layers and the hydroxyl and/or oxygen adsorption sites were covered by the alkyl chains. Hydrophobic interactions are generally considered to be weaker than polar ones as well as the hydrogen bonds formation, which can be expected to take part between the silicate sheets and the phenol hydroxyl groups due to the perpendicular orientation of phenol as mentioned above. Therefore, the lower phenol uptake on MMT can be explained by hindrance of the

water molecules strongly adhered to the silicate surface. The adsorption of the water and phenol molecules is competitive in this case (Gorb et al., 2000). The hydrophobised surface caused the higher phenol adsorption on modified MMT than on original MMT. The enhanced uptake of phenol on organo-montmorillonite has been also described in other studies (e.g., Mortland et al., 1986; Barhoumi et al., 2003; Jiang et al., 2002; Wu et al., 2001, Rawajfih et al., 2006). The adsorption abilities of CTMA-MMT and TMA-MMT are similar as demonstrated in Figure 1.

By the adsorption/intercalation of phenol only a little bit increase of the QAS-MMTs d_{001} values was observed. It can be explained so that TMA and CTMA may function as “pillars”, which keep the MMT layers apart and the modified interlayer enlarged only slightly in order to adopt itself to the size of guest phenol. The similar effect was observed when

smectites modified with CTMA and TMA were intercalated with naphthalene (Lee et al., 2004). Another feature of these organic „pillars” is stabilisation of the layered montmorillonite structure because its exfoliation, which was expected at so high phenol concentrations corresponding to the multilayer formation (Figure. 1), was not observed at all.

As already mentioned, the adsorption isotherms of phenol were of type III. It means that the phenol-phenol interactions were stronger than the phenol-silicate surface ones of the original and hydrophobised montmorillonite. Thus the phenol molecules created the separated islands, on which the subsequent layers were attached. Because MMT sustained the stable tabular structure even at the high concentrations of phenol, the multilayers should be formed on the external MMT surface. The multilayer formation of phenol and chlorophenols on surfactant-modified bentonite has been also found by Rawajfih et al. (2006).

ADSORPTION OF ANILINE

The adsorption of aniline is demonstrated in Figure 2. The multilayer adsorption classified as type II (IUPAC Recommendation, 1994) is exhibited by these data points. On the first aniline monolayers distinguished by the curves plateaus the subsequent layers were added at the higher concentrations. The monolayer adsorption was well described by Langmuir isotherms: $a_m = 1.86$ (mol kg^{-1}), $b = 0.020$ (l mmol^{-1}) for CTMA and $a_m = 0.97$ (mol kg^{-1}), $b = 0.358$ (l mmol^{-1}) for TMA (Kostelníková, 2007). Figure 2b provides a detail view, which exhibits that the aniline uptake on TMA-MMT is higher than that on CTMA-MMT. It is also obvious that aniline is more widely adsorbed on MMT than on QAS-MMTs.

At nearly neutral pH of the adsorption solutions used in this work (see above), the adsorption mechanisms of aniline cannot be explained by the ion-exchange reactions of Ar-NH_3^+ proposed by Čapková et al. (1999) because it is a weak acid ($\text{pK}_a \approx 4.6$) and exists in aqueous solutions as neutral molecule Ar-NH_2 at these conditions. Another way of the aniline adsorption onto montmorillonites has been proposed by, e.g., Yariv et al. (1969). According to these authors aniline is bound to the hydroxyl groups and/or oxygen atoms of the silicate sheets through the water molecules. The strong hydrogen bridge formation between aniline and the water molecules has been also confirmed by infrared spectra (Muller et al., 2006).

In this manner, the first aniline layer on the MMT silicate surface was probably created. The perpendicular orientation of intercalated aniline can be recognised from the d_{001} values as well as in the case of intercalated phenol. By mutual comparison of Figs. 1 and 2 it is evident that aniline is adsorbed in higher amounts than phenol. Therefore, we can conclude that the water molecules enable the adsorption of aniline but hinder to the adsorption of phenol.

When MMT was modified with QASs the water assisted sorption mechanism was replaced by the weaker hydrophobic interactions between the QAS alkyl chains and the aniline molecules. Thereby the adsorption ability of QAS-MMT was reduced. Small increase of the QAS-MMTs basal spacings (Table I) indicates the same effect already mentioned at the phenol intercalations: CTMA and TMA are able to act as the organic pillars stabilising the MMT tabular structure. We can suppose that the first aniline layer was created by the intercalation and adsorption on the external silicate sheets. The subsequent layers should be formed on the external surface only.

From Figures 1 and 2 it also follows that aniline was adsorbed in smaller amounts than phenol. In order to explain this fact the 1-octanol-water distribution coefficients (K_{OW}) can be used. There are $\log K_{OW} = 1.46$ (ATSDR, 1998) and $\log K_{OW} = 0.90$ (US EPA, 1985) for phenol and aniline, respectively. It means that phenol is more hydrophobic than aniline and therefore is largely adsorbed to the hydrophobised silicate surface of MMT in agreement with our observations.

CONCLUSIONS

The laboratory batch experiments revealed that phenol and aniline were efficiently adsorbed by modified and original montmorillonite according to the adsorption isotherms of type III and II, respectively. Aniline was adsorbed largely than phenol on original MMT. The water molecules probably enable the adsorption of aniline but hinder to the adsorption of phenol. The situation was quite opposite if the MMT surface was hydrophobised with QAS: Phenol was adsorbed in higher amounts than aniline because of its higher hydrophobicity.

The XRD patterns indicated that both aromatic compounds intercalated in the interlayer of modified and non-modified montmorillonite were oriented perpendicularly to the silicate sheets. From that it follows QASs act as the organic pillars between the MMT layers. In this way the tabular MMT structure was stabilised against its exfoliation at the high concentrations of phenol and aniline.

The obtained results indicate that phyllosilicates are capable for retention of phenol and aniline and could be used, e.g., for cleaning or decontamination of polluted water. Our next investigations will be focused on molecular modelling of the phenol and aniline interactions with the original and organically modified MMT silicate sheets.

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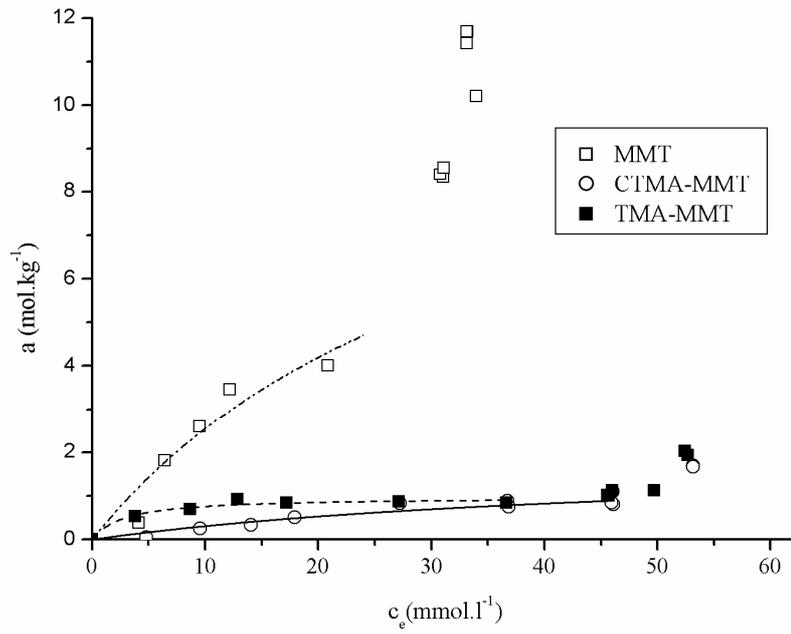


Fig. 2a Adsorption of aniline on original and modified montmorillonite. A whole graph.

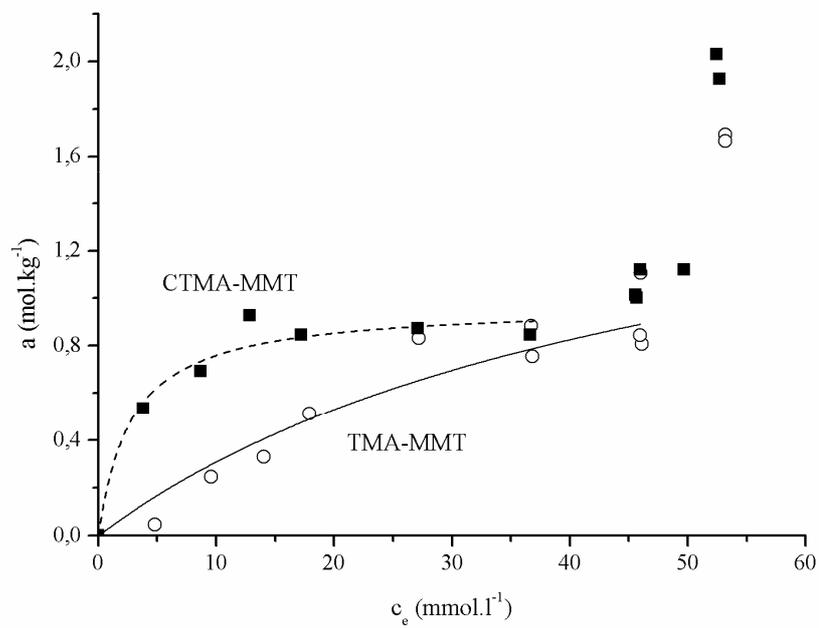


Fig. 2b Adsorption of aniline on original and modified montmorillonite. A detail view.

REFERENCES

- Agency for Toxic substances and disease registry (ATSDR): 1998, Toxicological Profile for Phenol (Update). Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA.
- Barhouni, M., Beurroies, I., Denoyel, R., Said, H. and Hanna, K.: 2003, Coadsorption of phenol and nonionic surfactants onto clays. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 223 (1-3), 63-72.
- Čapková, P., Burda, J.V., Weiss, Z. and Schenk, H.: 1999, Modelling of aniline - vermiculite and tetramethylammonium - vermiculite; Test of force yields. *J. Mol. Model.* 5 (2), 8-16.
- Gorb, L., Gu, J., Leszczynska, D. and Leszczynski, J.: 2000, The interaction of nitrobenzene with the hydrate basal surface of montmorillonite: an ab initio study. *Phys. Chem. Chem. Phys.* 2 (21), 5007-5012.
- IUPAC Recommendation, 1994: Recommendations for the characterization of porous solids. *Pure Appl. Chem.* 66 (8), 1739-1758.
- Janeba, D., Čapková, P. and Weiss, Z.: 1998, Molecular mechanics studies of montmorillonite intercalated with tetramethylammonium and trimethylphenylammonium. *J. Mol. Model.* 4 (6), 176-182.
- Jaynes, W.F. and Boyd, S.A.: 1991, Hydrophobicity of siloxane surfaces in smectites as revealed by aromatic hydrocarbon adsorption from water. *Clay. Clay Min.* 39(4), 428-436.
- Jiang, J.Q., Cooper, C. and Ouki, S.: 2002, Comparison of modified montmorillonite adsorbents. Part I: preparation, characterization and phenol adsorption. *Chemosphere* 47 (7), 711-716.
- Jesenák, K.: 2007, Polymeric clay nanocomposites. *Chem. listy* 101 (8), 657-664, (in Slovak).
- Kostelníková, H.: 2007, Using intercalated phyllosilicates as sorbents. Diploma thesis, VŠB-Technical University of Ostrava, Ostrava, 67 p.
- Kurková, M., Praus, P. and Klika, Z.: 2000, Using capillary isotachophoresis for the study of intercalation of quaternary salts into montmorillonite. *Chem. Listy* 94 (4), 241-244.
- Lagaly, G.: 1986, Interaction of alkylamines with different type of layered compounds. *Solid State Ionics* 22 (1), 43-51.
- Lee, S.Y., Kim, S.J., Chung, S.Y. and Jeong, C.H.: 2004, Sorption of hydrophobic organic compounds onto organoclays. *Chemosphere* 55 (5), 781-785.
- Madejová, J., Arvaiová, B., Komadel, P.: 1999, FTIR spectroscopic characterization of thermally treated Cu²⁺, Cd²⁺, and Li⁺ montmorillonites. *Spectrochim. Acta Part A*, 55 (12), 2467-2476.
- Mortland, M.M., Shaobai, S. and Boyd, S.A.: 1986: Clay-organic complexes as adsorbents phenol and chlorophenols. *Clay. Clay Miner.* 34 (5), 581-585.
- Muller, F., Bény, J.M. and Gautier, M.: 2006, Intercalation of aniline in wyoming monmorillonite exchanged with different cations. In *Abstract Book of 3rd Mid-European Clay Conference*, Opatija, 83.
- Pospíšil, M., Čapková, P., Měřínská, D., Maláč, Z. and Šimoník, J.: 2001, Structure analysis of monmorillonite intercalated with cetylpyridinium and cetyltrimethylammonium: Molecular Simulations and XRD Analysis. *J. Colloid Inter. Sci.* 236 (1), 127-131.
- Praus, P., Turicová, M., Študentová, S. and Ritz, M.: 2006, Study of the cetyltrimethylammonium and cetylpyridinium adsorption on montmorillonite. *J. Colloid Inter. Sci.* 304 (1), 29-36.
- Praus, P. and Turicová, M.: 2007, A physico-chemical study of the cationic surfactant adsorption on montmorillonite. *J. Braz. Chem. Soc.* 18 (2), 378-383.
- Rawajfih, Z. and Nsour, N.: 2006, Characteristics of phenol and chlorinated phenols sorption onto surfactant-modified bentonite. *J. Colloid Inter. Sci.* 298 (1), 39-49.
- Yariv, S., Heller, L. and Kaufherr, N.: 1969, Effect of acidity in montmorillonite interlayers on the sorption of aniline derivatives. *Clay. Clay Miner.* 17 (3), 301-308.
- U.S. Environmental Protection Agency: Health and environmental effects profile for aniline: 1985, Environmental Criteria and Assessment Office, Office of Health and Environmental Assessment, Office of Research and Development, Cincinnati, OH.
- Wu, P.X., Liao, Z.W., Zhang, H.F. and Guo, J.G.: 2001, Adsorption of phenol on inorganic-organic pillared montmorillonite in polluted water. *Environ. Inter.* 26 (5-6), 401-407.