



TREATMENT OF SOME PERSISTENT ORGANIC POLLUTANTS WITH CHEMICALLY MODIFIED SMECTITES ♦

Ingrid Buciscanu^{1*}, Stelian-Sergiu Maier¹, Viorica Deselnicu²

¹ „Gh. Asachi” Technical University, 700050, Blvd. D. Mangeron 67, Iași, Romania, Tel. 0040232279850, *E-mail: iiacomi@ch.tuiasi.ro

²Leather and Footwear Research Institute, 93 Ion Minulescu Street, 74259, Bucharest, Romania

Abstract: Some nanoparticulated sorbents, known in the specialty literature and practical use as *organoclays* were prepared, based on native sodium smectite modified with some quaternary ammonium cations – hexadecyltrimethylammonium (HDTMA), N-cetylpyridinium (NCPy), dimethyldioctadecylammonium (DDA) and alkylbenzyltrimethylammonium (ABDMA) – through a ion exchange reaction. The products were characterized by means of sorption isotherms over a range of 0 ÷ 250% satisfaction degree of the cation exchange capacity (CEC), by desorption tests and by TG analysis. Adsorptive properties were assessed by means of sorption isotherms towards several nonionic surfactants (NISs): two nonylphenol ethoxylates: NPEO₈ and NPEO₁₂ and one fatty alcohol ethoxylate with 10 ethoxy groups, EUSAPON OD. The HDTMA and NCPy-organoclays were effective adsorbents for both nonylphenol and fatty alcohol ethoxylates, with high sorption limits. The DDA-organoclay showed significantly lower sorption limits. The ABDMA proved to be inactive towards the nonionic surfactants.

Keywords: *organoclays, adsorbents, nonionic surfactants, wastewater*

♦ Paper presented at **COFrRoCA 2006: Quatrième Colloque Franco-Roumain de Chimie Appliquée**, 28 June – 2 July, Clermont-Ferrand, France

INTRODUCTION

Organic pollution has an increasing environmental impact, due to the diversification of synthetic organics, increasing concentrations and spreading in surface and ground waters. Of great concern are the synthetic organic micropollutants, which, even in small concentrations are hazardous to health due to their persistency and bioaccumulation. The main categories of toxic organic micropollutants are: polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), dioxine, pesticides, herbicides, non-ionic surfactants (NISs).

Removal of hydrophobic micropollutants by retention on different sorbents, of which the granular activated carbon (GAC) is the most common, proved to be a feasible solution for organic pollution treatment. During the last decades, extensive research has been dedicated to the interaction between organoclays and hydrophobic synthetic organics [1, 2] and actual treating technologies are in use [3, 4]. Organoclays are inorganic/organic hybrid materials, resulting from a host-guest interaction between smectite phyllosilicates and quaternary ammonium cations carrying flexible hydrocarbonated chains with 12 carbon atoms at least. Due to the hydrocarbonated coverage, the mineral surface turns from hydrophilic to lipophilic and the resulting organoclay act as selective sorbent to both nonionic and ionisable hydrophobic organics. Nonylphenol polyethoxylates (NPEOs), a class of surfactants widely used as detergents, emulsifiers, wetting and dispersing agents in numerous industrial and domestic activities, became an environmental issue when it was found that they caused estrogenic responses in a variety of aquatic organisms [5]; the impact on human health is also to be considered. At present, nonylphenol is listed as dangerous priority substance, based on the Water Framework Directive of the European Union. Even if the manufacture of NPEOs is beginning to be banned in several UE members and NPEOs are being replaced by fatty alcohol ethoxylates with less environmental risk, this class of surfactants is still in use and raises environmental concern.

NPEOs are commonly eliminated by biodegradation and chemical oxidation but in most cases these treatments achieve only a partial breakdown of the molecule, which results in bioaccumulative refractory metabolites which are proved endocrine disruptors for wildlife and humans.

Retention on sorbents appears to be a viable technique for NISs removal as well. Tange and Verstraete [6] reported that the sorption capacity of GAC for nonylphenol (NP) was at least 100 mg/g GAC; Rozzi *et al.* [7] tested the affinity of an adsorbent resin towards nonionic surfactants and found that the maximum sorption capacity of the polystyrene-divinylbenzene copolymer was 13.6 g NPEO as active substance/liter of resin.

Few work have been carried out on the adsorptive affinity of organoclays for pollutants others than aromatic derivatives. Sarmiento and Bello [8] found that an HDTMA-modified organoclay exhibits adsorptive behaviour towards a non-branched anionic surfactant.

In this paper, we intend to study the sorptive properties of some organoclays towards several nonylphenol and fatty alcohol ethoxylates, in order to evaluate the suitability of this kind of sorbents for “polishing” or “prepolishing” treatments of waters containing low concentrations of such pollutants.

EXPERIMENTAL

Materials

The substrate for the obtaining of organoclays was a native Na-bentonite from Valea Chioarului deposits, 91.6 % purity, with a CEC of 65 meq/g and Methylene Blue Index (MBI) of 352.5 mg/g. The quaternary ammonium compounds (QACs) HDTMA-Br, DDA-Br, NCPy-Cl and ABDMA-Cl were of synthesis grade and provided by Merck-Schuchardt. The other reagents were of analytical grade. The nonionic surfactants were commercial products with known active substance concentration, commonly used in leather and fur processing: two nonylphenol ethoxylates: NPEO₈ and NPEO₁₂ of local production and EUSAPON OD, one fatty alcohol ethoxylate with 10 ethoxy groups, produced by BASF. All the solutions and suspensions were obtained with deionised water.

Preparation of organoclay products

The organoclays were synthesized by exchanging large organic cations released by cationic surfactants for the inorganic interlayer cations on the bentonite. Bentonite samples of 2 g were swelled for 24 h with small amounts of water, some more water was added and the resulting suspensions were vigorously mixed for 1 hr at 40 °C for advanced hydration – dispersion and left to cool down to room temperature. Solutions of HDTMA, NCPy and ABDMA salts were prepared at 2.5×10^{-2} M concentration and added to the bentonite dispersions, so that the clay's CEC was satisfied in extents ranging from 10% to 250%. The reaction mass was completed with water so that the clay concentration reached 1% w/w and was vigorously stirred for 4 hours at room temperature and left overnight. Due to DDA-Br extremely low solubility, the DDA-organoclays were obtained through the following procedure: the corresponding amounts of DDA-Br were weighed, dispersed in a suited quantity of water, heated at 60 °C for solubilization and added to the bentonite suspensions. Thus, solubilization in organic solvents was avoided, but products with more than 100% completion of CEC could not be experimentally obtained. The resulting suspensions were vacuum filtered and washed till the reaction with AgNO₃ was negative. The filtrates were collected and analyzed for residual cationic surfactant concentration. The organoclays precipitates were dried at 105 °C and milled. The resulting products were named after the percent satisfaction of CEC: a 100 HDTMA-Be product means that the HDTMA surfactant covered 100% of the bentonite CEC.

Short-term desorption tests at room temperature were conducted on suspensions of 1% organoclays in the presence of 0.1M NaCl. Suspensions were prepared in capped flasks that were intermittently stirred for 1 hour, seven days in a row and the filtrates were analysed for the desorbed quaternary amines concentrations.

Thermogravimetric analysis

Several selected samples were submitted to TG analysis in a MOM device at a final temperature of 1000 °C in air, in order to determine the organic content and thus to confirm the hydrocarbonated matter retention onto the mineral support.

Procedure for surfactants sorption on organoclays

Stock solutions of 5 g/L, 2 g/L and 1 g/L active substance were prepared from all the surfactants, which were diluted to actual concentrations used in the sorption tests. Suitable amounts of organoclays were placed in 100 mL capped flasks so that 1 g/L and 2 g/L suspensions were finally obtained. Volumes of 100 mL nonionic surfactant solutions of concentrations ranging from 10 to 2000 mg/L were added; the resulting suspensions were periodically stirred for 1 hr, two days in a row. The third day, the mixtures were separated through filtration and the filtrates were analyzed to determine the residual concentrations of nonionic surfactants. In order to make an estimate of the sorptive behavior of organoclays, two sorption tests with 5 g/L 100HDTMA-Be and 65ABDMA-Be respectively, were performed on NPEO₈ solutions with concentrations ranging from 500 to 5000 mg/L. The subsequent tests were performed with 100HDTMA-Be and 100NCPy-Be products, in order to avoid possible contamination of treated samples with desorbed QACs. As it concerns the DDA-organoclay, we choose for the adsorption tests a product with 75 % satisfaction of CEC, namely the 75DDA-Be, in order to impart some porosity to the hybrid structure. A 100DDA-Be product would present complete filling of the interlayers with the voluminous hydrocarbonated tails and the resulting compact structure would exhibit lower adsorptive behaviour. This is in accordance with the observation that a DDA-organoclay partially exchanged for alkaline cations improve its adsorptive properties [9]. Former experiments showed that a dosage of 2 g/L is the optimal one. Further sorption tests were performed with this adsorbent dosage only.

Analytical methods

Quaternary amines were quantitatively determined through a two-phase titration developed by Furlong and Elliker [10] and described in [11]. Nonionic surfactants were determined through two methods: photocolometric CTAS – method for high concentrations and an adapted two-phase titration with sodium tetraphenylborate [12, 13] for low concentrations.

RESULTS AND DISCUSSION

Preparation of organoclay products

The percentages of QACs offer retained on the mineral substrate are given in Table 1. Both HDTMA and NCPy were sorbed beyond the CEC, being able to accumulate on the solid surface in quantities that exceed two times as much as the CEC. The DDA was

also entirely retained on the mineral substrate, up to 100% of CEC satisfaction and even exhibited the greatest affinity for the smectite clay. The ABDMA amine could not satisfy the CEC even at offers not exceeding 100% of the CEC. The desorption tests showed that at room temperature HDTMA, DDA and NCPy products are stable in electrolyte solutions, even if the amount of QAC exceeded 100% of the CEC. A 4 % and 6.8 % desorption of the adsorbed amine was recorded for 200HDTMA-Be and 200NCPy-Be products. The ABDMA-Be products showed extensive desorption of the organic cation, down to 65% of the CEC.

The interaction between the clay mineral and the organic cations was assessed in terms of sorption isotherms (see figure 1), the shape of which is consistent with the structures of the organic cations.

The HDTMA and NCPy cations have an asymmetrical head-tail structure that renders the hydrocarbonated chain flexible and allows the accumulation and steady accommodation of the guest cations in the interlamellar galleries, through cation exchange reactions and mineral-hydrocarbonated and inter-hydrocarbonated hydrophobic interactions. Experimental sorption isotherms fit a linear isotherm with no defined sorption limit, which confirms the multilayer covering of the mineral substrate in organoclays [14]. The DDA cation, with two tails, is considered to be the standard cation for flexible organic cations and expands the interlayers to a maximum extent. A linear isotherm is also to be expected, beyond the 100% of CEC satisfaction.

Table 1. Sorption of quaternary amines at different offer ratios

No.	QAC offer (% of CEC)	QAC adsorbed at equilibrium (% of CEC)			
		HDTMA	NCPy	DDA	ABDMA
1.	20	20	20	20	20
2.	40	40	40	40	40
3.	60	60	60	60	60
4.	65	-	-	-	65
5.	70	-	-	-	69.78
6.	80	80	80	80	78.94
7.	100	99.51	99.06	100	95.27
8.	150	148.53	147.9	-	97.02
9.	200	195.84	195.42	-	97.48
10.	250	244.25	224.67	-	97.56

The ABDMA cation exhibits a typical Langmuir isotherm, with well defined sorption limit, which indicates that the interaction is limited to cation exchange reactions at active sites. Even if a long C₁₂ - C₁₄ tail exists, the relative equilibration between the substituent volumes makes it rigid and inter-hydrocarbonated interactions impossible. Steric hindrance between voluminous cations make 35% of the active sites inaccessible, which is proved by massive and constant desorption of the ABDMA cation down to 65% of the CEC.

Thermogravimetical analysis

The weight losses recorded for the selected organoclays (Table 2) confirm the organic content calculated from the reaction stoichiometry. The first inflexion point is consistent with the melting point of the corresponding QAC.

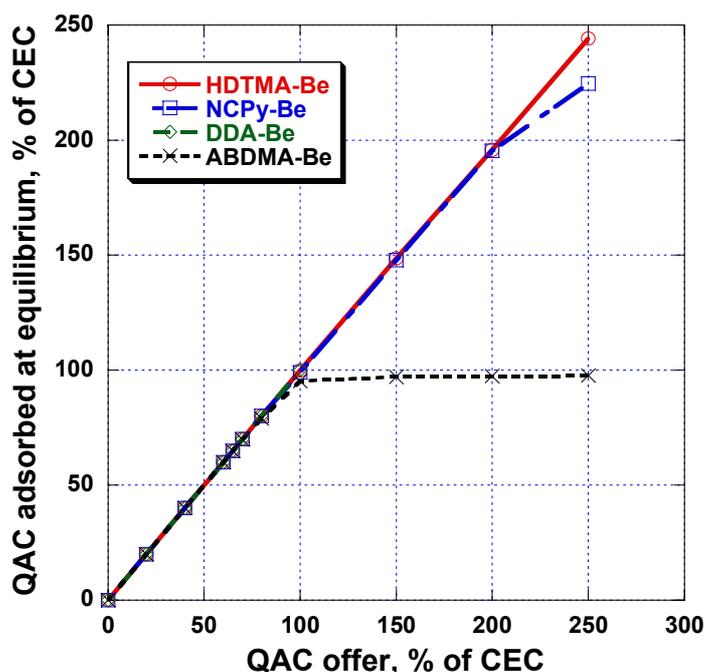


Figure 1. Sorption isotherms of quaternary amines on smectite

Table 2. Weight losses at TG analysis

No	Organoclay product	Organic matter loss [% w/w]
1.	100HDTMA-Be	20,87
2.	200HDTMA-Be	33,54
3.	100NCPy-Be	22,53
4.	100DDA-Be	34,06
5.	75DDA-Be	25,78

Sorption of NPEOs on organoclays

Preliminary tests indicated affinity between NPEO₈ and the HDTMA-Be product, as can be seen from the sorption isotherm (Figure 2) while the ABDMA-Be organoclay was inefficient as sorbent for the NIS.

Direct observation of the organoclay-NIS solution systems showed that:

(1) the dispersions of the NCPy-Be and DDA-Be were much more difficult to obtain than the dispersion of HDTMA-product, which suggests that the organoclay modified with the NCPy and DDA surfactant are more hydrophobic than the HDTMA-Be

organoclay. This may come from the different conformations of the organic cations; the NCPy cation has greater ability to accommodate parallel to the lamellar surface and form a compact hydrocarbonate layer on the mineral particle, while the HDTMA cations have a perpendicular orientation; as it concerns the DDA, the great concentration of hydrocarbonated tails imparts increased hydrophobicity to the hybrid structure;

(2) there is a critical concentration of the NIS below which the sorbent-sorbate system is easily separable from the aqueous phase through direct settling; beyond this concentration, stable colloidal dispersion arise, that need centrifugation for complete separation. At low concentrations, the NIS molecules are individually bonded through the hydrophobic head on the organoclay surface; increasing concentration lead to hemi-micelles formation, which does not affect the organoclay structural organization. When a critical concentration is exceeded, micellization takes place, the nonionic surfactant act as a colloid protector and brings the organoclay particles into a stable colloidal suspension. The experimental sorption isotherms, given in Figures 2, 3, 4, 5, 6 and 7, fit a Langmuir isotherm, which indicates strong solute uptake, with well defined sorption limit. The inflexion point on the isotherms coincides with the critical point beyond which the solid-liquid separation becomes difficult. The maximum uptake increase with increasing the organoclay concentration from 1 g/L to 2 g/L does not exceed 15%.

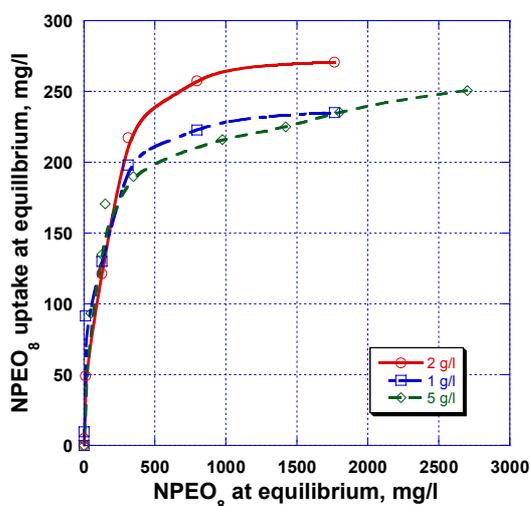


Figure 2. Sorption isotherms of NPEO₈ on HDTMA-Be.

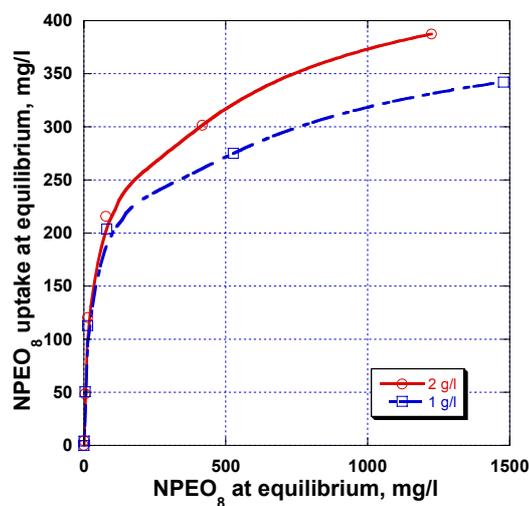


Figure 3. Sorption isotherms of NPEO₈ on NCPy-Be.

The relationship between the sorption limits of the two nonylphenol NISs and the exchange organic cation in the organoclay is consistent with the relationship between the sorbent and sorbate hydrophobicities. The NCPy-Be product has a greater affinity for NPEO₈ which is more hydrophobic than NPEO₁₂; consequently, the NPEO₁₂ will be easily retained on HDTMA-Be product.

The sorption limits are high – 387.5 mg on NPEO₈/g NCPy-organoclay and 359 mg NPEO₁₂/g on HDTMA-organoclay – but working concentrations must be limited to

values not exceeding the critical values, because beyond these, the effectiveness is low and phase separation is actually impossible.

The EUSAPON OD was effectively sorbed on the HDTMA-organoclay, with a sorption limit of 385 mg/g, which is consistent with the relationship between the sorbate and sorbent hydrophobicities (see Figure 6).

The DDA- Be exhibited significantly lower adsorption limits – 220 mg/g for NPEO8 and 80 mg/g for EUSAPON OD, probably due to the lack of porosity within the mass of sorbent. It is also to be noticed that even in the low concentrations domain, the adsorbed surfactant amounts are lower than those retained by the HDTMA-Be and NCPy-Be.

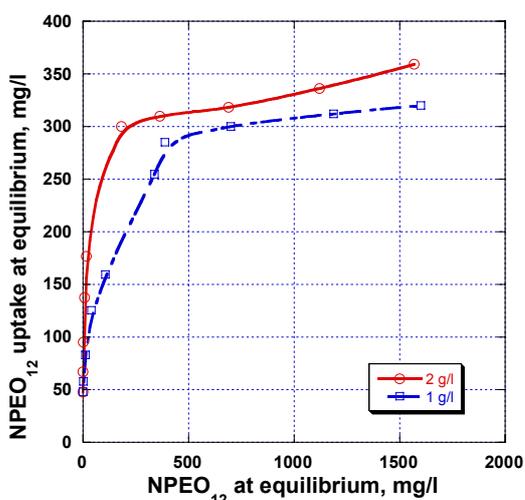


Figure 4. Sorption isotherms of NPEO₁₂ on HDTMA-Be

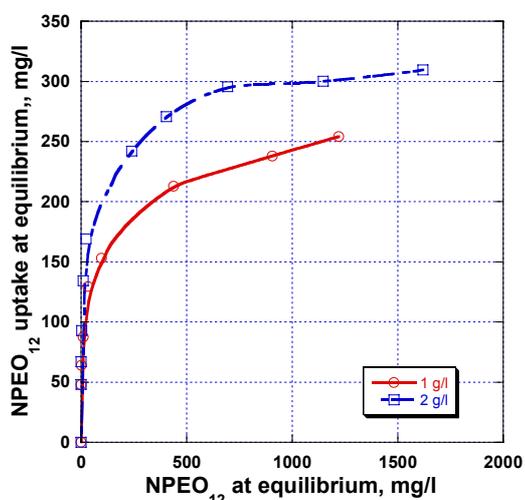


Figure 5. Sorption isotherms of NPEO₁₂ on NCPy-Be

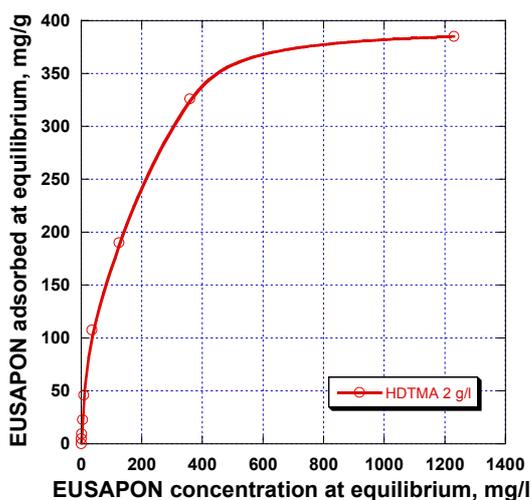


Figure 6. Sorption isotherm of EUSAPON on HDTMA-Be

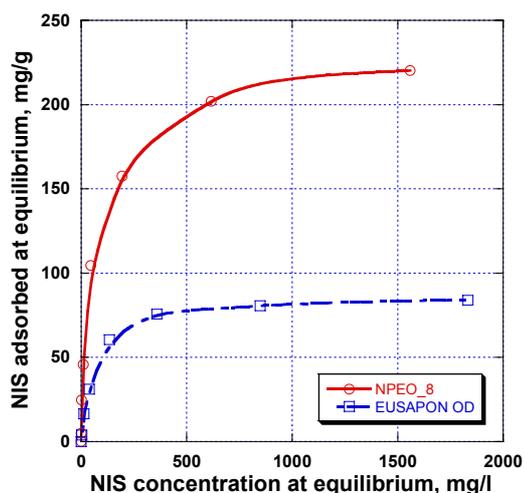


Figure 7. Sorption isotherms of NISs on DDA-Be

CONCLUSIONS

The Romanian native Na-bentonite is amenable to chemical transformations through host-guest reactions with QAC organic cations, resulting in hybrid products from the organoclays class.

The effectiveness of organoclays as sorbents for organic pollutants depend primarily on the structure of the QAC – the presence of a flexible tallow at least, able to cover as much as possible the inorganic surfaces, is indispensable.

Organophilic clays exhibit good adsorptive behavior towards ethoxylated surfactants. Langmuir-type isotherms prove strong uptakes in the low-concentrations range; the greater the sorbate hydrophobicity, the greater the organoclay affinity.

The HDTMA-organoclay proved once again to be the most effective organoclay sorbent, probably due to the best balance between the hydrophobic coverage and the required porosity for the sorbate uptake.

Practical applications can be feasible when waters with low concentrations of NIS are to be treated. Polishing treatments with organoclays can be an alternative to other advanced treatment techniques, provided a suitable contact technique is put in practice and the interference with other pollutants possibly present in the water is not significant.

REFERENCES

1. Koh, S.-M., Dixon, J.B.: Preparation and application of organo-minerals, as sorbents of phenol, benzene and toluene, *Applied Clay Science*, **2001**, 18, pp. 111-122.
2. Zhu, L., Ren, X., Yu, S.: Use of Cetyltrimethylammonium Bromide-Bentonite To Remove Organic Contaminants of Varying Polar Character from Water, *Environ. Sci. Technol*, **1998**, 32, pp. 3374-3378.
3. Alther, G.R.: Maximize water cleanup performance, *Environmental Protection*, **2000**, February, 37-40, www.eponline.com
4. Alther, G.R.: Organoclays Remove Oil, Grease, Solvents and Surfactants from Water, *CleanTech '99 Proceedings*, Rosemont Convention Center, **1999**, pp. 72-79.
5. Servos, M.R.: Review of the aquatic toxicity, estrogenic responses and bioaccumulation of alkylphenols and alkylphenol polyethoxylates, *Water Quality Research Journal of Canada*, **1999**, 34, pp. 123-177.
6. Tange, T., Verstraete, W.: Adsorption of Nonylphenol onto Granular Activated Carbon, *Water, Air & Soil Pollution*, **2001**, 131 (1-4), pp. 61-72.
7. Rozzi, A. *et.al.*: Removal by an Adsorbent Resin of Non-ionic Surfactants Used in Tannery Processes, *JSLTC*, **2000**, 84, pp. 266-270.
8. Sarmiento, D.Ch.R., Bello, J.A.P.: Adsorption of sodium dodecylbenzene sulfonate on organophilic bentonites, *Applied Clay Science*, **2001**, 18, pp. 173-181.
9. Meier, L.P., Nueesch, R., Madsen F.T.: Organic Pillared Clays, *Journal of Colloid and Interface Science*, **2001**, 238, pp. 24-32.
10. Furlong, T.E., Elliker P.R.: *J. Dairy Sci.*, **1953**, 36, pp. 225-234.

11. Zhang, Z.Z., Sparks, D.L., Scrivner, N.C.: Sorption and Desorption of Quaternary Amine Cations on Clays, *Environ. Sci. Technol.*, **1993**, 27 (8), pp. 625-1631.
12. Sakai, T., Teshima, N., Takatori, Y.: Simultaneous Determination of Cationic Surfactants and Nonionic Surfactants by Ion-Association Titration, *Analytical Sciences*, **2003**, 9, pp. 1323-1325.
13. * * * : Titrimetric/potentiometric determination of non-ionic surfactants, *Metrohm Application Bulletin No. 230/1e*, <http://www.metrohm.com/applications.html>
14. Bonczek, J.L., Harris, W.G., Nkedi-Kizza, P.: Monolayer to Bilayer Transitional Arrangements of Hexadecyltrimethylammonium Cations on Na-Montmorillonite, *Clays and Clays Minerals*, **2002**, 50 (1), pp. 11-17.