

SURFACTANT-MODIFIED CLAY SORBENTS FOR THE REMOVAL OF *p*-NITROPHENOL

RUTA OZOLA^{1*}, ANDREJS KRAUKLIS², JURIS BURLAKOV^{1,3}, MARIS KĻAVINS¹, ZANE VINCEVICA-GAILE¹, AND WILLIAM HOGLAND³

¹Department of Environmental Science, University of Latvia, Raina Blvd 19, Riga LV-1586, Latvia

²Department of Mechanical and Industrial Engineering, Norwegian University of Science and Technology, 7491 Trondheim, Norway

³Department of Biology and Environmental Science, Linnaeus University, 39182 Kalmar, Sweden

Abstract—Organic pollutants are widespread and a known problem for the environment. *p*-nitrophenol (PNP) is one such pollutant found in effluents from various industries involved with pesticides, pharmaceuticals, petrochemicals, plastic, paper, and other materials. The objective of this research was to prepare and test organically modified clays using four different surfactants and to evaluate the removal efficiency of PNP from aqueous solutions. Organically modified clays have attracted great interest due to their wide applications in industry and environmental protection as sorbents for organic pollutants. Two natural smectite-dominated clay types from outcrops in Latvia and Lithuania as well as industrially manufactured montmorillonite (Mt) clay were modified using different nonionic (4-methylmorpholine N-oxide (NMO) and dimethyldodecylamine N-oxide (DDAO)) and cationic (benzyltrimethyl ammonium chloride (BTMAC) and dodecyltrimethyl ammonium chloride (DTAC)) surfactants. Modified clay materials were characterized by Fourier-transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), and the Brunauer-Emmett-Teller method (BET) for surface area analysis. Sorption of PNP was investigated under various conditions, e.g. surfactant loading, initial PNP concentration, contact time, and pH. The novelty of the present study was to prepare innovative organo-sorbents based on manufactured as well as natural clay samples using cationic surfactants and nonconventional nonionic surfactants as modifiers. The sorption data combined with FTIR and XRD supplementary results suggests that nonionic organo-clay (Mt-DDAO_2) is the most effective sorbent and may serve as a low-toxicity immobilizer of pollutants such as phenols.

Keywords—Cationic and Nonionic Surfactants · Clay Sorbents · *p*-nitrophenol · Sorption · Water Treatment

INTRODUCTION

Clay minerals are aluminosilicates that include 1116 crystalline minerals and comprise ~80% of the sedimentary rocks in the Earth's crust (Seglins, 2010). Known properties such as plasticity, fire resistance, cation exchangeability, and wide distribution make them a resource used widely in industry (Murray, 2007). From the point of view of environmental engineering, the key properties of aluminosilicates are cation exchange capability, structure, texture, and surface area (Brovkina et al. 2012). Over recent decades, interest has increased the use of clay minerals as a potential sorbent material for organic (Ruiz-Hitzky et al. 2010) and inorganic pollutants (Anirudhan & Ramachandran 2015). Most modified clays are used as environmentally friendly or neutral sorbent materials (Brovkina et al. 2012). Clay modification with surfactants increases the ability of clay minerals to exchange metallic ions with other cationic, anionic-cationic, and nonionic molecules (Gamoudi et al. 2015). The generalized formula describing surfactants of interest is:



where R' refers to aliphatic compounds and R'' to aliphatic or aromatic compounds (Yariv & Cross, 2002; Guégan et al. 2015).

* E-mail address of corresponding author: ruta.ozola@lu.lv
DOI: 10.1007/s42860-019-00015-2

Inorganic cations are exchanged with surfactant cations and, thus, a hydrophilic surface of clay becomes hydrophobic; the derived material can then be referred to as organoclay (Guégan et al. 2015; Zhang, Zhang et al. 2015).

Organoclays are created mostly using smectite-group clay minerals that have a large surface area and a large cation exchange capacity – these properties are very important when characterizing sorbents (Seliem et al. 2011; Bertuoli et al. 2014). The choice of surfactant with chemical and textural properties that best fit the purpose is also of great importance (Guégan et al. 2015). Organoclay synthesis can be performed successfully by using surface-active organic (substituted) ammonium ions containing long alkyl chains (Paiva et al. 2008). Synthesis can be performed by various methods, e.g.: (1) cation-exchange reactions; (2) solid-state reactions; and (3) microwave irradiation (Paiva et al. 2008; Gamoudi et al. 2015).

Most chemical pollutants consist of organic compounds of which phenols are among the most widespread aquatic contaminants (Nayak & Singh, 2007) as they are used widely in oil, petroleum, coal, pharmacy, plastic, rubber, paper, dye, herbicide, pesticide, and many other industries (Nayak & Singh, 2007; Yan et al. 2007; Park et al. 2011; Lee & Tiwari, 2012; Luo et al. 2015).

In the aquatic environment a 96 h exposure to a phenolic concentration of >2 mg/L is toxic to fish, but exposure to 10–100 mg/L for the same period is lethal to all hydrobionts (Lee & Tiwari, 2012). Furthermore, human exposure, depending on the concentration, may lead to a variety of health risks, e.g. poisoning, eye and skin irritation, and damage to kidneys and liver (Xue et al. 2013; Zhang et al. 2015). Contamination by

derivatives such as *p*-nitrophenol (PNP) and *p*-chlorophenol (PCP) in drinking water causes bad odors even at very low concentrations (Park et al., 2013).

Various wastewater-treatment methods for phenolic contaminants are available, such as biological and chemical treatment, catalytic oxidation, ion exchange, solvent extraction, membrane filtration, and sorption methods (Luo et al. 2015). Sorption is considered to be more effective when the phenolic concentration is too high for biological treatment (Park et al. 2013; Luo et al. 2015). Nitrophenols are important chemical intermediates that serve as precursors for many pharmaceuticals and pesticides (Zhang et al., 2006). A range of industries, such as the plastics and paper industries, use nitrophenols extensively in their products. Significant amounts of nitrophenols are commonly present in the effluents of these industries and need to be treated before being discharged into the environment (Orshansky & Narkis, 1997; Li et al. 2002).

Various types of sorbents can be used for the removal of phenols (including PNP) from water: humic substances (Yang & Koopal, 1999), composite geomaterials (Houari et al. 2014), Mt modified with surfactants (Xue et al. 2013), and magnetic materials (Han et al. 2013). For instance, Fe-nano-zeolite was characterized as a sorbent, and its potential applications and efficacy at removing *o*-, *m*-, and *p*-nitrophenols from water was studied by Huong et al. (2016). Removal of nitrophenols from aqueous solutions using cationic β -cyclodextrin-modified zeolite as an adsorbent was investigated by Xiaohong et al. (2011) and using magnetic porous silica-graphene oxide hybrid composite by Liu et al. (2016). Zermane et al. (2010) modified hydroxyiron-Mt with cetyltrimethylammonium bromide (CTAB) and showed that the newly developed sorbent can remove both basic dye yellow 28 and PNP, and the presence of yellow 28 enhanced the uptake of PNP. Several authors have studied organically modified clay minerals (dominantly Mt) and their use for the removal of a wide variety of contaminants, including hydrophobic organic contaminants, heavy-metal cations, radioactive nuclides, etc. (Zhu et al. 2016).

In most research, cationic surfactants are used to produce organoclay sorbents, but, as an alternative, nonionic surfactants can be used. The main difference between cationic surfactants and nonionic surfactants is not only charge, but also low toxicity and potential biodegradability (Shen 2001). The present research focused on development of nonionic organoclay using 4-methylmorpholine N-oxide and dimethyldodecylamine N-oxide, comparing them to raw Mt clay, natural clay samples, and cationic organo-clays. The sorption properties of sorbent materials were studied by focusing on an organic pollutant – PNP.

MATERIALS AND METHODS

Materials and Chemicals

The following natural and manufactured clay samples were used in the experiments: (1) natural smectite-dominated clay of

Triassic age from the Saltiski deposit (Saltiski, Lithuania) – further labeled as T clay; (2) clay mixed with organic matter of Jurassic age from the Legemiki deposit (Nikrace, Latvia) – J clay; and (3) montmorillonite K 10 industrially produced clay, purchased from Sigma-Aldrich (Taufkirchen, Germany) – Mt clay.

The T clay contained mostly smectite-group minerals (66%) in the <0.001 mm fraction. The J clay was a mixture of equal amounts of illite-smectite, illite, smectite, chlorite, and kaolinite with admixture of ancient organic matter (3%); the amount of clayey fraction (<0.001 mm) varied between 15% and 20%. The Mt clay consisted mainly of montmorillonite (65%) with specific weight 300–370 kg/m³ and surface area 220–270 m²/g (according to the product's specification). The cation exchange capacities (CEC) of the Mt clay, T clay, and J clay were: 0.50 ± 0.03 mmol/g, 0.33 ± 0.03 mmol/g, and 0.25 ± 0.02 mmol/g, respectively.

The PNP (C₆H₅NO₃) used for sorption experiments was provided by Alfa Aesar (Haverhill, Massachusetts, USA). Two types of surfactants which operated as examples of nonionic and cationic surfactants, respectively: (1) dimethyldodecylamine N-oxide (DDAO, C₁₄H₃₁NO, M = 229.40 g/mol), 4-methylmorpholine N-oxide (NMO, C₅H₁₁NO₂, M = 117.15 g/mol); and (2) benzyltrimethylammonium chloride (BTMAC, C₁₀H₁₆CIN, M = 185.69 g/mol) and dodecyltrimethylammonium chloride (DTAC, C₁₅H₃₄CIN, M = 263.89 g/mol) were purchased from Sigma-Aldrich (Taufkirchen, Germany). All solutions were prepared using high purity deionized water (15 M Ω cm) obtained with a Millipore Elix 3 (Billerica, Massachusetts, USA) purification system.

Method of Clay Modification

Raw clay samples were saturated with sodium ions (Na⁺) by stirring 100 g of clay with 1 L of 0.5 M NaCl solution at 60°C for 24 h. Subsequently, the Na⁺-saturated clay sample was washed three or four times with deionized water until chloride ions were not detected by addition of 0.1 M AgNO₃; then the sample was dried in a Gallenkamp Plus II Oven (London, UK) at 60°C overnight. Such treated clay samples were labeled as Mt_Na, J_Na, and T_Na, respectively.

Modification of the Na⁺-saturated clay samples for the preparation of organoclays was performed as follows: 10 g of Na⁺-saturated clay sample was dispersed in 400 mL of deionized water using a Jenway 1000 hotplate/stirrer (Stone, Staffordshire, UK) for 30 min. A selected amount of each surfactant was dispersed in 100 mL of deionized water and stirred for 30 min. Dissolved surfactant was added slowly to the clay suspension at 60°C. The mixtures were stirred for 24 h at 60°C. The suspension was then washed several times with deionized water until no chloride ions were detected by addition of 0.1 M AgNO₃, filtered, dried at room temperature, and dried at 60°C overnight. Dried organoclays were triturated in an agate mortar and stored in a desiccator.

The BTMAC-modified Mt clay samples obtained were labeled as Mt_BTMAC_0.5, Mt_BTMAC_1, Mt_BTMAC_2, and Mt_BTMAC_3, where the number means the proportion of added surfactant/CEC; and the corresponding weight of the

surfactant was calculated using the following equation:

$$m_s = m_c \cdot \text{CEC} \cdot 10^{-3} \cdot Q_{\text{CEC}} \cdot M \quad (2)$$

where m_s is mass of the surfactant (g), m_c is mass of the clay sample used (g), CEC is cation exchange capacity of the clay samples used (mmol/g), Q_{CEC} is the proportion of surfactant added/CEC, and M is molecular weight of the surfactant (g/mol).

Characterization Methods of OrganoClay Sorbents

The modified clay materials obtained were characterized by X-ray diffraction (XRD), Brunauer-Emmett-Teller surface area analysis (BET method), Fourier-transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). The XRD data describing the mineralogy of sorbents were collected using a Bruker D8 Advance diffractometer (Billerica, Massachusetts, USA) using $\text{CuK}\alpha$ radiation. Surface area measurements were performed using a Micromeritics Gemini 2360 surface area and porosity analyzer (Norcross, Georgia, USA). The FTIR spectra were recorded using a Shimadzu IR-Tracer 100 spectrophotometer (Kyoto, Japan). The SEM images were obtained using a scanning electron microscope FE-SEM Hitachi S4800 (Tokyo, Japan).

Sorption Experiments

Sorption experiments were carried out to investigate the sorption capacity of raw and modified clays for the removal of PNP from aqueous solutions. For the sorption-isotherm studies, 0.3 g of a prepared sorbent material (organo-clays) was placed in a 100 mL glass vessel and supplemented with 20 mL of PNP at a concentration of 5, 10, 15, 20, or 25 mg/L. The mixture was agitated continuously on a multi-functional orbital shaker Biosan PSU-20i (Riga, Latvia) for 24 h at room temperature. After shaking, the mixture was centrifuged at 3000 rpm for 12 min and the supernatants were analyzed using a UV-Vis spectrophotometer (Shimadzu UV 1800, Kyoto, Japan) at 318 nm.

To undertake the sorption kinetics studies, 0.3 g of each of the sorbents (Mt_DDAO_2 and T_DDAO_2) was added to 20 mL of PNP solution (25 mg/L). The mixtures were agitated for 10–60 min with 10 min intervals and for 120–360 min with 60 min intervals. The pH of the PNP solution was adjusted to values ranging from 2 to 12 by adding either 0.1 M HCl or NaOH.

The quantity of the PNP sorbed on the organoclays was calculated using the following equation:

$$q_e = \frac{(C_i - C_e)}{m} \cdot v \quad (3)$$

where q_e is the amount of PNP sorbed on the sorbent (mg/g), C_i and C_e are initial and equilibrium liquid-phase concentrations of PNP (mg/L), respectively, v is the volume of solution (mL), and m is mass of sorbents used (g).

RESULTS AND DISCUSSION

Characterization of OrganoClay Sorbents

XRD X-ray diffraction patterns for clay sorbents modified with various proportions of BTMAC/CEC of Mt clay (Fig. 1a) revealed that the d_{001} peak for the Na-exchanged montmorillonite at 1.34 nm shifted to greater values as a result of the exchange of Na^+ ions with surfactant cations. For clay samples that were treated with surfactant/CEC ratios of 0.5, 1.0, 2.0, and 3.0, the interlayer distances increased by 0.17, 0.17, 0.18, and 0.18 nm, respectively (Table 1). Cation exchange by the other surfactants yielded a maximum increase in interlayer distance also with a surfactant/CEC ratio of 2.0, and did not change significantly when the surfactant concentration was increased.

Clay modification with the various surfactants at a surfactant/CEC ratio of 2 showed clearly an increase in the d_{001} spacing in every case (Fig. 1b, Table 1), indicating a successful intercalation by the organic molecules. The largest increase in interlayer spacing occurred with surfactant DDAO

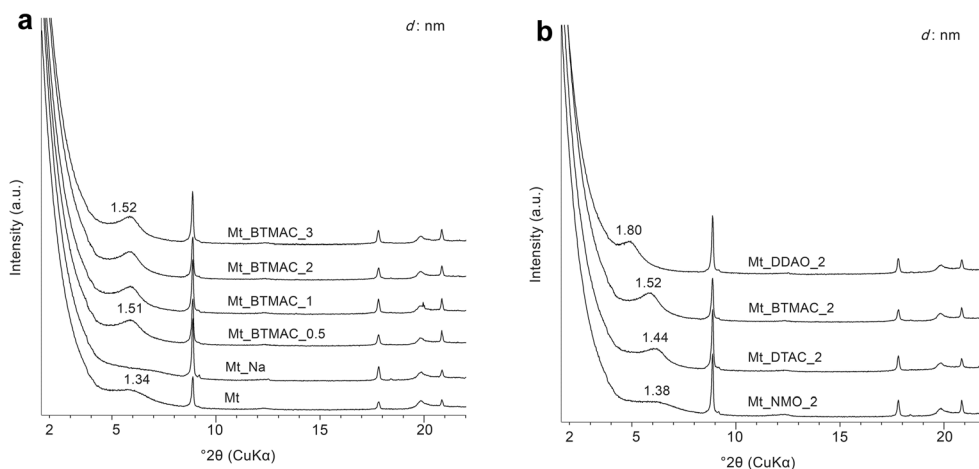


Fig. 1 XRD patterns of (a) Mt clay modified with BTMAC at various surfactant/CEC ratios and (b) modified with various surfactants at a surfactant/CEC ratio of 2.0

Table 1 Interlayer spacing of raw Mt clay and modified with various surfactants

Sample	d_{001} (nm)	Interlayer spacing (nm)	Interlayer space expansion (nm)
Mt	1.34	0.38	–
Mt_BTMAC_0.5	1.51	0.55	0.17
Mt_BTMAC_1	1.51	0.55	0.17
Mt_BTMAC_2	1.52	0.56	0.18
Mt_BTMAC_3	1.52	0.56	0.18
Mt_NMO_2	1.38	0.42	0.04
Mt_DTAC_2	1.44	0.48	0.10
Mt_DDAO_2	1.80	0.84	0.46

(0.46 nm), whereas a smaller change was observed with NMO (0.04 nm). These changes can be explained by the length of the surfactant alkyl chain (n_c , number of carbon atoms) (He et al. 2014). In the case of NMO, the value of n_c is 5, which is short compared to DDAO where n_c is almost three times longer at 14. In these organoclay samples, the alkyl chains of NMO, DTAC, and BTMAC formed only one parallel layer in the interlayer, as the basal 001 reflection was ≤ 1.5 nm, while in the case of DDAO, the alkyl chains were ordered in two parallel layers between the montmorillonite plates, indicated by the basal 001 reflection at 1.80 nm (Fig. 1a, b, Table 1) (Yariv & Cross, 2002; Zhu et al. 2007; Zhang et al. 2015).

Specific Surface Area Measurements Modification products were characterized also by their specific surface area, as this parameter is often used for sorption interpretation (Haydar et al. 2003). The specific surface area of Mt clay decreased from 245.88 m²/g (according to the one-point method) to 231.10 m²/g and 218.42 m²/g after treatment with 0.5 and 3.0 BTMAC/CEC ratios, respectively (Table 2). Similar results were achieved also in other studies (Zhou et al. 2008; Wu et al. 2012; Park et al. 2013; Parolo et al. 2014; Zhang et al. 2015).

Surfactant intercalation not only obstructs the clay mineral interlayer space, but also arranges a monolayer on the outer surface, creating a 'house of cards structure,' occupying pores among the clay particles. This process results in a reduction of pore size and molecular

nitrogen adsorption, thus decreasing reported values via BET of the specific surface area with an increasing degree of modification (Parolo et al. 2014; Zhang et al. 2015). As for clays treated with surfactants, the interlayer space is increased significantly; one might assume, therefore, that the specific surface area and pore size are not determining factors for the improvement of sorption capacity (Park et al. 2013; Zhang et al. 2015).

FTIR The functional groups and structural changes in clay after modification were determined by infrared spectroscopy. The characteristic bonds of montmorillonite that appear at 3621 cm⁻¹ as a sharp peak are assigned to OH-stretching vibrations of the structural OH group in the clay, whereas the broad band at 3428 cm⁻¹ is ascribed to hydrogen-bonded water molecules adsorbed within the interlayer space of the clay (Zhang et al. 2015). The bands at 1040 cm⁻¹ and 920 cm⁻¹ indicate the Si–O and Al–O bending vibrations (Zhou et al. 2011). The bands of quartz at 798 cm⁻¹, 515 cm⁻¹, and 460 cm⁻¹ are typical bending vibrations of O–Si–O (Alkaram et al. 2009).

After modification of Mt clay with surfactants, a pair of strong bands at 2930 cm⁻¹ and 2854 cm⁻¹ was observed which is assigned to the asymmetric and symmetric stretching vibrations of the methylene groups (CH₂), and their bending vibrations were detected at 1466 cm⁻¹ (Fig. 2) (Alkaram et al. 2009; Zhou et al. 2011; Wu et al. 2012; Zhang et al. 2015). These observations of the changes in the IR spectra confirmed the presence of surfactant molecules in Mt clay modified with BTMAC, DTAC, and DDAO.

SEM Irregular crystal morphology was observed for Mt clay (Fig. 3a). The surface of the particles was rough and the presence of a layer structure was revealed (Fig. 3b). Compared with Na clay, the SEM images showed similar irregular morphology, but in the case of Mt_BTMAC_2 aggregates were smaller (Fig. 3g, h). Although, in samples Mt_NMO_2 (Fig. 3c, d), Mt_DTAC_2 (Fig. 3e, f), and Mt_DDAO_2 (Fig. 3i, j), particles were bound into larger agglomerations.

Studies of removal of *p*-nitrophenol

Effect of Surfactant Loading Experimental results revealed that the sorption capacity of Mt clay for PNP was negligible (Fig. 6), but after modification of Mt clay with

Table 2 Specific surface area (by the BET method) of raw Mt clay and modified with BTMAC at various surfactant/CEC ratios

Sample	Multi-point method (m ² /g)	One-point method (m ² /g)	According to the Langmuir isotherm (m ² /g)
Mt	252.03	245.88	423.24
Mt_Na	262.16	256.04	439.76
Mt_BTMAC_0.5	238.41	231.10	402.05
Mt_BTMAC_1	236.98	229.52	399.95
Mt_BTMAC_2	235.75	228.79	396.78
Mt_BTMAC_3	224.46	218.42	376.58

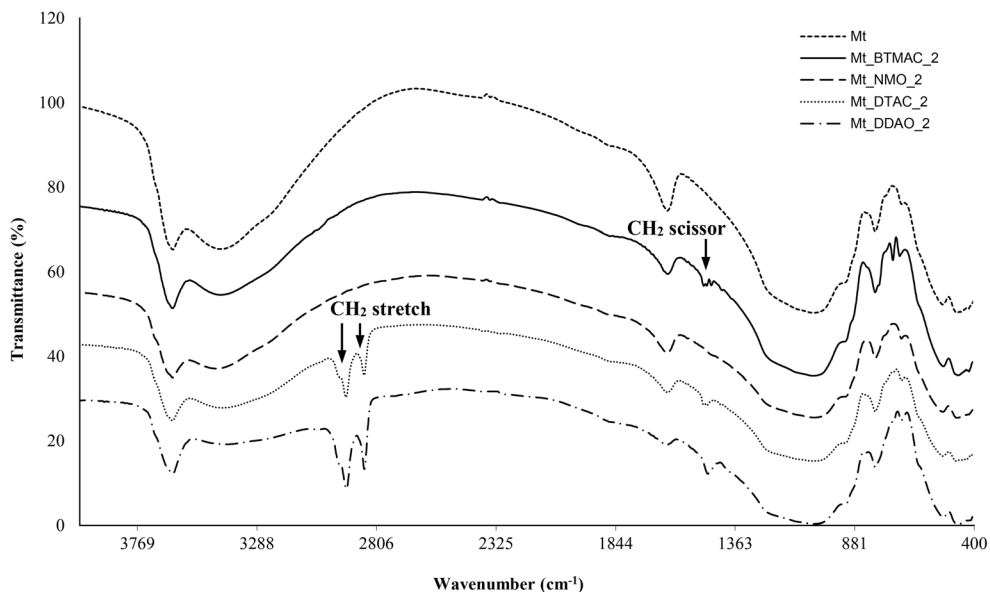


Fig. 2 FTIR spectra of Mt clay and modified with various surfactants at a surfactant/CEC ratio of 2.0

BTMAC the sorption capacity increased under a surfactant/CEC ratio of 2 (Fig. 4). The sorption capacities of the newly developed materials for PNP at surfactant/CEC ratios 0.5, 1.0, and 3.0 were relatively small (Fig. 4), however. Modification with natural clays and other surfactants was made, therefore, at a surfactant/CEC ratio of 2; these results indicated that the sorbed amount of PNP depends strongly on the amount of loaded surfactant and its distribution. Other studies (Zhou et al.

2008; Park et al. 2013) showed that, when surfactant loading is less than the CEC of the clay, surfactants replace the exchangeable cations in the interlayer space on montmorillonite. When surfactant loading exceeds the CEC of the clay, the surfactants occupy both the clay interlayer and the external space. Therefore, PNP sorption occurs not only due to hydrophobic interaction, but also through electrostatic interaction. While loaded surfactant molecules attract the dissociated PNP molecules

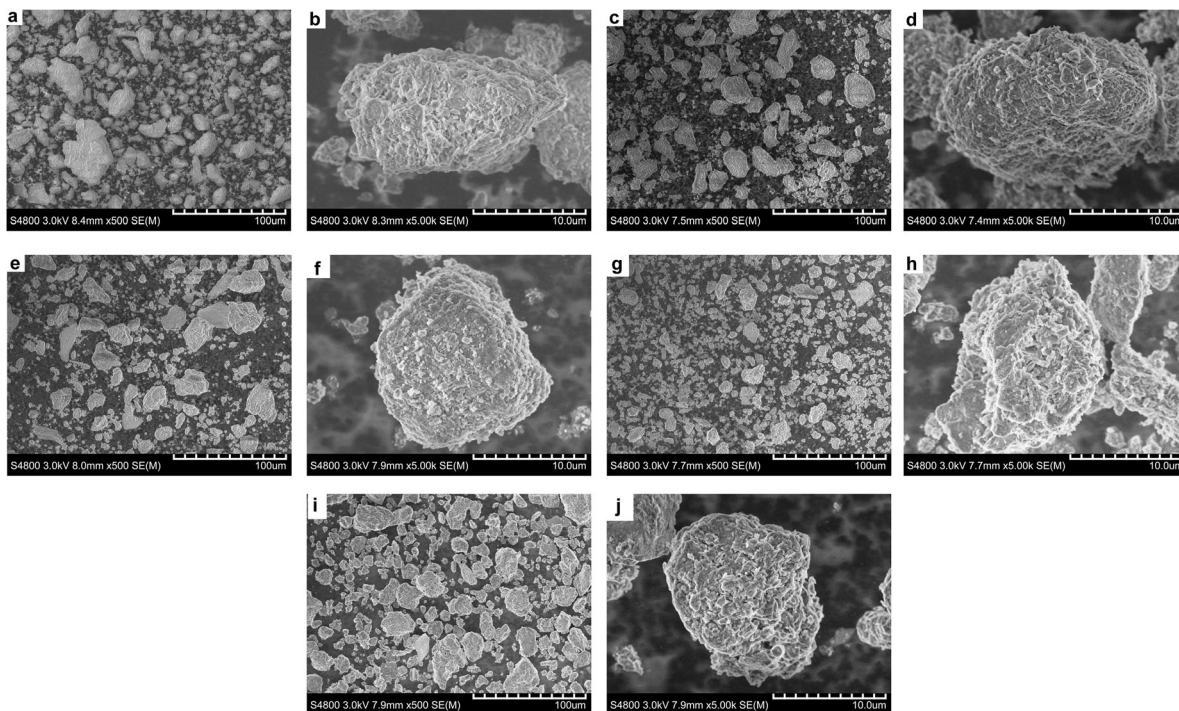


Fig. 3 SEM images of (a, b) Mt clay, (c, d) Mt_NMO_2, (e, f) Mt_DTAC_2, (g, h) Mt_BTMAC_2, (i, j) Mt_DDAO_2

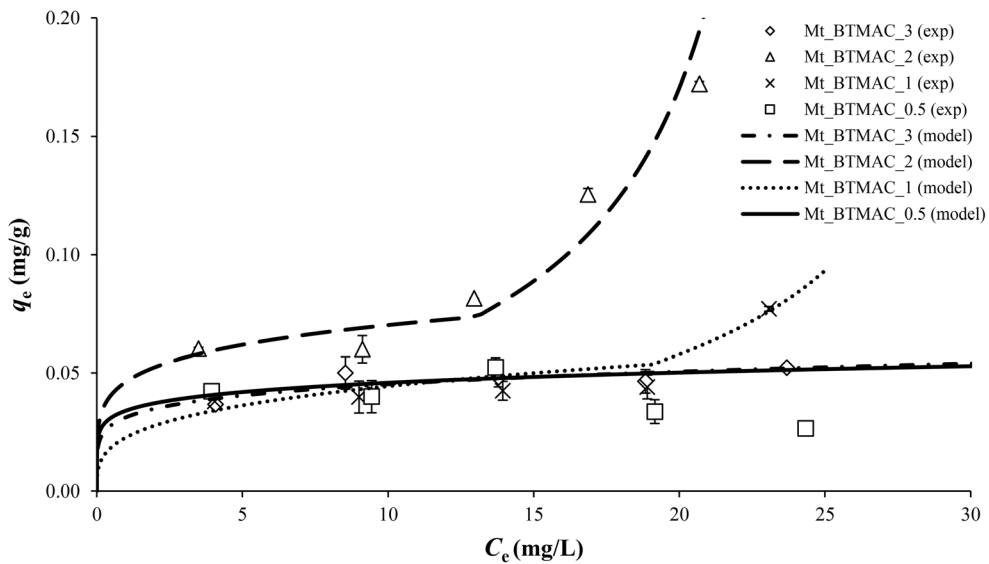


Fig. 4 Comparison of PNP sorption for Mt clay modified with BTMAC at various surfactant/CEC ratios (experimental conditions: initial PNP concentration = 5–25 mg/L, pH = 7, contact time = 24 h at room temperature)

through hydrophobic interaction, dissociated PNP anions bind to surfactant cations on the external surface of the clay through electrostatic interactions.

Effect of Initial Solution Concentration The initial concentration of PNP in the range 5–25 mg/L influenced the sorption of PNP on the modified clay materials at a surfactant/CEC ratio of 2 at room temperature and pH 7 (Figs. 5, 6 and 7). Initial increase in the PNP concentration resulted in an extended PNP sorption by modified clay materials. In the case of Mt_NMO_2, however, this

relationship was not observed, because sorption was small (~0.02 mg/g) (Fig. 5). The largest PNP sorption capacity was observed on Mt_DDAO_2 (0.36 mg/g) when the PNP concentration was 25 mg/L (Fig. 6). X-ray diffraction results (Fig. 2, Table 1) indicated that the largest interlayer space can be linked to the efficacy of PNP sorption (Park et al. 2013). The sorption capacity of Mt clay modified with DDAO was >18 times greater than that of raw Mt clay and three times greater than Mt_Na (Fig. 6). Due to the large size of hydrated Na⁺ ions (Zhu et al. 2014), the interlayer space during penetration was increased significantly, thus improving

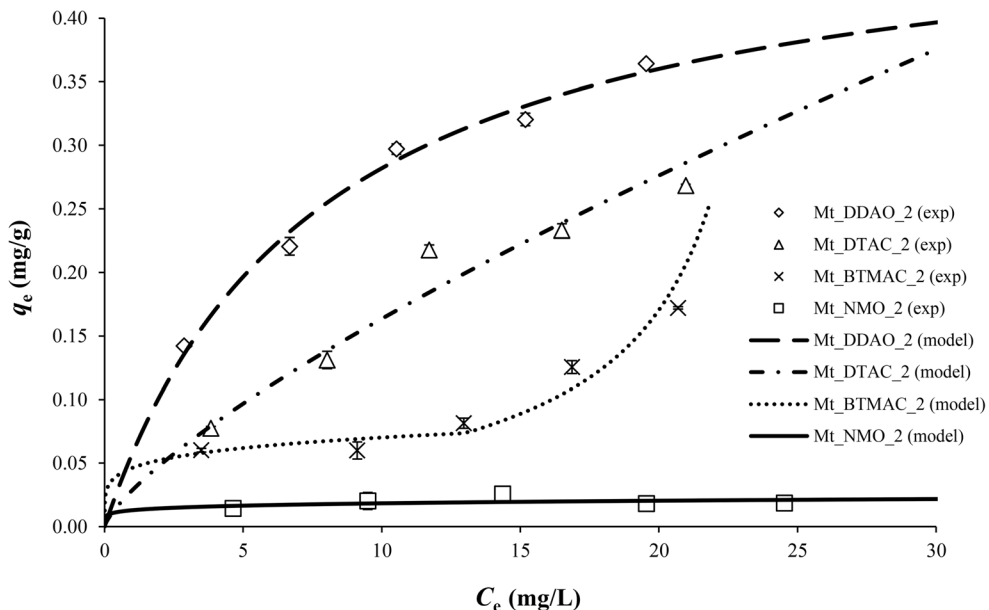


Fig. 5 Comparison of PNP sorption for modified Mt. clay with various surfactants at a surfactant/CEC ratio of 2.0 (experimental conditions: initial PNP concentration = 5–25 mg/L, pH = 7, contact time = 24 h at room temperature)

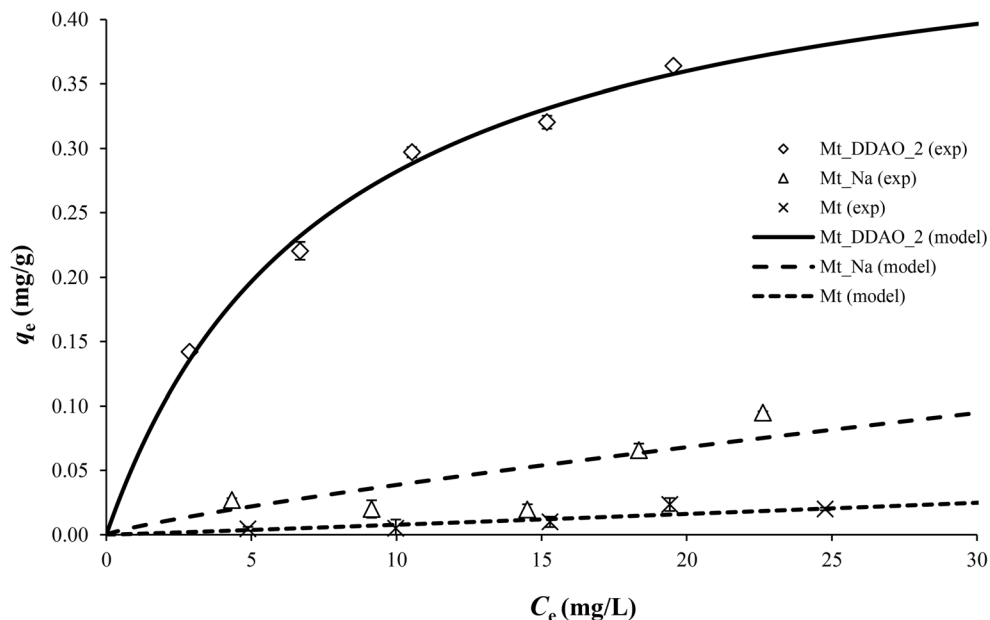


Fig. 6 Comparison of PNP sorption for raw Mt clay, Mt_Na, and modified with DDAO at organic phase loading of 2.0 (experimental conditions: initial PNP concentration = 5–25 mg/L, pH = 7, contact time = 24 h at room temperature)

sorption of organic molecules (Zhou et al., 2008). A larger BET specific surface area also was determined for samples treated with Na^+ ions (Table 2).

According to results obtained previously, natural clay was modified with DDAO at a surfactant/CEC ratio of 2. For natural, unmodified clays the sorption capacity was very small when the PNP concentration in the solution was 5 to 25 mg/L (Fig. 7). The greatest PNP sorption capacity was observed on T_DDAO_2, i.e. 0.15 mg/g, when the PNP concentration was 25 mg/L.

J clay modified with DDAO sorbed almost no PNP (on average 0.0072 mg/g); therefore, this material was excluded from sorption experiments in which the effect of pH and contact time were estimated.

Effect of Contact Time The PNP sorption rate was high at the beginning of the experiment (Fig. 8) because sorption sites were initially abundant and PNP molecules were easily sorbed on those sites. The sorption capacity of the PNP onto Mt_DDAO_2 and T_DDAO_2 reached a maximum within

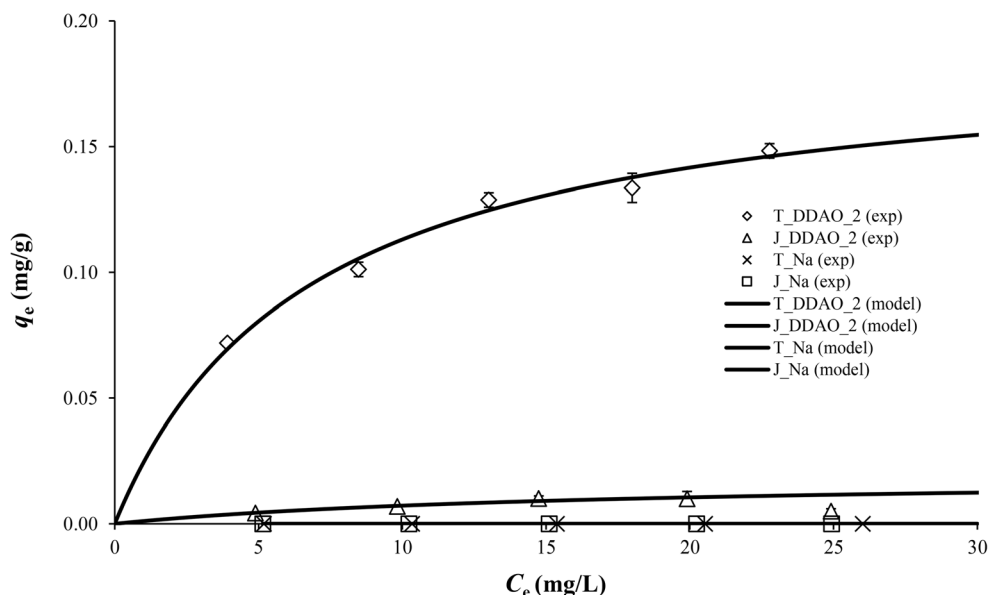


Fig. 7 Comparison of PNP sorption for J clay and T clay modified with DDAO at organic phase loading of 2.0 (experimental conditions: initial PNP concentration = 5–25 mg/L, pH = 7, contact time = 24 h at room temperature)

60 min, after which no substantial changes were observed. This can be explained, in part, by the reduced number of available vacant sorption sites and increased contact time (Zhang et al., 2015).

Effect of pH The effect of pH on PNP removal was investigated in the pH range 2 to 12 with the initial concentration of PNP of 25 mg/L at room temperature. High removal efficiency was obtained in an acidic environment (pH 2 to 4) for T_DDAO_2 and from pH 2 to 6 for Mt_DDAO_2 (Fig. 9). When the pH exceeded 6, the removal efficiency decreased significantly. Similar results were reported by other scientists (Zhou et al. 2008; Luo et al. 2015; Zhang et al. 2015; Park et al., 2013) and were explained by the clay surface charge and dissociation level of PNP. PNP is poorly soluble in water in acidic conditions with a dissociation constant (pK_a) of 7.15; when the pH is below pK_a ($pH < pK_a$), PNP may be a neutral molecule, but when pH is greater than the pK_a ($pH > pK_a$), PNP can exist as an anion. Based on the PNP dissociation conditions, sorption onto modified clay materials is more efficient when PNP is a neutral molecule. In acidic environments, a surfactant intercalated in the clay interlayer space provides effective environmental pollution removal due to Van der Waals forces and hydrophobic effects. When the solution is alkaline, PNP sorption decreases due to electrostatic repulsion forces between the negatively charged clay particles and PNP anions.

Sorption Isotherms

In this study, Langmuir and Freundlich isotherms were used to describe the relationship between the amount of sorbed PNP and its equilibrium concentration in the solution at room temperature and pH 7.

The Langmuir isotherm assumes that sorption occurs at specific homogenous sites on the surface of a sorbent. When a site is occupied by a sorbate molecule, no future sorption can

occur at this site. The Langmuir isotherm is expressed by the following equation:

$$q_e = \frac{q_{\max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (4)$$

where q_{\max} is the theoretical monolayer capacity (mg/g), K_L is the Langmuir equilibrium constant (L/mg) related to the affinity of binding sites, and C_e is the equilibrium solution concentration (mg/L) (Langmuir, 1918).

One of the essential characters of the Langmuir isotherm can be expressed by a dimensionless constant called the equilibrium parameter (R_L) and which is defined by the following equation:

$$R_L = \frac{1}{1 + K_L \cdot C_0} \quad (5)$$

where C_0 is the highest initial PNP concentration (mg/L) and the value of R_L indicates whether sorption will be favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), irreversible ($R_L = 0$), or linear ($R_L = 1$) (Weber & Chakravorti, 1974).

The Freundlich isotherm is an empirical equation based on sorption on heterogeneous surfaces, and is given by the following equation:

$$q_e = K_F \cdot C_e^{1/n} \quad (6)$$

where K_F (L/mg) and n are Freundlich constants defining relative capacity and sorption intensity, respectively (Freundlich, 1906).

The Langmuir and Freundlich isotherm constants and correlation coefficients (R^2) for the sorption of PNP onto modified clay samples at a surfactant/CEC ratio of 2 at a constant temperature and pH values are presented in Table 3. The R^2 values are >0.89 (Alkaram et al., 2009), indicating that both the

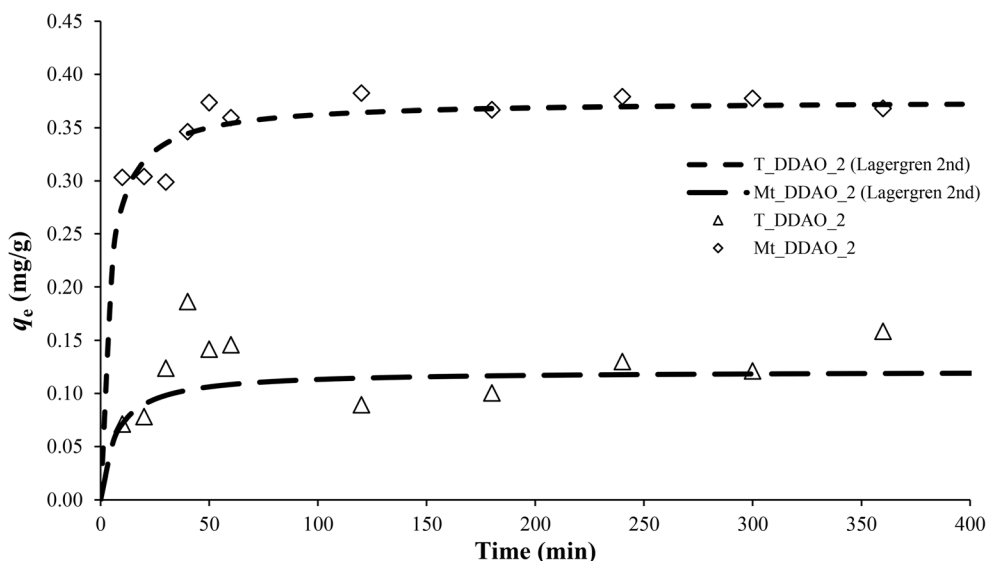


Fig. 8 Effect of contact time on the sorption of PNP onto modified Mt. clay and T clay (experimental conditions: initial PNP concentration = 25 mg/L pH = 7, at room temperature)

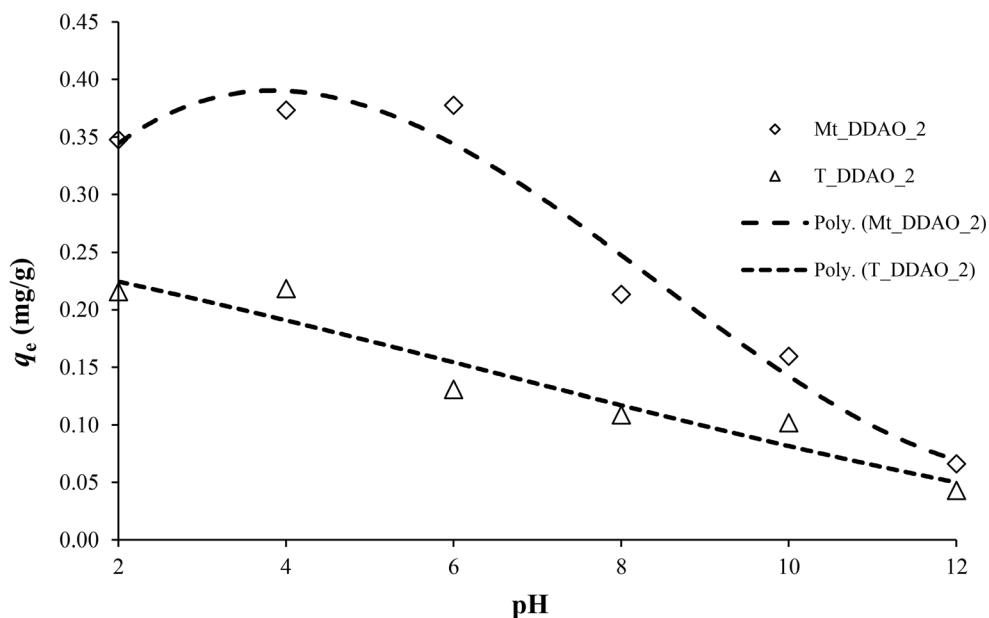


Fig. 9 Effect of pH on the sorption of PNP onto modified Mt. clay and T clay (experimental conditions: initial PNP concentration = 25 mg/L, contact time = 24 h at room temperature)

Langmuir and Freundlich isotherms can describe sorption data adequately. However, in the case of Mt_BTMAC_2, R^2 is < 0.89 , meaning that sorption cannot be described adequately by these isotherms. The suitability of the two isotherm models for the systems investigated indicates that both monolayer and multilayer sorption exist under the experimental conditions studied. The sorption of PNP onto these surfaces is thus complex, involving more than one mechanism (Febrianto et al. 2009). Similar results have been reported by Ko et al. (2007) for the sorption of PNP by organo-modified montmorillonite clay.

The Freundlich parameters n and K_F reflect the sorption intensity of PNP and the binding affinity constant and provide information about the sorption mechanism. The value of n observed for sorption of PNP solution is >1 ($n > 1$) and this indicated that the sorption of PNP onto the clay samples was effective over the entire range of concentrations, and sorption is determined by physical processes (Alkaram et al. 2009; Park et al. 2013). The largest value for the binding affinity constant,

K_F , was obtained in the sorption of PNP on the Mt_DDAO_2 sample and it fitted well with the experimental data.

In the Langmuir model, the values of K_L were 0.0340, 0.0367 and 0.1306, 0.1096 for Mt_BTMAC_2, Mt_DTAC_2 and Mt_DDAO_2, Mt_NMO_2, respectively. K_L values indicated that the affinity of binding sites for PNP increased when clay samples were treated with nonionic surfactants. R_L values ranged between 0 and 1; this also suggested that sorption of PNP by modified clay samples was favorable (Luo et al. 2015).

CONCLUSIONS

Organoclays prepared by intercalating cationic or nonionic surfactants are able to interact with organic molecules of a different polarity and serve as immobilizers for organic molecules and toxicants, e.g. phenols and nonionic organic compounds (NOCs). The sorbents developed revealed significantly improved performance in comparison to their unmodified counterparts, with a significant increase in *p*-nitrophenol

Table 3 Parameters of Langmuir and Freundlich isotherms for sorption of PNP onto modified clay samples at surfactant/CEC ratio of 2

Sample	Langmuir					Freundlich	
	q_{max} (mg/g)	K_L (L/mg)	R_L	R^2	n	K_F (L/mg)	R^2
Mt_BTMAC_2	0.34	0.0340	0.5408	0.2424	1.82	0.0248	0.6809
Mt_DTAC_2	0.63	0.0367	0.5214	0.8964	1.32	0.0287	0.9657
Mt_DDAO_2	0.50	0.1306	0.2345	0.9895	2.03	0.0864	0.9865
Mt_NMO_2	0.04	0.1096	0.2673	0.9818	1.95	0.0064	0.9977
T_DDAO_2	0.19	0.1500	0.2105	0.9921	2.45	0.0423	0.9815
J_DDAO_2	0.02	0.0596	0.4017	0.891	1.53	0.0015	0.9548

(PNP) sorption capacity up to 25 and 30.5 times in the cases Mt_DDAO_2 and Mt_DTAC_2, respectively. For a modified natural smectite dominated Triassic clay (T clay) and a mixed-content clay containing organic matter (J clay), sorption capacity with respect to PNP in aqueous solution significantly increased. The pH level dominates the efficiency of PNP sorption – an acidic environment promotes sorption for all modified clays, e.g. T_DDAO_2 was the most efficient within pH 2–4 and Mt_DDAO_2 within pH 2–6. The hypothesis that organoclays are more efficient sorbents than raw clays has been proved; furthermore, organoclays based on natural montmorillonite may be used for the removal of PNP, but with less efficacy than manufactured montmorillonite. Further studies must be performed to reveal improved properties in order to benefit wastewater treatment engineering and environmental remediation.

ACKNOWLEDGMENTS

This work was supported by the Latvian Research Council grant lzp-2018/1-0009, RBR-Reviving Baltic Resilience project No. STHB.02.02.00-22- 0092/16., Linnaeus University, and Geo IT Ltd.

REFERENCES

- Alkaram, U. F., Mukhlis, A. A., & Al-Dujaili, A. H. (2009). The removal of phenol from aqueous solutions by adsorption using surfactant-modified bentonite and kaolinite. *Journal of Hazardous Materials*, *169*, 324–332.
- Anirudhan, T. S., & Ramachandran, M. (2015). Adsorptive removal of basic dyes from aqueous solutions by surfactant modified bentonite clay (organoclay): Kinetic and competitive adsorption isotherm. *Process Safety and Environmental Protection*, *95*, 215–225.
- Bertuoli, P. T., Piazza, D., Scienza, L. C., & Zattera, A. J. (2014). Preparation and characterization of montmorillonite modified with 3-aminopropyltriethoxysilane. *Applied Clay Science*, *87*, 46–51.
- Brovkina, J., Lakevics, V., Stepanova, V., Ozolins, J., & Berzina-Cimdina, L. (2012). Development of effective sorbents on Latvian clay basis. *Material Science and Applied Chemistry*, *26*, 37–41.
- Febrianto, J., Kosasiha, A. N., Sunarsob, J., Jua, Y., Indraswati, N., & Ismadji, S. (2009). Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies. *Journal of Hazardous Materials*, *162*, 616–645.
- Freundlich, H. M. F. (1906). Over the adsorption in solution. *The Journal of Physical Chemistry*, *57*, 385–471.
- Gamoudi, S., Frini-Srasra, N., & Srasra, E. (2015). Influence of synthesis method in preparation of HDTMA⁺ – and HDPy⁺ – illites/smectites. *Applied Clay Science*, *116*, 78–84.
- Guégan, R., Giovanela, M., Warmont, F., & Motelica-Heino, M. (2015). Nonionic organoclay: A 'Swiss Army knife' for the adsorption of organic micro-pollutants? *Journal of Colloid and Interface Science*, *437*, 71–79.
- Han, S., Zhao, F., Sun, J., Wang, B., Wei, R., & Yan, S. (2013). Removal of p-nitrophenol from aqueous solution by magnetically modified activated carbon. *Journal of Magnetism and Magnetic Materials*, *341*, 133–137.
- Haydar, S., Ferro-Garcia, M. A., Rivera-Utrilla, J., & Joly, J. P. (2003). Adsorption of p-nitrophenol on an activated carbon with different oxidations. *Carbon*, *41*, 387–395.
- He, H., Ma, L., Zhu, J., Frost, R. L., Theng, B. K. G., & Bergaya, F. (2014). Synthesis of organoclays: A critical review and some unresolved issues. *Applied Clay Science*, *100*, 22–28.
- Houari, M., Hamdi, B., Bouras, O., Bollinger, J. C., & Baudu, M. (2014). Static sorption of phenol and 4-nitrophenol onto composite geomaterials based on montmorillonite, activated carbon and cement. *Chemical Engineering Journal*, *255*, 506–512.
- Huong, P. T., Lee, B. K., Kim, J., & Le, C. H. (2016). Nitrophenols removal from aqueous medium using Fe-nano mesoporous zeolite. *Materials and Design*, *101*, 210–217.
- Ko, C. H., Fan, C., Chiang, P. N., Wang, M. K., & Lin, K. C. (2007). P-Nitrophenol, phenol and aniline sorption by organo-clays. *Journal of Hazardous Materials*, *149*, 275–282.
- Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*, *40*, 1361–1403.
- Lee, M. S., & Tiwari, D. (2012). Organo and inorgano-organo-modified clays in the remediation of aqueous solutions: An overview. *Applied Clay Science*, *59–60*, 84–102.
- Li, A. M., Zhang, Q. X., Zhang, G. C., Chen, J. L., Fei, Z. H., & Liu, F. Q. (2002). Adsorption of phenolic compounds from aqueous solutions by a water-compatible hypercrosslinked polymeric adsorbent. *Chemosphere*, *47*, 981–989.
- Liu, F., Wu, Z., Wang, D., Yu, J., Jiang, X., & Chen, X. (2016). Magnetic porous silica-graphene oxide hybrid composite as a potential adsorbent for aqueous removal of p-nitrophenol. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *490*, 207–214.
- Luo, Z., Gao, M., Yang, S., & Yang, Q. (2015). Adsorption of phenols on reduced-charge montmorillonites modified by bispyridinium dibromides: Mechanism, kinetics and thermodynamics studies. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *482*, 222–230.
- Murray, H.H. (2007) Applied clay mineralogy: Occurrences, processing and application of kaolins, bentonites, palygorskite-sepiolite, and common clays. First Edition. Elsevier, Amsterdam, 188 pp.
- Nayak, P. S., & Singh, B. K. (2007). Removal of phenol from aqueous solutions by sorption on low cost clay. *Desalination*, *207*, 71–79.
- Orshansky, F., & Narkis, N. (1997). Characteristics of organics removal by PACT simultaneous adsorption and biodegradation. *Water Research*, *31*, 391–398.
- Paiva, L. B., Morales, A. R., & Díaz, F. R. V. (2008). Organoclays: Properties, preparation and applications. *Applied Clay Science*, *42*, 8–24.
- Park, Y., Ayoko, G. A., & Frost, L. R. (2011). Application of organoclays for the adsorption of recalcitrant organic molecules from aqueous media. *Journal of Colloid and Interface Science*, *354*, 292–305.
- Park, Y., Ayoko, G. A., Kurdi, R., Horváth, E., Kristóf, J., & Frost, R. L. (2013). Adsorption of phenolic compounds by organoclays: Implications for the removal of organic pollutants from aqueous media. *Journal of Colloid and Interface Science*, *406*, 196–208.
- Parolo, M. E., Pettinari, G. R., Musso, T. B., Sánchez-Izquierdo, M. P., & Fernández, L. G. (2014). Characterization of organo-modified bentonite sorbents: The effect of modification conditions on adsorption performance. *Applied Surface Science*, *320*, 356–363.
- Ruiz-Hitzky, E. R., Aranda, P., Darder, M., & Rytwo, G. (2010). Hybrid materials based on clays for environmental and biomedical applications. *Journal of Materials Chemistry*, *20*, 9306–9321.
- Seglins, V. (2010) Clays and clay minerals. <<https://www.lu.lv/vpp/arhivs/zeme/malu-petijumi/nodreigi-par-maliem/malu-minerali/>> (21 September 2017).
- Seliem, M. K., Komarneni, S., Cho, Y., Lim, T., Shahien, M. G., Khalil, A. A., & El-Gaid, I. M. A. (2011). Organosilicas and organo-clay minerals as sorbents for toluene. *Applied Clay Science*, *52*, 184–189.
- Shen, Y. H. (2001). Preparations of organobentonite using nonionic surfactants. *Chemosphere*, *44*(5), 989–995.
- Weber, T. W., & Chakravorty, R. K. (1974). Pore and solid diffusion models for fixed bed adsorbents. *American Institute of Chemical Engineers Journal*, *20*, 228–238.
- Wu, P., Dai, Y., Long, H., Zhu, N., Li, P., Wu, J., & Dang, Z. (2012). Characterization of organo-montmorillonites and comparison for Sr(II) removal: Equilibrium and kinetic studies. *Chemical Engineering Journal*, *191*, 288–296.

- Xiaohong, L., Baowei, Z., Kun, Z., & Xuekui, H. (2011). Removal of nitrophenols by adsorption using β -cyclodextrin modified zeolites. *Chinese Journal of Chemical Engineering*, 19, 938–943.
- Xue, G., Gao, M., Gu, Z., Luo, Z., & Hu, Z. (2013). The removal of *p*-nitrophenol from aqueous solutions by adsorption using gemini surfactants modified montmorillonites. *Chemical Engineering Journal*, 218, 223–231.
- Yan, L., Shan, X., Wen, B., & Zhang, S. (2007). Effect of lead on the sorption of phenol onto montmorillonites and organo-montmorillonites. *Journal of Colloid and Interface Science*, 308, 11–19.
- Yang, Y. H., & Koopal, L. K. (1999). Immobilisation of humic acids and binding of nitrophenol to immobilised humics. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 151, 201–212.
- Yariv, S., & Cross, H. (Eds.). (2002). *Organo-clay complexes and interactions* 680 pp. New York: Marcel Dekker, Inc..
- Zermane, F., Bouras, O., Baudu, M., & Basly, J. P. (2010). Cooperative coadsorption of 4-nitrophenol and basic yellow 28 dye onto an iron organo-inorgano pillared montmorillonite clay. *Journal of Colloid and Interface Science*, 350, 315–319.
- Zhang, W. M., Chen, J. L., Pan, B. C., Chen, Q., He, M. Y., & Zhang, Q. X. (2006). Modeling cooperative adsorption of aromatic compounds in aqueous solutions to nonpolar adsorbent. *Separation and Purification Technology*, 49, 130–135.
- Zhang, L., Zhang, B., Wu, T., Sun, D., & Li, Y. (2015). Adsorption behavior and mechanism of chlorophenols onto organoclays in aqueous solution. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 484, 118–129.
- Zhou, Q., He, H. P., Zhu, J. X., Shen, W., Frost, R. L., & Yuan, P. (2008). Mechanism of *p*-nitrophenol adsorption from aqueous solution by HDTMA+–pillared montmorillonite – Implications for water purification. *Journal of Hazardous Materials*, 154, 1025–1032.
- Zhou, Y., Jin, X. Y., Lin, H., & Chen, Z. L. (2011). Synthesis, characterization and potential application of organobentonite in removing 2,4-DCP from industrial wastewater. *Chemical Engineering Journal*, 166, 176–183.
- Zhu, L., Zhu, R., Xu, L., & Ruan, X. (2007). Influence of clay charge densities and surfactant loading amount on the microstructure of CTMA–montmorillonite hybrids. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 304, 41–48.
- Zhu, R., Zhao, J., Ge, F., Zhu, L., Zhu, J., Tao, Q., & He, H. (2014). Restricting layer collapse enhances the adsorption capacity of reduced-charge organoclays. *Applied Clay Science*, 88–89, 73–77.
- Zhu, R., Chen, Q., Zhou, Q., Xi, Y., Zhu, Y., & He, H. (2016). Adsorbents based on montmorillonite for contaminant removal from water: A review. *Applied Clay Science*, 123, 239–258.