

GÜLAY BAYSAL¹

APPLICATION OF SURFACTANT-MODIFIED MONTMORILLONITE IN NITROPHENOL REMOVAL BY ADSORPTION

Quaternary ammonium salts (QASs) such as 1-methyl-di-nonyl-1 phenyl ammonium iodide (QAS₁) and 1-methyl-di-dodecyl-1 phenyl ammonium iodide (QAS₂) were newly synthesized by complete alkylation reaction for modification of sodium montmorillonite (Mt). The sodium montmorillonite was modified via an ion-exchange reaction with QAS₁ and QAS₂, and two organoclays, Mt₁ and Mt₂, have been obtained. The synthesized quaternary ammonium salts were analyzed by nuclear magnetic resonance spectroscopy (NMR). The organoclays (Mt₁ and Mt₂) were characterized by a range of methods including X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The adsorption capacities of the synthesized organo-montmorillonites for the hydrophobic organic pollutant 4-nitrophenol (4-NP) have been evaluated. The distances between the organoclay layers showed a much better opening than that reported in the literature. The results show that the adsorption capacity increased in the order Mt₂ > Mt₁. The adsorption capacities of Mt₁ and Mt₂ for 4-NP were 77% and 81%, respectively.

1. INTRODUCTION

Ranging from medicinal to poisonous and from tinctorial to explosive materials, most of the fine chemicals include nitrophenol as input or intermediate. In other words, phenols and their derivatives found in nature are mainly the products of drugs, pesticides, plastics, papers, etc., from the pharmaceutical and petrochemical manufacturing industries [1]. The world production of these common pollutants has been up to 7800 Tg annually. Out of the main industrial pollutants, phenol-containing substances make clean water stinky and their damages to living organisms render critical contaminants, including 4-nitrophenol and *p*-chlorophenol despite their low concentrations [2].

¹Food Engineering, Engineering Faculty, Istanbul Aydin University, Istanbul, 34295, Turkey, e-mail address: gulaybaysal@aydin.edu.tr

It is important to note that wastewater management should prioritize the depollution policy and remove phenols from wastewater in concern with its obnoxious and venomous effects [3]. Several methods of wastewater treatment are used to process phenolic effluents, including catalytic oxidation, ion exchange, solvent extraction, and membrane separation as well as the adsorption, one of the most functional and widely-used techniques as regards to its convenience and success in purification and separation.

According to literature, activated carbon is the most commonly used adsorbent in nitrophenol adsorption. Although active carbon has a highly effective adsorption capacity for phenol and its derivatives, its regeneration is difficult and expensive [4]. It is very important that the adsorbent used should be original, cheap and easy to recover.

Adsorbents for carbon pollutants, rheological control agents, and reinforcing fillers for plastics and electronic materials are just a few of the modified clay minerals to perform a great number of operations in various major fields [5]. Sodium montmorillonite (Mt) is a positively charged nanomaterial with an inorganic character. Since nitrophenol adsorption takes place by ion exchange method, the clay needs to be converted into a positively charged cation by organic cation groups. Thus, the clay will acquire an organic character. This application will allow the clay layers to be spaced and will give nitrophenol adsorption ability to the clay. In this study, in addition to being an original and inexpensive adsorbent, an environmentally friendly and easily recyclable material that can be used in the adsorption of phenol compounds has been synthesized. The aim of this study was to investigate the structure of an organoclay formed with newly synthesized quaternary ammonium salts such as 1-methyl-di-nonyl-1 phenyl ammonium iodide (QAS₁), 1-methyl-di-dodecyl-1 phenyl ammonium iodide (QAS₂) and understand the adsorption of 4-NP by synthesized organoclays.

2. EXPERIMENTAL

Chemicals. Modifiers 1-methyl-di-nonyl-1 phenyl ammonium iodide (QAS₁) and 1-methyl-di-dodecyl-1 phenyl ammonium iodide (QAS₂) have been synthesized. 4-nitrophenol (4-NP,) montmorillonite (Sigma Aldrich), methyl iodide (Merck) and ethyl acetate (Merck) of analytical grade have been purchased. Some data on physical and chemical properties of Mt are given in Table 1.

Table 1

Physical and chemical properties of Mt

Chemical formula	(Na, Ca) _{0.33} (Al, Mg) ₂ Si ₄ O ₁₀ (OH) ₂ 6H ₂ O
Density, kg/dm ³	2.860
Specific surface area, m ² /kg	0.750
CEC, meq/kg	920
Composition, wt. %	1.40 Na, 2.44 Ca, 9.99 Al, 8.88 Mg, 20.7 Si, 35.53 O, 0.37 H

Apparatuses. Infrared spectra of the synthesized compounds were recorded using a Mattson 1000 infrared spectrophotometer by the potassium bromide disc technique in the wavelength range of 4000–400 cm^{-1} . ^1H -spin-lattice relaxation times and ^{13}C -NMR were measured with a Bruker DPX 400 MHz high performance digital FT-nuclear magnetic resonance spectrometer. X-ray diffraction (XRD) method was used because of its strength in measuring the degree of silicate scattering. The modified compounds were sampled for the characteristics of crystalline structure, mean size of particles, and concentrations of pollutants and the XRD patterns were described using Rigaku Rad B-Dmax II powder XRD. The morphology of the organoclays was examined with a JEOL JSM 5600 LV scanning electron microscopy (SEM) equipped with an energy dispersive X-ray detector to examine the morphology and effect of QASs⁺ on the Mt. The samples were analyzed using a Shimadzu UV-1010 spectrophotometer at a wavelength of 317 nm for the residual concentration of 4-NP.

Synthesis of 1-methyl-di-nonyl-1 phenyl ammonium iodide (QAS₁) and 1-methyl-dodecyl-1 phenyl ammonium iodide (QAS₂). First, methyl iodide (0.03676 mol) was mixed with N-dinonyl-N-(1-phenylethyl) amine at the ratio of 5.22 g/1 g N immediately after distillation. The following day, the thin layer chromatography, TLC was used to control the reaction in the ending process, in which no methyl iodide remained due to evaporation. The specific ethyl acetate or octyl (5:1) was vacated onto the mix and then emptied and dried up under vacuum [5]. The obtained products (Fig. 1) were analyzed by the NMR method.

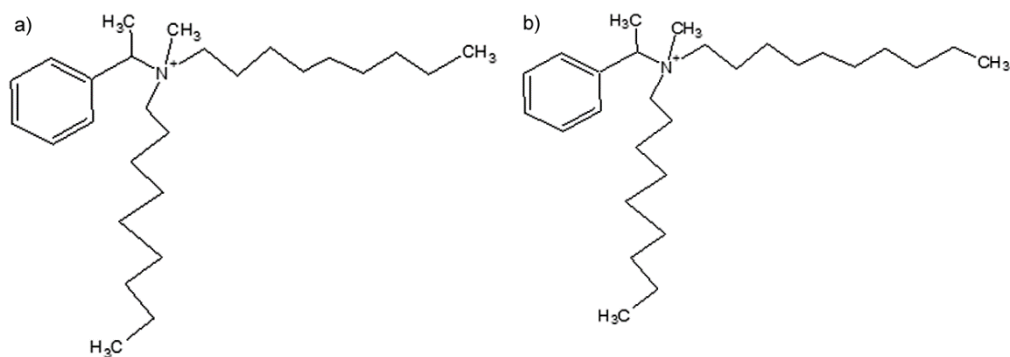


Fig. 1. The structure of 1-methyl-di-nonyl-1 phenyl ammonium cation (QAS₁) (a) and of 1-methyl-di-dodecyl-1 phenyl ammonium cation (QAS₂)

Preparation of the organoclay. In order to produce two organoclays from sodium montmorillonite, the cation exchange was performed between QAS₁ and QAS₂, with Mt₁ and Mt₂, respectively. One-hour blending Mt (1 g) and deionized water with ethanol (1:1) led to the swelled silicate layers at 298 K. The solvent (0.05 dm^3) at the same temperature was individually applied to the QAS₁ and QAS₂ for dissolution. Mixed with

clay dispersion, the dissolution was mechanically stirred at 298 K for 24 h. A disc filter funnel was used for deposit modification and filtration. To eliminate iodide ions, Mt₁ and Mt₂ were washed several times using the dissolvent (nearly 0.1 dm³). The

filtered residues were dried for 4 h at 343 K, and the fresh organoclays were grounded and screened with a 100-mesh sieve [5].

Adsorption experiments of 4-NP on the organoclay. Stock solutions of 4-NP in distilled water were prepared at room temperature. Kinetic studies were conducted in the flasks by shaking 4-NP solution (50 mg/dm³) with 10 g/dm³ of organo montmorillonites (Mt₁ and Mt₂) at 250 rpm on a mechanical shaker. The samples were withdrawn from the shaker at intervals from 15 to 240 min [6], and the concentrations of 4-NP were determined.

The organoclays Mt₁ and Mt₂ (10 g/dm³) were blended with solutions of 4-NP at the concentrations of 10, 20, 30, 40, 50, and 60 mg/dm³ 4-NP, shaken at 250 rpm/h for 4 h followed by the centrifugation at 3500 rpm/h for 15 min and then the concentration of 4-NP was measured. The tests were conducted at 298, 318 and 333 K.

The 4-nitrophenol (4-NP) uptake by organoclays was calculated from the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where q_e is the uptake of 4-NP, C_0 is the initial concentration, C_e the equilibrium concentration, V is the volume of the solution and m is the mass of the adsorbent [7, 8].

3. RESULTS AND DISCUSSION

3.1. CHARACTERIZATION OF ORGANOCLOYS

The results of the NMR analysis are given below to confirm that the synthesized quaternary ammonium salts are of specific characters.

Mt₁: ¹H NMR (400 MHz, CDCl₃) δ 0.87–0.91 CH₂CH₃ (m, 6H), 1.26–1.87 CH₂(CH₂)₇CH₃ (m, 28H), 1.93 ArCHCH₃ (d, 3H, $J = 7.2$ Hz), 3.17 N⁺CH₃ (s, 3H), 3.11–3.58 N⁺CH₂ (m, 4H), 5.05 ArCHCH₃ (q, 1H, $J = 7.2$ Hz), 7.49–7.64 Ar–H (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 14.08, 16.02, 22.62, 22.97, 26.51, 26.58, 29.06, 29.10, 29.16, 29.31, 29.38, 31.75, 31.78, 45.94, 59.45, 60.18, 129.40, 130.81, 132.19; IR: ν 3188.7, 2920.6, 2729.7, 2629.8, 1613.1, 1460.8, 1376.9, 1211.0, 1056.8, 931.4, 818.6, 775.2, 712.5, 463.8.

Mt₂: ¹H NMR (400 MHz, CDCl₃) δ 0.88–0.91 CH₂CH₃ (m, 6H), 1.26–1.88 CH₂(CH₂)₁₀CH₃ (m, 40H), 1.94 ArCHCH₃ (d, 3H, $J = 7.2$ Hz), 3.18 N⁺CH₃ (s, 3H),

3.10–3.59 N^+CH_2 (m, 4H), 5.04 ArCHCH_3 (q, 1H, $J = 7.2$ Hz), 7.50–7.63 Ar-H (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.10, 16.04, 22.67, 22.97, 26.58, 29.10, 29.16, 29.31, 29.37, 29.44, 29.47, 29.60, 31.89, 59.44, 60.16, 129.36, 130.76, 132.21; IR: ν 2921.6, 2852.2, 1611.2, 1461.7, 1391.4, 1210.1, 1159.0, 1077.0, 931.4, 778.1, 717.4, 468.6.

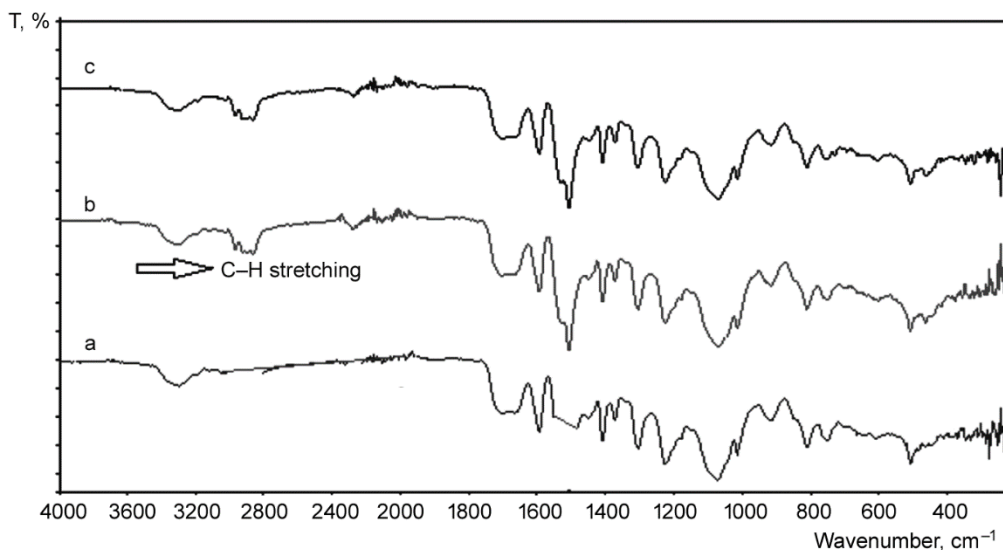


Fig. 2. FTIR spectra of Mt (a), Mt₁ (b), and Mt₂ (c)

The FTIR spectra of Mt, Mt₁ and Mt₂ are shown in Fig. 2. The mode A1 in the octahedral corresponds to the absorption at 3621 cm^{-1} within the spectrum of montmorillonite while hydrogen-bonded water (H–O–H) manifests itself through the band of 3436 cm^{-1} . Si–O stretching vibrations are regarded as an intensive band whereas the stretching modes of the QAS⁺ loaded organoclays were recorded at 2928, 2964, and 2854 cm^{-1} . The interjected surfactant molecules were characterized by a small increase in the wavelengths of C–H antisymmetric stretching modes [9].

The infrared spectra of Mt₁ and Mt₂ (Fig. 2) showed peaks at 1668 cm^{-1} assigned to carbon–carbon and carbon–nitrogen stretching vibrations in QASs⁺. Silicon–oxygen and aluminum–oxygen modes were observed at 990 and 1010 and 618 cm^{-1} , and magnesium–oxygen vibration was assigned to a band between 450 and 515 cm^{-1} .

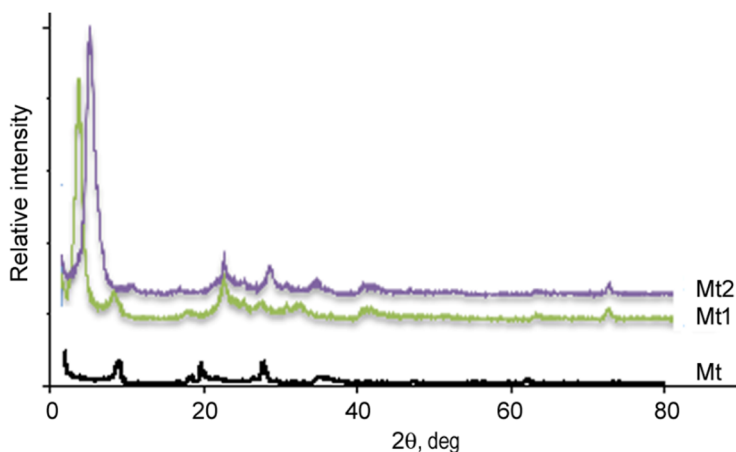
One-dimensional X-ray diffraction patterns of clay and organo montmorillonites are shown in Fig. 3. The d_{001} spacings were calculated (Table 2) from peak positions using Bragg's law equation $2d\sin\theta = n\lambda$ (d is the distance between atomic layers in a crystal, and λ is the wavelength of the incident X-ray beam, n is an integer). It is clear that the d spacing for Mt (9.7 \AA) increased to 21.85 \AA and 22.71 \AA since the small inorganic Na^+ cation was exchanged by quaternary ammonium salts's cation through an ion exchange process [10]. This result indicates that QAS⁺ cations were intercalated into the

montmorillonite interlayer space. Compared to similar studies in the literature such as [15] (the distances between of layer organoclays are 14.5 and 18.0 Å), [18] (the distances between of layer organoclays are 12.4 and 19.1 Å), and 19 (the distances between of layer organoclays are 17.8 and 20.6 Å), the findings show that the quaternary ammonium salts that we used widen the distance between the sheets by very high values.

Table 2

X-ray diffraction data for clay and organoclays

Sample	2θ [deg]	d -spacing [nm]
Mt	6.890	0.979
Mt ₁	4.040	2.185
Mt ₂	4.001	2.271

Fig. 3. XRD patterns of clay (Mt) and organoclays (Mt₁ and Mt₂)

This confirmed that the organoclay was intercalated between the layers. According to the obtained results, the increase in the spacing in the modified organoclays follows the order $Mt_2 > Mt_1$. The higher extent of intercalation corresponding to the largest interlayer distance of 2.271 nm in Mt_2 (compared to 0.973 nm for Mt) was obtained with QAS₂, which has a relatively bulkier cation than the other quaternary ammonium salt (QAS₁).

The fractured surface of organoclays is presented in Fig. 4 as the magnification rate of micrograph was 2.50. As a result of the interaction of clay particles with modifiers, the presence of surfactants increases energy levels and leads to surface tension. The resulting tension causes cracks on the surface. The increase in surface fractures provides mechanical strength to the synthesized organoclays. In this study, a rough surface was obtained as a result of fractures.

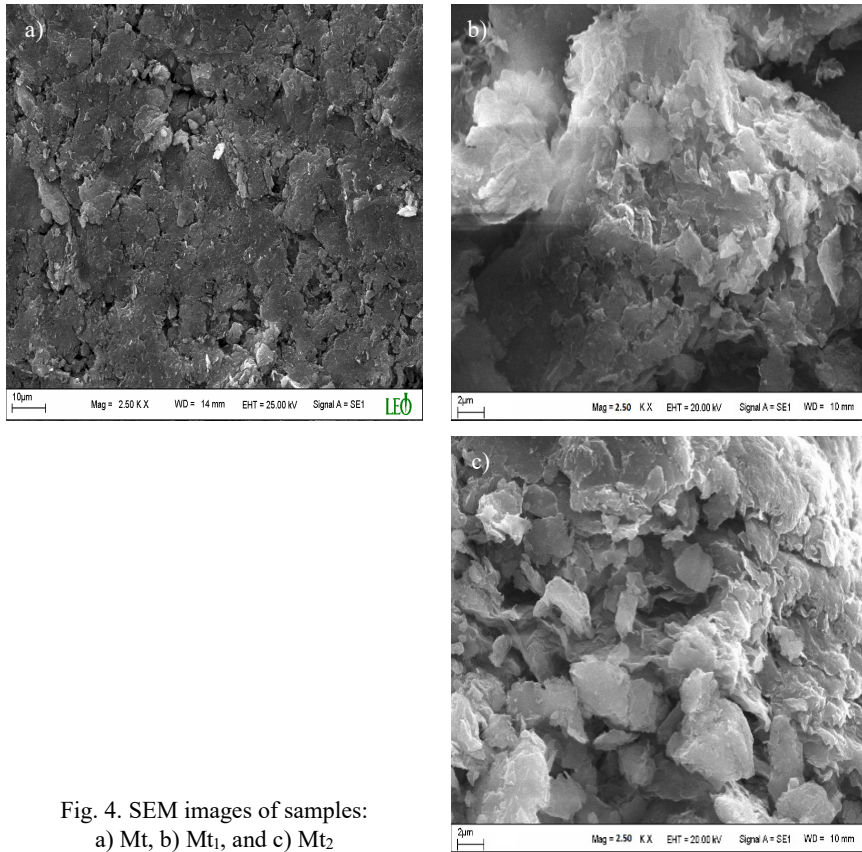


Fig. 4. SEM images of samples:
a) Mt, b) Mt₁, and c) Mt₂

3.2. ADSORPTION KINETICS AND THE EFFECT OF TEMPERATURE

Kinetic curves of 4-NP adsorption are given in Fig. 5. The results showed that 4-NP was adsorbed fast onto organoclays and a steady state was reached after 240 min. The results showed that Mt₂ exhibited higher adsorption rate than Mt₁. Because Mt₂ has been modified with the longer alkyl chain quaternary ammonium salt, it causes the clay layers to become more active, and the adsorption capacity increases. Other than the simplified kinetic models including pseudo-second order equation and intra-particle diffusion models, the most popular one is the pseudo-first order equation generated by Lagergren [11, 12].

The pseudo-first order model depicts properly the adsorption process:

$$\log(q_e - q_t) = \log q_e - \frac{k_{pf}t}{2.303} \quad (2)$$

where q_e and q_t are the amounts of nitrophenol adsorbed at equilibrium and at time t , respectively, and k_{pf} is the first-order rate constant.

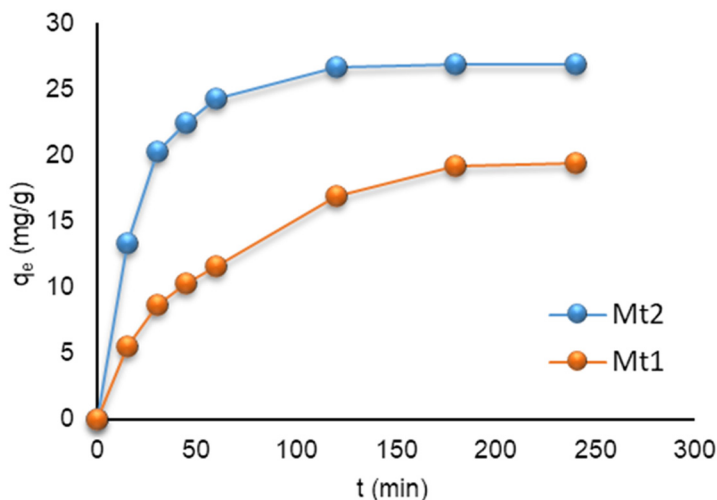


Fig. 5. The effect of contact time on the adsorption of 4-NP 298 K, adsorbent dose 10 g/dm³, C₀ 50 mg/dm³

The values $\log(q_e - q_t)$ were calculated from the kinetic data, plotted against time as shown in Fig. 6a, and the rate constant was calculated (Table 3). The numerical values of the intercept are 0.1294 for Mt₂ and 0.022 for Mt₁.

Table 3

Adsorption kinetic parameters of 4- nitrophenol on organoclays

Sample	First-order kinetic model			Second-order kinetic model			Constant for intraparticle mass transfer	
	k_{pf} [1/min]	q_e [mg/g]	R^2	k_2 [1/min]	q_e [mg/g]	R^2	k_{id} [1/min]	R^2
Mt ₁	0.012	1.09	0.952	0.024	1.110	0.961	0.081	0.798
Mt ₂	0.033	1.02	0.991	0.077	1.403	0.999	0.066	0.883

Despite a great number of sorption kinetic processes proceeding in accordance with the pseudo-first order mechanism, the pseudo-second order one was definitely observed to be more explanatory for phenolic substances adsorbing onto sorbents such as organoclays [13] and the rate control mechanism was chemisorption. The adsorption kinetics may also be described by a pseudo second-order reaction. The linear form of this model is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where k_2 (g/mg·min) is the rate constant of the pseudo-second order adsorption.

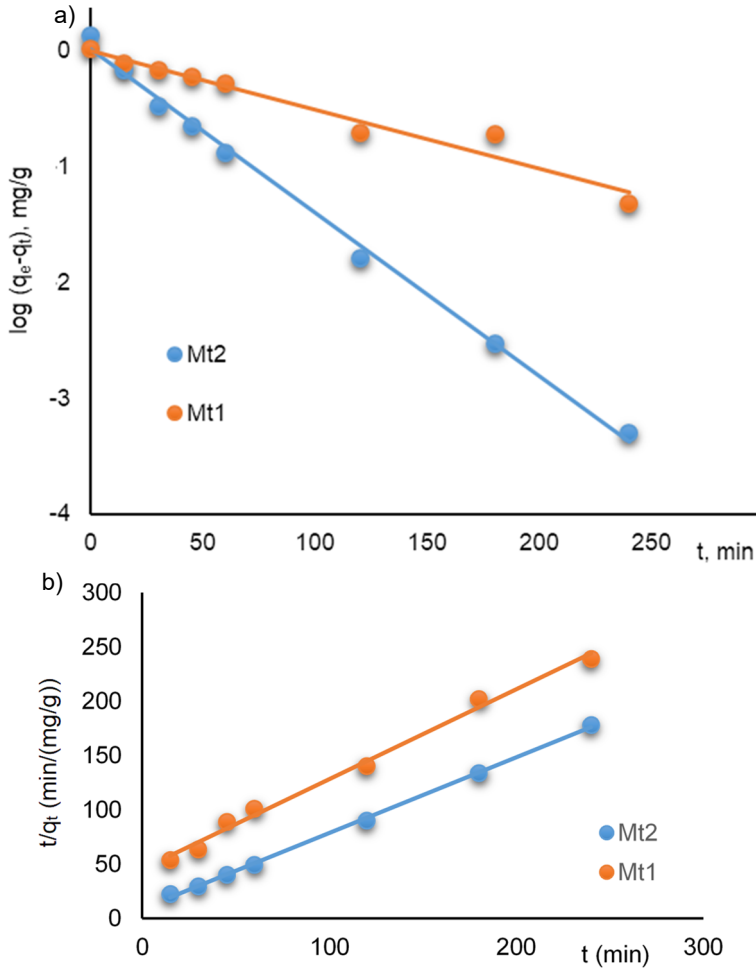


Fig. 6. Lagergren's plots for 4-NP on organoclays: a) pseudo-first order model, b) pseudo-second order model; 298 K, adsorbent dose 10 g/dm^3 , C_0 50 mg/dm^3

High correlation coefficients (0.96 and 0.997) indicated that the adsorption process is more compatible with a pseudo-second order rate mechanisms. The second-order rate constants were calculated from Fig. 6b. The rate constants k_{pf} of pseudo-first order adsorption for Mt₁ and Mt₂ were found 0.012 and 0.033 1/min, while the rate constant k_2 of pseudo-second order adsorption for Mt₁ and Mt₂ were found 0.024 and 0.077 g/mg.min, respectively (Table 3).

The rate constant for intraparticle mass transfer (k_{id}) is given as:

$$q_t = k_{id} t^{1/2} \quad (4)$$

where q_t is the amount adsorbed (mg/g) at time t . The plots of q_t vs. $t^{1/2}$ for Mt₁ and Mt₂ are shown in Fig. 7.

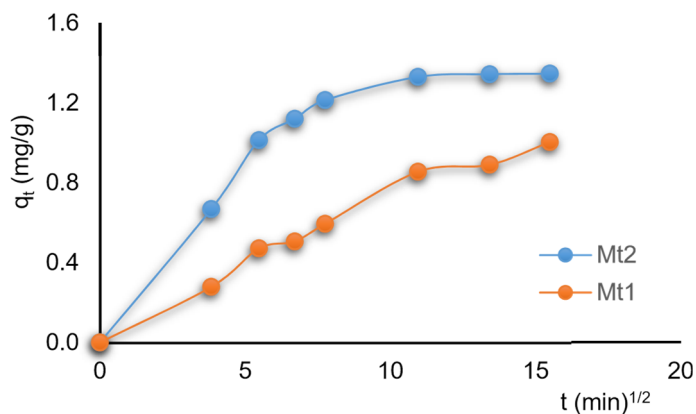


Fig. 7. Intraparticle mass transfer plots of 4-NPs on organoclays; 298 K, adsorbent dose: 10 g/dm³, C_0 50 mg/dm³)

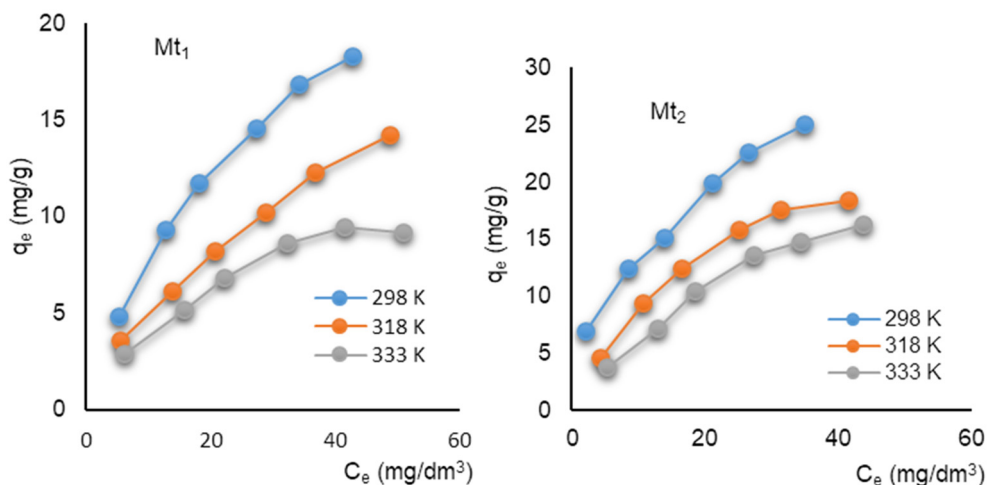


Fig. 8. Isotherms of Mt₁ and Mt₂ adsorption from solution at various temperatures, adsorbent dose 10 g/dm³, C_0 50 mg/dm³

The parameters of pseudo-first order, pseudo-second order and intraparticle mass transfer models were obtained (Table 3). The pseudo-second order kinetic model fitted better than the pseudo-first order model in this study. This indicates that the organoclays reached equilibrium time in the order Mt₂ > Mt₁. The results suggest that this adsorption system fit the pseudo-second order model based on the assumption that the rate-limiting step may be chemical adsorption or chemisorption, and the model provides the best

correlation of the experimental data [12]. Therefore, the chemical reaction in this study may be the rate controlling step.

The removal of 4-NP by organoclay was studied at 298, 318, and 333 K to determine the adsorption isotherms. The adsorption efficiency for 4-NP on organoclay decreased with increasing temperatures from 298 K to 318 and 333 K. (Fig. 8). It was observed that the increase in temperature from 298 K to 333 K decreased the adsorption capacity of bentonite, indicating an exothermic process of adsorption [14]. The decrease of adsorption with temperature was mainly due to the weakening of adsorptive forces between the active sites of organoclay and 4-NP [15].

3.3. ADSORPTION ISOTHERMS

In order to quantitatively describe the adsorption of nitrophenol by organo-montmorillonites, Langmuir and Freundlich equations were used. The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the adsorbed molecules [16]. The Langmuir adsorption model is typically used for homogenous surfaces, with monolayer onto the surface and decline the concept of multilayer adsorption as in case of heterogeneous surfaces [17].

The Langmuir equation is

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (5)$$

where q_e (mg/g) is the amount of 4-NP adsorbed per unit mass of adsorbent at equilibrium, C_e (mg/dm³) is the equilibrium liquid phase concentration of 4-NP, and b is the equilibrium constant (dm³/mg) which b relates to the affinity of binding sites to adsorb a given solute. q_m represents the adsorption capacity when the surface is fully covered with 4-NP molecules. The values of b and q_m were calculated from the slope and intercept of the straight lines of the plot of C_e/q_e vs. C_e .

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems:

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

and in the logarithmic form:

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (7)$$

where q_e is the nitrophenol amount (mg/g) adsorbed by organoclay in the equilibrium state, k_F (dm^3/g) is adsorption coefficient being an indicator of the adsorption capacity, C_e is the nitrophenol concentration (mg/dm^3) in equilibrium liquid phase, and n is the exponential coefficient, responsible for the adsorption intensity [16, 17] (Figs. 9, 10).

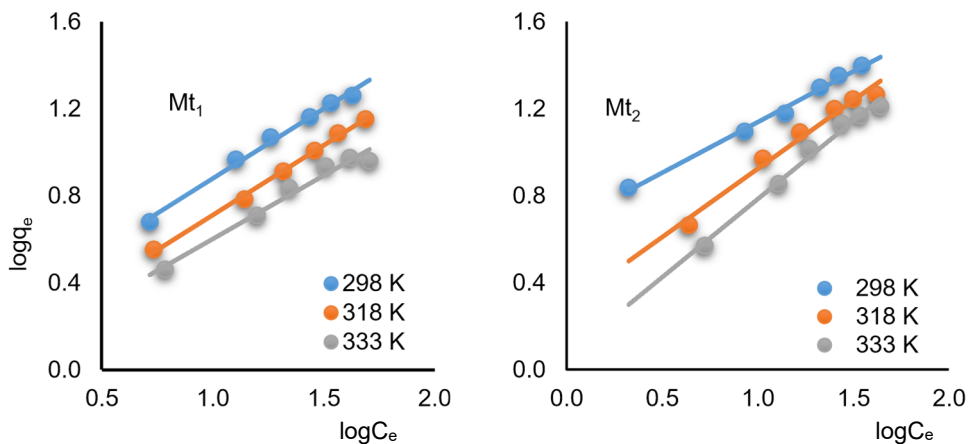


Fig. 9. Freundlich adsorption isotherms of 4-NP at various temperatures for Mt₁ and Mt₂

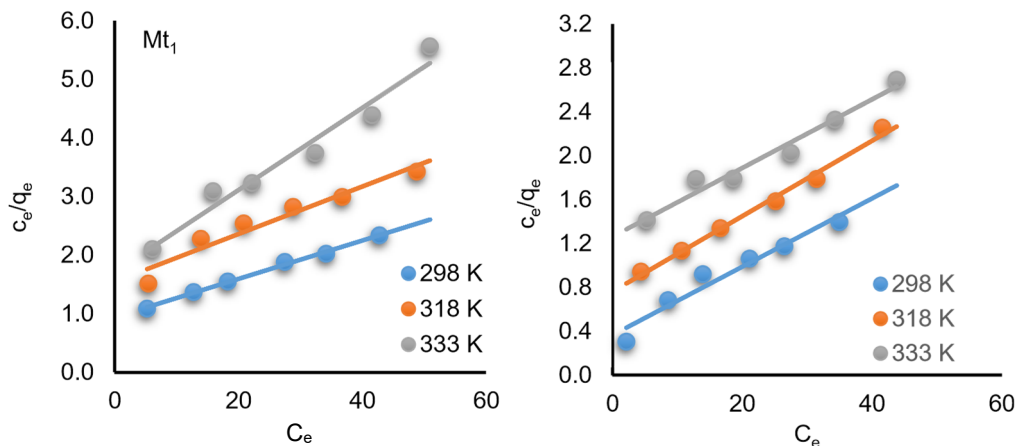


Fig. 10. Langmuir adsorption isotherms of 4-NP at various temperatures for Mt₁ and Mt₂

The values b , q_m , k_F , and n are summarized in Table 4. The isotherm data were calculated by the least square method, and the related correlation coefficients (R^2) are also given in Table 4. As seen in Table 4, the Freundlich isotherm fits well the experimental data ($R^2 = 0.97\text{--}0.99$ for Mt₁ and Mt₂, respectively), whereas, the lower correlation coefficients ($R^2 = 0.94\text{--}0.99$ for Mt₁ and Mt₂, respectively) show more poor agreement between the Langmuir isotherm and the experimental data.

Table 4

Langmuir and Freundlich isotherm constants for adsorption of 4-NP on organoclays

Sample	T [K]	Langmuir constants			Freundlich constants		
		q_m (mg/g)	b (dm ³ /mg)	R^2	k_F (mg/g)(mg/dm ³) ^{-1/n}	n	R^2
Mt ₁	298	14	0.041	0.96	1.27	1.56	0.99
	318	25	0.072	0.94	1.08	1.56	0.99
	333	30	0.035	0.99	1.02	1.72	0.97
Mt ₂	298	32	0.025	0.96	1.96	2.14	0.99
	318	29	0.045	0.99	1.35	1.59	0.98
	333	32	0.085	0.94	1.07	1.39	0.99

Generally, n represents a constant value indicating the affinity between adsorbent and adsorbate, and the range of 1–10 means the sufficient adsorption [7]. In this study, the constant n was favourably within the range of (1–10) (see Table 5).

Table 5

Adsorption capacities (k) and the adsorption coefficients (n) for 4-NP

Adsorbent	Freundlich constants		Reference
	k_F (mg/g)(mg/dm ³) ^{-1/n}	n	
DDTMA	0.578	0.316	[2]
Fe-SMPM	0.003	2.30	[8]
HDTMA ⁺ -Mt	20.83	1.73	[16]
CTAB	20.25	1.45	[18]
Mt ₁	1.27	1.56	present study
Mt ₂	1.96	2.14	

4. CONCLUSION

Montmorillonite was converted to hydrophobic organoclays by intercalation with cationic surfactants (QASs⁺) in order to improve its adsorption capacity for organic pollutants. The synthesized organoclays were characterized using various techniques.

New QASs⁺ were synthesized for this study, and organoclays were prepared using montmorillonite, 1-methyl-di-nonyl-1 phenyl ammonium iodide (QAS₁) and 1-methyl-di-dodecyl-1 phenyl ammonium iodide (QAS₂) as examples of surfactants with a long alkyl chain. The kinetic data may be best described by a pseudo-second order equation. Adsorption of 4-NP on QASs⁺-exchanged montmorillonites followed the Freundlich equation well. Due to the interlayer cation exchange by the QASs⁺ cation surfactant, the

adsorption of the 4-NP on organoclay was improved greatly, and the adsorption isotherms were linear. The organoclay obtained by modifying with the newly synthesized QAS_1^+ showed efficient adsorption for the 4-NP that is known as a pesticide.

ACKNOWLEDGMENTS

The author thanks Haluk Aydın, Serhat Uzan and Dicle University for their valuable support.

REFERENCES

- [1] SHEN H.M., ZHU G.Y., YU W.B., WU H.K., JI H.B., SHI H.X., SHE Y.B., ZHENG Y.F., *Fast adsorption of p-nitrophenol from aqueous solution using β -cyclodextrin grafted silica gel*, Appl. Surf. Sci., 2015, 356, 1155.
- [2] PARK Y., AYOKO G.A., KURDI R., HORVATH E., KRISTOF J., FROST R.L., *Adsorption of phenolic compounds by organoclays: Implications for the removal of organic pollutants from aqueous media*, J. Coll. Int. Sci., 2013, 406, 196.
- [3] PACURARIU C., MIHOC G., POPA A., MUNTEAN S., *Adsorption of phenol and p-chlorophenol from aqueous solutions on poly (styrene-co-divinylbenzene) functionalized materials*, Chem. Eng. J., 2013, 222, 218.
- [4] HATEM A.A., MAAH M.J., YAHYA R., BINABAS M.R., *Isotherms, kinetics and thermodynamics of 4-nitrophenol adsorption on fiber-based activated carbon from coconut husks prepared under optimized conditions*, Asian J. Chem., 2013, 25 (17), 9573.
- [5] BAYSAL G., AYDIN H., UZAN S., HOSGOREN H., *Investigation of antimicrobial properties of $QASs^+$ (novel synthesis)*, Russ. J. Phys. Chem. B, 2018, 12 (4), 696.
- [6] ZHOU Q., FROST R.L., HE H., XI Y., LIU H., *Adsorbed para-nitrophenol on HDTMAB organoclay. An TEM and infrared spectroscopic study*, J. Coll. Int. Sci., 2007, 307, 357.
- [7] AYDIN H., BAYSAL G., BULUT Y., *Utilization of walnut shells (Juglans regia) as an adsorbent for the removal of acid dyes*, Des. Water Treat., 2009, 2, 139.
- [8] ZERMANE F., BOURAS O., BAUDU M., BASLY J.P., *Cooperative coadsorption of 4-nitrophenol and basic yellow 28 dye onto an iron organo-inorgano pillared montmorillonite clay*, J. Coll. Int. Sci., 2010, 350, 316.
- [9] BAYSAL G., *Investigation analysis results and modification of Na^+ -montmorillonite with quaternary ammonium salt and ionic liquid*, Int. J. Food Eng., 2015, 1, 3.
- [10] KIM N.H., MALHOTRA S.V., XANTHOS M., *Modification of cationic nanoclays with ionic liquids*, Micropor. Mesopor. Mat., 2006, 96, 29.
- [11] ULLAH H., NAFEEES M., IQBAL F., SAIFULLAH M.A., SHAH A., WASEEM A., *Adsorption kinetics of Malachite Green and Methylene Blue from aqueous solutions using surfactant-modified organoclays*, Acta Chim. Slov., 2017, 64, 449.
- [12] PARK Y., AYOKO G.A., KURDI R., HORVATH E., KRISTOF J., FROST R.L., *Structural characterisation and environmental application of organoclays for the removal of phenolic compounds*, J. Coll. Int. Sci., 2013, 393, 319.
- [13] OFOMAJA A.E., UNUABONAH E.I., *Kinetics and time-dependent Langmuir modeling of 4-nitrophenol adsorption onto Mansonia sawdust*, J. Taiwan Inst. Chem. Eng., 2013, 44, 566.
- [14] VARANK G., DEMIR A., YETILMEZSOY K., TOP S., SEKMAN E., BILGILI M.S., *Removal of 4-nitrophenol from aqueous solution by natural low-cost adsorbents*, Indian J. Chem. Technol., 2012, 19, 9.
- [15] BORISOVER M., BUKHANOVSKY N., LAPIDES I., YARIV S., *Thermal treatment of organoclays. Effect on the aqueous sorption of nitrobenzene on n-hexadecyltrimethyl ammonium montmorillonite*, Appl. Surf. Sci., 2010, 256, 5539.

- [16] XIN X., WANG J., YU H.Q., DU B., WEI Q., YAN L.G., *Removal of o-nitrobenzoic acid by adsorption on to a new organoclay: montmorillonite modified with HDTMA microemulsion*, Environ. Techn., 2011, 32, 452.
- [17] NAFEEES M., WASEEM A., *Organoclays as a sorbent material for phenolic compounds: A review*, Clean Soil, Air, Water, 2014, 42 (11) available online, <https://onlinelibrary.wiley.com/doi/abs/10.1002/clen.201300312>
- [18] DOS S.A., VIANTEA M.F., POCHAPSKI D.J., DOWNS A.J., ALMEIDA C.A.P., *Enhanced removal of p-nitrophenol from aqueous media by montmorillonite clay modified with a cationic surfactant*, J. Hazard. Mater., 2018, 355, 141.
- [19] PARK Y., AYOKO G.A., FROST R.L., *Characterisation of organoclays and adsorption of p-nitrophenol. Environmental application*, J. Coll. Int. Sci., 2011, 360, 440.