Cleaning of pesticides from aqueous solution by a newly synthesized organoclay

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Abstract: In the present study, the novel quaternary ammonium salt (QAS^+), 1-methyl-di-octyl-1 phenyl ammonium iodide (QAS_1), was synthesized by complete alkylation reaction. Sodium montmorillonite (Mt) was modified via an ion-exchange reaction with QAS_1^+. The modified material and quarternary ammonium salt (Mt_1 and QAS_1) were analyzed by nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). Removal capacity of hydrophobic organic pollutants such as 4-nitrophenol (4-NP) and 2,4-dinitrophenol (2,4-DNP) from solution media of synthesized organoclay was evaluated. The optimum conditions and batch kinetics of adsorption of 4-nitrophenol and 2,4-dinitrophenol from aqueous solutions are reported. It was shown that the adsorption capacity decreased in the order 4-NP> 2,4-DNP. The total mass loss during the drying process was 66% and 78%, respectively. Thermodynamic parameters enthalpy (ΔH^0) and entropy (ΔS^0) and the mean free energy (E) for the adsorption of nitrophenol compounds (NCP) were determined.

Introduction

Hydrophilicity of the surfaces of clay minerals is resulted from inorganic cations hydrating from the sites of exchange, which contributes to the ineffectiveness of natural clays to be used as sorbent for organic compounds (Park et al. 2011, Shen et al. 2015, Zhou et al. 2008). This is, nevertheless, a handicap needed to be mounted via replacement of inorganic with organic cation ions (Frost et al. 2008).

In comparison of other sorbents (e.g. activated carbons) for adsorption by withdrawal, use of the clays altered in an organic way is increasingly popular because of its lower cost, among a variety of physicochemical and biological techniques to oust organic contaminants from effluent waters (Koyuncu et al. 2011).

Nitro compounds (e.g. nitrobenzene, nitrotoluenes and nitrophenols) available in either natural or effluent water can be derived from any causative actions, adding a disgusting taste and giving off stink into potable waters, (Varank et al. 2012) regardless their quantity of concentration, and thus analyzing these noxious compounds for living organisms is primarily significant to prevent environmental pollution. As a result of their universal use, they have a large quantity of water, soil and air (Marek et al. 2010, Pham and Chihiro 2019).

Within the ingredients of many synthetic compounds, pesticides, insecticides, and herbicides generated by the waste fluids of mine processing plants, metal casting foundries and metal finishing factories, a primary input is included, called nitrophenole, a normal bio-refractory organic compound. Chemical facilities often generate waste waters having these substances, which, in turn, makes the disposal activity more complicated (Al-Mutairi 2010).

The objective of this research is to use synthesized organoclay with a newly synthesized quaternary ammonium salt to adsorb 4-nitrophenol and 2,4-dinitrophenol from an aqueous solution. For this reason, 1-methyl-di-octyl-1 phenyl ammonium iodide (QAS_1) was synthesized as a modifier and the montmorillonite clay was modified with the synthesized quaternary ammonium salt. The characteristics of quaternary ammonium salts vary as the length of the alkyl chain in their structure increases. As the chain length increases, water solubility decreases and adsorption ability increases. Therefore, in this study, the long alkyl chain quaternary ammonium salt (QAS_1) was synthesized, and its adsorption capacity was evaluated by using it for organoclay synthesis. The newly synthesized organoclay was used to remove the aqueous solution of nitrophenol compounds by the adsorption technique and when compared with the literature, it was seen that it presents highly effective results.

As a result, this study can be considered as an alternative method for waste management and environmental pollution reduction (Gorka and Cimochowicz-Rybicka 2019).

Materials and methods

Materials

Modifier, 1-methyl-di-octyl-1 phenyl ammonium iodide (QAS_1) was newly synthesized. The nitrophenol compound that was used was of analytical grade. Montmorillonite (commercial tag: Cloisite-Na$^+$, CAS# 1318-93-0, Southern

Clay Products Inc.), methyl iodide (Merck) and ethyl acetate (Merck) were purchased. The physical and chemical properties of Mt are shown in Table 1.

Synthesis of QAS$_1$ (1-methyl-di-octyl-1 phenyl ammonium iodide)

Freshly distilled methyl iodide with a mass of 5.22 g (0.03676 mol) was added onto 1.0 g N,N-dinonyl-N-(l-phenylethyl) amine. Termination of the reaction was controlled by thin layer chromatography (TLC) on the next day. Excess methyl iodide was evaporated. The reaction mixture was irrigated with octyl:ethyl acetate with a ratio of 5:1 (v/v). The irrigation solvent was decanted. The remaining part was dried under a vacuum (Koyuncu et al. 2011).

The structure of QAS$_1$ is shown in Fig 1. The synthesized salt was analyzed by NMR technique.

Preparation of the organoclay

The cation-exchange method was effective to produce the organoclay (Mt$_1$), in which the sodium cations in Mt are replaced by the QAS$^+$. In general, the layered swollen silicates were achieved with mechanically 1-h blending Mt (1.0 g) with deionized water-ethanol v/v (1:1) (0.1 L) at 298 K. The diluted solution of the QAS$_1$ itself was produced through its dissolution (50% more than the clay CEC) in deionized water–ethanol

(0.05 L) at 298 K. The next step was to put the dispersed clay into this solution, using mechanical blending the mixture at 298 K for 24 h. The precipitates were altered and filtered using a disc filter funnel. Mt$_1$ was washed several times with deionized water–ethanol (about 0.1 L) to eliminate all iodide ions in the AgNO$_3$ solution. The remaining substance was dried in high temperatures like 343 K for 8 h. The new product of organoclay was finally had by means of grounding and screening the dried cake with a 100-mesh sieve (Baysal et al. 2018).

Adsorption experiments of the nitrophenol compounds on the organoclay

Adsorption kinetics

Stock solutions of 4-nitrophenol (4-NP; Fw = 139 g·mol^{-1}) and 2,4-dinitrophenol (2,4-DNP; Fw = 184 g·mol^{-1}) (1 g·L^{-1}) (Fig. 1) were obtained through dissolution of the adequate solute individually in distilled water at room temperature, and 4-h stirring (Zermane et al. 2010).

Kinetic studies were performed in an flasks at room temperature by blending sorbent (1.0 g; Mt$_1$) with solution (100 mL) containing 4-NP (30 mg·L^{-1}) and 2,4-DNP (10 mg·L^{-1}) at 250 rpm on a mechanical tool. The samples were picked up from the shaker at intervals from 15 to 240 min (Varank et al. 2012) and the concentrations (4-NP and 2,4-DNP) were detected under UV-visible spectrophotometry.

Table 1. The physical and chemical properties of Na$^+$- MMT

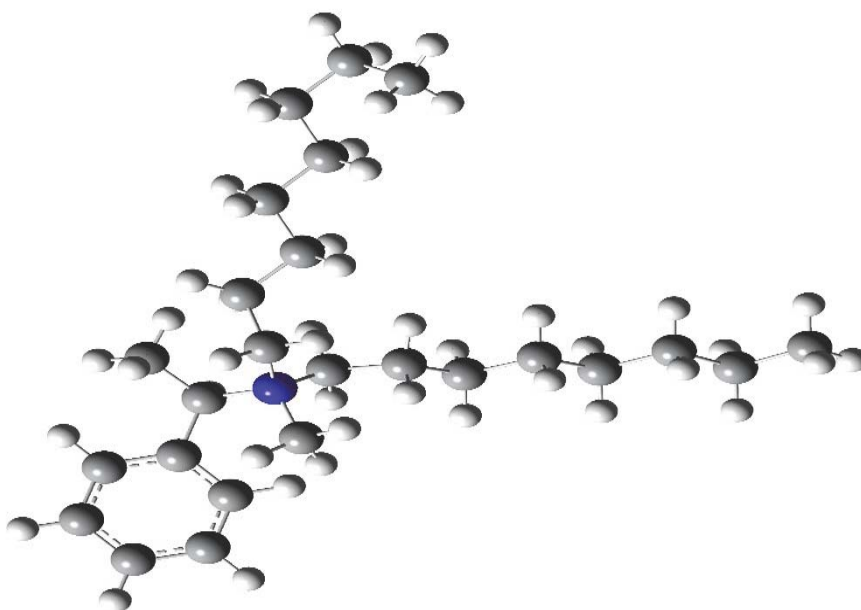| Molecule formula	(Na, Ca)$_{0.33}$(Al, Mg)$_2$ Si$_4$O$_{10}$(OH)$_2$ 6H$_2$O
The density [g·cm^{-3}]	2.86
pH (3% solution)	8
The specific surface area [m^2·g^{-1}]	750
CEC [meg·100 g^{-1}]	92
The percent of composition [%]	1.40 Na, 2.44 Ca, 9.99 Al, 8.88 Mg, 20.7 Si, 35.53 O, 0.37 H

Fig. 1. The structure of 1-methyl-di-octyl-1 phenyl ammonium iodide

Adsorption isotherms

Isothermic adsorption trials were made by shaking Mt_1 samples (1.0 g each) with diluted solution (50 mL). All flasks were initially filled with the solutions of nitrophenol compounds (50 mL) including different concentrations in quantity (15, 20, 25, 30, 35, 40 mg·L^{-1} for 4-nitrophenol and 5, 10, 15, 20, 25, 30 mg·L^{-1} for 2,4-dinitrophenol) at different temperatures (298, 318 and 333 K) and adsorbent doses (10, 20, 40, 60, 80, 100 mg·L^{-1}). Following 4-h stirring at 250 rpm and then 15-min centrifugation at 3500 rpm, the diluted concentrations (4-nitrophenol and 2,4-dinitrophenol) were observed on a Ultraviolence-Visible spectrophotometer at 317 nm (Zermane et al. 2010) and 361 nm, respectively.

In order to obtain thermodynamic results, these studies were done at different temperatures (298, 318 and 333 K). The retention level for organoclays (4-nitrophenol (4-NP) and 2,4-dinitrophenol (2,4-DNP)) was found by the following equation:

$$q_e = \frac{(c_0 - c_e) \cdot v}{m} \qquad (1)$$

Where:

q_e – is the retention level of nitrophenol compounds,
C_o – is the initial concentration,
C_e – is the concentration level at equilibrium,
V – is the volume of nitrophenol solution,
m – is the mass of the adsorbent (Baysal 2019, Frost et al. 2008).

Characterization of organoclay

Infrared spectra were carried out on Mattson 1000 infrared spectrophotometer using the potassium bromide disc technique in the wavenumber range of 4000–400 cm^{-1}. [1]H-spin-lattice relaxation times and ^{13}C-NMR were measured by Bruker DPX- 400 MHz high performance digital FT-Nuclear Magnetic Resonance spectrometer. The samples were characterized by X-ray diffraction (XRD) for the crystal structure, average particle size and the concentration of impurity compounds present. Rigaku Rad B-Dmax II powder X-ray diffractometer was used for X-ray diffraction patterns of these samples. Morphology of the composite was examined by a JEOL JSM 5600 LV scanning electron microscopy (SEM) equipped with an energy dispersive X-ray detector to examine the morphology and effect of QAS^+ in the Mt.

Results and discussion

NMR results

New synthesized QAS_1 was analyzed by NMR. The results are given below to confirm that the synthesized quaternary ammonium salt is of specific character.

1H NMR (400 MHz, CDCl$_3$) δ 0.696 -CH$_2$CH$_3$ (t, 6H, J=6.8), 1.116–1.716 CH$_2$(CH$_2$)$_4$CH$_3$ (m, 16H), 1.707 ArCHCH$_3$N$^+$ (d, 3H, J=6.8), 2.936 N$^+$CH$_3$ (s, 3H), 3.042–3.488 N$^+$CH$_2$ (m, 4H), 5.022 ArCHCH$_3$N$^+$ (q, 1H, J=6.8), 7.266–7.545 Ar-H (m, 5H); 13C NMR (100 MHz, CDCl$_3$) δ 13.73, 13.77, 15.96, 22.22, 22.30, 22.84, 22.92, 25.95, 26.06, 31.01, 45.90, 59.31, 60.07, 70.97, 129.05, 130.45, 131.02, 132.22; IR: ν 3437.15, 2954.43, 2924.54, 2857.04, 2185.93, 1457.93, 1390.44, 1378.87, 1282.44, 919.89, 712.58, 478.27.

FT-IR spectroscopy

FT-IR spectra are prepared for Mt and organoclay, as presented in Fig. 2 (a, b). Mt refers to broadband (3200 to 3800 cm^{-1}). The band of O-H represents water adsorption on the mineral of montmorillonite (shoulder) and its normal level is 3627 cm^{-1} (Fig. 2b) while the stretching wave number areas for O-H groups are 3416 cm^{-1}. The stretching region of C-H is related to the surface active molecules in the region of 2850–2928 cm^{-1} (see Fig. 2b). These bands are attributed to the C-H antisymmetric and symmetric stretching modes. For the QAS_1^+ loaded organoclays, stretching modes are found at 2928, 2964 and 2854 cm^{-1}. The C-H antisymmetric stretching modes are found to be slightly different, shifting towards greater wave numbers upon infiltration of the surface active molecules (Baysal et al. 2018).

The infrared spectrum of Mt_1 is referred to carbon-carbon and carbon-nitrogen stretching vibrations in QAS^+ (Fig. 2b) demonstrates the peak levels at 1668 cm^{-1}. Fig. 2 introduces a spectrum of organoclays, in which the silicon-oxygen bonds are identified at 990 cm^{-1}, and aluminum-oxygen bonds at 1010 cm^{-1} and 618 cm^{-1}, and magnesium oxide is represented by a band present in the range of 450 to 515 cm^{-1}.

X-ray diffraction analyses

The cation exchange from the sodium ion to the cationic surface active agent extends the layers on the montmorillonite. Such extension is simply evaluated using X-ray radiation. In Fig. 3,
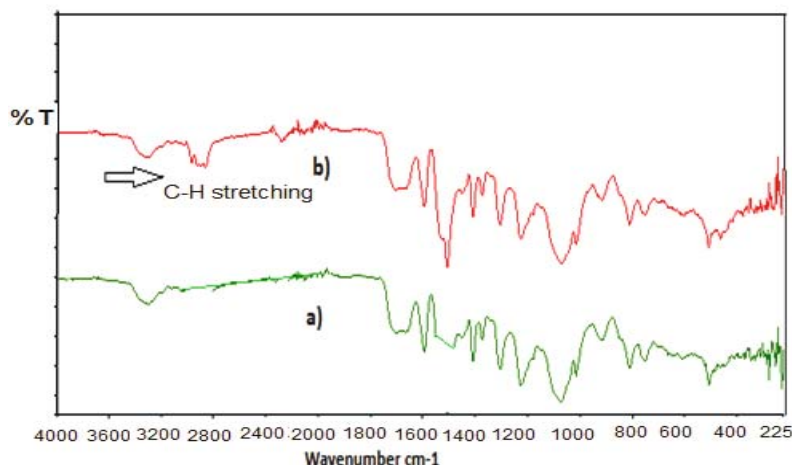

Fig. 2. FTIR spectra of (a) Mt and (b) Mt_1

XRD patterns of montmorillonite and its hybrid infiltrated by surfactant are presented. The distance between the layers of clay was calculated according to Bragg's law. Bragg's law refers to equation 2d sinθ = nλ, (the variable d is the distance between atomic layers in a crystal, and the variable lambda λ is the wavelength of the incident X-ray beam; n is an integer). As the loaded surface active agents proliferated, the values of d0 0 1 increased gradually as follows: 0.97 nm (Na$^+$-Mt)→1.71 nm (MMT-QAS$^+$), which means the enlargement of basal spacing from montmorillonite to Mt$_1$ (0.97 nm to 1.71 nm in value). It can be inferred from these outcomes that the cations of QAS$_1^+$ were infiltrated into the spacing between layers on the clay. In comparison to similar studies in the literature (the distances between the layers of the organoclays were 14.4, 14.5 and 18.0°A), the findings show that highly successful result were obtained (Borisover et al. 2010, Park et al. 2011).

Scanning electron microscopy

According to SEM analysis in accordance with a sampling method, several fractures occurred on the organoclay surfaces. In Fig. 4. the micrograph displays the fractured areas in the scale of 1 to 10. The stress and strain over the surface fractures become greater depending on dispersion and concentration on the clay as well as the modifier. From the results, it indicates that energy correlates with the stress and strain levels.

Contact time

Identification of the maximum level of adsorption and the equilibration process was described as the aim of this study, in which the independent variable was established as contact time. The time required for adsorption at equilibrium for the nitrophenol compounds was computed as about 240 min, and the process was rather fast at early times (see Fig. 5).

Adsorption kinetics

In the analysis of kinetics, the curves representing the results of 4-NP and 2,4-DNP suggested that the time period was shorter in 2,4-DNP than that of 4-NP in being adsorbed onto Mt$_1$; whereas the adsorption speed gradually declined for 240 min until the process ran for 4-NP and 2,4-DNP at a steady pace (see Fig. 5). The adsorption kinetics results showed that 4-NP exhibited a higher adsorption rate than 2,4-DNP because in the
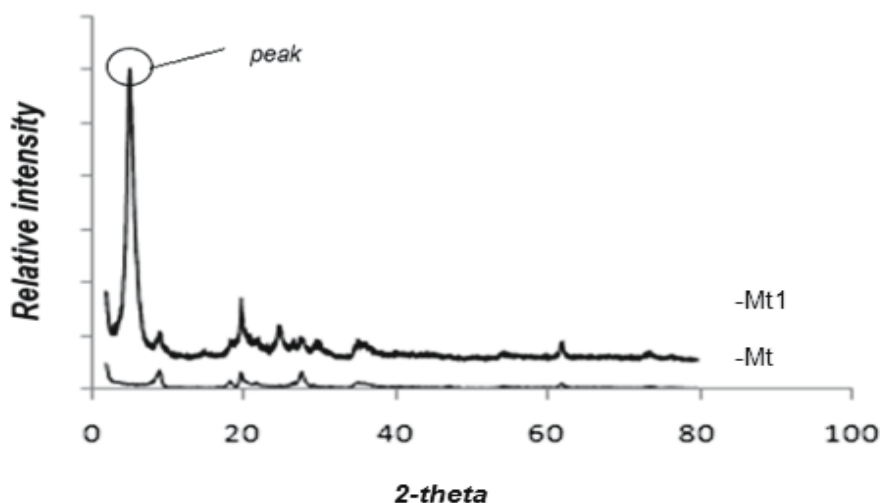

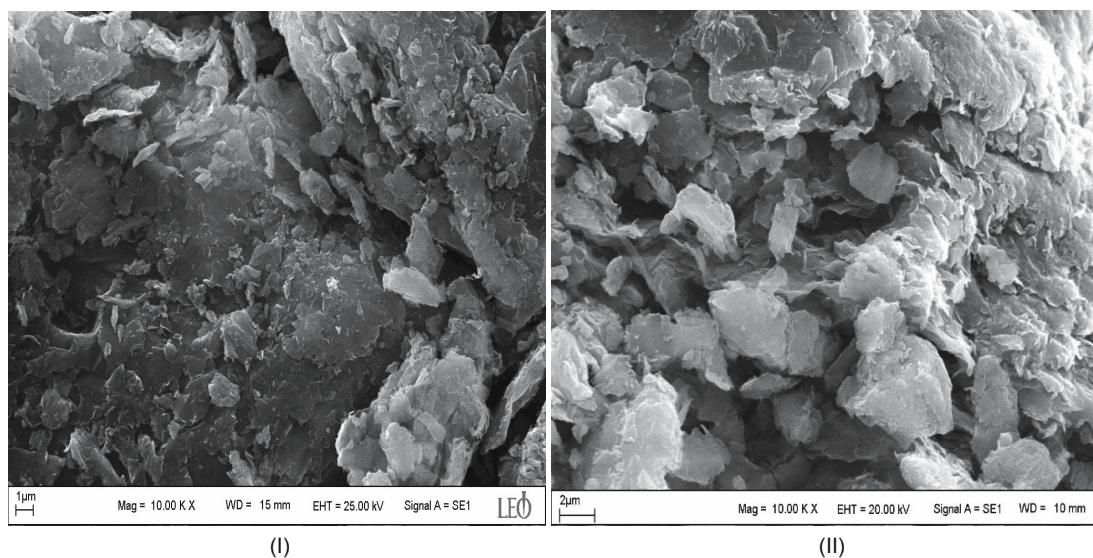**Fig. 3.** XRD patterns of clay (Mt) and organoclay (Mt$_1$)

Fig. 4. SEM images of samples, I) Mt, II) Mt$_1$

4-nitrophenol compound, the hydroxyl group was attached at the para position to the benzene rig. This provided resonant stability, and therefore, the adsorption capacity increased. When it reached equilibrium, the adsorption capacities were calculated as 78% for 4-NP and 66% for 2,4-DNP.

The results of the adsorption kinetics analysis are illustrated in Fig. 5. The plots represent the quantity of sorbent, qt in nitrophenol compound onto organo-montmorillonites versus time t. The initial concentrations were identified as 30 mg·L^{-1} for 4-NP and 10 mg·L^{-1} for 2,4-DNP, and at the end of the trials, it was observed that the equilibration process took 240 min for Mt$_1$.

In the literature, various studies reported that a pseudo-first--order rate mechanism is common to study adsorption kinetics, whereas a pseudo-second-order equation is undoubtedly used to uncover the process of phenolic compounds being adsorbed onto sorbents including organoclays.

The pseudo-first-order model depicts properly the adsorption process (Liu et al. 2008):

$$\log(q_e - q_t) = \log q_e - k_{pf} \cdot t \qquad (2)$$

Where:
q$_e$ and q$_t$ – are amount of nitrophenol adsorbed at equilibrium and at time t, [mg·g^{-1}],
k$_{pf}$ – is the first-order rate constant.

The values log (q$_e$–q$_t$) were calculated from the kinetic data and plotted against time as shown in Fig. 6. Good correlation coefficients (0.92 and 0.98) indicate that Lagergren's equation is applicable and the adsorption process is first order. The first--order rate constants (the adsorption rate constant) calculated from Fig. 6 are 0.16 and 0.025 min^{-1} for 4-NP and 2,4-DNP, respectively. The adsorption kinetics may also be described by a pseudo second-order reaction. The linear form of this model is:

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

Where:
k – is the rate constant of pseudo-second-order adsorption [g·mg^{-1}·min^{-1}].

The rate constant k$_{pf}$ of pseudo-first-order adsorption for 4-NP and 2,4-DNP was found 0.16 and 0.025 1·min^{-1}, while the rate constant k$_2$ of pseudo-second-order adsorption for 4-NP and 2,4-DNP was found 0.122 and 0.283 g·mg^{-1}·min^{-1}, respectively (Table 2).

The rate constant for intraparticle diffusion (k$_{id}$) is given as:

$$q_t = k_{td} \cdot t^{1/2} \qquad (4)$$

Where:
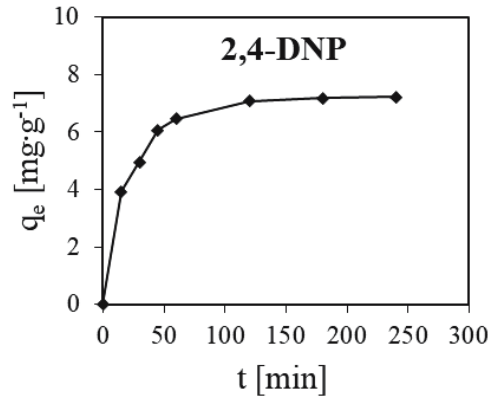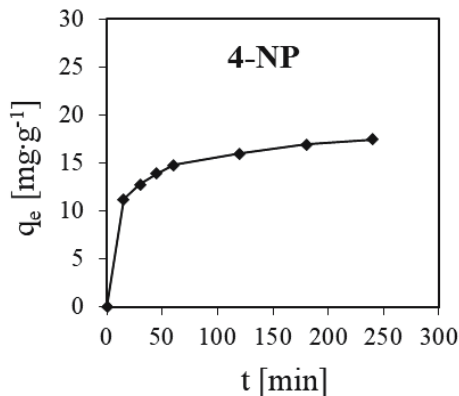q$_t$ – is the amount adsorbed [mg·g^{-1}] at time t [min].

Fig. 5. The effect of contact time on the adsorption of nitrophenols (T: 298 K, 4-NP-C$_o$ = 30 mg, 2,4-DNP-C$_o$: 10 mg, adsorbent = 1 g 0.1 L^{-1})
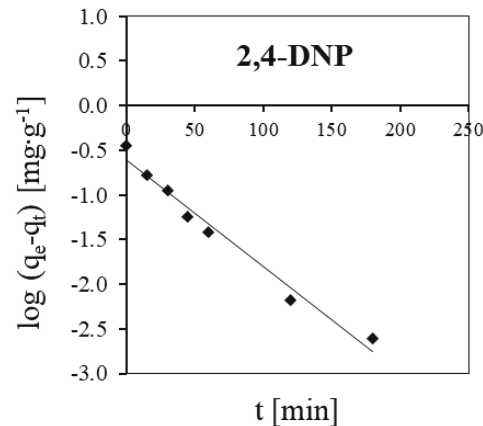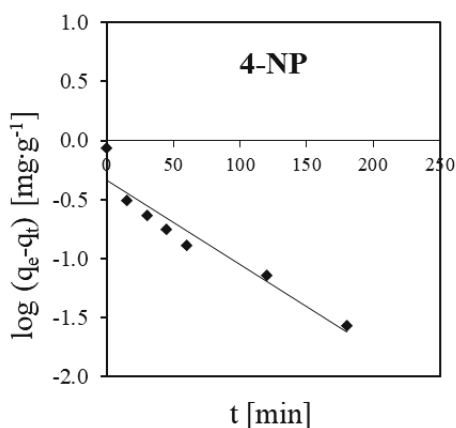

Fig. 6. Lagergren's plot for NPC on Mt$_1$ (T: 298 K, adsorbent = 1 g 0.1 L^{-1}, 4-NP-C$_o$ = 30 mg, 2,4-DNP-C$_o$: 10 mg)

The plots of q_t versus $t^{1/2}$ for Mt_1 are shown in Fig. 7.

The parameters of the pseudo-first-order, pseudo-second--order and intraparticle mass transfer models were obtained and are summarized in Table 2. In this study, it was seen that the adsorption system conformed to the pseudo second order model according to Table 2. This was because the correlation values of the pseudo-second-order model were closer to 1. In light of this result, the rate-limiting step in the adsorption system may be chemical adsorption or chemisorption. For this reason, the chemical reaction in this study expressively managed the rate-controlling step.

Effect of temperature

The equilibrium capacity of adsorption is most likely to vary with temperature. Studying the association of heat and its reaction makes contributions to the relevant literature with practical knowledge about the variables of enthalpy and entropy. The observations of nitrophenol compounds withdrawing from organoclay were taken in the trials conducted at 298, 318, and 333 K for the purpose of identifying adsorption isotherms and thermodynamic parameters.

It has been found that the adsorption of nitrophenol compounds (i.e. 4-NP and 2,4-DNP) onto organoclay is reversely associated with heating or temperature levels (from 298 K to 318 and to 333 K) Fig 8. In a study investigating such an association for bentonite in the way of increasing temperatures, it indicates exothermic adsorption process (Varank et al. 2012). The reason is why reduction of adsorption capacity is based on weakening of adsorptive forces available between the active sites of adsorbent and the adsorbates (i.e. organoclay and nitrophenol compounds, in the present study). In Fig. 8 the quantities of equilibrium adsorption between them are demonstrated at various temperatures.

Adsorption isotherms

The adsorption isotherm refers to the distribution of the adsorbates at equilibrium by type of phase, solid or liquid. The data analysis is made through benchmarking with any other
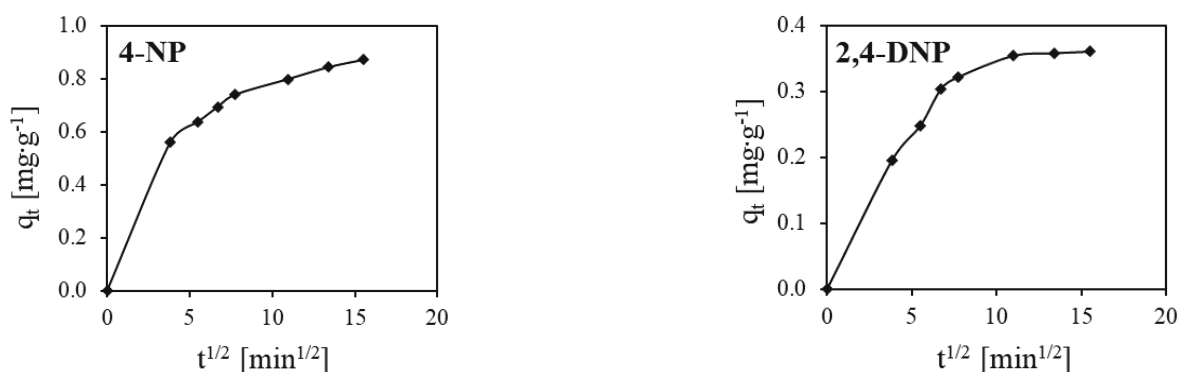

Fig. 7. Intraparticle diffusion plots of nitrophenol compounds on Mt_1 (T: 298 K, adsorbent: 1 g 0.1 L^{-1})

Table 2. Adsorption kinetic parameters of nitrophenol on Mt_1 (T: 298 K, adsorbent: 1 g 0.1 L^{-1})

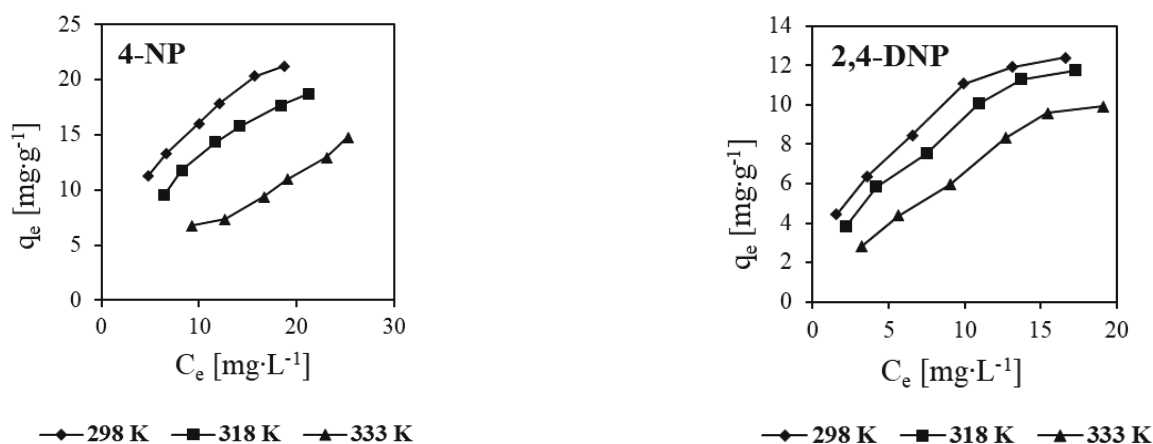| NPC	First-order kinetic model			Second-order kinetic model			Intraparticle diffusion	
	k_{pf} [min^{-1}]	q_e [$mg \cdot g^{-1}$]	R^2	k_2 [$g \cdot mg^{-1} \cdot min^{-1}$]	q_e [$mg \cdot g^{-1}$]	R^2	k_2 [$mg \cdot g^{-1} \cdot min^{-1/2}$]	R^2
4-NP	0.161	0.466	0.92	0.122	0.889	0.997	0.047	0.745
2,4-DNP	0.025	0.247	0.98	0.283	0.375	0.998	0.021	0.772

Fig. 8. Isotherms of dyes adsorption from solution at different temperatures (adsorbent: 1 g 0.05 L^{-1}, contact time: 240 min)

models as a template, and an appropriate model for design purpose can be found, which is really a significant action.

There are three common adsorption isotherm models to identify chemical adsorption behaviors: Langmuir, Freundlich and linear equations. Nevertheless, out of organic compounds, clay has some behavior in agreement with Freundlich adsorption isotherm equation (Liu et al. 2008). The present study focuses on the Langmuir and Freundlich models. Their linear forms are listed below:

$$\frac{c_e}{q_e} = \frac{1}{b \cdot q_m} + \frac{c_e}{q_m} \tag{5}$$

Where:

q_e – is the amount of nitrophenol compound adsorbed per unit mass of adsorbent particles at equilibrium [mg·g^{-1}],

C_e – is the equilibrium liquid phase concentration of the nitrophenol compound [mg·L^{-1}],

b – is the equilibrium constant [L·mg^{-1}].

The Langmuir constant b relates to the affinity of the binding sites (L·mg^{-1}), and q_m represents a practical limiting adsorption capacity when the surface is fully covered with nitrophenol compound molecules and assists the comparison of adsorption performance. The constants b and q_m are calculated from the slope and intercept of the straight lines of the plot of C_e/q_e versus C_e (Fig. 9).

Freundlich presented the earliest known empirical sorption isotherm model in 1906 by assuming an exponentially decaying adsorption site energy distribution that can be applied to nonideal sorption on heterogeneous surfaces, as well as multilayer sorption, and is expressed by the following equation:

$$q_e = k_F \cdot C_e^{1/n} \tag{6}$$

In the equation, q_e is the nitrophenol concentration [mg·g^{-1}] adsorbed by organoclay in equilibrium state, k_F is adsorption coefficient, C_e is the nitrophenol concentration [mg·L^{-1}] in equilibrium liquid phase, and a is the exponential item coefficient of C_e. In logarithmic form:

$$\log q_e = \log k_F + \frac{1}{n} \cdot \log C_e \tag{7}$$

Where:

k_F – is roughly an indicator of the adsorption capacity

$1/n$ – is an indicator of the adsorption intensity.

k_F and $(1/n)$ can be determined from the linear plot of $\log q_e$ versus $\log C_e$ (Fig. 10).

A higher rate constant for 4-NP indicates that the adsorbent (Mt_1) has higher affinity for 4-NP, which is consistent with its higher adsorption (q_m) (Table 3).
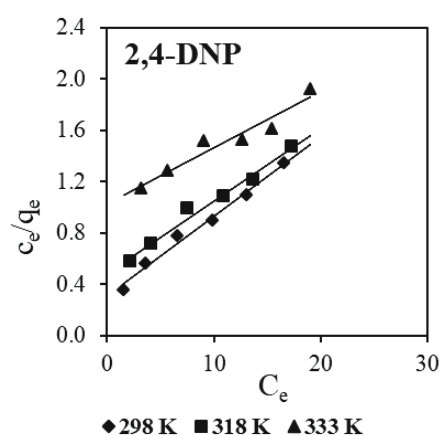

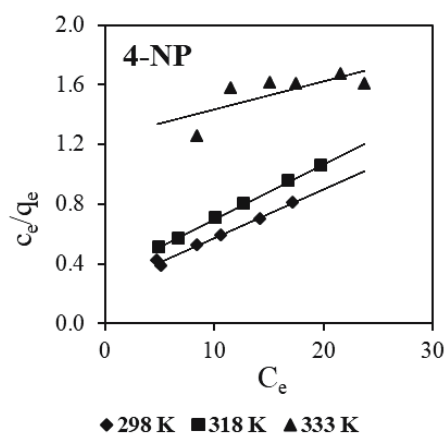**Fig. 9.** Langmuir adsorption isotherm at different temperatures (adsorbent: 1 g 0.05 L^{-1}, contact time: 240 min)
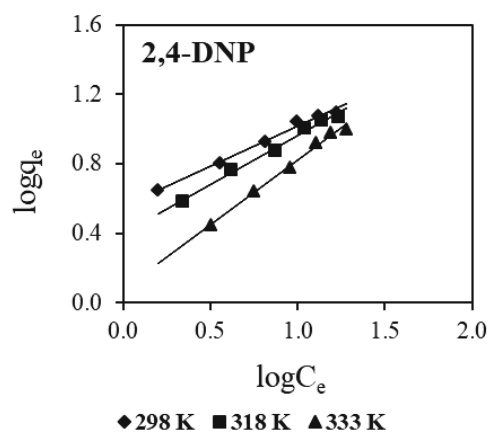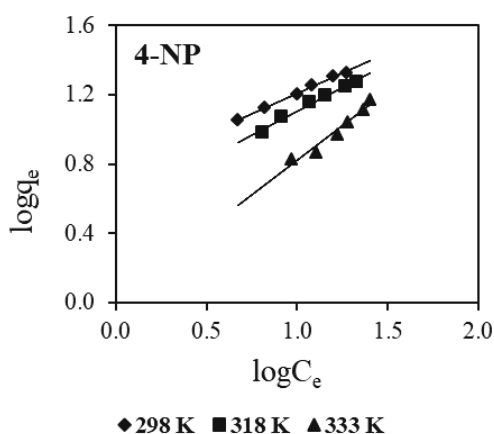

Fig. 10. Freundlich adsorption isotherm at different temperatures (adsorbent: 1 g 0.05 L^{-1}, contact time: 240 min)

It is generally stated that the values of n (n is a constant which shows greatness of relationship between adsorbate and adsorbent) in the range 1–10 represent good adsorption (Baysal 2019). In the present work, the exponent was $1 < n < 10$, indicating favorable adsorption. For the literature comparisons, the constants of n were used because the Freundlich isotherm was more compatible in Table 4.

The values b, q_m, k_F, and n are summarized in Table 3. The isotherm data were calculated from the least square method, and the related correlation coefficients (R^2 values) are given in the same table. As seen from Table 3, the Freundlich isotherm fits well the experimental data ($R^2 = 0.96$–0.99 for 4-NP and

2,4-DNP, respectively), whereas, the lower correlation coefficients ($R^2 = 0.73$–0.99 for 4-NP and 2,4-DNP, respectively) show poorer agreement between the Langmuir isotherm and the experimental data.

Effect of adsorbent dosage

As a significant variable in adsorption, the dosage of adsorbents identifies their adsorptive capacity where an initial concentration of adsorbates is given (Fig. 11). According to the results, the percentage of the adsorbed molecules was directly associated with adsorbent concentration, and significantly adversely with their quantity divided by the

Table 3. Langmuir and Freundlich isotherm constant for adsorption of NPC on Mt_1

Compound	T [K]	Langmuir Constants				Freundlich Constants		
		q_m [mg·g^{-1}]	b [L·mg^{-1}]	b [L·mol^{-1}]	R^2	k_F [(mg·g^{-1})(mg·dm^{-3})$^{-1/n}$]	n	R^2
4-NP	298	31	0.13	18209	0.99	5.4	2.1	0.99
	318	28	0.11	15151	0.99	3.6	1.8	0.98
	333	53	0.02	2085	0.73	1.1	1.25	0.96
2,4-DNP	298	16	0.19	36248	0.99	3.6	2.2	0.99
	318	18	0.12	21160	0.98	2.5	1.8	0.99
	333	23	0.04	7728	0.93	1.2	1.4	0.99

Table 4. Adsorption capacities (k) and the adsorption intensity (n) for nitrophenolic wastes

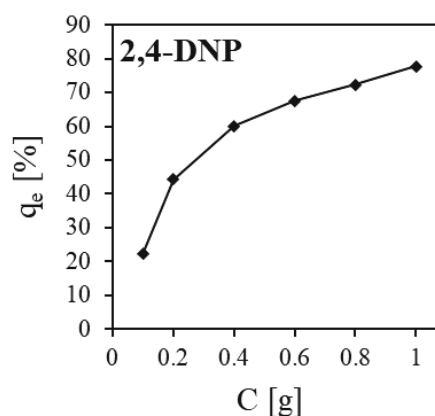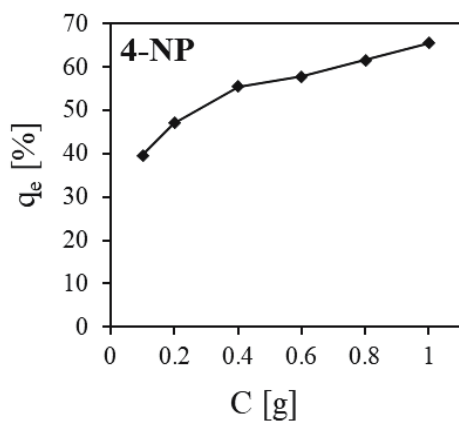| Adsorbent	Adsorbate	Freundlich Constants		References
		k	n	
HDTMA$^+$-MMT	4-nitrophenol	4.5	2.5	Zhou et al. 2008
HDTMA-B	p-nitrophenol	7.5	3.4	Koyuncu et al. 2011
HDTMA-B	m-nitrophenol	0.26	1.14	Koyuncu et al. 2011
Activated carbon	2,4-dinitrophenol	15.3–131.3	1.2–2.8	Al-Mutairi 2010
Date seeds	2,4-dinitrophenol	10.3–110.3	1.07–3.03	Al-Mutairi 2010
Organoclay	phenol	4.41–5.48	1.04–2.2	Al-Mutairi 2010
Fe-SMPM	4-nitrophenol	0.12	1.8	Zermane et al. 2010
Mt_1	4-nitrophenol	5.4	2.1	this study
Mt_1	2,4-dinitrophenol	3.6	2.2	this study

Fig. 11. Effect of adsorbent dosage on the adsorption of nitrophenol compounds (T: 298 K, contact time: 240 min)

adsorbents' mass. The adverse relationship between the adsorptive process of the adsorbates and the adsorbent doses was mainly caused by the unsaturated adsorption sites while the reaction occurred.

Estimation of thermodynamic parameters

The measurement of the quantity of nitrophenol compounds reacted in chemical adsorption process by Mt_1 is made in the temperature range of 25–60°C. The parametric relationships presented below were used to calculate thermodynamic values ΔG^0, ΔH^0 and ΔS^0:

$$\Delta G^0 = R \cdot T \cdot \ln b \qquad (8)$$

Where:

R – refers to the gas universal constant (1.987 cal·mol^{-1}·K^{-1}),
T – refers to the absolute temperature.

Also enthalpy (ΔH^0) and entropy (ΔS^0) changes can be estimated by the following equation (9):

$$\ln b = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R \cdot T} \qquad (9)$$

Accordingly, a plot of ln(b) versus 1/T should be on a straight line. ΔH^0 and ΔS^0 values were found with the slope and intercept of this plot, respectively. ΔG^0, ΔH^0, and ΔS^0 were calculated using the equations listed in Table 5.

The differences in free energy ΔG^0 for the adsorption of 4-NP and 2,4-DNP on Mt_1 were -5.8, -6.1 and -5.1; -6.2, -6.3 and -5.9 kcal·mol^{-1}, respectively at 308, 318, and 333 K. Natural spontaneity ($\Delta G^0 < 0$) demonstrates that the surface active molecules are so prone to nitrophenols in adsorption.

The changes in enthalpy (ΔH^0) of adsorption for 4-NP and 2,4-DNP were -14.08 kcal·mol^{-1} and 10.17 kcal·mol^{-1} respectively. The changes in entropy (ΔS^0) of adsorption for 4-NP and 2,4-DNP were -26.37 kcal·mol^{-1}·K^{-1} and -12.52 kcal·mol^{-1}·K^{-1} respectively. If ΔH is negative, the adsorption is an exothermic process for nitrophenol compounds on Mt_1. A negative ΔH value represents strong bonding between the sorbent and solute. The negative standard entropy change (ΔS^0) value corresponds to a decrease in the degree of freedom of the adsorbed species (Özcan and Özcan 2005).

Conclusions

A new QAS_1 was synthesized for this study, and an organoclay was prepared using montmorillonite and 1-methyl-di-octyl-1 phenyl ammonium iodide as an example of a surfactant with a long alkyl chain. Mt_1 presented impressive results for the adsorption of 4-NP and 2,4-DNP from aqueous solutions. The kinetic data may be best described by a pseudo-second-order equation. Adsorption of nitrophenol compounds and QAS^+-exchanged montmorillonites satisfied the Freundlich equation proficiently.

Due to the interlayer cation exchanged by QAS_1 cation surfactant, the adsorption of nitrophenol compounds to Mt_1 was greatly increased and the adsorption isotherms were linear. Consequently, the present study revealed that nitrophenol compounds which are known as pesticides presented a significantly efficient adsorption with organoclay modified with novel synthesized QAS_1. According to the literature, activated coal has a highly effective adsorption capacity in the adsorption of phenol compounds because it has a large surface area and complex pore structure. However, expensive methods are needed to recycle activated coal. The organoclay synthesized in this study was more easily regenerated, and it was possible to contribute to the literature as an advantage of being environment-friendly and inexpensive.

As a result, I have synthesized a novel material that removes the aqueous solution by adsorbing toxic substances with high performance, giving the literature a completely new and highly effective new adsorbent.

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Table 5. Values of thermodynamic parameters for the adsorption of 4-NP and 2,4-DNP on Mt_1

Temp.	4-NP			2,4-DNP		
T	$-\Delta G^0$	$-\Delta H^0$	$-\Delta S^0$	$-\Delta G^0$	$-\Delta H^0$	$-\Delta S^0$
[K]	[kcal·mol^{-1}]	[kcal·mol^{-1}]	[kcal·mol^{-1}·K^{-1}]	[kcal·mol^{-1}]	[kcal·mol^{-1}]	[kcal·mol^{-1}·K^{-1}]
298	5.808			6.216		
318	6.085	14.08	26.37	6.293	10.17	12.52
333	5.055			5.922		

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