Asian Journal of Chemistry; Vol. 28, No. 4 (2016), 871-876

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2016.19542

Removal of 4-Nitrophenol from Aqueous Solution by Organo-Montmorillonites Modified with Ionic Liquids

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Received: 31 July 2015; *Accepted*: 23 October 2015; *Published online*: 30 December 2015; AJC-17707

In this study, the removal capacity of organo-montmorillonite for a hydrophobic organic pollutant such as 4-nitrophenol was evaluated. Commercially available unmodified clay was treated under different conditions with aqueous solutions of three ionic liquids *viz.*, 1-butyl 3-methyl imidazolium tetrafluoroborate, 1-butyl 4-methyl pyridinium tetrafluoroborate and 1-methyl 3-octyl imidazolium tetrafluoroborate. The modified materials were characterized by FTIR and WXRD analysis. The Langmuir and Freundlich were tested to fit the adsorption isotherms. The results indicate that montmorillonite modified by ionic liquids can be used as adsorbent for *p*-nitrophenol because of its high adsorption capacity and low cost. This study can be useful for cleaning water or analytical purposes.

Keywords: Ionic liquids, Organo-montmorillonite, Adsorption kinetics, Adsorption isotherms, 4-Nitrophenol.

INTRODUCTION

The modified clay minerals, organo-montmorillonites, represent a family of materials which have a lot of applications in a range of key areas, such as rheological control agents, reinforcing fillers for plastics and electric materials [1,2], particularly adsorbents for organic pollutants [3-5].

Ionic liquids (IL) are gaining interest as a new reaction media for organic transformations. They can be used as solvents for a wide range of organic and inorganic reactions and their unique properties make them important candidates for the so-called "green chemistry" [6,7]. Because of their insignificant vapour pressures, low melting points, good solvent characteristics for organic, inorganic and polymeric materials, adjustable polarity, selective catalytic effects, chemical and thermal stability, low viscosity, non-flammability and high ionic conductivity, high ion content, they have generated significant interest for a wide range of industrial applications [8-11].

The most common organic cations containing nitrogen are imidazolium and pyridinium derivatives while other compounds are based on phosphonium or tetraalkylammonium cations. The commonly used anions include $[BF_4]^-$, $[PF_6]^-$, $[CF_3COO]^-$ and $[CF_3SO_3]^-$, *etc*. [12,13]. Imidazolium ionic liquids are popular because they have a low vapour pressure, a high conductivity in spite of a high viscosity and a large electrochemical window [14].

The presence of phenolic compounds in the environment is a cause of major concern because of their toxic effects on human health. These compounds have toxic effect on humans and animals as well as plants and they give an undesirable taste and odor to drinking water [15], even at very low concentration [16]. *p*-Nitrophenol (PNP) is one of the hazardous chemicals, which is widely used in industries. It is an important intermediate in the manufacturing of azo dyes and a number of pesticides. Thus, removal of these compounds prior to discharge into the environment is neccessary [17]. The objective of this research is to use organo-montmorillonite to adsorb 4-nitrophenol from an aqueous solution.

EXPERIMENTAL

Chemicals of high purity were obtained from various commercial sources, which consisted of ionic liquids (Fluka), silver nitrate (Merck), hydrochloric acid (Merck). Montmorillonite, Na^+-Mt, a hydrated aluminum silicate with sodium as the predominant exchangeable cation (trade name: Cloisite-Na^+, CAS# 1318-93-0, Southern Clay Products Inc.) is a powder with typical particle size less than 2 μm. Specific gravity of Na^+-Mt is between 2. 8 and 2.9, pH value of a 10% dispersion is 10 and its cation exchange capacity (CEC) as reported by the supplier is 92.6 meq/100 g clay. The physical and chemical properties of Na^+-Mt are included in Table-1.

Ionic liquids such as 1-butyl -3-methyl imidazolium tetrafluoroborate (IL_1), 1-butyl -4-methyl pyridinium tetrafluoroborate

TABLE-1
PHYSICAL AND CHEMICAL PROPERTIES OF Na^+-Mt

m.f.	$(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot 6H_2O$
Density (g/cm^3)	2.86
pH (%3 çözelti)	8
Surface area (m^2/g)	750
CEC (meg/100 g)	92
Composition (%)	1.40 Na, 2.44 Ca, 9.99 Al, 8.88 Mg, 20.7 Si, 35.53 O, 0.37 H

(IL_2), 1-methyl -3-octyl imidazolium tetrafluoroborate (IL_3) were used for clay modification.

Synthesis of organo clays: Cationic exchange of Na^+-Mt (Mt) was carried out with 1-butyl-3-methyl imidazolium tetrafluoroborate (IL_1), 1-butyl-4-methyl pyridinium tetrafluoroborate (IL_2) and 1-methyl-3-octyl imidazolium tetrafluoroborate (IL_3) and aqueous solutions stirring at 60 °C for 2 h and at 1X1 concentrations of the clay based on CEC. After filtration, all modified clays were repeatedly (more than 15 times) washed with distilled water. For clays modified with IL_1, IL_2 and IL_3 washing was continued until no residual halogen anion was detected by adding 0.1 M silver nitrate solution in the filtrate. It is to be noted that filtration time for all treated clays was significantly shorter than that for the unmodified one. After 24 h at room temperature, drying continued at 80 °C for 12 h under vacuum [18]. Abbreviations used to describe the modified clays are included in Table-2.

TABLE-2
EXPERIMENTAL DESCRIPTION AND ABBREVIATIONS OF Mts MODIFIED WITH IONIC LIQUIDS

Clay	Modifiers	Ionic liquids	Exchange temp./time/CEC amount used (C/h/stoichiometry)
Mt	–	–	–
Mt_1	$[C_8H_{15}BF_4N_2]$	IL_1	60/2/2 g
Mt_2	$[C_{10}H_{16}BF_4N]$	IL_2	60/2/2 g
Mt_3	$[C_{12}H_{23}BF_4N_2]$	IL_3	60/2/4 g

Adsorption of *p*-nitrophenol on the organo clays

Adsorption kinetics: Stock solutions of 4-nitrophenol (4-NP; Fw = 139 g mol^{-1}) (1 g L^{-1}) were prepared by dissolving the appropriate amount of each solute in distilled water at room temperature, shaken for several hours (4 h) [19].

Kinetic studies were conducted in Erlenmayer flask at room temperature by shaking 1 g of sorbent (Mt_1, Mt_2 and Mt_3) with 100 mL of solution containing 4-nitrophenol (50 mg L^{-1}) at 250 rpm on a mechanical shaker. The samples were withdrawn from the shaker at intervals from 15 to 240 min [15] and the concentrations of 4-nitrophenol were determined by UV–visible spectrophotometry.

Adsorption isotherms: Adsorption experiments were carried out by shaking 1 g of organo-montmorillonites samples with 50 mL aqueous solution. All flasks were filled with 50 mL of nitrophenol solutions of varying concentrations (10, 20, 30, 40, 50, 60 mg L^{-1} for 4-nitrophenol) and temperature (298, 318 and 333 K), initial concentrations of 4-nitro-phenol. The flasks were shaken for 4 min at 250 rpm. After shaking, the mixture was centrifuged at 3500 rpm for 15 min. After the centrifugation, the 4-nitrophenol concentrations in the aqueous phase were determined by a UV–visible spectrophotometer at 317 nm [19]. The adsorption studies were also carried out at different temperatures (298, 318 and 333 K) to determine the effect of temperature.

4-Nitrophenol uptake on organo-montmorillonites was calculated by the following equation:

$$Q = (C_o – C_e)\ V/m$$

where, Q is the uptake of 4-nitrophenol, C_o is the initial concentration, C_e is the equilibrium concentration, V is the volume of nitrophenol solutions and m is the mass of the adsorbent [20,21].

Fourier transform infrared spectroscopy: The IR spectra were recorded as KBr pellets in the spectral range of 4000–400 cm^{-1} on an ATI UNICAM systems 2000 Fourier transform spectrometer.

X-ray diffraction: The samples were characterized by X-ray diffraction 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.

UV spectroscopy: The samples were analyzed using a Shimadzu UV-1010 spectrophotometer at a wavelength of 317 nm for the residual concentration of 4-nitrophenol.

RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy (FT-IR): The FTIR spectra of Mt (a) and Mt modified with ionic liquids (b, c and d), are shown in Fig. 1. The absorption at 3621 cm^{-1}, in the spectrum of the montmorillonites, is typical for montmorillonite with a high amount of Al in the octahedral. The band at 3436 cm^{-1} shows H–O–H hydrogen-bonded water. The intensive band at 1036 cm^{-1} can be assigned to Si–O stretching vibrations. The spectrum of Mt_1 in Fig. 1(b) shows peaks for the imidazolium functional group in the range between 1650 and 1000 cm^{-1}; for example, the peaks in the range of 1600-1320 cm^{-1} are due to C–C and C–N vibrations; the conjugated strong peaks around 1630 and 1570 cm^{-1} are due to C–N–C or C–C bonds [9].

FT-IR spectrum of Mt_2, shown in Fig. 1(c). Infrared spectrum of IL_2 [pyridinium based, Fig. 1(c)] shows peaks at 1650, 1580, 1490 and 1460 cm^{-1} assigned to C–C and C–N stretching vibrations in pyridinium.

FT-IR spectrum of Mt_3 shown in Fig. 1(d). A longer hydrocarbon chain in IL_3 gives significantly strong peaks in the ranges of 3100–2800 cm^{-1} and 1640–1465 cm^{-1}. These peaks occur at 1570 and 1470 cm^{-1} and in the range of 3060–2860 cm^{-1} [refer to arrows in Fig. 1(d)], indicating the presence of IL_3 in the modified Mt_3.

X-ray diffraction (XRD): Fig. 2 shows typical XRD for the clay and organo-montmorillonites. The *d* 001 reflection has sharp intense peak at 2θ = 9.079, 6.620, 6.660, 6.320 for Mt, Mt_1, Mt_2 and Mt_3, respectively. The *d* 001 spacing was calculated and listed in Table-3 from peak positions using Bragg's law $d = \lambda/2 \sin\theta$. It is clear that the *d*-spacing for Mt (9.08 Å) increased to (13.97 Å) since the small inorganic Na^+ cation is exchanged by onium group through an ion exchange process. Fig. 2 presents three series of XRD corresponding to clays.

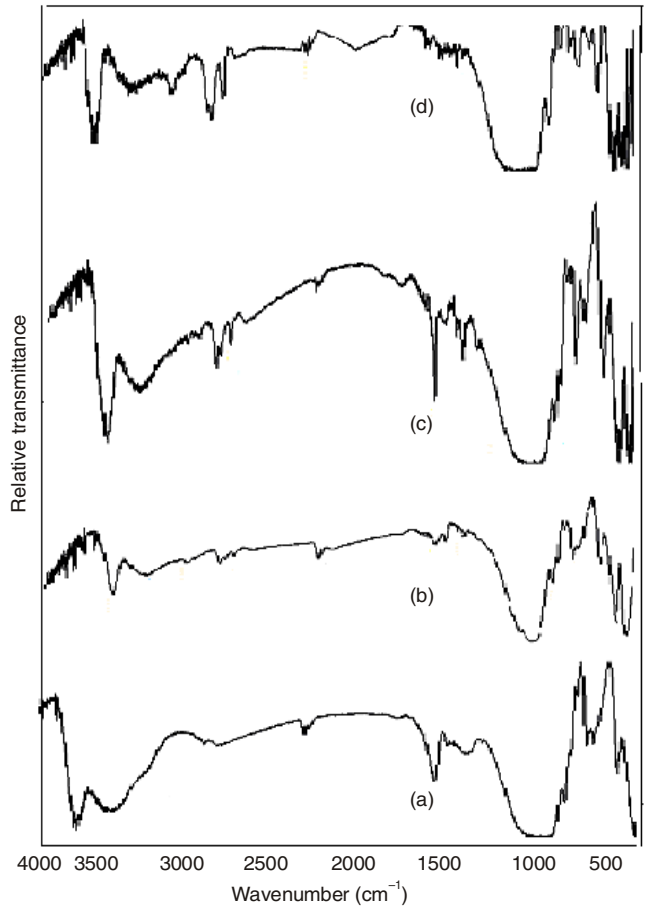

Fig. 1. FTIR spectra of (a) Mt, (b) Mt_1, (c) Mt_2 (d) Mt_3

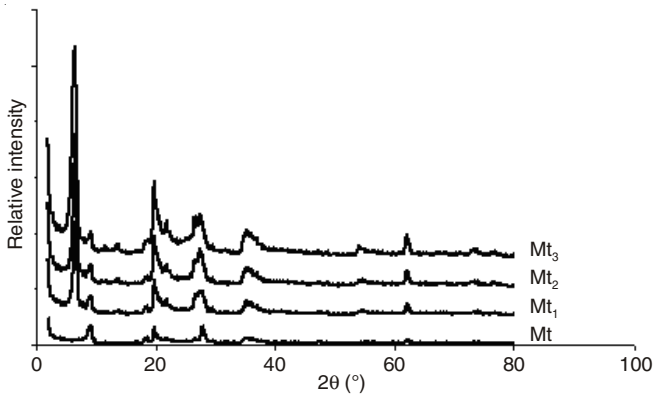

Fig. 2. XRD patterns of clay (Mt) and organo-montmorillonites (Mt_1, Mt_2, Mt_3)

TABLE-3
X-RAY DIFFRACTION DATA FOR THE SAMPLES

Sample	X-ray data	
	2θ	d-spacing
Mt	9.079	0.973
Mt_1	6.620	1.334
Mt_2	6.660	1.326
Mt_3	6.320	1.397

This confirmed that the organo-montmorillonite is intercalated between the layers. Increase in *d*-spacing *vs.* the washed unmodified Mt follows the order $Mt_3 > Mt_2 > Mt_1$. The higher extent of intercalation corresponding to the largest interlayer distance of 1.397 nm in Mt_3 (compare with 0.973 nm for Mt) is obtained with IL_3, which has a relatively bulkier cation than the other two ionic liquids. Results are comparable with those reported in for dimethyl imidazolium ionic liquids with variable alkyl chain length [22].

Adsorption experiments of 4-nitrophenol on the organo-montmorillonites

Contact time: The adsorption of *p*-nitrophenol increased with time and reached equilibrium at about 4 h (Fig. 3). The adsorption rate of *p*-nitrophenol can be determined by testing with intraparticle diffusion model, pseudo-first-order and pseudo-second order kinetic models, which are expressed in eqns. 1–3.

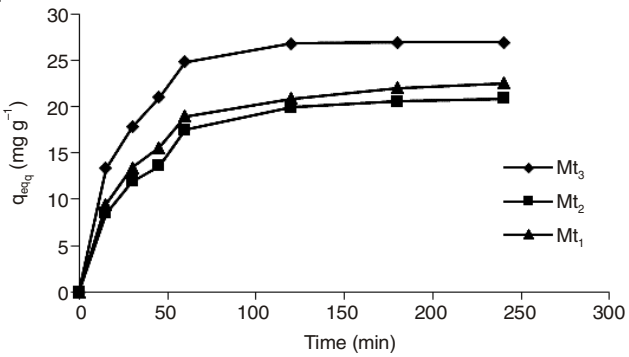

Fig. 3. Effect of contact time on the adsorrption of 4-nitrophenol

Adsorption kinetics: The results of the adsorption kinetics experiments are presented in Fig. 3. The plots represent the amount of 4-nitrophenol sorbed q_t onto organo-montmorillonites *versus* time t. For an initial 4-nitrophenol concentration of 50 mg L^{-1}, it was shown that the equilibrium time was 240 min for organo-montmorillonites. The results showed that Mt_3 adsorbed higher than Mt_2 and Mt_1; steady state was reached within 240 min for 4-nitrophenol.

Many studies have pointed out that the majority of adsorption kinetics can be represented as a pseudo-first-order rate mechanism. However, it was clearly found that the pseudo second- order equation, which agrees with chemisorption as the rate-control mechanism, was able to better describe the adsorption of phenolic compounds onto organo-montmorillonites and other sorbents [23,24].

The pseudo-first-order model depicts properly the adsorption process [18]:

$$\log (q_e-q_t)=\log q_{eq}- k_{pf}\, t/2.303 \quad (1)$$

where q_{eq} and q_t are the amount of nitrophenol adsorbed at equilibrium at time t, in mg g^{-1}, respectively and k_{pf} the first-order rate constant. The values log (q_{eq}-q_t) was calculated from the kinetic data (Fig. 3) and plotted against time as shown in Fig. 4. Good correlation coefficients (0.955 and 0.989) 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. 4 are 0.1612 and 0.0253 min^{-1} for 4-nitrophenol. The adsorption kinetics may also be described by a pseudo-second-order reaction. The linear form of this model is

$$t/q_t = 1/k_2q_e^2 + 1.t/q_e \quad (2)$$

TABLE-4
ADSORPTION KINETIC PARAMETERS OF 4-NITROPHENOL ON ORGANO-MONTMORILLONITES

4-Nitrophenol	First-order kinetic model			Second-order kinetic model			Intraparticle diffusion	
	k_{pf} (min^{-1})	q_{eq} (mg g^{-1})	R^2	k_2 (min^{-1})	q_{eq} (mg g^{-1})	R^2	k_2 (mg g^{-1} $min^{-1/2}$)	R^2
Mt_1	0.009	1.18	0.955	0.049	1.19	0.991	0.07	0.871
Mt_2	0.014	1.06	0.989	0.048	1.12	0.989	0.066	0.883
Mt_3	0.039	1.48	0.982	0.012	1.42	0.995	0.081	0.798

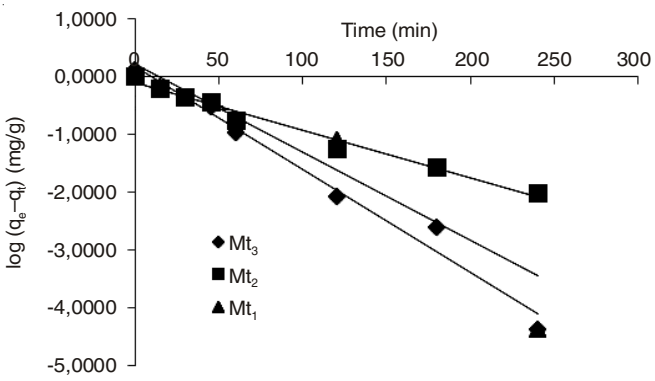

Fig. 4. Lagergren's plot for 4-nitrophenol on organo-montmorillonites (T = 298 K, adsorbents = 1 g 0.1 L^{-1}, 4-nitrophenol-C_o = 50 mg)

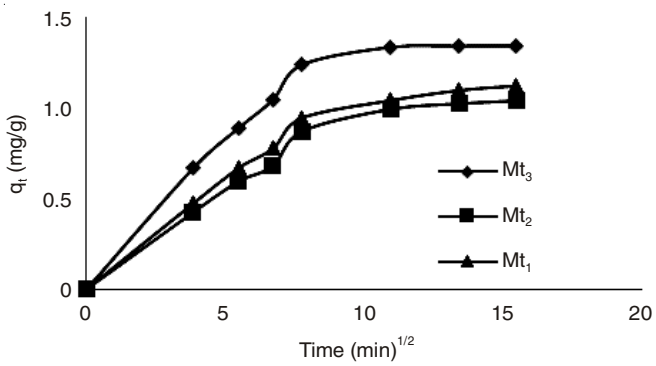

Fig. 5. Intraparticle diffusion plots of 4-nitrophenol on organo montmorillonites (T: 298 K, adsorbents: 1 g

where k_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo second-order adsorption.

The rate constant k_1 of pseudo-first-order adsorption and k_2 of pseudo-second-order adsorption ranged from 0.009 to 0.039 min^{-1} and 0.012 to 0.049 g/mg min, respectively (Table-4).

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

$$q_t = k_{id}\, t^{1/2} \quad (3)$$

were q_t is the amount adsorbed (mg g^{-1}) at time t (min). The plots of q_t *versus* $t^{1/2}$ for organo-montmorillonites are shown in Fig. 5.

Effect of temperature: The removal of 4-nitrophenol on organo-montmorillonites has been studied at 298, 318 and 333 K to determine the adsorption isotherms. Adsorption for 4-nitrophenol on organo-montmorillonites decreases with increasing from 298 K to 318 and 333 K (Fig. 6). It is observed that 4-nitrophenol adsorption capacity decreases with increasing temperature (Table-5). The increase in temperature from 298 to 333 K decreases the adsorption capacity of organo-montmorillonites, indicating the exothermic at the adsorption process [15]. The decreasing of adsorption with temperature is mainly due to the weakening of adsorptive forces between the active sites of organo-montmorillonites and 4-nitrophenol [21]. Fig. 6 shows the amount of equilibrium adsorption of 4-nitrophenol on organo-montmorillonites at different temperatures.

Adsorption isotherms: In order to quantitatively describe the adsorption of nitrophenol by organo-montmorillonites, Langmuir and Freundlich equation were used because the absorption behaviour of clays to organic compound usually accords with the Freundlich isotherm equation [25]. 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 sorbed molecules [26].

The widely used equilibrium-based isotherm models are Freundlich and Langmuir equations. Their linear forms are listed below:

$$C_{eq}/q_{eq} = 1/bq_m + C_{eq}/q_m \quad (4)$$

where q_{eq} (mg g^{-1}) is the amount of 4-nitrophenol adsorbed per unit mass of adsorbent particles at equilibrium, C_{eq} (mg L^{-1}) is the equilibrium liquid phase concentration of nitrophenol compounds, b is the equilibrium constant. Langmuir constantly relates to the affinity of binding sites (L mg^{-1}) or (L mol^{-1}) and

TABLE-5
LANGMUIR AND FREUNDLICH ISOTHERM CONSTANTS FOR ADSORPTION OF 4-NITROPHENOL ON ORGANO-MONTMORILLONITE

	Temp. (K)	Langmuir constants				Freundlich constants		
		Q_m (mg g^{-1})	b (L mg^{-1})	b (L mol^{-1})	R^2	k	n	R^2
Mt_1	298	32	0.040	5560	0.98	2.03	1.60	0.996
	318	36	0.020	2919	0.86	1.06	1.30	0.978
	333	11	0.040	5699	0.93	1.08	2.01	0.982
Mt_2	298	28	0.045	6255	0.98	2.10	1.70	0.995
	318	25	0.026	3614	0.90	1.16	1.60	0.994
	333	14	0.043	5977	0.97	1.04	1.70	0.969
Mt_3	298	39	0.039	5421	0.97	2.40	1.56	0.998
	318	45	0.018	2502	0.92	1.08	1.26	0.974
	333	67	0.008	1112	0.83	1.65	1.09	0.949

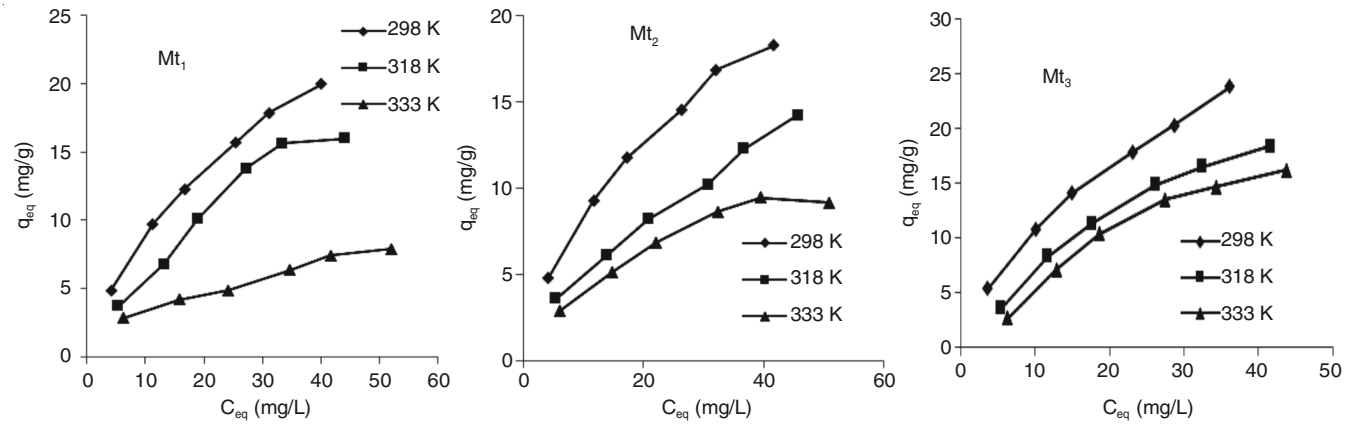

Fig. 6. Isotherms of 4-nitrophenol adsorption from solution at different temperatures (adsorbent = 1 g 0.05 L^{-1}, Contact time = 240 min)

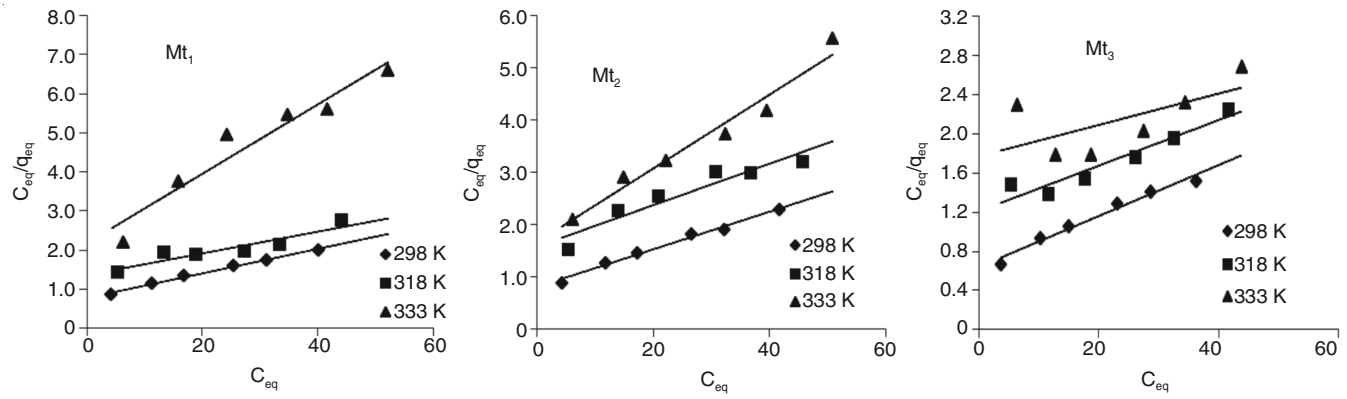

Fig. 7. Langmuir adsorption isotherm for adsorption of 4-nitrophenol

q_m represents a pratical limiting adsorption capacity when the surface is fully covered with nitrophenol compounds molecules and assists in the comparison of adsorption performance.

b and q_m are calculated from the slope and intercept of the straight lines of plot of C_{eq}/q_{eq} (Fig. 7).

Freundlich isotherm is an empirical equation employed to describe heterogeneous systems [15,27].

The Freundlich isotherm is given as:

$$q_{eq} = k_F C_{eq}^{1/n} \quad (5)$$

in the equation, q_{eq} is the nitrophenol concentration (mg/g) adsorbed by organo-montmorillonite in equilibrium state, K_F is adsorption coefficient, C_{eq} is the nitrophenol concentration (mg/l) in equilibrium liquid phase and a is the exponential item coefficient of C_{eq} [20,26,27].

In logaritmic form:

$$\log q_{eq} = \log k_F + 1/n \log C_{eq} \quad (6)$$

where k_F is roughly an indicator of the adsorption capacity and (1/n) of the adsorption intensity. k_F and (1/n) can be determined from the linear plot of log q_{eq} *versus* log C_{eq} (Fig. 8).

Conclusion

In this study, organo-montmorillonites were prepared by using montmorillonite and ionic liquids [1-butyl 3-methyl imidazolium tetrafluoroborate (IL_1), 1-butyl 4-methyl pyridinium tetrafluoroborate (IL_2) and 1-methyl 3-octyl imidazolium tetrafluoroborate (IL_3)] as an example of a surfactant with a long alkyl chain. The study obtained impressive results for the adsorption of 4-nitrophenol from aqueous solutions by

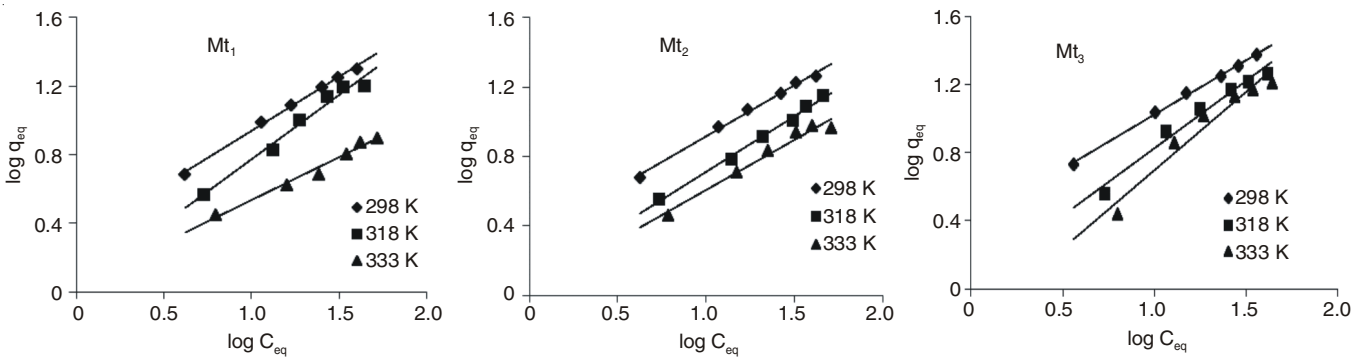

Fig. 8. Freundlich adsorption isotherm for adsorption of 4-nitrophenol

using organo-montmorillonites. The kinetic data can be best described by the pseudo-second-order equation. Adsorption of 4-nitrophenol and modified montmorillonites followed the Freundlich equation well (Table-6). This suggested that ionic liquids-modified montmorillonites are potential adsorbents for removing 4-nitrophenol from water. This study can be useful for cleaning water or analytical purposes.

TABLE-6
ADSORPTION CAPACITIES (k) AND ADSORPTION INTENSITY (n) FOR 4-NITROPHENOL

Adsorbent	Adsorbate	Freundlich constants		Ref.
		k	n	
$HDTMA^+$–MMT	4-Nitrophenol	4.5	2.5	[3]
Bentonite	4-Nitrophenol	0.16	1.16	[15]
Fe-SMPM	4-Nitrophenol	0.12	1.8	[19]
$HDTMA^+$–MMT	4-Nitrophenol	20.83	1.73	[26]
IL_s^+–MMT	4-Nitrophenol	2.4-1.04	2.1-1.09	[Present study]

REFERENCES

1. I.D. Sand, R.L. Piner, J.W. Gilmer and J.T. Owens, Organoclays as Processing Aids for Plasticized Thermoplastics, U.S. Eastman Chemical Company, USA, p. 8 (2003).
2. R.L. Frost, Q. Zhou, H. He and Y. Xi, *Spectrochim. Acta A*, **69**, 239 (2008).
3. Q. Zhou, H.P. He, J.X. Zhu, W. Shen, R.L. Frost and P. Yuan, *J. Hazard. Mater.*, **154**, 1025 (2008).
4. J.H. Kim, W.S. Shin, Y.H. Kim, S.J. Choi, Y.W. Jeon and D.I. Song, *Water Sci. Technol.*, **47**, 59 (2003).
5. Y. Park, G.A. Ayoko and R.L. Frost, *J. Colloid Interf. Sci.*, **360**, 440 (2011).
6. H. Zheng, K. Jiang, T. Abe and Z. Ogumi, *Carbon*, **203**, 44 (2006).
7. G. Baysal, H. Aydin, S. Koytepe and T. Seckin¸, *Thermochim. Acta*, **566**, 305 (2013).
8. H. Erdemi, Ü. Akbey and H.W. Meyer, *Solid State Ion.*, **181**, 1586 (2010).
9. V.V. Namboodiri and R.S. Varma, *Tetrahedron Lett.*, **43**, 5381 (2002).
10. H. Ohno and M.Yoshizawa, *Solid State Ion.*, **154-155**, 303 (2002).
11. R. Kanzaki, T. Mitsugi, S. Fukuda, K. Fujii, M. Takeuchi, Y. Soejima, T. Takamuku, T. Yamaguchi, Y. Umebayashi and S. Ishiguro, *J. Mol. Liq.*, **147**, 77 (2009).
12. M. Shamsipur, A.A.M. Beigi, M. Teymouri, S.M. Pourmortazavi and M. Irandoust, *J. Mol. Liq.*, **157**, 43 (2010).
13. N.E. Heimer, R.E. Del Sesto, Z. Meng, J.S. Wilkes and W.R. Carper, *J. Mol. Liq.*, **124**, 84 (2006).
14. A. Chagnes, H. Allouchi, B. Carre and D. Lemordant, *Solid State Ion.*, **176**, 1419 (2005).
15. G. Varank, A. Demir, K. Yetilmezsoy, S. Top, E. Sekman and M.S. Bilgili, *Indian J. Chem. Technol.*, **19**, 7 (2012).
16. J. Li, D. Kuang, Y. Feng, F. Zhang, Z. Xu and M. Liu, *J. Hazard. Mater.*, **201-202**, 250 (2012).
17. A. Tor, Y. Cengeloglu and M. Ersoz, *Desalination*, **242**, 19 (2009).
18. N.H. Kim, S.V. Malhotra and M. Xanthos, *Micropor. Mesopor. Mater.*, **96**, 29 (2006).
19. F. Zermane, O. Bouras, M. Baudu and J.P. Basly, *J. Colloid Interf. Sci.*, **350**, 315 (2010).
20. N.Z. Al-Mutairi, *Desalination*, **250**, 892 (2010).
21. H. Aydin and G. Baysal, *Desalination*, **196**, 248 (2006).
22. L.B. de Paiva, A.R. Morales and F.R. Valenzuela Díaz, *Appl. Clay Sci.*, **42**, 8 (2008).
23. L. Wei, H. Zhu, X. Mao and F. Gan, *Sep. Purif. Technol.*, **77**, 18 (2011).
24. M. Sathishkumar, A. Binupriya, D. Kavitha and S. Yun, *Bioresour. Technol.*, **98**, 866 (2007).
25. R. Liu, R.L. Frost, W.N. Martens and Y. Yuan, *J. Colloid Interf. Sci.*, **327**, 287 (2008).
26. X. Xin, J. Wang, H.Q. Yu, B. Du, Q. Wei and L.G. Yan, *Environ. Technol.*, **32**, 447 (2011).
27. M. Zahoor and M. Mahramanlioglu, *Sep. Sci. Technol.*, **46**, 1482 (2011).