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Development of surface reaction of nano-colloid minerals using novel ionic liquids and assessing their removal ability for Pb(II) and Hg(II)

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Abstract
The purpose of this study was to produce novel eco-friendly organoclays for removing toxic elements from aqueous environment. In the present research, nano-bentonite (Bent) and nano-montmorillonite (MT) minerals were treated with novel ionic liquids including 1-methyl-3-octylimidazolium chloride ([Omim][Cl]), 3,3′-(hexane-1,6-diyl) bis (1-methyl-imidazolium) bromide chloride ([H(mim)$_2$[Br][Cl]), and 1-hexyl-3-methylimidazolium chloride ([Hmim][Cl]) to produce organoclays with eco-friendly features. The products were investigated using X-ray diffraction (XRD); Fourier transformed infrared spectroscopy (FT-IR); carbon, hydrogen, and nitrogen elemental analysis (CHN); scanning electron microscope (SEM); and specific surface area (SSA) (via N$_2$-BET method) techniques. Finally, the mechanism involved in the adsorption of Pb(II) and Hg(II) onto organoclays from the aqueous phase was investigated by applying most three popular experimental adsorption isotherms including Langmuir, Freundlich, and Sips models. The results showed that by intercalating ILs, first XRD diffraction (d$_{001}$) of the modified clays was increased. Based on the results of Sips model, [H(mim)$_2$]-clays and [Omim]-clays had maximum adsorption capacity and maximum adsorption affinity. To the best of the authors' knowledge, the amount of removed toxic metals by the modified clays in this research was more than those in the previous researches. This research demonstrated that clay mineral modifications using ILs is enhanced clay d-spacing and facilitated diffusion of the large hazardous metal ions into clay interlayer spaces. These increased their potential for toxic metal immobilization as green adsorbents.

Keywords Bentonite · Green adsorbent · Toxic metal; Modification

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Introduction

Mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), and lead (Pb) are examples of toxic elements (TEs) that cause poisoning and toxicity at low concentrations. One of the main sources of TEs distribution into the environment is human activities. The anthropogenic origins have raised their toxicities in considerable amounts, and this phenomenon has become a global concern. The prevalent cancerous and noncancerous deices caused by TEs accumulation harm human health (Naderi et al. 2017; Jamal et al. 2018).

Thus, there is an on-going need for remediation of polluted systems by various methods like their mobilization through adsorbing agents (Zupancic et al. 2012), chelating/ complexing agents (Karczewska et al. 2011), and organic matters (Mendez et al. 2012). Immobilization of TEs is a low-cost method and reduces their bioavailability by their transportation from solution phase to solid phases (Porter et al. 2004).

Phosphate compounds (Bolan et al. 2003), liming materials (Garau et al. 2007), organic matters (Ahmad et al. 2014), goethite and humic acids (Unuabonah et al. 2016), and clay minerals (Lakshmi Narayanan et al. 2017; Zehhaf et al. 2015; Turan et al. 2011) are the most prevalent immobilizing components.

Silicate clay minerals are low-cost and abundant natural resources that are known as good alternatives for TEs adsorbing from natural environments even more preferentially than natural alkali and alkaline cations (Németh et al. 2011) via surface complexation, specially by covalent bonds and cation exchange phenomena (Swift and McLaren 1991; Stumm and Morgan 1981; Scheidegger et al. 1996; Jackson 1998). For modification and increasing their adsorption potential, large organic molecules are replaced with their natural interlayer cations (Oyanedel-Craver and Smith 2006; Say et al. 2008; Bergaya et al. 2011; Bergaya et al. 2012; Lagalya and Dekanyb 2013; Brown et al. 2013). Many studies showed that expansion in interior spaces of clay minerals by intercalating macromolecules has increased adsorption capacity of hazardous organic components (Cabrera et al. 2008; Nafees and Waseem 2014; Meng et al. 2015; Shen et al. 2018) and inorganic ions like TEs (Carvalho and de Vilhena 2005; Ma et al. 2010; Tashauoei et al. 2010; Özkahraman et al. 2011; Zhu et al. 2011; Venkatesan and Rajagopalan 2016; Sayed and Burham 2017; Yu et al. 2017; Park et al. 2017; Rusmin et al. 2017).

Quaternary ammonium salts (QAs) are the most common components that were utilized to modify clay minerals. Benzyldimethyltetradecylammonium, benzyltrimethylammonium, dioctadecylammonium (DMDOA), dodecyltrimethylammonium bromide, hexadecyltrimethylammonium bromide (HDTMA), hexadecylpyridinium, and tetramethylammonium are some of the high-usage QAs (Groisman et al. 2004; Okada et al. 2005; Pálková et al. 2015; Shichong He and Zhu 2016). The release of this kind of modified clay into the environments have hazardous effects and are toxic for biota (Sarkar et al. 2013). Hongping He et al. (2014) provided a concise review of recent advances about the production of organoclays with eco-friendly and biodegradable properties. Modification of clay minerals with environmentally friendly and biodegradable organic modifiers has received great attention recently (Zhao et al. 2018; Shichong He and Zhu 2016). Wu et al. (2011) reported that modification of nano-montmorillonite (MT) by humic acid as a natural modifier enhanced MT capacity in removal of Cu(II), Cd(II), and Cr(III) ions from the aqueous solutions.

Ionic liquid (IL) salt consists of a large organic cation and an inorganic anion which are poorly coordinated as well as the cation has low symmetry degree. It means there is so weak bond strength between the ingredients of the salts that its form is liquid at the temperatures below 100 °C (Paul et al. 2015). The ILs are suitable and eco-friendly solvents due to low melting points, low vapor, and high variety, have made them suitable and eco-friendly solvents, and have persuaded researchers to investigate about IL replacement with another solvents (Haixia et al. 2007; Hosseini et al. 2012). Generally, organic cations of ILs are sorted as imidazolium, pyridinium, and phosphonium cations (Gilman et al. 2002; Ha and Xanthos 2009; Ganguly et al. 2011; Yan et al. 2014). Livi et al. (2011) have synthesized dialkyl imidazolium and alkyl phosphonium to prepare ILs-modified organoclay. XRD results indicated that basal spacing of the ILs-modified MT was increased up to 41 Å. Souza et al. (2016) synthesized two types of organoclay that were modified with ILs and compared their characteristics with organosilane compounds. The first XRD diffraction of the clay layers (d_{001}) of the guest clay (12.3 Å) was increased in alkyl phosphonium, aryl phosphonium, and organosilane modified clays equated as 23.3, 18.4, and 15.2 Å, respectively.

In our previous research (Naderi et al. 2018), 2:1 nano-sized clays were treated using three green and novel imidazolium-based ILs. If ILs are released into any environment, they would be decomposed to their initial ingredients and would not produce secondary pollution. That is why, they have been categorized as the green adsorbents. Adsorption capacities of produced organoclays were explored in synthesized Cd(II) aqueous solutions with water matrix composition of distilled water and NO_3^-. The results were noteworthy and showed that the Cd(II) was adsorbed up to 94.6 mg per 1 g of adsorbent at the pH range of 6.5–7.5 and temperature of 25.0 °C. The water matrix in the case of pH test was composed of distilled water, NO_3^-, and both OH^{-1} and Cl^- as the anions of NaOH and HCl, respectively. Since various resource and dispersion agents like industrial installation, roads, traffic, streams, wind, and river would distribute TEs with different concentrates in the environment (Naderi et al. 2017), the adsorbents should be able to adsorb a wide range of TEs in different environments. The adsorption capacities of modified clays change from each metal and adsorption mechanisms of various TEs would differ on clay minerals (dos Santos et al. 2015). The various factors are ionic strength, type of anions in solution, pH, temperature, and cationic competition (Babel and Kurniawan 2003; Bhattacharyya and Gupta 2008; Andrejkovičová et al. 2010). Thus, the objective of the present study is to produce organoclays with green properties and test their abilities for high toxic TEs of Pb(II) and Hg(II). The synthesized ILs would not be harmful if they solely release into the environments and would be decomposed through microbial activities. The adsorption ability of the IL-modified clays for Pb(II) and Hg(II) adsorption from the aqueous medium is also investigated. The strong bond between clay and TEs ions through imidazolium ring is very important. This has a great effect on TE immobilization and is explored through

desorption experiments. We also explored multi-use of modified clays through desorption experiments that is important from the economical point of view. Furthermore, the removal ability of the IL-modified clays was compared with synthesized quaternary ammonium acid-modified clays in the same experimental condition. For this purpose, we modified gust clays with HDTMA that is one of the most applied modifiers in the previous researches.

Materials and methods

Chemicals

All chemicals were high-grade reagents (analytical reagent) and utilized without further purification. Chemicals such as 3-chloropropyltrimthoxysilane, 1-methylimidazolium, 1-chlorooctan, 1-chlorohexan, 1-bromo-6-chlorohexane, potassium hexafluorophosphate, and hexadecyltrimethylammonium bromide (HDTMAB) with a purity of 99% were purchased from Sigma–Aldrich (St. Louis, MO, USA). Ethanol (> 99.9%), Pb $(NO_3)_2$, and Hg $(NO_3)_2$ were purchased from Merck (Darmstadt, Germany) and 1000 mg L^{-1} of stock solution of Pb(II) and Hg(II) was made from Pb $(NO_3)_2$ and Hg $(NO_3)_2$. Paper filter (Amicon® Ultra, 3 kDa) and HCl (37%) and NaOH were purchased from Millipore and Merck (Darmstadt, Germany), respectively. The levels of pH of the sample solutions were adjusted using diluted solutions (0.1 mol L^{-1}) of HCl (37%) and NaOH. Double-distilled deionized water was utilized through all of the experiments. Na-Bent (from Southern Khorasan, IRAN) and nano-MT clay minerals (Sigma-Aldrich, St. Louis, MO, USA) were also purchased.

Instrumentation

The measurements of TEs ions contents were performed by atomic adsorption spectrometer (AAS) (Varian spectra AA-200, analytic Jena). The standard solution of 1000 mg L^{-1} (Pb $(NO_3)_2$ in H_2O) and Hg $(NO_3)_2$ in H_2O Titrisol® (Merck Company) is utilized to adjusted AAS instrument. To check the accuracy, each sample was read three times by atomic adsorption spectrometer. Then, precision and accuracy of Pb(II) and Hg(II) measurement was evaluated using relative standard deviations (%RSD) and measured the recovery test (%REC), respectively. The RSDs were applied to determine the precision of reading process through Eq. 1:

$$\%RSD = standard\ deviation/mean\ value \times 100 \qquad (1)$$

The REC was calculated using Eq. 2:

$$\%REC = C_s - C/C_{add} \times 100 \qquad (2)$$

where Cs is concentration of spiked sample (added sample + measured sample); C: concentration of unspiked sample (measured sample); C_{add}: concentration of added sample.

In case of obtaining high RSD and REC, the average of the three measured values of each sample would be reported in graphs and utilized for isotherm models.

By using XRD, the changes in basal spacing of the samples were determined. The XRD patterns used Bruker D8 Advance diffractometer, measured from 2° to 10° (2θ) with the step size of 0.01° (measurement temperature [°C]: 25.00, anode Material: Cu, K-Alpha1 [Å]: 1.54060, generator settings 30 mA, 40 kV, and diffractometer type: D8). In order to identify the functional groups of synthesized sorbents, FT-IR technique (Brucker, Tensor 27) was utilized. The SEM (VEGA, TESCAN-LMU) was applied to evaluated surface morphology of synthesized green organoclays. The N_2-BET method (Belsorp max, BET Japan) and CHN analyzer (vario EL cube) were utilized to determine specific surface area (SSA) and C, H, and N (carbon, hydrogen and nitrogen) contents of the studied clays, respectively. The pHs were measured using digital pH-meter (model 692, Herisau, Switzerland).

Production processes of modified clays

Preparation of nano-Ben

In this study, 2:1 clay minerals of Bent and MT were selected as the guest clays for modifying. The purchased MT was nano-sized originally. The nano-Bent was prepared from natural Bent through solvothermal reactions (Darvishi and Morsali 2011). To ensure successful nano-sizing of Bent, XRD and SEM tests were carried out. The size of Bent after solvothermal reaction was estimated by Scherrer equation (Eq. 3):

$$Crystal\ size = (k \times \lambda)/(\cos \theta) \qquad (3)$$

where $k = 0.9$, $\lambda = 1.54060$ Å, $\theta = 2\theta/2$, β = peak width at half maximum.

IL synthesis

Based on our previous study (Naderi et al. 2018), hydrophilic imidazolium-based ILs were synthesized (Table 1). In Table 1 reactants, their ratio (R1/R2) and experiment condition is described.

Converting water miscible ILs to immiscible types

All synthesized ILs were soluble in water because of Cl^- and Br^- anions (not bulky). The intercalated imidazolium cations into the organoclay would be solvated when it reacted with aqueous phase. To avoid this phenomenon happening, the immiscible ILs were prepared by replacing these anions with

Table 1   Procedure synthesis of hydrophilic imidazolium-based ILs

ILs types	Abbreviation	Reactant 1(R1)	Reactant 2 (R2)	R1/R2	Reaction condition
3,3′-(hexane-1, 6-diyl) bis (1-methylimidazolium) bromide chloride	[H(mim)$_2$][Br][Cl]	1-methylimidazole	1-bromo-6-chloro hexane	2	70 °C for 48 h in N$_2$ atmosphere
1-hexyl-3-methylimidazolium chloride	[Hmim][Cl]	1-methylimidazole	1-chlorohexane	1	70 °C for 72 h in N$_2$ atmosphere
1-methyl-3-octylimidazolium chloride	[Omim][Cl]	1-methylimidazole	1-chlorooctane	1	70–75 °C for 72 h N$_2$ atmosphere

bulky anions such as hexafluorophosphate (PF$_6^-$) (Haixia et al. 2007).

Modifiers intercalation into clay layers

The cation exchange capacity (CEC) of guest clays was determined by NH$_4^+$ method as described in the literatures (Page et al. 1982) and was 80.4 and 91.6 meq 100 g^{-1} for nano-Bent and nano-MT, respectively. The clay minerals were modified by ILs and HDTMA. In this procedure, 1 g of clay minerals was mixed with each modifier (equal to double amount of CEC) and under controlled experimental condition synthesis was carried out (Naderi et al. 2018). The schematic diagram of the preparation processes of organoclays and their symbols are shown in Fig. 1.

Adsorption experiments

All the batch adsorption experiments were conducted for removal of TEs from the aqueous phase at room temperature. First, a pre-test was carried out to find the amount of adsorbent dosage. The pH of solution did not adjust in this step and naturally was 6.8 in the suspension. The optimum pH in which maximum adsorption of TEs by the adsorbents would occur is calculated in the next steps. This pH was necessary for isotherm studies. The TEs solutions were prepared and diluted from 1000 mg L^{-1} standard solution of Pb(II) and Hg(II) in distilled water. For clay particle de-agglomeration and preparation of heterogeneous suspensions, each suspension was vibrated using ultrasonic processor (Qsonica, Q500) for 10 min. The suspension was stirred, centrifuged, and then collected analyzed by atomic adsorption spectroscopy.

Evaluation of optimum analytical parameters ranges on TEs adsorption

To find the most proper condition for isotherm studies, the adsorption of TEs was measured across various contact times (20, 40, 60, 80, 100, 120, and 140 min) and pH of sample solutions (2, 4, 6, 8, and 10). In each test, 50 mL of sample solution (300 mg L^{-1}) of Pb(II) and Hg(II) was added to 4 g L^{-1} of each green organoclays and placed on a shaker with 300 rpm and then was centrifuged at 4000 rpm to separate solid part. After reading concentration of the samples with atomic adsorption, the results with high accuracy and precision were reported for the isotherm studies. In all experiments, Pb(II) and Hg(II) adsorption percent values were determined by Eq. (4):

$$\%Removal = ((C_0 - C_e)/C_0) \times 100 \tag{4}$$

where C$_0$ and C$_e$ were respectively initial (before adsorption process) and final concentrations of TEs (after adsorption process) in solution.

Adsorption isotherm models

In this research, three most popular adsorption isotherms of Freundlich, Langmuir, and Sips (Repo et al. 2011) were fitted on adsorption data by Origin-Lab software (version 8) (Table 2).

Results and discussion

Properties of modified and unmodified clays

The SEM analysis of the natural Bent (Fig. 2a) and nano-Bent (Fig. 2b) confirmed that nano-Bent particles have finer size and are lower agglomerated. The intense and narrow XRD peak of natural Bent in position of about 2θ = 7 (Fig. 2c (1)) compared with a broad peak after solvothermal process in the same position (Fig. 2c (2)) confirmed that Bent particle sizes were decreased after solvothermal process. The calculated crystal size based on Scherrer equation (Eq. 1) of natural Bent (Fig. 2c (1)) estimated 96 nm, and it estimated 18 nm in nano-sized Bent (Fig. 2c (2)). A wide expansion of the modified clays compare with the untreated clays was observed (Fig. 2d).

The XRD graphs of the studied clays are shown in Fig. 3. The d$_{001}$ of B, B$_1$, B$_2$, and B$_3$ were 12.8, 16.7, 28.3, and 15.1
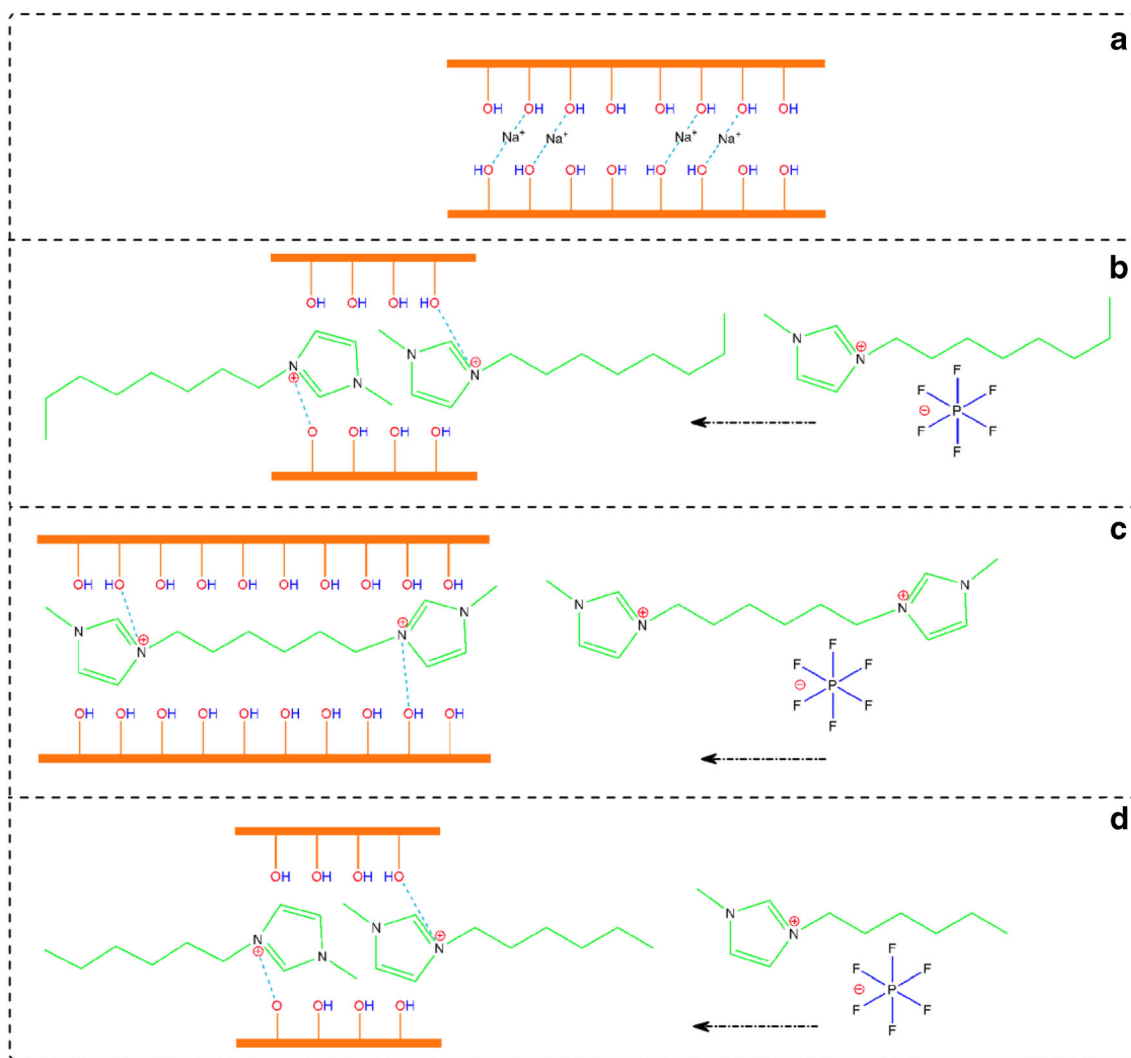
Fig. 1 Structure schematic of a Unmodified clay (MT/Bent), **b** B_1 and M_1 (nano-Bent/nano-MT+[Omim][PF_6]), **c** B_2 and M_2 (nano-Bent/nano-MT+ [H(mim)$_2$][(PF_6)$_2$]), and **d** B_3 and M_3 (nano-Bent/nano-MT+ [Hmim][PF_6])

Å, respectively, and d_{001} of M, M_1, M_2, and M_3 were 14.4, 15.1, 35.4, and 15.2 Å, respectively. The d_{001} of HDTMA-modified clays B_4 and M_4 were 17.4 and 19.2 Å, respectively. Accordingly, compared to the unmodified clays (B and M), the d_{001} peaks of the modified clays were shifted to the lower angles. The greatest d_{001} was obtained in B_2 and M_2 which

was modified with [H(mim)$_2$]. FT-IR spectra of the unmodified and ILs-modified clays with their relative ILs are shown in Fig. 4. The assignments of the peaks in Fig. 4 are listed in Table 3. The bands of 3620, 3420, 3200, 1631, 796, 693, and 627 cm^{-1} are due to stretching vibration of various bonds of unmodified clays. The wavelengths 830, 1400, 2000–2100,

Table 2 Components equations of isotherms

Isotherm equation	Component	Unit	Description	
Freundlich:	q_e	mg L^{-1}	Adsorbate per unit mass of adsorbent	Eq. (3)
$q_e = K_F C_e^{(1/n)}$	q_{max}	mg L^{-1}	Maximum adsorption	
	b	–	Energy of adsorption	
	C_e	mg L^{-1}	Equilibrium concentration	
Langmuir:	K_F	L mg^{-1}	Content of adsorption	Eq. (4)
$q_e = (q_{max} bC_e)/(1 + bC_e)$	n	–	Intensity of adsorption	
Sips:	K_S	–	Equilibrium constant	Eq. (5)
$q_e = (q_{max} K_S C_e^n)/(1 + K_S C_e^n)$				

Fig. 2 SEM images of **a** natural Bent, **b** nano-sized Bent, **c** (1) XRD pattern of natural Bent and (2) XRD pattern of nano-sized Bent, and **d** SEM image of ILs modified Bent
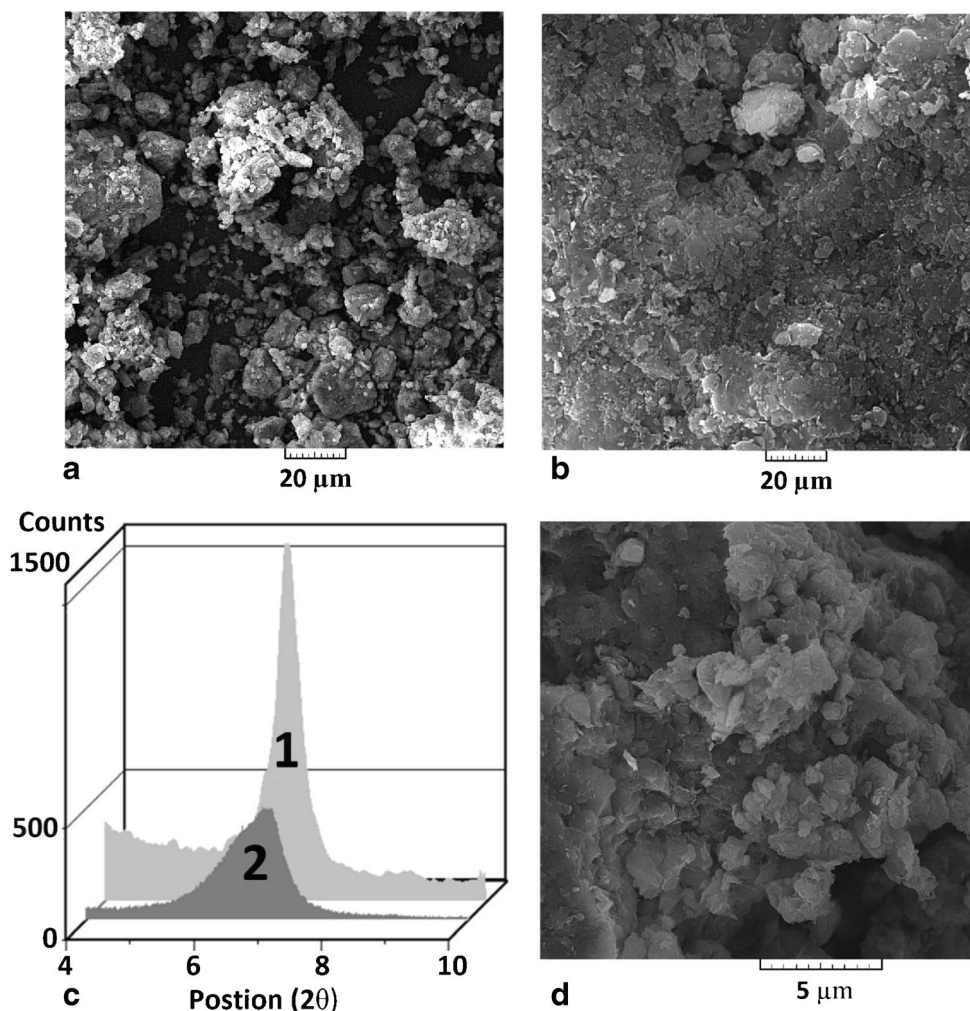
and 3100–31200 cm^{-1} are assigned to vibration of methyl imidazole ring in all IL-modified samples. The intensities of peak of 3200–3800 cm^{-1} and 3200–3800 cm^{-1} are increased since the stretching of water hydroxyl groups and C–C bond of octyl or hexyl chains of [Omim] and [Hmim] ILs. The

bands of 3113, 2860, and 3705 cm^{-1} are assigned to stretching of CH$_2$ functional groups in hexane and octane chains. The bands of 1470, 2852 cm^{-1} are due to stretching of C–C bonds, and 2948 cm^{-1} band is assigned to vibration of symmetric and asymmetric C–H cm^{-1}. The bands of 1481, 1842, and 1920
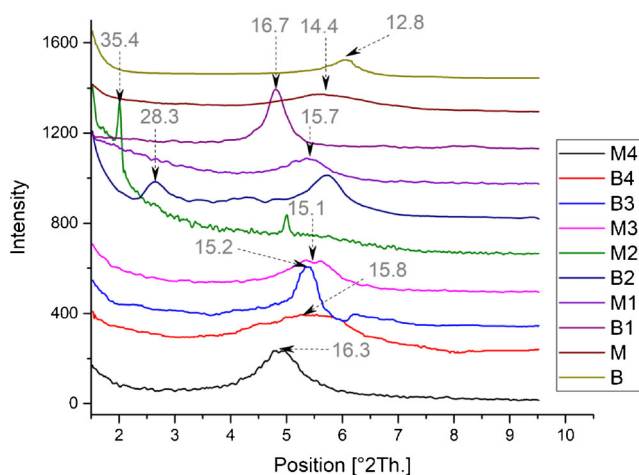

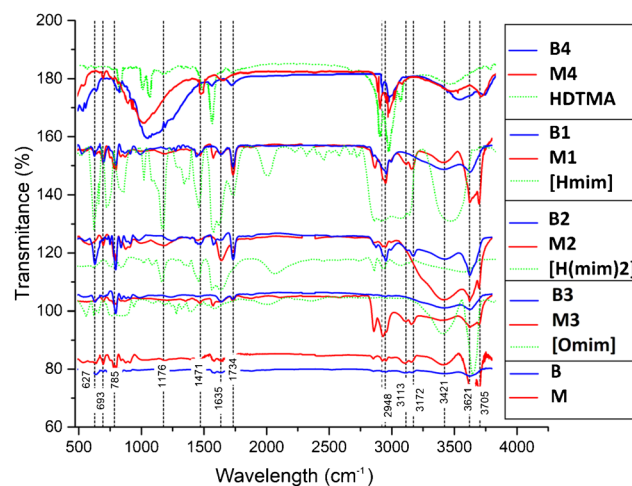**Fig. 3** XRD patterns of unmodified and modified clays

Fig. 4 FT-IR curves of unmodified and ILs-modified clays

Table 3 Positions and assignments of the FT-IR vibration bands

Position (cm^{-1})	Assignments	References
3620	Stretching of OH in Al–OH and Mg–OH	Frost and Kloprogge
3420	Stretching of OH in clay interlayer water	(2000)
3200	Hydroxyl groups linked to AL-Mg	
1631	OH deformation of interlayer water	
693, 627, 796	Si–O–Si and Si–O–Al stretching	
3200 to 3800	Stretching of water hydroxyl in [H(mim)$_2$] and [Omim]	Venegas-Sanchez et al. (2013)
830, 1400, 2000 to 2100, 3100 to 31200	Vibrational methyl imidazole ring	Li and Kobayashi (2016)
1470, 2852	C–C stretching	
2948	Vibration of C–H	Vaia et al. (1994); Xi et al. (2005)
2800 to 2900	C–C bond of octyl or hexyl chains [Omim] or [Hmim]	
3113, 2860, 3705	CH$_2$ functional group in hexane and octane chains	Ganguly et al. (2012)

cm^{-1} are assigned to HDTMA in B$_4$ and M$_4$. These bands of modifier agents were appeared in FT-IR curves of modified clays as an indication of the successful modification process. The result of the elemental analysis of the studied clays is given in Table 4. The high contents of nitrogen and carbon in all samples confirmed that intercalations of the organic cations have been performed. The highest nitrogen percentage in B$_2$ and M$_2$ is due to double methyl imidazole. The high carbon contents in B$_2$ and M$_2$ samples are due to long carbon chains that are in line with the result of FT-IR in that 2860 cm^{-1} band existed in these samples and was assigned to CH$_2$ of hexane chain. The results of N$_2$-BET test revealed that intercalation of ILs into natural clays have led to decrease in SSA of modified clays compared with unmodified clays (Table 4). The results of N$_2$-BET test showed that the SSA of Bent was increased from 61.78 m^2 g^{-1} to 71.78 m^2 g^{-1} after solvothermal process. The solvothermal process and Bent nano-sizing could have positive effects on modification process through higher SSA and enhancing grafted ILs cations.

TEs adsorption across various contact times

Figure 5 shows cumulative extraction percentage of Pb(II) (Fig. 5a) and Hg(II) (Fig. 5b) across times between 10 to 140 min. Overall, it seems that TE extraction was increased across contact time and remained constant at 80 min for all adsorbents. The adsorption sites of the clays modified with [Hmim] are fully occupied at 40 min. Apparently, short alkyl chains of [Hmim] have provided more vacant spaces that led to faster TE adsorption. Based on this test, all the adsorbents reached their maximum adsorption capacity after 80 min. Accordingly, the optimum reaction time was considered as 80 min for all clays.

pH effect on TEs adsorption

The changes in initial pHs of the solution significantly affected TE extraction. Adsorption of TEs was explored in pHs: 2–10 with the same TE initial concentration of 300 mg L^{-1} (Fig. 6). The graph illustrates that adsorption of Pb(II) (Fig. 6a) and Hg(II) (Fig. 6b) was increased dramatically from pH: 2 to 6 and then decreased gradually. In acidic pHs, hydronium ions (H$_3$O$^+$) compete with TEs to occupy activated sites of clays. The competitions between hydroxyl anion and negative charged of clays for interacting of TEs in alkaline pHs have led to lower TEs adsorption. According to the obtained results, pH of 6 was considered as the optimum pH in the conditions experimental tests performed. The results in Fig. 6 show that the adsorbents have removed TEs in wide pH range of 5 to 8 with adsorption efficiency above 80% of extraction. The most

Table 4 The results of CHN and SSA (N$_2$-BET) analysis

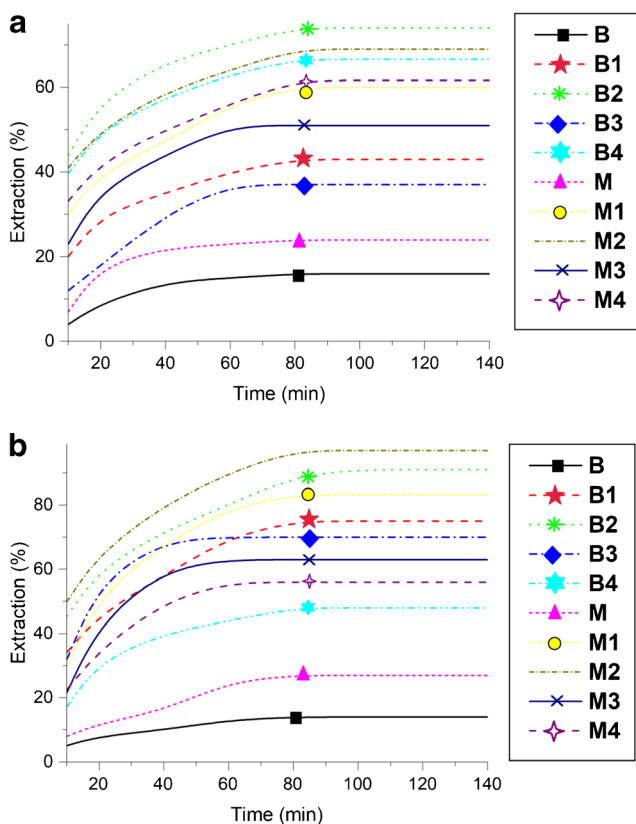| Element	Bent	B	B$_1$	B$_2$	B$_3$	M	M$_1$	M$_2$	M$_3$
N (%)	0.06	0.05	1.49	2.02	1.53	0.04	1.60	2.56	1.68
C (%)	0.10	0.09	7.40	6.54	6.53	0.01	8.39	6.89	3.85
H (%)	0.31	0.31	0.63	0.97	0.96	0.68	0.86	1.19	1.08
SSA (m^2 g^{-1})	61.45	71.78	10.30	28.21	20.02	75.05	12.53	27.67	17.35

Fig. 5 The cumulative extraction amount of the **a** Pb(II) and **b** Hg(II) across times (adsorbent dosage: 4 g L^{-1})

significant fact to emerge from these tests was the adsorption ability of IL-modified clays in wide pH ranges.

Isotherm studies

The study of TEs adsorption isotherms provided useful information about adsorption behavior of the studied clays at a constant temperature, pH: 6 and reaction time of 80 min (Fig. 7). The fitting results of Langmuir, Freundlich, and Sips models showed that the Sips model have the maximum fitting coefficient of determination (R^2). Therefore, the results of Freundlich and Langmuir models are not shown here. The most obvious pieces of information in the Fig. 7 are q_{max} of TE adsorption and adsorption affinity (Ks). The q_{max} values show the number of places that Pb(II) (Fig. 7a) and Hg(II) (Fig. 7b) linked with the adsorbed in the equilibrium concentration (C_e). The Ks constant specified adsorption energy or tendency to adsorption via adsorbent. The organoclays B_2 and M_2 had highest q_{max} of 93.14 and 85.28 mg g^{-1} for Pb(II) and 89.30 and 86.42 mg g^{-1} for Hg(II) respectively. The q_{max} of Pb(II) adsorption of clays in order of priority was $B_2 > M_2 > M_4 > B_4 > M_1 > B_1 > M_3 > B_3 > M > B$, respectively. The q_{max} of Hg(II) adsorption of clays in order of priority was also $B_2 > M_2 > M_1 > B_1 > M_3 > B_3 > M_4 > B_4 > M > B$. According to SSA results, nano-MT clay has more SSA (75.05 m^2 g^{-1}) than the nano-Bent clay (71.78 m^2 g^{-1}). The organoclays based on

MT have been able to obtain more q_{max} values than the organoclays based on Bent. Different charge density in MT and Bent is another possible reason for differences in Pb(II) and Hg(II) adsorption capacity (Souza et al. 2016). The Ks was at maximum for M_3 and B_3. It means that q_e at the initial or low-range concentrations was the highest among the samples. Overall, [Omim] has occupied lower volume due to shorter carbon chain that was accommodated with high SSA in B_3 and M_3 (Tables 4 and 5). The results of the present and previous research (Naderi et al. 2018) have demonstrated that clays modified with [H(mim)$_2$] have maximum q_{max} among the studied IL-modified clays. It was presumed that the large volume and high charge density of [H(mim)$_2$] have led to d$_{001}$ enhancing whereby the adsorption capacity was increased subsequently.

The q_{max} of TEs obtained from adsorption isotherms of the modified clays with various modifier in earlier studies (Lee et al. 2002; Şimşek et al. 2014; Huang et al. 2015; Lagadic et al. 2001; Anirudhan et al. 2012; Phothitontimongkol et al. 2009; Cruz-Guzman et al. 2006; Şölener et al. 2008; Stathi et al. 2007) and modified clays in this study are presented in Fig. 8.

In this regard, the maximum adsorbed Pb(II) and Hg(II) in mg g^{-1} of adsorbent for both green adsorbents like amine-containing compounds and other adsorbents are compared to those for the IL-modified clays. The gust clays in the earlier studies presented in Fig. 8 are the same type as that in this
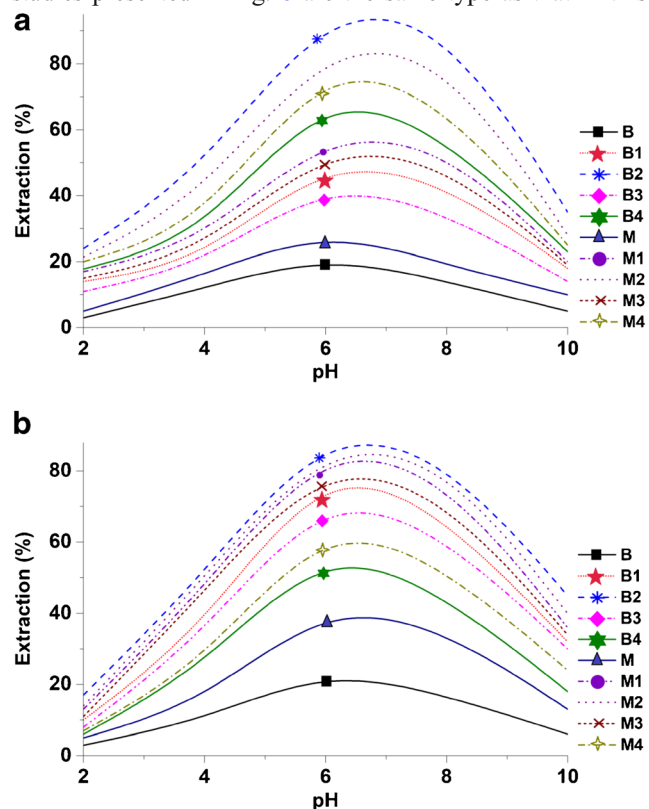

Fig. 6 Cumulative extraction amount of the **a** Pb(II) and **b** Hg(II) across various pHs (adsorbent dosage: 4 g L^{-1} and optimum reaction time: 140 min)
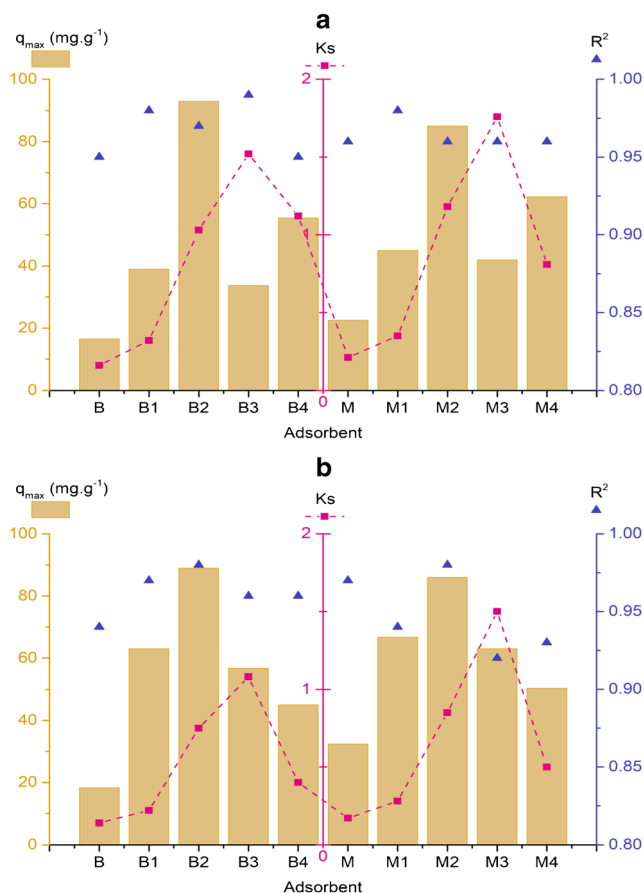
Fig. 7 The results of Sips adsorption isotherms of **a** Pb(II) and **b** Hg(II)

study including Bent and MT. One of the probable reasons for the relative-superiority adsorption capacity of the IL-modified clays could be the obtained d-spacing value after modification. Based on this comparison, the d-spacing value of ILs-clays has reached up to 28 nm which seems to be a considerable change. Another effecting factor is related to the molecular structure of modified agents. The imidazolium cations beside their large radius may occupy lower space in the modified interlayer space that other modified agents in the references researched. It could provide more free space for the metal adoption. The assertion is based on the length of hydrocarbon chain connected to the imidazolium ring. On the other hand, there is no special test in this research to improve the statement above, and this could be one of the possible reasons requiring further researches.

Table 5   The results of B_2 adsorption and desorption test

| HCl	Pb(II) adsorption percentage				Hg(II) adsorption percentage			
	C1	C3	C6	C9	C1	C3	C6	C9
0.1 M	100	99.6	96.6	88.3	100	98.3	96.4	89.3
0.5 M	91.2	83.7	80.6	78.9	90.7	86.4	83.8	77.9

Sorption mechanism of TEs

The mechanism of Pb(II) and Hg(II) adsorption on modified clay using ILs is shown in Fig. 9. The positive charge of nitrogen of imidazolium ring is bonded to hydrogen in clay interior hydroxyl groups to form a hydrogen bond. In fact, the positive charge delocalizes and as the result of that whole ring obtains the positive charge. After TE replacement ions with interior cation like Na$^+$, the nitrogen of methyl group was bonded with TEs through a coordinate (dative covalent) bond.

Desorption experiment

The stability of bonded ILs on the clay mineral surfaces was an important property. The multi-use of the modified clays and risk of TEs release due to decomposition and bond breaking of ILs was needed to be checked. This test was carried out using desorption experiment (stripping by acidic solution) through acidic solutions of 0.1 M and 0.5 M HCl (Table 5). In this part, 4 g L^{-1} of B$_2$ was utilized to remove TEs (concentration: 300 mg L^{-1} and pH 6). In each cycle (C), after removal process, the TEs were measured in the residual solution and centrifuged modified clays were washed with 10 mL of acid treatment. The results showed that the modified clays were able to remove TEs more than 95% after 6 cycles with 0.1 M of HCl, and this was decreased below 95% in next cycles. The adsorption percentage of TEs decreased in 0.5 M of HCl treatment. The OH–N bond between IL-Clay breaks in this pH. This test revealed that IL-Clays have considerable stability, and the products would highly resist again decomposition.

The analysis confirms that the modification of nano-bentonite/montmorillonite with the novel ILs has increased their potential for adsorbing Pb(II) and Hg(II). The modifier agents, ILs, are reported as the green salts (Abbott et al. 2006; Lozano et al. 2007; Vancov et al. 2012; Wanigasekara et al. 2010) where finally the modified clays in the present research are counted as the green sorbents. Generally, in all three types of the applied ILs, a large cation of imidazolium has intercalated into the interlayer of clay minerals and has been bonded with both electrostatic and hydrogen bonds to the negative-charged layers of nano-bentonite/montmorillonite. The exchanging of large imidazolium cations with small cations of Na$^+$ (or Ca^{2+}, Mg^{2+}, etc.) has been led to enhance both interlayer spacing and adsorption capacity for adsorbing large cations of Pb(II) and Hg(II). There is convenience evidence to say that the adsorption trends of the metals were affected by the type of imidazolium. For example, the modified clays using [Omim][Cl], the largest cation with two imidazolium rings, had highest adsorption capacities. Therefore, it seems that the radii of cations has been a crucial factor effecting the metal adsorption which is in line with previous researches

Fig. 8 The q_{max} obtained from adsorption isotherms of Pb(II) and Hg(II) ions in present and earlier studies
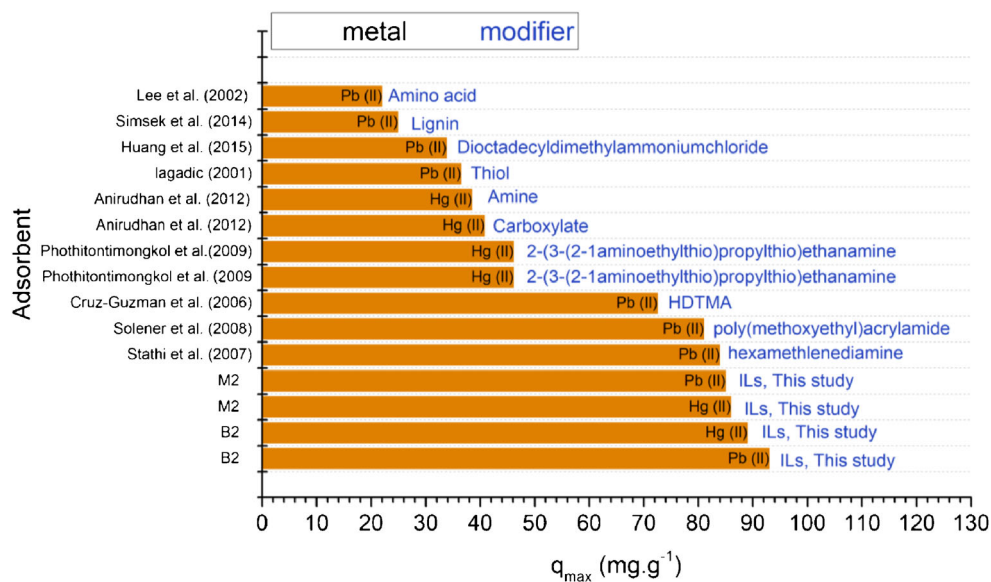
It is also important to say that the results showed both the natural bentonite and the purred montmorillonite had high capability in the ILs adsorption. Subsequently, the amounts of the TEs adsorbed by the modified-clays which were based on the natural bentonite were close to those which were based on the purred montmorillonite. Due to the low price of the natural bentonite compared to the purred montmorillonite as well their similar performance in TE adsorption, it seems that the natural bentonite is more appropriate and economical adsorbent for the modification. All in all, the natural bentonite as a guest clay could be a correct and qualified choice for producing IL-modified clays in industrial scale and mass production.

The generalization of the results is limited by applying the modified clays in polluted waste waters with various ingredients of toxic and non-toxic metals. Although the adsorbent had well performance for adsorbing the toxic metals in single phases, further researches should consider multi-phase solutions and industrial waste waters. As well, it is needed to find a solution to increase the bond strength between the ILs and clay minerals. For instance, covalent bonds and salinization (–Si–O–Si–) process keep imidazolium rings to the clay interlayer stronger than other bands.

Conclusions

This paper deals with the utilization of new several IL-based imidazolium cation synthesized to preparation of organoclays that could be utilized to remove TEs from the aqueous medium. The results showed that during modification processes, the interlayer spacing of modified clays was raised up to 35.4 and 28.3 Å for clays with Bent and Mnt base clay, respectively. These changes subsequently increased capacity of Pb(II)

Fig. 9 Schematic of TEs adsorption by ILs-modified clays
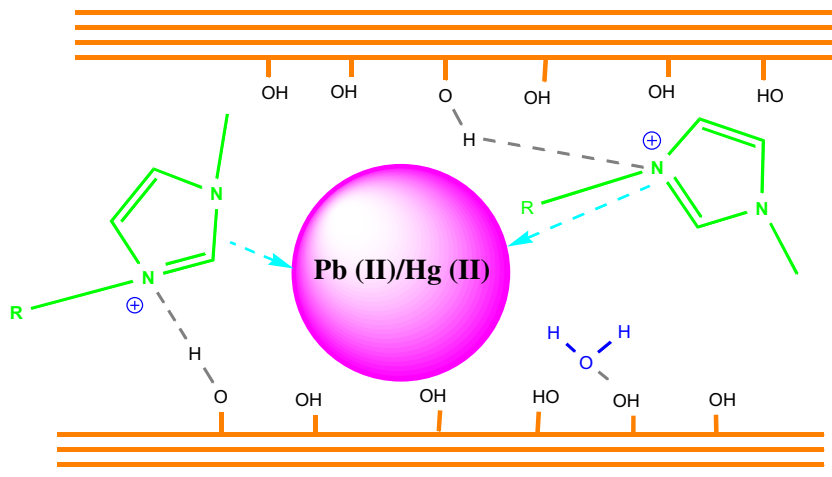
and Hg(II) adsorption. It was evident that the Bent modified with $[H(mim)_2][PF_6^-]$ had highest q_{max} of 93.14 and 89.30 mg g^{-1} for Pb(II) and Hg(II), respectively. The Mnt modified with $[H(mim)_2]$ had highest q_{max} of and 85.28 and 86.42 mg g^{-1} for Pb(II) and Hg(II), respectively. A comparative study of adsorption through adsorption isotherms showed that among the adsorbents, B_2 and M_2 which were synthesized by $[H(mim)_2][PF_6^-]$ were selected as the best sorbent. The ILs facilitated diffusion of Pb(II) and Hg(II) into clay interlayers that was significantly related to size of ionic cation and also d-spacing of produced organoclay. To sum up, the results of present study are important for producing green-organoclay. These green sorbents immobilize hazardous pollution agents, and these sorbents do not cause to secondary pollutions by releasing into environments.

Compliance with ethical standards

Conflict of Interest The authors declare that they have no conflict of interest.

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