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Modification of nano-clays with ionic liquids for the removal of Cd (II) ion from aqueous phase

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Abstract

The present study attempts to synthesize nano-modified clays of Na-bentonite (Bent) and montmorillonite (MT), using three imidazolium-based ionic liquids (ILs) including 3,3'-(hexyl)bis(3-methylimidazolium) bromide chloride ([H(mim)₂[Br][Cl]), 1-hexyl-3-methylimidazolium chloride ([Hmim][Cl]) and 1-octyl-3-methylimidazolium chloride ([Omim][Cl]). 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) (using N₂-BET) techniques provided evidence of successful modification of the guest clays. Removal of Cd (II) from aqueous phase was investigated using the modified clays under different experimental conditions of reaction time, pH and adsorbent dosage. Detailed isotherms and kinetic studies showed that the modified clays have much higher Cd (II) adsorption capacity compared to those of the starting clay minerals. The maximum Cd (II) adsorption capacities of 87.46 and 94.6 mgg⁻¹ were observed in [H(mim)₂]-MT and [H(mim)₂]-Bent with d-values of 35.4 Å and 28.3 Å respectively. The [Omim]-clays had the highest adsorption affinities of Cd (II) in initial concentrations of Cd (II). This study shows that ILs could enhance the clay capacity and tendency for Cd (II) adsorption with different trends based on the

ILs structures. The modified clays using ILs are green and eco-friendly adsorbents and due to substantial increase in their capacity for the removal of heavy metals, they could have positive economic and environmental impacts.

Keywords: Absorption, Clay modification, Green organoclay, Heavy metal.

1 Introduction

The heavy metals are low biodegradable elements with high atomic masses over 55.8 g mol^{-1} and densities higher than 5 g cm^{-3} that are considered as one of the most hazardous contaminants of environments (Mance and Worsfold 1988). Cadmium is the seventh most toxic heavy metal as per the agency for toxic substances and disease registry (ATSDR) ranking and also low level permissible exposure to humans (Kabata-Pendias, 2010). It has various anthropogenic sources of exposure like industrial activities and transportation, and natural factors like wind, topography and streams that distribute Cd (II) into the environment (Nadari et al., 2017). In trace quantities, Cd (II) has many hazardous effects on plants by disordering their metabolisms cycles (Shi et al., 2010; Nazar et al., 2012) and cause of many human diseases like digestive system, respiratory system, acute intoxication, kidney damage, bone damage and carcinogenicity (Godt et al., 2006).

Immobilization of heavy metals is a useful method which significantly decreases their bioavailability (Diels et al., 2002). Over the past few decades, the subject of heavy metals immobilization using modified clays has attracted a great deal of attention (Levy and Francis, 1976; Hamurcu et al., 2010). The smectite clay minerals have a wider range of use in processing and preparing of organoclay. It is due to their charge density, considerable interlayer expansion and ability to adsorb organic and inorganic contaminant using cation exchange and surface complex reactions (Bergaya and Lagaly, 2013). To increase the potential of a raw clay mineral for the adsorption, of they are modified with organic modifier and the produced component is named

organoclay. The organoclay is referred to reactions in which clay minerals through exchange reactions or surface bonds of organic compounds are modified (Bergaya and Lagaly, 2013; He et al., 2014). Hydrophilicity, hydrophobicity, high porosity, and high SSA of organoclays make these compounds the effective adsorbents for volatile organic compounds, organic contaminants and inorganic contaminants (Bergaya and Lagaly, 2001; Bouberka et al., 2009; Bergaya et al., 2011).

Quaternary ammonium cations (QACs) are polyatomic ions with positive charge with central nitrogen atom and connected alkyl or aryl group (NR_4^+). The R may vary from R1 to R4 that each R is a methyl, ethyl and longer alkyl chains with up to 18 carbons or an aryl group (McDonnell, 2007). QACs are further classified on the basis of the nature of the R groups. QACs alkyl or hydroxyl chain, the non-halogenated benzyl chain (including hydroxybenzyl, hydroxyethylbenzyl, naphylmethyl, dodecylbenzyl, and alkyl benzyl), the di- and tri-chlorobenzyl chain. They are all used to modify clay minerals and used as organo-adsorbents, largely because these salts can easily be exchanged with interlayered cations of expandable clay minerals. QACs such as DDBA¹, HDTMA², DTAB³ and OTAB⁴ are commonly used components for modifying clays (Boyd et al., 1988; Groisman et al., 2004; Okada et al., 2005; Pálková et al., 2015). The properties of modified clay is affected by alkyl chain length that d-values of modified clay with long-chain QACs ($n \geq 16$) is very different from that prepared using the QAC with a relatively short alkyl chain ($n < 16$) (He et al., 2014). Since QACs and other conventional modifier are harmful materials in essence and application of these salts in modification process will result in their release into the environment (He et al., 2010). The enrichment and spread of QACs into natural environment are

1 Didodecyldimethylammonium bromide
2 Hexadecyltrimethylammonium bromide
3 Decyltrimethylammonium bromide
4 Octadecyl trimethyl ammonium bromide

potentially adverse to both human and ecosystem health (Zhang et al., 2015). The release of the hazardous modifier has great concern due to their toxic effects on aquatic organisms (Qv and Jiang, 2013), such as daphnids, fish, algae, protozoan and microorganisms (Sánchez-Fortún et al., 2008; Liang et al., 2013; Chen et al., 2014), abatement efficiency of wastewater treatment plants like algae (Liang et al., 2013), reduction in bacteria susceptibility to biocide (Buffet-Bataillon et al.), increases antibiotic-resistance bacteria (Tandukar et al., 2013) and nitrification activities in soils (Hajaya and Pavlostathis, 2012).

New studies have shown that organic modifier application with eco-friendly or green properties such as betaine, ILs, and amino acids are advisable to avoid the hazardous effect of conventional modifier to produce green organoclays (He et al., 2014). The ILs are types of salts which have large cations such as imidazolium, pyridinium, alkyl ammonium, sulfonium and phosphonium and have low melting points of below 100 °C (Paul et al., 2015). The characteristics of ILs including low transition point, low vapor pressure and low toxicity and hazardous effects on environment have encouraged researchers to use these solvents instead of volatile organic solvents (Haixia et al., 2007; Hosseini et al., 2012). Imidazolium-based ILs have long-chains such as butyl, hexyl and octyl that increase interlayer space of clays in comparison with the length of their chains (Gilman et al., 2002). Generally ILs are moderate-low polarity salts (Wakai et al., 2005) and thermal stable components compare with the conventional organic modifiers. The cations and anions of ILs are completely divorces from each for preserving the charge neutrality, and facility in ion movement (Lui et al., 2011). This will result in better cation exchange and modification process.

Synthesis of imidazolium-based ILs compare with other ILs such as pyrrolidinium, alkyl ammonium, pyridinium, phosphonium, has advantages such as easy sample preparation and low cost. Furthermore, polarity of imidazolium ILs is higher because imidazolium structure has two

donor atoms (nitrogen) (Ha and Xanthos, 2009). Imidazolium based compounds has lower toxicity and hazard effect to environment compared to other ILs type. For example pyridinium ILs base has high toxicity (Carmichael and Seddon, 2000; Anderson et al., 2002; Shim et al., 2003).

This study attempts to modify clay minerals using green modifier, ILs, and to apply them for Cd (II) removal. Moreover, no study has been focused on the removal of Cd (II) from aqueous medium using the synthesized ILs. Thus, the objective of this study is to investigate the Cd (II) adsorption using modified 2:1 expandable clays, nano-MT and nano-Bent, by imidazolium-based ILs. In this research, three types of imidazolium-based ILs were synthesized and applied for modifying nano-MT and nano-Bent. The obtained products were characterized using complementary techniques such as XRD, FT-IR, CHN, SEM, N₂-BET and adsorption isotherms including Langmuir, Freundlich and Sips isotherms. Through this work, the influence of six laboratory ILs-modified clays on the Cd (II) absorption from aqueous phases under different experimental conditions of reaction time, pH and adsorbent dosage were studied.

2 Materials and methods

2.1 Materials

To synthesize the green organoclays, 1-methyl imidazole (as center cation), 1-chlorohexane (as alkyl chain), 1-chlorooctane (as alkyl chain), 1-bromo-6-chloro hexane (as alkyl chain) and potassium hexafluorophosphate (as counter ion) were purchased from Sigma-Aldrich (St. Louis, MO, USA). The stock solution of cadmium nitrate (Cd (NO₃)₂) (Merck (Darmstadt, Germany)), ethanol (99.99%) (Merck, EMSURE® ACS), millipore centrifuge filters (Amicon® Ultra, 3 kDa), standard solutions (HCl and NaOH 1 N) for adjusting the acidity and nano-MT (Sigma-Aldrich,

St. Louis, MO, USA) were purchased. The high purify raw Bent was prepared from Zaminkav company¹ in Tehran with origin of Korasan province plains.

2.2 Modification of clays

2.2.1 Preparation of the guest clays

To provide Bent nanoparticles, the raw Bent was dispersed in distilled water and then was shaken for 6 h. The particles with size of less than 2 μm (clay particles) were separated based on the sedimentation process (Stocks law) and then dried at 50 $^{\circ}\text{C}$. The dried fragments of clay were grounded and passed through a 200-mesh sieve. To synthesis Bent nanoparticles, raw Bent was mixed by ethanol with 1:20 ratio mixture and ultra-sound for 20 min. Then mixture was stirred, sealed and maintained at 170 $^{\circ}\text{C}$ for 48 h in Teflon-lined stainless-steel autoclave. The dispersion was filtered and dried in air at 80 $^{\circ}\text{C}$. It was then grounded and passed through a 200-mesh sieve (Darvishi and Morsali, 2011). The crystal sizes of raw Bent and Bent nanoparticles were measured using XRD patterns and Scherrer calculator (equation 1) by X'pert highscore software.

$$\text{Crystal Size} = (0.9 \lambda) / (d \cos\theta) \quad \text{Eq. (1)}$$

Where $\lambda = 1.54060 \text{ \AA}$ (in the case of $\text{CuK}\alpha$), $\theta = 2\theta/2$, d = the full width at half maximum intensity of the highest reflection.

¹ <http://www.zaminkav.com/>

2.2.2 Synthesis of the ILs

2.2.2.1 Synthesis of water soluble ILs

As presented in the Table 1, three types of ILs were synthesized for modifying guest clays with hydrophilic properties. In each case, imidazolium cations were bonded to different alkyl chains with the following methods.

Table 1

Synthesize of imidazolium-based ILs

Types of ILs	Synthesis of 3,3'-(hexyl)bis(1-methylimidazolium) bromide chloride ([H(mim) ₂ [Br][Cl])	Synthesis of 1-hexyl-3-methylimidazolium chloride ([Hmim][Cl])	Synthesis of 1-methyl-3-octylimidazolium chloride ([Omim][Cl])
Synthesis process description	A 0.1 mol (7.97 mL) of 1-methyl imidazole and 0.2 mol (29.84 mL) of 1-bromo-6-chlorohexane with a molar ratio of 1:2 underwent a reaction at 70-75 °C for 72 h under N ₂ gas conditions. Finally, a color cream was produced which was fragile at laboratory temperature and was miscible with water. The produced compound has solid state and to remove the loose and unbonded components, at first washed with distilled water and then with ethyl acetate for several times.	A 0.1 mol (7.97 mL) of 1-methyl imidazole and 0.1 mol (13.72 mL) of 1-chlorohexane with a molar ratio of 1:1 underwent a reaction at 70-75 °C for 72 h and under N ₂ gas conditions. The produced viscose yellow liquid was absolutely liquid at room temperature. The produced compound had a low viscosity and washed subsequently to remove the loose and unbonded components with ethyl acetate for several times.	A 0.1 mol (7.97 mL) of 1-methylimidazole and 0.1 mol (16.90 mL) of 1-chlorooctane with molar ratio of 1:1 underwent a reaction at 75-80 °C for 72 h under N ₂ gas conditions. The produced brown compound was absolutely liquid at room temperature. The produced compound had a low viscosity and washed subsequently to remove the loose and unbonded components with ethyl acetate for several times.

2.2.2.2 Insolubilizing of ILs in water

All of the synthesized ILs were water-soluble and in order to prevent fusion with water and to make them hydrophobic, chloride and bromide anions were replaced with hexafluorophosphate (PF₆) as a bulky and counter anion. Synthesis of 1-alkyl-3-methylimidazolium

hexafluorophosphate with the short name of $[C_x\text{mim}][\text{PF}_6]$ was performed based on the method presented by Haixia et al. (2007). Where x is the number of carbon atoms in the alkyl group (in present work, $x=C_6, C_8$). Analog salts of chloride $[C_n\text{mim}][\text{Cl}]$ ($n=4, 8, \text{ or } 12$) were prepared through adding identical moles of 1-methylimidazole and a precursor alkyl halide and keeping them at $80\text{ }^\circ\text{C}$ for 72 h. The produced compound had a high viscosity and for this reason it was washed with double distilled water for 6 times. It was then added gradually to potassium hexafluorophosphate (1:1-fold for 1-methylimidazole) so that chloride released into the water and $[C_x\text{mim}][\text{PF}_6]$ ($x=4, 8, \text{ or } 12$) were produced. The shaking process lasted for 6 h and then the upper acidic aqueous layer in the container was thrown away. In order to remove the extra chloride anions, the ILs formed in the lower part was washed 6 times with double distilled water. To ensure complete removal of chloride ion from the ILs, titration was performed using silver nitrate and the dispersion was dried using dryer freeze vacuum (Huddleston et al., 2001).

2.2.3 *Modification of guest clays by insoluble ILs*

The cation exchangeable capacity (CEC) of nano-Bent and nano-MT clays were measured by standard ammonium acetate method (Page et al., 1982) and were 80.4 and $91.6\text{ Cmol}(+)\text{kg}^{-1}$ respectively. Synthesis of the organoclay was performed using the method presented by Livi et al. (2011). For this purpose, 1 g of guest clay (Na-Bent or nano-MT) were distributed in ILs in amount of 2.0 clays CEC. The mixture was then scattered using ultrasound device for 20 min and subjected to $80\text{ }^\circ\text{C}$ for 24 h in a refluxed system through injection of N_2 gas in order for the reaction to be completed. Then dispersion of clay and liquid phase were centrifuged and washed with distilled water so that its electrical conductivity reached below $40\text{ }\mu\text{Sm}^{-1}$. Subsequently, the solid phase (clay) was dried at $50\text{ }^\circ\text{C}$ and the fragments of dried clay were grinded and passed through a 200-

mesh sieve. The schematic of the chemical structure for the guest and the synthesized clays are shown in Fig. 1.

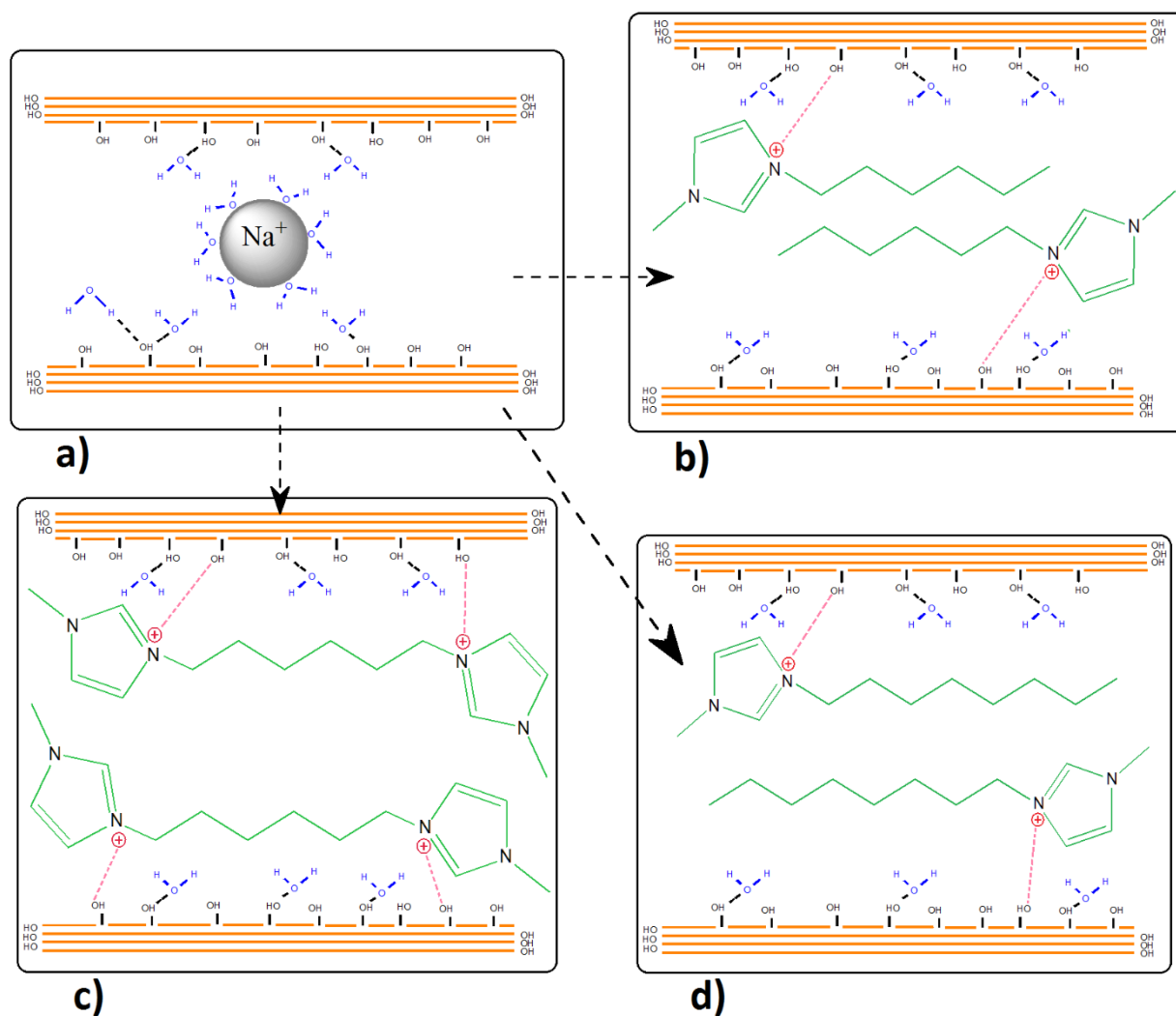


Fig. 1. Preparation stages of organoclays, a) Unmodified Bent, b) B₃, M₃ (nano-Bent/nano-MT + [Hmim][PF₆⁻]), c) B₂, M₂ (nano-Bent/nano-MT + [H(mim)₂][(PF₆⁻)₂]) and d) B₁, M₁ (nano-Bent/nano-MT + [Omim][PF₆⁻]).

The symbols of modified and unmodified clays is explained in Table 2. The guest clay and modifying agents is shown for each adsorbate.

Table 2

Components of modified and unmodified clays with corresponding symbols

Adsorbate	Components	Adsorbate	Components
B	Unmodified nano-Bent	M	Unmodified nano-MT
B ₁	nano-Bent + [Omim][PF ₆ ⁻]	M ₁	nano-MT + [Omim][PF ₆ ⁻]

B ₂	nano-Bent + [H(mim) ₂][(PF ₆ ⁻) ₂]	M ₂	nano-MT + [H(mim) ₂][(PF ₆ ⁻) ₂]
B ₃	nano-Bent + [Hmim][PF ₆ ⁻]	M ₃	nano-MT + [Hmim][PF ₆ ⁻]

2.3 Characteristics methods of the synthesized organoclays

X-ray diffraction analysis was used to determine the changes in interlayer spaces of modified clays compare to the raw clay minerals. The powder samples were analyzed using a Bruker D8 advance laboratory X-ray diffractometer equipped with a CuK α as a radiation source ($\lambda = 1.5418$ Å). To record the first 001 reflection and changes in clay interlayer space, XRD patterns were applied at the 2θ of 2-10, with a measurement of 0.01 degree per second speed and measurement temperature of 25.0°C. A position sensitive detector (Bruker Vantec), operating at voltage of 40 kV and current's intensity of 40 mA with a Bragg Brentano geometry was applied. The powder samples were prepared for analysis using McCrone micronizing mill. The XRD patterns were analyzed using X'pert highscore plus software and the graphs were drawn in OriginLab version 2016 software.

To detect the ILs in modified clay structures, FT-IR (Perkin Elmer, Spectrum GX) experiment was used and spectra over the 400-4000 cm⁻¹ range were obtained by the co-addition of 64 scans with a resolution of 4 cm⁻¹. To evaluate the structure and morphology of the synthesized clays, SEM (VEGA, TESCAN-LMU) was employed and images were taken in high vacuum mode and with a 20-kV accelerating voltage.

The SSA of the clays was measured using N₂-BET method (Belsorp max, BEL Japan, Inc.). The samples had previously been degassed in vacuum at 100°C for 12 h. The relative pressure (P/P₀) range between 0.05 and 0.99 was selected in deriving the nitrogen surface area by applying the BET equation. The percentage of carbon, hydrogen, and nitrogen in the studied clays were measured by CHN analyzer (CHN Analyzer vario EL cube). FT-IR and CHN tests directly are

shown ILs presence in structure of modified clay and confirm successfully modification process are conduct.

2.4 Adsorption of Cd (II) from aqueous phase

The purpose of this part was to assess the optimal condition of adsorption process. Thus the optimum contact time (range of 0.25-12 h), optimum pH of sample solution (range of 2-10) and effect of adsorbents dosage (range of 2-10 gL⁻¹) were studied. To calculate optimum time reaction, 50 mL of the synthetic solution with the concentration of 300 mgL⁻¹ of Cd (II) was poured into a 100-mL flask, to which 0.2 g (equivalent to 4 gL⁻¹) of each clay were added. The pHs of reaction mixture (50 mL of 300 mgL⁻¹ adsorbate + 4 gL⁻¹ adsorbent) were varied from 2 to 10. In this part the reaction time was equal to the calculated optimum time in previous step. The effect of adsorbent dosage was studied at the optimum contact times and in optimum pHs. For all sets of experimental performed, the mixture of organoclay and Cd (II) solution were placed on shaker at 300 rpm, and then this solid part was separated from the aqueous solution after centrifugation at 4000 rpm for 5 min.

The concentration of Cd (II) was measured using graphite furnace atomic absorption spectrometry (GF-AAS) (Varian spectra AA-200, Analytic Jena), and a mean of three reading replications was reported for each sample concentration. The device equipped with a hollow cathode lamp and a deuterium background corrector. The hollow cathode lamp of Cd (II) was operated at 4 mA, using the wavelength at 283.3 nm, slit of 0.7 nm, burner height of 8 mm and acetylene gas flow rate of 1.5 Lmin⁻¹. In order to prepare the standards of atomic device and Cd (II) solutions, standard Cd (II) titrozol solutions (Merck Co. Germany) were used. In order to ensure the accuracy of the device reading, titrozol samples were used to check and control the reading process. The absorption capacity of the adsorbents was measured using equation 2.

$$q_e = V (C_e - C_0) / m \quad \text{Eq. (2)}$$

Where q_e is the Cd (II) absorption capacity by the adsorbent in terms of mgg^{-1} , C_0 , C_e represents the initial and equilibrium concentrations of the metal in the solution in terms of mgg^{-1} , V denotes the volume of the solution per L, and m is the mass of the adsorbent in terms of gram. The values of Cd (II) absorption percentage were measured using equation 3.

$$\% \text{Removal} = ((C_0 - C_f) / C_0) \times 100 \quad \text{Eq. (3)}$$

Where C_0 and C_f are the initial and final concentrations of Cd (II) in the solution, respectively.

3.4. 1 Fitting data with absorption isotherm models

In order to evaluate the behavior of Cd (II) adsorbed into clays, three of the most popular isotherm models were applied to find the best fit model. The Langmuir, Freundlich and Sips relations were fitted onto the data nonlinearly (using OriginLab software 2016) to describe the absorption data. Langmuir model studies the behavior of standard equilibrium state assuming that the adsorbent has a constant number of absorption sites and adsorption on the surface of the material is monolayer. It is also assumed that the surface of the adsorbent is homogeneous and there is no interaction among the adsorbate molecules (Agrafioti et al., 2014). Langmuir model has been explained using equation 4.

$$q_e = (q_{\max} K_L C_e) / (1 + K_L C_e) \quad \text{Eq. (4)}$$

Where C_e represents the concentration of the metal at equilibrium state (mgL^{-1}), q_e shows the amount of the adsorbate per mass unit of the adsorbent at equilibrium state (mgg^{-1}), q_{\max} is the maximum absorption capacity (mgg^{-1}), and K_L is Langmuir constant related to the absorption of energy (Lmg^{-1}).

Freundlich model is assumed that adsorption on the surface of the adsorbent is multilayer and the adsorbent's surface is homogeneous. Freundlich equation is stated using equation 5.

$$q_e = K_f C_e^{(1/n)} \quad \text{Eq. (5)}$$

Where q_e is the amount of solute adsorbed mass unit of the adsorbent (mgg^{-1}), K_f is an index for the absorption capacity and $1/n$ is the intensity of absorption.

The nonlinear Sips (Freundlich – Langmuir) isotherm equation (Repo et al., 2011) is explained as equation 6.

$$q_e = (q_{\max} K_s C_e^n) / (1 + K_L C_e^n) \quad \text{Eq. (6)}$$

Where q_{\max} is the maximum absorption capacity (mgg^{-1}), K_s is equilibrium constant of Sips equation.

3 Results and Discussion

3.1 Characterization of modified clays

3.1.1 XRD analysis

The results of the XRD patterns are shown in Fig. 2. The interlayer space of the clay in 001 reflection for the nano-unmodified Bent (B), B₁, B₂, and B₃ clays were 12.8, 16.7, 28.3, and 15.1 Å, respectively. This space for nano-unmodified MT (M), M₁, M₂, and M₃ clays were 14.4, 15.3, 35.4, and 15.2 Å, respectively. The modified clays had a greater 001 reflection than unmodified clays, suggesting replacement of sodium ions by the imidazolium cations and swelling of the guest clays due to steric volume occupied by imidazolium. The modified clays of B₂ and M₂ considering the volume of Hmim₂ molecule and double ring of imidazolium, had the greatest interlayer space among the organoclay. The increase in interlayer space of modified clay has a direct relationship with volume and size of modifier cation and substituents chain length ILs (Ha and Xanthos, 2009). Beside the size of molecules, the arrangement of molecules in interlayer space is another controlling factor on organoclay d-values. For example, the d-values above 30 Å is due to paraffin

arrangement of imidazolium rings and shorter d-values about 19 Å, adopt pseudo trilayer arrangements (Souza et al., 2016).

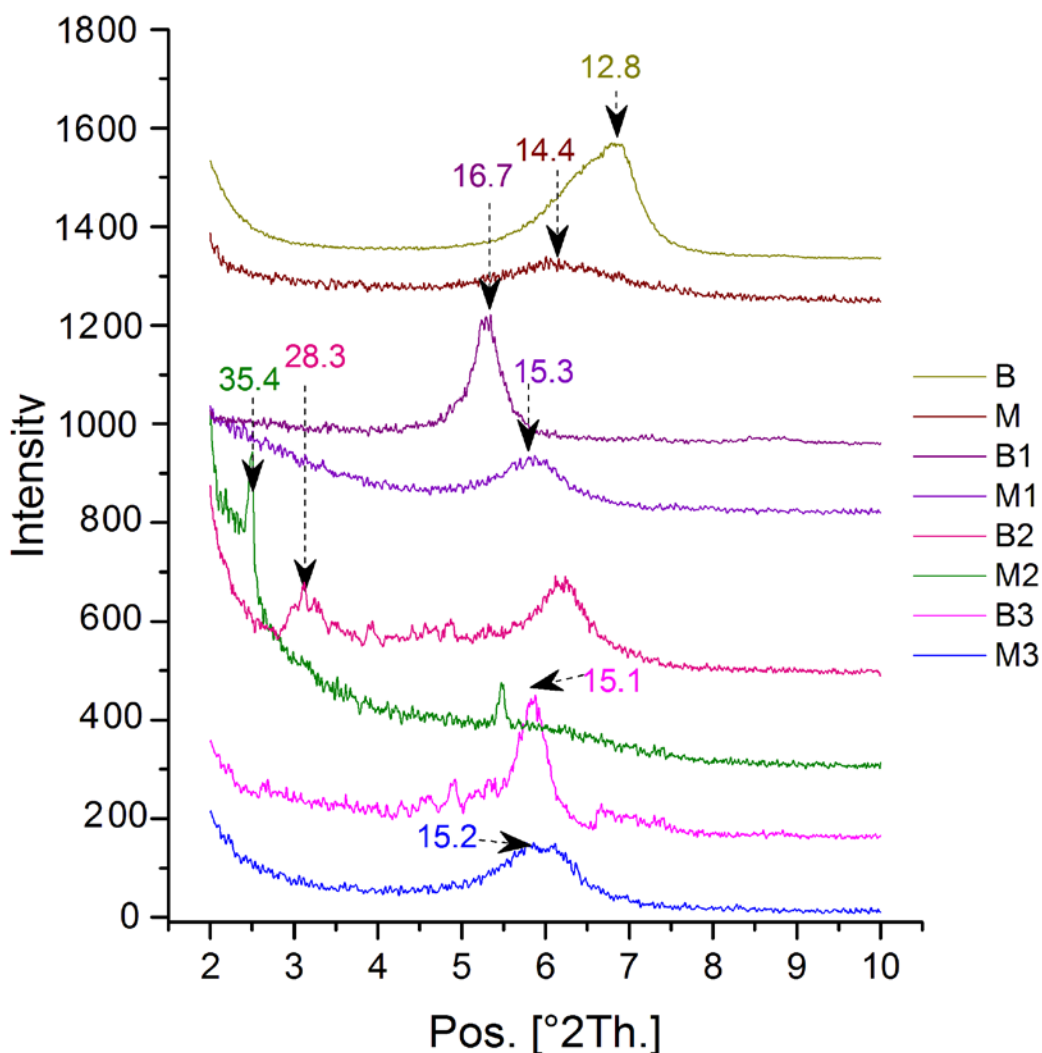


Fig. 2. XRD patterns of the studied clays.

3.1.2 FT-IR Spectra

FT-IR spectra of ILs are shown in Fig. 3. A broad reflection is appeared at 3200-3800 cm^{-1} in [Hmim], [H(mim)₂] and [Omim] samples. This reflection is assigned to hydroxyl stretching of ILs (Venegas-Sanchez et al., 2013). The wavelenghts of 830, 1400, 2000-2100, 3100-3120 cm^{-1} are assigned to vibrational methyl imidazole ring (C-C ring) in the ILs (Li and Kobayashi, 2016) that is appeared in B₁-B₃ and M₁-M₃ organoclays (Fig. 4). The wavelenghts of 1470, 2852 and 2948

cm^{-1} is related to stretching C-C chemical bond, symmetric and asymmetric C-H vibrations, respectively (Vaia et al., 1994; Xi et al., 2005). A broad reflection of 2800-2900 cm^{-1} is assigned to C-H bond of alkyl chain in [Omim], [Hmim] and [H(mim)₂] that is clearly appeared in B₁ and M₁ organoclays. The obtained results of FT-IR test for organoclays (Fig. 3) indicated that the wavelenghts of 3620, 3420, 1732, 1635 and 769 cm^{-1} are related to stretching of silanol, aluminum oxide and hydroxyls groups of raw Bent. The wavelenght of 3200 cm^{-1} band is related to hydroxyl groups linked to Al-Mg of MT. The wavelenghts of 3420 and 1635 cm^{-1} correspond to the hydroxyl stretching of absorbed water (Frost and Kloprogge, 2000). The wavelenghts of 3113, 2860 and 3705 cm^{-1} were detected in the modified clays that were related to stretching of CH₂ functional groups in hexane and octane chains (Patel et al., 2007; Ganguly et al., 2012).

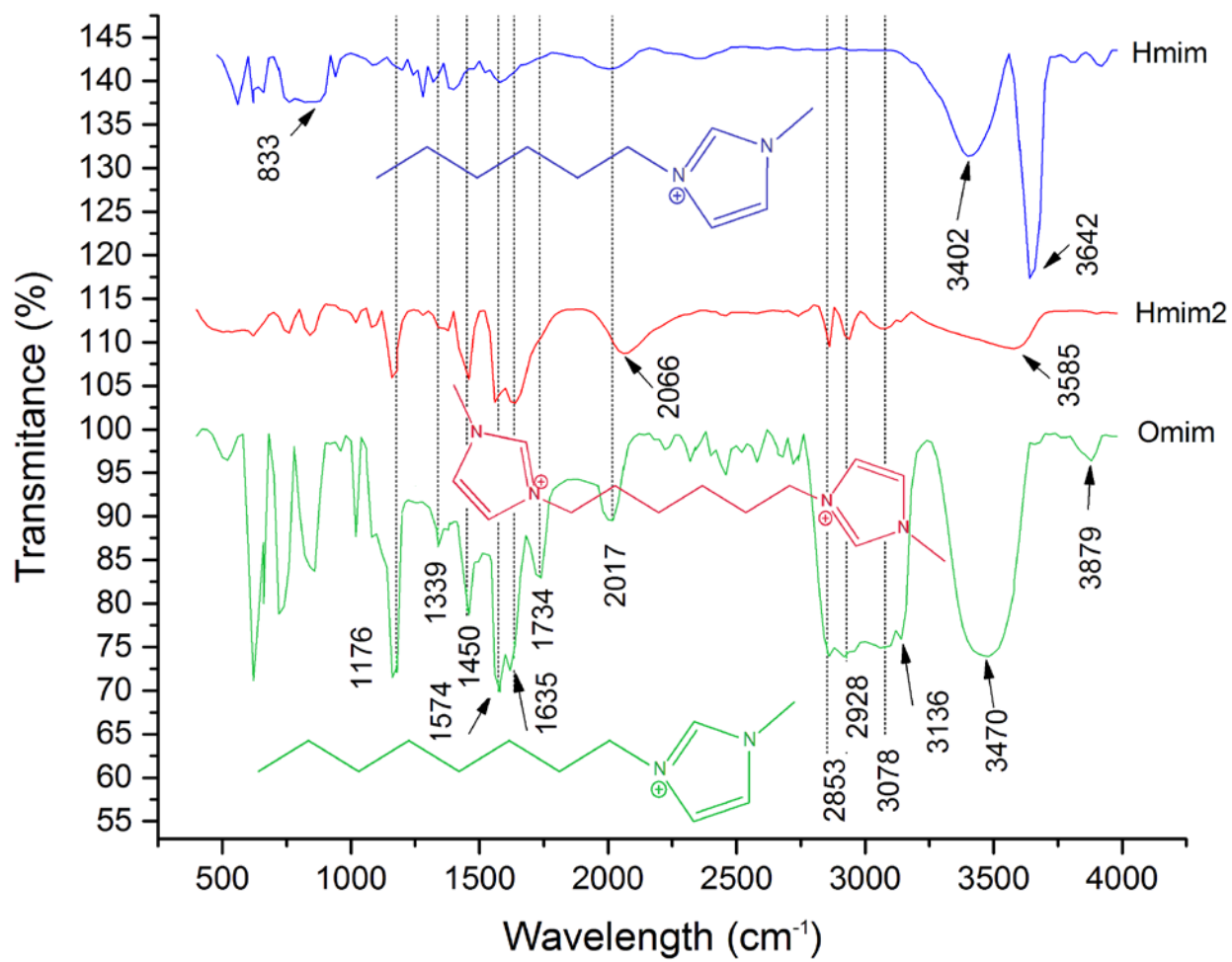


Fig. 3. FT-IR Spectra of synthesized ILs.

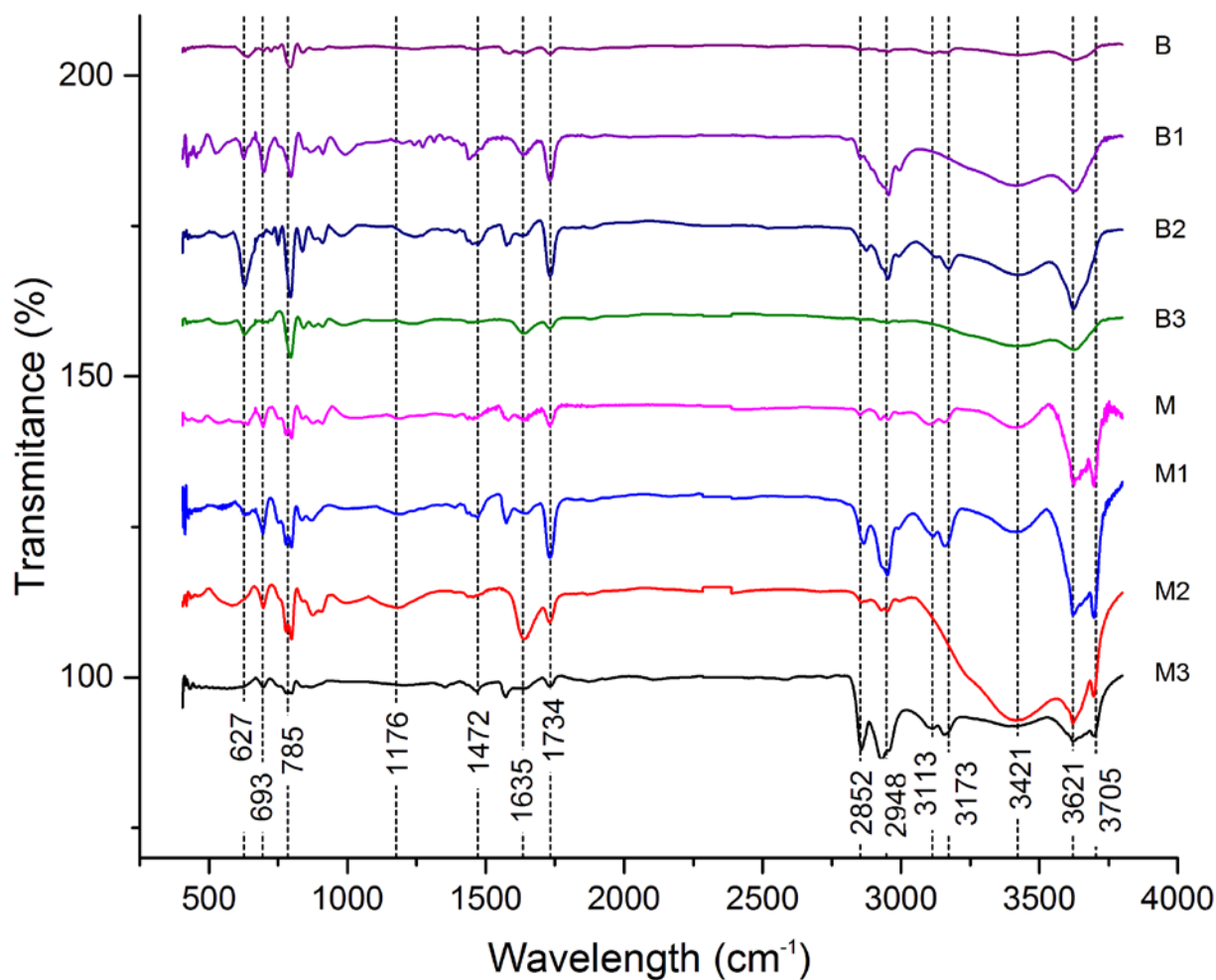


Fig. 4. FT-IR Spectra of the studied clays.

3.1.3 SEM analysis

The SEM images of the raw Bent and nano-Bent (B) prepared by the solvothermal process are presented in Fig. 5a and 5b. The morphology of nano-Bent (B) is finer than the raw Bent and based on Sherrer formula, the average size of raw Bent was 96 nm that was decreased to 18 nm in nano-Bent. The SEM images indicated that compare to the guest clay (Fig. 5c), the synthesized clay B₂ (Fig. 5d) have had a greater expansion and intercalating of ILs into the Bent clays had resulted in development of their organic units and volume growth. By revealing the same SEM results, organoclays were low agglomerated than the guest clays, B and M.

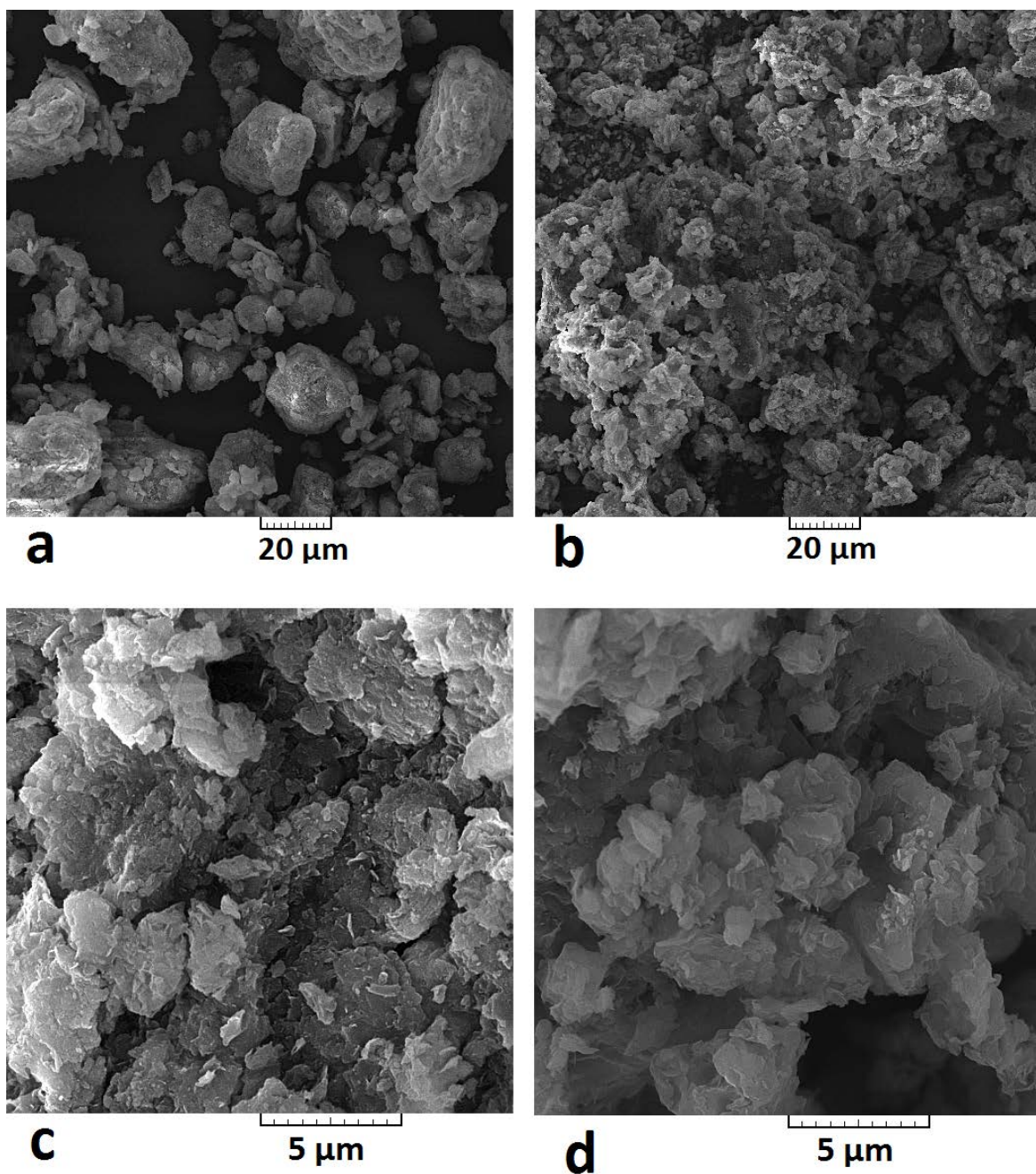


Fig. 5. SEM images of a) raw Bent, b) nano-Bent (B) and c) nano unmodified B₂ d) nano-modified B₂.

3.1.4 CHN and N₂-BET analysis

The results of carbon, nitrogen and hydrogen contents in the studied clays are presented in the Table 3 that shows the amounts of grafted ILs by the clays. Some parts of the ILs were not grafted with the clays in the reaction and are washed after modification process. The CHN values show the content of grafted ILs with the raw clays and confirm correctly clay modification. The modified

clays of M₂ and B₂ clays had the maximum nitrogen values of 1.86 and 1.98% and carbon values of 8.42 and 9.74%, respectively. This could be attributed to the presence of a thicker layer of [H(mim)₂] compound in the interlayer space of these clays considering the high interlayer distance in these compounds. The obtained results of N₂-BET analysis and measurement of the SSA showed decrease in internal surfaces of the modified clays (Table 3). The SSA of raw Bent (Bent), nano-Bent (B) and nano-MT (M) were 61.45, 71.78 and 74.43 m²g⁻¹, respectively. This revealed that: i) Bent nanoparticles had wider SSA compared to the raw Bent; and ii) MT based modified clay had more capacity for intercalating ILs.

Table 3
Elemental analysis (CHN) and SSA (N₂-BET) of studied clays.

Adsorbent		Bent	B	B ₁	B ₂	B ₃	M	M ₁	M ₂	M ₃
Elemental analysis (%)	Nitrogen	0.06	0.05	1.48	1.98	1.49	0.14	1.60	1.86	1.43
	Carbon	0.10	0.09	4.98	9.74	6.49	0.12	3.93	8.42	4.44
	Hydrogen	0.31	0.31	0.59	0.94	0.99	0.56	0.84	1.16	1.11
SSA (N ₂ -BET) (m ² g ⁻¹)		61.45	71.78	10.64	28.34	21.41	74.43	13.21	26.33	18.55

3.2 Effect of contact time on Cd (II) absorption

The results of cumulative amount of the Cd (II) extraction across different times (15 to 750 min) are shown in Fig. 6. The amount of Cd (II) absorption initially is very fast and has an ascending slope with the increase in the contact time from 15 to 60 min. From 60 to 180 min, the trend of extraction is smooth, suggesting that at these times the absorption sites have always been saturated by Cd (II) ion and the clays have no suitable efficiency during longer times. The optimal absorption time for the studied clays was considered as 180 min.

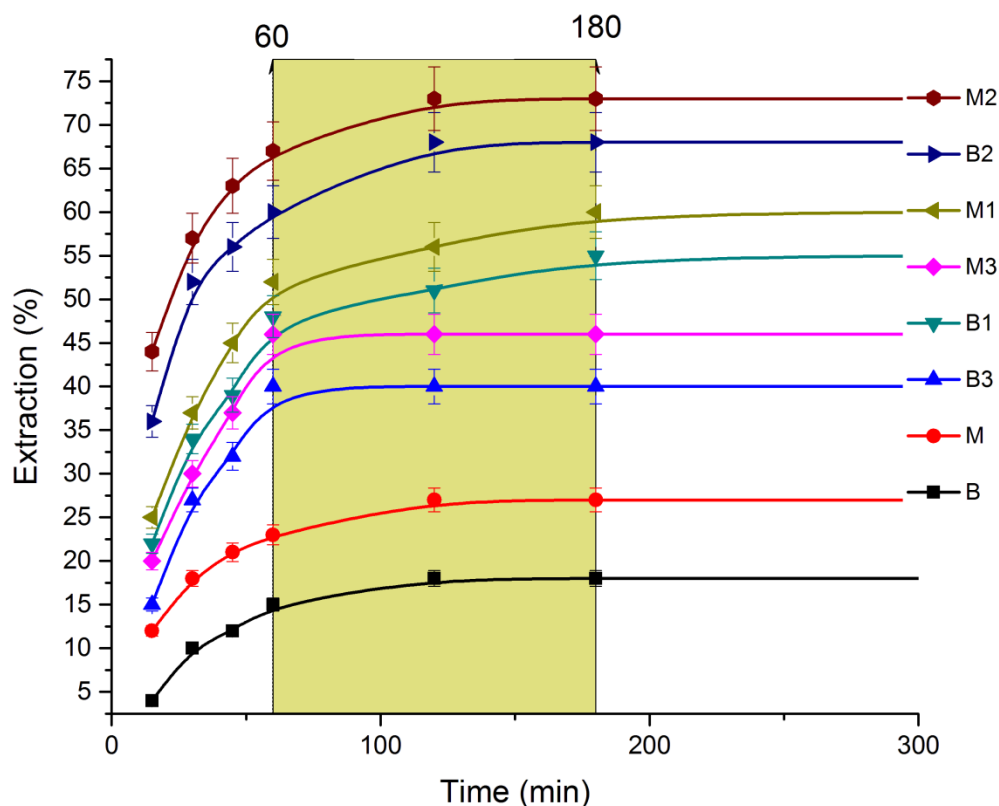


Fig. 6. Cumulative amount of the Cd (II) extraction across different times (with a constant value for the studied clays dosage: 4 gL^{-1}).

3.3 Effect of the pH on the Cd (II) absorption

The solution pH as one of the important parameters in removal process and absorption characteristics was studied in the range of 2-10 with a Cd (II) ion concentration of 300 mgL^{-1} and the adsorbent level of 4 gL^{-1} (Fig. 7). The results showed that the Cd (II) removal from aqueous phase using the studied clays has had a fast-ascending trend with the increase in the pH from 2 to 6. The adsorption reached its maximum value at the pH range of 6.5-7.5. The Cd (II) removal at this range of pH for the organoclays M_2 and B_2 was 81 and 74%, respectively. With the increase in the pH from 8 to 10, the absorption showed a descending trend. The low values of Cd (II) removal at low acidities environment are due to the competition between H_3O^+ ions and Cd (II) to

occupy the absorption sites of the clay. The results of these tests showed that pH of 7 was the optimum pH for Cd (II) adsorption.

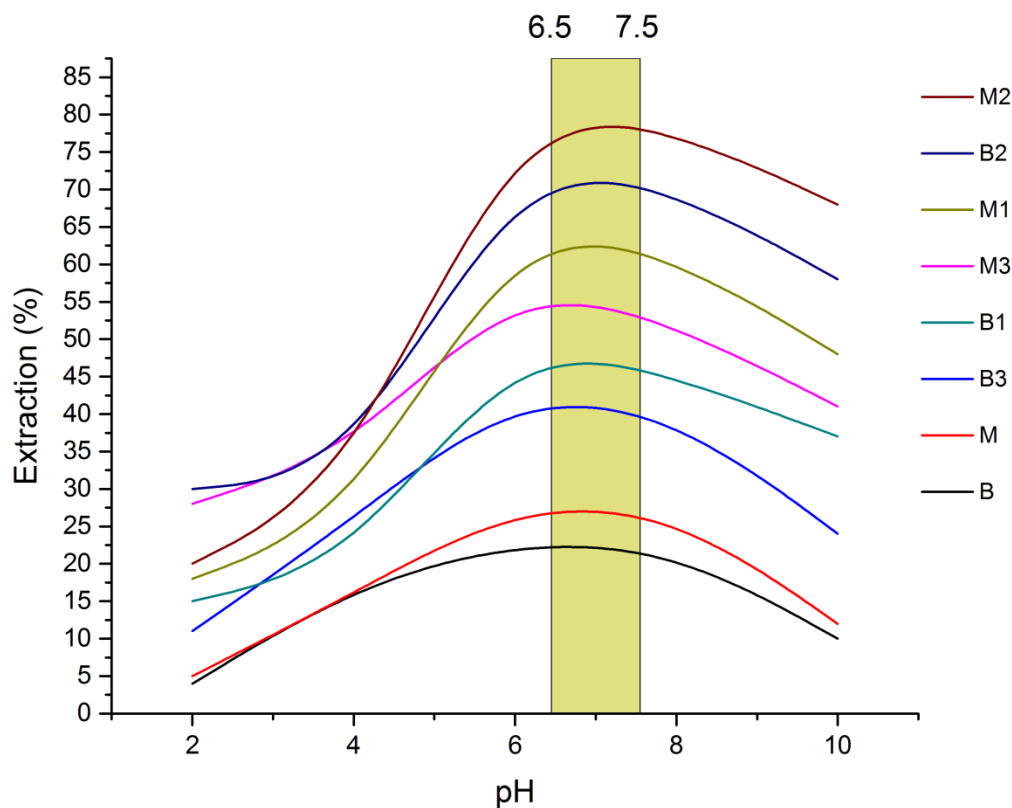


Fig. 7. Cumulative amount of the Cd (II) extraction across different pHs (with a constant value for the studied clays dosage: 4 gL^{-1} and optimum time for reaction: 180 min).

3.4 Effect of the adsorbent dosages on absorption

The results of adsorbent dosage on Cd (II) removal ions at the concentration of 300 mgL^{-1} and pH of 7 are presented in Fig. 8. With the increase in the adsorbent level from 2 to 10 gL^{-1} , the degree of absorption increased with different trends. The organoclays of M₂ and B₂ with 3 gL^{-1} removed 100% Cd (II) from aqueous phase at 2 gL^{-1} of the adsorbent. This test showed that Cd (II) extraction level by M₂ was 16% greater than B₂. Based on the obtained results across all of the studied clays, M₂ clay had the greatest ability for Cd (II) removal. M₁ and B₁ clays at 5 gL^{-1} and

M₃ and B₃ at 7 gL⁻¹ removed 100% of Cd (II) in solution. The Cd (II) removal ability across different clays followed the order of: M₂>B₂>M₁>B₁>M₃>B₃>M>B₂.

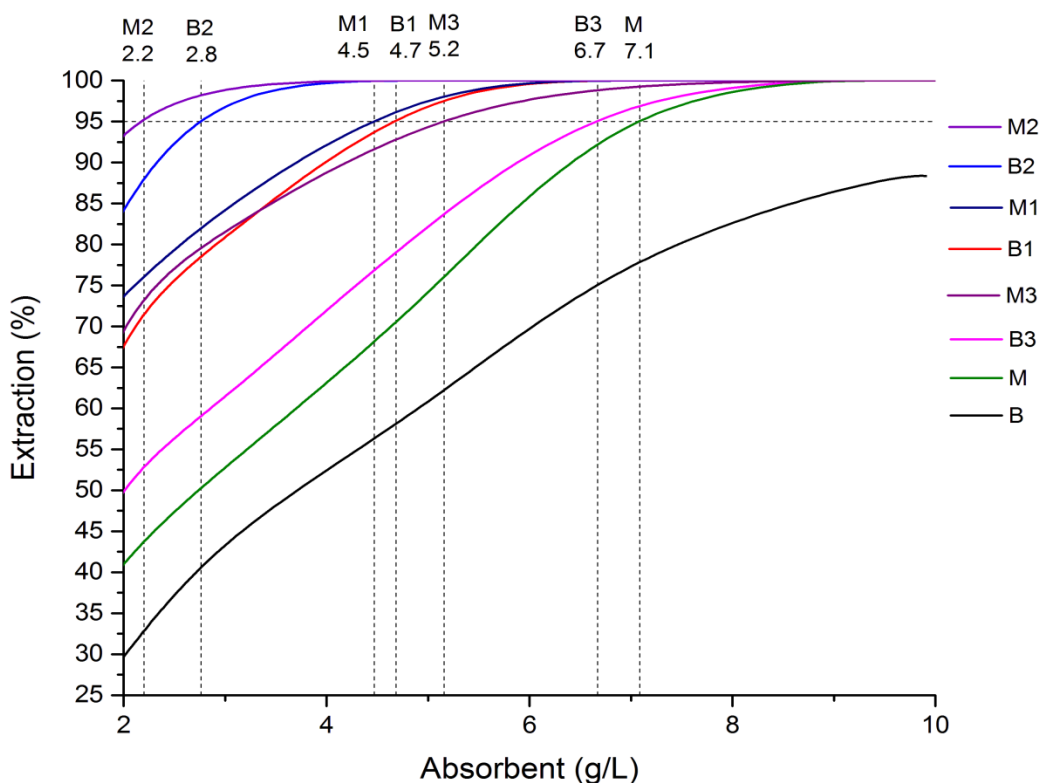


Fig. 8. The results of adsorbent dosage on Cd (II) extraction (at the optimum reaction pH of 7 and the optimum reaction time of 180 min).

3.5 The results of adsorption isotherm studies

In order to find the best equilibrium curves, experimental models of Langmuir, Freundlich and Sips were used and the results of model fittings including correlation coefficients and constant values are presented in Table 4. Overall, it was seen that the Sips model had the highest R² for Cd (II) adsorption data of studied clays and accordingly, it was the most appropriate fitting model compared to the Langmuir and Freundlich models.

In Langmuir and Sips models, q_{max}, as the total number of binding sites or theoretical monolayer saturation capacity of the studied clays, was obtained through calculation. Although these

equations do not present clear information about the absorption mechanism, represent the absorption ability as well as the absorption process by the adsorbent at the time of equilibrium. The range of q_{\max} for B₂ and M₂, were similar in Langmuir and Sips models with having higher adsorption contents (mgg^{-1}) than other clays. Adsorption values of 87.46 and 94.6 mgg^{-1} were calculated as the q_{\max} for B₂ and M₂ modified clays, respectively. The performance of the studied clays was investigated for both the level of absorption and tendency to Cd (II) absorption. Considering the q_{\max} values, the ability of absorption in the studied clays followed the order of: $M_2 > B_2 > M_1 > B_1 > M_3 > B_3 > M > B$.

The adsorption level of Cd (II) using unmodified and modified clays has been reported in several studies. The Cd (II) adsorption values of 6.3 mgg^{-1} (Dal Bosco et al., 2006), 22.7 mgg^{-1} and 30.7 mgg^{-1} (Gupta and Bhattacharyya, 2008) were reported for unmodified MT and adsorption values of 11.2 mgg^{-1} (Gupta and Bhattacharyya, 2008) and 30 mgg^{-1} (Alvarez-Ayuso and García-Sánchez, 2003) were reported for unmodified Bent. The Sips model showed that Cd (II) adsorption by Bent and MT were 19.52 and 30.74 mgg^{-1} respectively with no major difference in the presented results. Stathi et al. (2007) studied Cd (II) adsorption using three novel modified clays. The modified MT with hexamethylenediamine, 2-(dimethylaminoethanethiol hydrochloride), 5-aminovaleric acid, hexamethylenediamine-dithiocarbamate and reported maximum Cd (II) absorption of 160, 120, 204 and 306 mgg^{-1} respectively. Naidu and Harter (1998) reported that the q_{\max} values for organoclay synthesized with organic ligands such as acetate and citrate is 3.36 mgg^{-1} of clay. Lee et al (2011) used amino-clay (organoclay) and achieved the maximum values of 26.5 and 91.31 mgg^{-1} of clay, Cd (II), and lead adsorbed at natural acidity. Biswas et al. (2016) had modified Bent clay using surfactant cation and studied absorption of Cd (II) in aqueous solutions. They reported the maximum absorption level as 24.4 mgL^{-1} . The maximum absorption level in the

studied clays was mainly related to the interlayer distance values developed considering the type of organic liquid and the clay type. In this study, M₂ and B₂ clays with the highest interlayer distances value of 35.4 Å and 28.3 Å had the maximum q_{max} of 87.46 and 94.6 mgg⁻¹ respectively. Compare with the previous studies, the suitable absorption levels of Cd (II) for modified clays in this study has been achieved. Based on the results of N₂-BET test for the clays, unmodified nano-MT had higher internal surfaces (74.48 m²g⁻¹) in comparison with unmodified nano-Bent (71.78 m²g⁻¹). This fact has provided more interior SSA for interaction with ILs in modified clays with nano-MT as the starting or guest clay. In addition, higher Cd (II) adsorption capacity by modified MTs in comparison with modified Bents is due to higher SSA of MT.

Table 4

Langmuir, Freundlich and Sips isotherms constants for the adsorption of Cd (II) onto studied clays

Model	Parameters	Adsorbent							
		B	B ₁	B ₂	B ₃	M	M ₁	M ₂	M ₃
Langmuir	q _{max}	17.26	54.74	84.22	31.82	27.02	71.2	90.5	52.98
	K _L	1.40	1.10	1.57	2.08	1.73	1.40	1.48	2.13
	R ²	0.98	0.90	0.91	0.91	0.70	0.86	0.90	0.89
Freundlich	K _F	1.47	8.80	7.41	3.68	3.00	9.43	14.39	4.63
	N	0.37	0.69	0.53	1.81	0.47	0.81	0.83	1.27
	R ²	0.71	0.92	0.78	0.79	0.85	0.90	0.87	0.81
Sips	q _{max}	19.52	58.78	87.46	33.2	30.74	73.3	94.6	58.42
	K _S	2.32	2.45	2.05	1.13	1.54	2.65	1.85	1.04
	N	0.68	0.71	1.22	1.86	0.84	1.96	1.53	2.43
	R ²	0.98	0.96	0.95	0.94	0.90	0.96	0.98	0.90

The constant value of K in Sips and Langmuir equations is an indication of the adsorption by the adsorbent energy level (in the studied clays). The large values of K suggested higher tendency of the organoclays to adsorb the Cd (II). The constants of K_L (in Langmuir model) and K_S (in Sips model) show Cd (II) adoption affinities of the studied clays. The values of these constant were

highest in the modified clays with [Hmim] modifier. In this case, B1 and M1 were modified with shorter alkyl chain ILs of [Hmim], and this seems that these adsorbent are needed shorter time to adsorb Cd (II) on interior surfaces. Elfassy et al. (2016) reported in a case of [C₄mim] + [NTf₂]-ILs for the mercury adsorption, reported that ILs with longer alkyl chains has lower affinity in Hg (II) adsorption and the reaction between adsorbate and adsorbent was more time consumer.

Freundlich relation is an experimental equation in which the maximum amount of absorption by the adsorbent is not observed and logically is used for low to medium equilibrium concentrations. The K_F values were 9.43 and 8.80 for M₁ and B₁ clays respectively, which are higher than other clays with the same base and are congruent with the values of K_S and K_L factor in Sips and Langmuir equations. Accordingly, it reports the characteristics of absorption intensity or affinity to absorption in these two types of clay to be higher than other clays. On the other hand, the smaller the values of $1/n$ is, the more significant and higher the absorption is at low concentrations (Teng and Hsieh, 1998). The values of this parameter in Table 4 suggest high absorption intensity in M₁ and B₁ clays, and are in line with the results of other factors, which had been described in isotherms of absorption.

3.6 Sorption mechanism of Cd (II)

In the following schematic (Fig.9), the mechanism of Cd (II) adsorption is described. Base on the described schematic, firstly nitrogen atom with positive charge reacts with hydrogen of hydroxyl groups of clay interlayers in the form of hydrogen strength bonds. Then, contact of sample solution containing Cd (II) with green organoclay, co-ordinate (dative covalent) bonds forms between Cd (II) with nitrogen on methyl group of imidazolium cation.

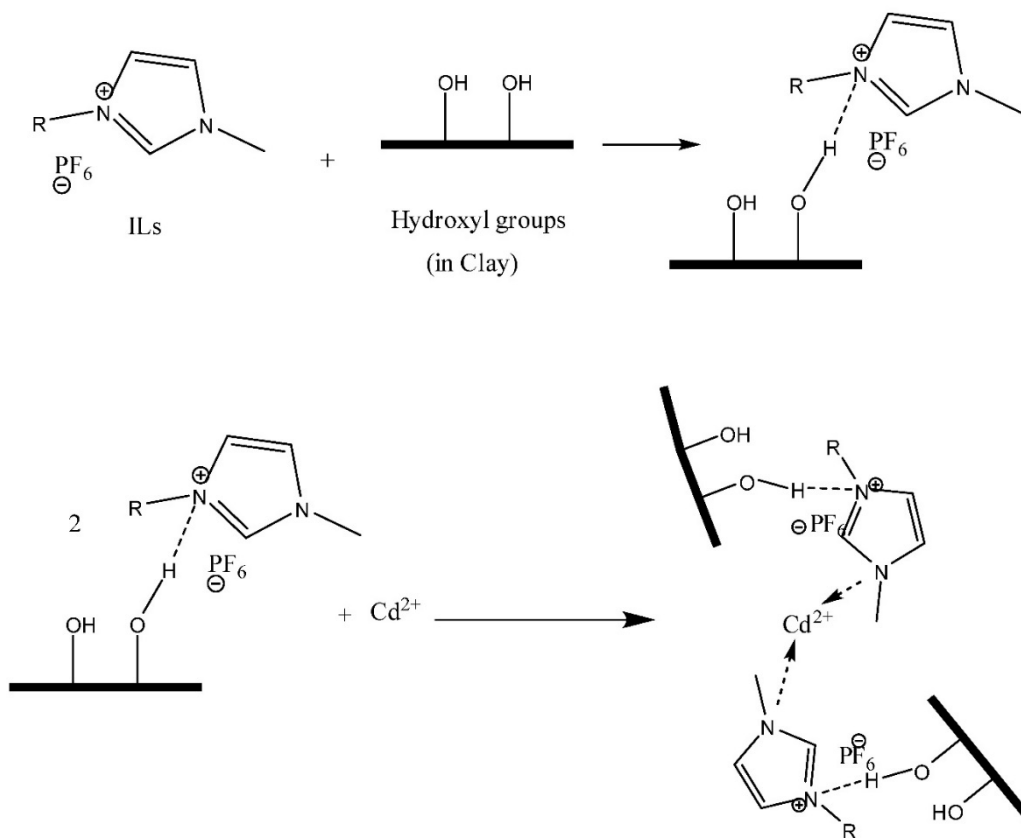


Fig.9. Schematic of cadmium adsorption with green organoclays.

In the aspect of the practical use of the adsorbent there is need to clarify the stability of the adsorbed Cd (II) and the possibility of regeneration and / or management of the used adsorbents. It is two possibilities for the prediction of stability of prepared green organoclays (adsorbent):

1- Replacement of Cd (II) ions with hydronium ions H_3O^+ after stripping of used adsorbent with medium acidic solution.

2- Breaking of bond between imidazolium-hydroxyl groups of clay and decomposition it.

We test stability of green organoclays after adsorption process and desorb (stripping by acidic solution) of Cd (II) on green organoclays with several common acidic solutions (0.1 M, 0.5 M of HCl and HNO_3) and results obtained present in Table 5. Condition of tests were done at calculated

optimum condition: Concentration of 300 mgL^{-1} for cadmium ions, sample solution pH of 7, volume of acidic solution is 10 mL and etc. Each cycle means: After extraction procedure of Cd (II) at optimum conditions. The organoclays of M_2 and B_2 with 3 gL^{-1} at 2 gL^{-1} of the adsorbent were applied.

Table 5

The stability test of green organoclays (B_2 and M_2) after adsorption and desorption process

Type of solution	Adsorption (%) of Cd(II) ion in presence of B_2				Adsorption (%) of Cd(II) ion in presence of M_2			
	Cycle 1	Cycle 3	Cycle 6	Cycle 9	Cycle 1	Cycle 3	Cycle 6	Cycle 9
0.1 M of HCl	99.4	99.2	95.6	88.1	98.6	98.3	96.7	91.2
0.5 M of HCl	87.6	80.6	78.9	75.9	90.2	85.5	80.5	79.1

Based on the obtained results in Table 5, for every green organoclay at presence of dilute hydrochloric acid solution (0.1 M), the ability of green organoclays were good and could be used for about 6 times. With increase concentration of stripping agent, because of probably decomposition of green organoclay with breaking of hydrogenic bonds between IL-Clay, it was observed that absorption capacity of green organoclays would be decreased. On if the main reason for select of HCl as stripping agent was inert effective it to decomposing of IL, because Cl^- could not replacing with PF_6^- in structure of hydrophobic green organoclay and Cl^- is leaving better group rather than the PF_6^- .

4 Conclusion

The results of different tests indicated that the ILs have been well transferred into the synthesized clays and resulted in increased distance between the clay mineral layers. The results of interaction between Cd (II) and other clays showed that the clays with nano-MT base have had better

characteristics and higher absorption level in comparison with raw Bent base clays. The order of absorption in the clays synthesized with ILs given the type of the ILs was [H(mim)₂], [Omim], and [Hmim], respectively. The Sips absorption isotherm was the most appropriate fitting model and indicated suitable maximum absorption values and a high affinity for absorption for the synthesized clays in comparison with other results of studies. High pure clay deposits like Bent as a result of sedimentation or extensive alteration of rocks, are very economic resources. For example, the cost of applied Bent in the present research is below 40 dollars for each ton. Important physio-chemical properties of clay minerals made them well chose as raw materials for industrial activities, agriculture and building, mitigation of environmental problems. The proper and eco-friendly modification of clay mineral make them a good and economical choice for removal of hazardous components in different environments. Therefore, application of ILs in synthesis of organoclay has been successful in terms of the level of Cd (II) absorption. Furthermore, these clays are harmless to the environment considering the suitable chemical characteristics of ILs. Accordingly, usage of ILs in this synthesis of ILs and removal of contaminations such as heavy metals can be a suitable substitute for other types of organoclay with harmful cations to the environment.

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