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Characterization, adsorption, and electrokinetic properties of modified sepiolite

Pınar Turan Beyli[a], Mehmet Doğan[a,*], Mahir Alkan[a], Aydın Türkyılmaz[b], Yasemin Turhan[a], Özkan Demirbaş[a], Hilmi Namli[a]

[a]*Faculty of Science and Literture, Department of Chemistry, Balıkesir University, 10145 Çağış/Balıkesir, Turkey, emails: pturan@balikesir.edu.tr (P. Turan Beyli), mdogan@balikesir.edu.tr (M. Doğan), malkan@balikesir.edu.tr (M. Alkan), yozdemir@balikesir.edu.tr (Y. Turhan), odemirbas@balikesir.edu.tr (Ö. Demirbaş), hnamli@balikesir.edu.tr (H. Namli)*
[b]*Faculty of Engineering and Architecture, Department of Enviromental Engineering, Kastamonu University, Kastamonu, Turkey, email: aydinturkyilmaz@gmail.com*

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ABSTRACT

The metal ion adsorption and electrokinetic properties of sepiolite modified by 3-(trimetoxysilyl)propyl metaacrylate was studied. The characterization of modified sepiolite was made by Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD), scanning electron micrograph (SEM), and differential thermal analysis/thermogravimetry (DTA/TG). The adsorption behavior of Fe(III), Mn(II), Co(II), Zn(II), Cu(II), and Cd(II) metal ions on modified sepiolite from aqueous solutions was investigated as a function of equilibrium pH, temperature, and ionic strength. The adsorption experiments were carried out using a batch method. The initial and final concentrations of heavy metals were determined by means of atomic absorption spectrophotometry. The zeta potential of the modified sepiolite suspensions was measured as a function of metal ion concentration and equilibrium pH using a Zeta Meter 3.0. The results showed that the amount of adsorbed metal ions increased with solution pH, and that the modified sepiolite adsorbed Cu(II) and Mn(II) ions more than other metal ions. It was found that the temperature had an important effect on metal ion adsorption and that the adsorption process was endothermic in nature. Equilibrium isotherms for the adsorption of metal ions were measured experimentally. Results were analyzed by the Freundlich and Langmuir equations and determined the characteristic parameters for each adsorption isotherm. The isotherm data were reasonably well correlated by Langmuir isotherm. Maximum monolayer adsorption capacity of modified sepiolite for Cu(II), Mn(II), Zn(II), Fe(III), Co(II), and Cd(II) metal ions was calculated from 12.3×10^{-5}, 11.7×10^{-5}, 9.0×10^{-5}, 8.2×10^{-5}, 5.7×10^{-5}, and 1.8×10^{-5} mol L^{-1}, respectively. The affinity order of adsorption was Cu(II) > Mn(II) > Zn(II)–Fe(III) > Co(II) > Cd(II). The results indicate that modified sepiolite is good adsorbent for the removal of metal ions from aqueous solutions.

Keywords: Modified sepiolite; Metal ions; Zeta potential; Adsorption; Characterization

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*Corresponding author.

1. Introduction

The release of heavy metals, especially Ni(II), Cu(II), Zn(II), Pb(II), Hg(II), Cd(II), Cr(VI), Co(II), etc., into the environment in aqueous waste streams is a potential threat these days due to their toxic and lethal effects, and soil quality as well as to plant, animal, and human health. Unlike organic pollutants, heavy metal ions are not biodegradable and tend to accumulate in living organisms, leading to several types of diseases and disturbances [1]. The stricter environment regulation on the discharge of heavy metals makes it necessary to develop various technologies for their removal [2]. Numerous techniques and treatment technologies have been developed to remove heavy metals from wastewaters, including chemical precipitation, ion exchange, membrane separation, chemical coagulation, solvent extraction, complexation/sequestration, cementation, electrochemical operation, coagulation–flocculation, biological treatment, and adsorption [1]. Traditional chemical precipitation is the most economic but is inefficient for dilute solution. Ion exchange and reverse osmosis are generally effective, but have rather high maintenance and operation costs and subject to fouling [2]. Adsorption is one of the effective separation techniques to remove dilute pollutants as well as offering the potential for regeneration, recovery, and recycling of the adsorbing material [3]. Currently, activated carbon is the most common adsorbent because of its higher adsorption capacity. However, because of its relatively high cost, in recent years, there has been an increasing interest in utilizing non-conventional adsorbents such as clay minerals as alternative low-cost adsorbents for the removal of heavy metal ions from aqueous solutions [4].

Sepiolite is a fibrous clay mineral that is formed of sheets as tetrahedral and octahedral oxides and it has channel cavities along the fiber. Due to its peculiar structure, sepiolite has considerable high sorption ability and can adsorb up to 200–250 times more water of its own weight [5,6]. Sepiolite is widely applied in many fields of adsorption technology including the removal of metals [1,2,7] and dyes [3,4,6]. The study of heavy metal ion adsorption onto a cost-effective modified sepiolite is significant in the industrial wastewater treatment system because it provides valuable insights into the mechanisms and the optimum operation parameters of adsorption processes. In our previous studies, we investigated the adsorption kinetics and mechanism of maxilon blue 5G and acid red dyes on sepiolite from aqueous solutions and found that the amount of maxilon blue 5G uptake increased with increase in contact time, initial dye concentration, pH and solution temperature, and decreased with increase in ionic strength [8,9]. In another work, the electrokinetic properties of sepiolite suspensions in different electrolyte media were studied and found that the sepiolite surface in water has a net negative charge at the natural pH of the suspension [10]. Again, we synthesized sepiolite/PVC nanocomposites and characterized using XRD, FTIR-ATR, DTA/TG, SEM and transmission electron microscopy (TEM) [11]. However, only a limited number of studies on the use of modified sepiolites as an adsorbent have been found in the literature. Eren et al. investigated the adsorption behavior of crystal violet from aqueous solution onto a manganese oxide-coated sepiolite sample and found that manganese oxide-coated sepiolite had a significant potential for removing basic dye from wastewater using the adsorption method [3]. In another study, natural and acid-activated sepiolites were used for the adsorption behavior of Pb^{2+} and Cd^{2+} heavy metal ions [12]. Fida et al. prepared bifunctional Ti–Fe kaolinite composite for Cr(VI) removal [13], and also Marjanovic et al. studied chromium(VI) adsorption from aqueous solutions onto thermo-acid activated sepiolite functionalized with (3-mercaptopropyl)trimethoxy-silane and [3-(2-aminoethylamino)propyl] trimethoxysilane [14]. But there has not been found any study on the modification of sepiolite by 3-(trimetoxysilyl)propyl metaacrylate, which is an organic modifier in the literature. Therefore, the aims of this study are (i) to modify the sepiolite surface by 3-(trimetoxysilyl)propyl metaacrylate, (ii) to characterize the modified sepiolite using FTIR, XRD, DTA/TG, BET, and SEM, (iii) to investigate the adsorption behavior and electrokinetic properties of heavy metal ions on modified sepiolite, (iv) to describe the equilibrium isotherm and (v) to determine whether modified sepiolite can be used as a chemical sensor for various metals. The effects of various parameters such as pH, ionic strength and temperature on metal ion adsorption and such as heavy metal ion concentrations and equilibrium pH on the electrokinetic properties have been investigated. Langmuir and Freundlich adsorption models were tested to describe the equilibrium isotherms and the isotherm constants were also determined.

2. Material and methods

2.1. Materials

Sepiolite sample used in this study was obtained from Aktaş Lületaşı Co. (Eskişehir, Turkey). The chemical composition of sepiolite has consisted of 53.47 SiO_2, 23.55 MgO, 0.71 CaO, 0.19 Al_2O_3, 0.16

Fe_2O_3, 0.43 NiO, and 21.49 loss of ignition as percent weight. The cation-exchange capacity of sepiolite is 25 meq 100 g^{-1}; the density is 2.55 g cm^{-3}; and particle size is in the range of 0–50 μm. All chemicals were obtained from Merck, Aldrich, Sigma and Fluka, were of analytical grade and used without further purification [15].

2.2. Methods

2.2.1. Surface modification of sepiolite with 3-(trimetoxysilyl)propylmetaacrylate

Sepiolite samples were treated before using in the experiments in order to obtain a uniform size sample of adsorbent as follows: the suspension containing 10 g L^{-1} sepiolite was mechanically stirred for 24 h, after two minutes, the supernatant suspension was filtered through filter paper. The solid sample was dried at 105˚C for 24 h, ground, and then sieved by 50 μm sieve. The particles under 50 μm were used in further experiments [16]. Sepiolite (5 g) suspended in toluene (100 mL) was refluxed and mechanically stirred for 1 h under dry nitrogen. To this suspension 3-(trimetoxysilyl)propyl metaacrylate (5.0 mL) was added dropwise. The mixture was refluxed for another 24 h, filtered and washed with water, followed by methanol and acetone. Modified sepiolite was dried at 110˚C [17].

2.2.2. Zeta potential

To determine the zeta potential of organo-modified sepiolite, electrophoretic mobility measurements were conducted using a Zeta Meter Model 3.0+ (Zeta Meter Inc., USA). The instrument determines the electrophoretic mobility of the particles automatically and converts it to the zeta potential using Smoluchowski's equation. The Smoluchowski's equation, the most elementary expression for zeta potential, gives a direct relation between zeta potential and electrophoretic mobility,

$$\zeta = \frac{4\pi\eta}{\varepsilon} \times U \tag{1}$$

where U is electrophoretic mobility at actual temperature, η is viscosity of the suspending liquid, ε is dielectric constant, π is constant and ζ is zeta potential. The pH measurements were performed using an Orion 920A pH meter with a combined pH electrode. Double-distilled water was used to prepare aqueous solutions for all experiments. For the electrophoretic mobility measurements, the suspensions were prepared in a polyethylene container by mixing 0.1 g of the modified sepiolite with 100 mL of double-distilled water, after the desired amounts of nitrate salts of heavy metals were added according to the experimental conditions. The zeta potential measurements were carried out as a function of the metal ion concentration and equilibrium pH. After agitation for 24 h in an incubator, the suspension was allowed to stand for 15 min to let the larger particles settle. An aliquot taken out from the suspension was slowly poured into the electrophoresis cell. Molybdenum anode and platinum cathode electrodes were inserted into the cell. After a desired voltage applied between the electrodes, the movement of particles was observed via a microscope nodule. Minimum 10 measurements were carried out to present the measured potential. The applied voltage during the measurements was varied in the range 50–150 mV. The pH that was made the zeta potential measurement was recorded as equilibrium pH. The instrument was tested prior to each test using the test colloid, as recommended by the supplier [18].

2.3. Adsorption procedures

Batch sorption experiments were performed at room temperature on an incubator at 150 rpm using 100-mL capped polyethylene bottles containing metal ion solutions and the adsorbent. About 0.1 g of modified sepiolite was added into 50 mL of metal solutions and shaken continuously at room temperature. A thermostated orbital shaker incubator was used to keep the temperature constant. Stock solutions were prepared in deionized water for each metal ion and further experimental solutions were prepared from the stock solution by successive dilution. The pH of the solutions was adjusted with NaOH or HNO_3 solution by using an Orion 920A pH meter with a combined pH electrode. The pH meter was standardized with NBS buffers before every measurement. A preliminary experiment revealed that about 24 h is required for metal ions to reach the equilibrium concentration. The effect of pH, ionic strength, and temperature on the adsorption of heavy metals (Cu(II), Mn(II), Zn(II), Fe (III), Co(II), and Cd(II)) was also studied. It was used the nitrate salts of metal ions in the experiments. At the end of the adsorption period, the solution was centrifuged for 15 min at 5,000 rpm. Five standard solutions for each metal ion were prepared in 100-mL flasks. Calibration graph for each batch of experiments was re-constructed by using the standard solutions.

Blanks containing no metal ion were used for each series of experiments. Filter paper was not used in any part of the experiments, since filter paper itself adsorbs about ≈30% of the present metal ions particularly at low concentration levels. Each run was repeated twice. The final concentration of metal ions in the solutions was determined by Unicam 929 flame atomic absorption spectrometer operating with an air-acetylene flame (AAS). The adsorbed amount of metal ions was calculated by the difference in initial and final concentrations.

$$q_e = (C_0 - C_e)\frac{V}{W} \tag{2}$$

where C_0 and C_e are the initial and equilibrium liquid-phase concentrations of metal ion solution (mol L^{-1}), respectively; V is the volume of metal ion solution (L), and W is the mass of the modified-sepiolite sample (g) [19].

2.4. Characterization

Infrared spectra of samples were obtained using a PerkinElmer BX 1600 FTIR. About 0.01 g of clay was mixed with 1 g of potassium bromide (KBr) and pelletized in the hydraulic press at 10 kPa. FTIR spectra were taken in the range from 4,000 to 400 cm^{-1} in the transmission mode. The interaction between the sepiolite surface and the modifier 3-(trimetoxysilyl) propylmetaacrylate, during the modification was investigated by a series of FTIR spectral analysis: (1) *modifier sample* (aimed to estimate the peaks arising from modifier and changes on it after modification), (2) *sepiolite sample* (to observe any changes on sepiolite during the modification process and comparing the modified sample), (3) *modified sepiolite sample* (to compare the peaks arise from the modifier and sepiolite), (4) *modified sepiolite with the sepiolite-background* (the peaks arising from sepiolite are omitted by subtracting the pure sepiolite spectrum from the modified one and the changes on the modifier will be appear more clear), and (5) *mechanical mixture* (to observe whether there is a chemical reaction or physically interaction between sepiolite and modifier). XRD measurements of natural and modified sepiolite samples were performed using a Analytical Philips X'Pert-Pro X-ray diffractometer equipped with a back monochromator operating at 40 kV and a copper cathode as the X-ray source (λ = 1.54 Å). A simultaneous DTA/TG system was used for differential thermal (DTA) and TG analysis (Perkin Elmer Diamond, DTA/TG). SEM measurements of sepiolite and modified sepiolite were performed by a Zeiss EVO LS 10. Most of the measurements were carried out using an accelerating voltage of 30 kV. The specific surface areas of sepiolite and modified sepiolite were estimated by the BET method using Hiden IMI PSA gas sorption device (Hiden Isochema).

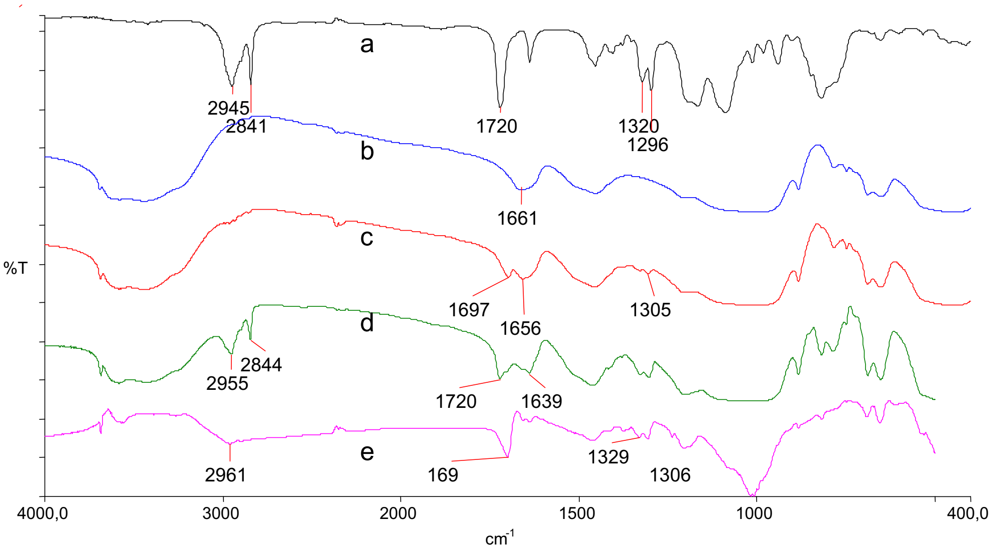

Fig. 1. FTIR spectra of (a) 3-(trimetoxysilyl)propylmetaacrylate, (b) sepiolite, (c) modified sepiolite, (d) mechanical mixture, and (e) sepiolite background.

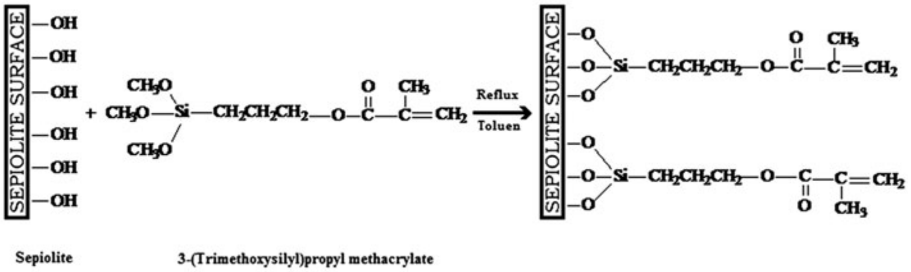

Fig. 2. The reaction between the methoxy groups of modifier and hydroxyl groups of the sepiolite.

3. Results and discussion

3.1. Characterization

3.1.1. FTIR analysis

Hydroxyl groups on the oxide surfaces as a result of hydrolysis play an important role as an active site in modification and adsorption processes. In the modification process, it is assumed that the modifiers hold the clay surface by chemical bonds and formed a monomolecular layer on the clay surface [20,21]. Infrared spectrum measurements, which depend on the band vibration of the functional groups in clay structure, can be used to determine whether or chemical bonding occurs, to understand the existence of different types of surface hydroxyl groups on oxide surface and to provide additional characterization not only of surface hydroxyl groups but also of other types of exposed site [22]. Fig. 1 has shown FTIR spectra of sepiolite samples. As seen from this figure, C=O peak at 1,720 cm^{-1} of modifier shifted to 1,697 cm^{-1} after the modification. The peak at 2,841 cm^{-1} arising from MeO groups of modifiers observed at 2,844 cm^{-1} after mechanical stirring. This peak was not observed in the modified sepiolite. The peak at 2,945 cm^{-1} of modifier shifted to 2,961 cm^{-1} after modification. This case can be seen from background spectrum of sepiolite. Moreover, the peak at 1,296 cm^{-1} of modifier shifted to 1,305 cm^{-1} after modification [23]. The reaction between the methoxy groups of modifier and hydroxyl groups of the sepiolite according to the above description can be seen at Fig. 2.

3.1.2. XRD characterization

XRD provides important information about the degree of crystallinity of the clay and, in some cases, about organic compounds [11]. Fig. 3 has shown XRD pattern before and after the modification of sepiolite. From Fig. 3, it has been observed some variations in the intensity of some peaks in XRD pattern of sepiolite by modification. The fact that the intensity of some peaks at 2θ of modified sepiolite changes has shown the occurring of a bond interaction between sepiolite and modifier.

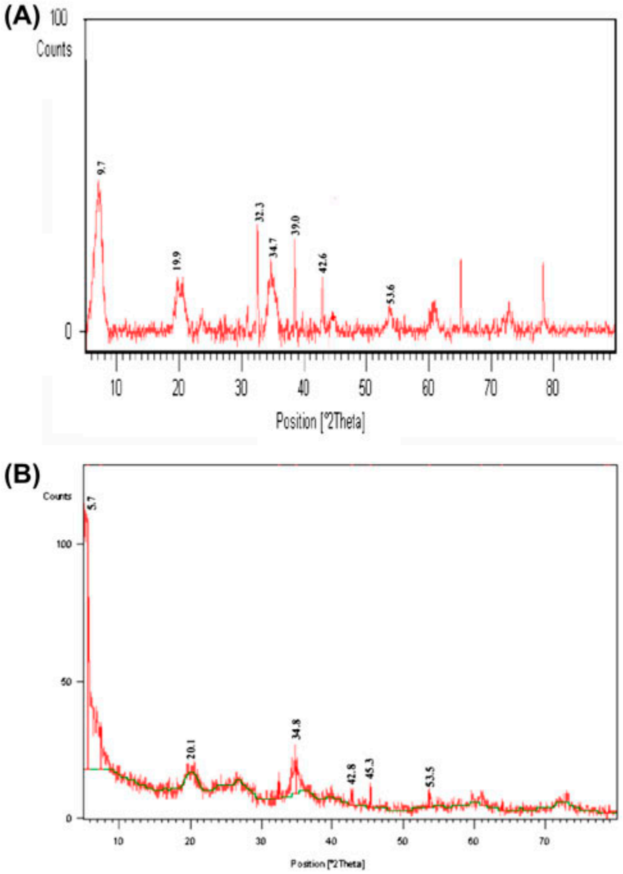

Fig. 3. XRD pattern of (A) sepiolite and (B) modified sepiolite.

3.1.3. DTA/TG characterization

DTA investigations of organo–clays are carried out to study the thermal properties and stability of the adsorbed organic matter; to establish whether organo–clay complexes are formed or whether the clay and the organic material are present merely as mixtures and to identify and differentiate between different clay minerals [24]. By using simultaneous DTA/TG, one can differentiate between peaks associated with weight loss and those associated with phase transition. DTA thermograms of organo–clays can be divided into three regions: the dehydration of clay, thermal oxidation of organic material, and dehydroxylation of clay [24]. The exothermic oxidation reaction during the gradual heating of the sample takes place in two steps, in the temperature range of 200–500˚C, oxidation of organic hydrogen and formation of water and charcoal, and in the temperature range of 400–750˚C, oxidation of charcoal and formation of CO_2 [25]. DTA/TG thermograms under the oxidizing gas atmosphere of clay samples modified by organosilane compounds give important information about the modification of clay surface, because the characteristic exothermic peaks belonging to organosilane compound in DTA/TG thermograms of unmodified clay sample are not observed. If the clay is modified, some new peaks in DTA/TG thermograms of organo–clay should be observed. These new peaks can be used as a proof of modification of clay by organosilane compound.

In this study, DTA/TG thermograms were recorded at a heating rate of 20˚C per min in the temperature range of 20–1,100˚C. Fig. 4 has shown DTA

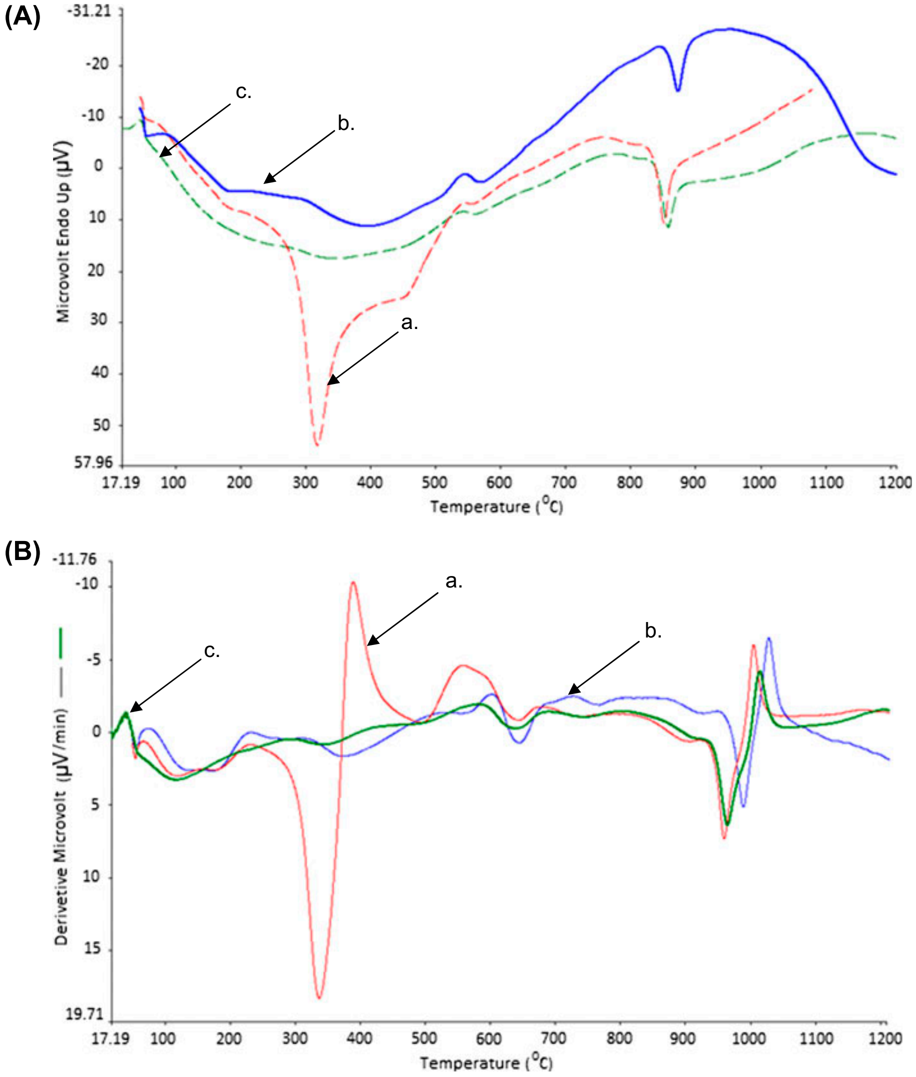

Fig. 4. (A) DTA and (B) d[DTA] spectra of natural and modified sepiolite samples under different conditions: (a) modified sepiolite under oxygen atmosphere, (b) modified sepiolite under nitrogen atmosphere, and (c) sepiolite under nitrogen atmosphere.

and d[DTA] thermograms of sepiolite and modified-sepiolite samples under oxygen and nitrogen atmosphere. As seen from this figure, the strong exothermic peaks on the DTA thermogram of modified sepiolite in the temperature range of 200–650˚C under oxygen atmosphere represent the oxidation of organosilane compound and the formation of H_2O and CO_2. During the thermal treatment of organo–clays in the temperature range of 200–320˚C, the organosilane group of the modified sepiolite is transformed into charcoal. The peak in the temperature range of 500–620˚C arises from the oxidation of charcoal and formation of CO_2. Differentiation between various clay–organic complexes is possible because, in air, each variety gives rise to characteristic exothermic peak temperatures. The DTA peak in the temperature range of 800–900˚C corresponds to the dehydroxylation of the residual sepiolite.

Fig. 5 shows the thermograms of percent weight loss versus. temperature and differential percent weight loss versus. temperature for sepiolite and modified sepiolite samples under nitrogen and oxygen. Sepiolite mineral is known to contain four types of water molecules in different chemical states: (i) hydroscopic water, (ii) zeolitic water, (iii) bound water, and (iv) structural water. These water molecules are removed with thermal dehydration [15]. As can be seen from Fig. 5, the removal of hydroscopic water

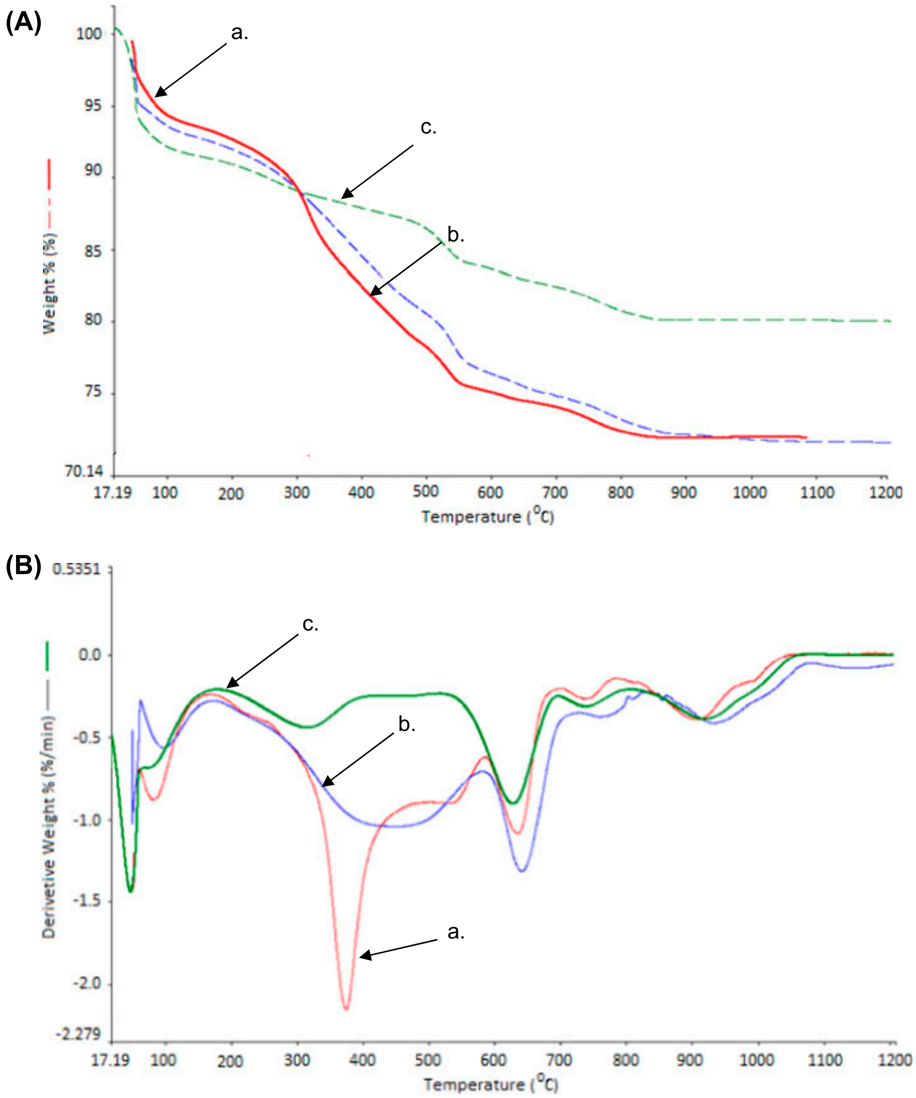

Fig. 5. (A) TG and (B) d[TG] spectra of natural and modified sepiolite samples under different conditions: (a) modified sepiolite under oxygen atmosphere, (b) modified sepiolite under nitrogen atmosphere, and (c) sepiolite under nitrogen atmosphere.

from the external surface and zeolitic water from the voids of the structure was completed by 200°C. The bound water molecules left the structure a higher temperature (200–600°C) than the hydroscopic and zeolitic water molecules. The removal of structural water molecules and hydroxyl groups was completed until 900°C. Percent weight losses for sepiolite under nitrogen and oxygen were determined as 9.5 and 9.4 in the temperature range of 0–200°C; 7.3 and 7.5 in the temperature range of 200–600°C; and 3.4 and 3.2 in the temperature range of 600–900°C, respectively. Total percent weight losses for sepiolite under nitrogen and oxygen were calculated as 20.2 and 20.1, respectively. Again, percent weight losses for modified sepiolite under nitrogen and oxygen were determined as 6.3 and 7.0 in the temperature range of 0–200°C; 15.7 and 17.6 in the temperature range of 200–600°C; and 4.1 and 3.1 in the temperature range of 600–900°C, respectively. Total percent weight losses for modified sepiolite under nitrogen and oxygen were calculated as 26.1 and 27.6, respectively. In addition, any weight loss was not observed by heating the samples up to 1,100°C. Results showed that the percent weight loss of modified sample increased. This result has shown that sepiolite was modified by organosilane compound and a chemical bond formed between the active sites on the sepiolite and modifier substance. Fig. 5 has shown that there is not a significant change in thermal

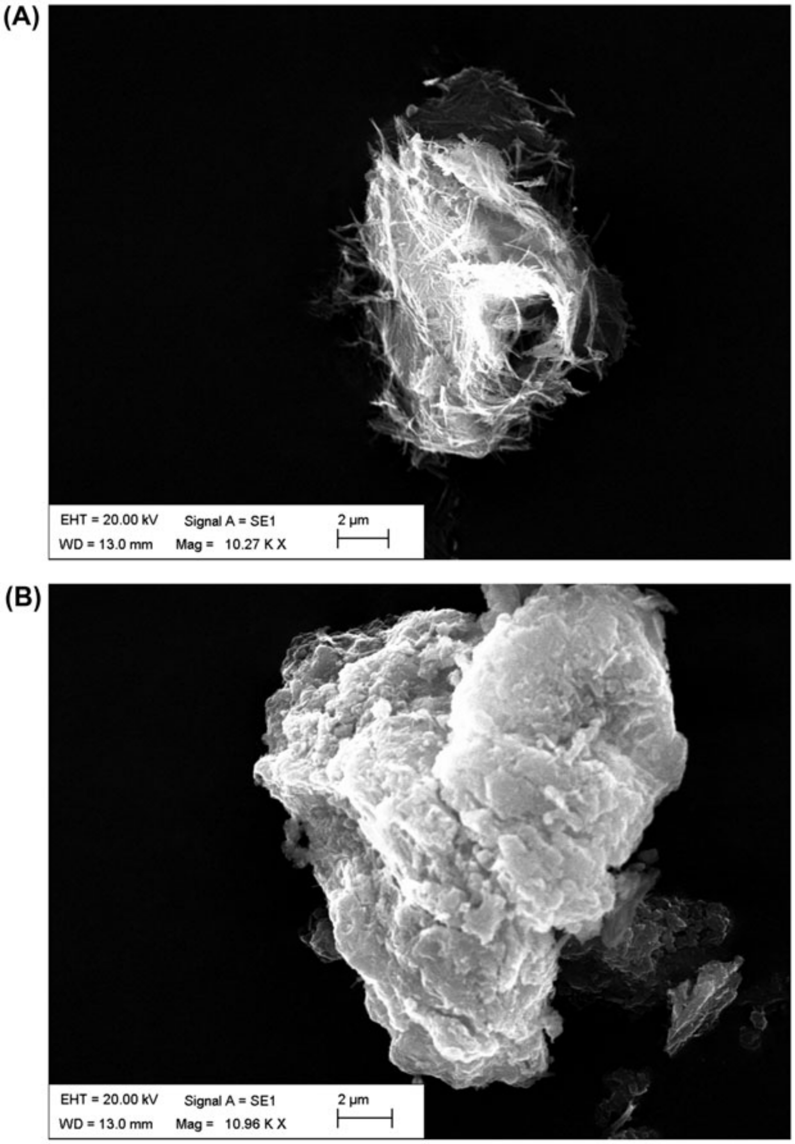

Fig. 6. SEM images of (A) sepiolite and (B) modified sepiolite.

degradation steps of sepiolite and modified sepiolite under oxygen and nitrogen. Moreover, in the low-temperature degradation step, there is a decrease in mass loss, which shows the increase of thermal stability at these temperatures.

3.1.4. SEM

Fig. 6 shows a SEM of sepiolite and modified sepiolite. The modification process produced a aggregate. When Fig. 6(a) and (b) are compared with each other, the results demonstrate that the sepiolite bundles are broken down into the sepiolite fibers. The large aggregates of sepiolite fibers are observed in the modified sepiolite. This confirms the modification of sepiolite.

3.1.5. BET analysis

The specific surface areas of sepiolite and modified sepiolite were measured as 342 and 180 m^2/g, respectively. Specific surface area is a property of solids which is the total surface area of a material per unit of mass solid or bulk volume or cross-sectional area. It has a particular importance for adsorption, heterogeneous catalysis, and reactions on surfaces. The specific surface area of sepiolite has decreased by organomodification. From SEM analysis, the sepiolite bundles are broken down into the sepiolite fiber during modification reaction and aggregates have formed. As a result of the modification, the specific surface area of modified sepiolite has decreased.

3.2. Zeta potential

All electrokinetic phenomena are related to the development of electrical double layer at the particle/electrolyte interface. The zeta potential, ζ, is the most important parameter of electrical double layer, which can be determined from the electrokinetic measurements. The ζ potential is defined as the potential of shear plane of the particle when it moves in liquid [10]. Fig. 7 shows the change of zeta potential of modified sepiolite suspensions in the presence of metal ions with solution equilibrium pH. The most important observations are that modified sepiolite does not have ieps over the pH range of 1.7–7, no charge reversal is observed over the entire pH range for dispersions containing different metal ions and modified sepiolite shows negative zeta potential.

The zeta potential of modified sepiolite in single aqueous solutions of Fe(III), Co(II), Cu(II), Zn(II), Mn(II), and Cd(II) was investigated. Although the zeta potential values of heavy metal cations in modified sepiolite suspensions are different, their tendency to change with pH is similar (Fig. 8). The values on the curves obtained for each heavy metal ion did not change the sign of zeta potential. As it is clearly observed from Fig. 8, zeta potential of modified sepiolite is sensitive to change in the cation concentration. In our previous study, we found that the zeta potentials of natural sepiolite suspensions in aqueous solutions of heavy metal ions are positive at low equilibrium pH values and that the pH at the iep (pH_{iep}) of natural sepiolite suspension is 6.6 [10]. The isoelectrical point is important because the sign of the surface charge has a major effect on the adsorption of all other ions, especially the counterions. Moreover, at the iep, there is no charge on the surface, and the total positive charge equals the total negative charge. The modified sepiolite surface is negatively charged and metal ions cannot specifically adsorb onto modified

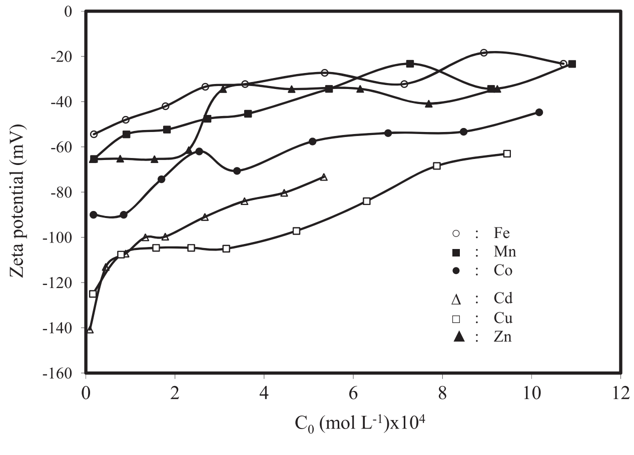

Fig. 7. Effect of heavy metal ion concentrations on zeta potential of modified sepiolite (○: Fe, ■: Mn, ●: Co, △: Cd, □: Cu and ▲: Zn).

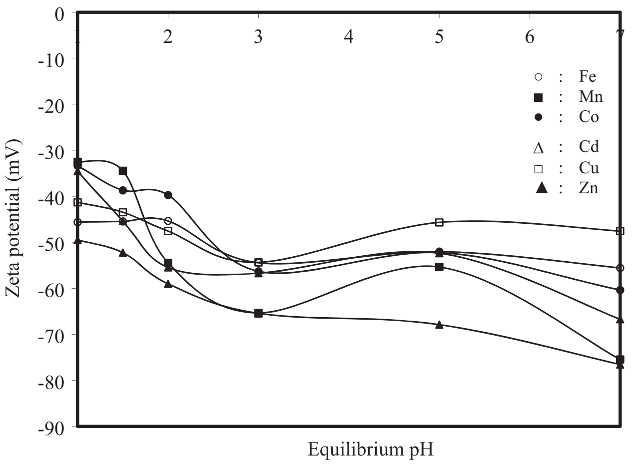

Fig. 8. Effect of pH on zeta potential of modified sepiolite (○: Fe, ■: Mn, ●: Co, △: Cd, □: Cu and ▲: Zn).

sepiolite surface and cannot change the magnitude of the zeta potential.

3.3. Adsorption

Adsorption, because of its simplicity, conveniency, and the availability of a wide range of adsorbents, is still one of the most extensively used methods [26]. The adsorption behavior of different heavy metals may be different for clay minerals. Universally consistent rules of metal selectivity cannot be given as it depends on a number of factors such as (i) the chemical nature of the reactive surface groups, (ii) the level of adsorption, (iii) pH at which adsorption is measured, (iv) ionic strength of the solution in which adsorption is measured, and (v) the presence of soluble ligands that could complex the free metal. All these variables may change the metal adsorption isotherms [27]. In this study, the adsorption of heavy metal ions on organo-modified sepiolite from aqueous solutions was investigated as a function of initial metal ion concentration, solution equilibrium pH, ionic strength and temperature. The results obtained are discussed below.

Fig. 9 has shown the adsorption isotherms obtained for the removal of metal ions, such as Cu(II), Zn(II), Cd (II), Co(II), Mn(II), and Fe(III), on modified sepiolite from aqueous solutions. The adsorption capacity of modified sepiolite is higher for Cu(II) and Mn(II) than that for other metal ions. This may be due to specific interactions between the ester functional group and metal ions, and to the specific adsorption of metal ions in the active sites on the unmodified sepiolite. In addition to this, as the acidic character of Mn(II), Fe(III), and Cu(II) is more than metal ions, Co(II), Fe(III), Zn(II), and Cd(II) ions are less adsorbed on modified sepiolite surface. It was found that the affinity of modified sepiolite to metal ions was in the form of Mn(II) > Cu(II) > Zn(II)–Fe(III) > Co(II) > Cd(II). In light of these observations, this material could be potentially applied as a selective electrode when the objective is to determine or identify Mn(II) and Cu(II).

The pH is an important parameter controlling the permeability through changes in the amount and charge of active sites on the edges of clay mineral particles [28]. Because of the protonation and deprotonation of the acidic and basic groups of the metal complexation ligand, its adsorption behavior for metal ions is influenced by the pH value, which affects the surface structure of sorbents, the formation of metal hydroxides, and the interaction between sorbents and metal ions [29]. Therefore, the pH dependence of adsorption of metal ions was investigated in detail. Fig. 10 shows the effect of solution equilibrium pH to the adsorption of metal ions on the modified sepiolite surface from aqueous solutions. As seen from Fig. 10, it was found that the adsorption of metal ions on modified sepiolite surface increased with increase in solution equilibrium pH. Oxygen atoms of organosilane compound in low solution equilibrium pH values are protonated, becomes positively charged, and therefore, the interaction of modified sepiolite surface with metal ions is quite difficult. However, the hydrogen ions holding the oxygen atoms of modifier are deprotonated into solution with increase of solution equilibrium pH, and therefore, the interaction between the oxygen atoms of modifier and metal ions increases. As a result, it can be said that the adsorption of metal ions increases with increase in solution equilibrium pH.

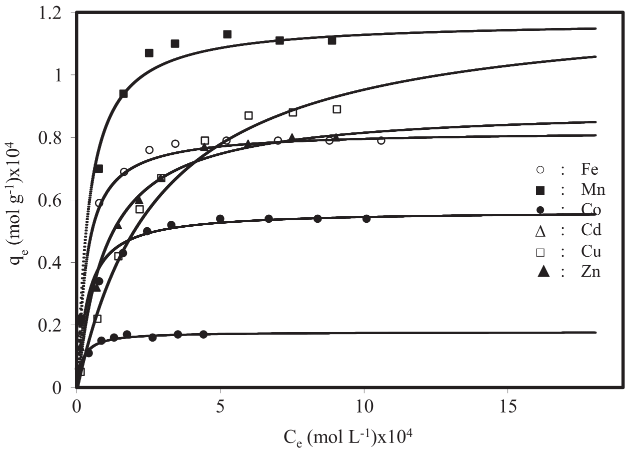

Fig. 9. Isotherm curves for adsorption data (○: Fe, ■: Mn, ●: Co, △: Cd, □: Cu and ▲: Zn).

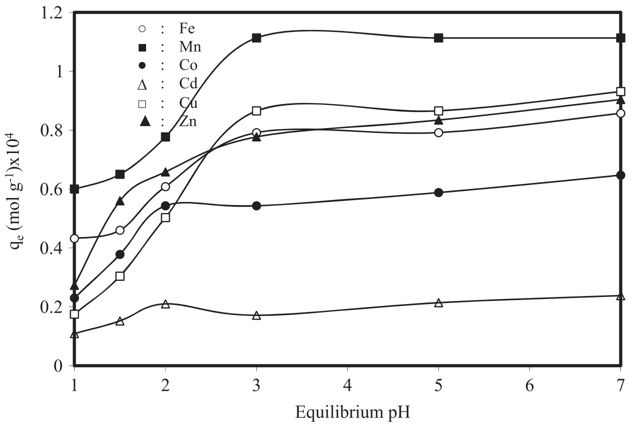

Fig. 10. Variation of the adsorption of metal ions with pH on modified sepiolite (○: Fe, ■: Mn, ●: Co, △: Cd, □: Cu and ▲: Zn).

Ionic strength affects the activity coefficients for OH^-, H_3O^+, and specifically adsorbable ions. Adsorption studies have shown that the removal degree of the waste significantly affects with the concentration and the nature of electrolyte ion species added to the medium [19]. In this study, NaCl was selected as a salt to examine the effect of ionic strength to the adsorption of various metal ions on the modified sepiolite surface. Fig. 11 shows the effect of ionic strength to the adsorption capacities of modified sepiolite for metal ions at 0, 1 × 10^{-2} ve 1 × 10^{-1} mol L^{-1} concentrations of NaCl. It was observed that the adsorption capacity of modified sepiolite for the metal ions slightly decreased in the presence of increasing concentrations of NaCl. In literature, it has been noted that ionic strength is nearly without effect on inner-sphere complex formation, and its increase generally induces a decrease of adsorption of outersphere forming ions. Some cases of increasing adsorption with increasing ionic strength are reported, but these results would be better attributed to the complexing properties of the electrolyte anion than to a direct contribution of ionic strength [30].

Temperature is an important parameter for adsorption processes. As study of the temperature dependence of adsorption, reactions give valuable information about the enthalpy change during adsorption. Greater adsorption is often found at lower temperatures, but the differences are usually small [18]. The adsorption capacity of modified sepiolite to metal ions such as Cu(II), Zn(II), Cd(II), Co(II), Mn(II), and Fe(III) was determined at constant temperature and pH in the temperature range of 25–55℃. Fig. 12 shows the effect of temperature to adsorption capacity of modified sepiolite samples for various heavy metal ions. The results have shown that adsorbed amount increased with increasing temperature. This increase may be as a result of the increase in moving of metal ions with temperature. This result shows that the adsorption process is an endothermic adsorption process [19,31].

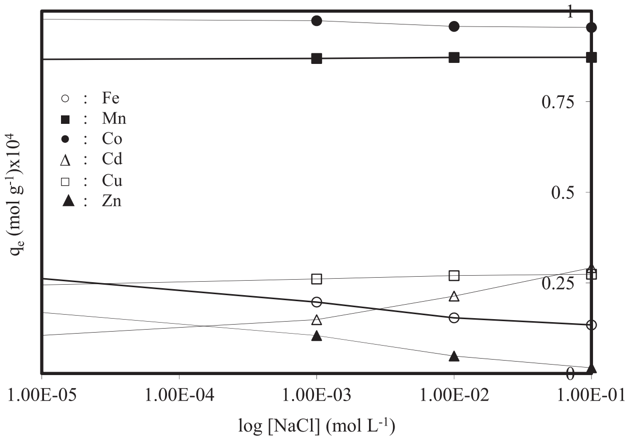

Fig. 11. Variation of the adsorption of metal ions with ionic strength on modified sepiolite (○: Fe, ■: Mn, ●: Co, △: Cd, □: Cu and ▴: Zn).

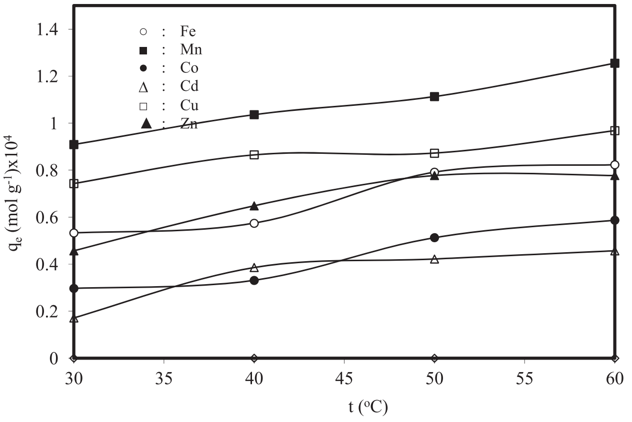

Fig. 12. Variation of the adsorption of metal ions with temperature on modified sepiolite (○: Fe, ■: Mn, ●: Co, △: Cd, □: Cu and ▴: Zn).

3.4. Adsorption isotherms

Adsorption data are most commonly represented by a so-called adsorption isotherm in which the quantity of anion or molecule adsorbed by a solid is plotted as a function of the concentration of that ion in the solution phase that is at equilibrium with the solid. The shape of the isotherms gives some information about the adsorbate–adsorbent interaction. The most common adsorption isotherm equations which are used to describe chemical adsorption isotherms are the Langmuir and the Freundlich equations. The characteristic feature of these isotherms is the decrease of slope at higher adsorption levels. The Langmuir equation can be written in the form:

$$q_e = \frac{q_m K C_e}{1 + K C_e} \tag{3}$$

Here, q_e is the quantity of solute adsorbed per unit weight of adsorbent (mol g^{-1}), C_e is the equilibrium concentration of solute remaining in the solution (mol L^{-1}), q_m and K are the Langmuir model constants. These constants are called the adsorption capacity (maximum surface coverage) and bonding energy constant, respectively. The parameters q_m and K can be calculated from adsorption data by converting Eq. (3) into the linear form:

Table 1
Isotherm constants calculated for the adsorption of metal ions on modified sepiolite

			Langmuir isotherm			Freundlich isotherm		
Metal ions	Temp. (℃)	pH	$q_m \times 10^5$ (mol g^{-1})	$K \times 10^{-4}$ (L mol^{-1})	R^2	n	$K_F \times 10^3$	R^2
Mn	30	4.0	11.7	2.5	0.998	2.8	1.6	0.8310
Cu	30	4.0	12.3	0.4	0.988	1.4	1.6	0.9480
Fe	30	3.0	8,2	3.1	0.998	3.0	1.0	0.7710
Zn	30	4.0	9.0	1.0	0.997	2.3	2.1	0.9480
Co	30	4.0	5.7	2.8	0.999	4.4	0.3	0.9300
Cd	30	4.0	1.8	5.3	0.998	3.7	6.3	0.910

Table 2
Adsorption capacities of metal ions on modified sepiolite and some other adsorbents

Adsorbate	Adsorbent	Adsorption capacity (mg g^{-1})	Refs.
Fe(III)	Modified sepiolite	4.59	In this study
	Olive stones	0.35	[34]
Mn(II)	Modified sepiolite	6.43	In this study
	Kaolinite	0.44	[35]
Co(II)	Modified sepiolite	3.36	In this study
	Kaolinite	0.92	[35]
Zn(II)	Modified sepiolite	5.87	In this study
	Unmodified jute fibres	3.55	[37]
	Fly ash	0.07	[38]
Cu(II)	Modified sepiolite	7.81	In this study
	Groundnut shells	4.46	[36]
	Unmodified jute fibres	4.23	[37]
Cd(II)	Modified sepiolite	2.02	In this study
	CNTs	1.10	[39]

$$\frac{C_e}{q_e} = \frac{1}{q_m K} + \frac{C_e}{q_m} \tag{4}$$

where q_m and K were calculated from the slope and intercept of the straight lines of the plot C_e/q_e vs. C_e [26].

The Freundlich model at logarithmic form is expressed as follows:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{5}$$

where K_F and $1/n$ are Freundlich isotherm constants. K_F and $(1/n)$ can be determined from the linear plot of $\ln q_e$ vs. $\ln C_e$ [27].

The isotherm constants were calculated from the least square method and presented in Table 1. The Langmuir equation represents the sorption process very well, since the correlation coefficient values, R^2, are higher for Langmuir isotherm than the Freundlich isotherm. This may be due to homogenous distribution of active sites on modified sepiolite surface [32,33]. Table 2 shows the adsorption capacities of metal ions on modified sepiolite synthesized in this study and some other adsorbents [34–39]. The results show that modified sepiolite has higher adsorption capacity for heavy metal ions than the other adsorbent given in Table 2.

4. Conclusions

A sepiolite surface with a new silylating agent was successfully modified. The modification process was characterized by FTIR, XRD, DTA/TG, SEM, and zeta potential measurements. The adsorption and electrokinetic properties of modified sepiolite was investigated in the presence of metal ions in aqueous solutions. Firstly, the sorption of metal ions from aqueous solutions onto modified sepiolite was studied, and then, a series of systematic zeta potential measurements were conducted to determine the electrokinetic behavior of modified sepiolite and the effects of Fe(III), Mn(II), Co (II), Zn(II), Cu(II), and Cd(II) on the zeta potential.

The adsorption of metal ions on the modified sepiolite increased with increased pH and temperature and decreased ionic strength. Modified sepiolite surface has a negative charge in the pH range of 1.7–7.0. This surface presents a high affinity for Mn(II) and Cu(II) due to the presence of oxygen centers. Adsorption on modified sepiolite can be expressed better with Langmuir-type adsorption isotherms and adsorption capacities order was found as Mn(II) > Cu(II) > Zn(II)–Fe(III) > Co(II) > Cd(II). Correlation coefficients for the isotherm models indicate that the Langmuir model best describes the metal adsorption process and experimental data are better fitted to the Langmuir isotherm. This anchored surface also presents a good adsorption capability for other divalent cations, which permits its use in the extraction of toxic metal ions from aqueous solutions. The separation of divalent cations with this surface suggests scope for exploitation in chromatographic applications. On the other hand, in exploring the selectivity in binding Mn(II) and Cu(II), this behavior suggests its possible use in the manufacture of a chemical sensor for this toxic metal. The results of this study indicate that modified sepiolite may be successfully used for the removal of metal ions from aqueous solutions.

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