1883

Characterization and Adsorption Properties of Chemically Modified Sepiolite

Yasemin Turhan, Pınar Turan, Mehmet Doğan,* Mahir Alkan, Hilmi Namli, and Özkan Demirbaş

Department of Chemistry, Faculty of Science and Literature, Balikesir University,
*10145 Cagis-Balikesir, Turkey*

Modification of sepiolite clay has been performed using triethoxy-3-(2-imidazolin-1-yl)propylsilane in the presence of toluene solution. The modified material was characterized by FTIR spectroscopy, XRD, and simultaneous DTA/TG analysis. It was found that the chemical bonding takes place between the hydroxyl groups and/or oxygen atoms within the structure of sepiolite and the silane group of the triethoxy-3-(2-imidazolin-1-yl)propylsilane by releasing the ethoxy groups to the solvent. Thermal decomposition of natural and modified sepiolites was carried out with a thermogravimetric analyzer. In TG and DTA analysis, during gradual heating in an oxidizing atmosphere, the modified sepiolite was oxidized, giving rise to significant exothermic peaks. The exothermic peak in the temperature range of 200–650 °C depended on the modifier loading and provided evidence of bond formation on the sepiolite surface. For natural sepiolite, a mass loss of 20.43% was observed up to 900 °C, whereas this value increased to 31.90% for modified sepiolite under oxygen atmosphere. Electrokinetic properties of the modified-sepiolite suspensions were also examined as a function of the initial electrolyte concentration and equilibrium pH using a Zeta Meter 3.0 instrument. To determine the adsorption capacity of modified sepiolite for metal ions, the experiments were examined as a function of pH, ionic strength, and temperature. The adsorption capacity of modified sepiolite increased with increasing pH and temperature, but ionic strength was found to have no significant effect. The experimental data were analyzed using the Langmuir and Freundlich adsorption models. Satisfactory agreement between the metal uptake capacities by the modified sepiolite was expressed in terms of the correlation coefficient (R^2). The Langmuir model represented the sorption process better than the Freundlich model, with R^2 values ranging from 0.9603 to 0.9977.

1. Introduction

Adsorption technology is currently used extensively for the removal of organic and inorganic pollutants from the aqueous phase,[1–3] and since its first introduction in the 1940s, activated carbon has been the water industry's standard adsorbent for the reclamation of municipal and industrial wastewater to potable water quality.[3–5] The use of carbon adsorption for the direct treatment of liquid industrial waste streams is a relatively recent practice but has been successfully utilized for the reclamation of metals from electroplating wastes and the removal of phenol from chloroalkali plant wastewater prior to recycling.[3,6] Despite the prolific use of this adsorbent in wastewater, carbon adsorption remains an expensive treatment process. This has prompted growing research interest in the production of low-cost alternatives to activated carbon from a range of carbonaceous and mineral precursors.[3,7,8] Many of the starting materials for these replacement adsorbents are from agricultural or industrial byproducts; hence, their use as secondary adsorbents contributes to waste minimization, recovery, and reuse.[3,9] For this reason, modification and impregnation techniques have long been used to increase surface adsorption, and thus removal capacity, and to add selectivity to activated carbon. Surface modification of clay minerals is important for improving the practical applications of clays such as fillers and adsorbents. The surfaces of clays can be changed from hydrophilic to hydrophobic or organophilic by organofunctional molecules, with surface hydroxyl groups, Lewis and Bronsted acidic sites, etc., by grafting organic groups onto the clay surface. Surface modification of adsorbents aims at altering their chemical and physical characteristics.[10,11] Surface modification techniques can be classified

as physical and chemical. Physical methods are accompanied by a topochemical compositional change on the top surface of the oxide.[12] Recent research has suggested that chemically modified clay minerals represent a new and promising class of adsorbents for water purification and industrial wastewater treatment with wider applications in soils.[13] Chemical modification methods can introduce various organic function groups on oxide surfaces without large geometric changes. Chemical modification in its real sense means the covalent bonding of functional groups to surfaces as a result of chemical reactions between surface species and appropriate reactants. Chemical modifications are achieved by alcohol treatments, coupling agents, graft polymerization, and mechanochemical methods. Difficulties sometimes arise in distinguishing whether a surface species being attached is chemisorbed, physisorbed, or only mechanically held on the metal oxide surface.[12]

One of the most important schemes of chemical surface modification involves silylation reactions and, in general, reactions with MX_m where M is a metal and X is a halide, alkoxide, alkyl, alyl, carbonyl, etc. Silylation is the displacement of an active hydroxyl group by an organosilyl group.[12,14] The silylating materials act as a means of bonding organic materials to oxide surfaces to obtain the advantages of reactive groups on a stable, insoluble substrate. Commercial silane coupling agents are, in general, of the type $RSiX_3$, i.e., they contain three groups that can potentially react with surface hydroxyl groups according to the equation[12]

$$3SiOH + X_3SiR \rightarrow -(Si-O)_3-SiR + 3HX \quad (1)$$
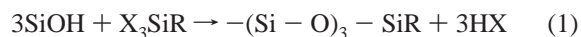
Zeta-potential measurement is a valuable tool for characterizing the surface properties of oxides and polymers, e.g., swelling, graft layer configuration, optimization of surface modification, and other physicochemical properties.[15] The effect

---

* To whom correspondence should be addressed. Tel.: +90 266 612 12 15. Fax: +90 266 612 10 00. E-mail: mdogan@balikesir.edu.tr.

of pretreatment of the oxide surface on electrokinetic characteristics is an interesting object for study, because oxide surfaces are increasingly widely used as substrates in the synthesis of oxide nanostructures of other chemical compositions using the method of molecular layer-by-layer deposition from the gaseous phase. In this case, the position of the isoelectric point (IEP) of the modified surface can serve as a criterion determining completeness of substrate surface-group substitution during synthesis.[16,17] Therefore, it is especially important to establish the extent of the changes in the characteristics of the original oxide surface under the conditions corresponding to the surface chemical reactions (temperature and additional surface treatment with various agents).

Sepiolite is a fibrous clay mineral that is formed of sheets of tetrahedral and octahedral oxides. It has fine channels running parallel to the fiber axis. These channels can accommodate water and other molecules.[18] It owes much of its industrial application to its molecular-sized channels and large specific surface area (more than 200 m²/g).[19] Sepiolite is used in a variety of industries, including cosmetics, ceramics, detergents, paper, and paint. The abundance and availability of sepiolite reserves, together with its relatively low cost, guarantee its continued utilization. Sorption depends heavily on experimental conditions such as pH, temperature, and ionic strength.[20,21] Sepiolite has attracted great attention because of its sorptive, rheological, and catalytic properties, and the use of sepiolitic clays is expanding.[22-24]

A limited number of studies have been performed on the evaluation of modified sepiolite. Lemic et al.[25] investigated the surface modification of sepiolite with quaternary amines; Alkan et al.[26] performed FTIR and zeta-potential measurements of sepiolite treated with some organosilanes; Torró-Palau et al.[27] examined the structural modification of sepiolite (natural magnesium silicate) by thermal treatment; Akyüz et al.[28] reported FTIR spectroscopic investigations of the adsorption of 3-aminopyridine on sepiolite and montmorillonite from Anatolia, Turkey; and Frost and Mendelovici studied the modification of fibrous silicate surfaces such as palygorskite, sepiolite, and chrysotile with a wide range of organic agents.[29] However, this study is the first to report the modification of sepiolite with triethoxy-3-(2-imidazolin-1-yl)propylsilane. The functionalized clay was characterized by Fourier transform infrared (FTIR) spectroscopy, X-ray powder diffraction (XRD), and differential thermal (DTA) and thermogravimetric (TG) analysis. One of the main aims of the present study is to provide an overview of the electrokinetic behavior of modified sepiolite by considering the major chemical and interfacial mechanisms affecting the surface charge characteristics. For this purpose, an attempt was made to evaluate the possibility of zeta-potential data as an indication of adsorption ability. Another primary aim of this study was to determine whether modified sepiolite can be used as a chemical sensor for various metals. Therefore, the following properties were evaluated: (1) the selectivity of the modified sepiolite for metal ions in aqueous solutions and (2) the effects of pH, ionic strength, and temperature on the adsorption capacity of modified sepiolite for metal ions in aqueous solutions. The mechanisms for heavy metal adsorption on modified sepiolite in contaminated systems are discussed in terms of the experimental results. It is anticipated that the data generated from this work will be useful in the application of modified sepiolite in cleanup of metal ions from industrial wastewater and in agriculture.

2. Material And Methods

2.1. Materials. The sepiolite sample used in this study was obtained from Aktaş Lületaşı Co. (Eskişehir, Turkey). The chemical composition (wt %) of the sepiolite was as follows: SiO_2, 53.47; MgO, 23.55; CaO, 0.71; Al_2O_3, 0.19; Fe_2O_3, 0.16; NiO, 0.43; and loss of ignition, 21.49. The cation-exchange capacity of sepiolite is 25 mequiv 100 g^{-1}; the density is 2.55 g cm^{-3}; the specific surface area is 342 m² g^{-1}; and the particle size is in the range of 0-50 μm.[30] All chemicals were obtained from Merck, Aldrich, and Fluka; were of analytical grade; and were used without further purification.

2.2. Surface Modification of Sepiolite with Silane Coupling Agent. Sepiolite samples were treated before use in the experiments to obtain a uniformly sized sample of adsorbent as follows:[31] A suspension containing 10 g L^{-1} sepiolite was mechanically stirred for 24 h; then about 2 min after stirring had stopped, the supernatant suspension was filtered through filter paper. The solid sample was dried at 105 °C for 24 h, ground, and then sieved with a 50-μm sieve. The particles under 50 μm were used in further experiments. Sepiolite (5 g) suspended in toluene (100 mL) was refluxed and mechanically stirred for 1 h under dry nitrogen. Triethoxy-3-(2-imidazolin-1-yl)propylsilane (5.0 mL) to this suspension was added dropwise. The, the mixture was refluxed for an additional 24 h; filtered; and washed with water, followed by methanol and acetone. The modified surface was dried at 110 °C.[32]

2.3. Characterization. About 0.01 g of clay was mixed with 1 g of potassium bromide (KBr) and pelletized in a hydraulic press at 10 kPa. Infrared spectra of solid samples were obtained using a Perkin-Elmer BX 1600 FTIR spectrometer. FTIR spectra were recorde in the range from 4000 to 400 cm^{-1} in transmission mode. The interaction between the sepiolite surface and the modifier [triethoxy-3-(2-imidazolin-1-yl)propylsilane] that occurred during the modification was investigated by a series of FTIR spectral analyses: (1) modifier sample (to estimate the peaks arising from the modifier and the changes to them after modification), (2) sepiolite sample (to observe any changes in the sepiolite during the modification process and compare to the modified sample), (3) modified-sepiolite sample (to compare the peaks arising from the modifier and the sepiolite), (4) modified sepiolite with the sepiolite background removed [to clarify the changes arising from the modifier; obtained by subtracting the pure sepiolite spectrum (spectrum 2) from the modified spectrum (spectrum 3) to omit the peaks arising from sepiolite], and (5) mechanical mixture (to determine whether there is a chemical reaction or a physical interaction between the sepiolite and the modifier). X-ray diffraction measurements of natural- and modified-sepiolite samples were performed using an 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 ($\lambda = 1.54$ Å). A simultaneous DTA/ TG system was used for differential thermal (DTA) and thermogravimetric (TG) analysis (Perkin-Elmer Diamond DTA/TG).

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

$$\zeta = \frac{4\pi\eta}{\epsilon}U \qquad (2)$$

where U is the electrophoretic mobility at the actual temperature, η is the viscosity of the suspending liquid, ϵ is the dielectric

constant, π is a constant, and ζ is the zeta potential. The pH measurements were performed using an Orion 920A pH meter with a combined pH electrode. Doubly distilled water was used to prepare aqueous solutions for all experiments for zeta-potential measurements. For electrophoretic mobility measurements, suspensions were prepared in a polyethylene container by mixing 0.1 g of the modified sepiolite with 100 mL of doubly 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 initial electrolyte concentration and equilibrium pH. After agitation for 24 h in an incubator, the suspension was allowed to stand for 15 min to allow the larger particles settle. An aliquot removed from the suspension was slowly poured into the electrophoresis cell. A molybdenum anode and a platinum cathode were inserted into the cell. After the desired voltage was applied between the electrodes, the movement of particles was observed via a microscope nodule. A minimum of 10 measurements were carried out to determine the measured potential. The applied voltage during the measurements was varied in the range of 50−150 mV. The solution pH at the time the zeta-potential measurement was made was recorded as the equilibrium pH. The instrument was tested prior to each experiment using the test colloid, as recommended by the supplier.[33]

2.5. 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. The containers were shaken during the adsorption experiments with a GFL thermostated orbital shaker incubator set to 150 rpm. A 0.1-g sample of modified sepiolite was added to 50 mL of metal solution each time, and the mixture was 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 using an Orion 920A pH meter with a combined pH electrode. The pH meter was standardized with NBS buffers before every measurement. The equilibrium pHs of the modified-sepiolite/metal-ion suspensions were between 2.37 and 5.43 for Co, between 1.33 and 6.38 for Cd, between 1.30 and 6.21 for Zn, between 1.33 and 6.38 for Mn, between 2.32 and 5.53 for Cu, and between 2.30 and 6.78 for Fe. A preliminary experiment revealed that about 24 h was required for the metal ions to reach their equilibrium concentrations. The metal concentrations in the experiments were in the ranges of $(0.17-13.57) \times 10^{-4}$ mol L^{-1} for Co, $(0.09-6.23) \times 10^{-4}$ mol L^{-1} for Cd, $(0.15-15.29) \times 10^{-4}$ mol L^{-1} for Zn, $(0.18-10.92) \times 10^{-4}$ mol L^{-1} for Mn, $(0.15-11.01) \times 10^{-4}$ mol L^{-1} for Cu, and $(0.17-12.53) \times 10^{-4}$ mol L^{-1} for Fe. The effects of pH, ionic strength, and temperature on the adsorption of heavy metals (Cu^{+2}, Co^{+2}, Zn^{+2}, Cd^{+2}, Mn^{+2}, Fe^{+3}) were also studied. The pHs of aqueous solutions of all metal ions except for Fe-(III) in adsorption experiments were constant at pH 4, whereas the pH for Fe(III) was 2.5. The nitrate salts of metal ions were used in the experiments. After the adsorption step, the aqueous phase was separated by centrifugation, and the final concentration of metal ion in solution was determined by atomic absorption spectroscopy (AAS). A Unicam 929 flame atomic absorption spectrometer operating with an air/acetylene flame was employed. At the end of the adsorption period, the solution was centrifuged for 15 min at 5000 rpm. A Nuve NF 800 model

centrifuge at 5000 rpm was used to separate the solid part from the solutions after complete adsorption. Five standard solutions for each metal ion were prepared in 100-mL flasks. A calibration graph for each batch of experiments was 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, as filter paper itself adsorbs ∼30% of the metal ions present, particularly at low concentration levels. Each run was repeated at least twice. The adsorbed amount of metal ions was calculated by the difference in initial and final concentrations as follows

$$q_e = (C_0 - C_e)\frac{V}{W} \qquad (3)$$

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).[31,34]

3. Results and Discussion

3.1. Characterization. The analysis methods most frequently applied in the study of organo−clay complexes are FTIR spectroscopy, XRD analysis, thermogravimetry (TG), and differential-thermal analysis (DTA). In this study, modified sepiolite was characterized by these methods as follows:

3.1.1. FTIR Characterization. The hydroxyl groups on the oxide surface, resulting from hydrolysis, act as active sites in the grafting reaction. The grafting agents are assumed to attach to clay surfaces by chemical bonding and adsorption to form a monomolecular layer or oligomer film on the clay mineral surfaces.[35] However, the adsorbed organic layer is often displaced by solvents or by compound formation. Chemical bonding gives rise to a solid linkage between the coupling agent and the clay surfaces, thus improving the properties of the polymer products.[36] Infrared spectral measurements based on changes in the absorption bands of functional groups in minerals can be used to determine whether chemical bonding has occurred. For the observation of the modification of the sepiolite with triethoxy-3-(2-imidazolin-1-yl)propylsilane, the previously described five-step FTIR measurement method was used.[26] In this method, the FTIR spectra of the pure modifier and sepiolite (KBr disk) were first measured before the modification was performed. After the modification, the FTIR spectrum of the modified sample was recorded directly as a KBr-background measurement, and a second sepiolite-background measurement was carried out to clarify the changes in the FTIR spectrum of modifier. Finally, the FTIR spectrum of a well-mixed mechanical mixture of the modifier and sepiolite was also recorded. Figure 1shows the FTIR spectra of the modifier, sepiolite, modified sepiolite, modified sepiolite with the sepiolite background, and mechanical mixture. The modifier [triethoxy-3-(2-imidazolin-1-yl)prophylsilane] contains three ethoxy groups bonded to the silane. As it is known that the modification occurs at the ethoxy site of the silane modifier, the C−H stretching due to the ethoxy group should decrease in intensity or even disappear according to the loss of one, two, or three ethoxy groups of the modifier during the modification. Mainly, we have observed the loss of all alkoxy groups upon surface modification of sepiolite in our previous works.[11,26,37]

First, the FTIR spectrum of the modifier was investigated. As shown in Figure 1a, the peak at 3385 cm^{-1} is due to hygroscopic water molecules, and those at 2973, 2930, and 2886 cm^{-1} are due to the asymmetric and symmetric C−H vibrations
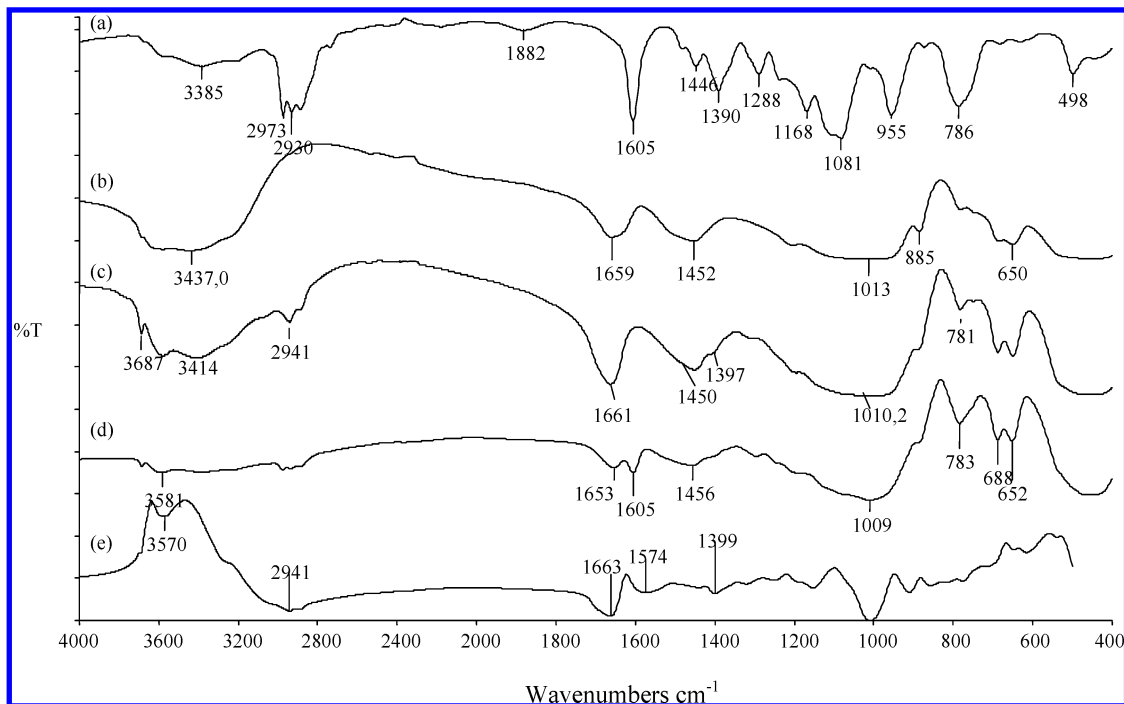
Figure 1. FTIR spectra of sepiolite samples: (a) pure modifier, (b) pure sepiolite, (c) modified sepiolite, (d) sepiolite-background, and (e) mechanical mixture.
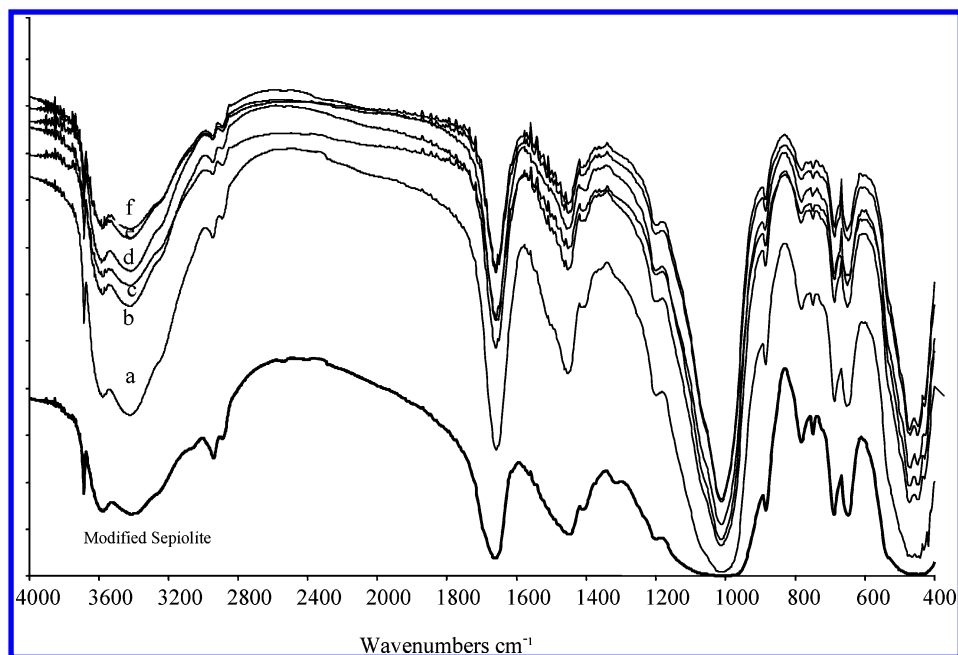

Figure 2. FTIR spectra of complex formation on a sepiolite surface modified by triethoxy-3-(2-imidazolin-1-yl)propylsilane: (a) Cd, (b) Co, (c) Cu, (d) Fe, (e) Mn, and (f) Zn.

of the ethoxy groups[38] and the CH_2 chains between the silane and the nitrogen. The cyclic hydrogens in the imidazolin structure also appeared in the same region. Because of the presence of a broad sepiolite peak between 3000 and 1800 cm^{-1} (Figure 1b),[39] the changes in the aromatic and nonaromatic hydrogens on the molecule can usually be informatively observed (Figure 1c, 2941 cm^{-1}). The peaks in the area of about 1650−1665 cm^{-1} are quite difficult to determine because of the overlap of the intense Si−O stretching of sepiolite[29,40] with the modifier structure.[41] Even the C═N vibration is very clear and intense in the modifier spectrum; it could not be seen in the spectrum of modified sepiolite. It was assumed that this peak was shifted downfield and overlapped with the intense Si−O stretch. The shift of the 1392 cm^{-1} peak in the sepiolite-

background spectrum (Figure 1d) to 1399 cm^{-1} and the presence of peaks at 2975 and 1605 cm^{-1} in mechanical mixture (Figure 1e) might be an indication of a chemical interaction occurring on the sepiolite surface during the modification. The appearance of peaks at 2973 and 2930 cm^{-1} in the spectrum of the mechanical mixture (Figure 1e), which were absent from that of the modified sepiolite (Figure 1c), can be accepted as a good indication of the loss of ethoxy groups during the modification process and the formation of a chemical bond between the sepiolite surface and the modifier silane structure. FTIR spectra obtained after complexation with metal ions were also examined; as no formation or breaking of chemical bonds occurred, the complexation spectra did not show the significant changes of the modified-sepiolite FTIR spectrum (Figure 2).
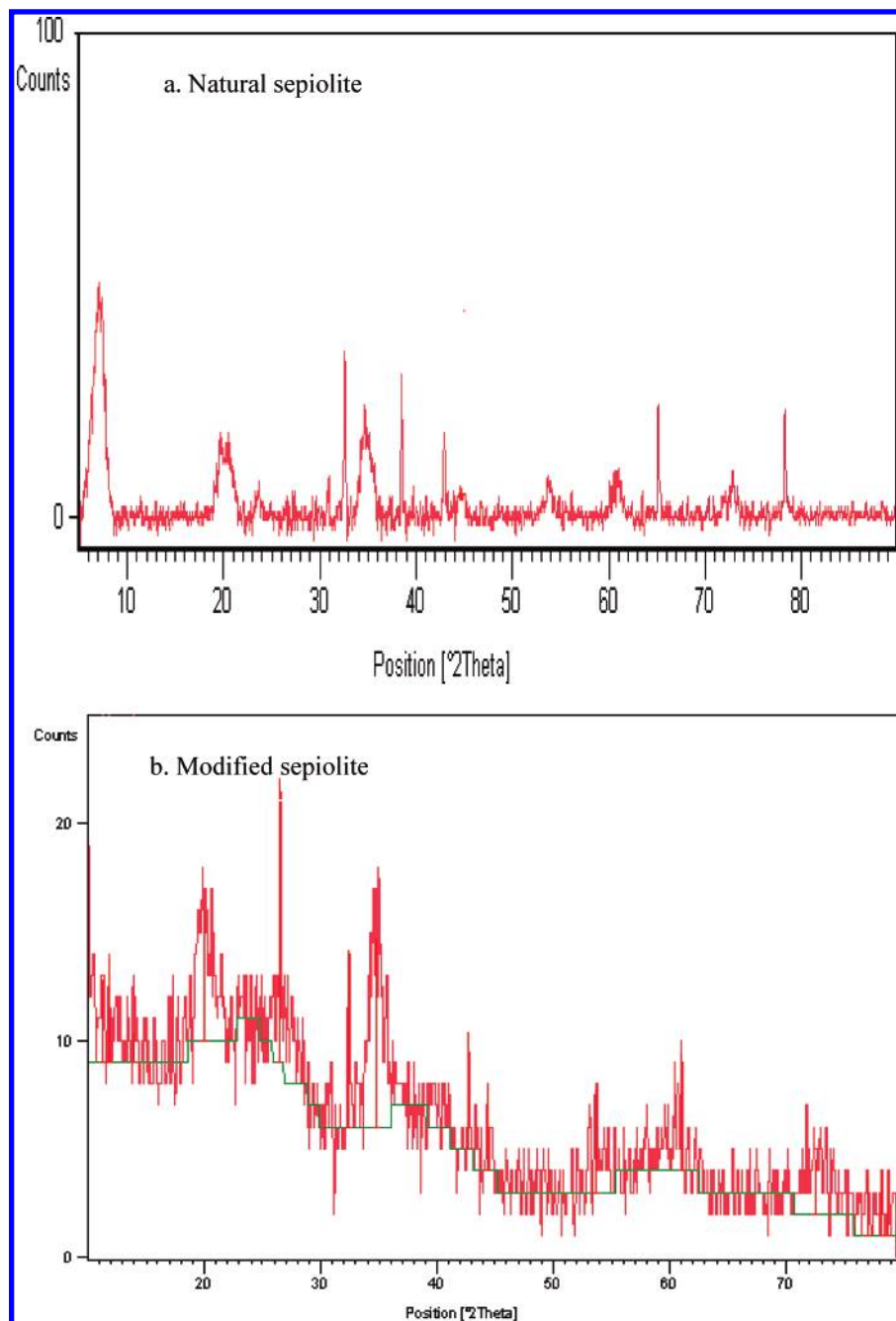
Figure 3. XRD spectra of natural- and modified-sepiolite samples.

3.1.2. XRD Characterization. XRD analysis can also provide important information about the modification of sepiolite by triethoxy-3-(2-imidazolin-1-yl)propylsilane. XRD patterns of the sepiolite before and after grafting are shown in Figure 3. These difractograms indicate that the grinding step in the presence of the chemical modifier was effective for generating a new modified product. The difractogram for clay ground without modifier shows that sepiolite was present in the sample. It can also be seen that some original peaks formed after grinding with modifier, and as can be seen in Table 1, the intensities of some peaks changed upon modification. The variations in XRD difractograms before and after the modification of sepiolite show that there is a covalent bonding interaction between natural sepiolite and the modifier. When a covalent bond is formed by the interaction between sepiolite and triethoxy-3-(2-imidazolin-1-yl)propylsilane, some structural distortions occur at the plane atoms in the sepiolite. As a result of these distortions, the peak intensities change.

Table 1. Changes in Peak Intensities of XRD Spectra of Natural and Modified Sepiolites

position (deg, 2θ)	intensity (%)	
	sepiolite	modified sepiolite
19.9760	34.16	10.15
26.0249	32.58	100.00
32.3018	100.00	62.44
34.7771	81.42	66.69
42.6689	55.27	41.21
53.6000	56.10	36.45
77.5474	31.58	23.24

3.1.3. Simultaneous DTA/TG Analyses. In modern instruments, DTA is recorded simultaneously with TG. By using simultaneous DTA/TG analysis, one can differentiate between peaks associated with mass loss and those associated with a phase transition. DTA has been used very widely in the study of thermal reactions of clay minerals. These reactions include
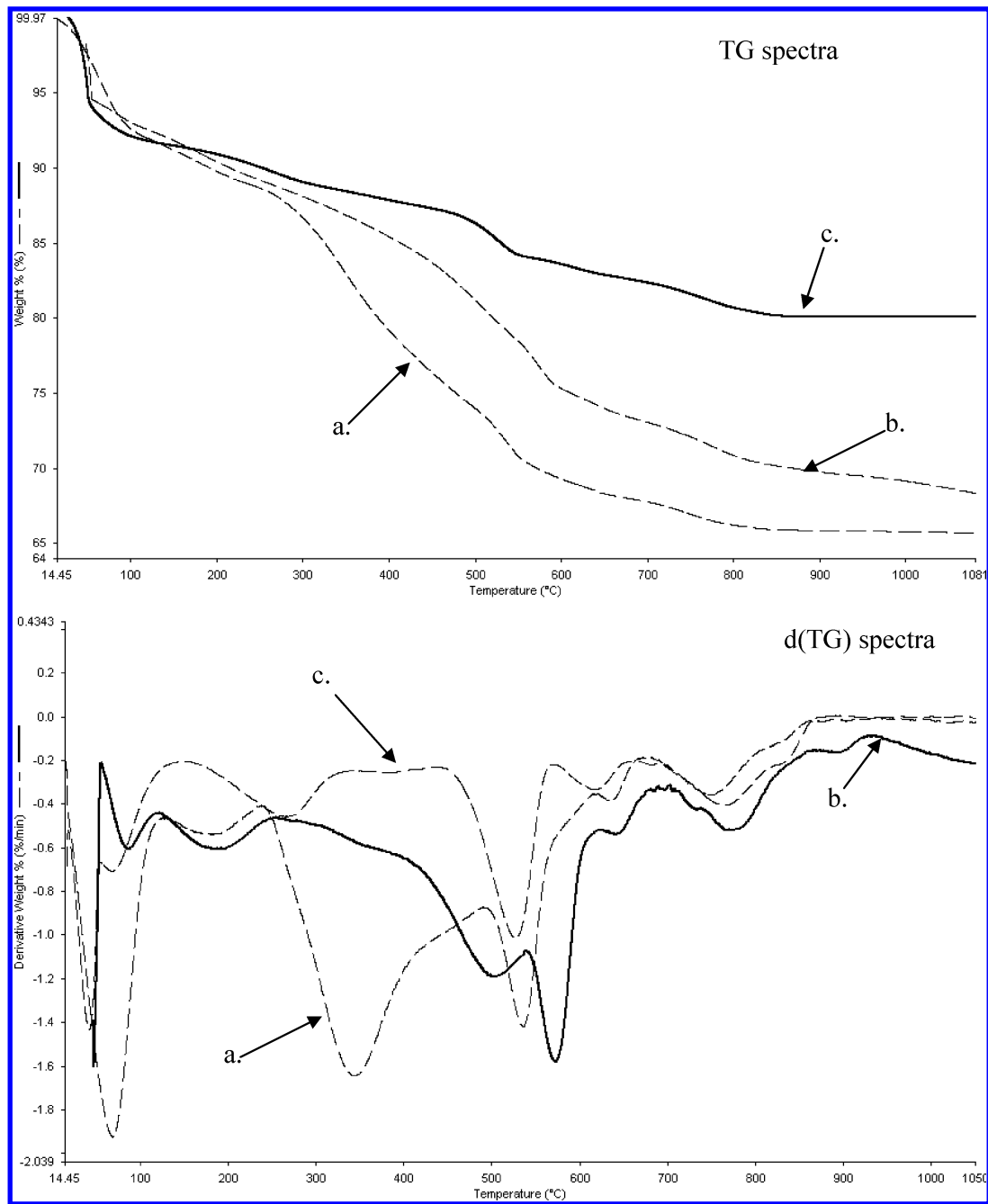
Figure 4. TG and d(TG) patterns of natural- and modified-sepiolite samples under different conditions: (a) modified sepiolite under oxygen atmosphere, (b) modified sepiolite under nitrogen atmosphere, and (c) natural sepiolite under nitrogen atmosphere.

dehydration of adsorbed water, dehydroxylation (evolution of water from hydroxyl groups contained in the clay skeleton), and the transformation of the clay to a meta phase and recrystallization of the meta phase into a crystalline phase.[42,43] Figure 4 shows the variation of percent mass loss with temperature (TG curves) and differential mass loss with temperature [d(TG) curves] for sepiolite and modified-sepiolite samples in oxidizing and inert enviroments in the temperature range of 20−1100 °C. Sepiolite mineral is known to contain four types of water molecules in different chemical states: (1) hydroscopic water, the moisture adsorbed on the sepiolite surface; (2) zeolitic water, the water molecules found in the channel-type voids of the structure; (3) bound water, the water molecules bound to the edges of the octahedral sheet; and (4) structural water, the hydroxyl groups associated with the octahedral sheet.[18] These water molecules are removed from the mineral by thermal dehydration, with the different types of

water molecules leaving the mineral at different temperatures. As can be seen in Figure 4, the removal of hydroscopic water from the external surface and zeolitic water from the voids of the structure was completed by 200 °C with mass losses of 9.65%, 9.10%, and 10.18% for the natural sepiolite under nitrogen atmosphere, for modified sepiolite under nitrogen atmosphere, and for modified sepiolite under oxygen atmosphere, respectively. The bound water molecules left the structure a higher temperature than the hydroscopic and zeolitic water molecules, with mass losses of 7.36%, 15.08%, and 15.05%, respectively, for the same three samples. It has been stated that the bound water is found in magnesium coordination in the crystal structure.[18] Its dehydration occurred in two steps, accompanied by structural changes. As can be seen in Figure 4, the first part of the bound water left the structure between 250 and 350 °C. During dehydration at around 400 °C, the percent mass loss became constant (after a small plateau in the
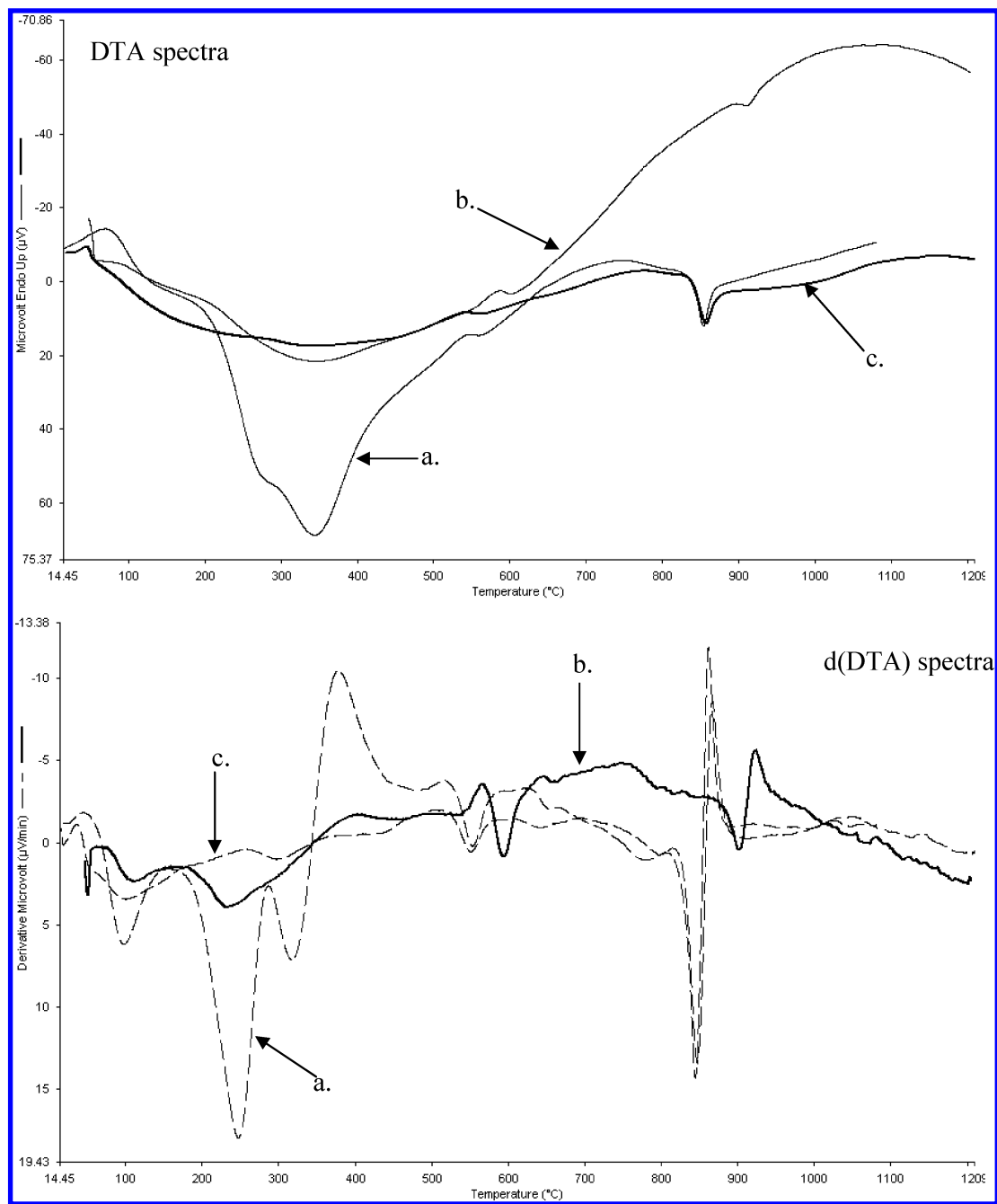
Figure 5. DTA and d(DTA) patterns of natural- and modified-sepiolite samples under different conditions: (a) modified sepiolite under oxygen atmosphere, (b) modified sepiolite under nitrogen atmosphere, and (c) natural sepiolite under nitrogen atmosphere.

TG curve); the remaining part of the bound water began to leave the structure at higher temperatures. The removal of bound water was completed at about 550 °C. This removal gave a particularly high peak in the d(TG) curve of modified sepiolite under oxygen atmosphere. One reason for this might be the mass loss of the organosilane compound from the modified sepiolite. The removal of structural water molecules and hydroxyl groups was completed with mass losses of 3.42%, 3.29%, and 6.67% by 900 °C for natural sepiolite under nitrogen atmosphere, for modified sepiolite under nitrogen atmosphere, and for modified sepiolite under oxygen atmosphere, respectively. No further mass loss was observed when two samples were heated to 1100 °C under different conditions.

The nature of the thermal reaction depends on the loading of the clay with the organic matter. DTA curves of organic substances recorded in oxidizing and inert environments show diagnostic exothermic and endothermic peaks, respectively,
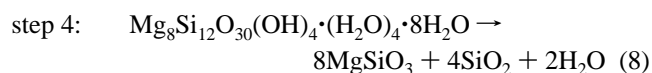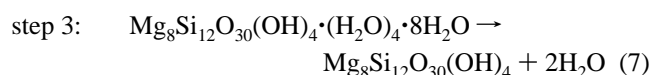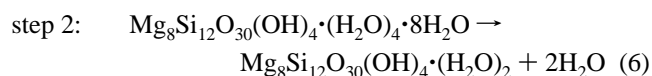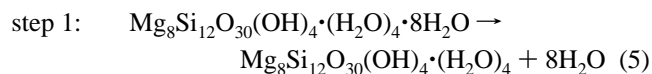
associated with combustion, decomposition, dehydration, fusion, vaporization, sublimation, and solid-state transitions.[44] The DTA peak temperatures are characteristic for each mineral, and DTA curves are applicable for the identification and determination of many clays.[45,46] Figure 5 shows the DTA and d(DTA) curves of natural and modified sepiolite under different conditions. The DTA curves for both samples show four important exothermic processes at 250, 320, 550, and 830 °C. The strong exothermic peaks observed in the DTA curves of the organo−sepiolite complexes in the temperature range of 200−650 °C represent the oxidation of organic matter (H and C) and formation of H_2O and CO_2. Combustion of the organic matter commences at a temperature that is independent of the amount of material present, but depends on the activation energy of the combustion reaction.[47] 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.

According to the explanation above, the modification reaction between triethoxy-3-(2-imidazolin-1-yl)propylsilane and sepiolite can be described as follows, where M represents metal ions such as Si and Mg

[4]
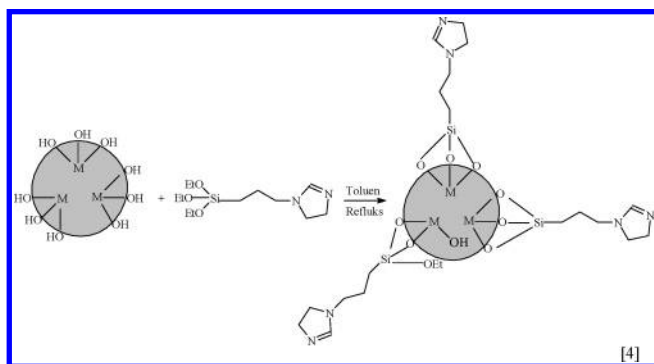
We compared our results with those of other studies. Frost and Ding[40] found four distinct mass losses for Vellecas sepiolite (Spain) in the temperature range of 50−820 °C. The first step occurred at 50 °C and was attributed to the loss of adsorbed water. The second step was observed at 246 °C. The third step was complex, with two overlapping mass-loss steps observed at 450 and 494 °C. The final step was also complex and involved two weight loss steps at 787 and 820 °C. Furthermore, Nagata et al.[48] proposed a set of four steps for the dehydration and dehydroxylation of a sepiolite. These steps correspond to (1) the loss of adsorbed water, (2) the loss of hydration water, (3) the loss of coordination water, and (4) the loss of water through dehydroxylation. Such a scheme is represented by the following equations

step 1:
$$Mg_8Si_{12}O_{30}(OH)_4 \cdot (H_2O)_4 \cdot 8H_2O \rightarrow$$
$$Mg_8Si_{12}O_{30}(OH)_4 \cdot (H_2O)_4 + 8H_2O \quad (5)$$

step 2:
$$Mg_8Si_{12}O_{30}(OH)_4 \cdot (H_2O)_4 \cdot 8H_2O \rightarrow$$
$$Mg_8Si_{12}O_{30}(OH)_4 \cdot (H_2O)_2 + 2H_2O \quad (6)$$

step 3:
$$Mg_8Si_{12}O_{30}(OH)_4 \cdot (H_2O)_4 \cdot 8H_2O \rightarrow$$
$$Mg_8Si_{12}O_{30}(OH)_4 + 2H_2O \quad (7)$$

step 4:
$$Mg_8Si_{12}O_{30}(OH)_4 \cdot (H_2O)_4 \cdot 8H_2O \rightarrow$$
$$8MgSiO_3 + 4SiO_2 + 2H_2O \quad (8)$$

Such a scheme is an oversimplification, as each of these steps can be subdivided into component mass-loss steps. For sepiolite samples, Nagata et al.[48] and Frost and Ding[40] found that the theoretical mass losses were 11.0% for step 1, 2.76% and 3.3% for step 2, 2.76% and 2.3% for step 3, and 5.21% and 2.1%, respectively. On the other hand, we found that the total theoretical mass loss for steps 1 and 2 was 9.65%, that for step 3 was 7.36%, and that for step 4 was 3.42%. As can be seen from the results above, the total mass losses for sepiolite samples in the three studies were 21.73%, 18.7%, and 20.43%, respectively. Thus, there is reasonable agreement between the predicted and observed mass losses.
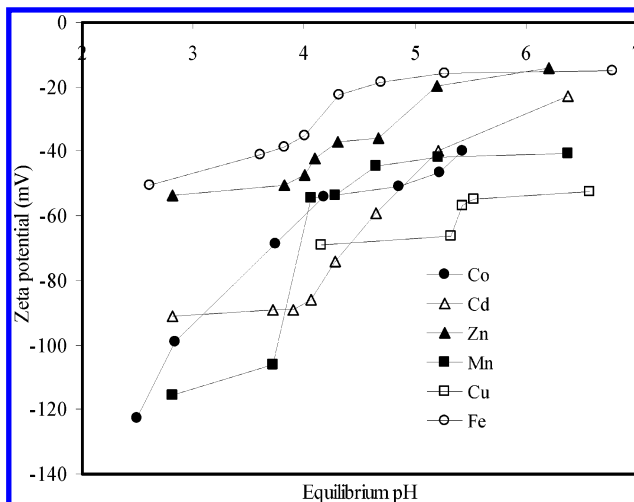

Figure 6. Effect of pH on the zeta potential of modified sepiolite.

3.2. ζ Potential. The zeta potentials of modified sepiolite in separate aqueous solutions of Co^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Fe^{3+}, and Cd^{2+} were investigated. Although the zeta-potential values with heavy metal cations were quite different, their tendencies to change with pH were similar (Figure 6). In our previous study,[49] we found that the zeta potentials of natural-sepiolite suspensions in aqueous solutions of heavy metals are positive at low equilibrium pH values and that the pH at the IEP (pH_{IEP}) of a natural-sepiolite suspension is 6.6. Moreover, we also found that pH_{IEP} value of natural-sepiolite suspensions in aqueous solutions of heavy metals vary as a result of the specific adsorption of the metal ions on the sepiolite. The isoelectrical point is the pH at which particles have zero zeta potential. The isoelectrical point of an oxide reflects the sum of all interactions occurring at the oxide/water interface such as the adsorption of H^+ and OH^- ions and the distribution of dissolved lattice ions. Moreover, at the IEP, there is no charge on the surface, and the total positive charge equals the total negative charge.[50] As can be seen in Figure 6, the zeta potential of modified-sepiolite suspensions is negative at low equilibrium pH values. This is another sign that the sepiolite surface was modified by triethoxy-3-(2-imidazolin-1-yl)propylsilane. For all metal ions, the zeta potential became less negative with increasing equilibrium pH. The zeta potentials measured in the presence of Co^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Fe^{3+}, and Cd^{2+} followed a common path and did not give the same pH_{IEP} of 6.6 in the studied pH range. The fact that the zeta potential at higher pH values increases might imply that metal ions interact with modified sepiolite and change its surface potential. They are preferentially adsorbed onto oxide surfaces to reduce the free energy requirement for adsorption. Each hydrolyzable metal ion has a distinct pH and concentration at which it first hydrolyzes. Surface precipitation is possible if heavy metal ions accumulate within the diffuse part of the electrical double layer, and accumulation occurs if there is a net negative charge on the solid surface. Thus, although the concentration of the metal ion in solution might be much lower than the solubility limit with respect to metal hydroxide and oxide solids, the solubility limit near the solid surface is exceeded, and precipitation onto the solid surface takes place. For example, it can be said that Fe^{3+} ions can hydrolyze and precipitate at pH values higher than 2.05. There is no change in the sign of the surface charge of modified sepiolite for any of the metal ions. The modified-sepiolite surface is negatively charged, and metal ions cannot specifically adsorb onto the modified-sepiolite surface and cannot alter the magnitude of the zeta potential. At low pH values, the adsorption of H_3O^+
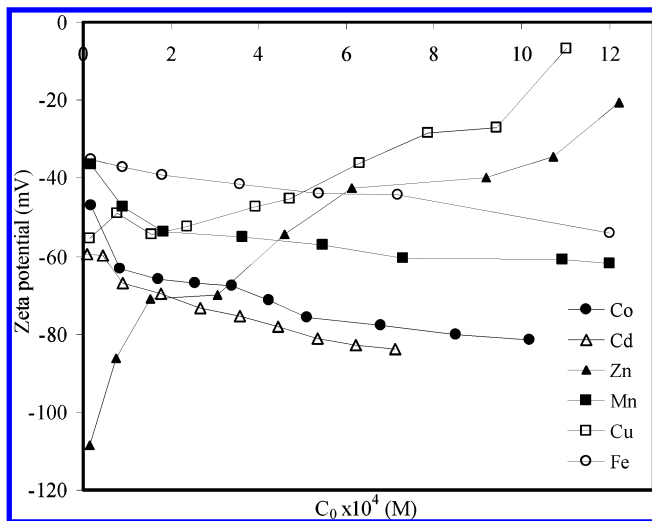
Figure 7. Effect of heavy metal ion concentration on the zeta potential of modified sepiolite.

Figure 8. Adsorption isotherm curve fitting.

hinders the specific adsorption of metal ions. For this reason, as the pH increases, the negative sign of the surface decreases because of the adsorption of metal ions.

Figure 7 shows the change of the zeta potential of modified sepiolite with electrolyte concentration in the presence of various electrolytes. As the concentrations of heavy metal ions increase in the solution, the zeta potential of sepiolite decreases (becomes less negative). For a cation to be a potential-determining ion (pdi), it should render the surface more positive with increasing concentration of the cation. As can be seen in Figure 7, the surface is, at first, more negatively charged, and then the negative charge decreases as the concentration of electrolyte increases. Note that, at the heavy metal ion concentrations studied, modified sepiolite does not exhibit a charge reversal. Indeed, charge reversal requires, in addition to ion exchange, specific adsorption of counterions in the electrical double layer (EDL), that is, in the inner Helmhotz plane (IHP) of the Stern layer. As the heavy metal cations did not reverse the sign of the surface, these cations adsorb as indifferent electrolytes onto modified sepiolite and are not capable of causing a charge reversal. Because of Coulombic attraction, they accumulate only as counterions in the EDL on the negatively charged modified sepiolite. Consequently, they compress the EDL and change the magnitude of the zeta potential of modified sepiolite.

3.3. Adsorption Equilibrium. The amounts of different heavy metal ions that adsorb can vary, and differences can be shown for different clay minerals. Universally consistent rules of metal selectivity cannot be given, as adsorption depends on a number of factors, such as (1) the chemical nature of the reactive surface groups, (2) the level of adsorption (adsorbate/adsorbent ratio), (3) the pH at which adsorption is measured, (4) the ionic strength of the solution in which adsorption is measured (which determines the intensity of competition by other cations for the bonding sites), and (5) the presence of soluble ligands that could complex the free metal. All of these variables can change the metal adsorption isotherms.[51] The ability of modified sepiolite to adsorb the cations from aqueous solution was evaluated by measuring the adsorption isotherms for a series of divalent and trivalent cations, including Co, Cu, Zn, Mn, Fe, and Cd. Under equilibrium conditions, the adsorption processes between adsorbent and adsorbate can be characterized by the amount of adsorbed metal ions per gram of modified sepiolite (q_e). This value was calculated from the initial concentration of cation added (C_0) and the concentration at the
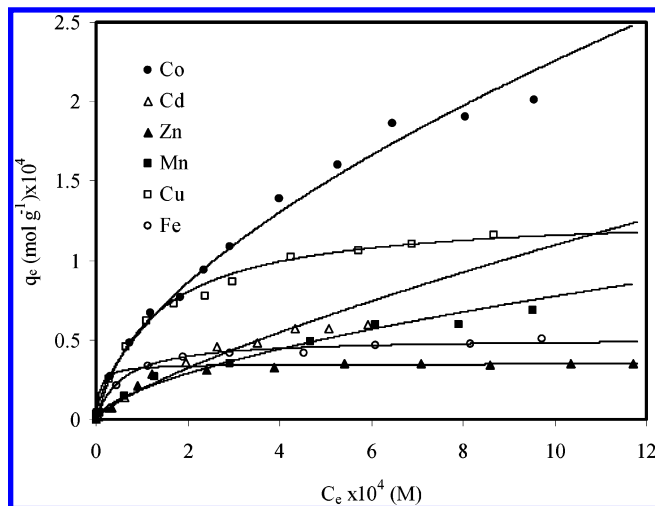
equilibrium point (C_e). Profiles of the adsorption isotherms for all cations in water are shown in Figure 8, representing the amount of adsorbed metal ions versus the concentration of solution under equilibrium conditions. A simple observation of these profiles, which define the maximum adsorption values, can lead to a perfect distinction of these cations, from the point of view of adsorption.[52] The isotherms presented in Figure 8 show that the adsorption follows the sequence Co > Cu > Cd $\approx$ Mn > Fe > Zn. The affinity of a metal ion for a surface is composed of two terms: the chemical affinity and the electrostatic affinity. The equilibrium constant, pK, determines the adsorption behavior of an individual heavy metal. Specific adsorption increases with decreasing pK value. The following order is given for specific adsorption (pK values in parentheses): Co^{2+} (9.7) < Cu^{2+} (7.7).[53] The adsorption capacity of modified sepiolite is higher for cobalt and copper than for the other ions. This behavior reflects the high affinity of the immidazolin ring for cobalt and copper and might be a result of the interaction between the metal ions and the chromophore group of modifier agent. In light of these observations, this material could potentially be applied as a selective electrode when the objective is to determine or identify cobalt and copper. The reaction between modified sepiolite and metal ions can generally be given as follows:
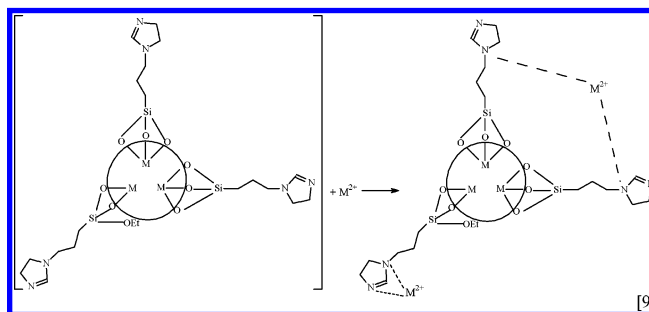
The pH is an important parameter controlling the permeability through changes in the amount and charge of active sites on the edges of clay mineral particles and, hence, flocculation.[54] The dependence of metal ion uptake on pH is related to the surface functional groups[55] and ion-exchange properties of sepiolite. To determine the influence of this parameter on the adsorption of metal ions, modified sepiolite was contacted with single-metal solutions at different equilibrium pH values ranging from 1.3 to 6.78 for a 24-h period. The results of the pH experiments are presented in Figure 9. It can be seen that the
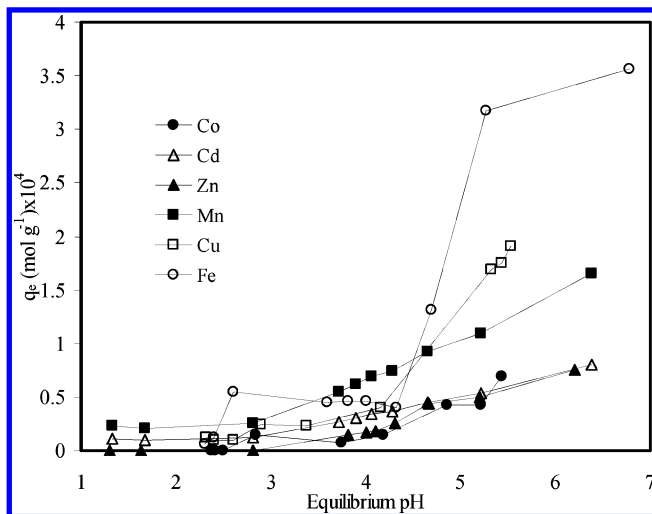
Figure 9. Variation with pH in the adsorption of metal ions on modified sepiolite.

Figure 10. Variation with ionic strength in the adsorption of metal ions on modified sepiolite.

Figure 11. Variation with temperature in the adsorption of metal ions on modified sepiolite.

adsorption of metal ions onto the modified sepiolite is markedly pH-dependent. Specifically, the adsorption of single metal ions increased with increasing pH. Higher adsorption at higher pH values might imply that the metal ions interact with modified sepiolite. Because of the protonation and deprotonation of the acidic and basic groups of the modifier agent, 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 the sorbents and the metal ions.[56] At lower pH values (<3.0), more hydrogen ions compete with the heavy metal ions for the functional groups, which reduces the chances for the formation of heavy metal ion−functional group complexes, so that fewer heavy metal ions are removed.[55] At moderate pH values (i.e., 3.0−5.0), linked H^+ is released from the active sites, and the amount of metal ions adsorbed is increased. In this pH range, it is believed that the ion-exchange and complex-formation processes are the major mechanisms for the removal of single metal ions from solution.[57] These observations are in line with earlier findings of Lafferty and Hobday.[58] In addition, increasing pH decreases the concentration of H^+, thus reducing the competition between metal ions and protons for adsorption sites on the modified-sepiolite surface. Another factor that could also contribute to enhancing metal ion adsorption is the increasing pH, which encourages metal ion precipitation from the solution in the form of hydroxides.[59] The pH values at which the chemical precipitation of metal hydroxides occurs are as follows: 7.73 at 13.57 $\times$ 10^{-4} for Co(II), 8.35 at 11.01 $\times$ 10^{-4} for Cu(II), 8.82 at 10.92 $\times$ 10^{-4} for Mn(II), 6.69 at 12.23 $\times$ 10^{-4} for Zn(II), 2.05 at 10.74 $\times$ 10^{-4} for Fe(III), and 8.47 at 7.11 $\times$ 10^{-4} mol L^{-1} for Cd(II). It can be said that the amounts removed up to these pH values might be due to the chemical precipitation of metal hydroxides. Up to pH 2 for Fe(III), there is an inflection point. The presence of the inflection point suggests the onset of a change in the mechanism for metal removal. Beyond pH 2, therefore, the ion-exchange mechanism becomes masked by precipitation and adsorption of hydrolyzed species.[60] With increasing pH, Fe^{3+} ions convert to $Fe(OH)^{2+}$, $Fe(OH)_2^+$, etc. Because of lower interactions of these types ions of decreasing charge with the modified-sepiolite surface, the adsorption of ferric ions in the pH range of 3.0−4.5 decreases slightly, and then the amount adsorbed increases with increasing pH as a result of precipitation. The strong removal of metal ions coincides with the pH at which a small fraction of the corresponding metal hydroxide species forms in the aqueous
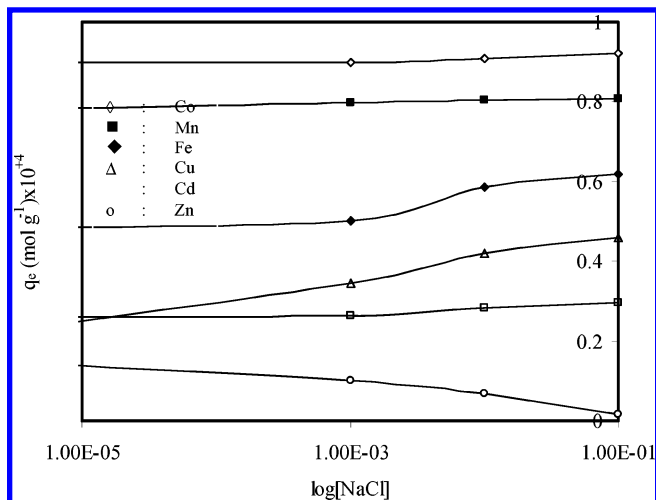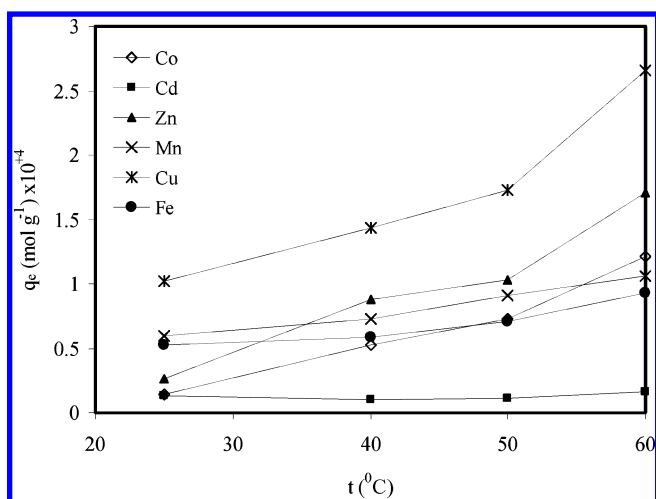
phase.[54] For example, Stumm and Morgan[61] reported that Cd speciates to $CdOH^+$ above pH 8, to $Cd(OH)_2$ above pH 9, and to $Cd(OH)_3^-$ above pH 11. Therefore, Cd^{2+} ions precipitate at higher pH values than the ions of other metals, if both ion exchange and metal hydroxide precipitation jointly contribute to metal removal from solution at high pH values. Another reason for the increase with pH in the amount of metal adsorbed might also be due to the ion-exchange mechanism, as shown by Kara et al. for Co adsorption on sepiolite.[62] They measured the amount of Mg(II) ion released as a function of pH in the absence and presence of Co(II) to identify the effect of cobalt ions on the solubility of magnesium ions and found the quantity of dissolved Mg(II) ions in the water/sepiolite system to be higher than that in Co(II)/water/sepiolite system up to pH 5 because of the release of additional Mg(II) ions by the H^+ ions of the acid used for adjusting pH.

Electrolytes and their ionic strengths are known to affect the adsorption of metal ions from aqueous solutions. Figure 10 shows the adsorption capacities of modified sepiolite for metal ions at different concentrations of NaCl. It was observed that, in the presence of increasing concentrations of NaCl, there was no significant change in the adsorption capacities of modified sepiolite for the metal ions.

The equilibrium values for the adsorption of metal ions on modified sepiolite were calculated at different temperatures at the equilibrium time (i.e., 24 h). As shown in Figure 11, the

Table 2. Isotherm Constants for the Adsorption of Metal Ions on Modified Sepiolite

metal ion	temperature (°C)	pH	Langmuir isotherm			Freundlich isotherm		
			$q_m \times 10^5$ (mol g^{-1})	$K \times 10^{-4}$ (L mol^{-1})	R^2	n	$K_F \times 10^4$	R^2
Mn	25	4.0	8.46	0.34	0.9603	1.6342	53.10	0.9915
Cu	25	4.0	13.04	0.80	0.9955	1.7550	85.02	0.9515
Fe	25	2.5	5.11	1.75	0.9954	2.8579	6.35	0.9566
Zn	25	4.0	3.51	12.17	0.9977	9.5057	0.73	0.7215
Co	25	4.0	28.53	0.24	0.9616	1.6680	141.90	0.9977
Cd	25	4.0	9.18	0.33	0.9785	1.3170	208.00	0.9843

adsorbed amount increases with increasing adsorption temperature, thus implying a strengthening of the adsorbate−adsorbent interactions at higher temperatures and indicating the process to be endothermic. This might be a result of an increase in the mobility of the metal ions with temperature. An increasing number of molecules might also acquire sufficient energy to undergo an interaction with active sites at the surface.

3.4. Adsorption Isotherm. The relationship between the amount of a substance adsorbed per unit mass of adsorbent at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. The Langmuir and Freundlich isotherms are the equations most frequently used to represent the data on adsorption from solution.[63]

3.4.1. Langmuir Isotherm. The Langmuir equation can be written as

$$q_e = \frac{q_m K C_e}{1 + K C_e} \quad \text{(nonlinear form)} \quad (10)$$

$$\frac{C_e}{q_e} = \frac{1}{q_m K} + \frac{C_e}{q_m} \quad \text{(linear form)} \quad (11)$$
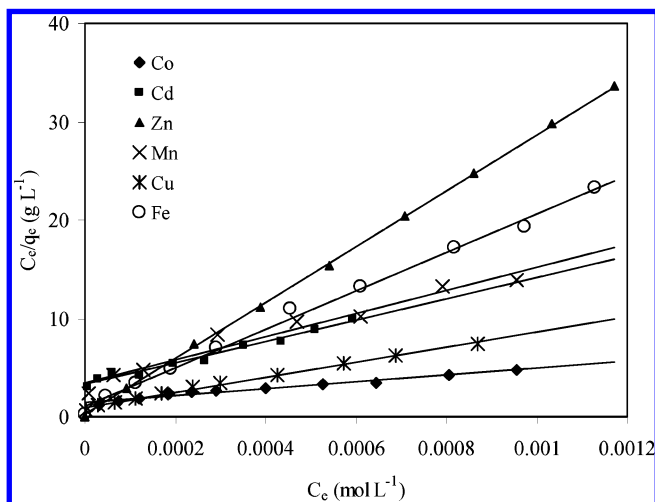
where C_e is the equilibrium concentration of the solution (mol L^{-1}), q_e is the amount adsorbed per unit mass of adsorbent (mol g^{-1}), q_m is the monolayer capacity (mol g^{-1}), and K is a constant related to the energy of adsorption (L mol^{-1}).[59]

3.4.2. Freundlich Isotherm. The Freundlich equation can be written as

$$q_e = K_F C_e^{1/n} \quad \text{(nonlinear form)} \quad (12)$$

$$\ln q_e = \ln K_F + (1/n) \ln C_e \quad \text{(linear form)} \quad (13)$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mol g^{-1}), C_e is the equilibrium concentration of solute in the bulk solution (mol L^{-1}), K_F is a constant indicative of the relative adsorption capacity of the adsorbent (mol g^{-1}), and $1/n$ is the constant indicative of the intensity of the adsorption.[59]

Computer simulation was used to fit the Langmuir and Freundlich equations to the adsorption data. The accuracy of these fits was estimated in terms of the computed correlation coefficients (R^2). The values of q_m, K, and R^2 for the Langmuir equation and the values of K_F, n, and R^2 for the Freundlich equation were determined for the adsorptions of all metal ions (see Table 2). Comparatively, the obtained R^2 values are more satisfactory for the Langmuir isotherm. Langmuir isotherms are presented in Figure 12 as plots of C_e/q_e versus C_e. Straight lines were obtained, with R^2 values in the range of 0.9603−0.9977 for modified sepiolite, which is an indication of the applicability of the Langmuir isotherm for the system under observation. The Langmuir adsorption isotherm is based on monolayer coverage of the adsorbate on the surface of adsorbent,[64−66] which is an indication of the fact that the sorption of metal ions onto the investigated sorbents leads to monolayer formation. The Langmuir constant, q_m, which is an indicator of the adsorption capacity, changed in the order of Co(II) > Cu(II) > Cd(II) > Mn(II) > Fe(III) > Zn(II).

3.5. Single-Stage Batch Adsorption. Adsorption isotherms can be used to predict the design of single-stage batch adsorption systems.[67] The schematic diagram for a single-stage adsorption process is shown in Figure 13. The solution to be treated contains a volume V (L) of water, and the metal concentration is reduced from C_0 to C_e in the adsorption process. In the treatment stage, a mass W (g) of adsorbent (metal-ion-free) is added, and the metal concentration on the modified sepiolite changes from $q_0 = 0$ to q_e. The mass balance that equates the metal removed from the liquid effluent to that accumulated on the modified sepiolite is

$$V(C_0 - C_e) = W(q_e - q_0) = W q_e \quad (14)$$

For the adsorption of metal ions on modified sepiolite, the Langmuir isotherm gives the best fit to experimental data. The

Figure 12. Lamgmuir isotherm plots for the data of Figure 8.
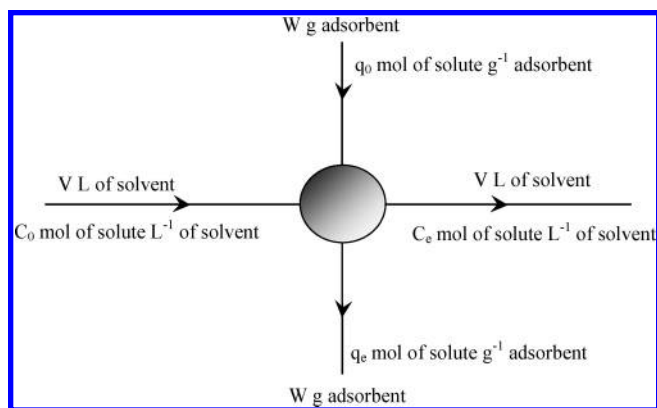
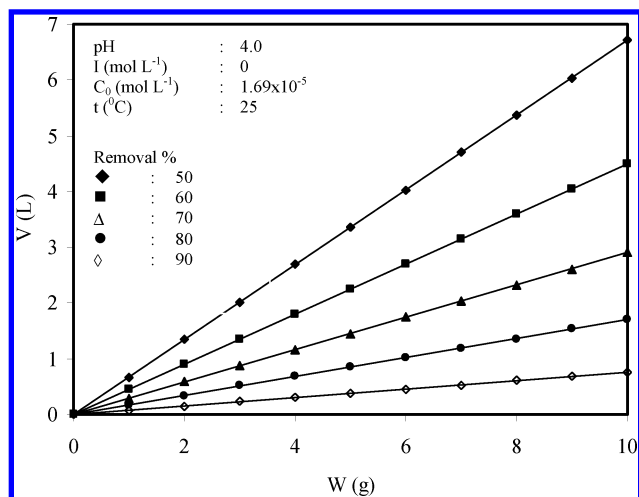**Figure 13.** Single-stage batch adsorber.

Figure 14. Volume of effluent (*V*) treated vs adsorbent mass (*W*) for different percentages of cobalt removal.

Langmuir data can now be applied to eq 14, which, upon substitution for q_e from eq 11 and rearrangement, gives

$$\frac{W}{V} = \frac{C_0 - C_e}{q_e} = \frac{C_0 - C_e}{\left(\dfrac{q_m K C_e}{1 + K C_e}\right)} \tag{15}$$

Equation 15 permits analytical calculation of the adsorbent solution ratio for a given change in solution concentration from C_0 to C_e. Figure 14 shows a series of plots derived from eq 15 for the adsorption of cadmium ions onto modified sepiolite. An initial cobalt concentration of 1.69×10^{-5} mol L^{-1} was assumed, and the figure shows the amount of effluent that can be treated to reduce the cadmium content by 90%, 80%, 70%, 60%, and 50% using various masses of modified sepiolite.

Conclusions

This broad physicochemical analysis verifies that the sepiolite surface modification examined involves the chemical reaction of the silanol groups on the sepiolite surface with the alkoxy groups of the organosilane molecule. The signs of modification of the sepiolite surface with triethoxy-3-(2-imidazolin-1-yl)-propylsilane compound are (1) the increased mass loss in TG patterns for modified sepiolite compared to natural sepiolite, (2) the presence of new exothermic peaks in the DTA patterns for modified sepiolite, (3) the changes in the peak intensities in the XRD spectra of modified sepiolite, and (4) the detection by FTIR spectroscopy of functional groups present on modified sepiolite. Thus, we showed that the position of the isoelectrical point under the selected conditions of the surface pretreatment is primarily affected by the preliminary annealing of the samples, which causes the IEP not to be observed. The reason for such a variation might be the change in the surface concentrations of various types of OH groups on the silica surface. The adsorption of metal ions onto modified sepiolite as an adsorbent increased with increasing pH and temperature, but ionic strength exhibited no significant effect on it. The affinity of metal ions for modified-sepiolite surface is a result of both chemical and electrostatic affinity. The adsorption followed the sequence Co > Cu > Cd ≈ Mn > Fe > Zn. The dependence of metal ion uptake on pH is related to the surface functional groups and ion-exchange properties of sepiolite. Adsorption equilibrium was correlated reasonably well by the Langmuir isotherm.

Literature Cited

(1) Suffet, I. H.; McGuire, M. J. *Activated Carbon Adsorption of Organics from the Aqueous Phase*; Ann Arbor Science: Ann Arbor, MI, 1980; Vols. 1 and 2.

(2) Slejko, F. L. *Adsorption Technology: A Step-by-Step Approach to Process Evaluation and Application*; Marcel Dekker: New York, 1985.

(3) Gupta, V. K.; Ali, I. Adsorbents for Water Treatment: Low-Cost Alternatives to Carbon. In *Encyclopedia of Surface and Colloid Science*; Hubbard, A., Ed.; Marcel Dekker Inc.: New York, 2002; pp 136−166.

(4) Cheremisinoff, P. N.; Ellerbusch, F. *Carbon Adsorption Handbook*; Ann Arbor Science Publishers: Ann Arbor, MI, 1979.

(5) Weber, W. J., Jr.; Vanvliet, B. M. Fundamental Concepts for Applications of Activated Carbon in Water and Wastewater Treatment. In *Activated Carbon Adsorption of Organics from the Aqueous Phase*; Suffet, I. H., McGuire, M. J., Eds.; Ann Arbor Science Publishers: Ann Arbor, MI, 1980; Vol. 1, p 16.

(6) Lyman, W. J. Applicability of Carbon Adsorption to the Treatment of Hazardous Industrial Waste. In *Carbon Adsorption Handbook*; Cheremisinoff, P. N., Ellerbusch, F., Eds.; Ann Arbor Science Publishers: Ann Arbor, MI, 1987; p 131.

(7) Srivastava, S. K.; Pant, N.; Pal, N. Studies on the Efficiency of a Local Fertilizer Waste as a Low Cost Adsorbent. *Water Res.* **1987**, *21*, 1389.

(8) Nawar, S. S.; Doma, H. S. Removal of Dyes from Effluents Using Low-Cost Agricultural By-Products. *Sci. Total Environ.* **1989**, *79*, 271.

(9) Patteson, J. W. Industrial Wastes Reduction. *Environ. Sci. Technol.* **1989**, *23*, 1032.

(10) Erdemoğlu, M.; Erdemoğlu, S.; Sayılkan, F.; Akarsu, M.; Şener, Ş.; Sayılkan, H. Organo-Functional Modified Pyrophyllite: Preparation, Characterisation and Pb(II) Ion Adsorption Property. *Appl. Clay Sci.* **2004**, *27*, 41.

(11) Demirbaş, Ö.; Alkan, M.; Doğan, M.; Turhan, Y.; Namli, H.; Turan, P. Electrokinetic and Adsorption Properties of Sepiolite Modified by 3-Aminopropyltriethoxysilane. *J. Hazard. Mater.* **2007**, *149*, 650.

(12) Monde, T. Chemically Modified Silica, Alumina, and Related Surfaces. In *Encyclopedia of Surface and Colloid Science*; Hubbard, A., Ed.; Marcel Dekker Inc.: New York, 2002; pp 1012−1016.

(13) Malakul, P.; Srinivasan, K. R.; Wang, H. Y. Metal Adsorption and Desorption Characteristics of Surfactant-Modified Clay Complexes. *Ind. Eng. Chem. Res.* **1998**, *37*, 4296.

(14) Plueddemann, E. P. *Silanes, Surfaces, and Interfaces*; Leyden, D. E., Ed.; Gordon and Breach: Amsterdam, 1980; pp 1−24.

(15) Uchida, E.; Ikada, Y. Zeta Potential of Polymer Surfaces. In *Encyclopedia of Surface and Colloid Science*; Hubbard, A., Ed.; Marcel Dekker Inc.: New York, 2002; pp 5657−5667.

(16) Ermakova, L.; Sidorova, M.; Bogdanova, N.; Klebanov, A. Electrokinetic and Adsorption Characteristics of (Hydr)Oxides and Oxide Nanostructures in 1:1 Electrolytes. *Colloids Surf.* **2001**, *192*, 337.

(17) Bergveld, P.; Sibbald, A. *Analytical and Biomedical Application of Ion-Selective Field-Effect Transistors*; Elsevier: Amsterdam, 1988.

(18) Balci, S. Thermal Decomposition of Sepiolite and Variations in Pore Structure with and without Acid Pre-Treatment. *J. Chem. Technol. Biotechnol.* **1996**, *66*, 72.

(19) Türker, A. R.; Bag, H.; Erdogan, B. Determination of Iron and Lead by Flame Atomic Absorption Spectrometry after Preconcentration with Sepiolite. *Freseius' J. Anal. Chem.* **1997**, *357*, 351.

(20) Balci, S. Effect of Heating and Acid Pre-Treatment on Pore Size Distribution of Sepiolite. *Clay Miner.* **1999**, *34*, 647.

(21) Bailey, S. E.; Olin, T. J.; Bricka, R. M.; Adrian, D. A Review of Potentially Low Cost Sorbents for Heavy Metals. *Water Res.* **1999**, *33*, 2469.

(22) Unal, H. I.; Erdogan, B. The Use of Sepiolite for Decolorization of Sugar Juice. *Appl. Clay Sci.* **1998**, *12*, 419.

(23) Daza, L.; Mendioroz, S.; Pajares, J. A. Mercury Adsorption by Sulfurized Fibrous Silicates. *Clays Clay Miner.* **1991**, *39*, 14.

(24) Inegahi, S.; Fukushima, Y.; Doi, H.; Kamigaito, O. Pore Size Distribution and Adsorption Selectivity of Sepiolite. *Clay Miner.* **1990**, *25*, 99.

(25) Lemic, J.; Tomasevic-Canovic, M.; Djuricic, M.; Stanic, T. Surface Modification of Sepiolite with Quaternary Amines. *J. Colloid Interface Sci.* **2005**, *292*, 11.

(26) Alkan, M.; Tekin, G.; Namli, H. FTIR and Zeta Potentials Measurements of Sepiolite Treated with Some Organosilanes. *Microporous Mesoporous Mater.* **2005**, *84*, 75.

(27) Torro-Palau, A.; Fernandez-Garcia, J. C.; Orgiles-Barcelo, A. C.; Pastor-Blas, M. M.; Martin-Martinez, J. M. Comparison of the Properties of Polyurethane Adhesives Containing Fumed Silica or Sepiolite as Filler. *Int. J. Adhesion Adhesives* **1997**, *17*, 111.

(28) Akyuz, S.; Akyuz, T.; Yakar, A. E. FT-IR Spectroscopic Investigation of Adsorption of 3-Aminopyridine on Sepiolite and Montmorillonite from Anatolia. *J. Mol. Struct.* **2001**, *565/566*, 487.

(29) Frost, R. L.; Mendelovici, E. Modification of Fibrous Silicates Surfaces with Organic Derivatives: An Infrared Spectroscopic Study. *J. Colloid Interface Sci.* **2006**, *294* (1), 47.

(30) Alkan, M.; Çelikçapa, S.; Demirbaş, Ö.; Doğan, M. Removal of Reactive Blue 221 and Acid Blue 62 Anionic Dyes from Aqueous Solutions by Sepiolite. *Dyes Pigm.* **2005**, *65*, 251.

(31) Alkan, M.; Doğan, M. Adsorption of Copper(II) onto Perlite. *J. Colloid Interface Sci.* **2001**, *243*, 280.

(32) Menezes, M. L.; Moreira, J. C.; Campos, J. T. S. Adsorption of Various Ions from Acetone and Ethanol on Silica Gel Modified with 2-, 3- and 4-Aminobenzoate. *J. Colloid Interface Sci.* **1996**, *179*, 207.

(33) Doğan, M.; Alkan, M.; Çakir, Ü. Electrokinetic Properties of Perlite. *J. Colloid Interface Sci.* **1997**, *192*, 114.

(34) Turan, P.; Doğan, M.; Alkan, M. Uptake of Trivalent Chromium Ions from Aqueous Solutions Using Kaolinite. *J. Hazard. Mater.* **2007**, *148*, 56.

(35) Roman, G. T.; Culbertson, C. T. Surface Engineering of Poly-(dimethylsiloxane) Microfluidic Devices Using Transition Metal Sol−Gel Chemistry. *Langmuir* **2006**, *22*, 4445.

(36) McKenzie, M. T.; Culler, S. R.; Koenig, J. L. Applications of Diffuse Reflectance FTIR to the Characterization of an E-Glass Fiber/Γ-APS Coupling Agent System. *Appl. Spectrosc.* **1984**, *38*, 786.

(37) Alkan, M.; Tekin, G.; Namlı, H. Zeta Potentials of Perlite Modified with Dimethyldichlorosilane, 3-Aminopropyltriethoxysilane and Dimethyloctadecylchlorosilane. *Fresenius' Environ. Bull.* **2005**, *14*, 795.

(38) Ignatyev, I. S.; Montejo, M.; Urena, F. P.; Sundius, T.; Lopez, Gonzalez, J. J. Vibrational Spectra and Structure of Methoxysilanes and Products of Their Hydrolysis. *Vib. Spectrosc.* **2006**, *40*, 1.

(39) Frost, R. L.; Locos, O. B.; Ruan, H.; Kloprogge, J. T. Near-Infrared and Mid-Infrared Spectroscopic Study of Sepiolites and Palygorskites. *Vib. Spectrosc.* **2001**, *27*, 1.

(40) Frost, R. L.; Ding, Z. Controlled Rate Thermal Analysis and Differential Scanning Calorimetry of Sepiolites and Palygorskites. *Thermochim. Acta* **2003**, *397*, 119.

(41) Frost, R. L.; Cash, G. A.; Kloprogge, J. T. 'Rocky Mountain Leather', Sepiolite and Attapulgite—An Infrared Emission Spectroscopic Study. *Vib. Spectrosc.* **1998**, *16*, 173.

(42) Smykatz-Kloss, W. *Differential Thermal Analysis. Application and Results in Mineralogy*; Springer: Berlin, 1974.

(43) Langier-Kuzniarowa, A. The Present State of Thermal Investigations of Clays. *Thermochim. Acta* **1989**, *148*, 413.

(44) Mitchell, B. D.; Birnie, A. C. Organic Compounds. In *Differential Thermal Analysis*; Mackenzie, R. C., Ed.; Academic Press: London, 1970; Vol. 1, pp 611−641.

(45) Mackenzie, R.C. *The Differential Thermal Investigation of Clays*; Clay Minerals Group, Mineralogical Society: London, 1957.

(46) Mackenzie, R. C. Simple Phyllosilicates Based on Gibbsite- and Brucite-Like Sheets. In *Differential Thermal Analysis*; Mackenzie, R. C., Ed.; Academic Press: London, 1970; Vol. 1, pp 497−537.

(47) Yariv, S. The Role of Charcoal on DTA Curves of Organo−Clay Complexes: An Overview. *Appl. Clay Sci.* **2004**, *24*, 225.

(48) Nagata, H.; Shimoda, S.; Sudo, T. On dehydration of bound water of sepiolite. *Clays Clay Min.* **1974**, *22*, 285.

(49) Alkan, M.; Demirbaş, Ö.; Doğan, M. Electrokinetic Properties of Sepiolite Suspensions in Different Electrolyte Media. *J. Colloid Interface Sci.* **2005**, *281*, 240.

(50) Alkan, M.; Doğan, M. Surface Titrations of Perlite Suspensions. *J. Colloid Interface Sci.* **1998**, *207*, 90.

(51) Bradl, H. Adsorption of Heavy Metal Ions on Clays. In *Encyclopedia of Surface and Colloid Science*; Hubbard, A., Ed.; Marcel Dekker Inc.: New York, 2002; pp 1−13.

(52) Prado, A. G. S.; Arakaki, L. N. H.; Airoldi, C.; Price, P. M.; Clark, J. H.; Macquarrie, D. J. *J. Chem. Soc., Dalton Trans.* **2001**, 2206.

(53) Bradl, H. Adsorption of Heavy Metal Ions on Clays. In *Encyclopedia of Surface and Colloid Science*; Hubbard, A., Ed.; Marcel Dekker, Inc., New York, 2002; pp 373−384.

(54) Altin, O.; Ozbelge, O. H.; Dogu, T. Effect of pH, Flow Rate and Concentration on the Sorption of Pb and Cd on Montmorillonite: I. Experimental. *J. Chem. Technol. Biotechnol.* **1999**, *74*, 1131.

(55) Chen, J. P.; Yang, L. Study of a Heavy Metal Biosorption onto Raw and Chemically Modified *Sargassum* sp. via Spectroscopic and Modeling Analysis. *Langmuir* **2006**, *22*, 8906.

(56) Duru, P. E.; Bektaş, S.; Genç, O.; Patır, S.; Denizli, A. Adsorption of Heavy-Metal Ions On Poly(ethyleneimine)-Immobilized Poly(methylmethacrylate) Microspheres. *J. Appl. Polym. Sci.* **2001**, *81*, 197.

(57) Ucer, A.; Uyanik, A.; Aygun, S. F. Adsorption of Cu(II), Cd(II), Zn(II), Mn(II) and Fe(III) Ions by Tannic Acid Immobilised Activated Carbon. *Sep. Purif. Technol.* **2006**, *47*, 113.

(58) Lafferty, C.; Hobday, M. Use of Low Rank Brown Coal as an Ion Exchange Material. 1. Basic Parameters and the Ion Exchange Mechanism. *Fuel* **1990**, *69*, 78.

(59) Adebowale, K. O.; Unuabonah, I. E.; Olu-Owolabi, B. I. The Effect of Some Operating Variables on the Adsorption of Lead and Cadmium Ions on Kaolinite Clay. *J. Hazard. Mater.* **2006**, *B134*, 130.

(60) Eligwe, C. A.; Okolue, N. B.; Nwambu, C. O.; Nwoko, C. I. A. Adsorption Thermodynamics and Kinetics of Mercury(II), Cadmium(II) and Lead(II) on Lignite. *Chem. Eng. Technol.* **1999**, *22*, 45.

(61) Stumm, W.; Morgan, J. J. *Aquatic Chemistry*; John Wiley and Sons: New York, 1970.

(62) Kara, M.; Yüzer, H.; Sabah, E.; Çelik, M. S. Adsorption of Cobalt from Aqueous Solutions onto Sepiolite. *Water Res.* **2003**, *37*, 224.

(63) Nadeem, M.; Mahmood, A.; Shahid, S. A.; Shah, S. S.; Khalid, A. M.; McKay, G. Sorption of Lead from Aqueous Solution by Chemically Modified Carbon Adsorbents. *J. Hazard. Mater.* **2006**, *B138*, 604.

(64) Lagergren, S. About the Theory of So-Called Adsorption of Soluble Substances. *K. Sven. Vetenskapsakad. Handl.* **1898**, *24*, 1.

(65) Mall, I. D.; Srivastava, V. C.; Agarwal, N. K. Removal of Orange-G and Methyl Violet Dyes by Adsorption onto Bagasse Ash and Kinetic Study and Equilibrium Isotherm Analyses. *Dyes Pigm.* **2006**, *69*, 210.

(66) Singh, K. K.; Singh, A. K.; Hasan, S. H. Low Cost Bio-Sorbent 'Wheat Bran' for the Removal of Cadmium from Wastewater: Kinetic and Equilibrium Studies. *Bioresour. Technol.* **2006**, *97*, 994.

(67) McKay, G.; Otterburn, S.; M.; Sweeney, A. G. The Removal of Colour from Effluent Using Various Adsorbents—IV. Silica: Equilibrium and Column Studies. *Water Res.* **1980**, *14*, 21.