Functionalized sepiolite for heavy metal ions adsorption

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Abstract

Surface modification of clays has become increasingly important due to the practical applications of clays such as fillers and adsorbents. The surface modification of sepiolite with [3-(2-aminoethylamino)propyl]trimethoxysilane has been employed. The modified sepiolite surface was investigated by FTIR, XRD and 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 methoxy groups of [3-(2-aminoethylamino)propyl]trimethoxysilane. The changes on electrokinetic properties of modified sepiolite particles were studied by measuring the zeta potential of particle as a function of metal concentration and equilibrium pH of solution. It was found that the zeta potential of the clay particles was always negative independent of the metal concentration in solution. This study also provides some evidence for the adsorption of metal ions on modified sepiolite. The adsorption of metal ions onto modified sepiolite has varied with the type of metal cations. The available basic nitrogen centers covalently bonded to the sepiolite skeleton were studied for Co(II), Cu(II), Mn(II), Zn(II), Fe(III) and Cd(II) adsorption from aqueous solutions. It was found that the amount of metal ion adsorbed onto modified sepiolite increases with increase in solution equilibrium pH and temperature, whereas it generally decreases with the ionic strength. The experimental data were correlated reasonably well by the Langmuir adsorption isotherm and the isotherm parameters (q_m and K) were calculated. The ability to adsorb the cations gave a capacity order of Zn(II) > Cu(II) ~ Co(II) > Fe(III) > Mn(II) > Cd(II) with affinities of 2.167×10^{-4}, 1.870×10^{-4}, 1.865×10^{-4}, 1.193×10^{-4}, 0.979×10^{-4} and 0.445×10^{-4} mol g^{-1}, respectively.

Keywords: Sepiolite; Modification; Zeta potential; Adsorption; Characterization; Metal ions

1. Introduction

Applications designed to improve analytical determinations and to improve the environment by metal removal have recently emerged [1–5]. The removal of toxic heavy-metal contaminants from industrial waste waters is one of the most important environmental issues to be solved today. The search for new and innovative treatment technologies has focused attention on the

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effect of heavy metal toxicity [6]. There are many methods for the removal of wastewater pollution from aqueous solutions such as adsorption, chemical precipitation, ion exchange, membrane processes, etc. [7].

Adsorption is the most popular method in which activated carbon or ion exchange resins are usually applied. Heavy metals in wastewaters can be removed by adsorption on solid matrices. Activated carbon, metal oxides, and agricultural products have been used as adsorbents for the adsorption of toxic heavy metal ions. Activated carbons have the advantage of high adsorption capacity for waste waters. However, because of its relatively high cost, there have been attempts to utilize low cost, naturally occurring adsorbents, to remove contaminants from wastewater [6,8]. In more recent times, inorganic oxides have received great attention not only due to their surface reactivity, but also to their ability in immobilizing organic molecules onto the surface. The importance of the evolution of this field of investigation in the last three decades reflects in significant review articles. Thus, the active silanol groups dispersed on oxides has a great ability for attaching with a myriad of different pendant functional organosilyl groups, to give some organic characteristics to the precursor inorganic support. Another feature related to these surfaces is the property of the functional groups already anchored onto oxide for reacting with an active molecule to enlarge the original organic chain. On the other hand, these organofuntionalized surfaces are resistant to removal from the surface by organic solvents or water, as well as having high thermal resistance [1]. Once the compounds are immobilised, the resultant new oxide can be applied in many academic and technological areas, such as catalysis for enzymatic reactions [9,10], for heterogeneous catalyst [11,12], biotechnological processes [13–15], cation preconcentration [16,17] agrochemical preconcentration [18], cation separation processes [19], and

development of agrochemicals with controlled released properties [19,20].

The use of chemically modified adsorbents containing a variety of functional groups on a pendant organic chain can be designed for the adsorption and preconcentration of metal ions from aqueous and non-aqueous solutions [1]. There are five types of surface modifications that have received attention: (1) adsorbed organic cations or polycations, (2) adsorbed polyvalent metal ions with attached organic acid groups (metal soaps), (3) surface silanol groups esterified with alcohols to cover the surface with SiOR groups, (4) polymeric organic coatings of various types, and (5) surface silanol groups reacted with organosilicon intermediates to produce a surface of $Si\text{-}O\text{-}SiR_3$ or similar multiply bonded $(SiO)_2SiR_2$ groups. It is only the last type of surface modification that has proved to be the most widely useful, probably because of the simplicity of application and stability of the resulting surface. However, all approaches are reviewed briefly [21]. The grafting of organic molecules onto the surface of an adsorbent can mainly proceed through reactions with its surface functional groups, i.e. silanol groups. This may result in the formation of covalent bonds and yield a material that exhibits hydrophobic properties. In this respect the most widely used reactants are silanes (alkoxy and chlorosilanes), metal alkoxides and organic condensation agents. Treatments with reactive silanes are among the major methods of modification used to convert silicas into materials carrying covalently bonded functional groups. In this respect alkoxy and chlorosilanes have a place of choice [22]. In a simple process, modified adsorbents have been considered for the selective removal processes of metals from aqueous solutions [23].

Adsorption mechanism at clay surfaces is strictly related to the dual nature of the surface charge, both of permanent and variable nature. Clays present exposed layer edges where exposed

-OH will exhibit weak acid–base behavior [24]. The acid–basic properties of such groups depend on the type of metal atom forming the oxide and on the number of metal atoms coordinating the hydroxyl group. The acid–basic reactions of the surface hydroxyl groups are responsible for the charge formation on the surface of metal oxide in electrolyte solutions [25]. Clays at layer edges have variable surface charge, i.e., that clays partially behave as oxide surfaces [24]. The isoelectric point is an important characteristic of a solid phase immersed in a liquid medium. By knowing the isoelectric point, one may conclude on the sign of surface charge, e.g., metal oxides are positively charged at $pH<pH_{iep}$ and negatively charged at $pH>pH_{iep}$, which helps in the understanding of coagulation and adhesion phenomena [26]. The differences in acid–base properties of clays and its modification will have effects on the zeta potential of the surfaces [27]. These changes may be the results of modification of clay surface.

Many studies concerning the use of modified materials for the adsorption of metal ions have been fullfilled. For example, [28] investigated the surface modification of sepiolite with quaternary amines; [29] FTIR and zeta potential measurements of sepiolite treated with some organosilanes; [30] the structural modification of sepiolite (natural magnesium silicate) by thermal treatment; [31] the effect of particle size on surface modification of silica nanoparticles by using silane coupling agents and their dispersion stability in methylethylketone; [32] the synthesis and characterization of epoxy resin modified with nano-SiO_2 and γ-glycidoxypropyltrimethoxy silane; [33] the effects of surface modification of fumed silica on interfacial structures and mechanical properties of poly(vinyl chloride) composites; [34] the grafting of trialkoxysilane on the surface of nanoparticles by conventional wet alcoholic and supercritical carbon dioxide deposition methods; [35] FT-IR spectroscopic investigation of adsorption of 3-aminopyridine on

sepiolite and montmorillonite from Anatolia; [36] the determination of vanadium, manganese, silver and lead by graphite furnace atomic absorption spectrometry after preconcentration on silica-gel modified with 3-aminopropyltriethoxysilane. But no studies about modification by [3-(2-amino-ethylamino)propyl]trimethoxysilane compound of sepiolite have been found.

Sepiolite is a non-swelling, lightweight, porous clay with a large specific surface area. Unlike other clays, the individual particles of sepiolite have a needle-like morphology. The high surface area and porosity, as well as the unusual particle shape of this clay account for its outstanding sorption capacity and colloidal properties that make it a valuable material for a wide range of applications. Chemically, sepiolite is a hydrated magnesium silicate with the ideal formula $Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4.8H_2O$. The outstanding sorptive and colloidal properties of sepiolite provide specific solutions for a wide variety of industrial applications such as cat and pet litters, industrial absorbents, waste treatment, carrier for chemicals, sepiolite absorbs, moisture control, fertilisers, roof panel, bitumens, construction additives, rheological additives [37].

In this paper, we firstly report the chemical functionalization of sepiolite with [3-(2-amino-ethylamino)propyl]trimethoxysilane in the presence of toluene solvent as a dispersing medium. An FTIR, XRD and DTA/TG analysis for the natural and modified sepiolite has been also performed for the purpose of exploring the nature of their surfaces. Then, the main interest in these resulting modified sepiolite is related to their high selectivity toward metals such as Co(II), Cu(II), Mn(II), Zn(II), Fe(III) and Cd(II). The aims of our study have determined (1) the electrokinetic properties of the modified sepiolite as a function of equilibrium solution pH and electrolyte concentration, (2) the selectivity of modified sepiolite toward divalent and trivalent metals, and studied the effect of different operating parameters on

these adsorption processes, such as initial concentration, pH, ionic strength and temperature. The experimental values have been analyzed according to Langmuir and Freundlich isotherms.

2. Material and methods

2.1. Materials

The sepiolite sample used in this study was obtained from the 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 (CEC) of sepiolite is 0.25 mmol g^{-1}; the density 2.55 g cm^{-3}; the specific surface area 342 m^2 g^{-1}; particle size in the range of 0 to 50 µm [38]. The found data for CEC in literature are in the 0.15 to 0.20 mmol g^{-1} interval for identical clay. The silylating agent [3-(2-aminoethylamino)propyl]trimethoxysilane (Aldrich) was used without previous purification. Solutions of all cations were prepared from reagent-grade nitrate salts.

2.2. Purification of sepiolite

Sepiolite samples were treated before using in the experiments in order to obtain a uniform size sample of adsorbent as follows [8]: the suspension containing 10 g L^{-1} sepiolite was mechanically stirred for 24 h, after waiting for about 2 min the supernatant suspension was filtered through filter paper. The solid sample was dried at 105°C for 24 h, ground then sieved by 50 µm sieve. The particles under 50 µm were used in further experiments.

2.3. Surface modification of sepiolite with a silane-coupling agent

Sepiolite (5 g) suspended in toluene (100 mL) was refluxed and mechanically stirred for 1 h

under dry nitrogen. To this suspension [3-(2-aminoethylamino)propyl]trimethoxysilane (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 surface was dried at 110°C [39].

2.4. Characterization

Infrared spectra of solid samples were determined in potassium bromide pellets. Fourier transform infrared (FTIR) spectra using the KBr pressed disk technique were performed on a Perkin Elmer BX 1600 FTIR. The spectra were collected for each measurement over the spectral range 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. 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 transmission mode.

X-ray powder diffraction (XRD) analysis was performed on 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 ($\lambda = 0.154$ nm). A simultaneous DTA-TG system was used for differential thermal (DTA) and thermogravimetric (TG) analysis (Perkin Elmer Diamond DTA/TG).

2.5. Zeta potential measurements

The zeta potential of modified sepiolite suspensions was measured using a Zeta Meter 3.0 (Zeta Meter Inc.) equipped with a microprocessor unit. The unit automatically calculates the electrophoretic mobility of the particles and converts it to the zeta potential using the Smoluchowski equation. The Smoluchowski 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 zeta potential measurements were carried out as a function of the initial electrolyte concentration and equilibrium solution pH. A sample of 0.1 g modified-sepiolite in 50 mL distilled water containing desired metal ions was added to an orbital shaker incubator and rinsed for 24 h at 25±1°C. The samples were allowed to stand for 1 min to let larger particles settle. An aliquot taken from the supernatant was used to measure the zeta potential. The average of 15 measurements was taken to represent the measured potential. The applied voltage during the measurements was generally varied in the range of 50–150 mV [40].

2.6. Adsorption

The capacity of the chemically modified sepiolite to adsorb cations from aqueous solution was determined using a batch process method, which consisted in suspending a series of 0.1 g samples of the modified sepiolite in 50 mL of aqueous solutions, containing each cation such as Co(II), Cu(II), Mn(II), Zn(II), Fe(III) and Cd(II) nitrates at several different concentrations, varying from 8.89×10^{-6} to 13.57×10^{-4} mol L^{-1} at 25°C and constant pHs, except those in which varying conditions of pH, ionic strength and temperature were investigated. The pH of the solution 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. Nitrate salts of metal ions were used in the experiments. The solutions were mechanically stirred for 24 h in an orbital shaker incubator at 298±1 K. A preliminary experiment revealed that about 24 h is required for metal ions to reach the equilibrium concentration. At the end of this process, the solid was separated by centrifugation during 15 min at 5000 rpm. The metal concentration adsorbed was determined by the difference between the initial concentration in the aqueous solution and that found in the supernatant, by using an AAS (Unicam 929) apparatus:

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

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 used (g) [7].

3. Results and discussion

3.1. Characterization

3.1.1. FTIR characterization

Since the introductions of Fourier transform instrumentation the application of the IR spectroscopy greatly increased in many types of clay modification research. The improvement on the FTIR spectrometers (enhanced frequency accuracy, high signal-to-noise ratios and high data acquisition speed) made it possible to design sample-handling accessories and new investigation methods [41]. Although there are many sampling techniques having the FTIR spectra, the traditional KBr pressed disk technique is the easiest and most informative one for the clay minerals. The modification of the sepiolite surface with the [3-(2-aminoethylamino)propyl]-trimethoxysilane is investigated by the KBr pressed disk technique.

In Fig. 1, the difference that has been observed in the vibration frequencies of FTIR spectrum of organosilane, [3-(2-aminoethylamino)propyl]-trimethoxysilane added sepiolite are considered as the indicators of the interaction between the modifying molecule and sepiolite particles. It is known that the adsorption of a molecule on to clay minerals effects the stretching vibrations of
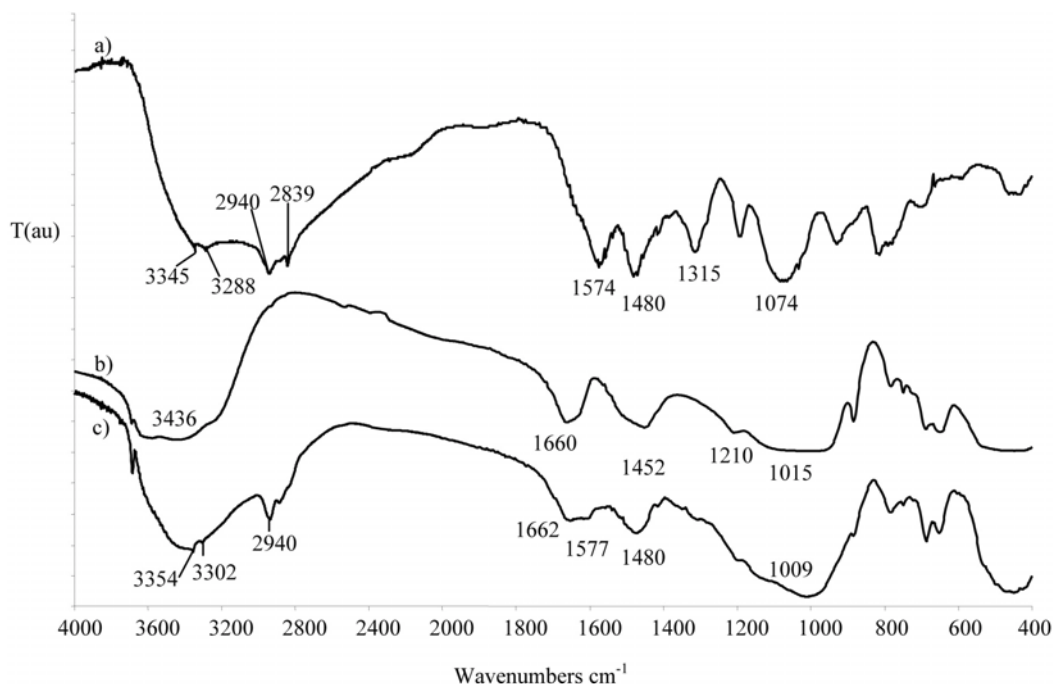
Fig. 1. FTIR spectra of (a) [3-(2-aminoethylamino)propyl]trimethoxysilane, (b) sepiolite and (c) modified structure in the KBr disks.

active Si–OH groups of external surface and causes to shift to lower wavenumbers [35]. On the other hand, the perturbation observed on the zeolitic and bound water vibrations of sepiolite indicates that some of organosilane molecules enter the interior channels and replace zeolitic water molecules. The frequency shifts may indicate the formation of new H-bonds between bound/zeolitic water and organosilane molecules whereas weakening in intensity of the m(OH) vibration of the zeolitic water is the indication that modifier molecules replace part of the zeolitic water [42].

A series of FTIR spectral analysis in KBr disk were performed in order to investigate the interaction between the sepiolite and the modifier [3-(2-aminoethylamino)propyl]trimethoxysilane during the modification process: (1) modifier sample (aimed to find the FTIR peaks arising from modifier), (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-will also show us the change in peaks with the first two spectra), (4) modified sepiolite with the sepiolite-background (aimed to omit the peaks arising from sepiolite and the changes on the modifier will be appear more clear) and (5) mechanical mixture, of sepiolite and modifier (categorise the interaction) has been measured.

The method used here [29] can allow to observe the changes on the modifier and sepiolite structure after modification. Scanning the equal amount of the sepiolite in KBr disk as background and having the spectra of the modified sample against only the modifier peaks appeared on the FTIR spectra. Comparing those peaks obtained from pure and modified peaks we may assume the changes on the modifier during the modification. For instance, as expected the peaks due to the methoxy group of the modifier

disappears on the background defined spectra and we can clearly see the modification happened between methoxy group and reactive Si-OH of the sepiolite. Reduce in the methoxy peaks intensity may be attributed to the one or two methoxy disappearance.

Sepiolite contains four different types of water molecules: (1) hygroscopic, (2) zeolitic, (3) bound and (4) hydroxyl water [43]. In sepiolite, the most probable binding sites on the sepiolite surface are surface hydroxyls and Lewis acidic centers. FTIR spectra of the sepiolite used for modification are shown in Fig. 1b. The Mg_3OH band at 3762–3578 cm^{-1} characterized by weak bonding strength is ascribed to the presence of OH groups in the octahedral sheet and the OH stretching vibration in the external surface of sepiolite [44]. On the other hand, the 3436 and 1660 cm^{-1} bands are respectively assigned to the OH stretching, representing the zeolitic water in the channels and bound water coordinated to magnesium in the octahedral sheet. The band at 1453 cm^{-1} developed due to the hydroxyl bending vibration again reflects the presence of bound water. The Si–O coordination bands at 1210 and 1015 cm^{-1} represent the stretching of Si–O in the Si–O–Si groups of the tetrahedral sheet [45].

Asymmetric and symmetric N-H stretching of secondary and primer amines in the modifier silane in Fig. 1a can be observed at 3345 and 3288 cm^{-1}. These two peaks can also be observed on the modified structure with a little shifts at 3354 and 3302 cm^{-1}, respectively. The careful inspection of the C-H vibrations for the methoxy and chain CH$_2$ groups at the 2940 and 2839 cm^{-1} for untreated modifier are the evident for the modification. The peak due to the chain at 2940 cm^{-1} is clearly seen while the C-H due to the O-CH$_3$ at 2839 cm^{-1} disappears. Since there are no C-H bond on the pure sepiolite the change in the C-H vibrations on the modified structure may be the best evidence for the modification of the [3-(2-aminoethylamino)propyl]trimethoxysilane. The change in the broad Si-O stretching at the
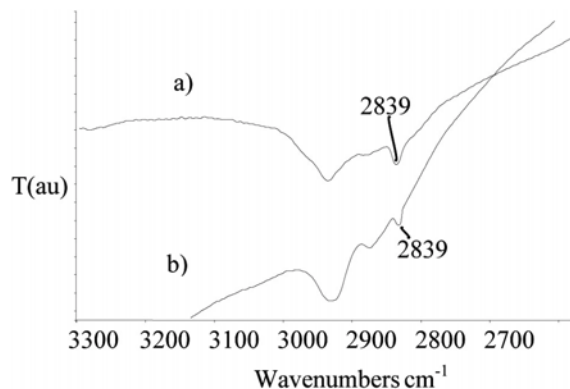

Fig. 2. FTIR C-H stretching area on the modified structure and mechanical mixture.

1480 and 1074 cm^{-1} may be attributed to the effect of the modification or the modification process.

The mechanical mixture spectra in Fig. 2c is more proof for the modification. The C-H vibrations appear at the 2839 cm^{-1} due to the OCH$_3$ (Fig. 2a) on the modifier ([3-(2-aminoethylamino)propyl]trimethoxysilane) is clearly seen in the mechanical mixture in Fig. 2c while it was not observed on the modified sepiolite structure in Fig. 2b. This is the indication of loosing methoxy groups as methanol during the modification.

According to the explanation above, the reaction between sepiolite and [3-(2-aminoethylamino)propyl]trimethoxysilane can be written as the following:
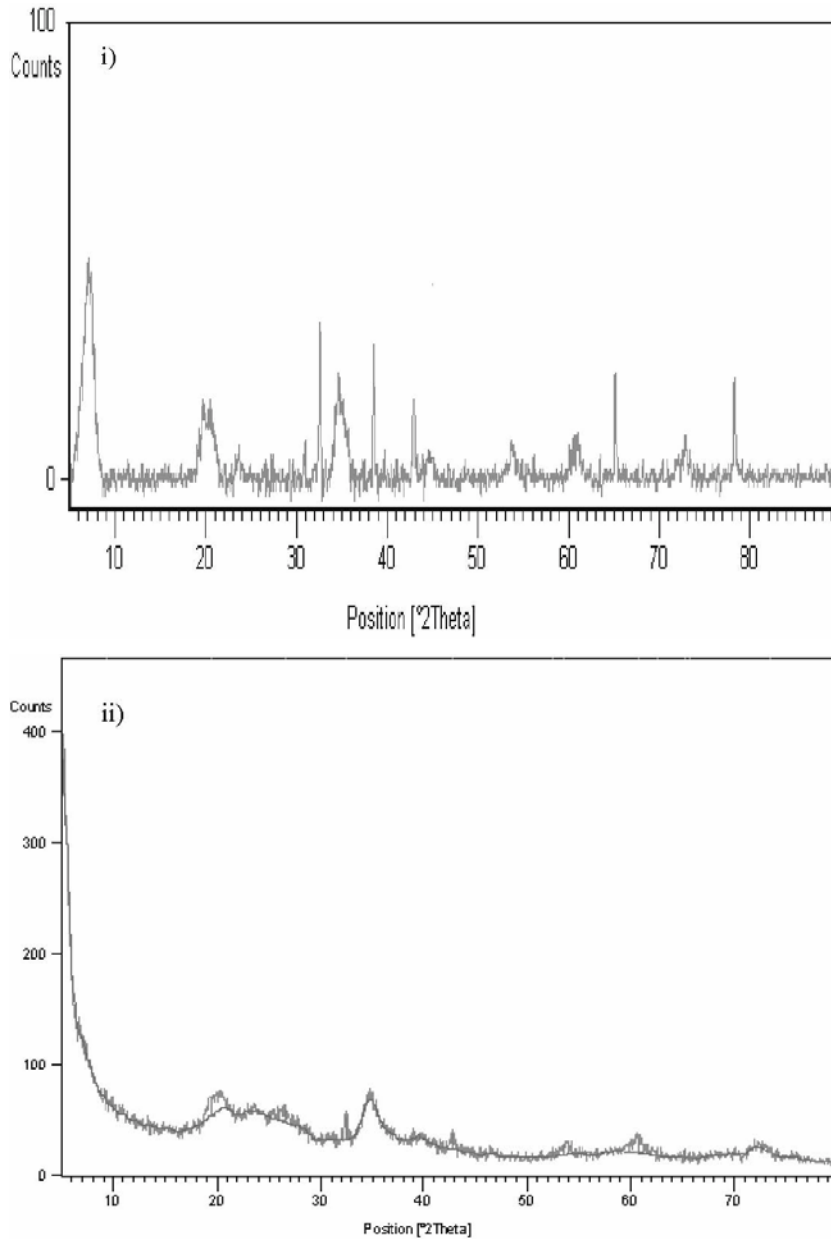

(3)
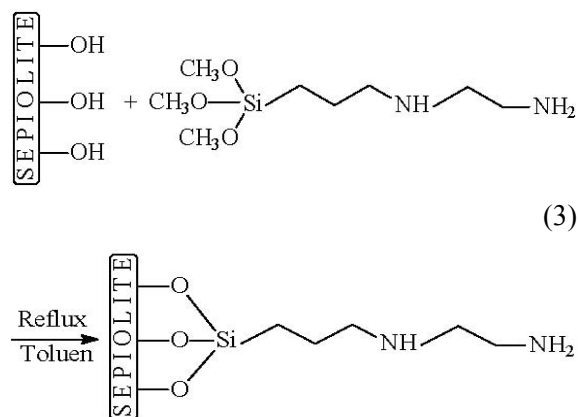
Fig. 3. XRD spectra of (i) natural and (ii) modified sepiolite samples.

3.1.2. XRD characterization

XRD provides a look into the extent of clay crystallization and in some cases a clue as to the organic incorporation. Fig. 3 includes the modified sepiolite for the comparison purposes with natural sepiolite. The XRD pattern of sepiolite is clearly affected by the incorporation of [3-(2-aminoethylamino)propyl]trimethoxysilane. Covalent bonding is formed because, as seen in Table 1, the some peak intensities both increased

Table 1
Changes in peak intensities of XRD spectra of natural and modified sepiolites

Position (2θ)	Intensity %	
	Sepiolite	Modified sepiolite
19.976	34.16	79.69
26.0249	32.58	62.22
32.3018	100	100
42.6689	55.27	75.24
53.6	56.1	45.27
60.3403	30.11	69.41
65.2608	24.51	36.64

and decreased by modification. When the covalent bonding is formed by the interaction between hydroxyl groups on sepiolite and [3-(2-aminoethylamino)propyl]trimethoxysilane, some structural distortions occur at the plane atoms in the sepiolite. As a result of these distortions, the peak intensity is changed.

3.1.3. DTA/TG analysis

By using simultaneous DTA-TG one can differentiate between peaks associated with weight loss and those associated with phase transition. DTA of organo-clay complexes supplies information on the thermal reactions and on the bonding between the organic species and the clay. During the gradual heating in oxidizing atmospheres the adsorbed organic material is oxidized, giving rise to significant exothermic peaks. DTA curves of organo-clays are divided into three regions: (1) the dehydration of the clay, (2) the thermal oxidation of the organic material and (3) the dehydroxylation of the clay. The exothermic oxidation reaction occurring during the gradual heating of the sample takes place in two steps, in the range 200–600°C, oxidation of organic hydrogen and formation of water and charcoal [46]. In this study, DTA and TG data curves were recorded in the temperature range 20 to 1100°C at a heating rate of 20°C min^{-1}. 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 [47]. DTA of organic material or of organo-clay complexes is carried out either in an oxidizing environment (in air or under a flow of oxygen) or under a flow of an inert gas (such as nitrogen or argon). Fig. 4 shows the DTA and d(DTA) curves of natural and modified sepiolite samples under different conditions. As seen in Fig. 4, the strong exothermic peaks observed on the DTA curves of the organo-sepiolite complexes in the temperature range 200–600°C represent oxidation of the 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 mater material present, but is dependent on the activation energy of the combustion reaction [46]. During the thermal treatment of organo-clays in the temperature range of 200–300°C, the organo-silane group of the modified sepiolite is transformed into charcoal. Peak in the temperature range of 500–600°C belongs to 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 process of the residual sepiolite.

The variation of percent weight loss with temperature (TG curves) and differential weight loss with temperature (d(TG) curves) for sepiolite and modified sepiolite samples are given in Fig. 5. Sepiolite mineral is known to contain four types of water molecules in different chemical states [48]. These water molecules are removed from the mineral by thermal dehydration. It has been stated that water molecules coordinated to magnesium lose until 500°C [29]. After losing four water molecules coordinated to magnesium,
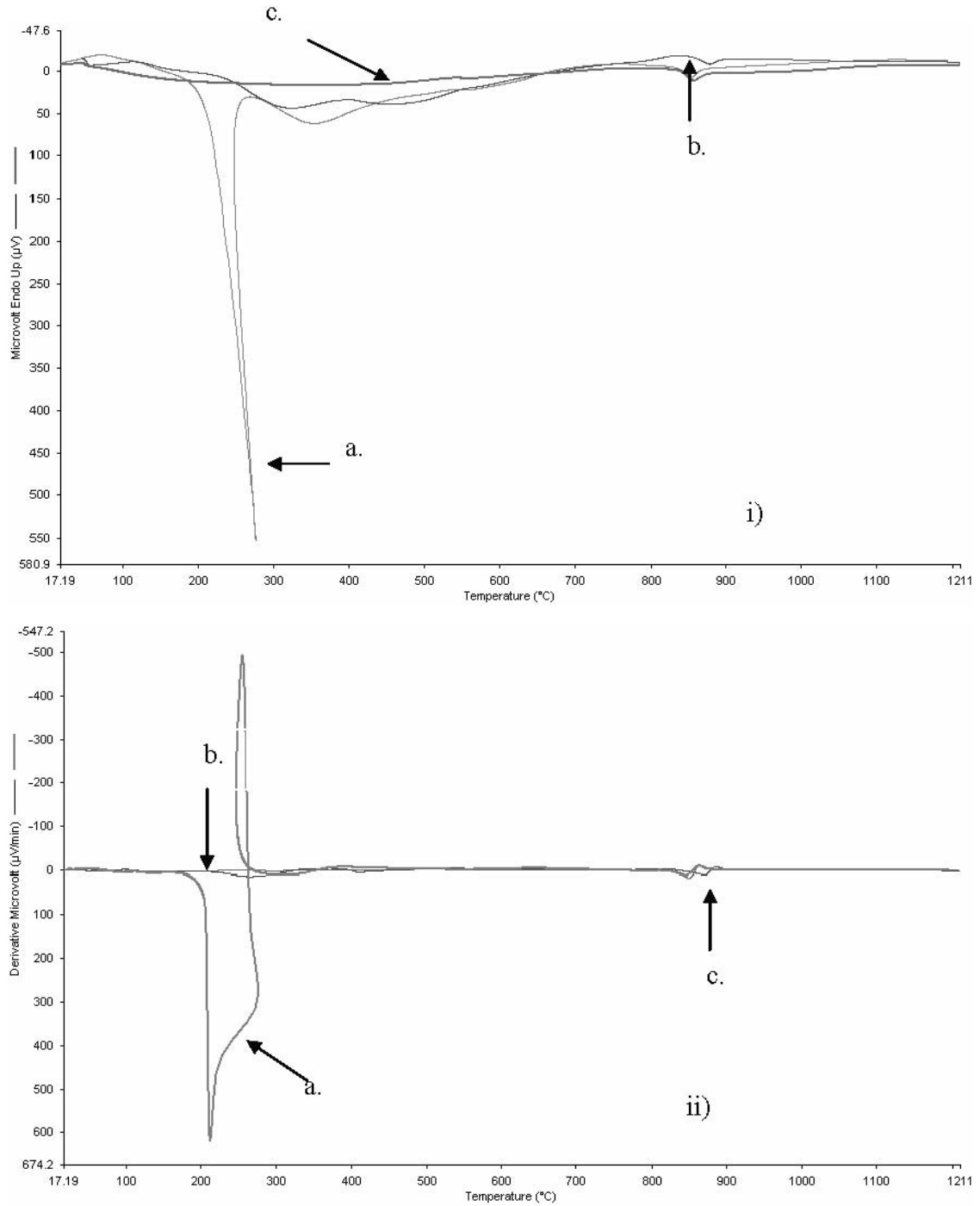
Fig. 4. (i) DTA and (ii) d(DTA) spectra of natural and modified sepiolite samples under different conditions: a. modified sepiolite under oxygen atmosphere, b. modified sepiolite under nitrogen atmosphere, and c. sepiolite under nitrogen atmosphere.
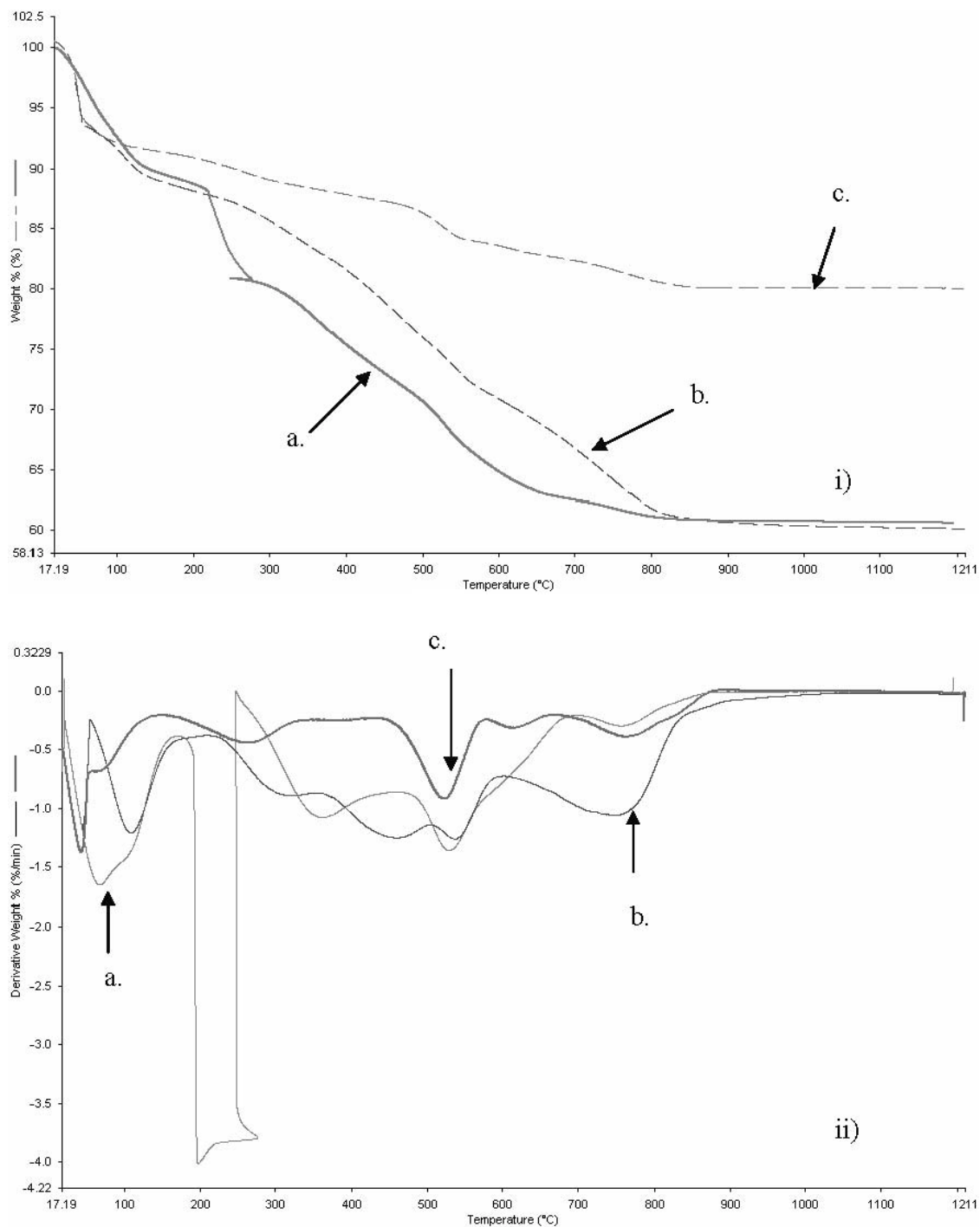
Fig. 5. (i) TG and (ii) d(TG) spectra of natural and modified sepiolite samples under different conditions: a. modified sepiolite under oxygen atmosphere, b. modified sepiolite under nitrogen atmosphere, and c. sepiolite under nitrogen atmosphere.

the structure folds. The different types of water molecules leave the mineral at different temperatures. The amount of hydroscopic water depends on the humidity of the environment. It leaves the mineral at lower temperatures. The zeolitic water is found in the channel-type voids and starts to leave the structure above room temperature. The bound water and structural water leave the mineral at higher temperatures. As seen in Fig. 5, the removal of hydroscopic water from the external surface and zeolitic water from the voids of the structure was completed up to 200°C with a 9.65% weight loss for sepiolite sample under nitrogen atmosphere, 5.44% weight loss for the modified sepiolite sample under nitrogen atmosphere, and 10.63% weight loss for the modified sepiolite sample under oxygen atmosphere, respectively. This weight loss is attributed to the loss of adsorbed water such as zeolitic and hydroscopic water. This removal gave a high peak in the d(TG) curve. The bound water was found in magnesium coordination in the crystal structure [49]. The bound water leaves the structure between 200°C and 600°C. In the present study, the bound water was evolved from the structure with a 7.36% weight loss for sepiolite sample under nitrogen atmosphere, 17.15% weight loss for modified sepiolite sample under nitrogen atmosphere, and 27.15% weight loss for the modified sepiolite sample under oxygen atmosphere, respectively. One reason for more mass loss for the modified sepiolite in this temperature range may be the oxidation of the organo-silane compound on the sepiolite surface. The removal of structural water molecules (hydroxyl groups) was completed at 3.42% weight loss up to 900°C for the sepiolite sample under nitrogen atmosphere, 10.08% weight loss up to 900°C for the modified sepiolite sample under nitrogen atmosphere, and 1.67% weight loss up to 900°C for the modified sepiolite sample under oxygen atmosphere, respectively. No further weight loss was observed until 1100°C.

3.2. Zeta potential

The magnitude of electrostatic interaction between modified sepiolite surface and metal ions is a function of electrokinetic potential (zeta potential). Fig. 6 shows the effect of the metal ion concentration on the zeta potential of modified sepiolite. The zeta potential values of modified sepiolite for iron were observed to increase lightly with increasing adsorbed metal amount as well as increasing metal ion concentration. But we did not found an important change on zeta potential of other metal ions suspensions. For iron, this increase may attributed to the precipitation of iron as $Fe(OH)_3$ or the formation of its hydrous complexes. Note that at low metal ion concentrations modified sepiolite does not give a charge reverse. Indeed, charge reversal requires, in addition to ion exchange, specific adsorption of counterions in electrical double layer, namely, in the iner Helmhotz plane of the Stern layer. But it was found that a charge reverse does not occur in the concentration ranges used in adsorption experiments, which are low metal concentrations. The result confirms that the adsorption of these metals on the surface of the modified sepiolite particle is due to the interaction between the basic group and these positively charged ions. These data support the hypothesis that binding of metal ions is essentially controlled by interaction with basic groups on the modified sepiolite surface [50].

Fig. 7 shows the zeta potentials of suspensions of modified sepiolite as a function of solution equilibrium pH in the presence of metal ions. By knowing the isoelectric point, one may conclude on the sign of surface charge, e.g., metal oxides are positively charged at $pH < pH_{iep}$ and negatively charged at $pH > pH_{iep}$, which helps in the understanding of coagulation and adhesion phenomena [26]. In our previous study [38], we found that the zeta potentials of natural sepiolite suspensions in aqueous heavy metal solutions were positive at low equilibrium pH values and natural sepiolite suspension had pH_{iep} at pH 6.6. As seen in Fig. 7,
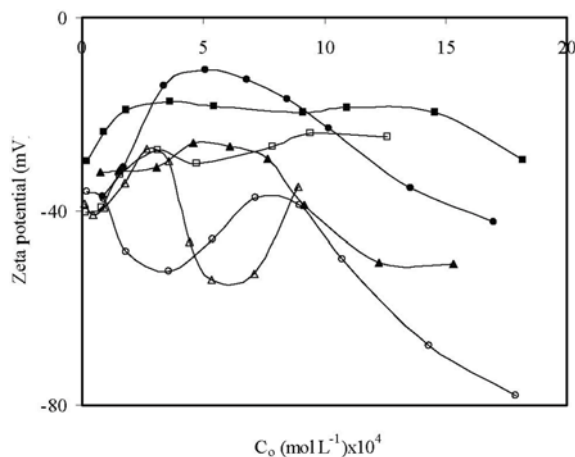
Fig. 6. Effect of heavy metal ion concentrations on zeta potential of modified sepiolite (o: Fe, ■: Mn, ●: Co, Δ: Cd, □: Cu and ▲: Zn).
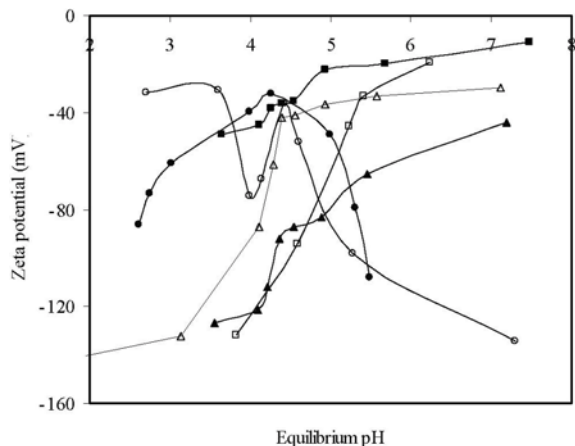

Fig. 7. Effect of pH on zeta potential of modified sepiolite (o: Fe, ■: Mn, ●: Co, Δ: Cd, □: Cu and ▲: Zn).

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 [3-(2-aminoethylamino)propyl]-trimethoxysilane. For all other metal ions except iron, the zeta potential became less negative with increasing equilibrium pH. For iron, the increase of the suspension pH results in an increase in the negative charge of modified sepiolite. This can be ascribed to either the precipitation of iron as

$Fe(OH)_3$ or the formation of its hydrous complexes, or the deprotonation of surface functional groups. For example, when the pH of solution increased, $-NH_2^+-$ and $-NH_3^+$ groups on modified sepiolite at low pHs can converte to the -NH- and $-NH_2$ groups due to the deprotonation of surface functional groups. On the other hand, the zeta potentials measured in the presence of Co(II), Cu(II), Mn(II), Zn(II) and Cd(II) followed a common path, and they 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 (become less negative) may imply that metal ions interact with modified sepiolite, and change its surface potential. The modified sepiolite surface is negatively charged and metal ions cannot specifically adsorb onto modified sepiolite surface and cannot change the magnitude of the zeta potential. At low pH values, adsorption of H_3O^+ hinders the specific adsorption of metal ions. For this reason, as pH increases, the negative sign of the surface decreases due to adsorption of metal ions.

3.3. Metal adsorption

The ability of modified sepiolite surface to adsorb cations from aqueous solution was evaluated by measuring the sorption isotherms for cations such as Co(II), Cu(II), Mn(II), Zn(II), Fe(III) and Cd(II). Profiles of the adsorption isotherms for all the cations in water are represented in Fig. 8. The number of moles adsorbed per gram of adsorbent versus the number of moles at equilibrium per volume of solution is illustrated for all cations. 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. The isotherms presented in Fig. 8 show that the adsorption followed the sequence Zn(II) > Cu(II) ~ Co(II) > Fe(III) > Mn(II) > Cd(II). The affinity of metal ion for one surface is composed of two terms, the chemical affinity and the
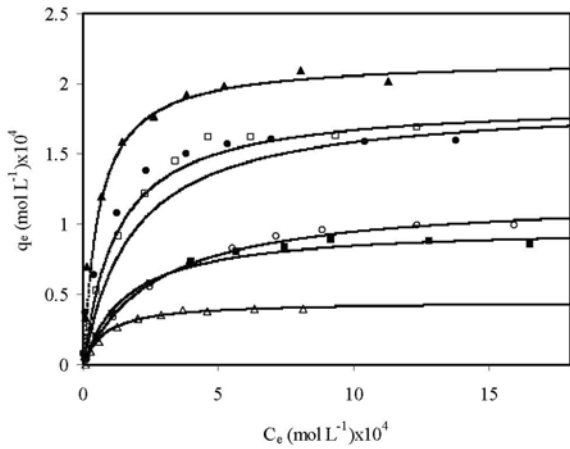
Fig. 8. Isothern curves for adsorption data (o: Fe, ■: Mn, ●: Co, Δ: Cd, □: Cu and ▲: Zn).

electrostatic affinity. The equilibrium constant pK determines the adsorption behavior of the single heavy metal. Specific adsorption increases with decreasing pK value. The following succession is given for specific adsorption (pK values in parentheses (Cd^{2+} (10.1) < Co^{2+} (9.7) < Zn^{2+} (9.0) < Cu^{2+} (7.7) [51]. The adsorption capacity of the modified sepiolite is higher for zinc, copper and cobalt than those for the other ions. This may be a result of the specific interaction between metal ions and the chromofore group (amine) of a modifier agent. In light of these observations, this material could be potentially applied as a selective electrode when the objective was to determine or identify cations. The reaction between the modified sepiolite and metal ions can generally be given as following:
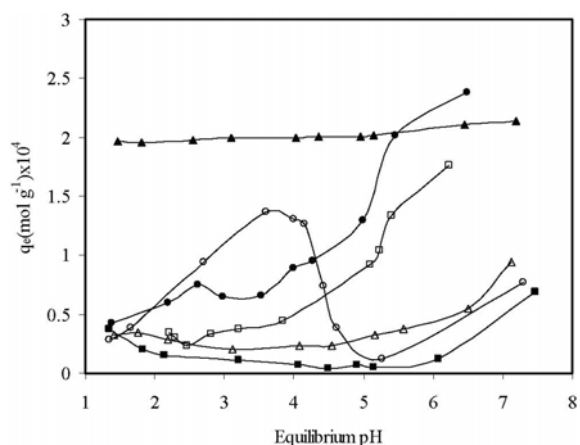

(4)
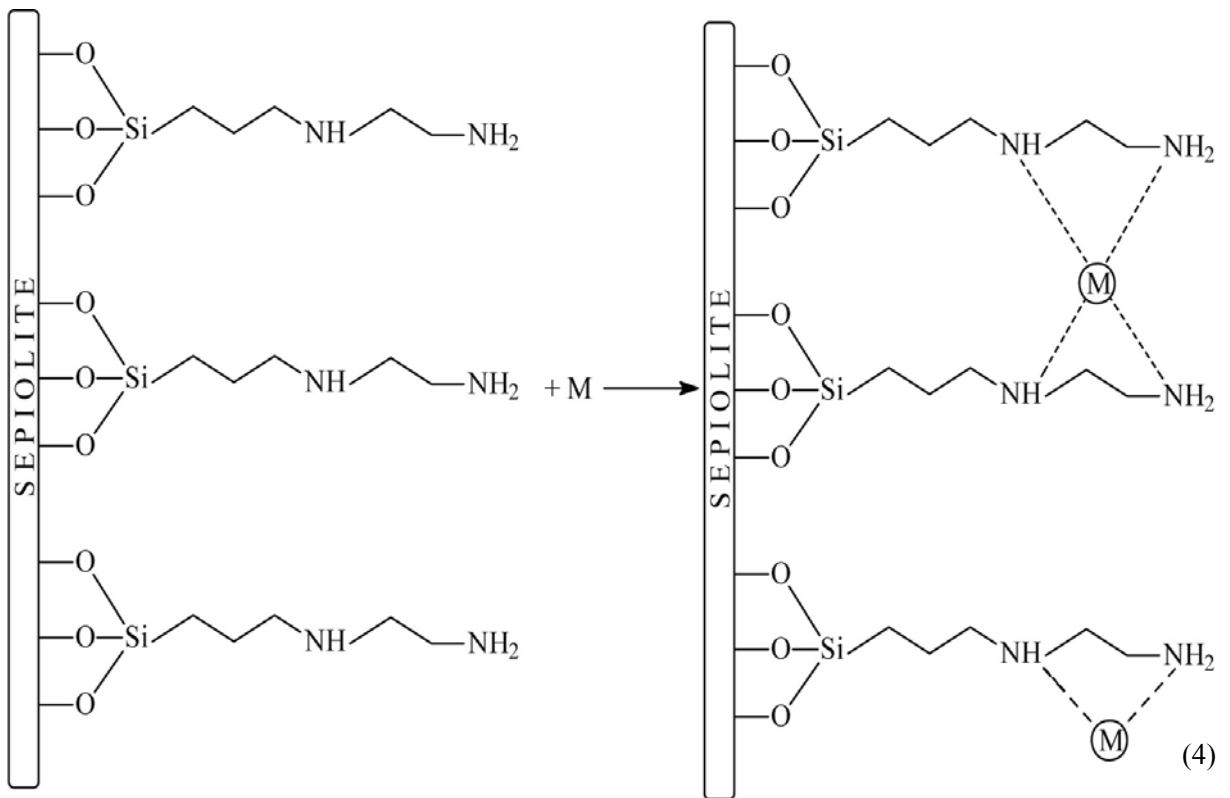
Fig. 9. Variation of the adsorption of metal ions with pH on modified sepiolite (o: Fe, ■: Mn, ●: Co, Δ: Cd, □: Cu and ▲: Zn).

The pH is one of the most important factors in controlling the adsorption of these cations at the surface. Solution speciation can have a deleterious effect upon metal ion sorption by a chemically bonded solid. The tendency for multivalent cations to be adsorbed onto solid surfaces has also been put to use in scavenging impurities from solution and for the selective preconcentration of a number of elements. The hydrous metal oxides have been used most frequently for these purposes, and the efficiency of removal of the metal ions from solution has invariably been found to be strongly pH dependent. A rapid increase in uptake of the metal ion usually occurs over a narrow pH range. This is particularly true for the strongly hydrolyzable cations [52] and has led many workers to view this uptake as an H^+–M^{2+} exchange reaction with the protons derived from the weakly acidic surface OH groups. Adsorption mechanism is clearly related to the dual nature of the surface charge in clays, both of a permanent and of a variable nature. The effect of equilibrium pH to the adsorption of metal ions onto modified sepiolite is given in Fig. 9, which indicates that the numbers of adsorbed metal ions increase with increase in equilibrium pH. At high pHs, the formation of

metal hydroxide species becomes significant. At low pHs, the surface bound [3-(2-aminoethylamino)propyl]trimethoxysilane moiety will be fully protonated [53]. Consequently, sorption of metals into the chemically bonded phase represents an ion-exchange reaction. The surface of modified sepiolite may have different charges depending on solution pH as following:
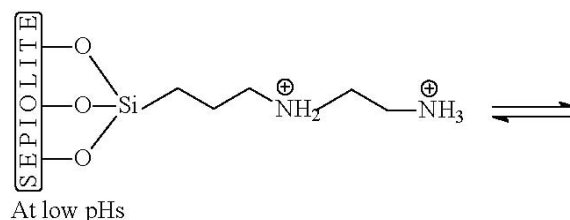
(5)
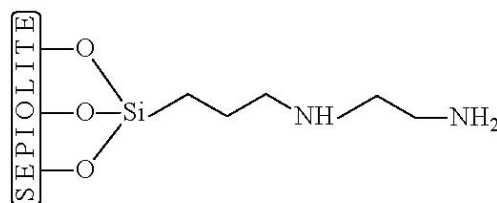
The pH values, which the chemical precipitation of metal hydroxides occurs, are 7.73, 5.35, 8.82, 6.69, 2.05 and 8.47 at 13.57×10^{-4}, 11.01×10^{-4}, 10.92×10^{-4}, 12.23×10^{-4}, 10.74×10^{-4} and $7.11\times10^{-4}\,mol\,L^{-1}$ for Co(II), Cu(II), Mn(II), Zn(II), Fe(III) and Cd(II), respectively. Up to pH 2 for Fe(III), there is an inflection point. The presence of the inflection point suggests an on-set 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 [54]. Strong removal of metal ions coincides with the pH condition where a small fraction of the corresponding metal hydroxide species forms in the aqueous phase [55]. For example, Stumm and Morgan [56] reported that Cd speciates to $CdOH^+$ after pH 8, $Cd(OH)_2$ after pH 9 and $Cd(OH)_3^-$ after pH 11. Therefore, Cd^{+2} ions precipitate at higher pH values than these of other metals. If pH
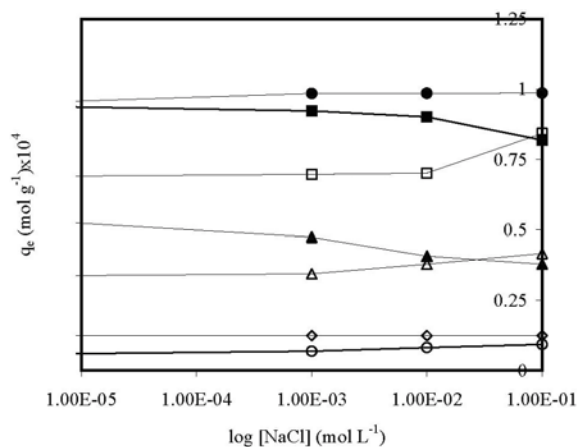
Fig. 10. Variation of the adsorption of metal ions with ionic strength on modified sepiolite (o: Fe, ■: Mn, ●: Co, Δ: Cd, □: Cu and ▲: Zn).

Fig. 11. Variation of the adsorption of metal ions with temperature on modified sepiolite (o: Fe, ■: Mn, ●: Co, Δ: Cd, □: Cu and ▲: Zn).

values are high, both ion exchange and metal hydroxide precipitation jointly contribute to metal removal from solution.

Ionic strength affects the activity coefficients for OH^-, H_3O^+, and specifically adsorbable ions. The effect of ionic strength onto the adsorption of metal ions on modified sepiolite is presented in Fig. 10. As seen in Fig. 10, the presence of inorganic salt has very little influence on the adsorption of metal ions. The metal adsorption decreases with the increasing ionic strength. In literature, it has been stated that ionic strength is nearly without effect on inner-sphere complex formation, and its increase generally induces a decrease of adsorption of outer-sphere 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 [57].

The temperature has two major effects on the adsorption process. Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of
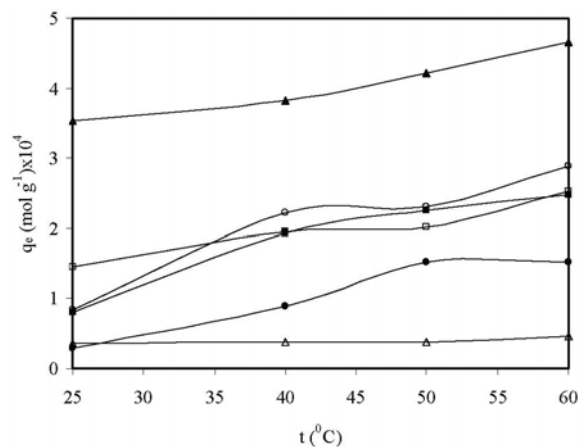
the solution. In addition, changing the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate [7]. The effect of temperature on the adsorption isotherm was studied by carrying out a series of isotherms at 25, 40, 50, and 60°C, as shown in Fig. 11. Results indicate that the adsorption capacity increases with increase in temperature. This may be a result of increase in the mobility of the metal ions with temperature. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface. Again, this result confirms endothermic nature of the on-going process [7].

3.4. Adsorption isotherm

The whole adsorption process can quantitatively be described by the adsorption isotherm which, at constant temperature, provides measured data relating to the amount adsorbed and the equilibrium pressure (or concentration) measured in the bulk phase after the adsorption equilibrium has completed. The most common adsorption isotherm equations used to describe adsorption phenomenons are the Langmuir and

the Freundlich equations. The characteristic feature of these isotherms is the decrease of slope at higher adsorption levels [58].

3.4.1. Langmuir isotherm

The physical and mathematical explanations of the adsorption and interpretation of the monolayer adsorption isotherms measured on homogeneous surfaces was started by Langmuir in 1916. This theory is based on the dynamic character of adsorption. At equilibrium, the number of adsorbed and desorbed molecules in unit time on unit surface are equal. Langmuir's theory does not take the lateral interactions and horizontal mobility of the adsorbed molecules into account [59]. The Langmuir equation can be written in the form:

$$q_e = q_m \left(\frac{KC_e}{1 + KC_e} \right) \tag{6}$$

where C_e is the equilibrium concentration of the solution (mol L^{-1}), q_e the amount of adsorbed per unit mass of adsorbent (mol g^{-1}), and q_m is the monolayer capacity (mol g^{-1}); K is the constant related to the energy of adsorption (L mol^{-1}). The steepness of the isotherm is determined by K. K can be considered to be a measure of the affinity of the adsorbate for the surface. The value of q_m is the upper limit for q_e and represents the maximum adsorption of adsorbate determined by the number of reactive surface adsorption sites. The parameters q_m and K can be calculated from adsorption data by converting Eq. (6) into the linear form

$$\frac{C_e}{q_e} = \frac{1}{q_m K} + \frac{1}{q_m} C_e \tag{7}$$

Then, the ratio C_e/q_e can be plotted against C_e. If the Langmuir equation can be applied, the

measured data should fall on a straight line with the slope of $1/q_m$ and the intercept of $1/q_m K$ [51].

3.4.2. Freundlich isotherm

The adsorption effects of metal ions on modified sepiolite surface can be interpreted with the Freundlich adsorption model, which depends on a heterogeneous surface with a continuous distribution of adsorption sites. The Freundlich equation has the form

$$q_e = K_F C_e^{1/n} \tag{8}$$

By the logarithmic linearization of Eq. (8), the two parameters of the Freundlich equation, K_F and $1/n$ could be estimated from the intercept and the slope of the straight line, respectively:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{9}$$

where q_e is the amount of metal ions adsorbed per unit weight of adsorbent; K_F the adsorption capacity; C_e the equilibrium concentration (mol L^{-1}); $1/n$ the adsorption intensity of the values of which range from less than 1.0 to greater than 1.0.

Adsorption isotherms were obtained in terms of Eqs. (7) and (9) by using experimental adsorption results in these equations. Fig. 12 shows the plots of Langmuir isotherm for the data of Fig. 8. Table 2 shows the results of Langmuir and Freundlich isotherm analyses calculated for adsorption of metal ions on modified sepiolite from aqueous solutions. The isotherm data were calculated from the least square method and the related correlation coefficients (R^2 values) are given in the same table. As seen from Table 1, the Langmuir equation represents the adsorption process very well; the R^2 values were all higher than 0.99, indicating a very good mathematical fit. From these data, the maximum adsorption capacity (q_m) was determined for each cation-matrix interaction through application of the Langmuir equation, where q_m and K were

Table 2
Isotherm constants for the adsorption of metal ions on modified sepiolite

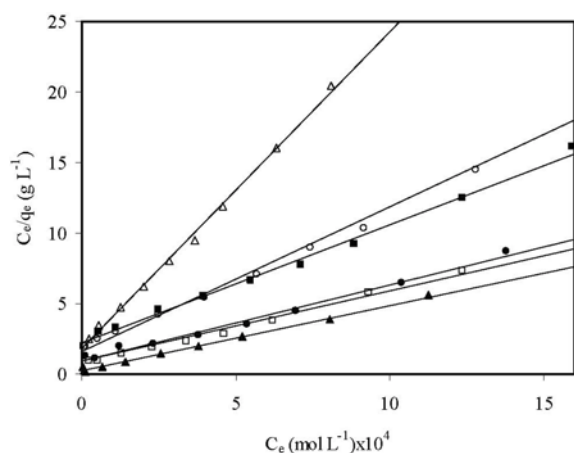| Metal	Parameters			Langmuir isotherm			Freundlich isotherm		
	Temp. (°C)	pH	[I] (mol L^{-1})	$q_m \times 10^4$ (mol g^{-1})	K (L mol^{-1})	R^2	n	$K_F \times 10^3$	R^2
Mn	25	4	0	0.979	6136	0.993	1.875	3.75	0.92
Cu	25	4	0	1.87	8137	0.995	1.474	26.4	0.87
Fe	25	2.5	0	1.193	3745	0.994	1.461	12.28	0.93
Zn	25	4	0	2.167	17941	0.995	1.995	9.62	0.81
Co	25	4	0	1.865	5546.4	0.991	1.647	12.89	0.92
Cd	25	4	0	0.445	12394	0.997	1.125	43.6	0.75

Fig. 12. Lamgmuir isotherm plots for the data of Fig. 9 (o: Fe, ■: Mn, ●: Co, Δ: Cd, □: Cu and ▲: Zn).

obtained from the curved and linear coefficients of the isotherm. Data calculated by applying the Langmuir equation show that the adsorption followed the sequence Zn(II)> Cu(II)~ Co(II) > Fe(III) > Mn(II) > Cd(II), respectively. The inter-active effect of zinc on the modified surface is much more effective than for other cations. As mentioned above, the modified sepiolite presented a larger cation adsorption capacity, suggesting its use in preconcentration and separation, especially for zinc. Such interactions can be interpreted due to the transference of cation from solution to the basic centers of the anchored [3-(2-aminoethylamino)propyl]trimethoxysilane molecule, by complexation of the cations through the available amine groups. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogenous distribution of active sites on sepiolite surface since the Langmuir equation assumes that the surface is homogenous [59].

3.4. Single-stage batch adsorption

Adsorption isotherms can be used to predict the design of single-stage batch adsorption systems [60]. The solution to be treated contains V L of water, and the metal concentration is reduced from C_0 to C_e in the adsorption process. In the treatment stage, W g adsorbent (metal ion free) is added and the metal concentration on modified sepiolite changes from $q_0 = 0$ to q_e. The mass balance that equates the metal removed from the liquid effluent to the that accumulated by modified sepiolite is

$$V\left(C_0 - C_e\right) = W\left(q_e - q_0\right) = Wq_e \qquad (10)$$

In the case of the adsorption of metal ions on modified sepiolite, the Langmuir isotherm gives the best fit to experimental data. The Langmuir data may now be applied to Eq. (10) and substituting for q_e from Eq. (6) and rearranging gives
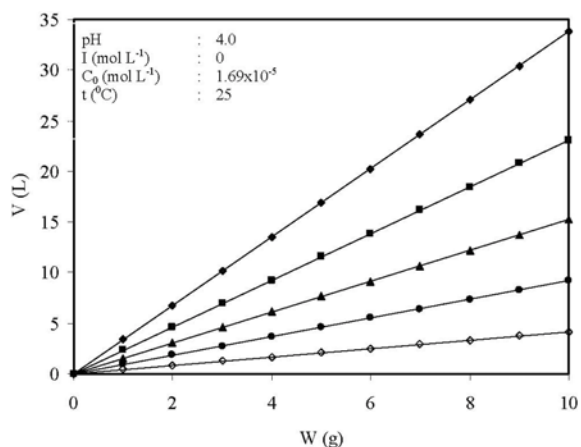
Fig. 13. Volume of effluent (V) treated against adsorbent mass (W) for different percentage zinc removal (removal % ♦: 50, ■: 60, ▲: 70, ●: 80, ◇:90).

$$\frac{W}{V} = \frac{C_0 - C_e}{q_e} \equiv \frac{C_0 - C_e}{\left(\dfrac{q_m K C_e}{1 + K C_e}\right)} \tag{11}$$

Eq. (11) permits analytical calculation of the adsorbent solution ratio for a given change in solution concentration, C_0 to C_e. Fig. 13 shows a series of plots derived from Eq. (11) for the adsorption of zinc ions on modified sepiolite. An initial zinc concentration of 1.69×10^{-5} mol L^{-1} is assumed and the figure shows the amount of effluent which can be treated to reduce the zinc content by 90, 80, 70, 60 and 50% using various masses of modified sepiolite.

4. Conclusions

The [3-(2-aminoethylamino)propyl]trimeth-oxysilane was successfully anchored onto the sepiolite. This new surface, with anchored pendant chains containing basic nitrogen atoms that are potential centers for cation removal, is a promising material to be applied for this operation, with good sorption capacity for the cations with ability in adsorbing Zn(II)> Cu(II)~ Co(II)> Fe(III)> Mn(II)> Cd(II). Equilibrium isotherms have been measured experimentally and analysed. It was found that the experimental data were correlated reasonably well by the Langmuir adsorption isotherm. This leads to the conclusion which shows the more homogeneous nature of the modified sepiolite. According to the Langmuir isotherm, the maximum adsorption capacity for metal ions of modified sepiolite was 2.167×10^{-4}, 1.870×10^{-4}, 1.865×10^{-4}, 1.193×10^{-4}, 0.979×10^{-4} and 0.445×10^{-4} mol g^{-1} for Zn(II), Cu(II), Co(II), Fe(III), Mn(II) and Cd(II), respectively. This surface has good separating matrices for metal ions. The high selectivity in bonding zinc suggests that this material may be useful for removal of this toxic heavy metal ion from waste waters. The characteristic of this matrix showed their ability to adsorb and separate toxic elements. This ability can be explored for applications in cleaning technologies, reinforcing the importance of developments in basic sciences for green chemistry.

Acknowledgments

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