© by PSP Volume 25 – No. 4/ 2016, pages 991-1006 Fresenius Environmental Bulletin

SYNTHESIS, CHARACTERIZATION, ELECTROKINETIC AND ADSORPTION PROPERTIES OF AN ORGANO-MODIFIED ADSORBENT FOR SELECTIVE REMOVING OF METAL IONS

Pınar Turan Beyli, Mehmet Dogan, Mahir Alkan[1], Aydın Türkyılmaz[2], Yasemin Turhan[1], Özkan Demirbas[1], Hilmi Namli[1]

[1]Balıkesir University Faculty of Science and Literture Department of Chemistry 10145 Çağış/Balıkesir-TURKEY
[1]Kastamonu University Faculty of Engineering and Architecture, Department of Enviromental Engineering Kastamonu-TURKEY

ABSTRACT

Firstly, sepiolite was modifed using N^1-[3-(trimethoxysiliylpropyl)]. In order to support the modification of sepiolite surface, FTIR, XRD, DTA/TG and SEM analyses were carried out. It was found that the chemical bonding took place between the hydroxyl groups and/or oxygen atoms within the structure of sepiolite and methoxy groups of N^1-[3-(trimethoxysiliylpropyl)] diethyltriamine. Then, the removal of heavy metal ions was systematically investigated as a function of pH, ionic strength and temperature using AAS. It was found that the amount of adsorbed metal ions increased with increase in solution equilibrium pH and temperature, whereas it generally decreased with the ionic strength. The experimental data were analyzed using Langmuir and Freundlich isotherms to identify the adsorption mechanism of metal ions on organo-modified sepiolite, and found that the isotherm data were reasonably well correlated by Langmuir isotherm. The Langmuir monolayer adsorption capacity of modified sepiolite was estimated as 118, 118, 110, 80, 37 and 30 mol g^{-1} for Cu(II), Zn(II), Fe(III), Mn(II), Cd(II) and Co(II), respectively. The affinity order of adsorption was Cu(II)=Zn(II)>Fe(III) >Mn(II)> Cd(II)> Co(II). The experiments demonstrated that Cu(II), Zn(II) and Fe(III) ions were more efficiently adsorbed than Cd(II) and Co(II) ions by modified sepiolite. The results show that modified sepiolite can be used as an alternative low-cost selective-adsorbent in adsorption process, in chromatographic purification process and in nanocomposite synthesis. Finally, the zeta potential of the modified sepiolite suspensions was measured and it was found that the zeta potential of the modified sepiolite in studied concentrations and pH values was negative.

KEYWORDS:
Metal ions, modified-sepiolite, zeta potential, selective-adsorption, characterization

INTRODUCTION

The release of heavy metals such as Ni(II), Cu(II), Zn(II), Pb(II), Co(II), etc. into the environment in aqueous waste streams is a potential threat to water and soil quality. Unlike organic pollutants, heavy metal ions are not biodegradable and tend to accumulate in living organisms, leading to several types of disseases and disturbances (Coruh and Geyikçi 2012). The removal of heavy metal ions from industrial wastewaters is a major problem. Numerous processes exist for removing dissolved heavy metals, including ion exchange, adsorption, precipitation, phytoextraction, ultrafiltration, reverse osmosis and electrodialysis. One of the major methods for the removal of pollutants from aqueous effluent is adsorption, especially using low-cost natural sorbets such as agricultural wastes, clay materials, zeolite, biomass, and seafood processing wastes. Activated carbon has been tested for the removal of inorganic ions from aqueous solutions. Despite its prolific use in water and wastewater industries, commercial activated carbon is not suitable in developing countries due to the high costs associated with production and regeneration of spent carbon. This has led to search for low-cost materials to remove pollutants (Coruh and Geyikçi 2012, Uğurlu 2009).

Clays and clay minerals are used for a large variety of environmental applications such as water purification, waste treatment mineral barries for waste deposits and slurry walls for the encapsulation of contaminated areas (Bradl 2002). The use of chemically modified clays and clays minerals 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. The preparation of solid adsorbents, to be applied for removal of these contaminants from waste effluent streams, is one of the major goals of green chemistry (Prado et al. 2002). 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-O-SiR_3 or similar multiply bonded $(SiO)_2SiR_2$ groups (Doğan et al. 2008). One of the most important schemes of chemically surface modification involves silylation reaction reacted with organosilicon intermediates, and in general, reactions with MXm where M is a metal and X is a halid, alkoxide, alkyl, alyl, carbonyl, etc. Silylation is the displacement of an active hydroxyl group by an organosilyl group. A major application for silylated surfaces has been in modified glass fibers and fillers for preparation of organic polymer composites and chromatographic materials (Monde 2002). At the same time, chemically modified adsorbents have been considered for the selective removal processes of metals from aqueous solutions.

Sepiolite is a natural clay mineral with a unit cell formula of magnesium hydrosilicate $Si_{12}Mg_8O_{30}(OH)_4(OH_2)_48H_2O$. It is structurally formed by blocks and channels extending in the fibre direction. Each structural block is composed of two inverted tetrahedral silica sheets and a central magnesium octahedral sheet. In the inner blocks, all corners of the silica tetrahedral are connected to adjacent blocks, but in the outer blocks, some of the corners are Si atoms bound to hydroxyls (Si–OH) (Kuncek and Sener 2010). These Si-OH groups play an important role in modification and adsorption processes. There are limited studies related to the modification of sepiolite, which may be used in the adsorption process, in chromatographic purification process and in nanocomposite synthesis due to increasing the mechanical properties. For example, Lemic et al. (2005) investigated the surface modification of sepiolite with quaternary amines; Alkan et al. (2005) the electrokinetic properties of sepiolite treated with some organosilanes; Torro-Palau et al. (1997) the structural modification of sepiolite by thermal treatment; Akyuz et al. (2001) the properties of adsorption of 3-aminopyridine on sepiolite and montmorillonite; but no studies about modification, adsorption and electrikinetic properties by N^1-[3-(trimethoxysiliylpropyl)] diethyltriamine compound of sepiolite have been found. It is therefore the objective of this study; i. to modify the sepiolite surface by N^1-[3-(trimethoxysiliylpropyl)] diethyltriamine, ii. to characterize the modified sepiolite using FTIR, XRD, DTA/TG and SEM, iii. to investigate the adsorption behavior and electrokinetic properties of heavy metal ions on modified sepiolite and iv. to describe the equilibrium isotherm. The effects of various parameters such as pH, ionic strength and temperature on metal ion adsorption and such as heavy metal ion concentrations and equilibrium pH on the electrokinetic properties have been investigated. Langmuir and Freundlich adsorption models were applied to describe the equilibrium isotherms and the isotherm constants were also determined.

MATERIAL AND METHODS

Materials. Sepiolite sample used in this study was obtained from Aktaş Lületaşı Co. (Eskişehir, Turkey). The chemical composition of sepiolite has been given in Table 1. The cation exchange capacity of sepiolite is 25 meq $100g^{-1}$; the density 2.55 g cm^{-3}; the specifice surface area 342 m^2 g^{-1}; particle size in the range of 0 to 50 µm. All chemicals were obtained from Merck, Aldrich, Sigma and Fluka, were of analytical grade and used without further purification (Alkan et al. 2005).

TABLE 1
The chemical composition of sepiolite

Composition	Weight (%)
SiO2	53.47
MgO	23.55
CaO	0.71
Al2O3	0.19
Fe2O3	0.16
NiO	0.43
Loss of ignition	21.49

Methods. Modification of sepiolite with N^1-[3-(trimethoxysiliylpropyl)]diethyltriamine. Sepiolite samples were treated before using in the experiments in order to obtain a uniform size sample of adsorbent as follows: the suspension containing 10 g L^{-1} sepiolite was mechanically stirred for 24 h, after waiting for about two minutes the supernatant suspension was filtered through filter paper. The solid sample was dried at 105 ^{o}C for 24 h, ground, and then sieved by 50 µm sieve. The particles under 50 µm were used in further experiments (Doğan et al. 2000). Sepiolite (5 g) suspended in toluene (100 mL) was refluxed and mechanically stirred for 1 h under dry nitrogen. To this suspension N^1-[3-(trimethoxysiliylpropyl)] diethyltriamine (5.0 mL) was added dropwise. The mixture was refluxed for another 24h, filtered and washed with water, followed by methanol and acetone. Modified sepiolite was dried at 110 ^{0}C (Menezes et al. 1996).

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

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

where U is electrophoretic mobility at actual temperature, η is viscosity of the suspending liquid, ε is dielectric constant, π is constant and ζ is zeta potential. The pH measurements were performed using a Orion 920A pH meter with a combined pH electrode. Double-distilled water was used to prepare aqueous solutions for all experiments. The samples were conditioned under the adsorption test conditions. For the electrophoretic mobility measurements, the suspensions were prepared in a polyethylene container by mixing 0.1 g of the modified sepiolite with 100 mL of double-distilled water, after the desired amounts of nitrate salts of heavy metals were added according to the experimental conditions. The zeta potential measurements were carried out as a function of the metal ion concentration and equilibrium pH. After agitation for 24 h in an incubator, the suspension was allowed to stand for 15 min to let the larger particles settle. An aliquot taken out from the suspension was slowly poured into the electrophoresis cell. Molybdenum anode and platinum cathode electrodes were inserted into the cell. After a desired voltage applied between the electrodes, the movement of particles was observed via a microscope nodule. Minimum 10 measurements were carried out to present the measured potential. The applied voltage during the measurements was varied in the range 50–150 mV. The pH that was made the zeta potential measurement was recorded as equilibrium pH. The instrument was tested prior to each test using the test colloid, as recommended by the supplier (Doğan et al. 1997).

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. 0.1 g of modified sepiolite was added into 50 mL of metal solutions and shaken continuously at room temperature. A thermostated orbital shaker incubator was used to keep the temperature constant. Stock solutions were prepared in deionized water for each metal ion and further experimental solutions were prepared from the stock solution by successive dilution. The pH of the solutions was adjusted with NaOH or HNO_3 solution by using an Orion 920A pH meter with a combined pH electrode. The pH meter was standardized with NBS buffers before every measurement. A preliminary experiment revealed that about 24 h is required for metal ions to reach the equilibrium concentration. The effect of pH, ionic strength and temperature on the adsorption of heavy metals such as Cu(II), Zn(II), Fe(III), Mn(II), Cd(II) and Co(II)) was also studied. It was used the nitrate salts of metal ions in the experiments. At the end of the adsorption period, the solution was centrifuged for 15 min at 5000 rpm. Five standard solutions for each metal ion were prepared in 100 mL flasks. Calibration graph for each batch of experiments were re-constructed by using the standard solutions. The blank experiments were simultaneously carried out without the adsorbent. Filter paper was not used in any part of the experiments, since filter paper itself adsorbs about ≈30% of the present metal ions particularly at low concentration levels. Each run was repeated at least twice. The final concentration of metal ions in the solutions was determined by Unicam 929 flame atomic absorption spectrometer operating with an air-acetylene flame (AAS). The amount of metal ions adsorbed onto modified sepiolite was calculated from the difference between initial and residual concentration in solution as follows:

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

where q_e is the amount adsorbed (mol g^{-1}), 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) (Alkan and Doğan 2001).

Characterization. Infrared spectra of samples were obtained using a PerkinElmer BX 1600 FTIR. About 0.01 g of clay was mixed with 1 g of potassium bromide (KBr) and pelletized in the hydraulic press at 10 kPa. FTIR spectra were taken in the range from 4000 to 400 cm^{-1} in the transmission mode. The interaction between the sepiolite surface and the modifier N^1-[3-(trimethoxysiliylpropyl)]diethyltriamine during the modification was investigated by a series of FTIR spectral analysis: 1. modifier sample, 2. sepiolite sample and 3. modified sepiolite sample. X-ray diffraction measurements of natural and modified sepiolite samples were performed using a Analytical Philips X'Pert-Pro X-ray diffractometer equipped with a back monochromator operating at 40 kV and a copper cathode as the X-ray source (λ = 1.54 Å). A simultaneous DTA/TG system was used for thermogravimetric (TG) analysis (PerkinElmer Diamond DTA/TG). To observe the surface topography of sepiolite and modified sepiolite, scanning electron micrographs (SEM) were performed using a Zeiss EVO LS 10. Most of the measurements were carried out using an accelerating voltage of 20 kV.

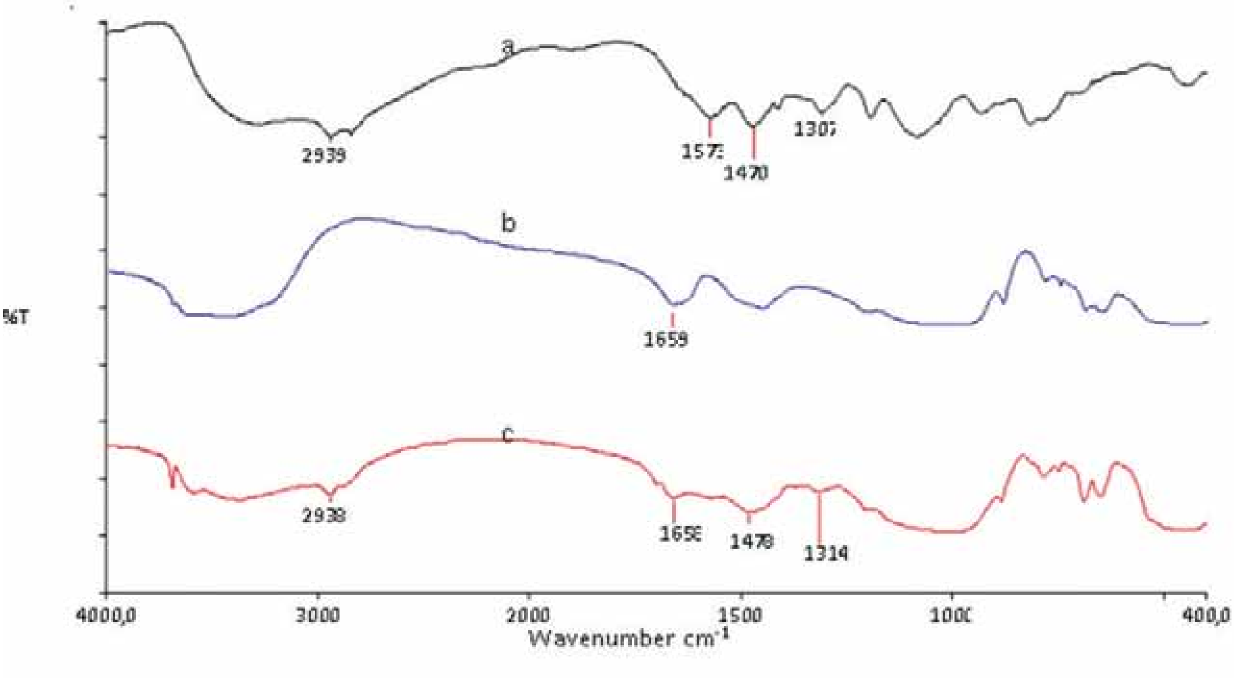
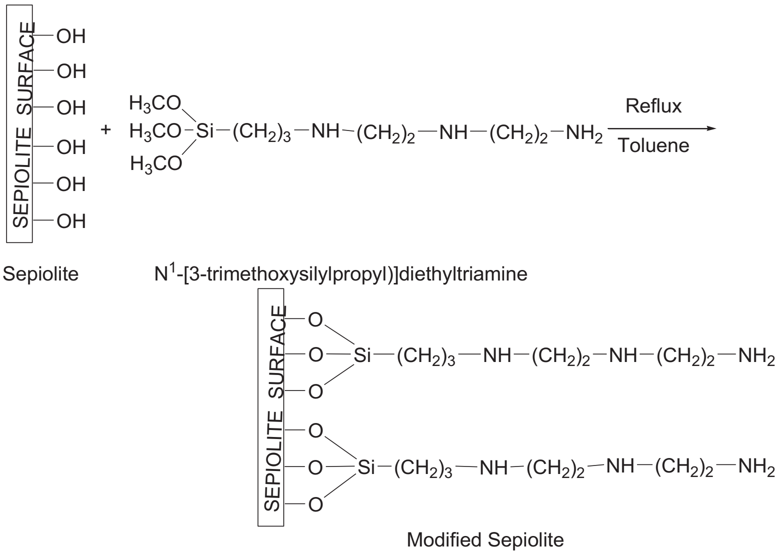


FIGURE 1
FTIR spectra of (a) N1-[3-(trimethoxysiliylpropyl)]diethyltriamine, (b) sepiolite and (c) modified structure in the KBr disks.

RESULTS AND DISCUSSION

Characterization of Modified-Sepiolite. FTIR Analysis. The existence of different types of surface hydroxyl groups on an oxide is easily recognized from infrared spectra, and the behavior of the hydroxyl groups when subjected to thermal treatments or modification processes may be fully characterized. Infrared spectra of adsorbed probe molecules are widely used to provide additional characterization not only of surface hydroxyl groups but also of other types of exposed site (Anderson and Rochester 2002). Figure 1 has shown FTIR spectra of sepiolite, modifier and modified sepiolite. As can be seen from spectra, there are important interactions between modifier and sepiolite. The peak at 2939 cm^{-1} of modifier due to alkyl groups was observed at 2938 cm^{-1} in modified sepiolite. Moreover, C-N peak of modifier at 1470 cm^{-1} shifted at 1478 cm^{-1} after modification process, and the peak of modifier at 1307 cm^{-1} shifted at 1314 cm^{-1}. According to the explanations above, the reaction between modifier and sepiolite can be written as following:



(3)

TG analysis. The variation of percent weight loss with temperature (TG curves) and differential weight loss with temperature (d[TG] curves) for sepiolite and modified sepiolite under nitrogen and oxygen atmospheres have been given in Figure 2. Sepiolite mineral is known to contain four types of water molecules in different chemical states; i. hydroscopic water, ii. zeolitic water, iii. bound water and iv. structural water (Alkan et al. 2005; Balci 1996) which are removed from the mineral by thermal dehydration at different temperatures. The amount of hydroscopic water depends on the humidity of the environment. It leaves the mineral at lower temperatures. In this case, the reaction may be written as following:

$$Mg_8Si_{12}O_{30}(OH)_4(H_2O)_48H_2O \rightarrow Mg_8Si_{12}O_{30}(OH)_4(H_2O)_4 + 8H_2O \quad (4)$$

The zeolitic water is found in the channel-type voids and starts to leave the structure above room temperature. The removal from the structure of zeolitic water can be given in following reaction:

$$Mg_8Si_{12}O_{30}(OH)_4(H_2O)_4 \rightarrow Mg_8Si_{12}O_{30}(OH)_4(H_2O)_2 + 2H_2O \quad (5)$$

The bound water and structural water leave the mineral at higher temperatures. The bound water is found in magnesium coordination in the crystal structure. It is known that dehydration of it occurres in two steps, accompanied by structural changes. Literature studies have shown that the first part of the bound water leaves the structure between 250°C and 450 ^{0}C. The following equation represents the explanations above:

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

By the removal of some parts of the bound water, rearrangements within the crystal structure may have occurred. The breakage of water molecules and the transportation of them from the small pores to the channel voids, become difficult due to the crystal folding. The remaining part of the bound water begins to leave the structure at higher temperatures.

$$Mg_8Si_{12}O_{30}(OH)_4 \rightarrow 8MgSiO_3 + 4SiO_2 + 2H_2O \quad (7)$$

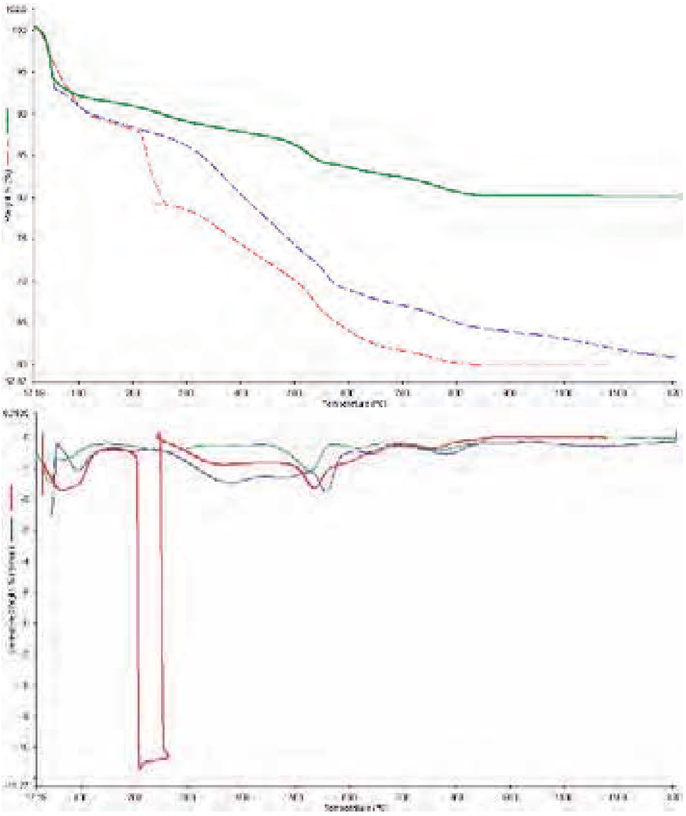


FIGURE 2
(A) TG and (B) d[TG] spectra of natural and modified sepiolite samples under different conditions: a. modified sepiolite under oxygen atmosphere, b. modified sepiolite under nitrogen atmosphere, and c. sepiolite under nitrogen atmosphere.

The removal of bound water is completed before 750°C. The removal of structural water molecules (hydroxyl groups) is completed up to 850°C (Balci 1996;) As can be seen from Figure 2, the removal of hydroscopic water from the external surface and zeolitic water from the voids of the structure was completed by 200 °C. The bound water molecules left the structure higher temperatures (200-600 ^{0}C) than the hydroscopic and zeolitic water molecules. The removal of structural water molecules and hydroxyl groups was completed until 850 ^{0}C. Percent weight losses for sepiolite under nitrogen and oxygen were determined as 9.6 and 9.4 in the temperature range of 0 to 200 ^{0}C; 7.4 and 7.5 in the temperature range of 200 to 600 ^{0}C; and 3.5 and 3.2 in the temperature range of 600 to 900 ^{0}C, respectively. Total percent weight losses for sepiolite under nitrogen and oxygen were calculated as 20.5 and 20.1, respectively. Again, percent weight losses for modified sepiolite under nitrogen and oxygen were determined as 4.5 and 11.8 in the temperature range of 0 to 200 ^{0}C; 19.6 and 24.0 in the temperature range of 200 to 600 ^{0}C; and 5.0 and 4.1 in the temperature range of 600 to 900 ^{0}C, respectively. Total percent weight losses for modified sepiolite under nitrogen and oxygen were calculated as 29.1 and 39.9, respectively. In addition, any weight loss was not observed by heating of the samples up to 1100 ^{0}C. Results showed that the percent weight loss of modified sample increased. In this case, it can be said that sepiolite was modified by organosilane compound and formed a chemical bond between the hydroxyl groups on the sepiolite and modifier substance.

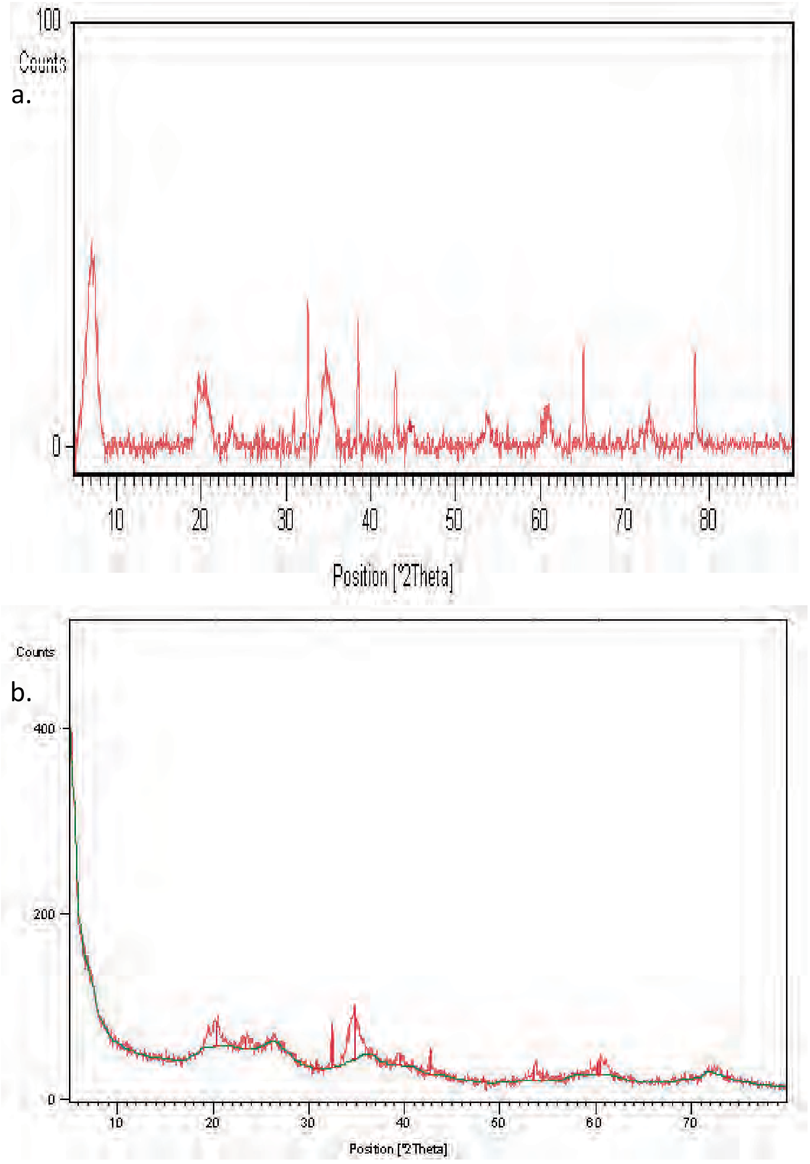


FIGURE 3
XRD spectra of (a) natural and (b) modified sepiolite samples.

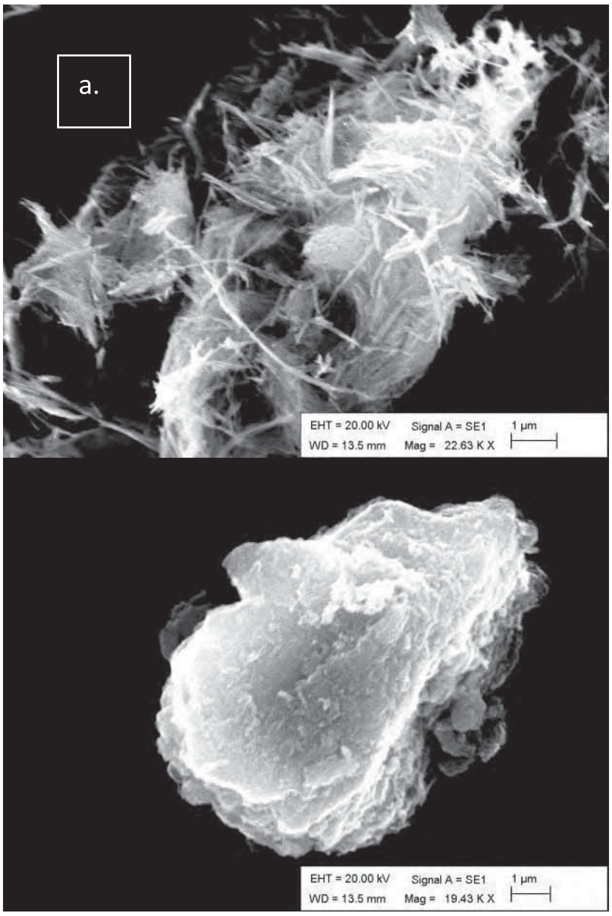


FIGURE 4
SEM images of (a) natural and (b) modified sepiolite samples.

XRD. Figure 3 shows XRD patterns of sepiolite and modified sepiolite. The XRD pattern of sepiolite is clearly affected by the incorporation of N^1-[3-(trimethoxysiliylpropyl)]diethyltriamine. Covalent bonding is formed because, as seen in Figure 3, the some peak intensities both increased and decreased by modification. When the covalent bonding is formed by the interaction between hydroxyl groups on sepiolite and N^1- [3-(trimethoxysiliylpropyl)] diethyltriamine, some structural distortions occur at the plane atoms in the sepiolite. As a result of these distortions, the peak intensity is changed.

SEM. Sepiolite and modified sepiolite were examined by SEM and representative micrographs are shown in Figure 4. The modification process produced a reduction in size of aggregates that showed flake type morphology. SEM image of modified sepiolite showed that sepiolite losed its fibrous morphology after modification process. This result has shown that sepiolite surface was modified by N^1-[3-(trimethoxysiliylpropyl)]diethyltriamine.

Electrokinetic properties. The zeta potential of modified sepiolite in single aqueous solutions of Cu(II), Zn(II), Fe(III), Mn(II), Cd(II) and Co(II) was investigated. Figure 5 illustrates the zeta potential of modified sepiolite as a function of different metal ion concentrations at natural pH. Since there is no experimental method for determining both the surface potential and Stern layer potential, the zeta potential is the measurable surface potential at the shear plane between the particle and the surrounding liquid (Kara et al. 2003). Although the zeta potential values with heavy metal cations are quite different, their tendency to change with zeta potential is similar (Figure 5). The values on the curves obtained for each heavy metal did not change the sign of surface negative charge. The results indicated that increasing metal ion concentration in solution decreased the negative charge of surface (becomes less negative) without changing the sign of the surface charge. This case can be explained the compression of the electrical double layer at the modified sepiolite surface. 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 from Figure 5, the surface is, at first, more negatively charged, and then the negative charge decreases as the concentration of metal ion 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, that is, in the inner Helmhotz plane 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 electrical double layer on the negatively charged modified sepiolite. Consequently, they compress the electrical double layer and change the magnitude of the zeta potential of modified sepiolite (Turhan et al. 2008).

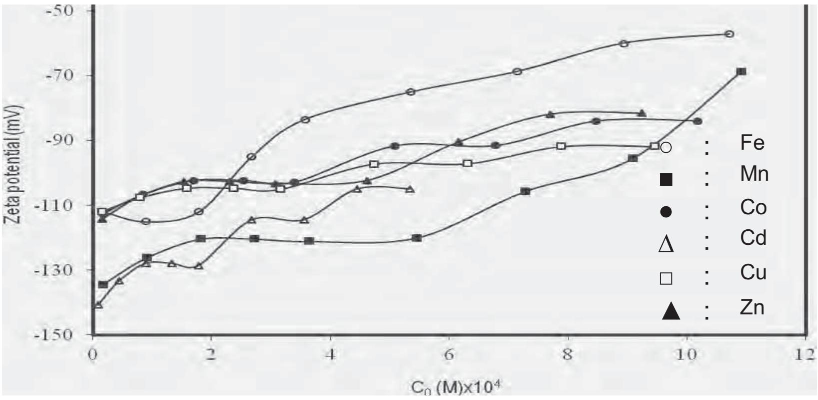


FIGURE 5
Effect of heavy metal ion concentrations on zeta potential of modified sepiolite.

The zeta potential curves as a function of pH for modified sepiolite in the presence of different metal ions are displayed in Figure 6. Previous investigations on the electrokinetic properties of different types of clay minerals indicated differences between various minerals in their pH dependence (Sondi and Pravdic 1996; Doğan et al. 2000). The pH-dependent changes are due to reactive hydroxyl groups at the edge surfaces. Indeed, the fraction of the edge surfaces and, thus, of reactive hydroxyl groups in the total surface area varies depending on the type of clay minerals. As seen from Figure 6, the most important observations are that modified sepiolite does not has isoelectrical point over the pH range of 1 to 7 and has negative zeta potential in the studied pH range. This is another sign that the sepiolite surface was modified by N^1-[3-(trimethoxysiliylpropyl)]diethyltriamine. For all metal ions, the zeta potential became more negative with increasing equilibrium pH. 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 sign of the zeta potential. At low pH values, the adsorption of H_3O^+ hinders the specific adsorption of metal ions. For this reason, as the pH increases, the negative sign of the surface increases because of the releasing of H^+ ions on two $–NH_2^+$- or one $–NH_3^+$ groups of modifier.

Adsorption properties. There are some physical and chemical parameters that influence the adsorption of heavy metal ions in aqueous solutions. The most important ones are pH, the presence of other cations in solution, and temperature. All these variables may change the metal adsorption isotherms (Bradl 2002). We have discussed the experimetal data obtained for adsorption of metal ions from aqueous solutions in this section.

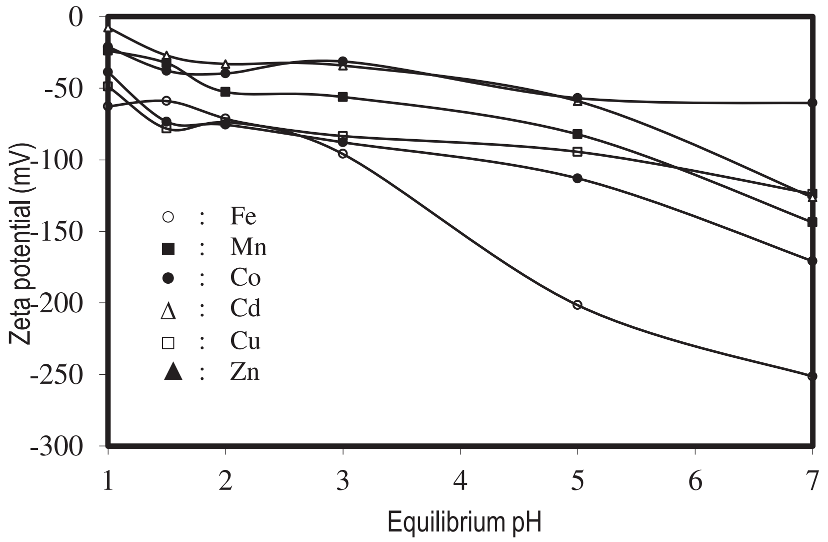


FIGURE 6
Effect of pH on zeta potential of modified sepiolite

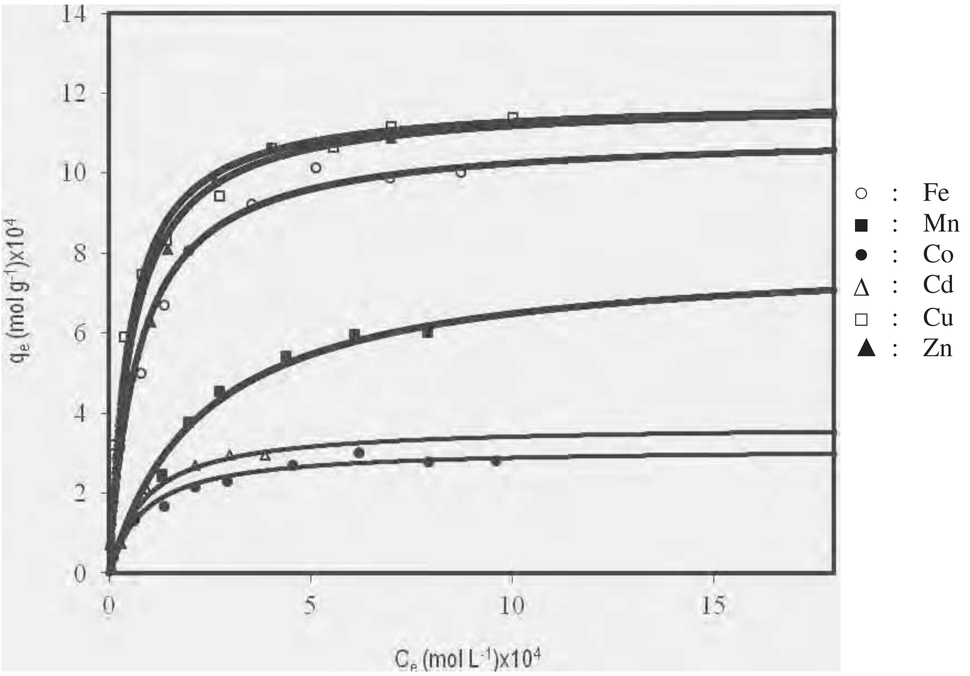
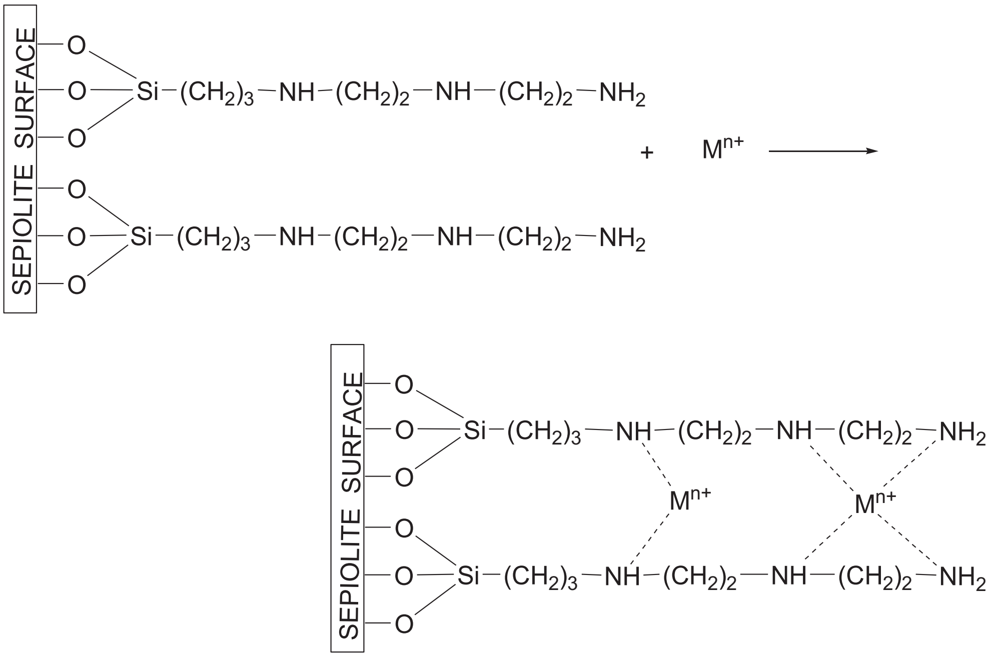


FIGURE 7
Isothern curves for adsorption data

After incorporating the silylating agent into clay structure, the pendant groups disposed on the structure enable this material to interact with a wide range of cations due to the presence of three basic centres; three characteristically hard basic centres. This fact improves the process of interaction with various metal ions (Prado et al. 2002). The changing of adsorbed metal ions versus the concentration of solution under equilibrium conditions has been given in Figure 7, which shows that the amount adsorbed of metal ions increased with increasing metal ion concentration. The higher the initial metal ion concentration, the larger the metal ion sorbed per unit weight of adsorbent at equilibrium. The selectivity of different adsorbents for metal ions cannot be given according to universally consistent rules as it depends on a number of factors such as i. the chemical nature of the reactive surface groups, ii. the level of adsorption, iii. the pH at which adsorption is measured, iv. the ionic strength of the solution in which adsorption is measured and v. the presence of soluble ligands that could complex the free metal [Bradl, 2002]. As seen from Figure 7, the adsorption capacity of modified sepiolite is higher for Cu(II), Zn(II) and Fe (III) ions than other ions. When Cu(II), Zn(II) and Fe (III) have hard and borderline acid character, the nitrogen atom of modifier has hard basic character (Yantasee et al. 2004). Based on the structural features presented by the pendant groups attached to the sepiolite surface, the hard basic atoms of modifier can easily bond to the hard or borderline cations. Thus, metal ion adsorption should be *via* nitrogen in the case of hard and borderline metal cations, as proposed in reaction (8).



(8)

The most important factor which controls the adsorption capacity of metal ions on different adsorbents is pH, which affects the surface structure of sorbents, the formation of metal hydroxides, and the interaction between sorbents and metal ions. Change of pH affects the adsorptive process because of the protonation and deprotonation of the acidic and basic groups on the adsorbent surface active sites (Kuncek and Sener 2010; Duru et al. 2001). Therefore, in this study, the pH dependence of adsorption for metal ions was investigated in detail. The pH dependence of metal ion uptake onto modified sepiolite is shown in Figure 8. The removal efficiency of metal ions generally increased with increasing pH in the pH range of 1 to 7. This can be explained by considering the surface charge of modified sepiolite. For clay minerals, the potential determining ions are H$^+$ and OH$^-$ and complex ions formed by bonding with H$^+$ and OH$^-$.

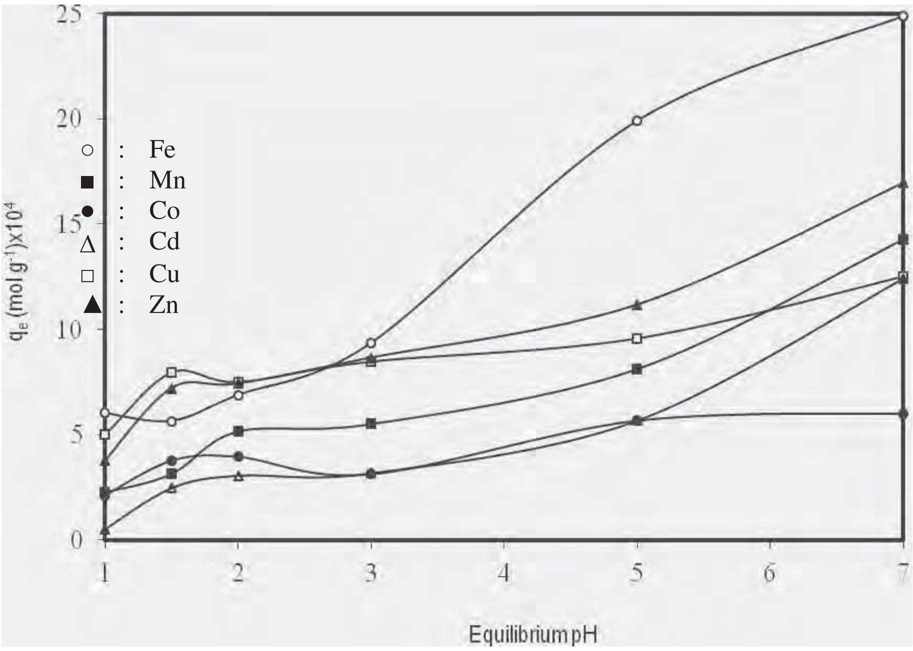
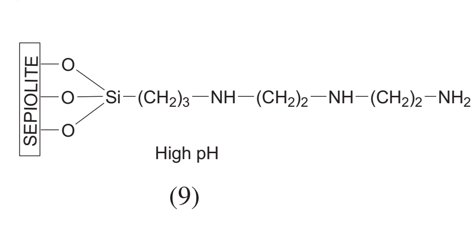


FIGURE 8
Variation of the adsorption of metal ions with pH on modified sepiolite

As the pH is lowered, the hydrogen ions compete with the metal ions for the sorption sites on the sorbent and may hinder the binding of positively charged metal ions. In this case, the adsorption of metal ions decreases. Increasing pH means decreasing H^+ concentration and more metal ions are able to occupy adsorption sites at the surface. Therefore, the adsorption of metal ions increases. As a result, as the pH of the system increases, the number of negatively charged sites increases due to deprotonation of the surface. A negatively charged surface site on the modified sepiolite favors the adsorption of metal cations. Lower adsorption of metal ions at acidic pH is probably due to the presence of excess H^+ ions competing with the metal cations for the adsorption sites. In low and high pH, the surface of modified sepiolite can be shown as following:



(9)

Figure 9 shows the adsorbed amount of metal ions on modified sepiolite from aqueous solutions in different NaCl concentrations. As seen in Figure 9, increasing the ionic strength of the solution slightly causes a decrease in the adsorption of metal ions onto the modified sepiolite surface. This indicates that the negative charge of the surface of modified sepiolite, which has no pHpzc in the pH range of 1 to 7, decreases with increasing ionic strength, resulting in reducing the adsorption capacity (Eren et al. 2010).

In order to study the effect of temperature to the adsorption of metal ions on modified sepiolite a series of experiment was conducted in the temperature range of 30 to 60 ^{0}C. The results are presented in Figure 10. There is an increase in the adsorbed amount of metal ions with a rise in temperature which may be due to higher adsorption caused by an increase in the thermal energy of the adsorbates. This indicates that the adsorption process is endothermic. The effect of temperature is fairly common and increasing temperature results in an increase in the rate of approach to equilibrium. In addition, the temperature coefficient for the reverse reaction is lower than for the forward reaction and consequently the equilibrium capacity increases with increased temperature (Kuncek and Sener 2010).

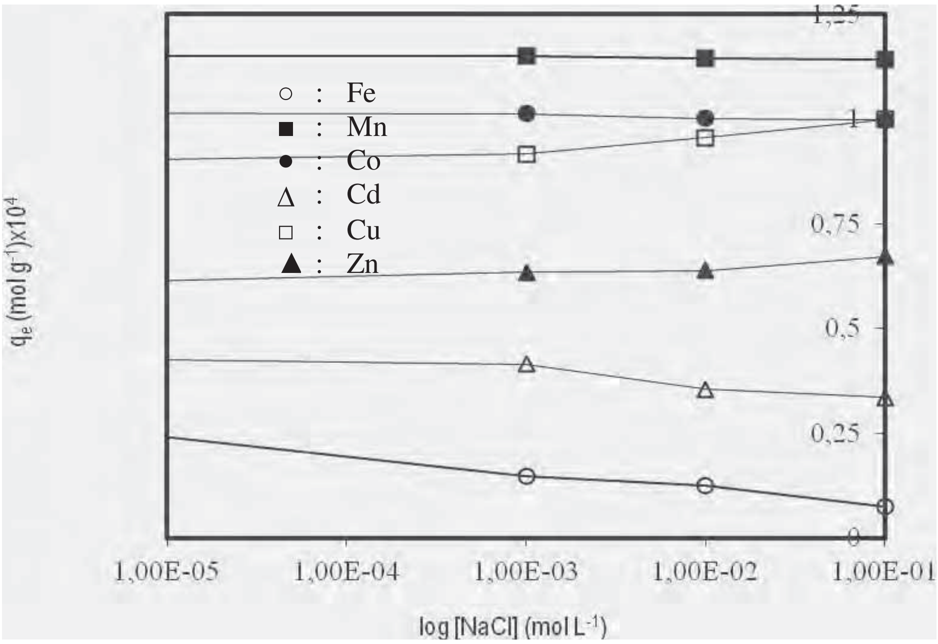


FIGURE 9
Variation of the adsorption of metal ions with ionic strength on modified sepiolite

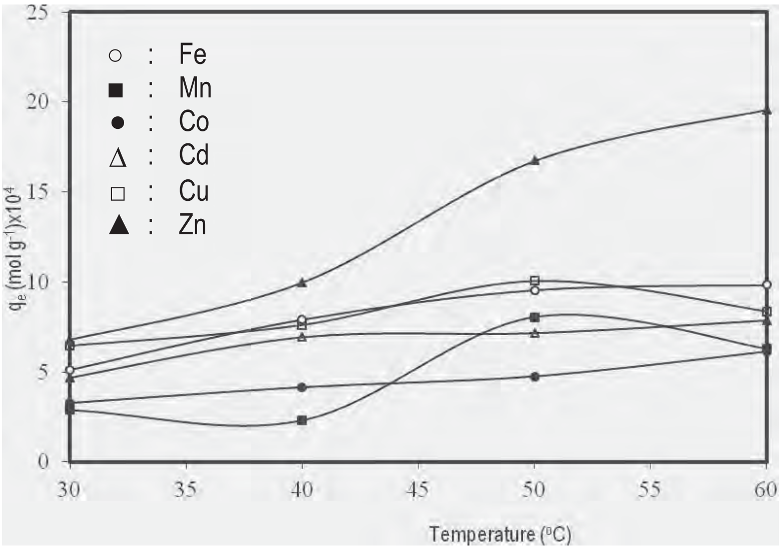


FIGURE 10
Variation of the adsorption of metal ions with temperature on modified sepiolite.

Adsorption isotherms. The analysis of the isotherm data is important to develop an equation which accurately represents the results and which could be used for design purposes. The adsorption curves were applied to both the Langmuir and Freundlich equations. The widely used Langmuir isotherm has found successful application to many real sorption processes and is expressed as in the linear form:

$$\frac{C_e}{q_e} = \frac{1}{q_m K} + \frac{C_e}{q_m} \tag{10}$$

where q_e is the amount adsorbed (mol g^{-1}), C_e is the equilibrium concentration of the adsorbate ions (mol L^{-1}), and q_m and K are Langmuir constants related to maximum adsorption capacity (monolayer capacity) and energy of adsorption, respectively. q_m represents a practical limiting adsorption capacity when the surface is fully covered with metal ions and assists in the comparison of adsorption performance. q_m and K are calculated from the slopes and intercepts of the straight lines of plot of C_e/q_e vs. C_e.

The Freundlich isotherm is given as,

$$q_e = K_F C_e^{1/n}$$

in logarithmic form,

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{11}$$

where K_F is roughly an indicator of the adsorption capacity and (1/n) of the adsorption intensity. K_F and (1/n) can be determined from the linear plot of $\ln q_e$ vs. $\ln C_e$.

The parameters of Freundlich and Langmuir isotherms are given in Table 2.

TABLE 2
Isotherm parameters for the adsorption of metal ions on the modified sepiolite

Metals	t (^{0}C)	pH	Langmuir isotherm			Freundlich isotherm		
			q_mx10^5 (mol g^{-1})	Kx10^{-4} (L mol^{-1})	R^2	n	K_F x10^3	R^2
Mn	30	4.0	80	4.34	0.981	1.67	49.29	0.965
Cu	30	4.0	118	2.05	0.998	3.71	8.31	0.918
Fe	30	3.0	110	1.39	0.998	2.06	41.17	0.928
Zn	30	4.0	118	1.77	0.996	2.47	23.75	0.968
Co	30	4.0	31	1.19	0.992	2.42	6.15	0.946
Cd	30	4.0	37	1.18	0.984	1.60	53.39	0.945

Langmuir isotherm fits quite well with the experimental data (correlation coefficient R^2>0.98), whereas the low correlation coefficients (R^2<0.96) show poor agreement of Freundlich isotherm with the experimental data.

The Langmuir isotherm models the monolayer coverage of the adsorption surface. Once metal ion occupies a site on the modified sepiolite surface, no further adsorption of metal ions can take place at that site. This model assumes that adsorption occurs at specific homogeneous adsorption sites within the adsorbent and intermolecular forces decrease rapidly with the distance from the adsorption surface. The Langmuir adsorption model further based on the assumption that all the adsorption sites are energetically identical and adsorption occurs on a structurally homogeneous adsorbent.

Theoretically, sepiolite has a finite capacity for adsorbing metal ions (Kocaoba 2009; Uğurlu 2009).

According to the equilibrium isotherms, the selectivity series is Cu(II)=Zn(II)>Fe(III)>Mn(II)>Cd(II)>Co(II). An inspection of the q_m values in Table 2 demonstrate that Cu(II), Zn(II) and Fe(III) are easily the most effective in binding to the pendant groups. This behaviour reflects the high affinity of the nitrogen basic centres for Cu(II), Zn(II) and Fe(III). This fact suggests that this surface is more favourable in reacting with hard and borderline cations. The selectivity of different clay minerals for heavy metal ions has changed. For example, it was found that the selectivity series for montmorrillonite was Ca>Pb>Cu>Mg>Cd>Zn, for illite Pb>Cu>Zn>Ca>Cd>Mg, for kaolinite

Pb>Ca>Cu>Mg>Zn>Cd, and for smectite Zn>Mn>Cd>Hg (Bradl 2002). In light of these observations, this material could be potentially applied as a selective electrode when the objective is to determine or identify hard and borderline acids. Another feature connected to the use of this surface is its good ability to separate these cations from a water solution.

CONCLUSIONS

Sepiolite surface was modified with N^1-[3-(trimethoxysiliylpropyl)]diethyltriamine. This surface presents a high affinity for Cu(II), Zn(II) and Fe(III) due to the presence of three basic nitrogen centres. This anchored surface also presents a good adsorption capability for other divalent cations. Modified sepiolite surface has a negative charge in solutions in the pH range of 1 to 7. The results of this study indicate that modified sepiolite can be successfully used for the removal of heavy metal ions from aqueous solutions. Correlation coefficients for the isotherm models indicate that the Langmuir model best describes the metal adsorption process, experimental data are better fitted to the Langmuir isotherm and adsorption capacities order was found as Cu(II)=Zn(II)>Fe(III)>Mn(II)>Co(II)>Cd(II). In summary, the surfaces of modified sepiolite present a high affinity for Cu(II), Zn(II) and Fe(III), and low affinity for Co(II) and Cd(II). This fact permits an excellent separation of Cu(II), Zn(II) and Fe(III) from other cations, and these surfaces may be useful in separating these cations. These abilities can be explored for applications in clean technologies reinforcing the importance of developments in basic sciences for green chemistry, in chromatographic applications and in the manufacture of a chemical sensor.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support of TUBİTAK (TBAG-2455 (104T067)).

REFERENCES

[1]Akyuz S, Akyuz T, Yakar AE (2001) FT-IR spectroscopic investigation of adsorption of 3-aminopyridine on sepiolite and montmorillonite from Anatolia. J. Molecular Struct. 565–566: 487–491.

[2] Alkan M, Çelikçapa S, Demirbaş Ö, Doğan M (2005) Removal of reactive blue 221 and acid blue 62 anionic dyes from aqueous solutions by sepiolite. Dyes and Pigments 65: 251-259.

[3] Alkan M, Doğan M (2001) Adsorption of copper(II) onto perlite. Journal of Colloid and Interface Science 243: 280–291.

[4] Alkan M, Tekin G, Namli H (2005) Zeta potentials of perlite modified with dimethyl-dichlorosilane, 3-aminopropyltriethoxysilane and dimethyloctadecylchlorosilane. Microporous and Mesoporous Materials 84(1-3): 75-83.

[5] Anderson JA, Rochester CH (2002) Infrared spectroscopy of silica, alumina, and related surfaces. Encyclopedia of Surface and Colloid Science. Marcel Dekker, Inc..

[6] Balci S (1996) Thermal decomposition of sepiolite and variations in pore structure with and without acid pre-treatment, J. Chem. Technol. Biotechnol 66: 72–78.

[7] Beene GM, Bryant R, Williams DJA (1991) Electrochemical properties of illites. J. Colloid Interface Sci. 147: 358–369.

[8] Bradl H (2002) Adsorption of heavy metal ions on clays. Encyclopedia of Surface and Colloid Science. Marcel Dekker, Inc..

[9] Coruh S, Geyikçi F (2012) Adsorption of copper (II) ions on montmorillonite and sepiolite clays: equilibrium and kinetic studies. Desalination and Water Treatment 45: 351–360. [11]Doğan M, Alkan M, Onganer Y (2000) Adsorption of methylene blue from aqueous solution onto perlite. Water, Air and Soil Pollution 120: 229-248.

[12] Doğan M, Turhan Y, Alkan M, Namli H, Turan P, Demirbas O (2008) Functionalized sepiolite for heavy metal ions adsorption. Desalination 230: 248–268.

[13] Duru PE, Bektas S, Genç Ö, Patır S, Denizli A (2001) Adsorption of heavy-metal ions on poly(ethylene imine)-immobilized poly(methyl methacrylate) microspheres. Journal of Applied Polymer Science 81:. 197–205.

[14] Eren E, Cubuk O, Ciftci H, Eren B, Caglar B (2010) Adsorption of basic dye from aqueous solutions by modified sepiolite: Equilibrium, kinetics and thermodynamics study. Desalination 252: 88–96.

[15] Hojati S, Khademi H (2013) Thermal behavior of a natural sepiolite from northeastern Iran. Journal of Sciences, Islamic Republic of Iran 24(2): 129-134.

[16] Kara M, Yuzer H, Sabah E, Celik MS (2003) Adsorption of cobalt from aqueous solutions onto sepiolite. Water Research 37: 224–232.

[17] Kocaoba S (2009) Adsorption of Cd(II), Cr(III) and Mn(II) on natural sepiolite. Desalination 244: 24–30.
[18] Kuncek I, Sener S (2010) Adsorption of methylene blue onto sonicated sepiolite from aqueous solutions. Ultrasonics Sonochemistry 17: 250–257.
[19] Lemic J, Tomasevic-Canovic M, Djuricic M, Stanic T (2005) Surface modification of sepiolite with quaternary amines. J. Coll. Interf. Sci. 292: 11–19.
[20] Menezes ML, Moreira JC, Campos JTS (1996) Adsorption of various ions from acetone and ethanol on silica gel modified with 2-, 3-, and 4-aminobenzoate. Journal of Colloid and Interface Science 179: 207-210.
[21] Monde T (2002) Chemically modified silica, alümina and related surfaces. Encyclopedia of Surface and Colloid Science. Marcel Dekker, Inc..
[22] Prado AGS, Arakaki LNH, Airoldi C (2002) Adsorption and separation of cations on silica gel chemically modified by homogeneous and heterogeneous routes with the ethylenimine anchored on thiol modified silica gel. Green Chemistry 4: 42–46. [23]Sondi I, Biscan J, Pravdic V (1996) Electrokinetics of pure clay minerals revisited. J. Colloid Interface Sci. 178: 514–522.
[24] Sondi I, Milat O, Pravdic V (1997) Electrokinetic potentials of clay surface modified by polymers. J. Colloid Interface Sci. 189: 66–73.
[25] Sondi I, Pravdic V (1996) Electrokinetic of natural and mechanically modified ripidolite and beidellite clays. J. Colloid Interface Sci. 181: 463–469.
[26] Sondi I, Pravdic V (2002) Electrokinetics of clay mineralssurfaces. Encyclopedia of Surface and Colloid Science. Marcel Dekker, Inc..
[27] Sondi I, Stubicjar M, Pravdic V (1997) Surface properties of ripidolite and beidellite clays modified by high-energy ball milling. Colloids Surf. 127: 141–149.
[28] Torro-Palau A, Fernandez-Garcia JC, Orgiles-Barcelo AC, Pastor-Blas MM, Martin-Martinez JM (1997) Structural modification of sepiolite (natural magnesium silicate) by thermal treatment: effect on the properties of polyurethane adhesives. Intern. J. Adhesion Adhesives 17: 111–119.
[29] Turhan Y, Turan P, Dogan M, Alkan M, Namli H, Demirbas O (2008) Characterization and adsorption properties of chemically modified sepiolite. Ind. Eng. Chem. Res. 47: 1883-1895.
[30] Uğurlu M (2009) Adsorption of a textile dye onto activated sepiolite. Microporous and Mesoporous Materials 119: 276–283.
[31] Williams DJA, Williams KP (1978) Electrophoresis and zeta potential of kaolinite. J. Colloid Interface Sci. 65: 79–87.
[32] Yantasee W, Lin Y, Fryxell GE, Alford KL, Busche BJ, Johnson CD (2004) Selective removal of copper(II) from aqueous solutions using fine-grained activated carbon functionalized with amine. Ind. Eng. Chem. Res. 43: 2759-2764.
[33] Zhou Z, Gunter WD (1992) The nature of surface charge of kaolinite. Clays Clay Miner. 40: 365–368.

Received: **01.06.2015**
Accepted: **06.03.2016**

CORRESPONDING AUTHOR

Pınar Turan Beyli
Balıkesir University
Faculty of Science and Literture
Department of Chemistry
10145 Çağış/Balıkesir - TURKEY

e-mail: pturan@balikesir.edu.tr

Mehmet Dogan,
Balıkesir University
Faculty of Science and Literture
Department of Chemistry
10145 Çağış/Balıkesir - TURKEY

e-mail: mdogan@balikesir.edu.tr