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Journal of Hazardous Materials 149 (2007) 650–656
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

# Electrokinetic and adsorption properties of sepiolite modified by 3-aminopropyltriethoxysilane

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Received 20 December 2006; received in revised form 5 April 2007; accepted 6 April 2007
Available online 19 April 2007

## Abstract

Surface modification of clay minerals has become increasingly important for improving the practical applications of clays such as fillers and adsorbents. An investigation was carried out on the surface modification of sepiolite with aminopropylsilyl groups in 3-aminopropyltriethoxysilane (3-APT). The zeta potential of the modified sepiolite suspensions was measured as a function of initial electrolyte concentration and equilibrium pH using a Zeta Meter 3.0 for modified sepiolite. The utility of the 3-APT-modified sepiolite was investigated as an adsorbent for removal of various heavy metal ions such as Fe, Mn, Co, Zn, Cu, Cd and Ni from aqueous solutions. The effects of various factors on the adsorption, such as pH, ionic strength and temperature of the solution were studied. The results showed that the amount adsorbed increases with solution pH in the pH range of 1.5 and 7.0; indicated that the modified sepiolite adsorbed Fe and Mn ions more than other metal ions such as Co, Zn, Cu, Cd and Ni. It was found that the temperature had an important effect on metal ion adsorption by the modified sepiolite. The adsorption isotherm has been determined and data have been analyzed according to the Langmuir and Freundlich models.

*Keywords:* Modification; Sepiolite; 3-Aminopropyltriethoxysilane; Zeta potential; Adsorption; Metal ions

## 1. Introduction

The toxic effects of heavy metals present many risks to humans, particularly in the case of water and food [1,2]. When heavy metal contents are monitored in natural water, of paramount importance is a reliable indication of the effect to the normal life of a given community [2,3]. Even low concentrations of heavy metals (ppb) in natural water supplies can have detrimental effects on wildlife and humans [4]. The presence of heavy metals in the environment has been of great concern because of their growing discharge, toxicity and other adverse effects on receiving waters. Therefore, the removals of heavy metals are very important in environmental remediation and clean up. Although there are several conventional methods of removing these metals, such as precipitation, reverse osmosis, ultra filtration, electrodeposition, solvent extraction, ion flotation, these techniques have limitations, such as metal solubility limits, high-pressure operation, etc. [5]. The adsorption on activated carbon has been applied for many years for the removal of heavy metals [6]. Despite the prolific use of activated carbon, it remains an expensive material since the higher the quality, the greater its cost. Due to the relatively high cost of activated carbons, there has been a substantial body of attempts to utilize low cost, naturally occurring adsorbents to remove environmentally toxic contaminants from wastewaters [7].

Clay minerals, synthetic or natural, are an important, plentiful, and low-cost class of materials with unique swelling, intercalation, and ion-exchange properties [8]. Clay minerals also exhibit wide surface properties that include surface modification through ion-exchange reactions and chemical modification with organosilanes (organochlorosilanes and organosiloxanes). In the first case, the presence of cation exchange sites at the edges offers an easy route for accommodating charged entities with specific functionalities. In the second case, the organosilane is attached to the clay edges through condensation reactions between the surface hydroxyl groups and the chloro- or alkoxy-groups of the organosilane, thus affording Si–O–Si or Al–O–Al covalent bonds [9,10]. The behavior of various materials functionalized with polypeptides and other

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doi:10.1016/j.jhazmat.2007.04.036

molecules is a topic of interest because of its applications in affinity separations, biosensors, and other uses involving site-specific interactions [11]. An example of the latter involves the removal of heavy metals from aqueous solutions [12–15]. The organofunctionalization of inorganic solid surfaces is normally used to introduce basic groups on anchored pendant chains [16,17]. The synthesised materials change the properties of the original matrix, with the preference for trace metals from solvents, by adsorbing these contaminants on the chemically modified surface [18,19].

Silane coupling agents are a family of organosilicon monomers, which are characterized by the general structure R–$SiX_3$. R is an organo-functional group attached to silicon in a hydrolytically stable manner. X designates hydrolysable alkoxy groups (usually methoxy, –$OCH_3$, or ethoxy, –$OC_2H_5$), which are converted to silanol groups by hydrolysis. Most commonly R is composed of a reactive group R′ separated by a propylene group from silicon, $R'–(CH_2)_3–SiX_3$. The reactive group can, for example, be vinyl (–$HC{=}CH_2$), amino (–$NH_2$), or mercapto (–SH) or can contain several chemical functional groups. If the silane should interact with a clay surface, and thus form chemical bonds at the interface, it must first be converted to the reactive silanol form by hydrolysis [7,20]. This hydrolysis can occur directly on the substrate surface by reaction with water on the surface (direct hydrolysis) or in a previous step during preparation of the aqueous solution of the silane (pre-hydrolysis). Silane coupling agents are capable of providing chemical bonding between an organic material and an inorganic material [21,22]. This sole property of silanes is utilized widely in the application of the silane coupling agents for the surface treatment of glass fiber products, performance improvement of fiber-reinforced plastics, improvement of paints and other coating materials and adhesives, modification of surface properties of inorganic fillers, and surface priming of various substrate materials [23].

Clays consist mainly of plate-like particles, which when in contact with water, usually have negatively charged faces and positively charged edges. The physical properties of clay–water systems such as sedimentation, filtration, swelling, viscosity, yield stress and structural strength are extremely sensitive to the nature of the electrical double layer around the particles and the tendency of the particles to aggregate. Zeta potential is an important and useful indicator of this charge which can be used to predict and control the stability of colloidal suspensions or emulsions. The greater the zeta potential the more likely the suspension is to be stable because the charged particles repel one another and thus overcome the natural tendency to aggregate. The measurement of zeta potential is often the key to understand dispersion and aggregation processes in applications as diverse as water purification, ceramic slip casting and the formulation of paints, inks and cosmetics. Zeta potential measurements provide particularly relevant information where colloid stability and/or ion adsorption is involved [24–26].

There are numerous studies evaluating the clay minerals modified by grafting coupling agents. But there are almost no studies reporting the modification of sepiolite, except our previous attempt, which was modified in this study [27]. Oztürk and Bektaş [28], and Alkan et al. [29] investigated the removal of different dyestuffs from aqueous solutions using various sepiolite samples. Sepiolite belongs to the phyllosilicate group of clay minerals with a 2:1 ribbon structure. It is composed of continuous and two-dimensional tetrahedral layers with $T_2O_5$ (T:Si, Al) composition and discontinuous octahedral layers. Octahedral layer discontinuity leads to the formation of internal channels in the structure, which provides high adsorption capacity [30,31]. The well-known sepiolite deposit in Turkey is in Eskisehir (Anatolia) [32,33].

One of main aims in this study has shown whether modified sepiolite can be used as a chemical sensor for various metals. Therefore, in this paper, it was firstly modified the sepiolite with 3-aminopropyltriethoxysilane (3-APT) in the presence of toluene solvent as a dispersing medium. Then, it has been investigated (i) the electrokinetic properties of the modified sepiolite as a function of equilibrium pH and electrolyte concentration, and (ii) the removal of metal ions from aqueous solutions by the modified sepiolite as a function of pH, ionic strength and temperature. The experimental values have been analyzed according to Langmuir and Freundlich isotherms. In the previous study, these properties of modified sepiolite have not been reported.

## 2. Material and methods

### 2.1. Materials

Sepiolite sample used in this study was obtained from Aktaş Lületaşı Co. (Eskişehir, Turkey). The chemical composition of sepiolite has consisted of 53.47 $SiO_2$, 23.55 MgO, 0.71 CaO, 0.19 $Al_2O_3$, 0.16 $Fe_2O_3$, 0.43 NiO and 21.49 loss of ignition as percent weight. The cation exchange capacity of sepiolite is 25 meq 100 $g^{-1}$; the density 2.55 g $cm^{-3}$; the specific surface area 342 $m^2$ $g^{-1}$; particle size in the range of 0–50 μm [34]. All chemicals were obtained from Merck and Aldrich, and were of analytical grade.

### 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 [35]: 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 are used in further experiments.

### 2.3. Surface modification of sepiolite with silane coupling agent

Sepiolite (10 g) suspended in toluene (100 mL) was refluxed and mechanically stirred for 1h under dry nitrogen. To this suspension 3-APT (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 and weighed [36]. The weight of sepiolite modified was determined as 10.364 g. In this case, it can be said that the mass difference is 0.364 g. The characterization of modified sepiolite was given in reference [27].

### 2.4. Zeta potential measurements

The zeta potential of 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's equation, the most elementary expression for zeta potential gives a direct relation between zeta potential and electrophoretic mobility,

$$\zeta = \frac{4\pi\eta}{\varepsilon}U \qquad (1)$$

where $U$ is electrophoretic mobility at actual temperature, $\eta$ the viscosity of the suspending liquid, $\varepsilon$ the dielectric constant, $\pi$ the constant and $\zeta$ is zeta potential. The zeta potential measurements were carried out as a function of the initial electrolyte concentration and equilibrium pH. A sample of 0.1 g the modified-sepiolite in 50 mL distilled water containing desired electrolyte 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 [37].

### 2.5. Adsorption experiments

Equilibrium data of the modified sepiolite with aqueous solution containing metal ions were obtained by batch operations. Adsorption experiments were carried out in 100-mL polyethylene flasks by shaking 0.1-g modified sepiolite samples with various amounts of stock metal ions at 25 °C and natural solutions pH, except those in which varying conditions of pH, ionic strength and temperature were investigated. A preliminary experiment revealed that about 24 h is required for metal ions to reach the equilibrium concentration. The modified sepiolite was placed in a flask containing 50 mL of metal solutions. The metal concentrations in the experiments were in the range of $1.53 \times 10^{-5}$ to $1.45 \times 10^{-3}$ mol $L^{-1}$. The flasks were shaken mechanically in terms of an orbital shaker incubator for 24 h at 25 °C. The effect of pH and temperature on the adsorption of heavy metals ($Cu^{+2}$, $Ni^{+2}$, $Co^{+2}$, $Zn^{+2}$, $Cd^{+2}$, $Mn^{+2}$, $Fe^{+3}$) was also studied. It was used the nitrate salts of metal ions in the experiments. A thermostated orbital shaker incubator was used to keep the temperature constant. 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. The concentration of metal ions was determined by AAS (Unicam 929). Blanks containing no metal ion were used for each series of experiments. The amounts of metal ions adsorbed were calculated from the concentrations in solutions before and after adsorption using equation below [38]:

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

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

## 3. Results and discussion

The experimental data obtained from zeta potential measurements and adsorption properties of modified sepiolite with 3-aminopropyltriethoxysilane has been discussed as follows.

### 3.1. Zeta potential

The properties of modified materials strictly differ. The surface charge can vary from negative to positive, depending on particle concentration. The metal adsorption process is influenced by the structure of modified material and accessibility [27]. Electrokinetic behavior of modified sepiolite in the presence of metal ions is shown in Fig. 1. 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 [39]. The zeta potential of modified sepiolite in the presence of various metal ions appears to exhibit similar trend. Adsorption of such ions onto sepiolite through specific attraction impart sepiolite more positive charges. Sepiolite is a clay mineral with ion exchange properties. Therefore, for each metal adsorbed, an equivalent amount of Mg(II) ion is released from the sepiolite surface [39]. The results indicate that increasing metal concentration makes the surface more positive with changing the sign of the surface charge. This strong dependency arises from the compression of the electrical double layer at the sepiolite surface as well as the exchange of metal ions by

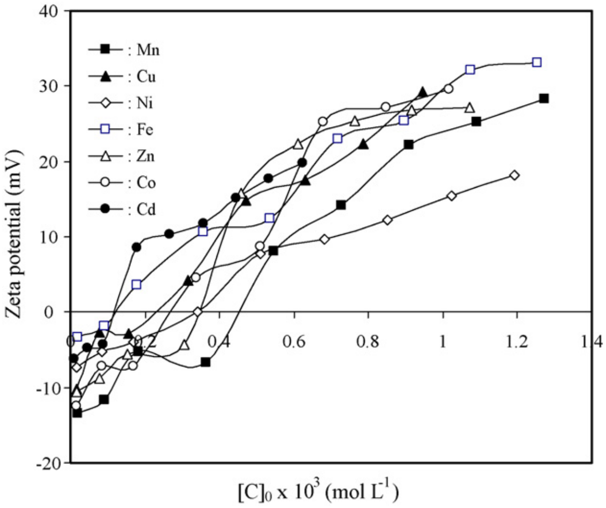


Fig. 1. The change in zeta potential with initial metal concentration.

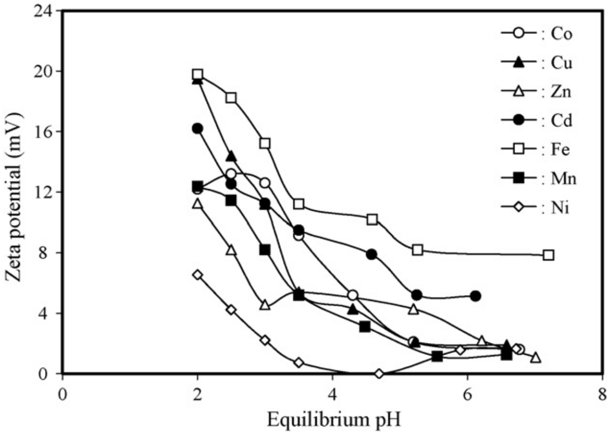


Fig. 2. The change in zeta potential with equilibrium pH.

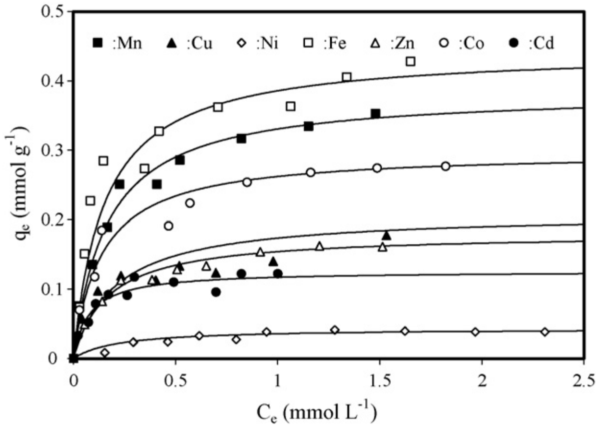


Fig. 3. The isotherm plots of metal ions on the modified sepiolite.

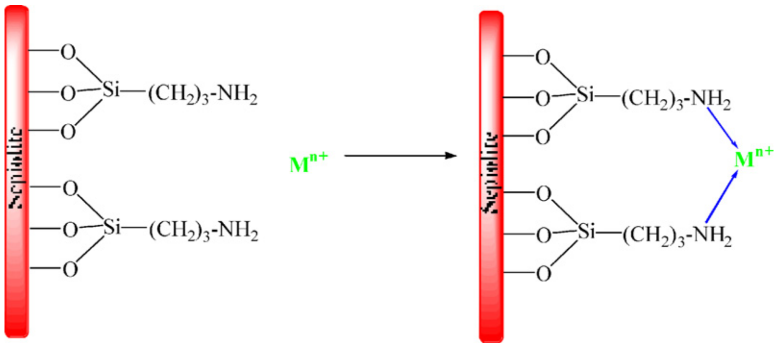
the Mg(II) ions in the sepiolite structure. In this case, it can be said that metal ions adsorb specifically on the modified sepiolite. Both mechanisms favor the surface to acquire more positive charges.

The zeta potential, which is dependent on pH, shows a characteristic behavior for the modified particles. A mixture of 0.3 g sepiolite in 100 mL of distilled water yields a natural pH of 7.13 [40]. Since the isoelectric point (iep) of natural sepiolite–water system was previously determined at pH 6.6 [40], the sepiolite surface at natural pH exhibits negative charges. These negative charges increase with increasing pH. Fig. 2 shows the changing of the zeta potential with equilibrium pH of sepiolite modified by 3-APT in the presence of different metal ions. As shown in Fig. 2, it is seen that the isoelectric point of the modified sepiolite in the presence of various metal ions shifts to higher pH values due to specific adsorption. These results are another clue showing the modification of natural sepiolite by 3-APT. Again, it can be said that the surface properties of natural sepiolite by modification change.

### 3.2. *Adsorption*

#### 3.2.1. *Equilibrium isotherm*

The ability of the modified sepiolite to adsorb the cations from aqueous solution was evaluated by measuring the adsorption isotherms for a series of divalent and trivalent cations, such as Fe, Mn, Co, Cd, Cu, Zn and Ni. Under equilibrium conditions, the adsorption processes between adsorbent and adsorbate can be characterized by the amount of adsorbed metal ions per gram of the modified sepiolite ($q_e$). This value was calculated from the initial concentration of cation added ($C_0$) and those at the equilibrium point ($C_e$). Profiles of the adsorption isotherms for all cations in water are shown in Fig. 3, representing the amount of adsorbed metal ions versus the concentration of the solution under equilibrium conditions. A simple observation of these profiles, which define the maximum adsorption values, can lead to a perfect distinction of these cations, from the point of view of adsorption [16]. The isotherms presented in Fig. 3 showed that the adsorption followed the sequence Fe > Mn > Co > Cd > Zn > Cu > Ni. This behavior reflects the high affinity of the amino basic centres for iron and mangane. This fact suggests that this surface is more favorable in reacting with hard cations. In the light of these observations, this material could be potentially applied as a selective electrode when the objective is to determine or identify hard acids [16]. The adsorbed amounts of modified and natural sepiolites were $3.01 \times 10^{-4}$ and $14.09 \times 10^{-4}\,\mathrm{mol\,g^{-1}}$ for Mn(II), $1.38 \times 10^{-4}$ and $29.0 \times 10^{-4}\,\mathrm{mol\,g^{-1}}$ for Cu(II), $0.21 \times 10^{-4}$ and $9.2 \times 10^{-4}\,\mathrm{mol\,g^{-1}}$ for Ni(II), $3.96 \times 10^{-4}$ and $33.6 \times 10^{-4}\,\mathrm{mol\,g^{-1}}$ for Fe(III), $1.25 \times 10^{-4}$ and $24.63 \times 10^{-4}\,\mathrm{mol\,g^{-1}}$ for Zn(II), $2.22 \times 10^{-4}$ and $13.52 \times 10^{-4}\,\mathrm{mol\,g^{-1}}$ for Co(II), and $1.12 \times 10^{-4}$ and $6.76 \times 10^{-4}\,\mathrm{mol\,g^{-1}}$ for Cd(II) at 25 °C, respectively. According to the explanation in above, it can be written the reaction between modified sepiolite and metal ions as follows:



(3)

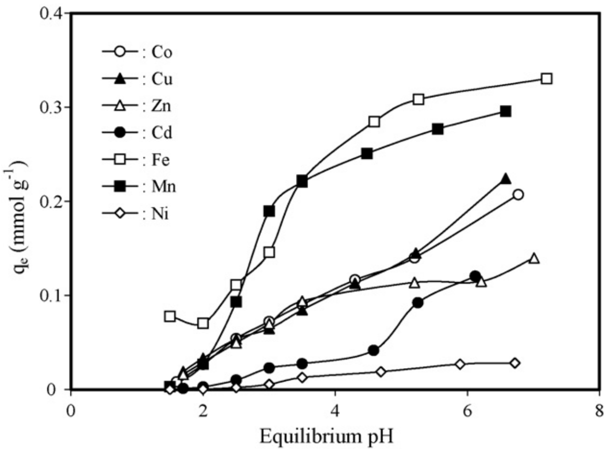


Fig. 4. The change in the amount adsorbed with equilibrium pH.

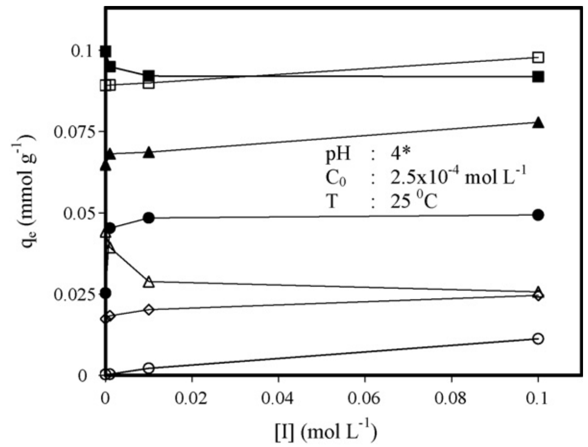


Fig. 5. The change in the amount adsorbed with ionic strength (○, Fe; ■, Mn; ●, Co; △, Cd; □, Cu; ▲, Zn; ◊, Ni), symbol '*' denotes pH 2.5 for Fe.

### 3.2.2. Effect of equilibrium pH

The adsorption of metal ions onto the modified sepiolite as a function of equilibrium pH is shown in Fig. 4. Metal ions were adsorbed on the modified sepiolite in the pH range 1.5–7.0. The pH values, which the chemical precipitation of metal hydroxides occurs, are 9.05, 5.62, 8.08, 2.48, 6.99, 8.10 and 8.77 at $3.63 \times 10^{-4}$, $3.15 \times 10^{-4}$, $3.41 \times 10^{-4}$, $3.58 \times 10^{-4}$, $3.06 \times 10^{-4}$ and $3.36 \times 10^{-4}$ mol L$^{-1}$ for Mn(II), Cu(II), Ni(II), Fe(III), Zn(II), Co(II) and Cd(II), respectively. It can be said that the removal amount up to these pH values may be due to the chemical preciptations of metal hydroxides. The adsorption of metal ions increases with increasing pH. It can be seen that the adsorption of metal ions onto the modified-sepiolite is markedly pH-dependent. As expected, the adsorption of metals decreases with decreasing pH because the hydroxyl groups on the unmodified-sepiolite and amine groups on the modified sepiolite are more protonated and, hence, they are less available to retain the investigated metals. The reason for this is that the surface complexation reactions are influenced by the electrostatic attraction between negatively charged groups at the modified-sepiolite surface and the ions [41,42].

### 3.2.3. Effect of ionic strength

Investigations carried out on adsorption revealed that the extent of waste uptake was strongly influenced by the concentration and nature of the electrolyte ionic species added to the aqueous media [38]. In this study, NaCl was chosen as a salt for investigating the effect of ionic strength to the adsorption of various metal ions on modified sepiolite surface. The effect of ionic strength on adsorption capacity of modified sepiolite was studied by carrying out a series of isotherms at $1 \times 10^{-3}$, $1 \times 10^{-2}$ and $1 \times 10^{-1}$ mol L$^{-1}$ NaCl salt concentrations at constant metal ion concentration as shown in Fig. 5. The results have shown that there is not an important changing in the adsorption capacity of modified sepiolite with increasing concentration of sodium chloride.

### 3.2.4. Effect of temperature

A study of the temperature dependence of adsorption reactions gives valuable information about the enthalpy change during adsorption. The effect of temperature on the adsorption isotherm was studied by carrying out a series of isotherms at 25, 35, 45 and 55 °C for the modified sepiolite, as shown in Fig. 6. As depicted in Fig. 6, the amount of metal ions adsorbed per unit of adsorbent increased from $13.1 \times 10^{-5}$ to $33.5 \times 10^{-5}$ mol g$^{-1}$; $6.1 \times 10^{-5}$ to $17.4 \times 10^{-5}$ mol g$^{-1}$; $11.6 \times 10^{-5}$ to $21.1 \times 10^{-5}$ mol g$^{-1}$; $11.4 \times 10^{-5}$ to $25.4 \times 10^{-5}$ mol g$^{-1}$; $11.3 \times 10^{-5}$ to $24.5 \times 10^{-5}$ mol g$^{-1}$; $4.2 \times 10^{-5}$ to $7.4 \times 10^{-5}$ mol g$^{-1}$; $1.2 \times 10^{-6}$ to $3.6 \times 10^{-5}$ mol g$^{-1}$ for Fe, Mn, Co, Zn, Cu, Cd and Ni, respectively, when temperature increased from 25 to 55 °C, which indicates that the temperature has an important effect on the adsorption. Results indicate that the adsorption capacity increases with increase in temperature. 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 greater than for the forward reaction and consequently the equilibrium capacity decreases with increased temperature [38]. The fact that the adsorbed amount of metal ions increases with increase in temperature shows that the adsorption process is an endothermic process.

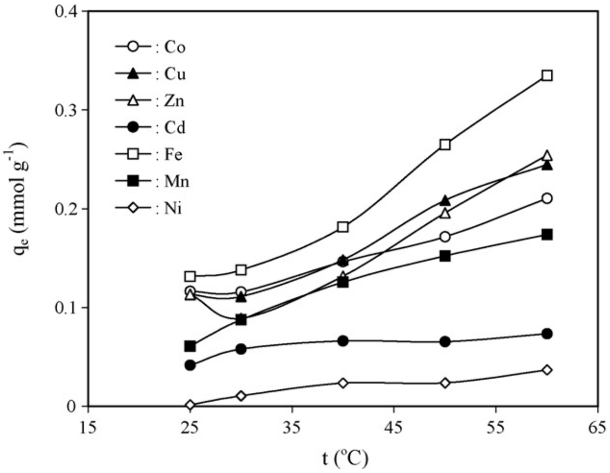


Fig. 6. The change in the amount adsorbed with temperature.

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

| Metals | $t$ (°C) | pH | Langmuir isotherm | | | Freundlich isotherm | | |
|---|---|---|---|---|---|---|---|---|
| | | | $q_m \times 10^4$ (mol g$^{-1}$) | $K \times 10^5$ (L mol$^{-1}$) | $R^2$ | $n$ | $K_F \times 10^3$ | $R^2$ |
| Mn | 25 | 4.0 | 3.840 | 0.096 | 0.996 | 2.605 | 4.917 | 0.936 |
| Cu | 25 | 4.0 | 1.452 | 0.224 | 0.998 | 3.872 | 0.978 | 0.866 |
| Ni | 25 | 4.0 | 0.446 | 0.061 | 0.988 | 3.610 | 0.929 | 0.745 |
| Fe | 25 | 3.0 | 4.442 | 0.130 | 0.990 | 2.871 | 4.409 | 0.824 |
| Zn | 25 | 4.0 | 1.810 | 0.086 | 0.994 | 2.895 | 1.698 | 0.940 |
| Co | 25 | 4.0 | 2.976 | 0.114 | 0.993 | 3.138 | 2.295 | 0.914 |
| Cd | 25 | 4.0 | 1.263 | 0.115 | 0.981 | 3.104 | 1.254 | 0.848 |

### 3.3. Adsorption isotherm

The equilibrium isotherm for the sorption of metal ions was measured experimentally and the experimental points are shown in Fig. 3 as a plot of equilibrium solid phase concentration, $q_e$, versus equilibrium liquid phase concentration $C_e$. The data were analyzed by two isotherm equations, namely the Langmuir and Freundlich equations. The Langmuir isotherm can be derived from the Gibbs approach. The Langmuir equation for a liquid state sorption system is as follows [25,34,35,37,38,43]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K} + \frac{1}{q_m} C_e \qquad (4)$$

where $C_e$ is the equilibrium concentration of adsorbate in solution (mol L$^{-1}$), $q_e$ the equilibrium loading of adsorbate on adsorbent (mol g$^{-1}$), $q_m$ the ultimate adsorption capacity (mol g$^{-1}$), and $K$ is the relative energy of adsorption (L mol$^{-1}$). The Langmuir model can be linearized to obtain the parameters $q_m$ and $K$ from experimental data on equilibrium concentrations and adsorbent loading.

The most important multi-site adsorption isotherm for heterogeneous surfaces is the Freundlich adsorption isotherm:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (5)$$

where $K_F$ and $n$ are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. So, the plot of $\ln q_e$ against $\ln C_e$ of Eq. (5) should give a linear relationship, from which $1/n$ and $K_F$ can be determined from the slope and the intercept, respectively. The two isotherm equations were linearized and minimized using a Microsoft Excel program to obtain the optimum isotherm coefficients. The coefficients are presented in Table 1. The correlation coefficients of each isotherm equations are also shown in Table 1. The Langmuir isotherm exhibits extremely high correlation coefficients, which provides considerably better fits to the experimental data than the Freundlich isotherm. The Freundlich isotherm was developed to describe heterogeneous surface isotherms. In this case, there is a continuously varying energy of adsorption as the most actively energetic sites are occupied first and the surface is continually occupied until the lowest energy sites are filled at the end of adsorption process. The main characteristic of the Langmuir equation is that it is based on the assumption that all sites have equal adsorption energies.

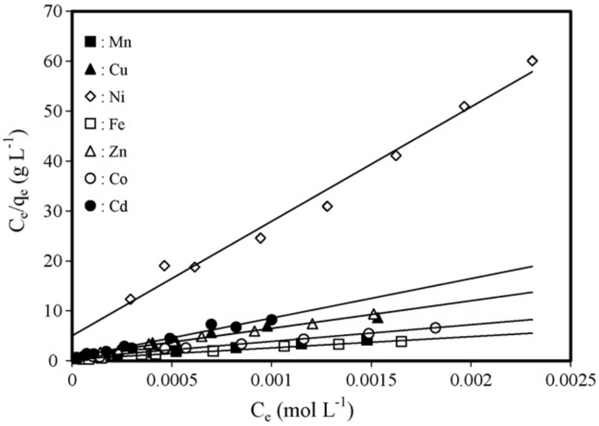


Fig. 7. Langmuir isotherm plots for the data of Fig. 3.

Fig. 7 shows Langmuir theoretical curves for the experimental data in Fig. 3. The maximum adsorption capacities ($q_m$) were $4.442 \times 10^{-4}$, $3.840 \times 10^{-4}$, $2.976 \times 10^{-4}$, $1.810 \times 10^{-4}$, $1.452 \times 10^{-4}$, $1.263 \times 10^{-4}$, $0.446 \times 10^{-4}$ mol g$^{-1}$ for Fe, Mn, Co, Zn, Cu, Cd and Ni, respectively. An inspection of the $q_m$ values above demonstrate that iron and mangane is easily the most effective in binding to the pendant groups.

### 3.4. Conclusions

According to our results, the modified sepiolite presents a high affinity for metal ions, due to the presence of a basic amino centre. This surface also presents a good adsorption capability for other divalent cations, which permits its use in the adsorption of toxic metal ions from aqueous solutions. Adsorption isotherm of Fe, Mn, Co, Cu, Cd, Ni and Zn from aqueous solution suggests that adsorption density follows the sequence Fe > Mn > Co > Cd > Zn > Cu > Ni. The adsorption of metal ions on the modified sepiolite decreases with decreasing pH. At low pH values, the hydrogen ion competes with heavy metals towards the superficial sites and, moreover, the Si–O$^-$ and Al–O$^-$ groups are less deprotonated and they form complexes with bivalent and trivalent ions in solution with greater difficulty. The separation of divalent cations with this surface suggests scope for exploitation in chromatographic applications. On the other hand, in exploring the selectivity in binding Fe and Mn, this behavior suggests its possible use in the manufacture of a chemical sensor for this toxic metal.

## Acknowledgment

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

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