

## Adsorption of copper (II) ions onto sepiolite and electrokinetic properties

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### Abstract

We investigated the electrokinetic properties of sepiolite suspensions using the microelectrophoresis technique as a function of pH in the presence of various electrolytes such as, LiCl, NaCl, KCl, Cu(NO<sub>3</sub>)<sub>2</sub>, CaCl<sub>2</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, AlCl<sub>3</sub> and Fe(NO<sub>3</sub>)<sub>3</sub> and then, the adsorption of Cu(II) ion onto sepiolite from aqueous solutions as a function of pH, ionic strength and temperature. We found that (1) zeta potential of sepiolite suspensions increased with increasing ionic strength, (2) zeta potential values of sepiolite suspensions in different valence electrolyte solutions in the studied pH ranges increased with increase in electrolyte valence, (3) sepiolite had an isoelectrical point at pH 6.6, (4) the monovalent electrolytes showed similar behavior in the studied pH ranges but di- and trivalence electrolytes different behaviour, (5) Cu(II) ion adsorption increased with increase in pH and temperature, and decrease in ionic strength. Furthermore, experimental data were correlated reasonably well by the Langmuir adsorption isotherm. Adsorption enthalpy was calculated as 24 kJ/mol. The interaction between the sepiolite surface and Cu(II) ions was concluded to be a physical process.

*Keywords:* Sepiolite; Zeta potential; Adsorption; Electrolyte; Copper; Adsorption isotherm

### 1. Introduction

Developments in technology have led to the release of heavy metals which are hazardous to the environment [1]. The presence of metals in aquatic environments has been known to cause several health problems to animals and human

beings [2]. Because of their toxicity and non-biodegradable nature, metals are of special significance. The heavy metal levels in wastewater, drinking water, and water used for agriculture must be reduced to the maximum permissible concentration. For example, copper concentration in the drinking water samples was in the range of 0.17–1.19 mg/L [3]. Precipitation, ion exchange, solvent extraction, electrolysis, reverse osmosis

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and ultrafiltration carbon are the conventional methods for the removal of heavy metal ions from aqueous solutions [2,4–8] but due to high maintenance cost these methods do not suit the needs of developing countries [9]. On the other hand, adsorption process modeling is nowadays a topic of interest for the prediction of the metal partitioning between the aqueous solution and the solid surface, and its subsequent application to the design of adsorption treatment units, as well as for the evaluation of the fate of heavy metals in natural environments [2]. The adsorption process is used especially in the water treatment field and the investigations have been made to determine low cost and good adsorbents [8]. It has been demonstrated that certain cheaply available, naturally abundant clays have the potential to remove heavy metals from dilute wastewater by an adsorption process and thus offer an alternative to existing technologies.

Sepiolite is a hydrous magnesium silicate characterized by its fibrous morphology and intracrystalline channels. It owes much of its industrial applications to its molecular sized channels and large specific surface area (more than 200 m<sup>2</sup>/g) [10]. Sepiolite is used in a variety of industries including cosmetics, ceramics, detergents, paper and paint. High-capacity values were also observed for heavy metal removal and wastewater treatment [11,12]. The abundance and availability of sepiolite reserves together with its relatively low cost guarantee its continued utilization. Most of the world's sepiolite reserves are found in Turkey. Thus, it is important to characterize this clay mineral and evaluate how its relevant physicochemical properties are altered during chemical and thermal treatment. Sorption depends heavily on experimental conditions such as pH, temperature and ionic strength [13,14]. Sepiolite has attracted remarkable attention by its sorptive, rheological and catalytic properties, and the use of sepiolitic clays is expanding [15–18].

Charge formation, density and changes due to adsorption and desorption of solutes are directly

reflected in the electrokinetic behaviour of clay minerals. All electrokinetic phenomena are related to the development of electrical double layer at the particle/electrolyte interface [19–21]. The study of the electrochemical properties of the clay/water interface is important to understand a large number of properties of clay-rich porous media and colloid suspension of clays [22]. Otherwise, electrokinetic properties such as the isoelectric point (iep) and potential determining ions (pdi) of fine particles in an aqueous solution play a significant role in understanding the adsorption mechanism of inorganic and organic species at the solid/solution interface [23]. The zeta potential ( $\zeta$ ) is defined as the potential of shear plane of the particle when it moves in liquid. The principal reason for determining the  $\zeta$ -potential was to obtain an indication of the magnitude of the potential at the beginning of the diffuse double layer around the particle [20,21].

There are a number of works related to the removal of metal ions from aqueous solutions. For example, Hadjar et al. investigated the adsorption of heavy metal ions on composite materials prepared by modification of natural silica [24]; Basci et al. biosorption of copper (II) from aqueous solutions by wheat shell [25]; Chuah et al. rice husk as a potentially low-cost biosorbent for heavy metal and dye removal [26]; Sarioglu et al. the removal of copper from aqueous solutions by phosphate rock [27]; Larous et al. the experimental study of the removal of copper from aqueous solutions by adsorption using sawdust [28]; Kocaoba et al. the kinetics and equilibrium studies of heavy metal ions removal by use of natural zeolite [29].

It has been reported that sepiolite has a high adsorptive capacity for many gases and vapours, especially when the dimensions of their molecules allow them to penetrate into the channels of the adsorbent [30,31]. It has been also used as adsorbent of dyes [32–34] and pesticides [35], as a catalyst support [36,37], and also as a support material on the methanogenesis from sewage

sludge, reducing the toxic effect of some heavy metals [38]. The aim of this research is to investigate (1) the  $\zeta$ -potential of sepiolite suspensions as a function of pH for better understanding of the electrical properties of contaminated minerals, and (ii) the adsorption of Cu(II) ion onto sepiolite from aqueous solutions as a function of pH, ionic strength and temperature. Adsorption isotherms and thermodynamic parameters of the adsorption are also presented.

## 2. Material and methods

### 2.1. Material

The sepiolite sample used in this study was obtained from Aktaş Lületaşı (Eskişehir, Turkey). All chemicals were obtained from Merck, and were of analytical grade. Some physicochemical properties of sepiolite used in this study have been given in Table 1 [33]. X-ray powder diffraction (XRD) analysis was performed on an Analytical Philips X'Pert-Pro X-ray diffractometer equipped with a back monochromator operating 40 kV and a copper cathode as the X-ray source ( $\lambda = 0.154$  nm). Fig. 1 shows XRD spectra of copper loaded and natural sepiolites.

### 2.2. Purification of sepiolite particles

Sepiolite samples were treated before using in the experiments in order to obtain a uniform size sample of adsorbent as follows [39]: the suspension containing 10 g/L sepiolite was mechanically stirred for 24 h, after waiting for about 2 min

Table 1  
Physicochemical properties of sepiolite

Parameters	Value
Surface area ( $\text{m}^2 \text{g}^{-1}$ )	342
Density ( $\text{g cm}^{-3}$ )	2.5
Cation exchange capacity ( $\text{meg } 100\text{g}^{-1}$ )	25
pH of solution	7.8–8.3

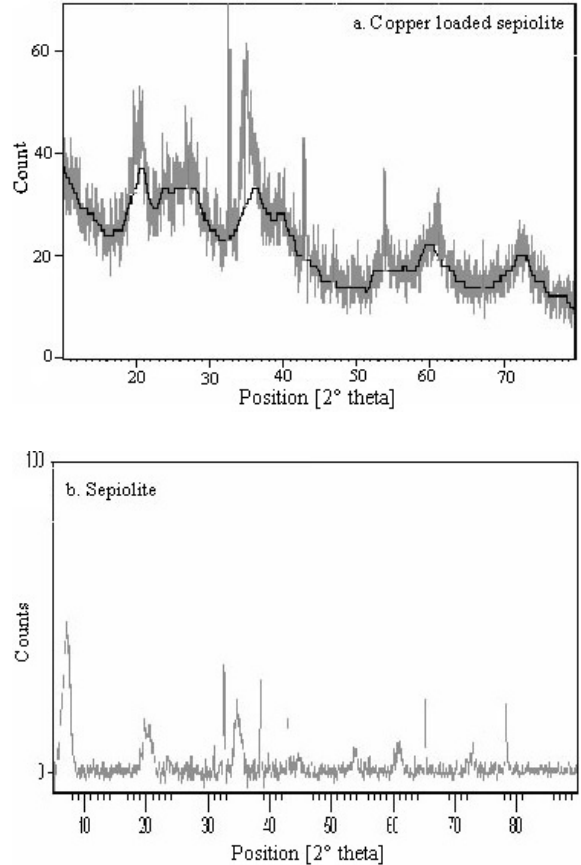


Fig. 1. XRD spectra of sepiolite samples.

the supernatant suspension was filtered through white-band filter paper ( $\Phi = 12.5$  cm). The solid sample was dried at  $105^\circ\text{C}$  for 24 h, ground then sieved by a  $75 \mu\text{m}$  sieve. The particles under  $75 \mu\text{m}$  are used in further experiments.

### 2.3. Zeta potential measurements

The zeta potential of sepiolite suspensions was measured using a Zeta Meter 3.0 (Zeta Meter) 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:

$$\zeta = \frac{4\pi V_t}{D_t} \times EM \quad (1)$$

where  $EM$  is electrophoretic mobility at actual temperature (Volt s/cm<sup>2</sup>),  $V_t$  is viscosity of the suspending liquid (cm<sup>2</sup>/s),  $D_t$  is the dielectric constant,  $\pi$  is constant and  $\zeta$  is the zeta potential (mV) [39]. The zeta potential measurements were carried out as a function of the solid to liquid ratio and pH. A sample of 0.3 g sepiolite in 100 mL distilled water containing desired electrolytes was added to a thermostatic shaker bath 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.

#### 2.4. Adsorption experiments

The adsorption experiments were carried out by mechanically shaking 0.25 g of the sepiolite with 50 mL of aqueous solution containing the desired concentration of copper ion for the required pH, ionic strength and temperature in 100 mL sealed plastic polyethylene containers. Cu(II) aqueous solutions were prepared from copper nitrate. Constant ionic strength at 1×10<sup>-2</sup> M NaCl was used in all experiments as background electrolyte. The solution pH was controlled by addition of 0.1 M HCl and NaOH. The desired solution temperature was controlled by the use of a constant temperature water bath. The resulting supernatant was analyzed for residual copper-ion concentration by atomic absorption spectroscopy (Unicam 929). The amount of copper adsorbed by sepiolite was determined by the difference between the total concentration of

copper at the beginning of the experiment and the copper concentration on sepiolite measured by AAS after adsorption according to Eq. (2):

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

where  $C_0$  and  $C_e$  are the initial and equilibrium liquid-phase concentrations of copper solution (mol/L), respectively;  $q_e$  is equilibrium Cu(II) concentration on adsorbent (mol/g),  $V$  is the volume of Cu(II) solution (L), and  $W$  is the mass of sepiolite sample used (g) [40].

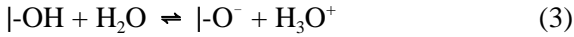
### 3. Results and discussion

#### 3.1. Electrokinetic properties

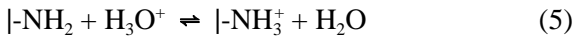
Discussing the source of surface charges on the oxide surfaces may be more useful before investigating the change of zeta potential with equilibrium pH of sepiolite suspensions in various electrolyte media. There are few processes leading to charge separation at interfaces and the resulting formation of double layers. Electrokinetic properties of oxides are greatly affected by edge faces. Active hydroxyl sites are located on these planes. The surface of a colloid particle in an electrolyte solution is almost always electrically charged. There are three main mechanisms responsible for the charging of the surface: (1) ion adsorption, (2) surface dissociation, and (3) isomorphic replacement of ions of the solid phase by others of a different charge [20,41].

Changes in pH of aqueous solution affect the ion-exchange mechanism controlling the electrostatic forces. An electrically charged particle surface attracts the ions of opposite sign (counter ions) and repels the ions of the same sign of the particle (co-ions) [42]. An electrical charge winning of oxide surfaces usually occurs as a result of the chemical ionization, which is a Brönsted acid/base type process. Functional groups usually bind –OH, –COOH or –NH<sub>2</sub>

groups on the polymers, silica or oxides. Ionization processes for –OH, –COOH or –NH<sub>2</sub> groups on surface can be given as follows [20,41].



and



The surface hydroxyl groups of the oxides have very important effect on the adsorption process. The silicon atoms at the oxide surfaces tend to maintain their tetrahedral coordination with oxygen [43,44].

In general, the effect of solid concentration on zeta potential is an important parameter governing the surface charge generation. This means that the ionic species produced at the solid–liquid interface increase with increased solid concentration and that using inadequate solid concentrations can lead to erroneous interpretation of zeta potential measurements. Experimental results have shown that solid concentration used has no significant effect on zeta potential (figure not shown). Therefore, in the subsequent zeta potential measurements, the solid-to-liquid ratio has been kept constant at 3 g/L.

Fig. 2 shows the variation of zeta potential with equilibrium pH of sepiolite suspensions at different concentrations of KCl electrolyte. As seen in the figure, the zeta potential value of sepiolite suspensions decreases with increase in its equilibrium pH and has approximately an isoelectrical point in the pH range of 6.6–6.7. The isoelectrical point is described as pH, at which particles have zero zeta potential. The isoelectrical point of an oxide is the sum of all interactions occurring at oxide/water interface such as the adsorption of H<sup>+</sup> and OH<sup>–</sup> ions and the distribution of dissolved lattice ions [45]. The hetero-

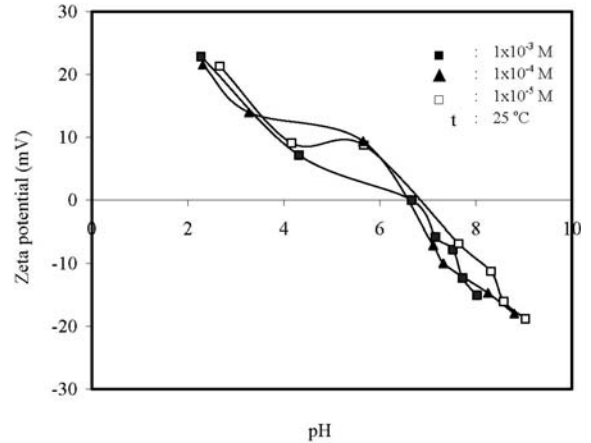


Fig. 2. Variation of zeta potential with equilibrium pH of sepiolite suspensions at different KCl concentrations.

geneity of oxide surfaces, any detected impurities and different pre-treatments such as leaching, washing, ultrasonic scrubbing may cause important changes in the iep and zeta potential values [46,47]. As the equilibrium pOH of suspension increases, the value of zeta potential changes from positive to negative. In this case, the zeta potential of sepiolite suspensions does not importantly change with increase in electrolyte concentrations. Therefore, KCl only affects the thickness of electrical double layer with increase in electrolyte concentrations. This means that KCl is an indifferent electrolyte [48]. As a result, the increase in the electrolyte concentration causes an increase in surface potential.

The results obtained in this study can also be explained with Debye–Hückel models. According to this model, the thickness of electrical double layer can be calculated with the following equation [19]:

$$\kappa = \left( \frac{2000 \cdot e^2 \cdot N_A \cdot I}{\epsilon_0 \epsilon k T} \right)^{1/2} \quad (6)$$

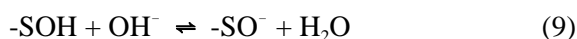
where 1/κ is the thickness of the diffuse layer; ε<sub>0</sub> is the permittivity of free space (C<sup>2</sup>m<sup>2</sup>/N); ε is the

relative permittivity of the medium;  $e$  is the electronic charge ( $\text{C}$ );  $k$  is Boltzmann's constant ( $\text{J/K}$ );  $N_A$  is the Avagadro's constant ( $\text{mol}^{-1}$ );  $T$  is the temperature ( $\text{K}$ ); and  $I$  is the solution ionic strength ( $\text{mol/L}$ ). The ionic strength of the solution as  $\text{mol/L}$  can be calculated as follows:

$$I = 0.5\sqrt{c_i z_i^2} \quad (7)$$

where  $c_i$  is the concentration of  $I$  ionic type and  $z_i$  is the valence of  $I$  ionic type. The thickness of the ionic atmosphere at particle surface depends on the ionic strength of aqueous media. According to Eq. (6), for a monovalent electrolyte, the thickness of electrical double layer decreases with increase in electrolyte concentration.

The electrical charge at the oxide surface/ aqueous phase on protonation/deprotonation of the surface hydroxyl can be described as [49].



and, at iep,

$$[-\text{SOH}_2^+] = [-\text{SO}^-] \quad (10)$$

The fact that sepiolite has an iep shows that the reaction responsible for the surface charge of the solid is mainly the reaction in Eq. (8) below the iep and in Eq. (9) above the iep, respectively. As seen in Fig. 2, at low pH the suspensions are positively charged, while at high pH the suspensions are negatively charged. Fig. 2 shows that sepiolite  $H_{iep}$  is approximately 6.6. In this case, Eq. (10) is valid. It can be said that the sepiolite surface protects its neutral character even though most silicates or clay minerals have an iep in the pH range of 2 to 4.

Fig. 3 also shows the effect of equilibrium pH on zeta potential of sepiolite suspensions in  $1 \times 10^{-3}$  mol/L LiCl, NaCl and KCl solutions.

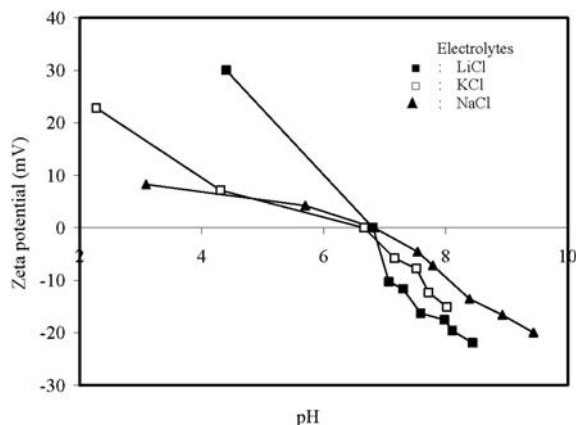


Fig. 3. Variation of zeta potential with equilibrium pH of sepiolite suspensions in the presence of different monovalent electrolytes at constant concentration.

Sepiolite suspensions have positive zeta potential at low equilibrium pH values and negative zeta potential at high equilibrium pH values. Again, as seen in Fig. 3, sepiolite suspensions for various electrolyte types have an isoelectric point in the pH range of 6.6 to 6.8. It seems that LiCl presents a different behaviour at pHs below the iep. The monovalent alkali cations naturally form a sequence, known as the Hofmeister series, based on the influence of the ion on the water in its vicinity. The Hofmeister series orders ions from the least hydrated ions to the most hydrated ions. Most investigations find that the adsorption sequence of monovalent cations on to silica surface follows the Hofmeister series ( $\text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ ) in greater quantities than  $\text{Li}^+$ . Electrophoretic mobility measurements generally indicate that the magnitude of the negative zeta potential at high pH increases as the Hofmeister series ( $\text{Cs}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+$ ) produce lower magnitude negative zeta potentials than  $\text{Li}^+$  [50,51].

The effect of equilibrium pH on zeta potential of sepiolite suspensions in  $1 \times 10^{-3}$  mol/L  $\text{CaCl}_2$ ,  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Cu}(\text{NO}_3)_2$  solutions is given in Fig. 4 where the zeta potential exhibited different behavior depending on electrolyte types. In  $\text{Cu}(\text{NO}_3)_2$  case, sepiolite suspensions have posi-

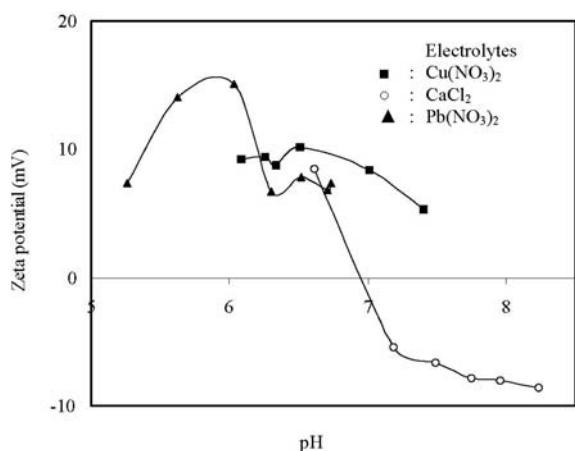
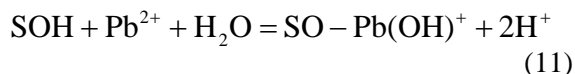


Fig. 4. Variation of zeta potential with equilibrium pH of sepiolite suspensions in the presence of different divalent electrolytes at constant concentration.

tive zeta potential in the equilibrium pH range of 6.0 to 7.5 and not to iep. This result has shown that the interactions between sepiolite and Cu(II) ions are very strong. As similar to behaviour of  $\text{Cu}(\text{NO}_3)_2$ , sepiolite suspensions in  $\text{Pb}(\text{NO}_3)_2$  solutions have exhibited positive zeta potential in the equilibrium pH range 5.2 to 6.7, and not to iep. Lead ions can find various forms as depending on pH values. For example, it finds  $\text{Pb}^{2+}$  form in the pH range of 4.0–5.5;  $\text{Pb}(\text{OH})^+$  form in the pH range of 5.5–9.0; and  $\text{Pb}(\text{OH})_2$  form in the pH range of 9.0–12.0 [52]. Therefore, lead ions in the pH range 5.2–6.0 are the  $\text{Pb}(\text{OH})^+$  form as shown in the reaction below:



The results obtained in this study can be explained by considering the  $\text{H}^+/\text{M}^{2+}$  stoichiometry: since specific adsorption of multivalent cations almost always involves proton exchange as indicated by the reaction above, an important characteristic of this adsorption process is the number of protons released, or hydroxide ions adsorbed, for each cation adsorbed. The fact that

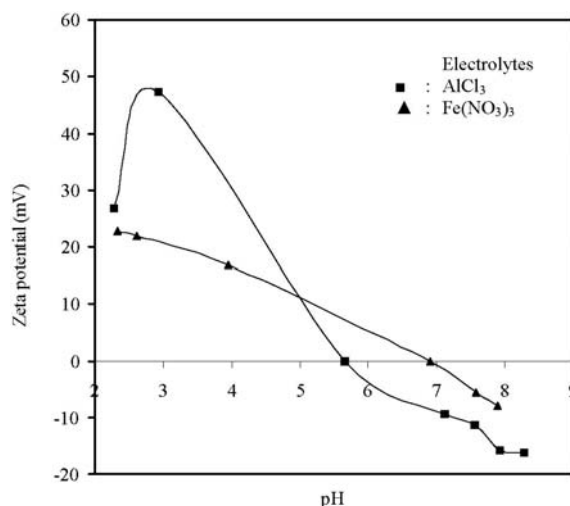


Fig. 5. Variation of zeta potential with equilibrium pH of sepiolite suspensions in the presence of different trivalence electrolytes at constant concentration.

the  $\text{H}^+/\text{M}^{2+}$  exchange stoichiometry is usually less than two for divalent cation adsorption means that the surface charge becomes increasingly positive, which is reflected in a charge in the electrokinetic properties of the interface. A similar observation is also possible for trivalent cations. In this case, the specific adsorption reverses the sign of the effective charge of the surface [39,53]. If in  $\text{CaCl}_2$  case, sepiolite suspensions have an iep at pH 6.9, approximately.

Fig. 5 shows the effect of equilibrium pH on zeta potential of sepiolite suspensions in the presence of trivalence electrolytes such as  $\text{AlCl}_3$  and  $\text{FeCl}_3$ . Sepiolite suspensions in the presence of  $\text{AlCl}_3$  and  $\text{FeCl}_3$  electrolytes have isoelectrical points at pH 5.6 and 6.8, respectively. There is an important changing at iep of sepiolite for  $\text{AlCl}_3$ . The  $\text{AlCl}_3$ -based changes in the electrokinetic behaviour of sepiolite are likely to be due to the adsorption of the lower charged Al(III) hydrolysis products. Al(III) forms a variety of hydrolysis products as depending on pH values. Precipitation and surface adsorption of Al(III)-based hydrolysis products occurs at high pH values

(6–12). At high pH, a significant quantity of dissolved cations is present in solution. At lower pH values, sepiolite surface interactions  $\text{Al}^{3+}$  ions. Therefore, it can be said that  $\text{Al}^{3+}$  ions on sepiolite surface adsorb specifically. In this case,  $\text{AlCl}_3$  compresses the electrical double layer. As a result, the isoelectric point of sepiolite suspension in the presence of  $\text{AlCl}_3$  is significantly lower than that of pure sepiolite [48,54].

### 3.2. Adsorption

The adsorption of copper on sepiolite from aqueous solutions has been investigated as a function of pH, ionic strength and temperature.

#### 3.2.1. Effect of pH

pH is one of the most important parameters affecting adsorption and ion-exchange properties of the clay minerals. The reaction mechanisms involving the transport of heavy metals in an aqueous phase in contact with minerals have been studied to predict the evolution and movement of groundwater contaminants. The mechanisms underlying the adsorption of solute on solid particles can be said to comprise the following main steps: (1) solute transfer from the bulk solution to the adsorbent surface; (2) transfer from the surface to the structural active sites via exchange; (3) uptake on the active site, via complexation, sorption, precipitation, hydrolysis [55]. The type of sorption process which occurs is highly dependent on the quantity and type of mineral phase present. Solution conditions, such as pH, ionic strength, metal ion concentration and the presence and concentration of other sorbing species also play a major role in determining the extent and type of operative sorption process. Adsorption and complexation occur rapidly, whereas the exchange of the solute with cations inside the structure can be rapid or very slow [56]. Oxide surfaces contacting with aqueous solution have hydroxyl groups and can adsorb the counter ions in aqueous media with ionization of hydroxyl

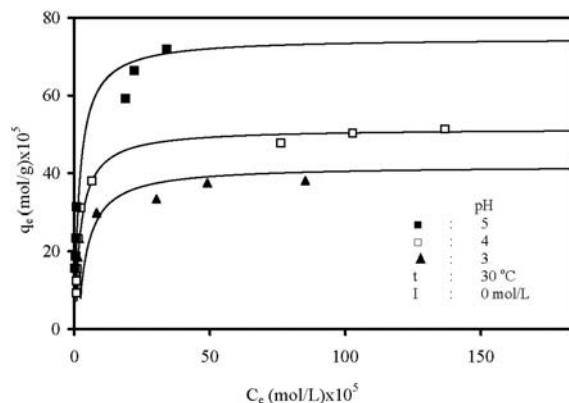


Fig. 6. Effect of solution pH on the adsorption of Cu(II) ions onto sepiolite.

groups [57]. Therefore, these hydroxyl groups on oxide surfaces are very important for controlling of adsorption. Fig. 6 shows the effect of pH to the adsorption of Cu(II) ions onto sepiolite from aqueous solutions. The adsorbed amount of Cu(II) on sepiolite depends on the number of hydroxyl groups on surface and the pH controls the concentration of hydroxyl groups [58]. Moreover, the adsorbed amount depends also on the structure of minerals. Electrolyte concentration along with pH influences the development of positive and negative surface charges, which directly affect the surface adsorption. The adsorption of Cu(II) ions on sepiolite surface is pH-dependent as can be observed in Fig. 6. The amount of cation adsorbed increases with increase in pH. A rapid increase in uptake of the metal ion usually occurs over a narrow pH range. The changing at the adsorption amount with pH can be explained by the concentration and activity of hydrogen ions [48] and ion exchange mechanism. From the measurements of zeta potential, we found that sepiolite had an iep at pH 6.6. The increase of the suspension pH results in an increase in the negative charge of sepiolite. This can be ascribed to either the adsorption of  $\text{OH}^-$  ions onto the positive charge centers of sepiolite or the deprotonation of surface hydroxyl



groups. As a result, we can say that the removal of Cu(II) ions increases since interaction of Cu(II) ions with sepiolite surface occurs more easily. At low pH values, hydrogen ions at active sites on the sepiolite surface compete with Cu(II) ions for adsorbing each other. In this case, hydrogen ions can adsorb at active sites on sepiolite. Again, at high hydrogen concentrations, negative charge density will decrease at active sites on sepiolite, and therefore, the adsorbed amount will decrease. The increase in adsorbed amount with pH may also be due to the ion exchange mechanism, as shown by Kara et al. [59] for Co adsorption on sepiolite. Clay minerals are highly reactive due to their large surface area [21] because they commonly carry a charge forming is the basis for their exchange capacity and their swelling properties. The ion exchange capacity of the clays is the property to clay minerals in adsorbing ions and retaining them in an exchangeable state, i.e., these ions are exchangeable for other cations and anions by treatment with such ions in a water solution. These ion exchange reactions generally do not affect the structure of the clay mineral. Ion exchange is of very great importance because the physical properties of clay materials are frequently dependent on the exchangeable ions carried by the clay. Ion exchange is a reversible chemical reaction wherein an ion from solution is exchanged for a similarly charged ion attached to an immobile solid particle [21].

Kara et al. measured the released Mg (II) ion against pH in the absence and presence of Co (II) to identify the effect of cobalt ions on the solubility of magnesium ions, and found the quantity of dissolved Mg (II) ions in water-sepiolite system is higher than that in Co (II)-water-sepiolite system up to pH 5 due to the release of additional Mg (II) ions by the H<sup>+</sup> ions of the acid used for adjusting pH [59]. On the other hand, this effect ceases in the pH range of 5–8.2 above which the amount of dissolved Mg (II) ions becomes equal to the adsorbed Co (II) ions onto sepiolite. As a result, in this pH interval the

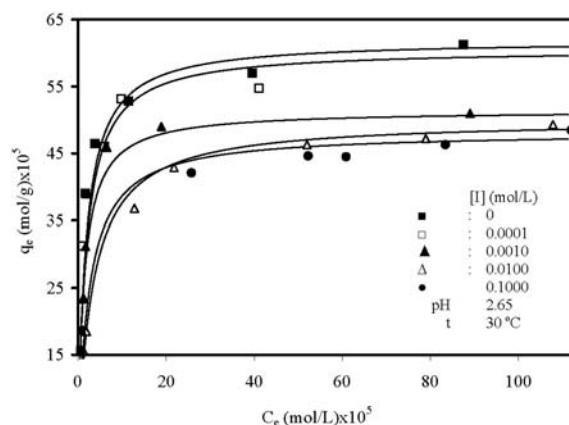


Fig. 7. Effect of ionic strength on the adsorption of Cu(II) ions onto sepiolite.

adsorption mechanism was ascertained as the ion exchange.

### 3.2.2. 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 [44]. In this study, NaCl was chosen as a salt for investigating the effect of ionic strength to the adsorption of Cu(II) ions on sepiolite surface. The effect of ionic strength on adsorption capacity of sepiolite was studied by carrying out a series of isotherms at 0,  $1 \times 10^{-4}$ ,  $1 \times 10^{-3}$ ,  $1 \times 10^{-2}$  and  $1 \times 10^{-1}$  mol/L concentrations as shown in Fig. 7. As pointed out in Fig. 7, increasing ionic strength has significantly decreased the adsorption of Cu(II) ions on sepiolite. Since the salt screens the electrostatic interaction of opposite charges of the oxide surface and Cu(II) ions, the adsorbed amount should decrease with increase of NaCl concentration [60–62].

### 3.2.3. Effect of temperature

The temperature dependence of adsorption reactions gives valuable information about the

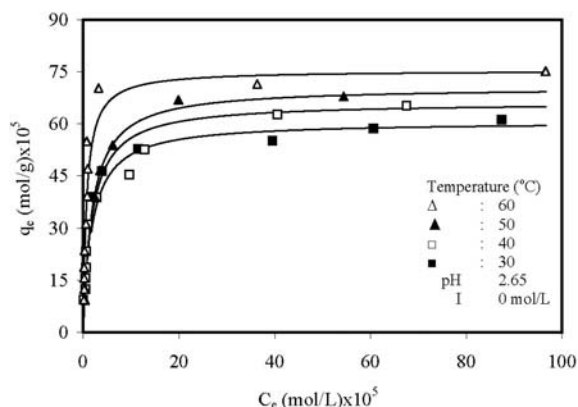


Fig. 8. Effect of temperature on the adsorption of Cu(II) ions onto sepiolite.

adsorption enthalpy change. The adsorption of Cu(II) ions onto sepiolite was endothermic as shown in Fig. 8 and the adsorption amount increased as temperature increased. Meena et al. [63] reported that the increase in adsorption with temperature may be attributed to either increase in the number of active surface sites available for adsorption on the adsorbent or the decrease in the thickness of the boundary layer surrounding the adsorbent with temperature, so that the mass transfer resistance of adsorbate in the boundary layer decreases. Moreover, increasing temperature results in an increase in the rate of approach to equilibrium. Increase in raising temperature of the adsorption capacity of sepiolite implies that the enthalpy change has positive values, indicating that the adsorption process of Cu(II) ions on sepiolite was endothermic, which was opposite to the exothermic adsorption usually encountered.

From the adsorption data at various temperatures, the enthalpy change for Cu(II) adsorption can be estimated from the van't Hoff isochore [57,64]:

$$\left[ \frac{\partial \ln K}{\partial (1/T)} \right]_{\theta} = -\frac{\Delta H_{ads}^0}{R_g} \quad (12)$$

The subscript  $\theta$  means that the equilibrium where  $R_g$  is the gas constant;  $q_m$  is the ultimate

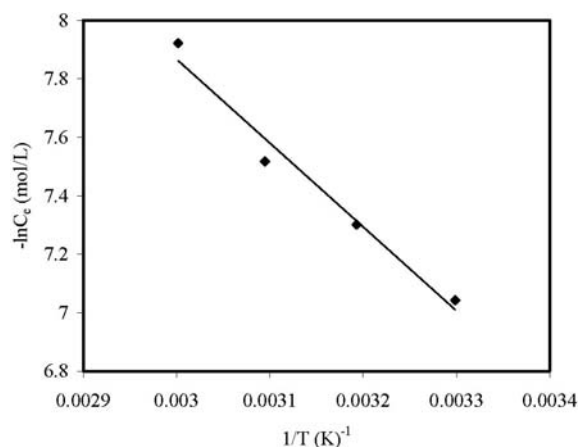


Fig. 9. Plot of  $-\ln C_e$  vs.  $1/T$  for Cu(II) adsorption onto sepiolite.

constant at each temperature is measured at constant coverage. Under these conditions, from the Langmuir equation at  $\theta = q_e/q_m = 0.5$ ;  $K = 1/C_e$  and so

$$\left[ \frac{\partial \ln C_e}{\partial (1/T)} \right]_{\theta=0.5} = \frac{\Delta H_{ads}^0}{R_g} \quad (13)$$

adsorption capacity (mol/g);  $q_e$  is the equilibrium loading of adsorbate on adsorbent (mol/g);  $C_e$  is the equilibrium concentration of adsorbate in solution (mol/L); and  $K$  is the relative energy of adsorption (L/mol).

This value of  $\Delta H_{ads}$  is called the isosteric heat of adsorption referring to the fact that it applies to a certain value of the coverage. The Langmuir model implies that  $\Delta H_{ads}^0$  should be constant, but it is more likely to be a function of coverage ( $\theta = q_e/q_m$ ). The values of  $\Delta H_{ads}^0$  were calculated as 24 kJ/mol from the data given in Fig. 9 according to Eq. (13). The results show that the interactions between surface and adsorbate molecules are physical interactions. Again, as seen in the XRD spectra in Fig. 1, it can be said that an important interaction between copper ions and sepiolite particles does not occur because of physical interactions among them.

### 3.3. Adsorption isotherms

The adsorption data obtained for equilibrium conditions have been analyzed by using the linear forms of the Freundlich and Langmuir isotherms. Langmuir and Freundlich models are the simplest and most commonly used isotherms to represent the adsorption of components from a liquid phase onto a solid phase [65,66]. The Langmuir model assumes monolayer adsorption while the Freundlich model is empirical in nature. The data are analyzed to obtain Freundlich and Langmuir parameters. The linear plot for the Langmuir isotherm has been obtained using following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m K} + \frac{C_e}{q_m} \quad (14)$$

The Langmuir model can be linearized to obtain the parameters  $q_m$  and  $K$  from experimental data on equilibrium concentrations and adsorbent loading.

The Freundlich model at logarithmic form is expressed as

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (15)$$

where  $K_F$  and  $1/n$  are Freundlich isotherm constants.

Sorption equations were obtained by experimental data with Eqs. (14) and (15). The isotherm constants were calculated from the least square method and are presented in Table 2. The Langmuir equation represents the sorption process very well since the correlation coefficient values,  $R^2$ , are higher for Langmuir isotherm than the Freundlich isotherm. This may be due to homogenous distribution of active sites on the sepiolite surface [67,68].

The shape of the isotherm may also be considered with a view to predicting if an adsorption system is “favorable” or “unfavorable.” The

essential characteristic of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor or equilibrium parameter,  $R_L$ , [67] which is defined by the relationship

$$R_L = \frac{1}{1 + KC_e} \quad (16)$$

According to the value of  $R_L$  the isotherm shape may be interpreted as follows:

Value of $R_L$	Type of adsorption
$R_L > 1$	: Unfavorable
$R_L = 1$	: Linear
$0 < R_L < 1$	: Favorable
$R_L = 0$	: Irreversible

The results given in Table 2 show that the adsorption of Cu(II) ions on sepiolite is favorable.

### 3.4. Designing batch adsorption from isotherm data

In a single-stage adsorption process, the solution to be treated contains  $V$  L solvent, and the copper concentration is reduced from  $C_0$  to  $C_e$  in adsorption process at equilibrium. In the treatment stage  $W$  g sepiolite is added and the copper concentration on sepiolite changes from  $q_0 = 0$  (initially) to  $q_e$  at equilibrium. The mass balance equates the copper removed from the liquid to that accumulated at equilibrium by the solid is

$$V(C_0 - C_e) = W(q_e - q_0) = Wq_e \quad (17)$$

For the adsorption of copper on sepiolite the Langmuir isotherm has given the best fit to experimental data. Consequently, the equation can be best substituted for  $q_e$  in the rearranged form of Eq. (14) giving adsorbent/solution ratios for this particular system:

$$\frac{W}{V} = \frac{C_0 - C_e}{q_e} \equiv \frac{C_0 - C_e}{(q_m KC_e / 1 + KC_e)} \quad (18)$$

Table 2  
Isotherm constants for Cu(II) adsorption onto sepiolite

Temp., °C	[I] (mol/L)	pH	Langmuir isotherm			Freundlich isotherm	
			$q_m$ (mol/g) $\times 10^{-4}$	$K$ (L/mol) $\times 10^{-4}$	$R^2$	$R^2$	$R_L$
30	—	—	6.06	5.39	0.9994	0.973	0.021–0.521
40	—	—	6.62	5.44	0.9994	0.953	0.027–0.978
50	—	—	7.06	5.31	0.9996	0.925	0.034–0.833
60	—	—	7.54	13.82	0.9996	0.834	0.007–0.870
30	0.1	—	4.82	4.04	0.9994	0.909	0.022–0.860
30	0.01	—	5	3.01	0.9998	0.974	0.029–0.815
30	0	—	6.18	4.05	0.9998	0.991	0.027–0.828
30	0	—	6.64	4.75	0.9997	0.982	0.034–0.804
30	—	3	4.19	2.87	0.9998	0.915	0.018–0.830
30	—	4	5.15	4.35	0.9997	0.881	0.017–0.757
30	—	5	7.48	5.2	0.9998	0.998	0.034–0.804

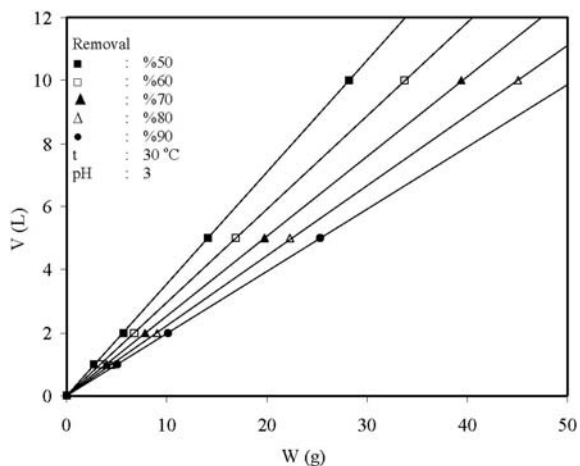


Fig. 10. Volume of effluent ( $V$ ) tread against adsorbent mass ( $W$ ) for different percentages of Cu(II) adsorption.

Fig. 10 shows a series of plots derived from Eq. (18) for the adsorption of copper ions on sepiolite. An initial copper concentration of  $2.36 \times 10^{-3}$  mol/L at  $30^\circ\text{C}$  and at pH 3 is assumed and the figure shows the amount of effluent, which can be treated to reduce copper ions content by 50, 60, 70, 80 and 90% using various masses of adsorbent. As seen in Fig. 10, in order

to remove 90% of the copper ions for an initial copper concentration of  $2.3 \times 10^{-3}$  mol/L, it is necessary to add sepiolite at the amounts of 5.07, 10.14, 23.35 and 50.70 g into 1, 2, 5 and 10 L solution, respectively. This result has shown that sepiolite can effectively be used to remove the copper ions from aqueous solutions.

#### 4. Conclusions

The work presented here describes the electrokinetic and adsorption properties of sepiolite suspensions. It was found that:

- The sepiolite amount had no important effect on zeta potential;
- Sepiolite suspensions had an isoelectrical point at pH 6.6, approximately;
- KCl was an indifferent electrolyte;
- $\text{Li}^+$  ions approach more on sepiolite surface than  $\text{Na}^+$  and  $\text{K}^+$ ;
- Sepiolite suspensions in  $\text{CaCl}_2$  solutions had an isoelectrical point at pH 6.9, but not to  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Cu}(\text{NO}_3)_2$ ;
- $\text{AlCl}_3$  specifically adsorbed on sepiolite and

the thickness of electrical double layer decreased with increase of ion valence;

- The adsorption data were correlated reasonably well by Langmuir adsorption isotherm;
- The amount of  $\text{Cu}^{+2}$  ions adsorbed increased with increasing pH and temperature and otherwise decreased with increasing ionic strength;
- The dimensionless separation factor showed that sepiolite could be used for removal of  $\text{Cu}^{+2}$  ions from aqueous solutions; and,
- The adsorption process was endothermic and the value of  $\Delta H_{\text{ads}}$  was calculated as 24 kJ/mol.

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