

ELECTROKINETIC AND ADSORPTION PROPERTIES OF SEPIOLITE MODIFIED BY 1-[3-(TRIMETHOXYSILYL)PROPYL]UREA

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SUMMARY

Surface modification of clay minerals has become increasingly important for improving the practical applications. Modification of sepiolite clay has been performed using 1-[3-(trimethoxysilyl)propyl]urea (TMSPU) in the presence of toluene solution. The utility of the TMSPU-modified sepiolite as an adsorbent for removal of various metal ions from aqueous solutions was investigated. Extensive physicochemical evaluation of the obtained modified sepiolite was conducted using FTIR and XRD techniques, and it was suggested that chemical bonding takes place between the hydroxyl groups and/or oxygen atoms within the structure of sepiolite and methoxy groups of TMSPU. Electrokinetic properties of the formed sepiolite suspensions were also examined by determining their zeta potential. The adsorption capacity of the modified sepiolite for Fe(III), Mn(II), Co(II), Cu(II), Zn(II) and Cd(II) was determined. The effects of pH and temperature on the adsorption process were studied. Toward Fe(III) and Mn(II), the adsorption capacity of the modified sepiolite was high. The adsorption isotherm has been determined and the data have been analysed according to the Langmuir and Freundlich models.

KEYWORDS: Sepiolite, 1-[3-(trimethoxysilyl)propyl]urea, modification, zeta potential, adsorption, metal ions.

INTRODUCTION

Surface modification of adsorbents aims at altering their chemical and physical characters. Efficiency of the modification depends upon the type of bonds, which are formed between functional groups on adsorbent surface and those of the modifying and pro-adhesive compounds [1, 2]. For classifying surface modification from the standpoint of the techniques employed, the subject is divided into two groups, physical and chemical ones. Physical methods

are accompanied by a topo-chemical compositional change on the top surface of the adsorbent. Chemical modification methods can introduce various organic functional groups on adsorbent surfaces without large geometrical changes. Chemical modification in its real sense means the covalent bonding of functional groups to surfaces as a result of chemical reactions between surface species and appropriate reactants. Difficulties sometimes arise in distinguishing whether a surface species being attached is chemisorbed, physisorbed, or only mechanically held on the metal oxide surface [3]. Impregnation or organic modification process is accomplished through the replacement of inorganic exchangeable cations. After this replacement, organic molecules are adsorbed within the crystalline structure of the clay, and then swell in the presence of organic contaminants. These organic ions attached to the clay, readily adsorb other organic species [4-6].

Among various modifying compounds, compounds of the coupling agent group, which contain three groups, that can be potentially react with surface hydroxyl [7, 8], deserve particular attention. These groups are capable to undergo condensation with silanol groups of adsorbent surfaces. Organo-functionalization or grafting of silane molecules on a clay surface is another interesting method of modification. In surface modification, most frequently applied are silane coupling agents [9, 10] of the general formula $(RO)_3\text{-Si-X}$, where X corresponds to the functional organic group, linked to Si atom by an alkyl chain, while RO corresponds to an easily hydrolysable group (most frequently an alkoxy group). Silane coupling agents are capable of providing chemical bonding between an organic and an inorganic material. In literature of the subject and in analytical practice, several investigative techniques have been suggested for controlling the mechanism of organo-silane reaction with silanol groups of silica surfaces. The FTIR and XRD technique has proven to be very useful for examination of chemical structure and surface interactions [11, 12]. The combination of the two techniques allows for a clear description of physical and chemical interactions between organo-silanes and adsorbent surface.

The differences in acid-base properties of clays and their modification will have effects on the zeta potential of the surfaces and, consequently, the zero net charge [13]. 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 [14, 15]. 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 suspensions of clays [16]. 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 [17].

Modified adsorbents are of interest in many fields of chemistry. In each field, interactions with specific types of molecules are effected. In analytical and physical fields, organic compounds [18] and metal ions [19] are selectively adsorbed. The chemical field aims at the immobilization of metal complexes for use as catalyst centers [20]. Enzymes are immobilized in the biochemical field [21]. In the industrial field, interaction with polymers and ceramics is realized [7]. Heavy metals are present in nature and industrial wastewaters. Due to their mobility in natural water ecosystems and their toxicity, the presence of heavy metals in surface water and groundwater poses a major inorganic contamination problem [22]. With industrial advances, current interests in the study of water pollution problems have stimulated interest for the removal of heavy metal ions from aqueous solutions by various methods [23]. These include chemical (precipitation/neutralization) or physical (ion exchange, membrane separation, electroanalysis and active carbon adsorption) methods [24, 25]. Adsorption is one of the more popular methods for the removal of heavy metals from wastewater, offering significant advantages. When compared with many conventional methods, especially from an economical and environmental point of view, it is the cheapest, most easily available and profitable, easy to operate and most efficient methodology. Activated carbon is widely used as an adsorbent due to its high surface area, high adsorption capacity, but it is relatively high in price, which limits its usage [26]. In recent years, attention has been focused on the various adsorbents, such as chitosan, zeolites, fly-ash, coal, oxides, sawdust and various clay minerals, which have organic and inorganic-binding capacities, and are able to remove unwanted hazardous species from contaminated water at low cost [27]. Among the new adsorbents, clays, such as kaolinite [28], perlite [15,29], bentonite [30], montmorillonite [31], smectite [32] etc. are being considered as alternative low-cost adsorbents.

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 [33]. 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 using sepiolite [34, 35]. 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 [36, 37]. Sepiolite has attracted remarkable attention by its sorptive, rheological and catalytic properties, and the use of sepiolitic clays is expanding [38, 39].

There are many studies of the adsorption properties of some metal ions by modified adsorbents, but we did not find any study related to characterization and its electrokinetic and adsorption properties of sepiolite modified by 1-[3-(trimethoxysilyl)propyl]urea (TMSPU). Of many surface modification materials, TMSPU is an alkoxysilane having an amine-group and $(\text{CH}_3\text{O})_3\text{-Si}$ moieties in its structure, and exhibiting a unique property. In this paper, we firstly report the chemical functionalization of sepiolite with TMSPU in the presence of toluene as a dispersing medium. The functionalized clay has been characterized with different techniques, such as Fourier transform infrared spectroscopy (FTIR) and XRD. Secondly, the electrokinetic properties of the modified sepiolite in various metal ion media have been reported, and finally, the effects of pH and temperature on the adsorption capacity of the metal ions onto modified sepiolite from aqueous solution were studied. The adsorption results have been discussed according to the isotherm equations.

MATERIALS AND METHODS

Materials

Sepiolite sample used in this study was obtained from Aktaş Lületaş Co. (Eskişehir, Turkey). The chemical composition and some physicochemical properties of sepiolite clay are given in Tables 1 and 2, respectively [40]. 1-(3-[trimethoxysilyl]propyl)urea was obtained from the Aldrich Chemical Company Inc., USA. Other chemicals were of analytical grade and obtained from Merck.

TABLE 1 - Chemical composition of sepiolite.

Component	Weight %
SiO ₂	53.47
MgO	23.55
CaO	0.71
Al ₂ O ₃	0.19
Fe ₂ O ₃	0.16
NiO	0.43
LoI	21.49

LoI: Loss of ignition

TABLE 2 - Some physicochemical properties of sepiolite.

Colour	Cation exchange capacity (meq 100g ⁻¹)	Density (g cm ⁻³)	Specific surface area (m ² g ⁻¹)	Particle size (µm)
White	25.00	2.55	342	50

Grafting process

Sepiolite samples were treated before use in experiments, in order to obtain a uniform size sample of adsorbent as follows [15]: the suspension containing 10 g L⁻¹ sepiolite was mechanically stirred for 24 h, after waiting for about two min, the supernatant suspension was filtered through filter paper. The solid sample was dried at 105 °C for 24 h, ground, then sieved by a 50-µm sieve. The particles under 50 µm were used in further experiments. The grafting reaction was carried out in 100 mL toluene solution. A quantity of 5 mL of TMSPU was firstly introduced into 100 mL toluene, and temperature was kept at 80 °C. Then, 5 g of clay was added, and the mixture was stirred under reflux for 24 h. The crude product was filtered and washed twice times using toluene, followed by methanol and acetone. This resultant product was dried at 80 °C for 24 h, and then placed in a sealed container for characterization [41].

Characterization

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 using a Perkin–Elmer BX 1600 spectrophotometer operated in the transmission mode. The interaction between the sepiolite surface and the modifier (TMSPU) during the modification has been investigated by a series of FTIR spectral analyses:

1. **Modifier sample** (aimed to estimate the peaks arising from modifier, and changes on it after modification)
2. **Sepiolite sample** (to observe any changes on sepiolite during the modification process, and comparing the modified sample)
3. **Modified sepiolite sample** (to compare the peaks arising from the modifier and sepiolite)
4. **Modified sepiolite with the sepiolite-background** (the peaks arising from sepiolite are omitted by subtracting spectrum, and the changes on the modifier will appear more clear)
5. **Mechanical mixture** (to observe if there is a chemical reaction between sepiolite and modifier).

X-ray diffraction measurements were performed using an Analytical Philips X'Pert-Pro X-ray diffractometer equipped with a back monochromator operating at 40 kV and a copper cathode as X-ray source ($\lambda = 1.54 \text{ \AA}$).

Zeta potential measurements

The zeta potential of the modified sepiolite suspensions was measured using a Zeta-meter 3.0 (Zeta Meter Inc.) equipped with a microprocessor unit. The unit automatically calculates the electrophoretic mobility of the particles, and converts it to the zeta potential using the Smoluchowski equation. The Smoluchowski'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; V_t is viscosity of the suspending liquid; D_t is dielectric constant; π is constant and ζ is zeta potential [42]. A sample of 0.1 g modified sepiolite in 100 mL distilled water containing the desired electrolyte was added to a 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 applied voltage during the measurements was generally varied in the range of 50–150 mV.

Adsorption experiments

Adsorption experiments were carried out in 100-mL polyethylene flasks by shaking 0.1 g modified sepiolite with various amounts of stock metal solutions at constant pH and 25 °C, except those in which varying conditions of temperature and pH were investigated. Each run was repeated, at least twice. A preliminary experiment revealed that about 24 h is required for metal ions to reach equilibrium concentration. The flasks were shaken mechanically for 24 h at 25 °C. A thermostated shaker incubator was used to keep the temperature constant. The pH of the solution was adjusted with NaOH or HNO₃ solution by using an Orion 920A pH-meter with a combined pH electrode. The pH-meter was standardized with NBS buffers before every measurement. At the end of the adsorption period, the solution was centrifuged for 15 min at 5000 rpm. The concentration of metal ions in the supernatant was determined by AAS (Unicam 929). Blanks without metal ions were used for each series of experiments. The amounts of metal ions adsorbed were calculated from the concentrations in solutions before and after adsorption.

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

where q_e is the amount of adsorbed metal ions on modified sepiolite at equilibrium (mol g⁻¹); C_0 and C_e are the initial and equilibrium liquid-phase concentrations of metal ions (mol L⁻¹), respectively; V is the volume of metal ion solution (L), and W is the mass of the modified sepiolite sample used (g) [15].

RESULTS AND DISCUSSION

Characterization of surface grafting

Modification of the sepiolite surface with TMSPU was investigated by FTIR, XRD and zeta potential.

FTIR Analysis: The hydroxyl groups on the oxide surface, resulting from hydrolysis, act as active sites in the

grafting reaction. The grafting agents are supposed to attach to clay surfaces by chemical bonding and adsorption to form a monomolecular layer or oligomer film on the clay mineral surfaces [13]. However, the adsorbed organic layer is often displaced by solvents or during compounding. Chemical bonding gives rise to a solid linkage between the coupling agent and the clay surfaces, thus improving the properties of the polymer products [43]. Infrared spectrum measurement based on the absorption band changes of functional groups in minerals can be used to determine if there is a chemical bonding. In Figures 1-4, the differences that have been observed in the vibration frequencies of the FTIR spectrum of TMSPU-added sepiolite are considered as the indicators of the interaction between the modifying molecule and sepiolite particles. The adsorption of a polar or a nonpolar molecule perturbs the stretching vibrations of Si-OH groups of external surface and causes shifting to lower wave-number [44]. On the other hand, the perturbation observed on the zeolitic and bound water vibrations of sepiolite indicates that some of the organosilane molecules enter the interior channels and replace zeolitic water molecules. The frequency shifts may indicate the formation of new H-bonds between bound/zeolitic water and organosilane molecules, whereas weakening in intensity of the m(OH) vibration of the zeolitic water is the indication that modifier molecules replace a part of the zeolitic water [45].

The method [12] used here can allow following the changes on the modifier and sepiolite after modification. Scanning the equal amount of the sepiolite as background, and having the spectra of the modified sample, we get only the modified compounds peaks appearing on the FTIR spectra. Comparing those peaks obtained from pure and modified peaks, we may assume the changes on the modifier during the modification. For instance, when the peaks due to the methoxy group of the modifier disappear after modification, we can clearly see the modification that happened between methoxy group and OH of the sepiolite. Reduce in the methoxy peaks intensity may be attributed to

the one or two methoxy disappearance(s), and reaction style of the sepiolite and modifier.

Sepiolite contains four different types of water molecules: (i) hygroscopic, (ii) zeolitic, (iii) bound, and (iv) hydroxyl water [46]. In sepiolite, the most probable binding sites on the sepiolite surface are surface hydroxyls and Lewis acidic centers [45]. FTIR spectra of the original sepiolite samples are shown in Figure 1a. The Mg₃OH band at 3762–3578 cm⁻¹ characterized by weak bonding strength is ascribed to the presence of OH groups in the octahedral sheet, and the OH stretching vibration in the external surface of sepiolite. On the other hand, the 3430 and 1660 cm⁻¹ bands are, respectively, assigned to the OH stretching, representing the zeolitic water in the channels and bound water coordinated to magnesium in the octahedral sheet. The band at 1453 cm⁻¹ developed due to the hydroxyl bending vibration again reflects the presence of bound water. The Si-O coordination bands at 1208 and 1016 cm⁻¹ represent the stretching of Si-O in the Si-O-Si groups of the tetrahedral sheet [47].

The modifier, TMSPU, shows very clear FTIR spectra due to the carbonyl group (1657 and 1606 cm⁻¹) and NH (3348 cm⁻¹) bonds in the urea. The C-H stretching at the propyl groups (2943-2842 cm⁻¹) is also a good indication for the modification, since the sepiolite does not have any peaks around this region (Figure 1b).

Indication of the modification can be observed from the comparison of sepiolite (a), modifier (b) and modified sepiolite samples (c) in FTIR spectrum (Figure 2). While sepiolite gives intense peaks at the O-H region, it is difficult to see the urea N-H stretching due to the overlap of large O-H stretching at 3100-3650 cm⁻¹. But as mentioned above, the propyl chain C-H can easily be seen at 2944 cm⁻¹. Other indication for the modifications is the carbonyl group of the urea. The peaks (1655 and 1604 cm⁻¹) can also clearly be found in the modified sepiolite spectrum (Figure 2c). The peak at 2842 cm⁻¹ (Figure 2b) assumed to be the C-H

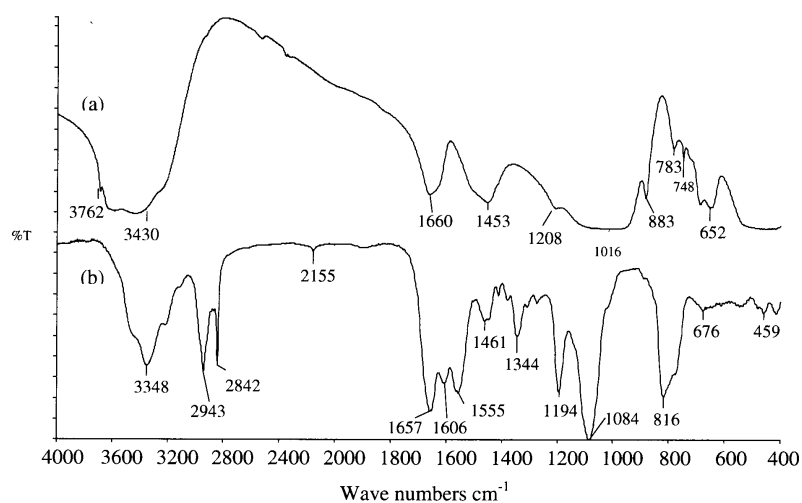


FIGURE 1 - FTIR (KBr) spectra of the sepiolite (a) and modifier (b) used for modification.

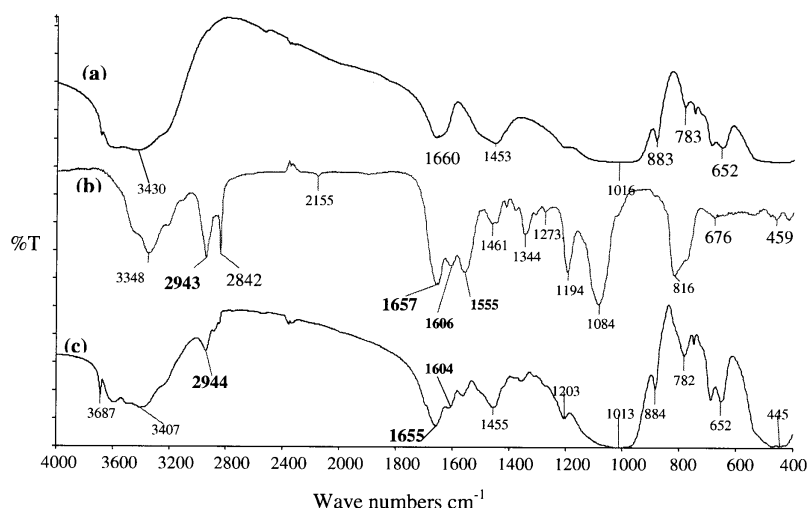


FIGURE 2 - The FTIR spectra of the sepiolite (a), modifier (b) and modified sepiolite (c) in KBr.

stretching for the methoxy group. Disappearance of the related peak after the modification may be attributed to the loss of the methoxy group as methanol.

To support the above assumption, the direct mixture of the sepiolite and modifier was also investigated. In the physical absorption case, the FTIR spectrum of the modified structure and the mechanical mixture should give the same spectra. When the modifier has any change during the modification, this change may be observed in the difference between the modified and mechanical mixture. As can be seen from Figure 3, while the mechanical mixture shows the same peaks of the modifier and sepiolite, the modified sample has differences in both, especially disappearance of the methoxy group and change in the surface of the sepiolite.

The mechanical mixture clearly shows that the methoxy groups of the modifier are still on the molecule without any change. The peak due to the methoxy C-H at 2842 cm^{-1} in the modifier spectra in KBr (Figure 4a) was observed at 2847 cm^{-1} with a little shift in the mechanical mixture spectra (Figure 4d), which was not observed in the modified sample (Figure 4c), being a good indication of the surface reaction.

Abundance of the Si-OH in the sepiolite gives very intense peaks for Si-O and O-H bond stretching. Due to these intense peaks in the case of less modification, it is difficult to observe the peaks arise from the modifier. Having a background, as sepiolite omits the peaks arising from it, only the modifier peaks will appear more clearly as shown in Figure 4e.

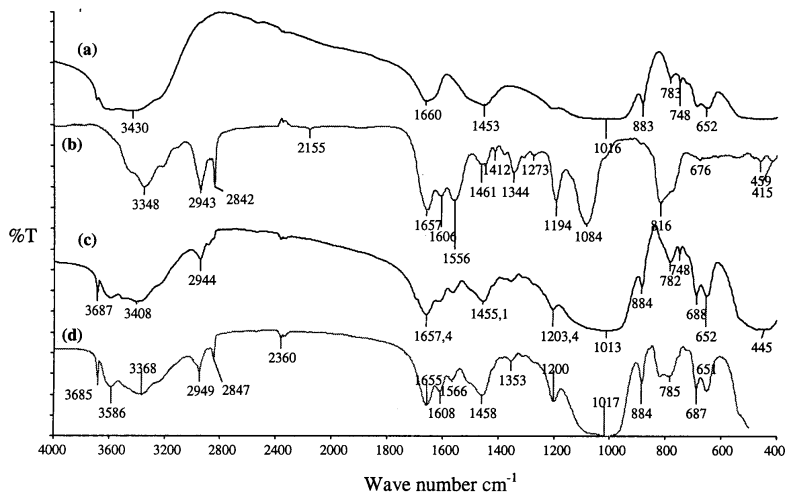


FIGURE 3 - The infrared absorption spectra of the modifier (a), sepiolite before modification (b), after modification with TMSPU (c), mechanical mixture of sepiolite, and modifier (d).

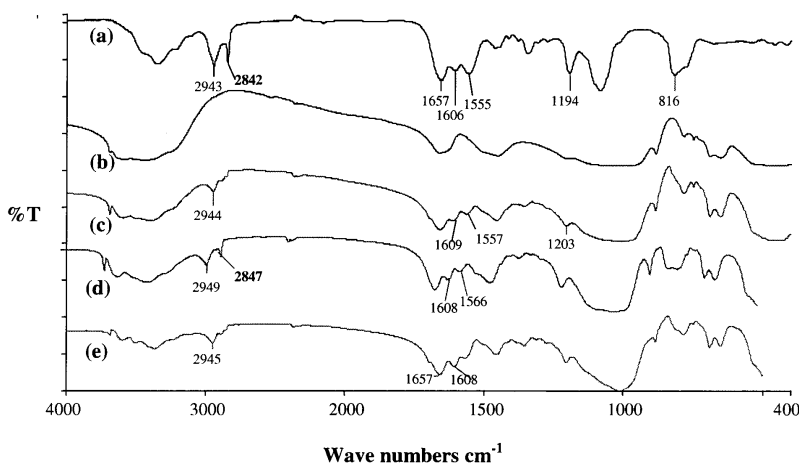
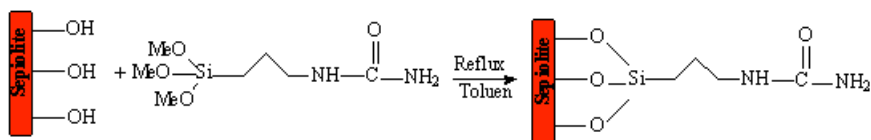


FIGURE 4 - The infrared absorption spectra of the modifier (a), sepiolite before modification (b), after modification with (TMSPU) (c), mechanical mixture of sepiolite and modifier (d) and modified sepiolite with the sepiolite-background (e).

According to the explanation above, the reaction between hydroxyl groups of sepiolite and methoxy group of modifier can be written as follows:



(3)

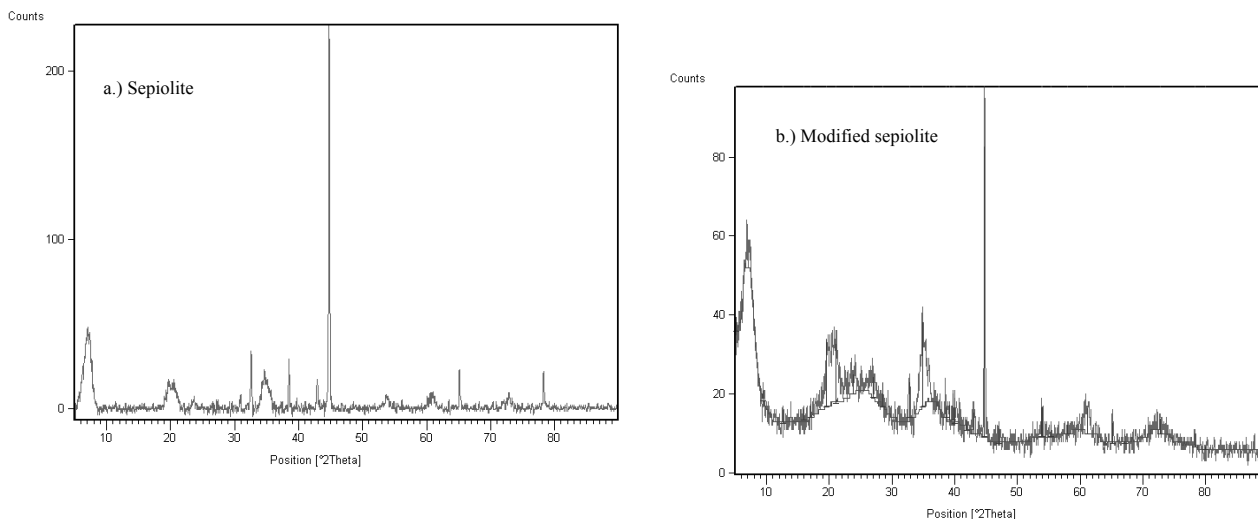


FIGURE 5 - XRD patterns of the sepiolite and modified sepiolite.

XRD Analysis: XRD analysis can also provide an important information about the modification of sepiolite by TMSPU. The XRD patterns of the sepiolite before and after grafting are shown in Figure 5. As seen in Figure 5, XRD pattern of sepiolite is affected by modification with TMSPU, as observed by the change in some peaks. It is clear that there is a bonding interaction between sepiolite and TMSPU, since the intensity of some peaks has especially changed in the position range of 20-40 in the XRD pattern of TMSPU-modified sepiolite.

Zeta potential

Interfacial interaction between an adsorbent and a metal ion through an adsorption process from aqueous solution is a phenomenon of central importance and of great technological and scientific interest, because of its application in commercial processes. In addition, adsorption is a process of considerable complexity and an interesting challenge in understanding the solution and interfacial behaviour of suspensions. Therefore, it is necessary to investigate the electrokinetic properties of adsorbent suspensions. The study of zeta potential can also lead to a better knowledge of the double-layer region, especially for ionic solids [48]. The variation of zeta potential of the modified sepiolite with the different initial metal concentrations and equilibrium pH are shown in Figures 6 and 7, respectively. As can be seen, the zeta potential values of the modified sepiolite are negative. This has shown that a bonding interaction between the active sites on sepiolite and the modifier occurred, and that sepiolite surface was modified. We previously found that sepiolite had an isoelectric point (iep) at pH 6.6 [48]. The iep of a mineral represents the sum of all interactions occurring at the mineral/water interface, e.g., H⁺ and OH⁻ adsorption, distribution of dissolved lattice ions, if

FIGURE 6 - The variation of zeta potential with equilibrium pH of the modified sepiolite suspensions in the presence of metal ions.

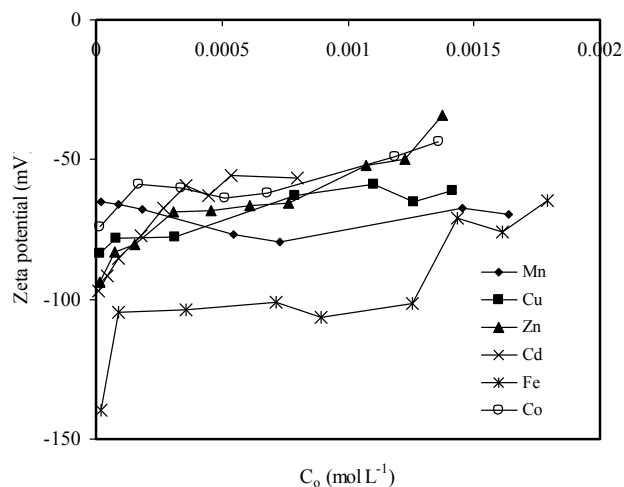
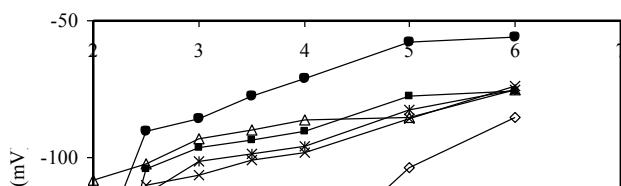


FIGURE 7 - The variation of zeta potential with initial metal concentration of the modified sepiolite suspensions.



present, or hydrolytic reactions of H^+ and OH^- with the dissolved lattice ions at the interface. The iep also indicates that at this point (or pH) there is no charge at the surface; that is, the total positive charges are equal to the total negative ones. Comparing with our previous results, we can say that some changes occur on the sepiolite surface by modification due to not observing the isoelectrical point in the pH range studied. For a cation to be a potential-determining ion (pdi), it should render the surface more positive with an increase in the concentration of the cation. As seen in Figure 7, the surface is, at first, more negatively charged, and then the negative charge decreases as the concentration of electrolyte increases. It can be said that these cations adsorb specifically, and are capable of causing a charge reversal at high electrolyte concentrations.

Adsorption equilibrium

The adsorption of metal ions on the modified sepiolite by TMSPU from aqueous solutions has been investigated as a function of pH and temperature.

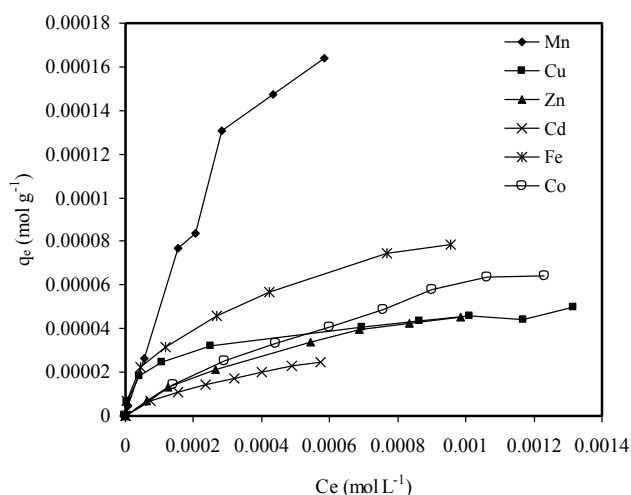
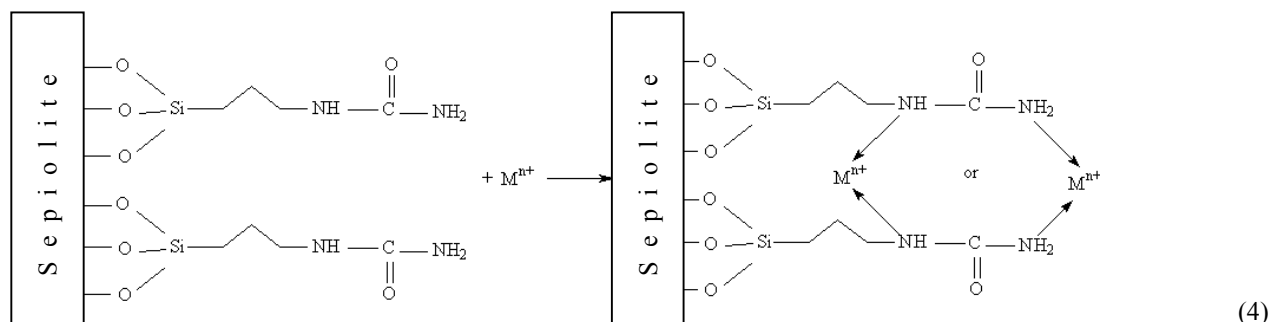


FIGURE 8 - The adsorption isotherm curves of metal ions on modified sepiolite.

Adsorption isotherm: Figure 8 shows the isotherm plots for the adsorption of metal ions, such as Fe(III), Mn(II), Co(II), Cu(II), Zn(II) and Cd(II), from aqueous solutions on the modified sepiolite by TMSPU. The adsorption capacity of the modified sepiolite is higher for Fe(III) and Mn(II) than for the other ions. This may be a result of i) specific interaction between metal ions and the chromophore group (amine) of modifier agent, and ii) the specific adsorption of metal ions at active sites on the unmodified sepiolite. In addition to that, acidic characters of Fe(III) and Mn(II) (hard acids) are more than the other ions, such as Co(II), Cu(II), Zn(II) and Cd(II) (relatively hard acids). Owing to the presence of acids harder than Co(II), Cu(II), Zn(II) and Cd(II), the Co(II), Cu(II), Zn(II) and Cd(II) ions are less adsorbed on the TMSPU-modified sepiolite. The reaction between the modified sepiolite and metal ions can generally be given as follows:



(4)

Effect of pH: The pH is an important parameter controlling the permeability through changes in the amount and charge of active sites on the edges of clay mineral particles and, hence, flocculation [49]. Because of the protonation and deprotonation of the acidic and basic groups of the modifier agent, its adsorption behavior for metal ions is influenced by the pH value, which affects the surface structure of sorbents, the formation of metal hydroxides, and the interaction between sorbents and metal ions [50]. Therefore, the pH dependence of adsorption for metal ions was investigated in detail. The adsorption of the metal ions on the modified sepiolite from aqueous solutions was studied over the equilibrium pH range 2–7 for a fixed adsorbent dose of 1 g L^{-1} at $25 \text{ }^\circ\text{C}$ (Figure 9). This figure shows that the adsorption behavior of metal ions is sensitive to pH changes. The experiments were carried out for pH values below that pH where the chemical precipitation of metal hydroxides occurs, which has been estimated as pHs 5.5; 9.8; 9.1; 7.7; 8.9 and 9.3 at 1.07×10^{-3} , 9.10×10^{-4} , 1.35×10^{-3} , 1.10×10^{-3} , 1.07×10^{-3} and $6.20 \times 10^{-4} \text{ mol L}^{-1}$ for Fe(III), Mn(II), Co(II), Cu(II), Zn(II) and Cd(II), respectively. In these conditions, metal removal can be related to the adsorption process. The inhibition of metal adsorption with a decrease in pH has been observed by several authors for different sorbents [51]. The increase in the metal removal, as the pH increases, can be explained on the basis of a decrease in competition between proton and metal species for the surface sites, and by the decrease in positive surface charge, which results in a lower coulombic repulsion of the sorbing metal [52]. This decrease can be due to protonation of the nitrogen atom in the modified sepiolite, especially in the low initial pH value [53]. In the range of pHs studied, it was observed that the adsorption capacities increased with increasing pH, reaching plateau values around pH 4.5 for Cu(II) and Zn(II) metal ions; and up to pH 6.5 for Mn(II) and pH 7.0 for Cd(II) metal ions. On the other hand, for Fe(III) and Co(II), it was found that maximum adsorption occurred a pH 4. As the pH increases, the ion exchange sites become increasingly ionized and the metal ions become adsorbed. In this case, the ion-exchange process for Mn(II), Cu(II), Zn(II) and Cd(II) is the major mechanism for removal of metals from solution. These observations are in line with earlier findings of Lafferty and Hobday [54]. At pH 4.0 for Co(II) and Fe(III), there was an inflection point. The presence of the

inflection point suggests an on-set of a change in the mechanism for metal removal. Beyond pH 4.0, therefore, ion-exchange-mechanism becomes masked by pre-precipitation and adsorption of hydrolyzed species [55]. Strong removal of metal ions coincides with the pH condition where a small fraction of the corresponding metal hydroxide species is formed in the aqueous phase [49]. For example, Stumm and Morgan [56] reported that Cd speciates to CdOH^+ after pH 8, Cd(OH)_2 after pH 9 and Cd(OH)_3^- after pH 11. Therefore, Cd^{+2} ions precipitate at higher pH values than those of other metals. If at high pH values, both ion exchange and metal hydroxide precipitation jointly contribute to metal removal from solution.

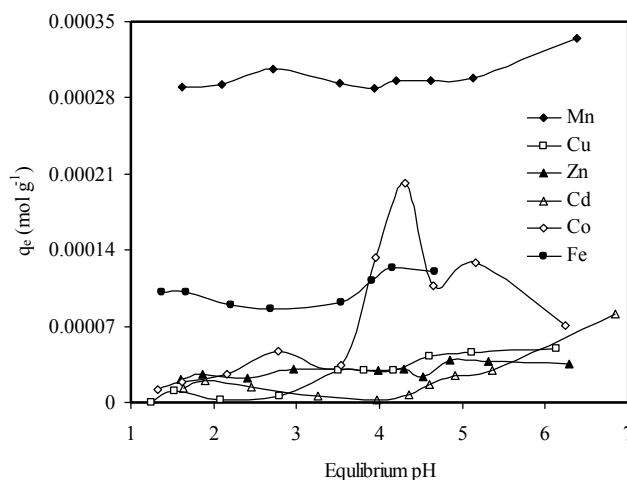


FIGURE 9
Effect of pH to the adsorption of metal ions on modified sepiolite.

Effect of temperature: In the temperature range of 25–55 $^\circ\text{C}$, the adsorption capacity of the modified sepiolite for the metal ions, such as Fe(III), Mn(II), Co(II), Cu(II), Zn(II) and Cd(II), at constant concentration was determined. The results of the studies of the influence of temperature on cation adsorption are presented in Figure 10, in terms of amount of metal removed versus temperature. It can be seen that temperature has an effect on adsorption. The results indicate that the distribution ratio increased with increase of solution temperature. This shows that the adsorption is

an endothermic and a chemical adsorption process [53]. The effect is stronger for Fe(III) than for the others.

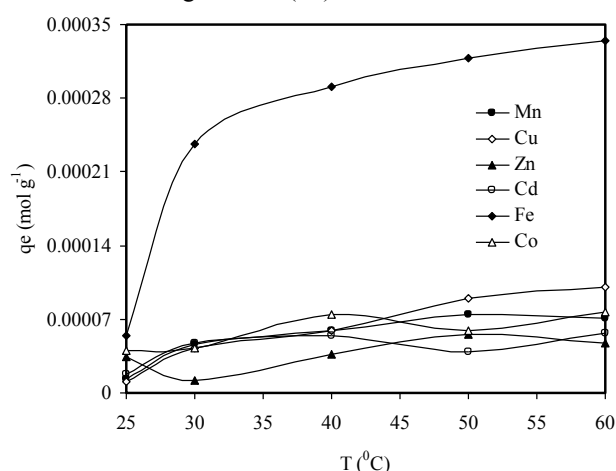


FIGURE 10 - Effect of temperature on the adsorption of metal ions on modified sepiolite.

Effect of competing metal ions: The amount of adsorption of different heavy metals can vary, and differences can be shown for different clay minerals. In order to examine the effect of the competing metals, adsorption experiments were conducted by the constant concentration of metal ions and summarized in Table 3. As seen from Table 3, the modified sepiolite adsorbed more Fe(III) and Mn(II) according to the other metals. When the initial concentrations of Fe(III) and Mn(II) were $1.07 \times 10^{-3} \text{ mol L}^{-1}$ and $9.1 \times 10^{-4} \text{ mol L}^{-1}$, the removal percentages are 16 and 14 %, respectively. On the other hand, the removal percentages of the other metals by the modified sepiolite are very low, being between 1-2 %. This result shows that there is a stronger interaction between metals, such as Fe(III) and Mn(II), and the amine group of the modifier. Again, the more adsorption of Fe(III) ions may be due to the specific adsorption of iron ions at the active sites on the unmodified sepiolite surface. Universally consistent rules of metal selectivity cannot be given, as it depends on a number of factors such as the following: i) the chemical nature of the reactive surface groups, ii) the level of adsorption (adsorbate/adsorbent ratio), iii) the pH at which adsorption is measured, iv) the ionic strength of the solution in which adsorption is measured (determines the intensity of competition by other cations for the bonding sites), and v) the presence of soluble ligands that could complex the free metal [57].

TABLE 3 - Some values belonging to metal ions r competing for adsorption.

Metals	pH	C_0 (mol L ⁻¹)	K_{sp}	(OH) (mol L ⁻¹)	q_e (mol g ⁻¹)
Fe(III)	4	1.07×10^{-3}	1.6×10^{-39}	3.46×10^{-10}	1.75×10^{-4}
Mn(II)	6	9.10×10^{-4}	1.6×10^{-13}	6.84×10^{-5}	1.27×10^{-4}
Co(II)	4	1.35×10^{-3}	1.3×10^{-15}	1.37×10^{-5}	2.65×10^{-5}
Cu(II)	6	1.10×10^{-3}	4.8×10^{-20}	4.57×10^{-7}	1.85×10^{-5}
Zn(II)	5.5	1.07×10^{-3}	3.0×10^{-16}	8.43×10^{-6}	1.86×10^{-5}

Cd(II) 7 6.20×10^{-4} 5.5×10^{-15} 2.08×10^{-5} 8.36×10^{-6}

T: 25 °C and pH:3

Adsorption models

The metal adsorption data for the modified sepiolite have been analyzed using the Langmuir and Freundlich models, to evaluate the mechanistic parameters associated with the adsorption process.

Langmuir isotherm: Langmuir's isotherm model assumes uniform energies of adsorption onto the surface, and no transmigration of adsorbate in the plane of the surface. The linear form of the Langmuir isotherm is represented by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m K} + \frac{1}{q_m} C_e \quad (5)$$

where q_e is the amount adsorbed on the modified sepiolite (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 [58]. When C_e/q_e is plotted against C_e , a straight line with slope $1/q_m$ and intercept $1/q_m K$ is obtained (figure not given). The values for the Langmuir variables, q_m and K , and correlation coefficients are shown in Table 4.

Freundlich isotherm: The adsorption for metal ions has also been analyzed using the logarithmic form of the Freundlich isotherm as shown below:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

where K_F and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. When $\ln q_e$ is plotted against the $\ln C_e$, a straight line with slope $1/n$ and intercept $\ln K_F$ is obtained (Figure 11). The results reflect the satisfaction of the Freundlich isotherm model for the adsorption of metal ions. The intercept of the line, $\ln K_F$, is roughly an indicator of the adsorption capacity and the slope, $1/n$, is an indication of adsorption intensity [58]. The values obtained for the Freundlich variables for the adsorption of metal ions are given in Table 4.

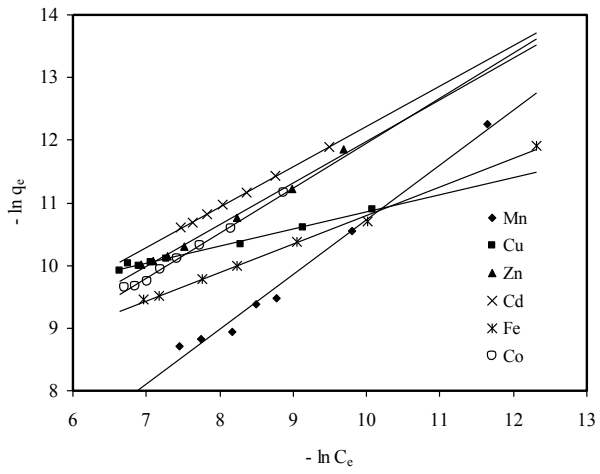


FIGURE 11 - Freundlich isotherm plots for Figure 7.

TABLE 4 - Isotherm parameters for the adsorption of metal ions on the modified sepiolite.

Metal ions	Temperature (°C)	pH	Langmuir isotherm			Freundlich isotherm		
			q_m (mol g ⁻¹)	K (L mol ⁻¹)	R ²	R ²	n	K _F
Mn	25	4.0	3.58x10 ⁻⁴	1597.4	0.8824	0.9866	1.14	1.3785 x10 ⁻¹
Cu	25	4.0	4.96x10 ⁻⁵	10834.8	0.9893	0.9916	3.65	2.9923 x10 ⁻⁴
Fe	25	3.0	8.84x10 ⁻⁵	6103.4	0.9646	0.9966	2.19	1.9623 x10 ⁻³
Zn	25	4.0	7.17x10 ⁻⁵	1726.2	0.9937	0.9920	1.51	4.8387 x10 ⁻³
Co	25	4.0	1.33x10 ⁻⁴	797.9	0.9540	0.9942	1.39	8.4668 x10 ⁻³
Cd	25	4.0	4.35x10 ⁻⁵	2202.5	0.9723	0.9998	1.57	3.0380 x10 ⁻³

CONCLUSIONS

The modification of sepiolite with TMSPU was firstly studied. For modification, a silane-coupling agent was used. The performed broad physicochemical analysis proved that sepiolite surface modification involved chemical reaction of sepiolite surface silanol groups with alkoxy groups of an appropriate silane molecule. The respective proof was provided by spectrophotometric experiments (FTIR and XRD).

At least 20 metals are known to be toxic, and fully half of these, including cadmium, arsenic, mercury, chromium, copper, lead, nickel, selenium, silver, and zinc, are released into the environment in quantities that pose a risk to human health. The removal of heavy-metal ions from aquatic systems is carried out with classical methods of adsorption techniques. TMSPU-modified sepiolite was applied to the removal of heavy metal ions from aqueous solutions. TMSPU-modified sepiolite showed great promise in the removal of heavy metal ions from aqueous media. The adsorption capacity increased with increasing pH, reaching plateau values around pH 4.5 for Cu(II) and Zn(II) metal ions; and up to pH 6.5 for Mn(II) and pH 7.0 for Cd(II) metal ions. On the other hand, for Fe(III) and Co(II), it was found that maximum adsorption occurred at pH 4. At low pH values (2.0), the hydrogen ions compete with heavy metal cations, and the percentage removals of metals decline. Above pH 4.5 for some metals, precipitation becomes dominant, especially for Fe(III) ions. The study indicates that the Fe(III) and Mn(II) ions have more affinity to the modified sepiolite. The metal adsorption was affected by the pH. In the case of the competing mixture, when Cu(II), Cd(II), Co(II) and Zn(II) adsorb at low rates (1-2%), Fe(III) and Mn(II) adsorb in the range of 14-16 %. An adsorption isotherm was used to characterize the interaction of each heavy metal ion with the adsorbent. This provided a relationship between the concentration of heavy metal ions in the solution and the amount of heavy metal ions adsorbed onto the solid phase, when both phases were at equilibrium.

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