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Removal of copper ions by modified sepiolite samples

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ABSTRACT

This paper presents the adsorption of Cu(II) from aqueous solution by raw sepiolite (RS), manganese oxide-coated sepiolite (MCS), and base activated sepiolite (BAS) samples. Adsorption of Cu(II) by sepiolite samples was investigated as a function of the initial Cu(II) concentration, solution pH, ionic strength, temperature and the presence of an inorganic ligand (Cl^-). Changes in the surface and structure were characterized by means of XRD, IR and N_2 gas adsorption data. The Langmuir monolayer adsorption capacities of RS, MCS and BAS in 0.1 M KNO_3 solution were calculated to be 5.55, 6.70 and 13.46 mg/g, respectively. ΔG, ΔH and ΔS were determined as –18.94 kJ/mol (at 303 K), 25 kJ/mol and 145 J/mol K, –19.51 kJ/mol (at 303 K), 2 kJ/mol and 71 J/mol K and –20.51 kJ/mol (at 303 K), 31 kJ/mol and 170 J/mol K for RS, MCS, and BAS, respectively.

Keywords: Sepiolite; Adsorption; Thermodynamic; Clay; Copper ions

1. Introduction

The contamination of water by heavy metals through the discharge of industrial wastewater is a worldwide environmental problem. The main heavy metal removal methods are chemical precipitation, membrane filtration, ion exchange and adsorption [1]. Adsorption processes provide attractive alternative treatment options to other removal techniques because they are more economical and readily available [2,3]. A lot of non-conventional, low-cost and easily obtainable adsorbents have been tested for heavy metal removal such as clay minerals [4,5], biomaterials [6–9] and industrial solid wastes [10–13].

Sepiolite is a clay mineral, a complex magnesium silicate, a typical formula for which is $Mg_4Si_6O_{15}(OH)_2.6H_2O$. Adsorption studies using modified sepiolite are relatively scarce. Adsorption is due to the presence of active adsorption centres on the sepiolite surfaces [14]. Few works related to Cu(II) adsorption on raw and modified sepiolite have been reported [15–17]. In these studies, Vico [15] found that three possible mechanisms that could be involved in the interaction between metal ions like Cu(II) and the surface of the mineral: (1) A process of ion exchange in which Cu(II) replaces Na^+; (2) Adsorption of Cu(II) on urface –SOH sites on the broken edges of the mineral with simultaneous release of protons; (3) Replacement of Mg(II) in the edges of octahedral sheet for Cu(II) could be another mechanism that contributes to the total adsorption phenomena. Sancheza et al. [16] have reported that the maximum retention capacity for Orera sepiolite was obtained as 6.9 mg/g for Cu(II). Ozkan et al. [17] reported that aminopropyltriethoxysilane modified sepiolite was effective for removal of Cu(II) from aqueous solution. Sepiolite, which has a high surface area, should provide an efficient surface for the manganese oxides. At the same time, the manganese oxides can improve the Cu(II) adsorption capacity of sepiolite. The resulting composite adsorbent could become a very efficient way to

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remove Cu(II) from aqueous solution. To our knowledge, however, so far there has been no report in the literature of the study of the interaction between Cu(II) and manganese oxide-coated sepiolite (MCS).

The aim of this paper is to examine the effectiveness of manganese oxide-coated sepiolite (MCS) and base activated sepiolite (BAS) in removing Cu(II) from aqueous solution and to determine the adsorption characteristics of Cu(II) onto the MCS and BAS samples. The reason for choosing manganese oxides is that relative to Fe or Al oxides, manganese oxides have a higher affinity for cations [18]. Although several investigators have suggested applications for manganese oxides in water and wastewater treatment [19–22], sepiolite has never been used as a support for manganese oxide for heavy metal removal from wastewater. Due to this reason, MCS was proposed and studied in this research. The reason for choosing a base activation process is that the use of alkaline conditions should facilitate the breakdown of Si–O–Si bonds. Enhanced silanol groups of BAS particles produced by base activation can easily form a more stable unit with heavy metals.

In this work, RS, MCS, and BAS were examined in batch experiments for the removal of Cu(II) from aqueous solution (i.e. simulated wastewaters) in order to examine whether this separation technique may improve sepiolite performance as a Cu(II) adsorbent. The influence of pH, ionic strength, ligand (Cl^-) and temperature on the adsorption of Cu(II) by the RS, MCS, and BAS samples was investigated to better understand the Cu(II) adsorption process. The materials were characterized by infrared spectroscopy (IR), X-ray diffraction (XRD), and N_2 adsorption/desorption experiments (BET method).

2. Materials and methods

2.1. Materials

All reagents used, such as NaCl, KNO_3, HNO_3, NaOH, H_2O_2 and $MnCl_2$ were all of analytical grade and all solutions were prepared with double distilled water. A solution of 1.0 mM Cu(II) was prepared from $Cu(NO_3)_2.5H_2O$ by dissolution in deionisied water. The stock was diluted to prepare a working solution. RS was composed of 51.95% SiO_2, 2.14% Al_2O_3, 0.41% Fe_2O_3, 2.77% CaO, 23.35% MgO, 0.22%, Na_2O, 0.36% K_2O, 0.08% TiO_2, 0.52% SO_3. The ignition loss of the RS at 1273 K was also found to be 18.46%.

2.1.1. Preparation of MMS

The RS was dispersed into 150 ml of 0.1 M $MnCl_2$ aqueous solution. 300 ml of 0.1 M NaOH aqueous solution was added slowly with a drop rate. The oxidation was performed in aqueous supension system at room temperature. The $Mn(OH)_2$ intercalated compound prepared as above was dispersed in 50 ml of 1.5 M H_2O_2 basic solution and vigorously sitirred. The color of the sample immediately turned from original light color to dark brown, indicating the oxidation of the hydroxide into oxide phase. For equilibrium, the suspension was further stirred for 24 h. The powder sample was washed repeatedly with deionized water and seperated cenntrifugally, then dried in vacuum at 313 K [21,22].

2.1.2. Preparation of BAS

20 g of RS was added to a 1 M aqueous solution of NaOH (300 ml) and the suspension was refluxed for 72 h. After this, the suspension was centrifuged and the solid thoroughly washed with distilled water. Homoionic sodium sepiolite was obtained by using a liquidesolid ratio of 10 and 1 M of NaCl at room temperature for 24 h. The powder sample was washed repeatedly with deionized water and seperated cenntrifugally, then dried in vacuo at 313 K [23].

Infrared (IR) spectra of the sepiolite samples were recorded in the region (4000–400) cm^{-1} on a Mattson-1000 FTIR spectrometer at a 4 cm^{-1} resolution. The mineralogical compositions of the RS, MCS and BAS samples were determined from the X-ray diffraction (XRD) patterns of the products taken on a Rigaku 2000 automated diffractometer using Ni filtered CuKa radiation. A Tri Star 3000 (Micromeritics, USA) surface analyzer was used to measure the nitrogen adsorption isotherm at 77 K in the range of relative pressure 10^{-6} to 1. The data in Table 1 indicate the surface areas, pore volumes and average pore diameter for RS, MCS, and BAS samples.

2.2. Adsorption dependence on Cu(II) concentration

The experiments of adsorption equilibrium were carried out in a similar fashion to that described before [22]. The adsorption percentage of Cu(II) was calculated by the difference of the initial and final concentration using the following equation:

$$R = (C_0 - C_e) / C_0 \times 100 \qquad (1)$$

where C_0 is the initial concentration of Cu(II) solution (mg/L), C_e the equilibrium concentration of the Cu(II) solution (mg/L), R the retention of Cu(II) in % of the added amount.

The equilibrium data have been analyzed using the Langmuir and Freundlich isotherms and the characteristic parameters for each isotherm have been determined [24,25]. A clear review of the equations and their application is in the literature [21]. The data conform to the linear form of the Langmuir model [24] [Eq. (2)] expressed below:

$$C_e / q_e = C_e / q_m + 1 / K_L q_m \qquad (2)$$

where C_e is the equilibrium concentration of Cu(II) (mg/L) and q_e is the amount of the Cu^{2+} adsorbed (mg) per unit of

Table 1
Porous structure parameters of the sepiolite samples

Sample	S_{BET} (m^2/g)	S_{ext}^{a} (m^2/g)	$S_{mic.}$ (m^2/g)	V_t (cm^3/g)	$V_{mic.}$ (cm^3/g)	$V_{meso.}$ (cm^3/g)	D_p^{b} (nm)
RS	160	34	126	0.36	0.017	0.343	8.95
MCS	14	2	12	0.043	0.001	0.042	12.58
BAS	130	23	107	0.374	0.012	0.362	11.46

[a] $S_{ext} = S_{meso}$.
[b] $4V/A$ by BET.

sepiolite (g). q_m and K_L are the Langmuir constants related to the adsorption capacity (mg/g) and the equilibrium constant (L/g), respectively.

The adsorption equilibrium data was also applied to the Freundlich model [25] [Eq. (3)] given below:

$$\log q_e = \log K_f + (1/n)\log C_e \tag{3}$$

where K_f and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The Freundlich parameters (K_F and n) indicate whether the nature of adsorption is either favorable or unfavorable.

The thermodynamic parameters of the adsorption process can be determined from the experimental data as described before [21].

$$\ln K_d = \Delta S/R - \Delta H/RT \tag{4}$$

$$\Delta G = \Delta H - T\Delta S \tag{5}$$

$$K_d = q_e / C_e \tag{6}$$

where K_d is the distribution coefficient for the adsorption, ΔS, ΔH and ΔG are the changes of entropy, enthalpy and Gibbs energy, T (K) is the temperature, R (J mol^{-1}K^{-1}) is the gas constant. The values of ΔH and ΔS were determined from the slopes and intercepts of plots of ln K_d vs. $1/T$.

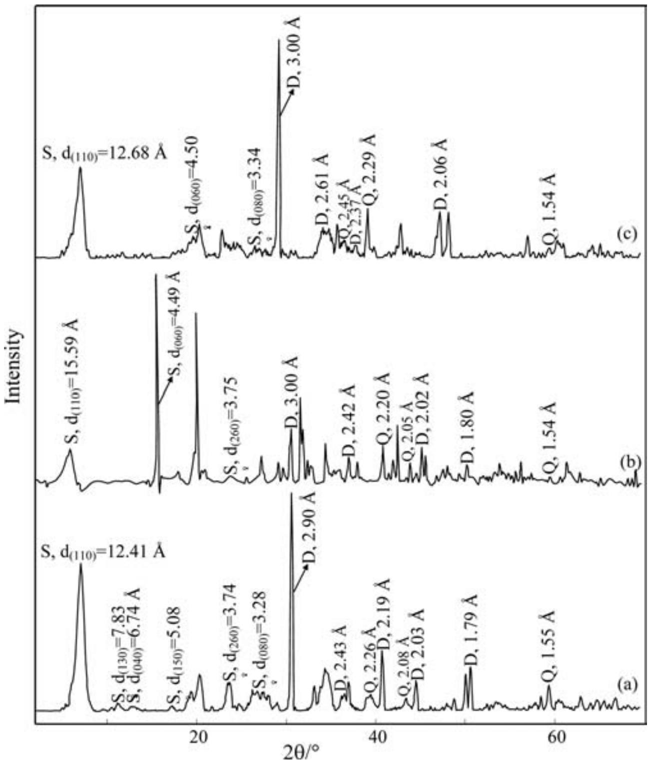


Fig. 1. The X-ray diffraction patterns of the RS (a), MCS (b), and BAS samples (S: sepiolite, D: dolomite, Q: quartz). Figs. 1a,b are from [26].

3. Results and discussion

3.1. Material characterization

The XRD patterns of the RS, MCS, and BAS samples are presented in Fig. 1. Some of the structural properties of the MCS used in this study have been described in Eren at al. [26]. The authors demonstrated that the manganese oxide-coating process has caused structural changes in the sepiolite sample. The Mn oxide-coating process affected mainly the intensities of the 110 and 260 reflections which have been reduced, and also the 130, 040, 150 and 080 reflections of RS disappeared after the oxide-coating process (Table 2). The formation of a new structure was also illustrated by the peak appearing at a lower angle i.e. <5.66° (15.59 Å) in the XRD pattern of the MCS. The structure of RS changed after the base activation process as shown by the reduction in intensity of the 110 reflection at 12.41 Å and the appearance of a weaker smectite peak at 15 Å (Fig. 1b). The position of the d110 peak of the RS sample shifted from 12.41 to 15.60 Å (Fig. 1c) which was accompained by a intensity decrease from 78 to 55% (Table 2). The intensity of weak sepiolite diffraction peak at 26.24° (3.34 Å) also decreased, and 130, 040, 150 and 260 diffraction peaks at 7.83, 6.74, 5.08 and 3.74 Å completely disappeared (Table 2).

The IR spectra of the RS, MCS, and BAS samples are presented in Fig. 1. Recently Eren et al [26] synthesised manganese oxide coated sepiolite and compared the IR spectral characteristics of the raw sepolite with the earlier reported data. The spectral data are reported in Table 1.

Table 2
d-spacing and intensity values of reflections for sepiolite samples

Reflection	RS		MCS		BAS	
	d, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0
d_{110}	12.41	78	15.59	12	12.68	55
d_{130}	7.83	3	—	—	—	—
d_{040}	6.74	2	—	—	—	—
d_{150}	5.08	3	—	—	—	—
d_{060}	—	—	4.49	10	4.50	13
d_{260}	3.74	13	3.75	8	—	—
d_{080}	3.28	12	—	—	3.34	8

The IR spectrum of MCS contains a peak at the 523 cm^{-1} from a Mn–O vibration [26,28], and a vibrational band for Mn_3O_4 species is located at 627 cm^{-1} [29]. As shown in Fig. 2c, the sepiolite-like product obtained as a result of the base activation. The two peaks observed at 1429 and 1381 cm^{-1} arise from dolomite impurities. The absorbances at 689 and 651 cm–1 are weaker than corresponding absorbances for the RS, suggesting fewer chemical bonds that absorb at these positions and thinner, more disordered crystals of the BAS than the RS reference [30] (Fig. 2a).

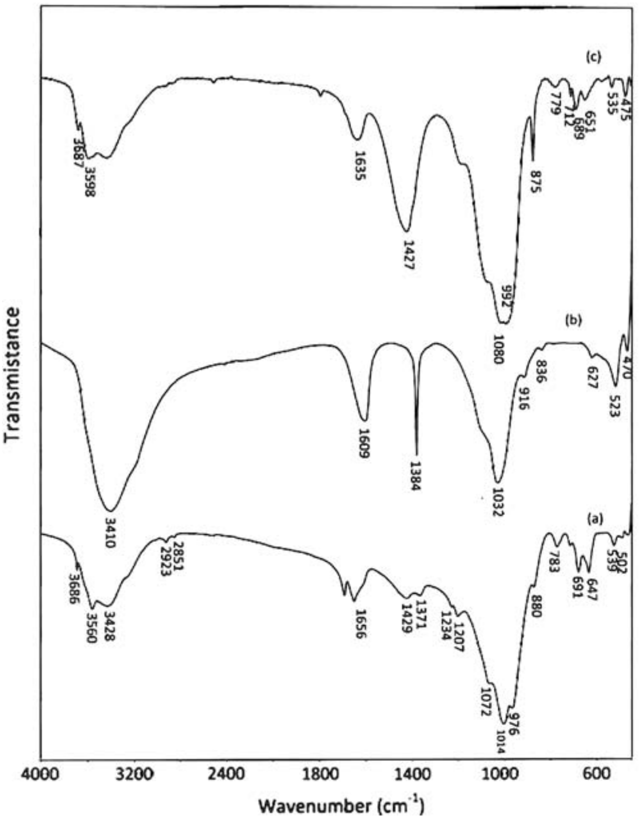


Fig. 2. IR spectra of the RS (a), MCS (b), and BAS (c) samples. Figs. 2a,b are from [26].

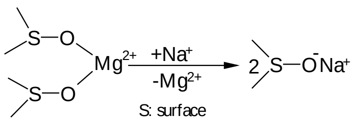
3.2. Adsorption isotherms and parameters

The equilibrium data for Cu(II) adsorption on sepiolite samples were fitted to the Langmuir equation: an equilibrium model able to identify the chemical mechanism involved. Linear plots of C_e/q_e vs. C_e (Fig. 3) were employed to determine the value of q_m (mg/g) and K_L (L/mg). The data obtained with the coefficients of determination (R^2) are listed in Table 3. The Langmuir monolayer adsorption capacities of RS, MCS and BAS in 0.1 M KNO_3 solution were estimated to be 5.55, 6.70 and 13.46 mg/g, respectively (Table 3). It is evident that the base activation process significantly enhanced the adsorption of Cu(II). This may be due to the following two reasons:

i) It is conceivable that more silanol groups of BAS particles produced by base activation could be an important reason. The specific adsorption involving monodentate and bidentate complexation onto Si–OH sites of the BAS particles may predominate under the adsorption conditions. It is known that the use of alkaline conditions should facilitate the breakdown of Si–O–Si bonds by the following reaction:

$$\text{–Si–O–Si–} + 2OH^- = H_2O + 2\text{–Si–}O^- \tag{8}$$

ii) Corma and co-workers [31] have reported that it is possible to replace part of the Mg^{2+} located at the edges of the channels by Na^+ after the base activation process. Once the Na^+ form of the RS is obtained, the ion exchange of Na^+ by copper ions can be easily achieved.



(9)

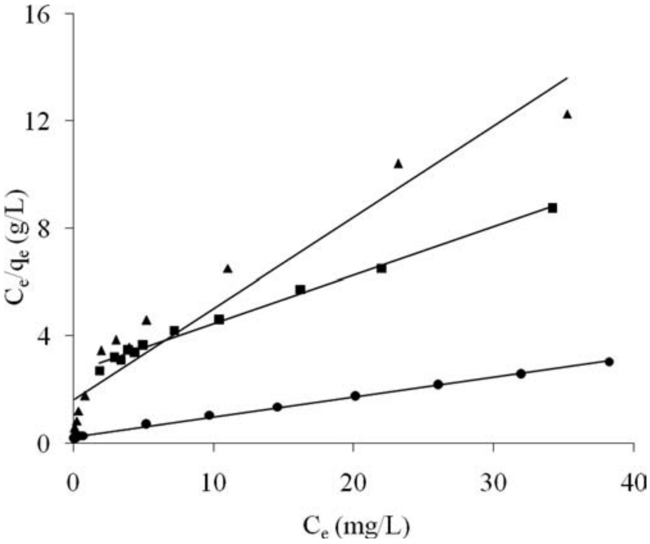


Fig. 3. Langmuir isotherm plot for the adsorption of Cu(II) onto sepiolite samples, RS; triangles, MCS; circles, BAS; squares. T = 295 K, initial pH = 6.0, m = 2 g/L, ionic strenght (IS) is 0.1 M KNO_3 (controlled by KNO_3).

Table 3
IR absorption bands of RS and MCS samples

Suggested assignments	RS [26,27]	MCS [26]
SiOH hydroxyl stretch	—	—
MgOH (trioctahedral) stretch	3686	3686
MgOH (dioctahedral) stretch	—	—
OH- stretch from coordinated water	3560	3560
Water OH-stretch	3428	3446
Water OH-stretch	—	—
Water OH bend	1698	—
Water OH bend	1656	—
Water OH bend	—	1609
Carbonate impurity	1429	—
Carbonate impurity	1371	1384
SiOH stretch	1207	—
SiOH stretch	1072	1032
SiOH stretch	1014	991
OH deformation	967	—
OH deformation	—	916
OH translation	783	—
OH translation	691	—
OSiO bends	647	—
OSiO bends	502	523
OSiO bends	474	470
OSiO bends	—	—

The adsorption capacities of samples for the removal of Cu(II) has been compared with adsorption capacities of different sepiolites reported in the literature and the values of the adsorption capacities are presented in Table 4. The values are reported in the form of monolayer adsorption capacity. The experimental data of the present investigation are comparable with the reported values [16,17,32–35]. From this table, it is also appears that the surface properties of RS could be improved upon modification of manganese oxide as previously reported by other researchers [32–34]. The equilibrium data were also fitted to Freundlich equation, and a fairly satisfactory empirical isotherm can be used for non-ideal adsorption. The constants K_F and n were calculated from Freundlich plots (Fig. 4). In adsorption systems, a value of $n > 1$ which indicates that the adsorption intensity is favorable over the entire range of concentrations studied. The K_F value of the Freundlich equation (Table 3) also indicates that BAS has a very high adsorption capacity for copper ions in aqueous solutions.

3.3. *Effect of ionic strength, pH and inorganic ligand*

The adsorption of Cu(II) onto the sepiolite samples as a function of ionic strength and pH is shown in Figs. 5a–c. The three sepiolite samples showed an identical behaviour of increased uptake of Cu(II) per unit mass with gradually increasing pH, and the shape of the curves is dependent on the sepiolite surfaces.

As shown in Fig. 5a, Cu(II) adsorption by the RS sample decreased when pH decreased. This result suggests that the adsorptive decrease was caused by competition for exchange sites between hydrogen and Cu(II) cations. There is also a decrease in Cu(II) adsorption with increas-

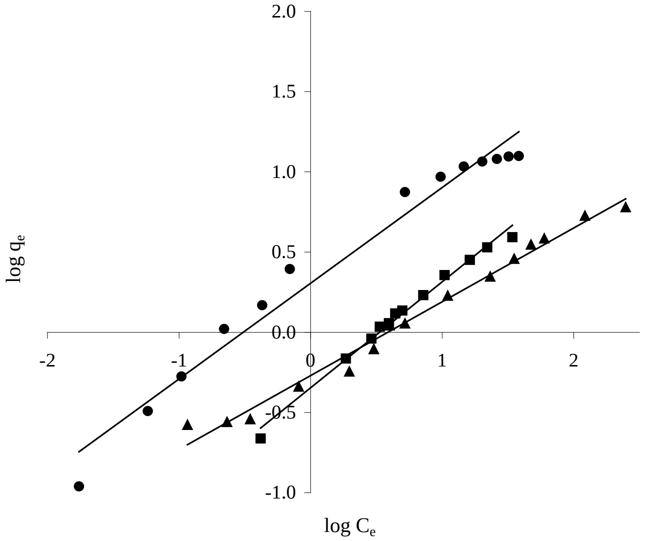


Fig. 4. Freundlich isotherm plot for adsorption of Cu(II) onto sepiolite samples, RS; triangles, MCS; circles, BAS; squares. T = 295 K, initial pH = 6.0, m = 2 g/L, IS is 0.1 M KNO_3 (controlled by KNO_3).

Table 4
Langmuir and Freundlich isotherm parameters for the adsorption of Cu(II) onto sepiolite samples

Sample	Langmuir isotherm constants			Freundlich isotherm constants		
	q_m (mg/g)	K_L (L/mg)	R^2	n	K_F ((mg/g)(L/mg)$^{1/n}$)	R^2
RS	5.55	0.067	0.994	1.51	0.45	0.971
MCS	6.70	0.030	0.991	2.07	0.52	0.980
BAS	13.46	0.331	0.997	1.68	2.02	0.974

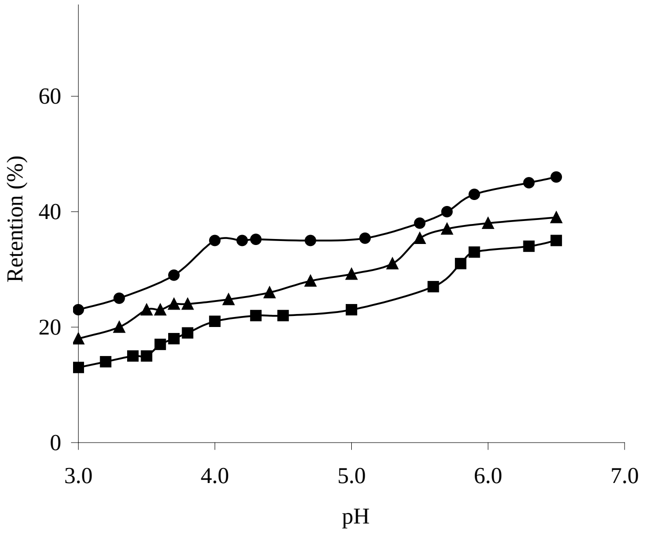


Fig. 5a. Adsorption of Cu(II) (3.2 mg/L) by RS (2 g/L) as function of pH and ionic strenght, squares, 0.1 M; triangles, 0.05 M; circles, 0.01 M.

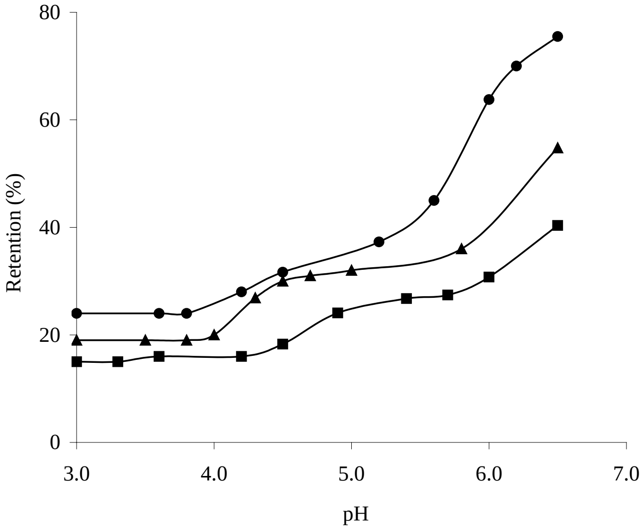


Fig. 5b. Adsorption of Cu(II) (3.2 mg/L) by MCS (2 g/L) as function of pH and ionic strenght, squares, 0.1 M; triangles, 0.05 M; circles, 0.01 M.

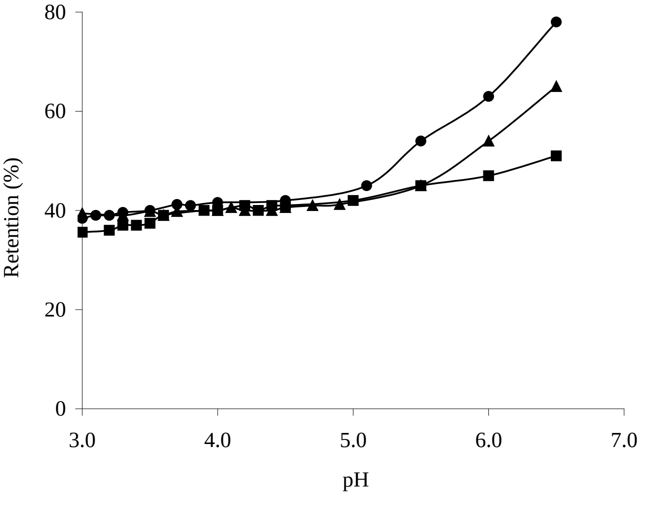


Fig. 5c. Adsorption of Cu(II) (3.2 mg/L) by BAS (2 g/L) as function of pH and ionic strenght, squares, 0.1 M; triangles, 0.05 M; circles, 0.01 M.

ing ionic strength. This can be explained by competition of Cu(II) cations with the background cation potassium at the face sites. The adsoption curves for RS are characterized by two distinct adsorption edges. For example, in the presence of 0.1 M KNO_3, the first stage adsorption edge commenced at about 13 % Cu(II) adsorption at pH ~3.0 and ended at pH ~3.8, at about which 20% of the total Cu(II) had been adsorbed. The second stage started at pH ~4.3 and continued up to pH 6.5 where about 35% of the total Cu(II) was adsorbed. The adsorption of Cu(II) onto the RS appears to involve two distinct mechanisms:

(1) the interlayer of sepiolite through an ion exchange reaction at permanent-charge sites are responsible for cation uptake at in the range $3 < pH < 4$. This assertion is based on the following experimental evidence that Cu(II) cations are sorbed by RS at low pH values.

(2) Cu(II) forms surface complexes with silanol and aluminol groups at the edges of the crystals at $pH > 4.3$. The adsorption of Cu(II) onto the MCS sample as a function of ionic strength and pH is shown in Fig. 5b.

The adsorption reduction for pH less than 4 can be explained by the mechanism involved in cation adsorption. This is in good agreement with the adsorption data of Karamanis et al. [36]. In this study, the reduction has been attributed to the excess of hydronium ions that compete for the exchangeable positions in the interlayer space of manganese oxide leading to a material conversion to hydrogen form. The adsoption curve of BAS have a different shape from that of RS sample, and the adsorption capacity of this material is higher than RS and MCS (Fig. 5c). The adsoption curve for this sample is characterized by one distinct adsorption edge. In the pH range 3 to 5.5, increasing ionic strength did not led to a significant change in the Cu(II) adsorption. The percent Cu(II) adsorbed in the the presence of 0.01 M KNO_3 at pH 6.5 is ≈78%, compared to 51 % at the same pH but in the presence of 0.1 M KNO3 for the BAS sample.

The adsorption of Cu(II) by the sepiolite samples was influenced by the presence of Cl^- (Fig. 6). It is clear that aqueous speciation by inorganic ligand influences Cu(II) adsorption. The adsorbed Cu(II) in the presence of Cl^- may also be attributed to a high specifity of the surfaces for Cu(II) relative to the ligand. The percent Cu(II) adsorbed in the 0.01 M Cl^- system at pH 6.5 are 41, 35 and 40% for the RS, MCS and BAS samples, compared to 35, 41 and 51% at the same pH but in the absence of Cl^-. These results suggest that the observed Cu(II) adsorption behavior in the sepiolite suspensions is influenced by both aqueous speciation and surface ligand complexation of Cu(II) ions. The increased amount of adsorbed Cu(II) on RS can be explained in terms of solution chemistry, because Cu–Cl, CuOH–Cl complexes are the dominant Cu(II) species in the presence of 0.01 M Cl^-. Thus, the specifically adsorbed ligand enhances Cu(II) retention by the surface complexation of Cu(II). Also, the reductions in Cu(II) adsorption on the MCS and BAS samples in the presence Cl^- might be due to ion competition with the various Cu(II) species for adsorption sites {$[XOH^+ – Cl^-$}.

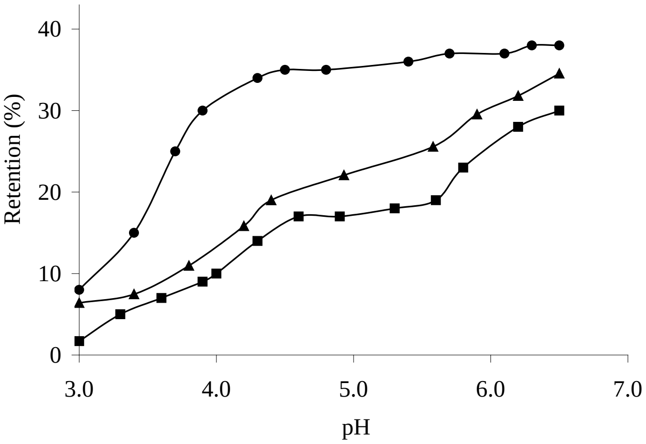


Fig. 6. Adsorption of Cu(II) (3.2 mg/L) by sepiolite samples (2 g/L) as function of pH and in the presence of Cl^- [IS is 0.1 M (KNO_3)], squares, RS; triangles, MCS; circles, BAS.

Table 5
Adsorption results of Cu(II) ions from the literature by various adsorbents

Adsorbent	Adsorption capacity (mg/g)	Ref.
Sepiolite	6.93	[16]
Organo-sepiolite	9.22	[17]
Raw bentonite	42.41	[32]
Manganese oxide coated raw bentonite	105.38	[32]
Diatomite (pH 5, 24 h)	24.0	[33]
Mn-diatomite (pH 5, 24 h)	99.0	[33]
Carbon nanotube (pH 5)	≈26.24	[34]
Mn oxide-coated carbon nanotube (pH 5)	78.74	[34]
Biomass	25.32	[35]

3.4. Thermodynamic studies

DG, DH, and DS were evaluated at 303 K for RS, MCS, and BAS as –18.94 kJ/mol, 25 kJ/mol and 145 J/mol K; –19.51 kJ/mol, 2 kJ/mol and 71 J/mol K; and –20.51 kJ/mol, 31 kJ/mol and 170 J/mol K, respectively (Table 6). The negative values for the Gibbs energy change, ΔG, show that the adsorption process for the three sepiolite samples is spontaneous and the degree of spontaneity of the reaction increases with increasing tempreature. The values of ΔG are more negative for the MCS and BAS suggesting that the adsorption process for these materials is more spontaneous. These results suggest that the internal domains of these samples are more suitable environments for Cu(II) cations than the RS sample. Weng et al. [37] noted that $\Delta G°$ values up to 20 kJ/mol are consistent with electrostatic interaction between adsorption sites and the metal ion while $\Delta G°$ values more negative than 40 kJ/mol involve charge sharing or transfer from the adsorbent surface to the metal ion to form a coordinate bond. The values of ΔG obtained in this work, range from –18.21 to –19.66 kJ/mol indicating that electrostatic interaction may play a significant role in the adsorption process. It may be suggested that a surface complexation reaction is the major mechanism responsible for the Cu(II) adsorption process. The heats of adsorption are positive for each sepiolite sample. The low ΔH value for MCS shows that the interactions between MCS and Cu(II) are weak. These positive values of ΔH suggest that a large amount of heat is consumed to transfer the Cu(II) ions from aqueous so-

Table 6
Thermodynamic parameters for the adsorption of Cu(II) onto sepiolite samples

Sample	ΔH (kJ/mol)	ΔS (J/molK)	ΔG (kJ/mol)				R^2
			303	313	323	338	
RS	25	145	–18.94	–20.39	–21.84	–24.01	0.931
MCS	2	71	–19.51	–20.22	–20.93	–22.00	0.983
BAS	31	170	–20.51	–22.21	–23.91	–26.46	0.998

lution into the solid phase. As was suggested by Nunes and Airoldi [38], the transition metal ions must give up a larger share of their hydration water before they could enter the smaller cavities. Such a release of water from the divalent cations would result in positive values of ΔS. This mechanism of the adsorption of Cu(II) ions is also supported by the positive values of ΔS, which show that Cu(II) ions are less hydrated in the sepiolite layers than in the aqueous solution. Also, the positive value of ΔS indicates the increased disorder in the system with changes in the hydration of the adsorbing Cu(II) cations.

The experimental adsorption thermodynamic data of the present investigation are comparable with reported values. Weng et al. [37] have reported that $\Delta G°$, $\Delta H°$ and $\Delta S°$ for adsorption of Cu(II) on spent activated clay have values of –26.85 kJ/mol, 14.51 kJ/mol, and 138.78 J/molK, respectively. Bhattacharyya and Gupta [39] calculated that $\Delta H°$ of Cu(II) adsorption on TBA-montmorillonite, ZrO–kaolinite and montmorillonite as 29.2, 50.5 and 50.7 kJ/mol, respectively, for the temperature range 303–313 K. Lin and Juang [40] have found that ΔG, ΔH and ΔS for Cu(II) adsorption on surfactant modified montmorillonite are –9.66 kJ/mol, 7.05 kJ/mol, and 9.09 J/K mol, respectively. Yavuz et al. [41] have reported that $\Delta G°$, $\Delta H°$ and $\Delta S°$ for adsorption of Cu(II) on kaolinite are 4.61 kJ/mol, 39.52 kJ/mol, and 0.117 J/K mol, respectively. The entropy values reported in above references are comparatively smaller than the values obtained in the present study. This indicates the considerable change in surface configuration due to the interactions and the strong affinity of Cu(II) towards the used sepiolite samples is supported by an entropy increase. In the present study, calculated $\Delta G°$ values were found to be more negative than the above literature values. This result also confirms that the adsorption process is a high preference of Cu(II) for the used sepiolite samples.

4. Conclusions

In the present work, a cheap, readily available and effective adsorbent material has identified sepiolite as a potentially attractive adsorbent for the treatment of Cu(II) contaminated aqueous solutions after modification with manganese oxides and sodium hydroxide. The adsorption of Cu(II) by sepiolite samples was influenced by pH, ionic strength, and the presence of Cl^-. The adsorption isotherm studies indicate that the adsorption of Cu(II) follows both the Langmuir and Freundlich isotherms. From the values of the Langmuir monolayer capacity, qm, it is concluded that the treatment with manganese oxide and sodium hydroxide does increase the number of adsorption sites to a large extent. Since there is a huge deposit of sepiolite in Turkey, there is great potential for its utilization in wastewater treatment.

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