

Equilibrium and thermodynamic studies of Cu(II) removal by iron oxide modified sepiolite

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ABSTRACT

This paper presents the adsorption of Cu(II) from aqueous solution by raw sepiolite (RS) and iron oxide-coated sepiolite (ICS) 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^- , SO_4^{2-} and HPO_4^{2-}). Changes in the surface and structure were characterized by means of XRD, IR and XRF techniques. The Langmuir monolayer adsorption capacities of RS and ICS in 0.1 M NaNO_3 solution at 298 K were estimated to be 14.96 and 21.56 mg/g, respectively. ΔG , ΔH and ΔS were evaluated for RS and ICS to be -14.14 kJ/mol (at 298 K), 39.03 kJ/mol and 178 J/mol K, and -16.09 kJ/mol (at 298 K), 32.99 kJ/mol and 165 J/mol K, respectively.

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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. A lot of non-conventional, low-cost and easily obtainable adsorbents have been tested for heavy metal removal such as clay minerals [2–5], biomaterials [6–9] and industrial solid wastes [10–13].

Sepiolite is a clay mineral, a complex magnesium silicate, a typical formula for which is $\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$. Adsorption studies using modified sepiolite are relatively scarce. Adsorption is due to the presence of active adsorption centres on the sepiolite surfaces [14]. Sepiolite, which has a high surface area, should provide an efficient surface for the metal oxides. At the same time, the metal oxides can improve the Cu(II) adsorption capacity of sepiolite. The resulting composite adsorbent could become a very efficient way to 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 iron oxide-coated sepiolite (ICS).

The aim of this paper is to examine the effectiveness of iron oxide-coated sepiolite (ICS) in removing Cu(II) from aqueous solution and to determine the adsorption characteristics of Cu(II) onto the ICS sample.

Although several investigators have suggested applications for iron oxides in water and wastewater treatment [15–18], sepiolite has never been used as a support for iron oxide for heavy metal removal from wastewater. Due to this reason, ICS was proposed and studied in this research. For this aim, RS and ICS 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, inorganic ligands (Cl^- , SO_4^{2-} and HPO_4^{2-}) and temperature on the adsorption of Cu(II) by the RS and ICS samples was investigated to better understand the Cu(II) adsorption process. The materials were characterized by infrared spectroscopy (IR), X-ray diffraction (XRD), and X-ray fluorescence (XRF) techniques.

2. Materials and methods

2.1. Materials

All reagents used, such as NaCl, NaNO_3 , HNO_3 , NaOH, and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 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 $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ by dissolution in deionised water. The stock was diluted to prepare a working solution.

The preparations of the iron oxide coated clay sample have already been discussed in previous work [19]. The system was prepared by mixing 20.0 g of RS, 100 mL of freshly prepared 1.0 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution, and 180 mL of 2.0 M NaOH solution in a 2-L polyethylene flask. The addition of NaOH solution was rapid and with stirring. The

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analysis. The Si can be taken as a reference element due to it is a structural element of the sepiolite. Coating of the RS with iron oxide resulted in an increase of SiO_2/MgO ratio from 1.81 to 2.08 wt.%. It is most likely that the extraction of Mg^{2+} cations from octahedral positions under the working conditions applied during the coating process. Coating of RS with iron oxide resulted in the increase of Fe_2O_3 content from 0.22 to 15.45 wt.%. The loss on ignition (LOI) comes from the total water of minerals, carbonates and organic matter. There was a significant difference in LOI values of the RS and ICS. It is most likely that different types of water molecules from layers were removed during the thermal activation process of iron saturated sepiolite sample.

The XRD patterns of RS and ICS samples were presented in Fig. 1. For the XRD pattern of RS, main reflection was observed in the region $2^\circ < 2\theta < 8^\circ$ (Fig. 1a). This corresponds to the 7.10 (2θ) value from which the interlamellar distance was found to be 12.44 Å. The XRD results show that iron oxide-coating process has caused structural changes in the sepiolite sample. The position of d_{110} peak of RS sample shifted from 7.10 to 7.14 Å (Fig. 1b) which was accompanied by a intensity decrease from 129 to 65.5 (Table 2). The formation of a new structure was illustrated by the peak appearing at lower $<4.40^\circ$ (20.06 \AA) in the XRD pattern of the RS. The XRD peak intensities for ICS is less than those for some of the peaks for RS. Iron oxide-coating process of the RS has reduced mainly the intensities of the 110, 131 and 082 reflections, and the 370, 441 and 321 reflections of RS disappeared after oxide-coating process. It is known that XRD intensity is closely related with the crystallinity and particle size of the sample. The decrease of peak intensity in XRD pattern of ICS points out that iron oxide could be dispersed in the internal structure of sepiolite. This may be the reason for the broader and less intense peaks of the ICS sample compared with that for RS. Thus, the broader and less intense peaks for the ICS sample show its smaller crystal size and poorer crystal structure. In addition to this, introduction of the iron into the channels of sepiolite may also decrease the crystallinity of the sepiolite.

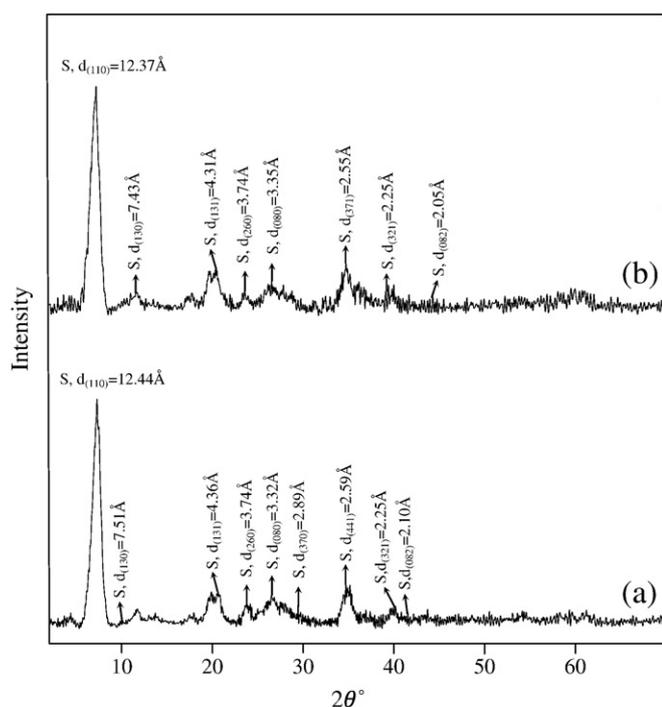


Fig. 1. The X-ray diffraction patterns of the RS (a) and ICS (b) samples (S: sepiolite).

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

Reflection	RS		ICS		Ref. [26,27]
	d, Å	I	d, Å	I	
d_{110}	12.44	129	12.37	65.5	12.07
d_{130}	7.51	2.4	7.43	2.4	7.48
d_{131}	4.36	16.9	4.31	4.1	4.30
d_{260}	3.74	6.7	3.74	4.1	3.74
d_{080}	3.32	6.0	3.35	7.3	3.37
d_{370}	2.89	7.4	–	–	2.92
d_{441}	2.59	16.2	–	–	2.61
d_{321}	2.25	5.9	–	–	2.26
d_{082}	2.10	19.6	2.05	1.6	2.07

The IR spectra of the RS and ICS samples are presented in Fig. 2. The bands in the IR spectrum of RS (Fig. 2a) may be summarised as follows: (i) the band of the triple bridge group Mg_3OH is at 3686 cm^{-1} ; (ii) the absorption of the structurally bound water is seen at 3560 cm^{-1} ; and (iii) the stretches at 3428 cm^{-1} and the OH-bending mode at 1660 cm^{-1} are associated with zeolitic water. The lattice vibrations are given as follows: (a) the Si–O combination bands at ($1207, 1072$ and 967 cm^{-1}); (b) the basal plane of the tetrahedral units exhibiting the Si–O–Si plane vibrations at (1014 and 474 cm^{-1}), and (c) Mg_3OH bending vibration at 647 cm^{-1} [28]. Noticeable changes were detected for bands which are related to the OH vibrations in the region between 3700 and 3000 cm^{-1} . As the RS altered to ICS, changes in the IR absorption bands of the sample were noted at $3687, 3561$, and 3428 cm^{-1} (Fig. 2b). The broad band at 3561 cm^{-1} , due to the zeolitic water in the RS, disappeared upon modification. It is also known that intermolecular hydrogen bonding causes the appearance of bands at $3550\text{--}3200 \text{ cm}^{-1}$. The band at about 3450 cm^{-1} results from monomeric structures, whereas the absorption near 3200 cm^{-1} arises from “polymeric” structures [29–31]. For the ICS sample, the bands at $3687, 3561$ and 3428 cm^{-1} were replaced by a broad band at 3436 cm^{-1} . The broad band at 3436 cm^{-1} for ICS sample indicates the monomeric hydrogen bond vibrations. The observed shift toward lower frequency points out the increase in hydrogen bonding for ICS. Doula [31] and Cornell [32] agree that the

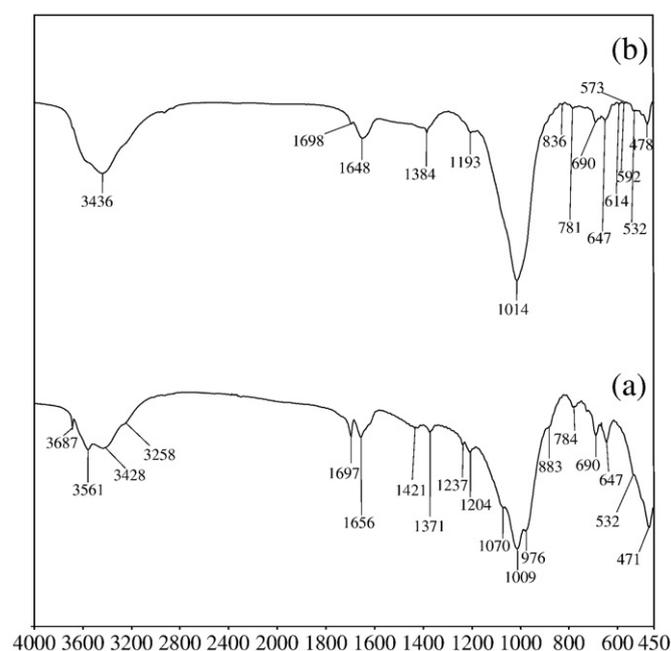


Fig. 2. IR spectra of the RS (a) and ICS (b) samples.

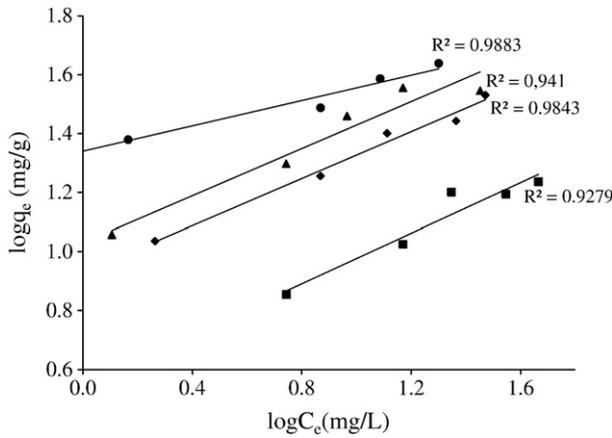


Fig. 6. Freundlich isotherm plot for the adsorption of Cu(II) onto RS sample at different temperatures. Squares, 298 K; diamonds, 318 K; triangles, 318 K; circles, 328 K, initial pH = 5.0, m = 1 g/L, ionic strength (IS) is 0.1 M NaNO₃ (controlled by NaNO₃).

while $n > 1$ means that adsorption intensity is favorable at high concentrations but much less at lower concentrations [36,37]. The Freundlich adsorption capacity (K_F) for the RS sample was found to be lower than that for the ICS. In the adsorption systems, the n values are higher than 1 which point out that adsorption intensity is favorable at high concentrations.

There are few works related to Cu(II) adsorption on raw and modified sepiolite which have been reported [38–41]. Sanchez et al. [38] have reported that the maximum retention capacity for Orera sepiolite was obtained as 6.9 mg/g for Cu(II). Aminopropyltriethoxysilane modified sepiolite was reported to be 9.22 mg/g for the removal of Cu(II) from aqueous solution by Ozkan et al. [39]. Dogan et al. [40] have reported that q_m for adsorption of Cu(II) on [3-(2-aminoethylamino)propyl]trimethoxysilane modified sepiolite sample is 11.88 mg/g. Doğan et al. [41] have reported a Langmuir monolayer capacity, q_m , of 30.61 mg/g for Cu(II) adsorption onto sepiolite. From these observations, it also appears that the surface properties of RS could be improved upon modification of iron oxide.

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 was shown in Fig. 7a and b. The two sepiolite samples showed an identical behavior of increased uptake of Cu(II) per unit mass with gradually increasing pH, and the shape of curves dependent on the sepiolite surfaces. The experiments, however, could not be done at pH > 6.0 due to insoluble copper hydroxide starts precipitating from the solution.

Table 3

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

Sample	T (K)	Langmuir constants			Freundlich constants		
		q_m (mg/g)	K_L (L/mg)	R^2	n	K_F ((mg/g)(L/mg) ^{1/n})	R^2
RS	298	14.96	0.05	0.941	2.49	2.27	0.969
	308	26.82	0.14	0.997	2.65	6.06	0.939
	318	31.84	0.14	0.93	2.37	6.32	0.897
	328	39.83	0.18	0.98	2.37	8.73	0.940
ICS	298	21.56	0.08	0.972	2.33	3.53	0.984
	308	38.99	0.15	0.962	2.51	8.47	0.984
	318	40.91	0.26	0.981	2.51	10.69	0.939
	328	44.52	0.71	0.976	4.65	21.88	0.988

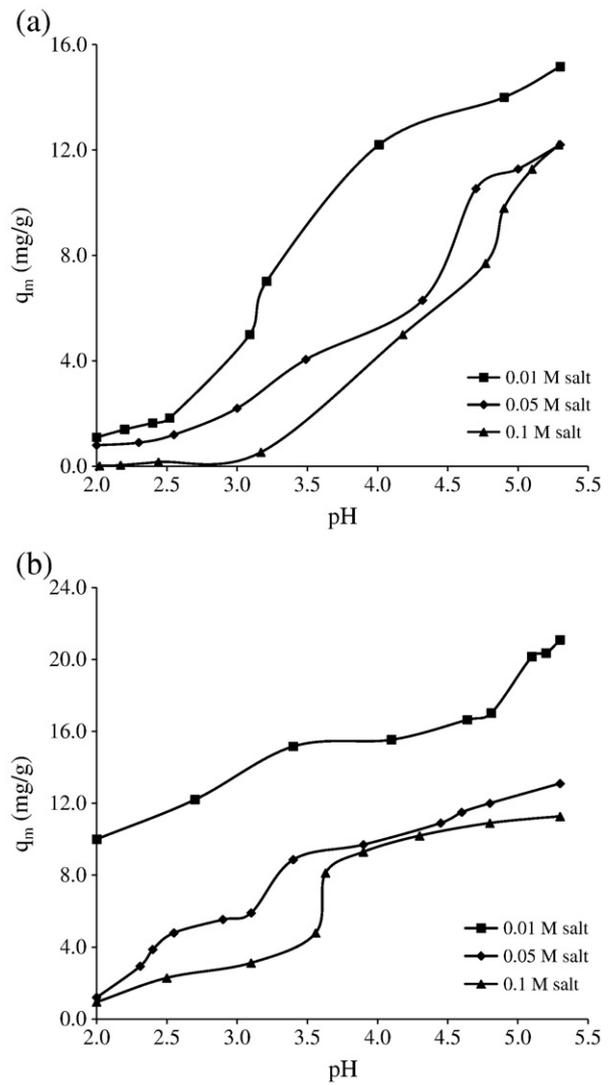


Fig. 7. a. Adsorption of Cu(II) (38.1 mg/L) by RS (1 g/L) as function of pH and ionic strength, squares, 0.1 M; diamonds 0.05 M; triangles, 0.01 M. b. Adsorption of Cu(II) (38.1 mg/L) by ICS (1 g/L) as function of pH and ionic strength, squares, 0.1 M; diamonds 0.05 M; triangles, 0.01 M.

The adsorption curve of RS have a different shape from that of ICS sample, and the adsorption capacity of this material is lower than ICS (Fig. 7a). The adsorption curve for this sample is characterized by one distinct adsorption edge. In the pH range 2.0 to 5.3, increasing ionic strength did not lead to a significant change in the Cu(II) adsorption. The percent of Cu(II) adsorbed onto the RS sample in the presence of 0.01 M NaNO₃ at pH 6.5 is ≈ 39%, compared to 32% at the same pH but in the presence of 0.1 M NaNO₃.

As shown in Fig. 7b, Cu(II) adsorption by the ICS sample decreased when pH decreased. There is also a decrease in Cu(II) adsorption with increasing ionic strength. Increasing the ionic strength from 0.01 to 0.1 led to a significant decrease in the Cu(II) ions' adsorption for ICS sample. The percent of Cu(II) ions adsorbed in the presence of 0.01 M NaNO₃ at pH 5.3 is ≈ 55%, compared to 29% at the same pH but in the presence of 0.1 M NaNO₃ for the ICS sample. The adsorption curves for ICS are characterized by two distinct adsorption edges. For example, in the presence of 0.1 M NaNO₃, the first stage adsorption edge commenced at about 3% Cu(II) adsorption at pH ~ 2.0 and ended at pH ~ 3.5, at about which 5% of the total Cu(II) had been adsorbed. The second stage started at pH ~ 4.0 and continued up to pH 5.3 where

about 29% of the total Cu(II) was adsorbed. This may be due to the following two reasons: i—the effect of ionic strength on metal adsorption may be explained by the formation of outer-sphere complexes since Na^+ in the background electrolyte could compete with the copper ions adsorbed on the outer-sphere adsorption sites and reduced the adsorption, whereas Na^+ would not have competed for the inner-sphere sites. ii—The electrostatic attraction seems to be a significant mechanism, as indicated by the results where at high ionic strength, the increased amount of NaNO_3 can help render the surface of the ICS to be not easily accessible to Cu(II) ions. According to the electrical diffuse double layer theory, when solid adsorbent is in contact with sorbate species in solution, they are bound to be surrounded by an electrical diffused double layer, the thickness of which is significantly expanded by the presence of electrolyte. Such expansion may be inhibited between the approaching ICS particles and Cu(II) cations.

The adsorption of Cu(II) by the sepiolite samples was influenced by the presence of inorganic ligands (Fig. 8a and b). It points out that aqueous speciation by inorganic ligand influences Cu(II) adsorption.

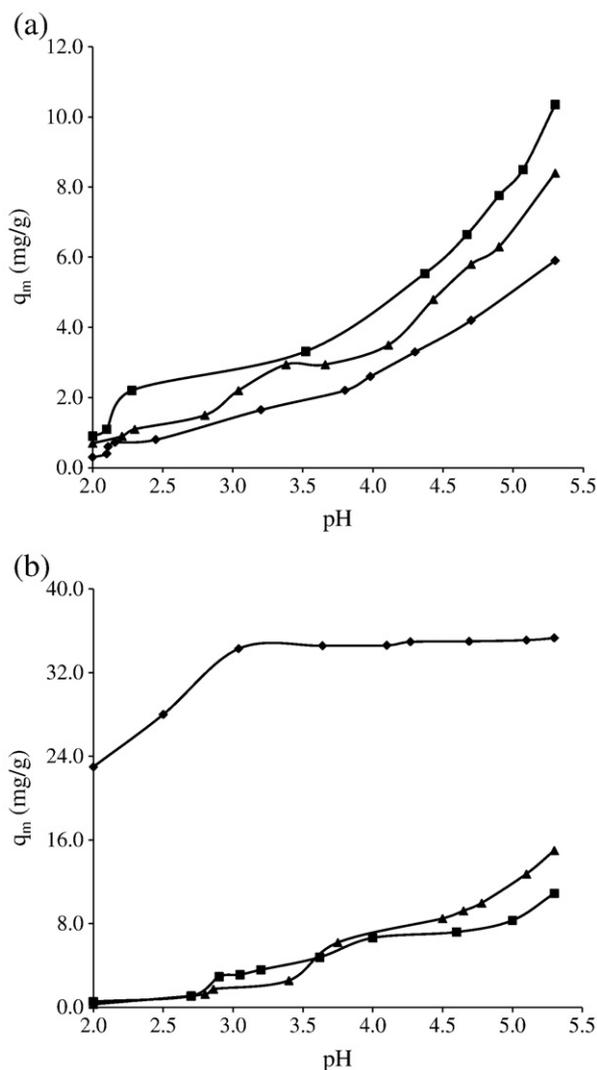


Fig. 8. a. Adsorption of Cu(II) (38.1 mg/L) by RS sample (1 g/L) as function of pH and in the presence of inorganic ligands. [IS is 0.1 M (NaNO_3)], squares, Cl^- ; diamonds, SO_4^{2-} ; triangles, HPO_4^{2-} . b. Adsorption of Cu(II) (38.1 mg/L) by ICS sample (1 g/L) as function of pH and in the presence of inorganic ligands. [IS is 0.1 M (NaNO_3)], squares, Cl^- ; diamonds, SO_4^{2-} ; triangles, HPO_4^{2-} .

The adsorbed Cu(II) in the presence of ligands may also be attributed to a high specificity of the surfaces for Cu(II).

As shown in Fig. 8a, the retention of Cu(II) ions by RS surface was decreased in the presence of 0.01 M inorganic ligands. The decreased amount of adsorbed Cu(II) ions can be explained in terms of solution chemistry. These ions effectively decrease the degree of hydrolysis of Cu(II) ions by blocking some of the coordination positions. Also, the reduction in Cu(II) ions' adsorption on the RS sample in the presence of Cl^- , SO_4^{2-} and HPO_4^{2-} might be due to ion competition with the various Cu(II) species for adsorption sites {e.g. $[\text{XOH}^+-\text{Cl}^-]$, $[\text{XOH}^+-\text{SO}_4^{2-}]$ and $[\text{XOH}^+-\text{HPO}_4^{2-}]$ }.

The adsorption of Cu(II) ions by the ICS sample was influenced by the presence of SO_4^{2-} and HPO_4^{2-} (Fig. 8b). The percent of Cu(II) ions adsorbed in the 0.01 M SO_4^{2-} and HPO_4^{2-} systems at pH 5.3 are 92 and 33%, respectively, compared to 29% at the same pH but in the absence of these ligands. This result suggests that the observed Cu(II) ions' adsorption behavior in the ICS suspensions is influenced by both aqueous speciation and surface ligand complexation of Cu(II) ions. The specifically adsorbed ligand enhances Cu(II) ions' retention by the surface complexation of Cu(II) ions. The increased amount of adsorbed Cu(II) on ICS can be explained in terms of solution chemistry, because Cu-L (L: SO_4^{2-} or HPO_4^{2-}), and CuOH-L complexes are the dominant Cu(II) species in the presence of 0.01 M SO_4^{2-} or HPO_4^{2-} . Thus, the specifically adsorbed ligand enhances Cu(II) retention by the surface complexation of Cu(II). Fig. 6 also showed that the retention of Cu(II) ions by ICS surface was not changed in the presence of 0.01 M Cl^- ligand. In the ICS suspensions, the percent of Cu(II) ions adsorbed in the 0.01 M Cl^- system at pH 5.3 is 28%, at the same pH but in the absence of the Cl^- ligand this value is 29%.

3.4. Thermodynamic studies

ΔG , ΔH , and ΔS were evaluated at 298 K for RS and ICS as -11.14 kJ/mol, 39.03 kJ/mol and 178 J/mol K; -16.09 kJ/mol, 32.99 kJ/mol and 165 J/mol K, respectively (Table 4). The negative values for the Gibbs energy change, ΔG , show that the adsorption process for the two sepiolite samples is spontaneous and the degree of spontaneity of the reaction increases with increasing temperature. The values of ΔG are more negative for the ICS suggesting that the adsorption process for this material is more spontaneous. This observation suggests that the internal domains of this samples are more suitable environments for Cu(II) cations than the RS sample. Weng et al. [42] noted that ΔG° values up to 20 kJ/mol are consistent with electrostatic interaction between adsorption sites and the metal ion while ΔG° 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, indicate 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 were calculated as positive for sepiolite samples. These positive values of ΔH suggest that a large amount of heat is consumed to transfer the Cu(II) ions from aqueous solution into the solid phase. As was suggested by Nunes and Airoldi

Table 4
Thermodynamic parameters for the adsorption of Cu(II) (51 mg/L) onto sepiolite samples.

Sample	ΔH (kJ/mol)	ΔS (J/molK)	ΔG (kJ/mol)				R^2
			298	308	318	328	
RS	39.03	178	-14.14	-15.92	-17.70	-19.49	0.855
ICS	32.99	165	-16.09	-17.74	-19.39	-21.03	0.963

