Adsorption studies of Cu(II) onto biopolymer chitosan and its nanocomposite 5%bentonite/chitosan

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ABSTRACT

Chitosan (CS) and nanocomposite 5%bentonite/chitosan (5%Bt/CS) prepared from the natural biopolymer CS were tested to remove Cu(II) ions using a batch adsorption experiment at various temperatures (25, 35 and 45 °C). X-ray diffraction, Fourier transform infrared spectroscopy, and thermogravimetric analysis/differential thermal analysis (TGA/DTA) were used in CS and the nanocomposite characterisation. This confirmed the exfoliation of bentonite (Bt) to form the nanocomposite. The adsorption kinetics of copper on both solids was found to follow a pseudo-second-order law at each studied temperature. The Cu(II) adsorption capacity increased as the temperature increased from 25 to 45 °C for nanocomposite adsorbent but slightly increased for CS. The data were confronted to the nonlinear Langmuir, Freundlich and Redlich–Peterson models. It was found that the experimental data fitted very well the Langmuir isotherm over the whole temperature and concentration ranges. The maximum monolayer adsorption capacity for the Cu(II) was 404–422 mg/g for CS and 282–337 mg/g for 5%Bt/CS at 25–45 °C. The thermodynamic study showed that the adsorption process was spontaneous and endothermic. The complexation of Cu(II) with NH2 and C=O groups as active sites was found to be the main mechanism in the adsorption processes.

Key words | adsorption, bentonite, chitosan, Cu(II), isotherm, nanocomposite

INTRODUCTION

Nowadays, the issue of heavy metals has become a growing concern. A common feature of industrial effluents is related to the fact that they almost always contain heavy metals, such as Zn(II), Cu(II), Pb(II), Ag(I), while many efforts are made to mitigate their adverse effects. Among the toxic heavy metals, Cu(II) is considered a priority pollutant, which is widely used in metal processing, electroplating, tanning paint and the pigment industry (Jarup 2003; Nicholson et al. 2005; Steinhögl et al. 2005; Alvarez et al. 2007). It is known that excessive copper in water may cause toxic and harmful effects to the living organisms (Gündoğan et al. 2004; Rengaraj et al. 2007). Therefore, it is of great significance to remove excess Cu(II) from wastewater because of their high toxicity towards aquatic organisms, human and other forms of life.

Conventional processes, such as chemical precipitation, membrane separation, ion exchange complexation and electrochemical treatment, have been used in the treatment of polluted water. However, these processes have the disadvantages of high cost and, sometimes, ineffectiveness for low metal concentration (Feng 2000). Thus, adsorption becomes an alternate method to remove heavy metals from diluted solutions.

In recent years, many low cost and widely available materials have been identified as suitable adsorbents for the removal of heavy metals from wastewaters (tea waste: Amarasinghe & Williams 2007; titanate nanotubes: Lee et al. 2009; maple wood sawdust: Rahman & Islam 2009; chitosan/rectorite; chitosan/clinoptilolite). Chitosan (CS), which is a natural adsorbent, has generally been considered by many researchers to be a potential material for the removal of heavy metals from wastewater because of the presence of amino (NH2), C=O and hydroxyl (OH) groups in its structure. These groups can serve as chelation sites and environmentally friendly adsorbents (Darvishi Cheshmeh Soltani et al. 2013; Zavareh et al. 2015). However, pure
CS bead has many drawbacks, such as unsatisfied mechanical properties, severe shrinkage, solubility in acidic conditions and deformation after drying (Mir et al. 2008). In order to overcome these disadvantages, many types of nanocomposite material based on CS were synthesised and used in the adsorption processes to remove heavy metal cations (Wan et al. 2004; Gotoh et al. 2004). Amongst all the potential nanocomposites, those based on clay have been widely investigated because of the availability of clay materials, and because their intercalation chemistry has been studied for a long time. CS is a powerful chelating agent that easily forms complexes with transition heavy metals. Many applications of CS were found in water treatment as well as metal cations and dyes (Wang et al. 2005). However, little research (Hussein et al. 2012; Wang et al. 2005) has paid attention to the chelating processes mechanism, especially the nature of active sites to remove the heavy metal by CS.

In this study, CS and the prepared 5% bentonite/chitosan (5%Bt/CS) were used as adsorbents. The objective was to combine the advantages of CS and Bt as the promising adsorbent in the treatment of wastewater loaded with Cu(II) ions. In addition, the nature of the adsorption sites involved in the adsorption of Cu(II) was discussed based on the characterisation of solids by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and thermogravimetric analysis/differential thermal analysis (TGA/DTA) before and after adsorption of Cu(II) by the proposed materials. The effects of various parameters, namely temperature, contact time and initial metal ion concentration were considered. Isotherms data were confronted to nonlinear Langmuir, Freundlich and Redlich–Peterson (R–P) adsorption isotherms, and those of kinetics were tested with the pseudo-first-order and pseudo-second-order kinetic models.

MATERIAL AND METHODS

Material

The CS used in this study was obtained from deacetylation of chitin extracted from shrimp shells collected in Morocco and had a deacetylation degree of 76%, as described in previous work (Ahlafi et al. 2013). Bt was purchased from Rhône–Poulenc (France) and it was used without any treatment. CH₃COOH; (CuSO₄, 5H₂O); NH₄OH; HCl and NaOH were of analytical grade and were purchased from Sigma-Aldrich Chemicals. NaOH and HCl solutions were used for pH adjustment, and NH₄OH was used to complex the residual amount of Cu(II) ions by NH₃.

Synthesis of nanocomposite 5%Bt/CS

The preparation of the nanocomposite 5%Bt/CS was carried out as follows: the CS was dissolved in acetic acid aqueous solution (2%v/v) and centrifuged to remove insoluble materials. Bt was first swelled by 50 mL distilled water, added slowly to 50 mL of CS solution, and stirred at 60°C for 6 h. The resulting nanocomposite 5%Bt/CS was centrifuged for 10 min, washed with distilled water and dried overnight at 80°C.

Characterisation methods

To characterise the prepared adsorbents before and after their contact with Cu(II) ions in solution, different methods such as XRD, thermal analysis TGA/DTA, and FTIR were used. XRD was used to determine the basal spacing d(001) value. The XRD patterns were obtained using a X’Pert MPD-PRO wide angle X ray powder diffractometer provided with a diffracted beam monochromator and Ni filtered CuKα radiation (λ = 1.5439 Å). The 2θ angle was scanned between 4 and 80°. The FTIR spectra of the studied samples were carried out using Fourier Transform Infrared Spectrometer (Shimadzu FTIR, JASCO 4100) in the range of 400 and 4,000 cm⁻¹. Samples were prepared in KBr pellets (2 mg/200 mg KBr). Thermal properties were investigated with simultaneous thermal analyser TGA/DTA under air flow from room temperature to 600°C at a rate of 20°C/min in a TA60 Shimadzu.

Adsorption trials

Batch experiments were performed to investigate the adsorption capacities of CS and 5%Bt/CS for the removal of Cu(II). The kinetic adsorption of Cu(II) was carried out by dispersing 0.1 g of the adsorbents in 20 mL of Cu(II) solution (C₀=1 × 10⁻³M). The mixture was shaken at 300 rpm at the desired temperature (25–45°C) for predetermined time intervals, ranging from 0.5 to 800 min. The mixture pH was adjusted to the optimum pH-value of 5 by adding HCl (0.1N) or NaOH (0.1N) (the initial precipitation of Cu(II) ions is pH = 6) (Dinu & Dragan 2010; Zeng et al. 2015). The adsorption equilibrium isotherms were tested by varying the initial concentration of metal ions [10⁴–500 mg/L]. After agitating at 300 rpm for 12 h at temperature T(°C), the adsorbent was separated from the liquid phase with a
0.45μm membrane. The residual Cu(II), which remained in the filtrate at each contact time and each adsorption temperature, was mixed with excess NH₄OH solution (C = 1N) to form the complex Cu(NH₃)₂. The concentrations of Cu(II) were determined by UV-visible spectrophotometer at λ = 610 nm which corresponds to the maximum absorption of the complex Cu(NH₃)₂. The copper uptake at equilibrium was calculated by the following equation:

\[ q_e = \frac{C_0 - C_e}{m_{\text{ads}}} \times V_{\text{sol}} \text{(mg/g)} \]  

(1)

where \( q_e \) is the equilibrium concentration of copper ion in solid phase, (mg/g), \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations in liquid phase (mg/L), respectively, \( m_{\text{ads}} \) is the amount of adsorbent (g) and \( V \) is the volume of the solution in L.

**RESULTS AND DISCUSSION**

**Characterisation of CS and 5%Bt/CS**

**XRD**

Figure 1 illustrates the XRD patterns of Bt, CS and 5%Bt/CS. The XRD pattern of the Bt shows a reflection peak at \( d_{001} = 14.92 \, \text{Å} \). The XRD pattern of CS shows the characteristic peaks at \( d = 9.04 \) and 4.57 Å. It can be observed in the spectrum of 5%Bt/CS that the peak at \( d_{001} = 14.92 \, \text{Å} \), characteristic of Bt, disappears and is substituted by a shoulder peak at lower 2θ angle, which indicates the exfoliated structure.

**FTIR**

The FTIR spectra of CS, Bt and 5%Bt/CS are presented in Figure 2. Compared to Bt, the infrared spectrum of CS exhibits the characteristic bands at 2,920 cm⁻¹, 2,850 cm⁻¹ and at 1,430 cm⁻¹, attributed to the \( \nu \text{CH} \) antisymmetric, symmetric stretching and deformation vibrations of C–H bonds, respectively. The vibration bands of CS appearing in 5%Bt/CS spectrum can be established as follows: the absorption band around 3,420 cm⁻¹, revealing the stretching vibration of N–H and O–H groups in CS, and those at 1,650 and 1,565 cm⁻¹ confirm the acetamide (amide I, C–O stretching vibration) and amine (N–H stretching vibration) groups. The peaks at 1,157 and 1,026 cm⁻¹ are related to C–O stretching in the \( \beta-1,4\)-glycosidic linkage present in CS (Zeng et al. 2015). The band around 1,065 cm⁻¹ is attributed to the combined effects of C–N stretching vibrations of primary amines. These spectra also exhibit absorption bands at 3,420 cm⁻¹ (O–H stretching vibration) and at 1,080 cm⁻¹ (–CO stretching vibration in –COH), and at low frequency at 800, 650 and 530 cm⁻¹, indicating the presence of Al–Mg–OH, Al–O–Si and Si–O vibrations (Eren & Afsin 2008). The presence of these bands confirms that the CS polymer was inserted into the interlayer space of the Bt to form the 5%Bt/CS nanocomposite. The disappearance of the functional groups at 3,630 cm⁻¹ (O–H), and the decrease of the intensities of amine bands in the nanocomposite are the result of the intercalation of CS into Bt interlayer spaces.
Sorption kinetics

The influence of contact time on the adsorption capacity of CS and 5%Bt/CS at pH = 5, C₀(Cu(II)) = 10⁻³M and at different temperatures (25, 35 and 45 °C) was determined (Figure 3). Figure 3 shows that the removal of Cu(II) increased rapidly in the initial time (t < 30 min) and remains constant after contact time t = 100 min for CS and t = 300 min for 5%Bt/CS, which corresponds to the equilibrium. It can be observed that the amount of adsorbed Cu(II) increased with increasing temperatures for the same Cu(II) concentration, indicating the endothermic nature of the process. This behaviour is more pronounced for 5%Bt/CS than CS. The increase in temperature would provide a faster rate of diffusion of adsorbate ions from the solution to the adsorbent (Huang et al. 2013). Similar profiles were found by Dong-Wan Cho (Cho et al. 2012) and Lixuan Zeng et al. (Zeng et al. 2015), when they studied the adsorption of Cu(II) on CS/clay/magnetite composite and on cross-linking CS/rectorite nano-hybrid composite, respectively. They also observed that adsorption of Cu(II) ions on CS was less affected by temperature. It is suggested that the sorption of Cu(II) by CS and 5%Bt/CS may involve chemical sorption (Han et al. 2006). As indicated by Cho et al. (2012), adsorption of Cu(II) on CS/clay/magnetite composite occurs both on the surface/pores of CS/clay/magnetite composite and on the amine and hydroxyl groups of cross-linked CS. These adsorption sites were readily accessible from the outer interface, and thus resulted in rapid adsorption process (Gandhi et al. 2012).

In order to analyse the adsorption rate of Cu(II) on these samples at different temperatures, both the pseudo-first-order kinetic model (Equation (2)) and the pseudo-second-order kinetic model (Equation (3)) have been used to model the kinetic data:

\[
\log(qe - qt) = \log(qe) - \left(\frac{K_1}{2.303}\right)t \\
\frac{t}{q_t} = \frac{1}{K_2q_e^2} + \frac{t}{q_e}
\]

where qₑ and qₜ are the adsorbed quantities of metal ions (mg/g) at equilibrium times and desired times, respectively. K₁ (min⁻¹) and K₂ (g/(mg.min)) are the pseudo-first and the pseudo-second rate constants, respectively.

Figure 4 shows that the experimental data fit the linear pseudo-second-order equation more appropriately because of higher correlation coefficients R² values compared to the pseudo-first-order for both samples at three studied temperatures (Table 1). In addition, there is a very close value between the amount of Cu(II) ions on adsorbents at equilibrium (qₑ) acquired by experiments, and qₑ(cal) calculated from the model. Also, the calculated equilibrium adsorption capacity qₑ(cal) for the pseudo-second-order kinetic model was well approximated to the experimental value, indicating that the rate determining step involved chemisorptions at each temperature. This is in agreement with the suggested mode of Cu(II) adsorption on acid-activated clay, CS/clinoptilolite composite (Dinu &...
Dragan 2010) and N-(2-Carboxyethyl) CS (Huang et al. 2015) that involved specific interaction with surface functional groups.

### Adsorption isotherms

The relationship between the amount of Cu(II) ions adsorbed onto CS and 5%Bt/CS, and its equilibrium concentration in the solution at different temperatures of 25, 35 and 45 °C, are presented in Figure 5. The obtained isotherms were analysed using the nonlinear Langmuir, Freundlich and R-P equations (Kumar et al. 2008; Yang et al. 2014; Fathi et al. 2015).

**Langmuir:**

\[
q_e = \frac{q_m K_L C_e}{1 + K_L C_e}
\]

**Freundlich:**

\[
q_e = K_F C_e^{1/n}
\]

**R-P:**

\[
q_e = \frac{K_{RP} C_e}{1 + a_{RP}(C_e)^eta}
\]

Where \(K_L\), \(K_F\) and \(K_{RP}\) are the Langmuir, Freundlich and R-P constants, respectively, and \(n\) relates to adsorption intensity, \(\beta\) is the exponent which lies between 1 and 0, \(q_e\) (mg/g) is the adsorption capacity at equilibrium, and \(q_m\) (mg/g) is the maximum amount of adsorption which completes monolayer coverage on the adsorbent surface (mg/g).

Figure 5 shows a plot between \(C_e\) versus \(q_e\) and Table 3 shows a nonlinear Langmuir, Freundlich and R-P models.
and parameters values obtained at different temperatures of Cu(II) adsorption onto CS and 5%Bt/CS. It can be seen that the adsorption capacity of CS was more significant at 25, 35 and 45 °C than its nanocomposite 5%Bt/CS. This could be due to the blockage of micropores in Bt after chemical modification. For all temperatures, the nonlinear Langmuir isotherm exhibited the highest values of determination coefficients (Table 2), which produced a better fit compared with the Freundlich and R–P isotherms. It can also be seen that the values of \( \beta \) in the R–P model are far to 0, which means the isotherms are not approaching the Freundlich isotherm which is a special case of R–P isotherm when constant \( \beta \) is about unity. It was also observed from Figure 5 that the Langmuir isotherm exactly overlapped the experimental equilibrium data of Cu(II) onto CS and 5%Bt/CS.

Furthermore, the affinity between the adsorbent and Cu(II) can be predicted by the Langmuir parameter of the dimensionless separation factor or equilibrium parameter, \( R_L \), which is expressed in Equation (7). The value of \( R_L \) was calculated to indicate whether the adsorption system

![Figure 5](image)

Figure 5 | Nonlinear regression models of Langmuir, Freundlich and R–P isotherms for adsorption of Cu(II) onto CS and 5%Bt/CS at different temperatures.

<table>
<thead>
<tr>
<th>Solid</th>
<th>T(°C)</th>
<th>( Q_m ) (mg/g)</th>
<th>( K_L ) (L/mg)</th>
<th>( R^2 )</th>
<th>( K_F ) (mg/g)</th>
<th>( 1/n )</th>
<th>( R^2 )</th>
<th>( K_{RP} ) (L/g)</th>
<th>( a_{RP} ) (L/mg)</th>
<th>( \beta )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS</td>
<td>25</td>
<td>404.35</td>
<td>8.4 \times 10^{-4}</td>
<td>0.817</td>
<td>17.48</td>
<td>0.339</td>
<td>0.786</td>
<td>0.295</td>
<td>8.1 \times 10^{-5}</td>
<td>1.24</td>
<td>0.831</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>605.68</td>
<td>2.8 \times 10^{-2}</td>
<td>0.941</td>
<td>39.64</td>
<td>0.252</td>
<td>0.922</td>
<td>0.465</td>
<td>5.4 \times 10^{-2}</td>
<td>0.59</td>
<td>0.763</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>422.21</td>
<td>5.5 \times 10^{-3}</td>
<td>0.989</td>
<td>73.87</td>
<td>0.201</td>
<td>0.795</td>
<td>4.9 \times 10^{4}</td>
<td>0.3 \times 10^{4}</td>
<td>0.87</td>
<td>0.759</td>
</tr>
<tr>
<td>5%Bt/CS</td>
<td>25</td>
<td>282.49</td>
<td>5.5 \times 10^{-2}</td>
<td>0.976</td>
<td>34.79</td>
<td>0.197</td>
<td>0.928</td>
<td>0.578</td>
<td>3.5 \times 10^{-3}</td>
<td>0.98</td>
<td>0.954</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>236.22</td>
<td>2.0 \times 10^{-3}</td>
<td>0.913</td>
<td>18.67</td>
<td>0.288</td>
<td>0.896</td>
<td>0.422</td>
<td>6.3 \times 10^{-2}</td>
<td>0.61</td>
<td>0.770</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>337.07</td>
<td>5.8 \times 10^{-3}</td>
<td>0.871</td>
<td>16.78</td>
<td>0.346</td>
<td>0.820</td>
<td>11.742</td>
<td>0.778</td>
<td>0.64</td>
<td>0.864</td>
</tr>
</tbody>
</table>

Table 2 | Langmuir, Freundlich, and R–P isotherm constants for the adsorption of Cu(II) onto CS and 5%Bt/CS at different temperatures.
is unfavourable \( (R_L > 1) \), linear \( (R_L = 1) \), favourable \( (0 < R_L < 1) \) or irreversible \( (R_L = 0) \) (Hall et al. 1996; Bayramoglu et al. 2009; Dinu & Dragan 2010; Cho et al. 2011).

\[
R_L = \frac{1}{1 + K_L C_0} \tag{7}
\]

Values of \( R_L \) for Cu(II)/CS and Cu(II)/5%Bt/CS systems have been calculated for all temperatures and concentrations \( C_0 \) [10^4–500 mg/L]. As shown in Figure 6, all values of \( R_L \) lie between 0 and 1, indicating the Langmuir model is favourable. The figure also shows that \( R_L \) value decreased with increasing initial Cu(II) concentrations suggesting that the adsorption process was more favourable at higher concentration.

**Thermodynamic study**

The feasibility and nature of any reaction can be better explained by studying the thermodynamics of the process. The thermodynamic parameters studied are changes in Gibbs free energy \( (\Delta G^\circ) \), standard enthalpy \( (\Delta H^\circ) \), and standard entropy \( (\Delta S^\circ) \). The Gibbs free energy change of adsorption is defined as:

\[
\Delta G^\circ = -RT \ln K_L \tag{8}
\]

The values of \( (\Delta H^\circ) \) and \( (\Delta S^\circ) \) were calculated using the van ’t Hoff equation:

\[
\ln(K_L) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{9}
\]

where \( K_L \) is the Langmuir equilibrium constant, \( R \) is the universal gas constant and \( T \) is the temperature.

A plot of \( (\log K_L) \) versus \( (1/T) \) produces a straight line with slope equal to \( -\Delta H^\circ /RT \) and an intercept equals to \( \Delta S^\circ /R \). Figure 7 shows linear relation between \( (\log K_L) \) and \( (1/T) \) for the adsorption of Cu(II) onto CS and 5%CS/Bt/CS. The values of \( (\Delta H^\circ) \) and \( (\Delta S^\circ) \) are calculated from the slope and the intercepts of straight lines in Figure 7 and listed in Table 3. The values of standard Gibbs free energy \( (\Delta G^\circ) \) were calculated using Equation (9) and are also listed in Table 3. The negative values of \( (\Delta G^\circ) \) indicate the spontaneous nature of the process, and the positive value of \( (\Delta H^\circ) \) indicates that the adsorption is an endothermic process, and the positive value of \( (\Delta S^\circ) \) reflects the increased randomness at the solid/solution interface (Cho et al. 2012; Zeng et al. 2015). The results in Table 3 show that the negative value of \( (\Delta G^\circ) \) increases with increasing temperature, indicating the spontaneous nature of adsorption of Cu(II). This indicates that the adsorption of Cu(II) on 5%Bt/CS is favoured at higher temperatures.

**Figure 6** | Plot \( R_L \) against initial Cu(II) concentration at different temperatures.
demonstrated by Chu (2013) in the study of the copper removal capability of prawn shell was the presence of Binding sites on the prawn shell. Beppu et al. (2004) demonstrated that the interaction between heavy metal ions and the CS microsphere (He et al. 2013) is mainly affected via coordination with the amine (–NH2) and O–H functional groups on CS. Many studies reported the Langmuir model as best describing the equilibrium isotherms of Cu(II) on CS (Chu 2002; Wan et al. 2004; Wan Ngah et al. 2004; Ngah & Fatnathan 2008; Laus & de Fávere 2011; Futalan et al. 2012). A study of the copper removal capability of prawn shell was demonstrated by Chu (2002), where the extended Langmuir model or the competitive Langmuir model was adopted because of the competition between proton and copper for binding sites on the prawn shell. Beppu et al. (2004) illustrated that the interaction between heavy metal ions and the CS included both chelating and ion exchange mechanisms. According to our study, the solution pH was 5; therefore, the –NH2 and O–H groups of the adsorbent are protonated in the presence of H+ ions. Consequently, the electrostatic attractions between the positively charged amino and OH groups of the surface and the positively charged Cu(II) are uncertain. So, it could be deduced that the copper ions are adsorbed on the sorbent through an inner-sphere complex via surface chelation ion exchange or by donor/acceptor mechanism rather than electrostatic interaction (Liu et al. 2015).

Infrared spectra of Cu/CS and Cu/5%Bt/CS samples shown in Figure 8(a) and 8(b), indicate a neat difference in the evolution of the bands of NH (amine) and of amide I (C = O) in the 1,500–1,650 cm⁻¹ range of wavenumbers, compared with the initial spectra of CS and of 5%Bt/CS. As it can be observed in detail in the spectra represented in Figure 8(b), the transformation of these bands is different in the case of the two solids, indicating that Cu(II) complexing sites on these solids are probably not similar. The bands at 1,660 cm⁻¹ and at 1,570 cm⁻¹ of Cu(II) are observed in the DrTGA (derivation of TGA) curves for Cu/CS and Cu/5%Bt/CS. These bands persist after adsorption of Cu, with an intensification of their bands. The same behaviour was observed for the C–H stretching vibration at 2,890 cm⁻¹ and in the range of 900–1,200 cm⁻¹, which were linked to the cleavage of C = N bonds (Schiff bases generated by crosslinking) appearing around 1,650 cm⁻¹ (Thatte et al. 2014) and the formation of Cu–O bond (bands at 606 cm⁻¹ and 615 cm⁻¹), respectively (Thatte et al. 2014; He et al. 2014; Zavareh et al. 2015). Moreover, it can be noted that the band at 3,400 cm⁻¹ has not changed its position and intensity, which avoids the involvement of O–H groups in the interaction with Cu(II). These results are in accordance with the recent conclusions of He et al. (2014) and Zeng et al. (2015) that indicate the NH2 and C = O groups of CS are the only active sites for metal ions’ adsorption.

To confirm these chemical changes in both adsorbents after adsorption of Cu(II), the analyses by TGA/DTA were performed between 25 and 550 °C (Figure 9(a) and 9(b)). It is observed in the DrTGA (derivation of TGA) curves (Figure 9(b)) that the weight loss of CS took place in two steps, while the weight loss of Cu/CS exhibits more than two steps. The first peak at T < 112 °C corresponds to desorption of physically adsorbed water. The second step with the peak at 338 °C corresponds to the decomposition of CS. In the DrTGA curve of Cu/CS, the two peaks observed at T = 297 °C and at T = 365 °C were assigned to the deacetylation and cleavage of glycosidic linkages while the last peak at T = 500 °C was attributed to the cleavage of the C = N bond in Ca(II) –CS microsphere (He et al. 2014).
Moreover, DrTGA spectra recorded after Cu adsorption onto the nanocomposite 5%Bt/CS contain several peaks. The main observation is that Cu/CS and Cu/5%Bt/CS have lower thermal stability than CS and 5%Bt/CS, due to the effect of complexation between Cu(II) and CS molecular chains via the NH$_2$ groups (Wang et al. (2018); Zavareh et al. (2018)). These results indicate that in the complexation mechanism, the major interactions occur between the pair of nitrogen (amine) and the amide (H$_2$N-C = O) with Cu(II).

These results were also supported by XRD spectra recorded for Cu/CS and Cu/5%Bt/CS shown in Figure 10. Changes in the diffractogram of CS were observed when Cu/CS complex is formed. It was noticed that the characteristic peaks of CS changed their positions from $d = 9.04$ to $10.02$ Å and $d = 4.57$ to $4.67$ Å, accompanied with increase in the peaks intensity. The same result was found by Webster et al. (Webster et al. 2007) when they studied the complexation of CS with different transition metal cations. They attributed the changes observed between $9^\circ < 2\theta < 23^\circ$ to the formation of Cu/CS complexes through -NH$_2$ binding in different ways. However, in the Cu/5%Bt/CS diffractogram, new diffraction peaks appeared, indicating the formation of a new regular crystalline phase in which the
diffraction peaks of CS were weakened because the hydrogen bonds within CS were destroyed by metal ions that chelate with –NH2 and H2N–C=O groups. These changes are consistent with those found by M. H. M. Hussein et al. (2012) and Xiaohui Wang et al. (2005). From these observations, it can be concluded that the copper adsorption mechanism on the two solids is different. In contrast, Rangel-Mendez et al. (2009), indicate in their study of pH (4, 5 and 7) effect on CS selectivity for removing cadmium(II), copper(II), and lead(II) that the nature of complexing sites are mainly –NH2 and –OH groups. They also found that in slightly acidic pH (pH = 5), no participation of –OH groups was observed, and the experimental results do not discard the possibility that this could happen in a small proportion. The oxygen atom in the hydroxyl group has a stronger attraction to its electron lone pairs over the nitrogen atom in the amino group. Therefore, the amino group is more likely to donate the lone pairs to a metal ion as Lewis base (Jin & Bai 2002; Morales et al. 2011).
CONCLUSIONS

The results obtained indicate that CS and 5%Bt/CS, prepared from natural raw materials, are effective adsorbents to remove Cu(II) from aqueous solutions, showing a removal capacity at $T = 45\, ^\circ\mathrm{C}$ of up to 400 mg/g for CS and 342 mg/g for 5%Bt/CS. FTIR, XRD and TGA/DTA analyses were performed to confirm the observed results. Kinetic and adsorption isotherm modelling of the experimental data shows that the kinetic of Cu(II) adsorption on both samples was fitted well by the pseudo-second-order model, and the experimental isotherms were described by the Langmuir model. The separation factor in the study was $0 < R_q < 1$, indicating the favourable uptake of Cu(II) onto the CS and Bt/CS nanocomposite. It was also found that the reaction of Cu(II) adsorption on both solids is spontaneous ($\Delta G < 0$) and endothermic ($\Delta H > 0$). The results show that the NH$_2$ and the amide C=O groups are the major active sites for the Cu(II) adsorption.

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