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ORIGINAL PAPER

Adsorption of copper and zinc onto natural clay in single and binary systems

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Abstract Calcareous and smectitic clay samples from the Coniacian–Lower Campanian system, Tunisia, were used as adsorbents for the removal of copper and zinc from aqueous solutions in single and binary systems. Calcareous clay sample was treated with acetic acid to obtain carbonate-free sample that was also used for metals removal. The adsorption of metal ions onto natural clay was tested in a batch method by mixing 1 g/L of each sample with a metal ion solution of zinc (300 μmol/L) and/or copper 600 μmol/L under the operating pH of 6, and agitation speed of 200 rpm within the equilibrium time of 60 min at 25 °C for single and binary systems. Our results showed that natural clay samples were mainly composed of silica, alumina, iron, and magnesium oxides. Adsorption data showed that the studied clay samples removed substantial amounts of heavy metals in single and mixed systems. Initial solution pH and carbonates contents enhanced the removal capacities of the studied clay samples, confirming their strong influencing effects. Thermodynamic parameters indicated an endothermic adsorption for metals removal by calcareous clay, but exothermic process for the smectitic sample. These results suggest that the Late Cretaceous clays, Tunisia, can be effectively used as natural adsorbents for the removal of toxic heavy metals in aqueous systems.

Keywords Clays · Competitive Langmuir model · Heavy metals · Thermodynamic · Sorption

Introduction

Various industrial processes, including metal plating, fertilizer production, mining, metallurgy, battery manufacturing and textile dyeing, and others, are the main sources of heavy metals (Barhoumi et al. 2009; Messaoudi et al. 2009; Eloussaief and Benzina 2010). The fate of the metals in aquatic system can be variable, depending upon their initial form and the chemical and physical characteristics of the receiving water body. Metals may be in solution as free ions, soluble salts, associated ions with dissolved inorganic or organic ligands, or bound to particulate matter. Unlike organic contaminants, heavy metals are non-biodegradable; they accumulate in living organisms causing adverse effects to many vital functions. That is why toxic metals like zinc, copper, nickel, mercury, cadmium, lead, and chromium have to be removed from industrial wastewaters before being discharged in the ecosystem. Remediation of metal-contaminated media is a time-consuming and expensive process. The use of natural clays in the removal of Cu(II) and Zn(II) from aqueous solutions is of particular interest for environmental clean-up since the use of natural adsorbents is particularly beneficial for the development of cost-effective process for heavy metal removal from wastewaters. Adsorption is the most preferred method for removal of heavy metals from aqueous solutions due to its simplicity and its high

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effectiveness (Sdiri et al. 2011, 2012a, b). In this regards, multiple researchers studied the effectiveness of various type of clay in removing heavy metals from aqueous solutions including kaolinite (Sari et al. 2007; Schaller et al. 2009), bentonite (Ulmanu et al. 2003; Kaya and Hakan Ören 2005; Eren et al. 2009), illite (Ozdes et al. 2011), sepiolite (Guerra et al. 2010), montmorillonite (Lin and Juang 2002), and other adsorbents (Al-Degs et al. 2006; Engates and Shipley 2011). Many other studies have been undertaken to evaluate the adsorptive capacity of various bioadsorbents in the removal of inorganic pollutants (Ahmad et al. 2010; Das 2012; Dubey and Shiwani 2012; Revathi et al. 2012; Eren 2010). They found that those cheap adsorbents could be used in the removal of different metal cations [e.g., Cd(II), Pb(II), Cu(II), Zn(II) … etc.]. For instance, Ahmad et al. (2010) used activated sludge biomass (ASB) for the biosorption of Cd(II), Pb(II), and Zn(II). They mentioned that ASB removed substantial amounts of Cd(II) and Pb(II), but low quantity of Zn(II). Wang and Li (2009) investigated the competitive removal of copper and nickel by non-living biomass, showing that Cu(II) was preferably adsorbed over Ni(II). Those studies were limited to the adsorption of single metals, despite the fact that contaminated wastewaters contain more than one pollutants [e.g., Pb(II), Cd(II), Cu(II), and Zn(II)] that have to be removed before the final discharge in the receiving ecosystems. The Coniacian–Lower Campanian clays of the Aleg formation, Tunisia, showed high adsorptive capacities for heavy metal (Sdiri et al. 2011, 2012b). While most sorption studies that are conducted on clays usually start by the removal of non-clay minerals (e.g., carbonate minerals, and quartz) in order to concentrate the clay minerals and improve the sorption properties of the adsorbent (Al-Degs et al. 2006), the effects of carbonates impurities have not been studied in details. Adsorption onto cost-effective natural materials is the most commonly utilized technique due to its simplicity when compared to other methods like ion exchange and precipitation. Therefore, we attempted to study the effects of carbonate minerals as well as the competitive cations on the adsorption of heavy metals by calcareous and smectitic clays. Moreover, natural clay samples without any pre-treatment were used in order to decrease the cost of the removal process. The importance of understanding the mechanisms involved in heavy metals removal from wastewaters is a cornerstone in the elucidation of the interactive mechanism between both clay and metal removed, and between metal cations [i.e., Cu(II) and Zn(II)] in binary system.

This work has been carried out in the laboratory of Soil Environmental Chemistry, Faculty of Life and Environmental Sciences, University of Tsukuba, and finalized at the National Institute for Materials Science, Japan. Most of the adsorption experiments were performed in 2012.

Materials and methods

Characterization of clay

The calcareous clay sample was collected from the Coniacian–Early Campanian outcroppings of the Gafsa area (south of Tunisia). To study the effect of carbonate minerals on the adsorptive capacity, the collected sample was treated with acetic acid (1 mol/L) in a water bath at 80 °C. Both original and carbonate-free clay materials were saturated with 1 M NaCl solution. The obtained Na^+ homoionic clay samples were then dialyzed several times to remove chloride (Jarraya et al. 2010). Finally, Na^+ homoionic clay materials were dried at 105 °C for 24 h and then crushed to collect the desired particle size ranges of <210 μm. Hereafter, we use the abbreviations RS and TS to refer to original and treated clays, respectively. To clarify the effects of carbonates on the adsorption process, additional smectitic clay (RY), collected from the Gabes area, was used for comparative purposes (Sdiri et al. 2011, 2012b).

Chemical compositions of the original and treated samples were determined by subjecting the pelleted clay powders to an electron microprobe equipped with X-ray dispersive spectrometer (JXA8621 Superprobe; JEOL, Japan). N_2 adsorption methodology was used for porosity measurement using Coulter instrument (SA3100, Beckman Coulter, USA). The adsorbent was also characterized using an FT-IR spectrophotometer (FT-720; Horiba Ltd., Japan) at room temperature.

Batch adsorption

All the chemicals used were of analytical reagent grade supplied by Wako Pure Chemical Industries, Ltd. (Japan). Stocks of copper and zinc solutions (1,000 mg/L) were prepared by dissolving appropriate amounts of $CuCl_2 \cdot 2H_2O$ and $ZnCl_2$ in 1,000 mL of ultrapure water. Working standards were prepared by dilution of the stock solution. 0.1 M HCl and 0.1 M NaOH solutions were used for pH adjustment. The adsorption of metal ions [i.e., Cu(II) and Zn(II)] onto natural clay was tested in a batch method by mixing 1 g/L of each original (RS and RY) and treated (TS) sample with a metal ion solution of Zn(II) 300 μM and Cu(II) 600 μM under the operating pH of 6, and agitation speed of 200 rpm within the equilibrium time of 60 min at 25 °C for single and binary systems, unless otherwise specified by the study design (i.e., to examine the effects of pH, temperature, initial metal concentration, and contact time). After shaking, 10 mL of supernatant were withdrawn and filtered with 0.45 µm syringe driven filter (Millex-LH, PTFE, Millipore Corp., Ireland). The filtrates were analyzed for the Cu(II) and Zn(II) concentrations using an ICP-AES Instruments, Optima 7300 DV series (PerkinElmer Inc., Japan). All experiments were run in triplicate.

The amount of removed heavy metal (µmol/g) was calculated from the difference between initial and final concentrations as defined by the following equation:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \tag{1}$$

where q_e is the amount of metal ions adsorbed on the clay (µmol/g), C_0 and C_e are the initial concentrations in solution (µM), respectively, V is the volume of the medium (L), and m the mass of the clay sample (g).

The influence of initial metals concentration on the sorption of Cu(II) and Zn(II) onto original and treated clay was studied by varying the concentrations tested from 150 µM to 1.6 mM and 100 to 600 µM for single and binary systems, respectively, as were the temperature (25 °C), clay concentration (1 g/L), and metal solution pH (6). To study the effect of pH, the initial pH of the solution was adjusted to 2, 3, 4, 5, or 6. The contact time in the pH experiments was fixed at 60 min, and the shaking rate was 200 rpm; metal concentrations were held at 600 µM Cu(II) and 300 µM Zn(II). Temperature effect was evaluated by conducting this method at 25, 30, and 35 °C, while maintaining the initial pH at 6, contact time at 60 min, and clay concentration at 1 g/L.

Adsorption isotherm models

Langmuir and Freundlich isotherm models were used in this study to establish the relationship between the amount of adsorbed metal onto clays and its equilibrium concentration in aqueous system.

Langmuir adsorption isotherm (Langmuir 1918) is based on the assumption of monolayer adsorption onto a surface with a finite number of identical sites. Langmuir isotherm could be arranged in its linear form as following:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{2}$$

where C_e is equilibrium concentration of the metal (µM) and q_e is the amount of the metal adsorbed per gram of adsorbent (µmol/g). q_m and K_L are Langmuir constant relating adsorption capacity (µmol/g) and the energy of adsorption (L/g), respectively. These constants can be calculated from the slope and intercept of the linear plots of C_e/q_e versus C_e, respectively.

The dimensionless parameter of adsorption (R_L) (defined as $R_L = \frac{1}{1+K_L C_0}$, where C_0 (µM) is the initial concentration) was used as an indicator to assess the extent of adsorption.

Depending on the R_L value, there are four possibilities for adsorption: (1) favorable adsorption if $0 < R_L < 1$, (2) unfavorable adsorption when $R_L > 1$, (3) linear adsorption for $R_L = 1$, and (4) irreversible adsorption for $R_L = 0$ (Sari et al. 2007; Baccar et al. 2010).

The adsorption data were also fitted to Freundlich isotherm (Freundlich 1906), which is described by the linear form following the equation:

$$\log q_e = \log K_F + n \log C_e \tag{3}$$

where K_F and n are Freundlich constants, determined from the intercept and slope of the linear plot of $\log q_e$ versus $\log C_e$.

Thermodynamic parameters

The removal of copper and zinc by natural clay samples was studied from thermodynamic viewpoint to ascertain the nature of adsorption process under the condition of the current study. To achieve this goal, three thermodynamic parameters, including Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy change ($\Delta S°$), were determined by the following equations (Eloussaief and Benzina 2010; Eloussaief et al. 2011; Ozdes et al. 2011)

$$K_d = \frac{C_s}{C_e} \tag{4}$$

$$\Delta G° = -RT \ln K_d \tag{5}$$

$$\ln K_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{6}$$

where C_s and C_e are the removed and remaining concentrations, respectively. K_d is the distribution coefficient for the adsorption, $\Delta S°$, $\Delta H°$, and $\Delta G°$ are the changes of entropy, enthalpy, and the Gibbs energy, T (K) is the temperature, and R (8.314 J/mol K) is the gas constant. The values of $\Delta H°$ and $\Delta S°$ were determined from the slopes and intercepts of the plots of $\ln K_d$ versus $1/T$.

Model validation

To evaluate the fit of the above-mentioned theoretical models to the experimental data, linear coefficients of determination and non-linear χ^2 test were used. The linear coefficient of determination, R^2, represents the percentage of variability in the dependent variable that has been explained by the regression line.

The χ^2 test statistic was also used to calculate the sum of the squares of the differences between the experimental data and those calculated from the model. The equivalent mathematical statement could be described as following:

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \tag{7}$$

where q_e and $q_{e,m}$ are the experimental and calculated the equilibrium capacity (mg/g), respectively. If the data obtained from the model are similar to the experimental data, χ^2 will be a small number, if not, and χ^2 will be a bigger number.

Results and discussion

Characterization of clay samples

Chemical analysis by XRF showed that the original (RS and RY) and treated (TS) clays are mainly composed of silica, aluminum, and iron oxides (Table 1). The results indicated that RS clay, collected from Gafsa area, contained high amount of calcium, and its chemical composition was significantly affected by acetic acid treatment. In comparison between RS and TS, the percentage of silica increased from 40.096 to 57.144 %, with a significant increase in the mass fraction of aluminum and iron oxides. The data also indicated that the fraction of CaO and MgO decreased from 26.667 to 2.372 % and from 4.667 to 2.751 %, respectively. Based on the chemical properties, it was expected that the studied clay samples show variable adsorptive behaviors.

Table 1 Physicochemical properties of the studied clay samples

Chemical composition (% by weight)	RS	RY	TS
SiO_2	40.096	57.567	57.144
Al_2O_3	16.320	21.138	22.495
Fe_2O_3	7.386	10.181	9.891
CaO	26.667	2.370	2.372
MgO	4.667	3.615	2.751
TiO_2	1.158	1.111	1.472
K_2O	3.060	1.744	3.604
Na_2O	nd	0.605	–
P_2O_5	0.429	0.901	0.015
CuO	0.002	0.003	nd
ZnO	0.018	0.020	0.024
Structural parameters			
S_{BET} (m^2/g)	17.843	71.940	10.222
Fine fraction of <2 μm (%)	42.751	88.533	–
Moisture content (%)	16.365	15.794	–
CEC [cmol(+)/kg]	37.450	36.871	20.171
Total pore volume (cm^3/g)	0.042	0.123	–

nd Not detected

The specific surface areas of the original and treated clay samples (<210 μm-sized powders) were estimated to be 17.843, 71.841, and 10.222 m^2/g for RS, RY, and TS, respectively (Table 1). The obtained FTIR spectra of the bulk (RS and RY) and the decarbonated (TS) clay samples showed the stretching vibrations of the surface hydroxyl groups (Si–Si–OH, or Al–Al–OH) near at 3,694.94 and 3,619.73 cm^{-1}. The other vibration at 1,635.34 cm^{-1} was attributed to the bending of adsorbed water (Sdiri et al. 2011, 2012b). The stretching bands near 1,435.34, 871.67, and 711.60 cm^{-1}, found in the original sample, were assigned to calcite, but disappeared after the removal of carbonate minerals by acid treatment (Sdiri et al. 2010, 2011). Detailed mineralogical, geological, and spectroscopic characterization of the studied clay samples can be found in Sdiri et al. (2011, 2012b).

Adsorption in single-element system

The adsorption of the selected metal ions was carried out with concentrations of Zn(II) 300 μM and Cu(II) 600 μM under the operating pH of 6 and agitation speed of 200 rpm within the equilibrium time of 60 min. As shown in Fig. 1, more than 315 μmol/g of Cu(II) was removed by RS due to the precipitation as metal carbonate, but the removal capacity decreased to 165 μmol/g for TS because of the removal of carbonate minerals. Due to the presence of carbonates minerals, Cu(II) removal occurred mainly via the precipitation of copper carbonates ($CuCO_3$). The lower precipitation pH of $CuCO_3$ (pH 6) and the solubility product constant ($K_{sp} = 1.4 \times 10^{-10}$ at 25 °C) would explain this phenomenon. Above pH 6, solid phase of $CuCO_3$ should form, leading to a high sorption capacity, since the equilibrium pH increased to 7.7 after the addition of carbonaceous clay (RS sample). The same behavior was observed with Zn(II) removal, but to a much lower extent. This was expected because of the higher precipitation pH (pH 6.8) for zinc carbonates; therefore, lower solubility constant ($K_{sp} = 1.4 \times 10^{-11}$ at 25 °C) (Al-Degs et al. 2006). Sdiri et al. (2012b) mentioned that carbonaceous materials have high affinity to Cu(II) and Pb(II) due to their enhanced relative binding strength. As for RY clay, the removal efficiency was lower than the original RS clay because of the small amounts of carbonate (Table 1).

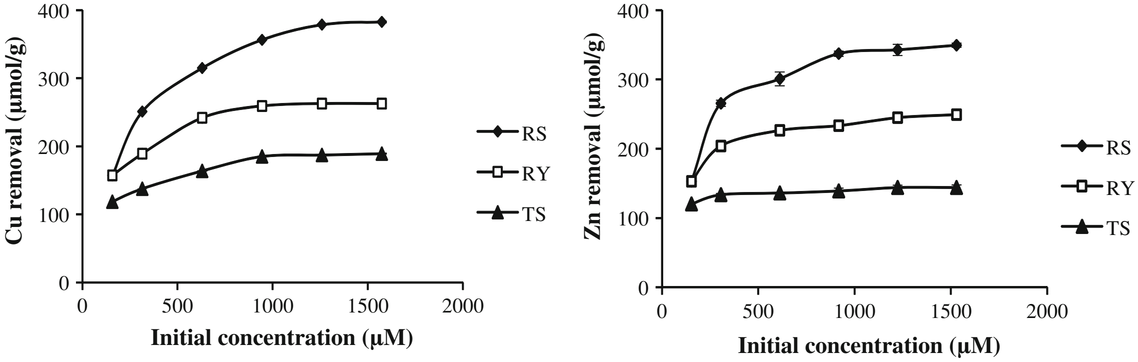

Fig. 1 Effect of initial concentration on Cu(II) and Zn(II) adsorption onto natural clays

Effect of initial concentration

The effect of initial concentration on the adsorption of Cu(II) and Zn(II) was carried out with concentrations of 150, 300, 600, 900, 1,300, and 1,600 µM under the operating pH of 6 and agitation speed of 200 rpm within the equilibrium time of 60 min. As shown in Fig. 1, the removal amount increased with increasing initial metal concentration until the saturation of available adsorption site. After that, metal cations will not be adsorbed anymore and the adsorbed amount will attain a plateau. Our results indicated that 600 and 300 µM were the optimal concentrations for Cu(II) and Zn(II) removal, respectively; they were used in all subsequent experiments. Carbonaceous clay (RS sample) showed the highest removal efficiency due to precipitation as metal carbonate. After the equilibration time of 60 min, the removal of Zn(II) decreased from more than 265.550 to 133.685 µmol/g because of the removal of carbonate minerals. The same behavior was observed with Cu(II) as described earlier. In comparison with RY clay sample, the original RS clay removed higher amounts of copper and zinc, but the treated form showed much lower removal efficiency (Fig. 1). Thus, it was clear that the removal of both metals was strongly influenced by carbonate content.

Adsorption isotherms

The isotherm constants for the removal of Cu(II) and Zn(II) are summarized in Table 2. Our results showed that the calculated Freundlich parameters (k_F and n) indicate favorable adsorption ($0 < n < 1$). In addition, the separation factor (R_L) varied between 0 and 1, confirming favorable adsorption under the experimental conditions of the study (Table 2). The maximum adsorbed capacity q_0, calculated from Langmuir model, reached 434.78 µmol/g. Moreover, the high coefficient of correlation ($R^2 \approx 1$) indicated that Langmuir isotherm fitted the experimental data better than Freundlich isotherm. Sdiri et al. (2011) applied the D–R model to clarify the adsorption nature of various metal cations onto montmorillonitic and calcareous clay. The adsorption energy (E) was less 8 kJ/mol, suggesting a physical removal process.

Effect of contact time

The effect of equilibration time on the sorption of copper and zinc was analyzed kinetically over a range of 5–120 min. The reaction was stimulated by shaking with clay samples (raw and carbonate-free samples) at 200 rpm at 25 °C for 60 min to reach equilibrium with the initial metal solution of pH6. The initial solution concentration was 600 µM and 300 µM for Cu(II) and Zn(II), respectively, while the amount of clay was 1 g/L. Figure 2 indicate that more than 95 % of the total adsorptive capacity occurred within 30 min, after what the removal further increased but with a much slower rate. From theoretical point of view, adsorption process requires long equilibration time, while the practical approach needs a short contact time. Based on the kinetic results, an equilibration time of 60 min was selected as a compromise between theoretical and practical approach.

Both metals [i.e., Cu(II) and Zn(II)] were removed faster by the RY sample than any of the others, confirming the significant role of chemisorption as a removal mechanism for zinc, as well as for copper. In the carbonaceous clay (RS), metal binding was lower at the beginning of the experiment, probably because of the surface interaction (physisorption) combined with slow dissolution of carbonate minerals that usually constitutes the first step of metal removal by carbonates (Sanchez and Ayuso 2002; Aziz et al. 2008; Sdiri et al. 2012a). However, the difference in removal rates between the RS and RY samples gradually diminished with contact time, and the effects of carbonates was clearly shone after

Table 2 Adsorption isotherm constant values for Freundlich and Langmuir models in single and binary systems

	Freundlich				Langmuir				
	k_F	n	R^2	χ^2	q_0 (μmol/g)	k_L (L/μmol)	R_L	R^2	χ^2
Single system									
Copper									
RS	146.882	0.142	0.9139	130.502	434.783	0.188	0.949	0.9891	84.421
RY	90.823	0.162	0.8903	2.791	277.778	0.472	0.979	0.9946	4.757
TS	51.619	0.19	0.9737	0.469	204.082	0.259	0.963	0.9893	3.364
Zinc									
RS	199.620	0.080	0.9350	1982.918	344.828	0.069	0.125	0.9979	6.346
RY	12.886	0.456	0.7965	4.456	238.095	0.097	0.093	0.9936	7.990
TS	134.325	0.005	0.1251	2.885	161.290	0.008	0.552	0.9915	1.342
Binary system									
Copper									
RS	24.559	0.514	0.8721	212.029	370.370	0.029	0.255	0.9325	29.763
RY	23.551	0.339	0.9774	24.319	172.414	0.030	0.245	0.9952	5.055
TS	25.991	0.282	0.8954	15.732	140.845	0.034	0.229	0.9814	3.583
Zinc									
RS	28.018	0.084	0.9552	1.750	38.168	0.198	0.048	0.9976	0.998
RY	37.829	0.178	0.8575	265.205	102.041	0.114	0.080	0.9986	2.363
TS	25.476	0.112	0.9557	240.094	49.751	0.098	0.092	0.9987	0.323

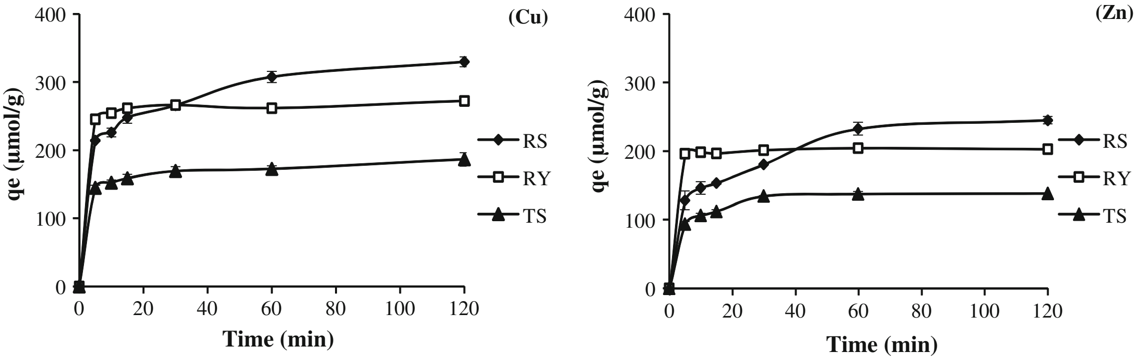

Fig. 2 Effect of contact time on Cu(II) and Zn(II) adsorption onto natural clays

60 min (Fig. 2), suggesting an enhanced removal efficiency by RS clay.

Effect of pH

The initial solution pH was varied from 2 to 6 while maintaining the other parameters constant. Effects of initial solution pH on the removal of Cu(II) and Zn(II) are shown in Fig. 3, indicating that the sorption capacity of both copper and zinc onto natural clays increased with pH (Fig. 3) due to the increase of surface negative charge. This was expected because of the fact that in acidic environment ($pH < 4$), the sorption of metal ions was suppressed by the excessive presence of H^+ which compete for available reactive sites. pH increase was combined with augmentation of removal rates and gradual decrease of H^+ competitive effects. It is noteworthy to mention that the sorption capacity of the calcareous clay (RS) was stable in the pH range of 4–6, indicating a possible ion-exchange mechanism. This finding could be ascribed to the contribution of precipitation as metal carbonates.

Our results confirmed that the initial solution pH is a key adsorption parameter that strongly affects heavy metal

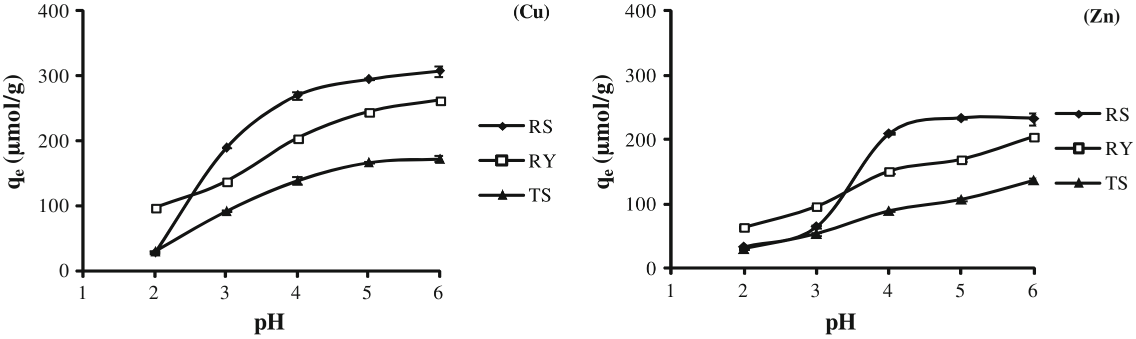

Fig. 3 Effect of initial pH on Cu(II) and Zn(II) adsorption onto natural clays

removal because of the decrease of positive charges on the adsorbent surface with increasing the solution pH (Eloussaief et al. 2009).

The possible removal mechanisms that may take place near neutral pH involve precipitations as metal hydroxides according to the following reactions:

$$\mathrm{Cu(II)} + 2\mathrm{OH} \Leftrightarrow \mathrm{Cu(OH)_2} \tag{8}$$

$$\mathrm{Zn(II)} + 2\mathrm{OH} \Leftrightarrow \mathrm{Zn(OH)_2} \tag{9}$$

The theoretical precipitation pH calculated from solubility products was 7.75 and 8.66 for $Cu(OH)_2$ ($K_{sp} = 2.2 \times 10^{-20}$ at 25 °C) and $Zn(OH)_2$ ($K_{sp} = 1.2 \times 10^{-17}$ at 25 °C), respectively. However, the experimental precipitation pH was 5.78 and 7.30 for $Cu(OH)_2$ and $Zn(OH)_2$ as ascertained from the maximum concentration of copper and zinc, respectively. These values were calculated from the following equation (Al-Degs et al. 2006):

$$\mathrm{pH_{ppt}} = 14 - \log\sqrt{\frac{\mathrm{M}^{2+}}{K_{\mathrm{sp}}}} \tag{10}$$

where $\mathrm{pH_{ppt}}$ is precipitation pH and M^{2+} is metal concentration (mol/L).

The removal of copper and zinc by carbonaceous clay occurred via precipitation of metal carbonates with a substantial contribution to the total sorption capacities in aqueous solution. It was found that more than 40 % of the total removal capacities were achieved by carbonates impurities found in the natural clay sample. For instance, acetic acid treatment decreased the removal capacity of copper with 44 %. Sanchez and Ayuso (2002), Karageorgiou et al. (2007), Sdiri et al. (2012a), and Sdiri and Higashi (2013) mentioned that calcite dissolution preceded the interaction of metal cations with reactive sites at the surface of the sorbent. The mutual interactive behavior of carbonates and metal ions could be described by the following reactions (Al-Degs et al. 2006):

Table 3 Thermodynamic parameters of Cu(II) and Zn(II) adsorption onto natural clays

	$-\Delta G$ (kJ/mol)			$-\Delta H$ (kJ/mol)	$-\Delta S$ (J/mol × K)
	298 K	303 K	308 K		
Cu					
RS	1.66	0.25	0.77	−40.572	−133.146
RY	2.20	1.09	1.09	18.831	57.280
TS	3.22	2.24	2.26	16.711	46.602
Zn					
RS	3.526	7.399	8.814	−83.930	−298.590
RY	1.282	0.938	1.010	5.113	13.310
TS	0.095	1.229	0.991	14.508	50.406

$$\mathrm{CaCO_{3(s)}} \leftrightarrow \mathrm{Ca^{2+}_{(aq)}} + \mathrm{CO^{2-}_{3(aq)}} \tag{11}$$

$$\mathrm{CO^{2-}_{3(aq)}} + \mathrm{M^{2+}_{(aq)}} \leftrightarrow \mathrm{MCO_{3(\mathit{s})}} \tag{12}$$

In addition, the ion exchange may also operate as a possible sorption mechanism as follows:

$$\mathrm{M^{2+}} + \mathrm{CaCO_3} \Leftrightarrow x \cdot \mathrm{Ca^{2+}} + \mathrm{M}_y\mathrm{Ca}_{(1-x)}\mathrm{CO_3} + (1-y) \cdot \mathrm{M^{2+}} \tag{13}$$

Effect of temperature

The effect of temperature on the sorption of Cu(II) and Zn(II) onto natural clay samples was studied at 25, 30, and 35 °C. The thermodynamic parameters are listed in Table 3. The sorption capacity of both metals by the original RS clay increased as temperature increased from 298 to 308 K indicating an endothermic sorption process (Fig. 4). The positive $\Delta H°$ value further indicated the endothermic process. The decrease of sorbed amounts with temperature suggests an exothermic sorption process, as indicated by negative ΔH^0 values.

The changes in entropy ($\Delta S°$) were −133.146, 57.260, and 46.602 J/mol × K for copper removal by RS, RY, and

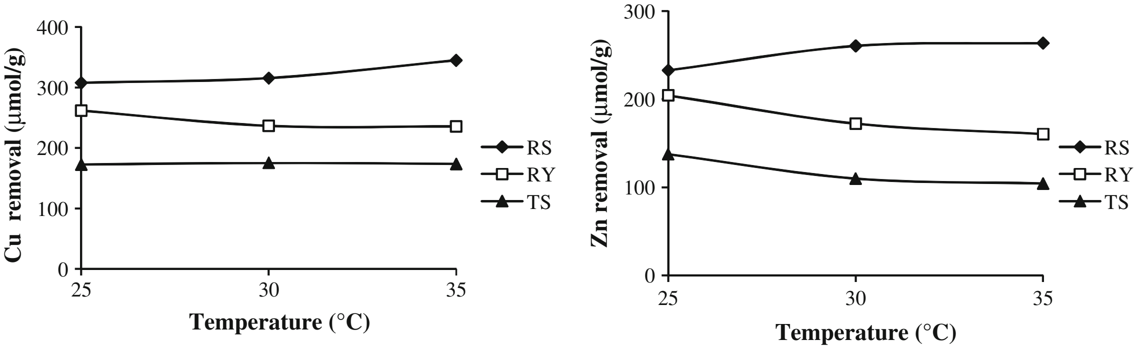

Fig. 4 Effect of temperature on Cu(II) and Zn(II) adsorption onto natural clays

TS, respectively. The negative value of $\Delta S°$ indicated that the reactions occurred via an arrangement of metal cations at the surface of the sorbent. This is an additional proof for the precipitation of metal carbonates, while the positive value of RY and TS indicated an enhanced disorder during the sorption reaction (Unuabonah et al. 2007). The change of free energy (ΔG^0) for all metals was negative indicating that the sorption of both metals onto natural clays (i.e., original and treated) was spontaneous in nature (Table 3).

Table 4 Inhibitory effect of a metal on the adsorption of competing metals

Sample	Inhibited	Inhibitor	
		Cu(II)	Zn(II)
RS	Cu(II)	–	10.179
	Zn(II)	88.501	–
RY	Cu(II)	–	46.422
	Zn(II)	62.603	–
TS	Cu(II)	–	18.704
	Zn(II)	72.222	–

Adsorption in binary system

Figure 5 shows the removal quantities of Cu(II) and Zn(II) by the original and treated clay samples at pH 6 in binary systems. The results showed that Cu(II) showed the highest removal efficiency with the removal amounts in the presence of Zn(II) of 199.210, 126.780 and 108.226 µmol/g for RS, RY and TS samples, respectively. The carbonaceous clay (RS) removed 199.210 µmol/g of Cu(II), but dramatically decreased for its carbonate-free form (TS) (Fig. 5). Thus, the presence of carbonates in RS sample enhanced Cu(II) removal because of the precipitation of $CuCO_3$. In contrast, smectitic clay samples (RY) showed an intermediate removal capacities that is lower than the original sample (RS), but somewhat higher than its treated from (TS). The removal efficiency of Zn(II) decreased substantially in the presence of Cu(II) compared with single-element system (Figs. 1, 5). Therefore, Cu(II) strongly depressed Zn(II) adsorption with an inhibitory effect on Zn(II) removal [defined as IE (%) $= \frac{Zn_{(Zn)} - Zn_{(Cu-Zn)}}{Zn_{(Zn)}}$ where $Zn_{(Zn)}$ and $Zn_{(Cu-Zn)}$ are Zn(II) removal quantity (µmol/g) in single and binary system, respectively] of 88.5, 62.6, and 72.22 % for RS, RY, and TS samples, respectively (Table 4). Inversely, the inhibitory effect of Zn(II) on Cu(II) removal occurred to a much

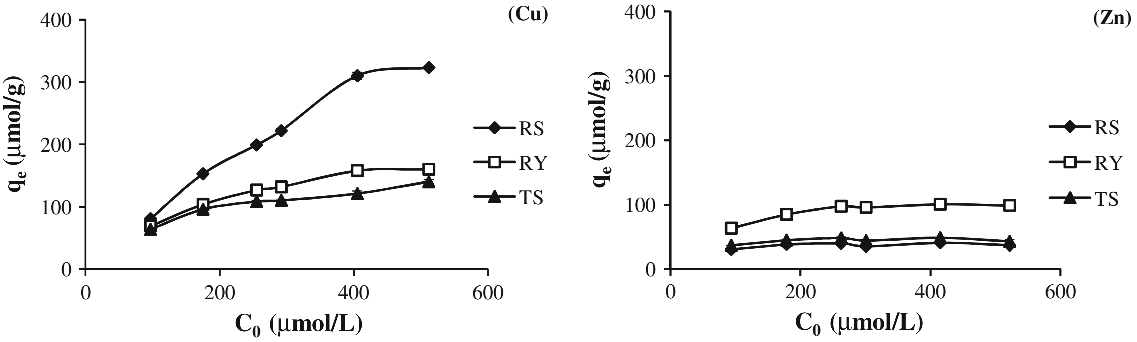

Fig. 5 Adsorption of Cu(II) and Zn(II) by natural clays in binary systems

Table 5 Comparison of Langmuir constant in single and binary systems

Sample	$\frac{(q_{0,\mathrm{Cu}})_{(S)}}{(q_{0,\mathrm{Zn}})_{(S)}}$	$P_i = \frac{(q_{0,i})_{(S)}}{(q_{0,i})_{(M)}}$		$\frac{(q_{0,\mathrm{Cu}})_{(M)}}{(q_{0,\mathrm{Zn}})_{(M)}}$
		Cu(II)	Zn(II)	
RS	1.261	1.174	9.034	9.704
RY	1.167	1.611	2.333	1.690
TS	1.265	1.449	3.242	2.831

lower extent because of the higher selectivity for Cu(II) combined with the low competitive ability of Zn(II) with regards to Cu(II), despite their similar ionic radii. The calculated inhibitory effects of Zn(II) on Cu(II) were 10.18, 46.42, and 18.70 % for RS, RY, and TS, respectively. This was expected since Cu(II) was predominantly adsorbed by all the studied samples over Zn(II) because of its higher relative binding strength and lower ionization potential (Sdiri et al. 2012b).

The competitive Langmuir (CLM) and *P* factor models were applied to the experimental result to analyze competitive sorption behaviors of copper and zinc. The CLM is an extended form of the Langmuir model that allows predicting the amount of a sorbed solute *i* per unit weight of a sorbent, q_i in the presence of other solutes. The CLM isotherm can be described by the following equation (Srivastava et al. 2006; Park et al. 2012):

$$q_i = \frac{k_{L,i} q_{0,i} C_i}{1 + \sum_{j=1}^{2} k_{L,j} C_j} \tag{14}$$

where q_i (μmol/g) and C_i (μmol/L) are the solid phase and the liquid phase equilibrium concentration of a solute *i* in bi-solute competitive sorption, respectively. $q_{0,i}$ (μmol/g) and $k_{L,i}$ (L/μmol) are the parameters determined by fitting the Langmuir model to the single-solute sorption data of solute *i*.

P factor model was also used to simulate the competitive sorption behavior of copper and zinc in bi-solute system. This model assumed a simplified approach to compare and correlate single-solute sorption with those of the multi-component systems by introducing a "lumped" capacity factor P_i (Valderama et al. 2010):

$$P_i = \frac{(q_{0,i})_{(S)}}{(q_{0,i})_{(M)}} \tag{15}$$

where $(q_{0,i})_{(S)}$ and $(q_{0,i})_{(M)}$ are the sorbent monolayer capacity for component *i* in single and binary component systems, respectively.

Table 6 Comparison of adsorption capacity with those of previous removal studies with natural clays

Adsorbent	Adsorption capacity (μmol/g)		pH	References
	Cu	Zn		
Single system				
RS	307.651	232.722	6	Present study
RY	261.701	204.434		
TS	172.473	137.615		
Fly ash	140.002	115.000	4–5	Pehlivan et al. (2006)
Illitic clay	207.723	–	5.5	Eloussaief et al. (2009)
Sewage sludge	295.107	166.667	5	Gupta et al. (2009)
Red mud	310.326	192.508	7	Lopez et al. (1998)
Hydroxyapatite	16.000	15.000	–	Corami et al. (2007)
Natural bentonite	–	159.021	4	Kaya and Hakan Ören (2005)
Natural bentonite	–	195.719		
Cu–Zn binary system				
RS	276.335	26.584	6	Present study
RY	202.216	76.652		
TS	140.214	38.226		
Calcareous soil	12.589	4.587	6.7	Mesquita and Vieira e Silva (1996)
Acid soil	20.002	6.004		Arias et al. (2006)
Hydroxyapatite	1510.009	1,170.030	–	Corami et al. (2007)
Illite	157.366	64.220	–	Oubagaranadin et al. (2010)

Our results indicated that the removal of copper and zinc better fitted to the Langmuir isotherm in single and binary systems. The maximum sorption capacities calculated from Langmuir model in bi-solute system were lower than those calculated in single-solute system, because of the existence of competing metal ion.

Effects of competitive metals on the sorption of heavy metals (i.e., copper and zinc) onto natural clays are summarized in Table 5. $\frac{(q_{0,\mathrm{Cu}})_{(S)}}{(q_{0,\mathrm{Zn}})_{(S)}}$ and $\frac{(q_{0,\mathrm{Cu}})_{(M)}}{(q_{0,\mathrm{Zn}})_{(M)}}$ ratios were higher than unity indicating the predominant sorption of copper over zinc in single and binary system. This further indicates the preferential sorption of copper over zinc due to its physical properties. In all cases, the high P_i values ($P_i >> 1$) confirmed that the sorption was hindered by the presence of competing ions. It was worth to mention that the sorption of Zn(II) showed high P_i value when compared with Cu(II) because of the strong inhibitory effect that exert the latter on Zn(II) removal, especially for the original clay (RS clay).

Comparison to other studies

Based on previous relevant studies, the amount of heavy metals removed by various clay materials is highly variable (Table 6). In the current study, calcareous clay sample (RS) demonstrated an enhanced removal rate when compared with the treated form (TS) and smectitic clay (RY). Sdiri et al. (2011, 2012b) mentioned that the removal efficiency was dependent upon the physicochemical characteristics of the clay and the metal removed, which was the case of the present clay samples. After the removal of carbonates, the calculated Langmuir capacity decreased from 434.783 to 204.082 µmol/g for copper removal by the calcareous clay sample, confirming the tight relationship between the physicochemical properties of the adsorbent and its removal capacity. These results indicate much higher removal efficiency for the present clay samples than that shown by Bhattacharyya and Gupta (2008), who reviewed the removal of metals like lead, cadmium, and copper by various kinds of clay (Table 6). We found that the natural clay from southern Tunisia exhibited greater removal efficiency than those reported in the literature, confirming their beneficial use for the removal Cu(II) and Zn(II) from aqueous solutions.

Conclusion

Calcareous clay of the Coniacian–Early Campanian Aleg formation, Tunisia, showed high removal capacities due to the presence of carbonates impurities, suggesting its potential use as metal sorbent. The adsorption of Cu(II) and Zn(II) in single and binary systems fitted to the Langmuir isotherm. In binary system, the adsorption capacity decreased for each metal due to competitive effect. Nevertheless, the removal of Cu(II) ions showed greater potential than the removal of Zn(II) in the presence of Cu(II). Our study showed that good adsorptive capacities could be achieved under the operating conditions of 60 min contact time, pH 6, and clay concentration of 1 g/L at 25 °C. The obtained results demonstrated the predominant role of carbonate impurities in the removal of Cu(II) and Zn(II). Therefore, the precipitation as metal carbonates may be effectively involved as immobilization mechanism. The positive $\Delta H°$ value for the sorptive removal of Cu(II) and Zn(II) by the carbonaceous clay (RS) indicated an endothermic process. However, sorptions by the smectitic clay (RY) and the acetic acid treated clay (TS) were exothermic ($\Delta H° < 0$). The negative $\Delta G°$ values confirmed the feasibility of sorption processes and their spontaneous nature. Despite these trends in thermodynamic values, it seems that the retention of Cu(II) and Zn(II) by natural clays was independent from temperature in the range investigated. Therefore, it can be concluded that the effect of carbonate overwhelmed that of temperature in the condition of our study. Finally, the use of natural clay from the Aleg formation, Tunisia, as a starting material to develop clay-based cost-effective adsorbents with enhanced surface area and strong adsorptive capacities for various environmental pollutants in aqueous systems, could be envisaged.

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