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ORIGINAL ARTICLE

Simultaneous removal of heavy metals from aqueous solution by natural limestones

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Abstract Two natural limestone samples, collected from the Campanian–Maastrichtian limestones, Tunisia, were used as adsorbents for the removal of toxic metals in aqueous systems. The results indicated that high removal efficiency could be achieved by the present natural limestones. Among the metal ions studied, Pb^{2+} was the most preferably removed cation because of its high affinity to calcite surface. In binary system, the presence of Cu^{2+} effectively depressed the sorption of Cd^{2+} and Zn^{2+}. Similarly Cu^{2+} strongly competed with Pb^{2+} to limestone surface. In ternary system, the removal further decreased, but considerable amount of Pb^{2+} and Cu^{2+} still occurred regardless of the limestone sample. The same behavior was observed in quadruple system, where the selectivity sequence was $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+}$. From these results, it was concluded that the studied limestones have the required technical specifications to be used for the removal of toxic metals from wastewaters.

Keywords Heavy metals · Limestone · Sorption · Precipitation · Competitive effects · Wastewater

Introduction

Numerous activities including metal plating, fertilizer industry, mining operations, metallurgy, battery manufacturing and textile dyeing generate a huge volume of wastewater contaminated with various metals (Eloussaief and Benzina 2010; Eloussaief et al. 2011, 2012; Sdiri et al. 2012a). These metals constitute a real threat for the environment because of their adverse effects on living organisms and water quality (Barhoumi et al. 2009; Messaoudi et al. 2009). Therefore, the levels of such pollutants in water body have to be reduced to the minimum. The use of natural sorbent for removing various metals from wastewater has been found to be an effective alternative. Especially, the use of natural limestones as cheap medium for toxic metals removal has been investigated by multiple researchers (Aziz et al. 2001; Sanchez and Ayuso 2002; Godelitsas et al. 2003; Prieto et al. 2003; Komnitsas et al. 2004; Cave and Talens-Alesson 2005; Rouff et al. 2006; Aziz et al. 2008; Sdiri et al. 2012b), pointing out that limestones could be an efficient natural geological materials for the treatment of heavy metals in contaminated water. Martins et al. (2004) mentioned that zinc sorption was favored as water hardness (i.e., Ca^{2+}) increased. Al-Degs et al. (2006) also studied the process that governs the interaction between Pb^{2+} and Zn^{2+} and calcite (eventually calcium). They mentioned that based on some theoretical assumptions, the removal of lead should be preferred over zinc. The released calcium in the solution was in tight relationship with the removed metal (i.e., lead and zinc). These may serve as a guide when studying the interactive behavior of calcium and metals. However, most of the reported metal removal efficiency of limestone dealt with single-element system. Desired intensive remediation is usually concerned with contaminated water that contains more than one heavy metal. To date, no attempt has been made to study the interactive mechanisms involved in metal–carbonates interactions in mixed systems. Therefore, the present study provided an attempt to (1) examine the adsorption behavior of several divalent metals onto natural limestones in single

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and multi-element systems, (2) to determine the mechanisms involved in the removal processes, (3) to study the competitive sorption of Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} in single, binary, ternary and quadruple systems and (4) to discuss the feasibility of using natural limestones from Tunisia in wastewater cleanup.

Materials and methods

Limestones samples used

Two limestone samples (S and Z) of the Campanian–Maastrichtian Abiod formation were collected from the outcroppings in the areas of Gafsa (southern Tunisia, Z samples) and Bizerte (northern Tunisia, S sample) where the geological particularities of the material allow its use in a wide range of industrial and environmental applications (Bouaziz et al. 2007; Aloui and Chaabani 2007). The collected limestone blocks were crushed, sieved and a grain size of less than 210 μm was used for batch sorption.

All of the chemical reagents were of analytical grade supplied by Wako Pure Chemical Industries, Ltd. (Japan). Ultrapure water (UPW) produced with a Milli-Q system (Millipore Corp., France) was used throughout the experiments. Working standards were prepared by the dilution of the stock solution (1,000 mg/L), prepared by dissolving proper amount of copper, cadmium, lead and zinc chloride in 100 mL of hydrochloric acid (0.1 mol/L). Solutions of 0.1 M HCl and 0.1 M NaOH were used for pH adjustment.

Batch sorption

Batch sorption, a technique commonly used to obtain data on the removal efficiency of a given sorbent under static conditions, was selected as an appropriate technique in the current study. Polypropylene tubes containing 20 mL of metal solution and 3 g/L of limestone powder from the <210 μm-sized samples (S or Z) were shaken at 200 rpm at 25 °C for 60 min to reach equilibrium. In single, binary and multi-element systems, 10 mg/L of each metal was used as an initial concentration to achieve similar concentration for all systems (molar concentration: $[Pb] = 4.82 \times 10^{-5}$ mol/L, $[Cd] = 8.89 \times 10^{-5}$ mol/L, $[Cu] = 1.57 \times 10^{-4}$ mol/L and $[Zn] = 1.52 \times 10^{-4}$ mol/L). For instance, in quadruple system, 5 mL of each metal stock solution (1,000 mg/L) were introduced in 500 mL volumetric flask and then diluted with UPW to obtain an initial concentration of 10 mg/L for each metal. The initial pH of the solution was adjusted to 6 with 0.1 M HCl and 0.1 M NaOH prior to mixing with limestone powder (Sdiri et al. 2012b). After shaking, 10 mL of supernatant were withdrawn and filtered through a 0.2 μm syringe-driven filter (Millex-LG, PTFE, Millipore Corp., Ireland). After the reaction, the sample solutions were stored at 4 °C until analysis for Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} with an ICP-AES instrument, Optima 7300 DV series (PerkinElmer Inc., Tokyo, Japan). The amount of a metal removed from the solution was calculated as the difference between initial and final concentrations. The same experimental conditions were maintained for mixed systems (i.e., binary, ternary and quadruple mixtures). All experiments were run in triplicate.

Results and discussion

Characterization of limestone samples

Chemical composition was determined by subjecting the pressed limestone samples to an electron microprobe equipped with an X-ray dispersive spectrometer (JXA8621 Superprobe; JEOL, Tokyo, Japan). It showed that the limestone samples collected from the southern area (i.e., Z sample) was characterized by its high purity, while the northern S sample contained more than 16.856 % SiO_2 and minor amounts of iron and aluminum oxides (Table 1).

Mineralogical analysis was carried out for powder samples with an X-ray diffractometer (RAD-X; Rigaku Intl. Corp., Tokyo, Japan). XRD patterns of the studied limestone samples showed the presence of characteristic peaks of calcite (Sdiri et al. 2010). In the northern S sample, the additional peak prevailing at 3.34 Å showed the presence of quartz (Fig. 1). The specific surface areas, determined using the N_2-sorption method (SA 3100, Beckman Coulter, USA), were 6.25 and 1.03 m^2/g for S and Z samples, respectively.

The studied limestone samples were also characterized by FTIR spectrophotometer (FT-720; Horiba, Ltd., Tokyo, Japan) over a range of 4,000–650 cm^{-1} at room temperature. The obtained spectra showed broad bands near 1,400, 875 and 711 cm^{-1}, characteristic of calcite. The maximum absorption recorded at 1,095.37, 1,064.51 and 985.447 cm^{-1} was attributed to the asymmetric stretching of Si–O (Fig. 2). The presence of high amount of silica may effectively enhance the adsorptive capacity of S sample when compared with the pure Z limestone (Sdiri et al. 2010).

Table 1 Chemical composition of the studied limestone samples (by weight %)

Sample	$CaCO_3$	SiO_2	Al_2O_3	Fe_2O_3	K_2O	MnO	SO_3	SrO	TiO_2	Total
S	76.671	16.856	3.003	2.056	0.831	0.117	ND	0.228	0.238	100
Z	99.609	0.391	ND	ND	ND	ND	ND	ND	ND	100

ND not detected

Sorption experiments of heavy metals by a batch method

Sorption in single-element system

Sorption experiments of the selected metal cations were performed by shaking the known amount of natural limestone powder with metal solution at room temperature (25 °C). The initial concentration of metal was kept at 10 mg/L (i.e., [Pb] = 4.82×10^{-5} mol/L, [Cd] = 8.89×10^{-5} mol/L, [Cu] = 1.57×10^{-4} mol/L and [Zn] = 1.52×10^{-4} mol/L). The dose of limestone sample was 3 g/L and the heavy metal solution of pH 6 was introduced. Preliminary results showed that Pb^{2+} was totally removed under the experimental conditions of this study (Sdiri et al. 2011). This indicates that the removal of lead ions by limestone is predominantly governed by the precipitation of lead carbonate (Sanchez and Ayuso 2002; Davis et al. 2006; Karageorgiou et al. 2007). The lower precipitation pH of $PbCO_3$ (pH 5.3) and the solubility product constant ($K_{sp} = 7.4 \times 10^{-14}$ at 25 °C) would explain this phenomenon. Above that pH value, $PbCO_3$ solid phase should be formed, leading to high sorption capacity, since equilibrium pH increased to 7.7 after the addition of limestone. Several previous works confirmed that carbonate precipitation was especially effective for the removal of lead (Godelitsas et al. 2003; Rouff et al. 2006). That is why, subsequent experiments in single-element systems focused only on Cd^{2+}, Cu^{2+} and Zn^{2+} sorption. In binary and multi-component systems, Pb^{2+} was re-introduced because of its decreased removal percentage under competitive conditions.

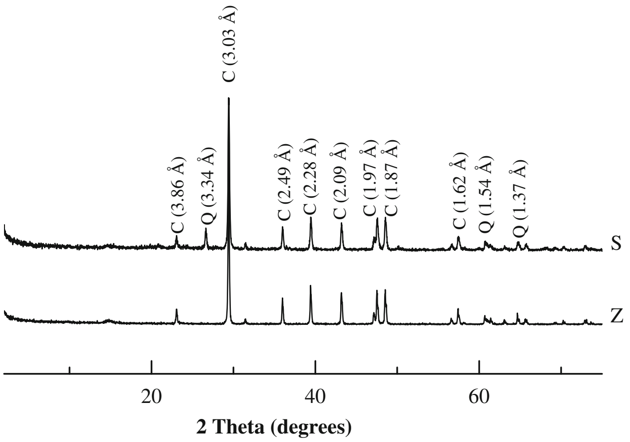

Fig. 1 XRD patterns of the studied limestone samples

While the theoretical precipitation of $CdCO_3$ ($K_{sp} = 1 \times 10^{-12}$ at 25 °C) begins at pH 8.5, an initial

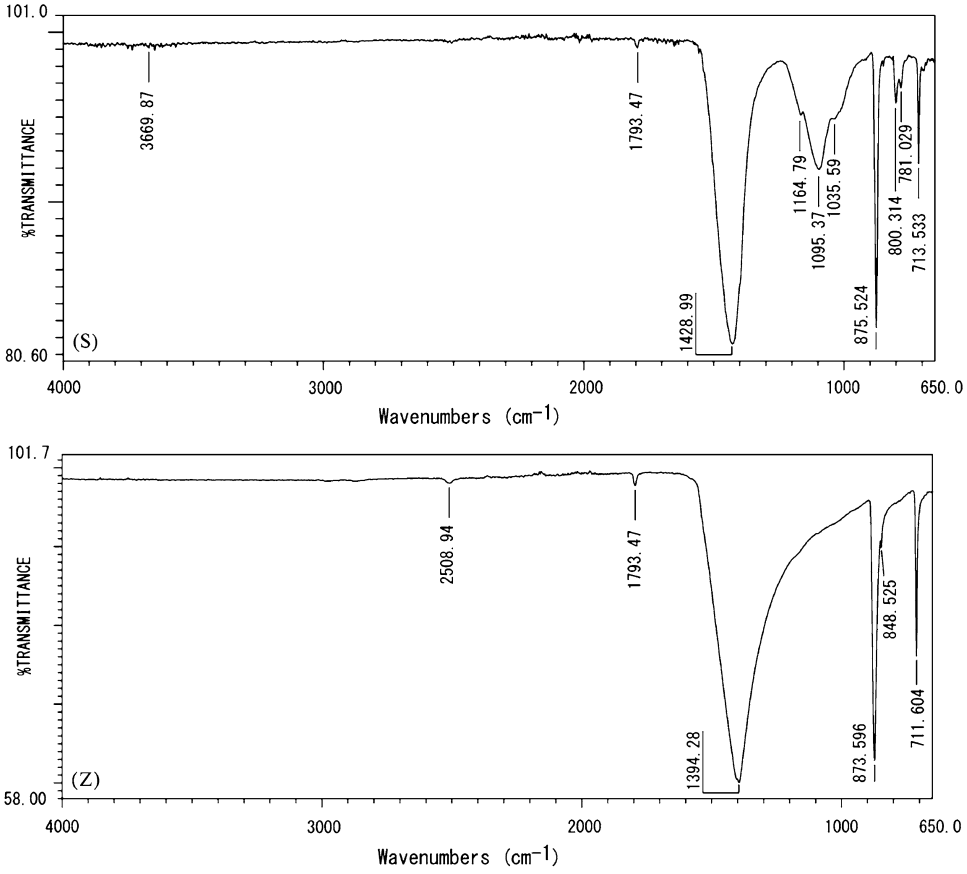

Fig. 2 FTIR spectra of the studied limestone samples

chemisorption step may also serve as a removal mechanism (Pickering 1983). Our results clearly showed that higher removal efficiency from the lower grade limestone sample (S) was probably related to its higher specific surface area, combined with elevated concentrations of silica and other impurities, as indicated earlier in this paper. To get more insights on the removal mechanisms, the dissolved calcium during the present sorption study was measured and compared in the case of Pb and Cd removal by limestone. It was confirmed that the presence of lead favored calcite dissolution, while cadmium inhibited calcium carbonate dissolution to some extent. Calcium concentration exceeded 40 mg/L in the case of lead removal, but less than 25 mg/L during the removal of cadmium regardless of the limestone sample. Similar findings were reported by Alkattan et al. (2002), Martin-Garin et al. (2003) and Cubillas et al. (2005) while studying the effect of metal sorption on calcite dissolution.

The sorption of single metal (Cd^{2+}, Cu^{2+} and Zn^{2+}) onto limestone is shown in Fig. 3. The overall removal percentage for Cd^{2+} was 95.00 and 14.68 % for S and Z sample, respectively. Although it has been reported that cadmium is the metal cation which replaces Ca^{2+} more easily, due to the similarity of their ionic radii (Sanchez and Ayuso 2002; Al-Degs et al. 2006), it was observed that the exchange mechanism for cadmium occurs to lower extent. Moreover, it could be presumed that cadmium could exert an inhibitory effect on calcite dissolution (Martin-Garin et al. 2003), resulting in the reduction of the available site for metal sorption. Similar findings were reported by Alkattan et al. (2002) and Cubillas et al. (2005) while studying the effect of metal sorption on calcite dissolution. These results may explain the lowest removal capacity of the purest limestone (Z sample). The efficiency of copper removal varied from 37.68 to 91 %, indicating that pure limestone had better affinity to this element in comparison with cadmium. The high removal percentage of copper was also favored by the presence of bicarbonate ions in the aqueous medium leading to the precipitation as copper carbonates. The precipitation pH of $CuCO_3$ (pH 6) was lower than the final pH (pH 7.7) indicating that the precipitation mechanism governed most of copper removal. As for zinc, less than 20 % removal was achieved by the pure Z sample that is much lower than the removal percentage (73 %) by S sample (Fig. 3). According to Pickering (1983) and Sanchez and Ayuso (2002), the available sites that bind preferably to Zn^{2+} represent less than 10 % of the total active sites. Our results showed that the higher removal efficiency, completed by the lower grade limestone sample (S), was probably related to its higher specific surface area combined with the high amounts of silica and other impurities, as discussed earlier (Fig. 3).

Sorption in binary system

Sorption experiments of heavy metals were also studied in mixed systems by shaking 60 mg of natural limestone (<210 µm-sized powder) with 20 mL of metal solution at

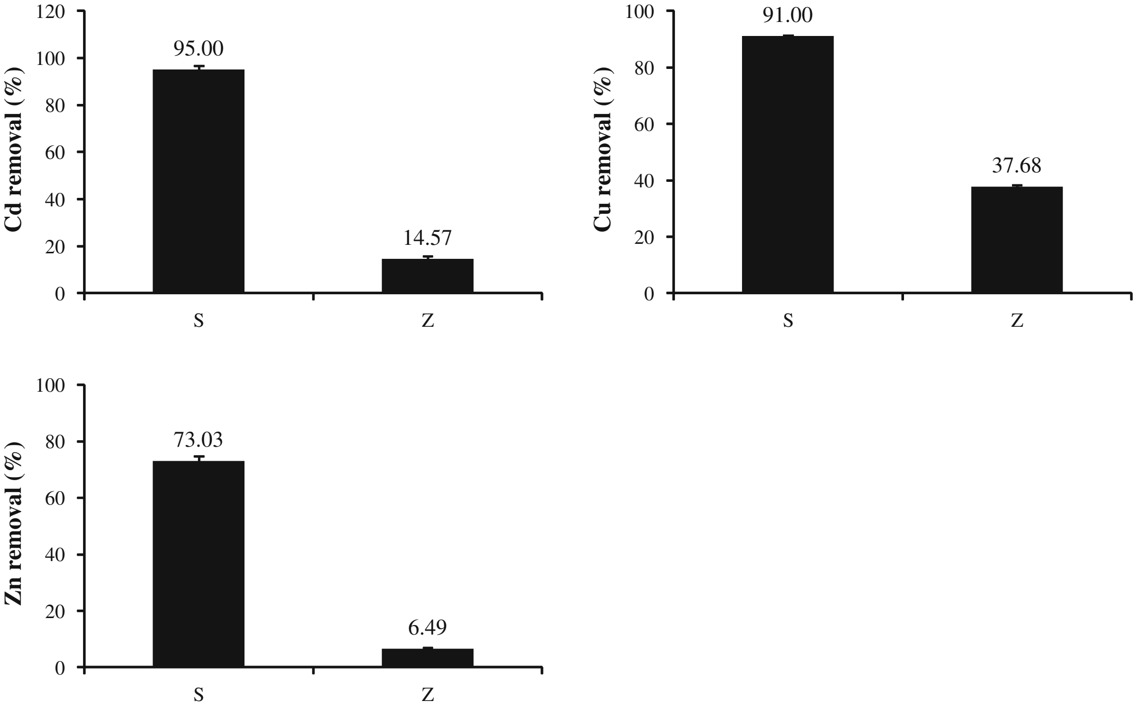

Fig. 3 Sorption of Cu, Cd and Zn in single system

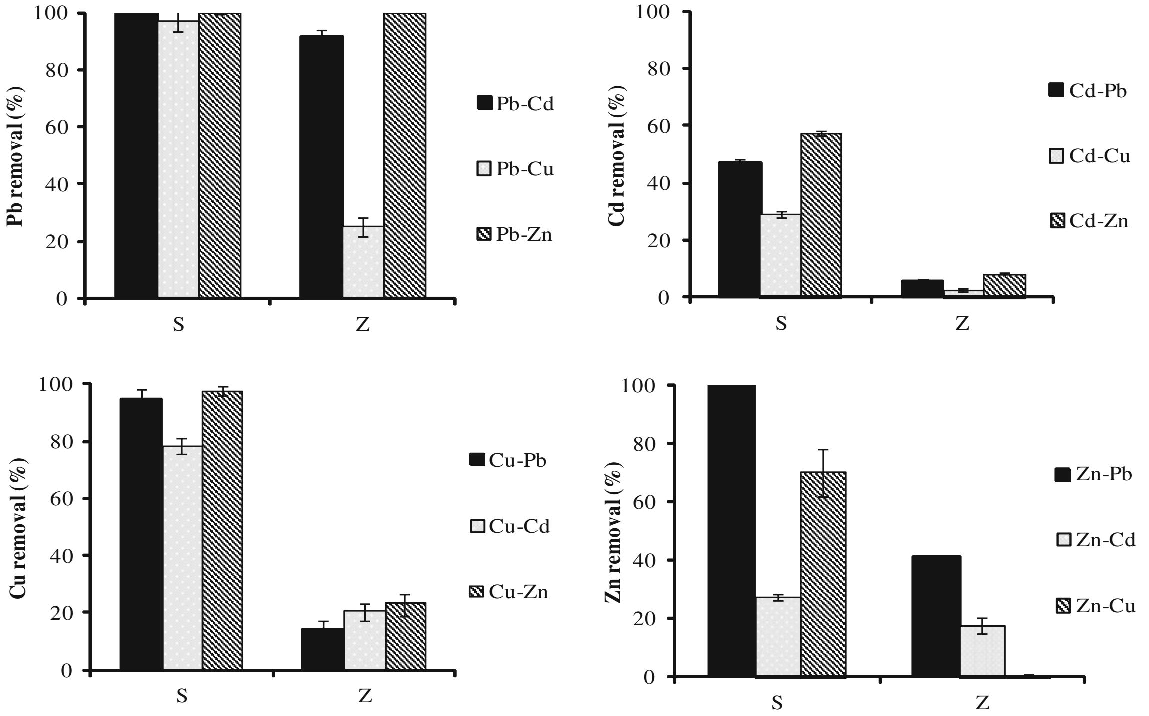

Fig. 4 Sorption of Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} in binary systems

room temperature (25 °C) for 60 min. The initial concentration of metal was fixed at 10 mg/L for each metal and pH 6. Figure 4 shows the removal percentage of Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} sorbed onto S and Z limestone samples at pH 6 for all possible metal combinations in binary systems. The results showed that S limestone sample showed higher removal efficiency regardless of the metal to be removed. Generally, the removal rate by S limestone sample was much higher than that achieved by Z sample, suggesting that the enhanced removal capacity correlated with the presence of impurities. In Pb–Cd systems, more than 91.5 % removal of Pb^{2+} was observed in all cases. The removal percentages in the presence of Cd^{2+} were 99.67 % for S sample and 91.42 % for Z sample. The removal efficiency of Cd^{2+} decreased substantially in the presence of Pb^{2+} compared with single-element system (Figs. 3, 4). Therefore, Pb^{2+} strongly depressed Cd^{2+} sorption onto limestone samples, showing an inhibitory effect on Cd removal [defined as $\text{IE}\ (\%) = (\text{Cd}_{(\text{Cd})} - \text{Cd}_{(\text{Pb-Cd})})/\text{Cd}_{(\text{Cd})}$ where $\text{Cd}_{(\text{Cd})}$, $\text{Cd}_{(\text{Pb-Cd})}$ are Cd removal percentage in single and binary system, respectively] of 50.82 % and 60.60 % for S and Z samples, respectively. This was further confirmed by the removal efficiencies of Cd^{2+}, which decreased to 46.72 and 5.74 % for S and Z limestone samples, respectively. Inversely, the inhibitory effect of Cd^{2+} on Pb^{2+} removal occurred to much lower extent because of higher selectivity for Pb^{2+}. The interactive behavior of Pb–Cu system showed that Pb^{2+} had somewhat higher affinity to limestone than Cu^{2+}. Similar results were reported by Xue et al. (2009), who studied competitive adsorption of heavy metals onto basic oxygen furnace slag. It was found that the presence of Pb^{2+} strongly prevented the removal of Cu^{2+} by the limestone sample (Z) with an IE of 62.52 %, but not S sample (Table 3). Interestingly, Pb^{2+} slightly enhanced the removal of Cu^{2+} with S limestone sample probably due to the presence of high affinity sites that adsorb both Pb^{2+} and Cu^{2+} under the conditions of our experiments. This behavior was confirmed by the poor effect of Cu^{2+} on Pb^{2+} removal, though higher than those of Cd^{2+} and Zn^{2+}. For Z limestone sample, the inhibitory effect of copper over lead exceeded 50 %. Cu^{2+} also showed strong inhibitory effects over Cd^{2+} and Zn^{2+}. This was expected since copper was predominantly sorbed by all the studied samples over cadmium and zinc because of its higher relative binding strength and lower ionization potential (Table 2). As for Cd–Zn system, it was observed that Cd^{2+} strongly prevented the removal of Zn^{2+} cations. Similarly, Zn^{2+} inhibited the removal of Cd^{2+} to the same order of magnitude, though slightly lower. Moreover, in Pb–Zn system, the coexistence of these two metals favored the removal of Zn^{2+}, but not Pb^{2+}. This meant that there was simultaneous binding of both metals with the same binding sites. Hence, it is plausible to account for an uncompetitive sorption or

Table 2 Physical characteristics of the studied cations (Kinraide and Yermiyahu 2007)

Cation	RBS	PE	IR	IP	HR	$-\log K_{H_2O,M}$	HI
Ca^{2+}	1.44	1	0.99	6.11	4.12	12.7	0.181
Cd^{2+}	2.15	1.69	0.97	8.99	4.26	10.1	0.081
Cu^{2+}	2.66	1.9	0.73	7.73	4.19	7.5	0.104
Pb^{2+}	2.68	2.33	1.19	7.42	4.01	7.6	0.131
Zn^{2+}	2.2	1.65	0.74	9.39	4.3	9	0.115

RBS relative binding strengths, *PE* Pauling electronegativity, *IR* ionic radius, *IP* ionization potential, *HR* hydrated radius, $-\log K_{H_2O,M}$ log of the first hydrolysis constant, *HI* hardness index

Table 3 Inhibitory effect (%) of a competing metal on other metals sorption onto limestones

Sample	Inhibitor	Inhibited			
		Pb^{2+}	Cd^{2+}	Cu^{2+}	Zn^{2+}
S	Pb^{2+}	–	0.330	2.970	0.001
	Cd^{2+}	50.822	–	69.441	45.768
	Cu^{2+}	−3.991	13.934	–	−7.187
	Zn^{2+}	−36.933	62.625	4.217	–
Z	Pb^{2+}	–	8.582	75.002	0.003
	Cd^{2+}	60.603	–	81.949	41.935
	Cu^{2+}	62.520	45.806	–	39.039
	Zn^{2+}	−531.741	–	100	–

even a favorable sorption for Zn^{2+} in the presence of Pb^{2+}, despite their different properties (Table 2). The increased removal of zinc in the presence of lead would suggest a coprecipitation mechanism that enhances the removal of zinc. However, other mechanisms (i.e., sorption and precipitation) would contribute to the removal efficiency. The sorption of Zn cations on $Pb(OH)_2$ is not to be excluded, but it contributed to a very low extent because of the fact that the precipitation as lead hydroxide started at pH 7.6, that was bit lower than the final pH (of 7.7). This was further confirmed by the negative IE exerted by Pb^{2+} on Zn^{2+} (Table 3).

Sorption in ternary system

Competitive sorption experiments were also performed by simultaneous removal of three metals under the same experimental conditions described earlier. That is, sorption experiments performed by shaking 60 mg of natural limestone (<210 μm-sized powder) with 20 mL of metal solution at room temperature (25 °C) for 60 min. The initial concentration of metal was fixed at 10 mg/L for each metal and an initial pH of 6. The results of removal percentages are shown in Fig. 5, where it was indicated that S limestone sample removed the highest amounts of heavy metal, while Z sample retained the lowest amounts regardless of the removed cation and the studied mixture. Moreover, the affinity of the studied metal cations for limestone sample followed the sequence of $Pb^{2+} > Cu^{2+} > Zn^{2+} \approx Cd^{2+}$. Similar sequence has been reported for the competitive adsorption of several metals onto basic oxygen slag (Xue et al. 2009), who found a sequence of $Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+}$, confirming that Pb^{2+} had the highest affinity to the surface of carbonate than others. Nevertheless, according to the above-mentioned work, the sequence changes considerably in single-element system that was not the case for the present study. Comparing the data obtained for lead, cadmium, copper and zinc, strong relationship between metal removal percentage and its first hydrolysis constant was observed (Kinraide and Yermiyahu 2007; Appel et al. 2008; Zhu et al. 2010). Lead removal capacity of S limestone sample clearly increased from 78.66 % in Pb–Cd–Cu mixture to 90.75 % in Pb–Cd–Zn system. Similar results were obtained for Z sample, with an increasing percentage of 61.93 % (Table 4). In Pb–Cu–Zn system, the removed amounts of lead were higher than those observed in Pb–Cd–Cu system, but much lower than those recorded in Pb–Cd–Zn mixture. Since copper suppressed the removal of Pb^{2+}, it was expected that lead removal would be lower in the presence of Cu^{2+}. In the presence of Zn^{2+}, the removal of lead jumped to more than 75 % for all samples in Pb–Cd–Zn system, but decreased in Pb–Cu–Zn mixture. These results indicate the antagonistic effect of Zn^{2+} and Cu^{2+}. Such explanation also applies for cadmium removal by the studied limestone samples. As for copper, the removal efficiency of Z sample in Pb–Cd–Cu system has readily increased in Pb–Cu–Zn and Cd–Cu–Zn (Table 4). Finally, it is worth noting that zinc removal remained roughly unchangeable in all cases probably because of its low electronegativity combined with high ionization potential (Table 2).

Sorption in quadruple system

Mixed metal sorption of Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} ions by natural limestone samples was also investigated to establish the effect of the presence of three metal ions on the removal of each one of them in equal concentration of 10 mg/L. Figure 6 revealed that the studied limestone samples had high affinity to Pb^{2+}, leading to the highest removal percentages. Lead removal efficiency was 75.02 and 6.57 % for S and Z samples, respectively. The sorption capacity of Cu^{2+} was about 59.5 % for S sample, but only 7.05 % for Z sample. This also indicated the high affinity to Cu^{2+}, but somewhat lower than Pb^{2+}. As for Cd^{2+} and Zn^{2+}, low removal percentage was achieved by S limestone sample, but Z sample, considered as pure limestone samples, was not able to remove measurable amounts of Cd^{2+} and Zn^{2+}. It could be assumed that the studied limestones

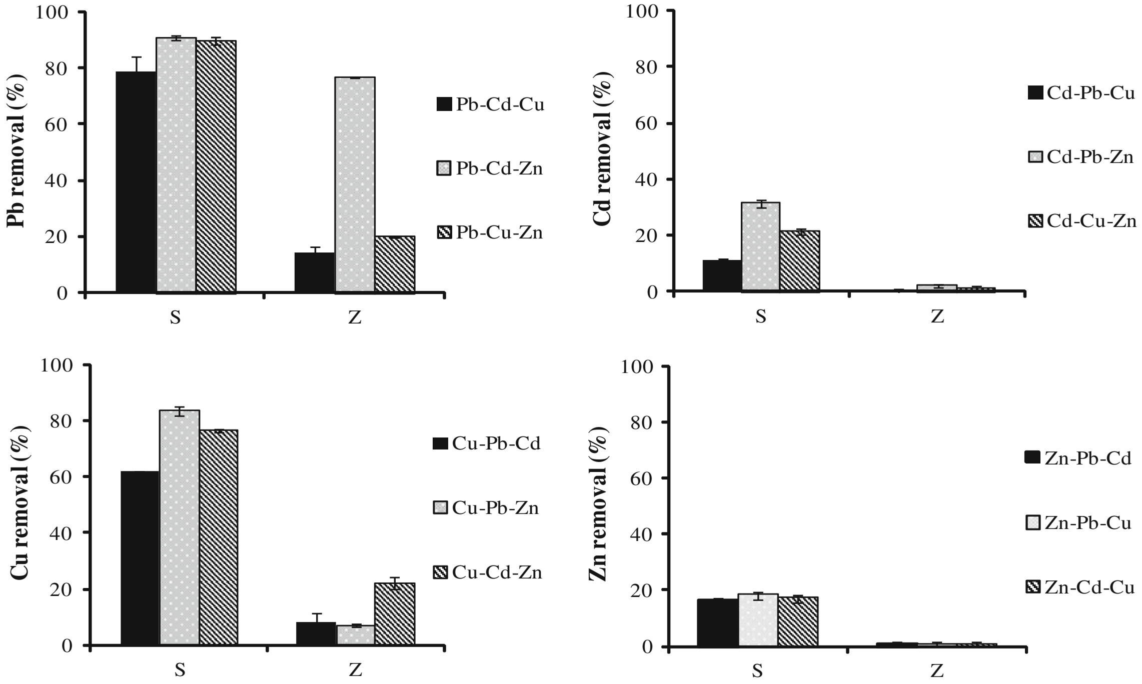

Fig. 5 Sorption of Pb, Cd, Cu and Zn in ternary systems

Table 4 Removal percentage of heavy metals in ternary system by natural limestone (in %)

Metal	Sample	Pb–Cd–Cu	Pb–Cd–Zn	Pb–Cu–Zn	Cd–Cu–Zn
Pb	S	78.66	90.75	89.72	
	Z	14.45	76.42	20.14	
Cd	S	11.11	31.33		21.40
	Z	0.31	2.11		1.23
Cu	S	62.04		83.43	76.50
	Z	7.99		7.23	22.23
Zn	S		16.38	18.27	17.19
	Z		1.13	0.35	0.57

removed the following sequence $Pb^{2+} > Cu^{2+} > Cd^{2+} \approx Zn^{2+}$. This indicated that the studied metals competitively interacted with limestone samples.

Interaction with calcium

Heavy metal sorption onto natural limestones started with calcium carbonate dissolution, leading to the release of calcium in the solution (Aziz et al. 2001; Alkattan et al. 2002; Sanchez and Ayuso 2002). It was clearly observed that the studied heavy metals interacted with limestone in different ways, leading to variable concentration of Ca^{2+} in the solution. In single-element system, more than 23 mg/L of Ca^{2+} was released in the solution. The presence of cadmium depressed calcite dissolution when compared to other metals (Martin-Garin et al. 2003). The concentration of released Ca^{2+} in the presence of cadmium was 28.04 mg/L for S sample and 23.74 mg/L for Z sample. These concentrations were the lowest when compared with the released calcium in the presence of other metals. Although it has been reported that, of the metal cations that have been studied, cadmium most easily replaces Ca^{2+}, due to the similarity of their ionic radii (Sanchez and Ayuso 2002; Al-Degs et al. 2006), it was observed that the exchange mechanism for cadmium operates at a slow rate. It is worth noting that the presence of zinc showed the highest concentration of released Ca^{2+}, exceeding 35.74 mg/L for the studied limestone samples. This was also verified in binary and ternary systems (Fig. 7). Inversely, the presence of cadmium decreased calcite dissolution, therefore calcium concentration. Furthermore, the inhibiting effect of cadmium was strong enough to overcome the improving effect caused by the presence of zinc. In the quadruple system, the presence of other metals strongly depressed calcium concentration because of its low electronegativity (Pauling electronegativity = 1.00) compared to other metals studied, therefore its easier displacement by other competitive metals. The released calcium decreased substantially to less than 16.8 and 4.74 mg/L for S and Z samples, respectively. For each charge class, Kinraide and Yermiyahu (2007) mentioned that binding strength increased with increasing electronegativity (Table 2). It is, therefore, probable that the

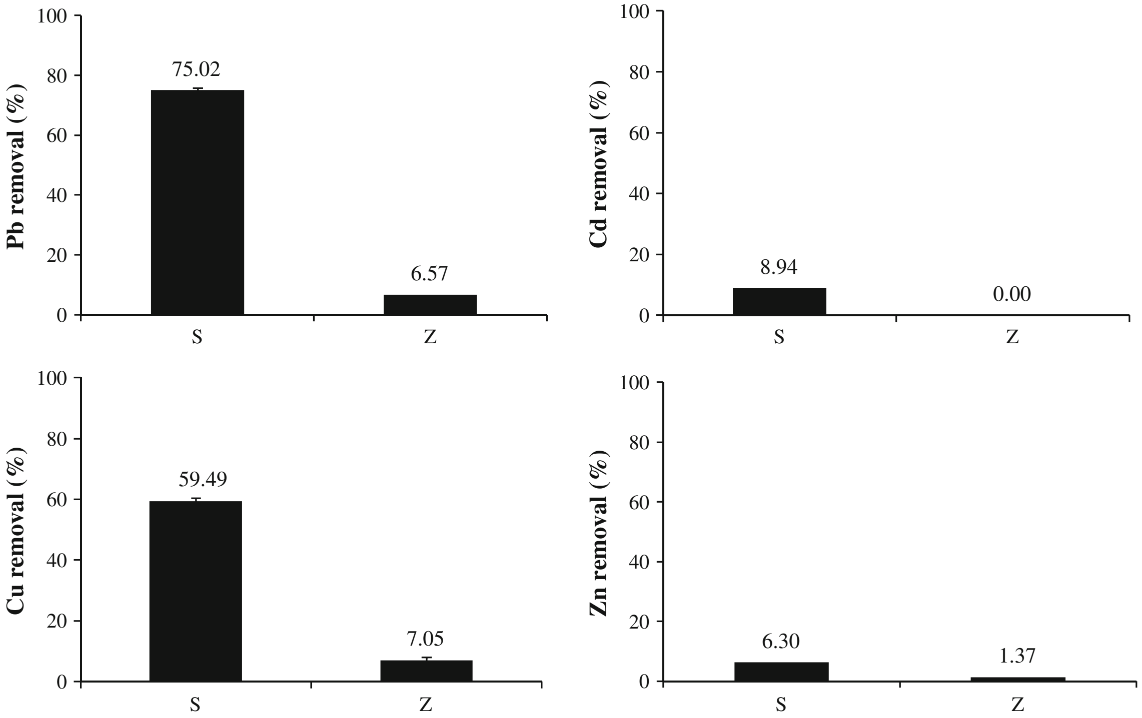

Fig. 6 Sorption of Pb, Cd, Cu and Zn in mixed systems

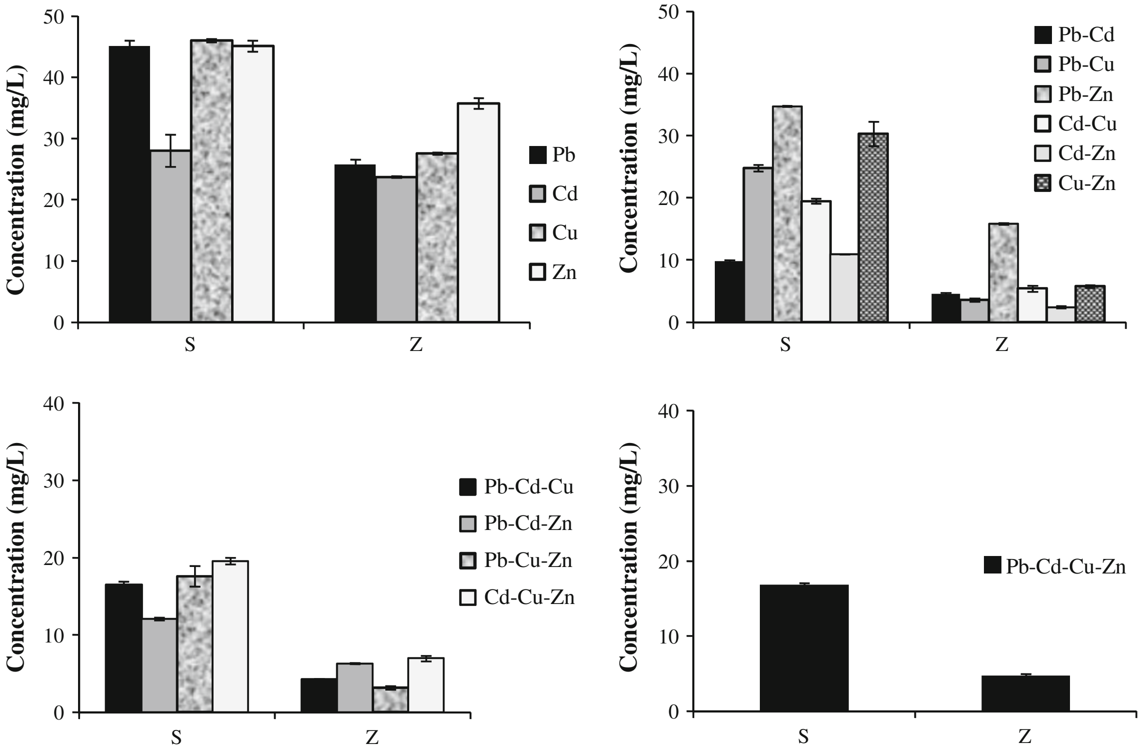

Fig. 7 Released calcium in single and multi-element systems

differences between metal sorption capacities would depend only on their affinity to the surface of calcite.

Discussion

The removal percentages of metal cations in single and multi-element systems were compared. In single element removal, the studied limestone samples revealed higher removal efficiency than do in mixed systems. Furthermore, the limestone samples used in this study have variable chemical composition that may explain the difference in the metal adsorptive capacities. Al-Degs et al. (2006) mentioned that, based on conventional theory, metals with higher electronegativity should adsorb more readily as was the case of the studied metals. The same theory suggested that metals of higher hydrolysis constants have better adsorptive capacity (Appel et al. 2008). Moreover, differences in limestone affinity for the studied metals (i.e., Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+}) are mainly contingent upon those metals physico-chemical properties including electronegativity, ionic radius, hydrated radius, hydrolysis constant among others (Apiratikul and Pavasant 2006; Appel et al. 2008). This assumption can give a reasonable explanation for the higher removal of Pb^{2+} and Cu^{2+} compared to Cd^{2+} and Zn^{2+}. For example, Pauling electronegativity of Pb^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+} are 2.33, 1.90, 1.69 and 1.65, respectively. Our experimental results showed that limestone sample's affinity followed the order $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+}$, which is consistent with the electronegativity values. Furthermore, the hydrated radius showed the sequence $Zn^{2+} = 4.3$ Å $> Cd^{2+} = 4.26$ Å $> Cu^{2+} = 4.19$ Å $> Pb^{2+} = 4.01$ Å, indicating that smaller radius favored metal interaction with the sorbent surface (Appel et al. 2008). Numerous studies, including Godelitsas et al. (2003), Al-Degs et al. (2006) and Karageorgiou et al. (2007), reported that metals of ionic radius close to that of Ca^{2+} adsorb stronger. According to those works, Cd^{2+} should have higher sorption capacity than Cu^{2+} and Zn^{2+}; however, this was not the case for the present study. In multi-element system, physical properties of metals still play an important role in the removal process. Srivastava et al. (2005) found that lead had a higher affinity than copper, which in turn had a higher affinity than cadmium and zinc. He stated that cadmium could not effectively compete with other metals because of its restricted adsorption to charge sites. Among the metal ions studied, Pb^{2+} was the most preferably removed cation because of its high affinity to calcite surface. Considering this observation, Pagnanelli et al. (2003) concluded that the metal with highest affinity is not significantly influenced by the presence of other heavy metals in solutions. However, the present study showed that the presence of copper strongly inhibited the removal of lead, especially in the pure limestone (Z sample). As for S limestone sample, the presence of copper slightly decreased lead removal. This was attributed to the availability of numerous binding sites, the presence of which may render the competitive effect insignificant (Apiratikul and Pavasant 2006). It is worth noting that the presence of Pb^{2+} in the system more effectively decreased the sorption capacity of Cu^{2+} and Cd^{2+}, but enhanced the removal of Zn^{2+}. Therefore, these metals had only a minor competitive effect on Pb^{2+} adsorption and did not appear to compete with this metal for high affinity sorption sites. Both Cd^{2+} and Zn^{2+} have similar hydrated radii of 4.26 and 4.30 Å, respectively (Table 2), and low electronegativities than Cu^{2+} and Pb^{2+}, which minimize electron sharing or covalent bond formation with the sorbent surface. Thus, coulombic interactions with surfaces were favored for Zn^{2+} and Cd^{2+}. Echeverria et al. (1998) and Appel et al. (2008) reported decreased sorption of Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} when these metals were sorbed in mixed systems compared to single element removal. It is to be mentioned that the effect of competing ions was stronger on Zn^{2+} and Cd^{2+} removal in ternary and quadruple systems than in binary system because of the preferential sorption. Performances of natural limestones for the removal of several heavy metals from wastewaters were clearly dependent on various parameters including the physico-chemical characteristics of the limestone sample and the metal to be removed. Furthermore, the feasibility of heavy metal removal by natural limestones seemed to be related to the concentration of the metal ions, essentially. For instance, the removal of lead was the highest among the studied metals due to the high affinity to calcite surface when compared with other metals like copper, cadmium and zinc. In summary, the studied Camapanian-Maastrichian limestones of the Abiod formation, Tunisia exhibited high removal efficiency in single and multi-element systems, and therefore, was found to be suitable for removing Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} from aqueous solutions.

Conclusions

The present study showed that natural limestones effectively removed high percentage of heavy metals. The adsorption behavior of Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} onto limestones in single and mixed systems is governed by physical properties of the studied metal. The limestone from northern Tunisia, containing higher impurities such as silica and iron and aluminum oxides, showed better removal efficiency than the limestones of southern area. For all the studied metals, higher removal percentage was achieved by the low grade limestone sample from the solution of 10 mg/L in single and mixed systems.

The selectivity sequence of the studied metal was $Pb^{2+} > Cu^{2+} > Zn^{2+} \approx Cd^{2+}$ in single and mixed systems. Due to their chemical properties (high electronegativity, small hydrated radius and high hydrolysis constant), copper and lead were sorbed onto limestone surface more than cadmium and zinc. These results indicated that Campanian–Maastrichtian limestones from Tunisia are expected to be promising natural resources for the removal of toxic heavy metals from wastewaters.

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