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Studies on divalent ion uptake of transition metal cations by calcite through crystallization and cation exchange process

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The uptake of transition metal cations of Fe, Cu, Zn, Cd and Pb with calcium carbonate in the form of calcite was investigated. The uptake reaction was found to be in the following order: $Pb^{2+} > Cu^{2+}$ $Zn^{2+} > Cd^{2+} \approx Fe^{2+}$; and the amount of uptake (meq/g) cations has been found to increase with the increase of the metal ion concentration and reaction time. The uptake of these ions was mainly considered to be due to the crystallization that happens through decomposition reaction mechanism as in case of Pb^{2+}, Cu^{2+} and Zn^{2+} and cation exchange of surface Ca^{2+}-ions present in lattice structure of carbonate solid with metal cations, as in the case of Fe^{2+} and Cd^{2+}. The different affinities of calcite toward these cations can be used for waste ions fixations or decontamination. *© 2003 Kluwer Academic Publishers*

1. Introduction

Numerous methods have been proposed to immobilize or fix the pollutant heavy metal ions in natural and waste water and also in nuclear wastes using various types of inorganic materials such as layered zirconium phosphates, clay minerals, framework of alumino-silicates, calcium silicate hydrates and hydroxyaptities. The removal of heavy metals takes place mostly via cation exchange reactions as in the case of calcium silicate hydrates [1–7] and hydroxyaptities [8–10].

TABLE I XRF chemical analysis of calcite ($CaCO_3$) sample

CaO	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO	K_2O	Na_2O	SO_3	Cl	Total	$CaCO_3$
55.71	n.d.	0.078	n.d.	0.105	0.233	0.014	n.d.	0.034	0.003	56.177	99.482

n.d. = not detected.

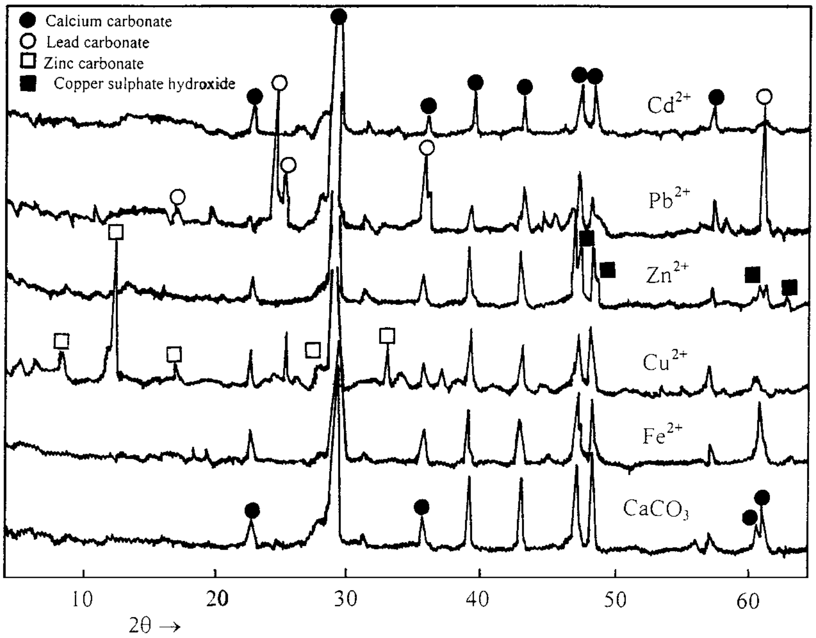

Figure 1 XRD patterns of $CaCO_3$ reacted with 2000 mg/l of Fe^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, or Cd^{2+} or Cd^{2+} for 24 h.

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The Pb^{2+} ions were shown [9, 10] to be fixed by hydroxyapatites. Ions such as Pb^{2+}, Cd^{2+}, Sr^{2+} and Ba^{2+} form insoluble carbonates around neutral pH. Gamsjer *et al.* [11] reported the fixation of Pb^{2+} ions in aqueous solution on calcite and aragonite and the adsorption of Cd^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+} and Sr^{2+} ions on calcium carbonates suggested by others [12–14]. They, however, used very dilute aqueous solutions of heavy metals which reacted partially with calcite or aragonite. Calcium carbonate in the form of calcite ($CaCO_3$) is

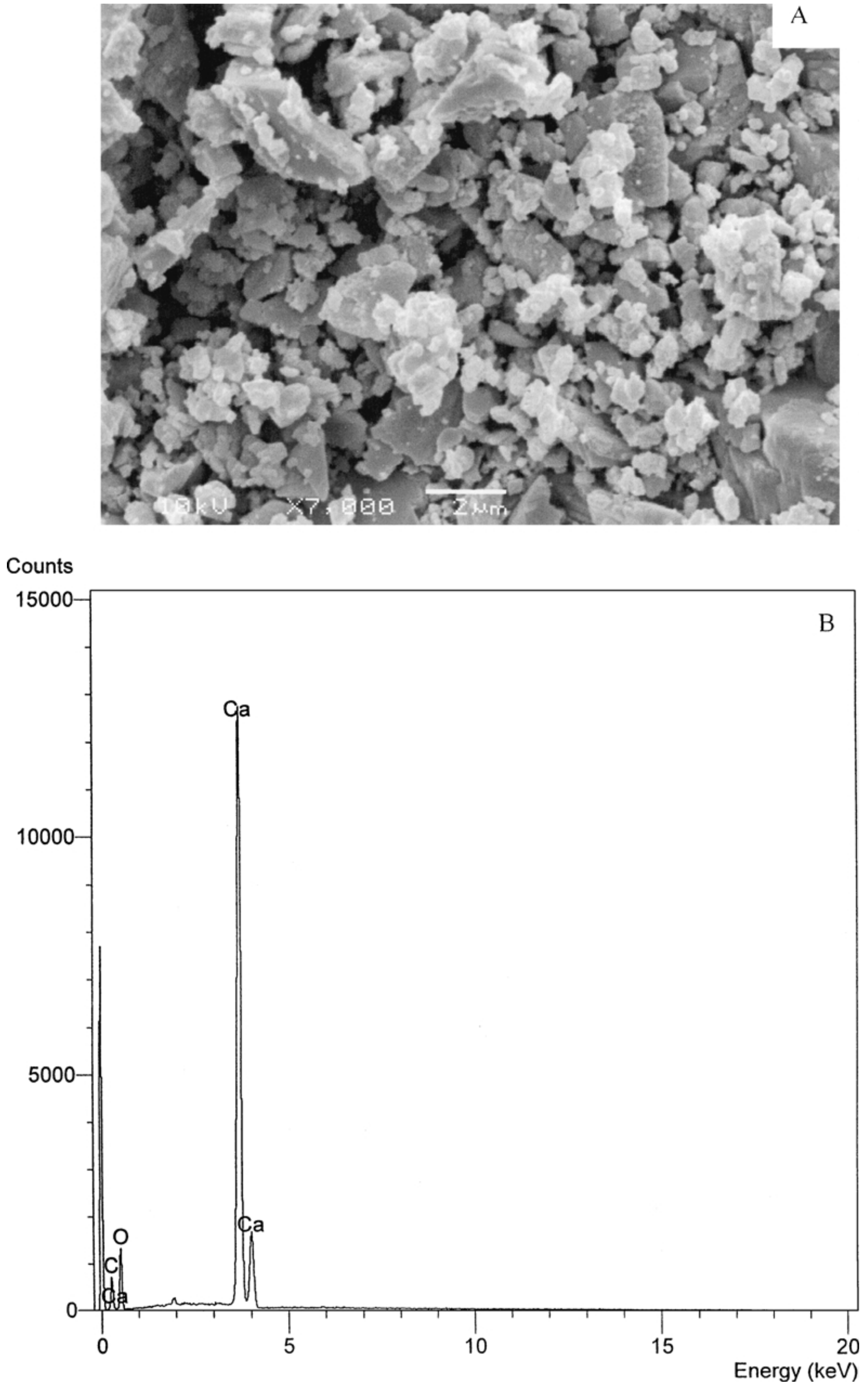

Figure 2 (A) SEM photographs show subhedral crystals or $CaCO_3$ and (B) EDAX of $CaCO_3$.

TABLE II Change in pH-values on reaction of M^{2+}-ions with $CaCO_3$

	Metal ion																								
	Fe^{2+}					Cu^{2+}					Zn^{2+}					Pb^{2+}					Cd^{2+}				
Reaction time/h	200	400	800	1000	2000	200	400	800	1000	2000	200	400	800	1000	2000	200	400	800	1000	2000	200	400	800	1000	2000
													Concentration (ppm)												
0	2.54	2.37	2.09	1.93	1.73	5.03	4.76	4.57	4.41	4.35	6.01	5.54	6.05	6.09	6.10	5.01	4.80	4.91	4.95	4.85	6.17	6.01	6.18	6.15	5.90
1	3.41	3.07	2.72	2.10	1.92	6.33	7.49	7.66	7.44	4.47	6.48	6.63	6.83	6.93	6.08	7.44	7.22	6.46	7.45	7.40	5.86	6.03	6.53	6.38	6.35
6	3.65	4.24	2.99	2.30	1.97	5.40	6.11	6.92	6.53	4.47	6.59	6.25	6.32	6.57	5.99	7.32	7.21	7.26	7.31	7.25	5.90	5.94	6.22	6.10	6.21
12	3.91	4.75	2.78	2.15	1.83	4.90	5.29	6.33	5.51	4.52	6.53	6.13	6.07	6.39	6.09	7.14	7.12	7.13	7.21	7.20	5.60	5.90	5.99	6.01	6.11
24	3.68	4.65	2.68	2.25	1.88	4.64	5.19	6.32	5.33	4.73	6.49	6.07	6.13	6.27	6.18	6.39	7.03	6.86	6.96	7.02	5.75	5.91	5.87	5.99	6.13

ubiquitous and the above studies show that such materials may be useful for waste ions decontamination.

Other carbonates as barium carbonate were used in the removal of SO_4^{2-}, Ca^{2+}, Zn^{2+} and Cd^{2+} from industrial effluents [15]. SO_4^{2-} removal was very effective when it was associated with calcium. On the other hand Sm^{3+}, can be also removed by carbonates of alkali earth metals from Na and K chloride solutions [16]; while Ln^{3+} and Nd^{3+} ions can be separated using carbonates of alkali earth metals of Mg, Ca and Ba [17].

Lime in the presence of inorganic additives as Na_2CO_3 was also used in heavy metals removal from acid mine drainage [18]. Removal of humic acids,

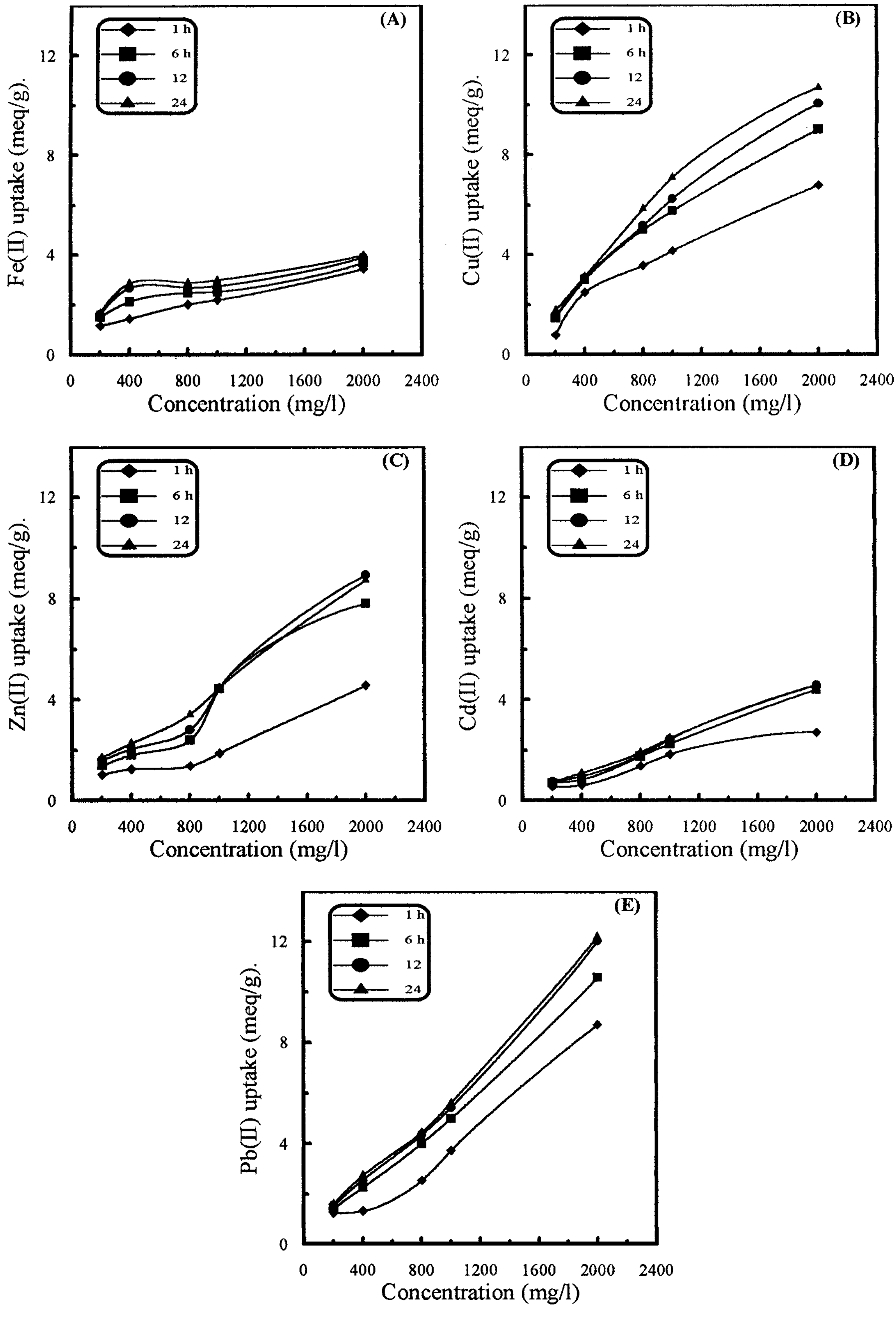

Figure 3 (A–E) Concentration and time dependence of the M^{2+}-ions uptake from aqueous solutions by $CaCO_3$.

colour, permanganate and some heavy metals was also studied using closed-bed lime-stone reactor [19].

The objectives of the present research have been to examine the uptake reaction of transition metal cations of Fe, Cu, Zn, Cd and Pb from diluted and very concentrated aqueous solutions by natural calcium carbonate in the form of calcite; where it is a common constituent of cement and concrete and hence the latter as inorganic materials may be useful in waste ion fixation or decontamination.

2. Experimental and method

The uptaked Fe^{2+}, Cu^{2+}, Zn^{2+} Cd^{2+} and Ni^{2+} by calcium carbonate in the form of calcite obtained, from Sinai peninsula (Egypt) was examined. X-ray fluorescence (XRF) analysis provides a rapid convenient, and accurate method of determining the elements present in the calcite sample.

Uptake experiments were conducted as follows: 100 mg of solid was equilibrated with the respective cations at different periods of time (1–24 h) in glass vials at room temperature, without shaking together with 25 ml of Cl^-, $SO_4{}^{2-}$ or $NO_3{}^-$ solution of 200, 400, 800, 1000 or 2000 mg/l of Fe^{2+}, Cu^{2+}, $Zn^{2+}Cd^{2+}$ or Pb^{2+}; $NO_3{}^-$ was used for Pb^{2+}; Cl^- for Cd^{2+} and $SO_4{}^{2-}$ for Cu^{2+}, Fe^{2+} or Zn^{2+}. Calcium carbonate of 100 mg contains 1.0 mmol of reactive calcium ions. After different periods of equilibration, the solid phases in the glass vials were separated by centrifugation and a part of the supernatant solutions was collected for M^{2+} chemical analysis using atomic absorption spectroscopy (AAS). Change in pH-values on reaction of M^{2+}-ions solutions with $CaCO_3$ solid was measured immediately after centrifuge using digital pH-meter (Fisher Scientific, Model 825 MP) with combined glass electrode equipped with Ag/AgCl reference electrode. The glass electrode has been calibrated using different buffer solutions of pH's 4.004 and 9.18.

It should be mentioned here that, Fe^{2+} solutions were slightly acidified by very diluted solution of H_2SO_4 to prevent precipitation of Fe^{2+} as hydroxide during the reaction. The solids after reactions dried at 80°C for 24 h and then characterized by X-ray powder (XRD) diffraction (Philips diffractometer using Ni filter with Cu K_α radiation), scanning electron microscopy (SEM) by means of JEOL scanning electron microscope JSM-5600 attached to an energy dispersive X-ray (EDAX) (ISIS OXFORD) source and IR spectra in range 4000 – 200 cm^{-1} (Perkin Elmar 1430 Ratio Recording Infrared spectrophotometer).

3. Results and discussion

The chemical analysis of calcium carbonate sample using XRF is given in Table I.

Powder XRD analysis (Fig. 1) showed that one single phase of $CaCO_3$ (calcite) agreed with ASTM card no.5-0586 and the chemical analysis (Table I). The carbonate phase consisted of aggregating of subhedral crystals on examination by SEM (Fig. 2A), while EDAX detected a radiation peaks of Ca, C and oxygen only (Fig. 2B). On the other hand, IR-spectra (Fig. 4) shows strong absorption bands found at 1435, 875 and 715 cm^{-1}, in addition to weak bands at 2530 and 1797 cm^{-1}. These bands are characteristic for $CaCO_3$ (calcite) [20].

The pH-values of the initial metal solutions varied with the type of salt and also change during the reaction course (Table II). This change is attributed to the ions uptake by the solids and crystallization during the reaction.

Results of the uptake reaction of Fe^{2+}, Cu^{2+}, $Zn^{2+}Cd^{2+}$ or Pb^{2+} with $CaCO_3$ are shown in Fig. 3 (A → E). Generally, the amount of metal ions taken up by $CaCO_3$ solid increases with the increase the initial concentration and/or reaction time in the order: $Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+} \approx Fe^{2+}$. At 200 mg/l concentration of M^{2+}, the uptake was found to be: 92, 88, 76, 53 and 61% for Pb^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+} and Cd^{2+} respectively. While at 2000 mg/l concentration used, the uptake was found to be: 58, 51, 40, 32 and 26% for the above metal cations respectively. The uptakes referred to here are given as examples and they were used after 24 h reaction time.

TABLE III Change in the main interlayer distance 104 (*hkl*) at dA° equal to 3.05 in the presence of different M^{2+}

Species	$CaCO_3$ (ref.)	Fe^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}
dA°	3.052	3.0694	3.052	3.0694	3.0871	3.0694
2θ	29.288	29.068	29.238	29.068	28.898	29.068

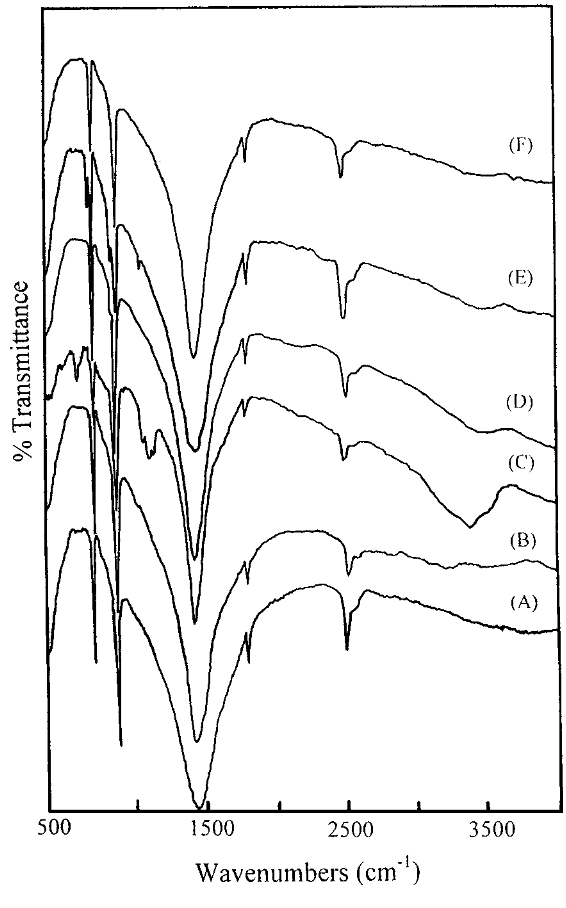

Figure 4 IR-Spectra of $CaCO_3$ (A) and $CaCO_3$ reacted with 2000 mg/l Fe^{2+} (B), Cu^{2+} (C), Sn^{2+} (D), Pb^{2+} (E), and Cd^{2+} (F) for 24 h.

Amounts of Ca^{2+}-ions were detected in solutions ranging from 0.006–0.864 meq/g. This is ascribed to the slightly acidic nature of the M^{2+} solutions (Table II) and probably to presence of exchange reaction between surface Ca^{2+} of the solid with M^{2+}. The latter is supported by the change in the main interlayer distance (shift) of $CaCO_3$ (104, *hkl*) at 3.05 and $dA^\circ 2\theta = 29.288$ as indicated in Table III. The diffraction angle of XRD apparatus has been corrected using gypsum ($CaSO_4 \cdot 2H_2O$) and potassium hydrogen phthalate (KHP) as standers, and the dA°-values have been calculated using the known W. Bragg's equation: $n\lambda = 2d \sin\theta$.

Since many carbonates of formula $M^{II}CO_3$ have the same structure as calcite (such as Zn^{2+}, Fe^{2+} and Cd^{2+}

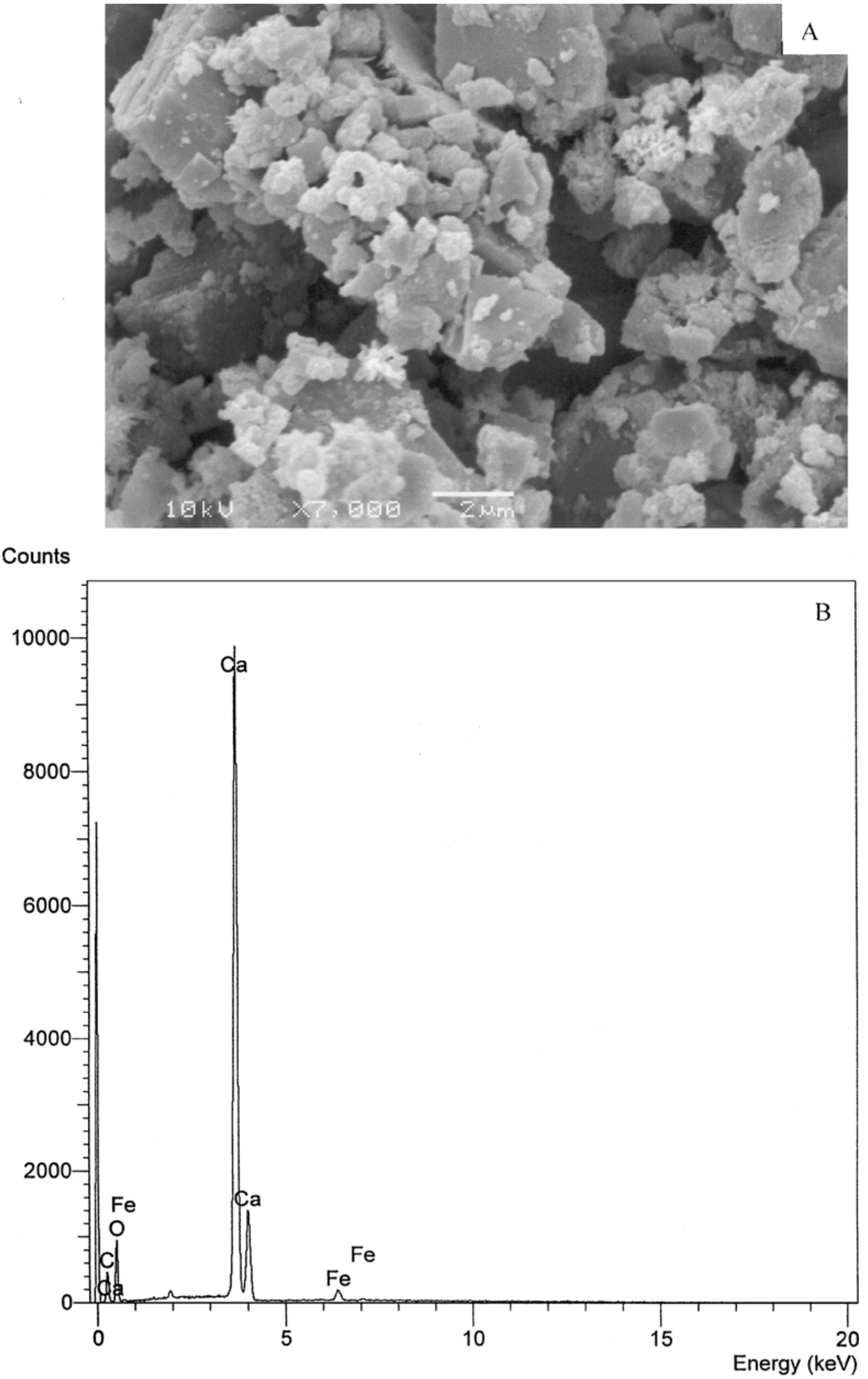

Figure 5 (A) SEM of $CaCO_3$ reacted with 2000 mg/l Fe^{2+} solution of 24 h and (B) EDAX of $CaCO_3$ reacted with 2000 mg/l Fe^{2+} for 24 h.

carbonates) or aragonite (such as $PbCO_3$) [21]. In this respect, Michihihiro *et al.* [22] reported that the uptake of Pb^{2+} ions by calcite is similar to that by aragonite, whereas Cd^{2+} does not reacted with calcite. This result is in contradiction with that reported by Gasmjager *et al.* [11] who found that the uptake of Pb^{2+} ions by aragonite was faster than by calcite. But Cd^{2+} ions in the present study have been found to react with $CaCO_3$ (calcite). This is confirmed by EDAX data (Fig. 8B) and from the decrease in the relative intensities of $CaCO_3$ peaks, even thought $CdCO_3$ crystallization are not detected in XRD (Fig. 1).

There is a shift in dA°-values of the main interlayer distance (3.052 A°) of $CaCO_3$ solid on reaction with

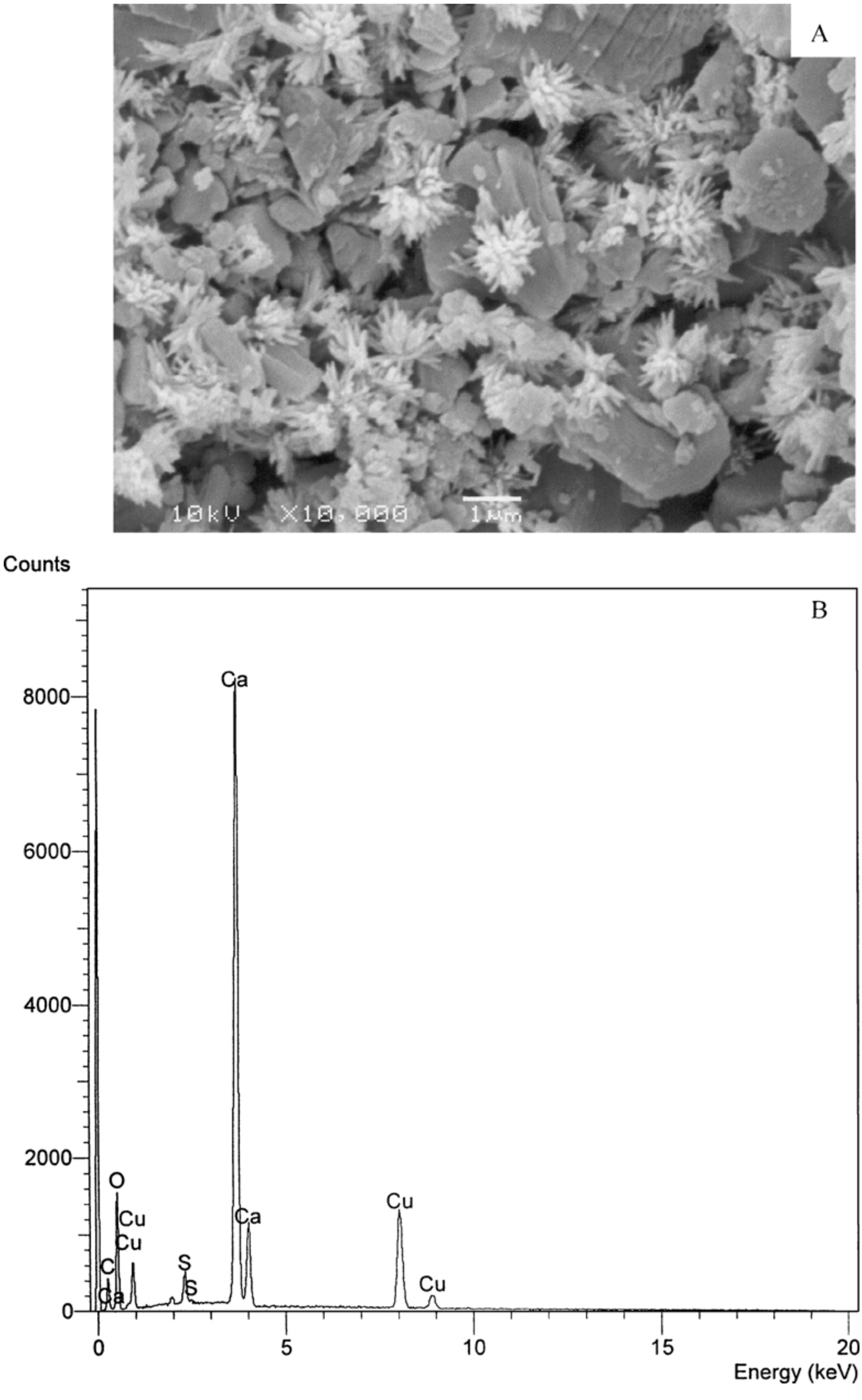

Figure 6 (A) SEM of $CaCO_3$ reacted with 2000 mg/l Cu^{2+} solution for 24 h and (B) EDAX of $CaCO_3$ reacted with 2000 mg/l Cu^{2+} for 24 h.

Fe^{2+}, Cd^{2+}, Cd^{2+}, Zn^{2+} and/or Pb^{2+} (Table III) and in some of the minor peaks. This means that the uptake of these cations take place mainly via cation exchange with surface Ca^{2+}- ions present in the lattice the solid, since many carbonate of formula $M^{II}CO_3$ have the same structure of calcite or aragonite ($M = Zn^{2+}$, Fe^{2+}, Cd^{2+} or Pb^{2+}) [21]. There is no detectable crystallization for Cd-salt as shown in XRD pattern (Fig. 1) or even on microstructure examined by SEM (Fig. 8A). While in the case of Fe^{2+} there is no crystallization detection for iron-salts. For the same system there is a decrease in relative intensity and a presence of shift in dA°-values of XRD patterns of Calcite, however, a vermicular form deposition of ill-crystallized crystals

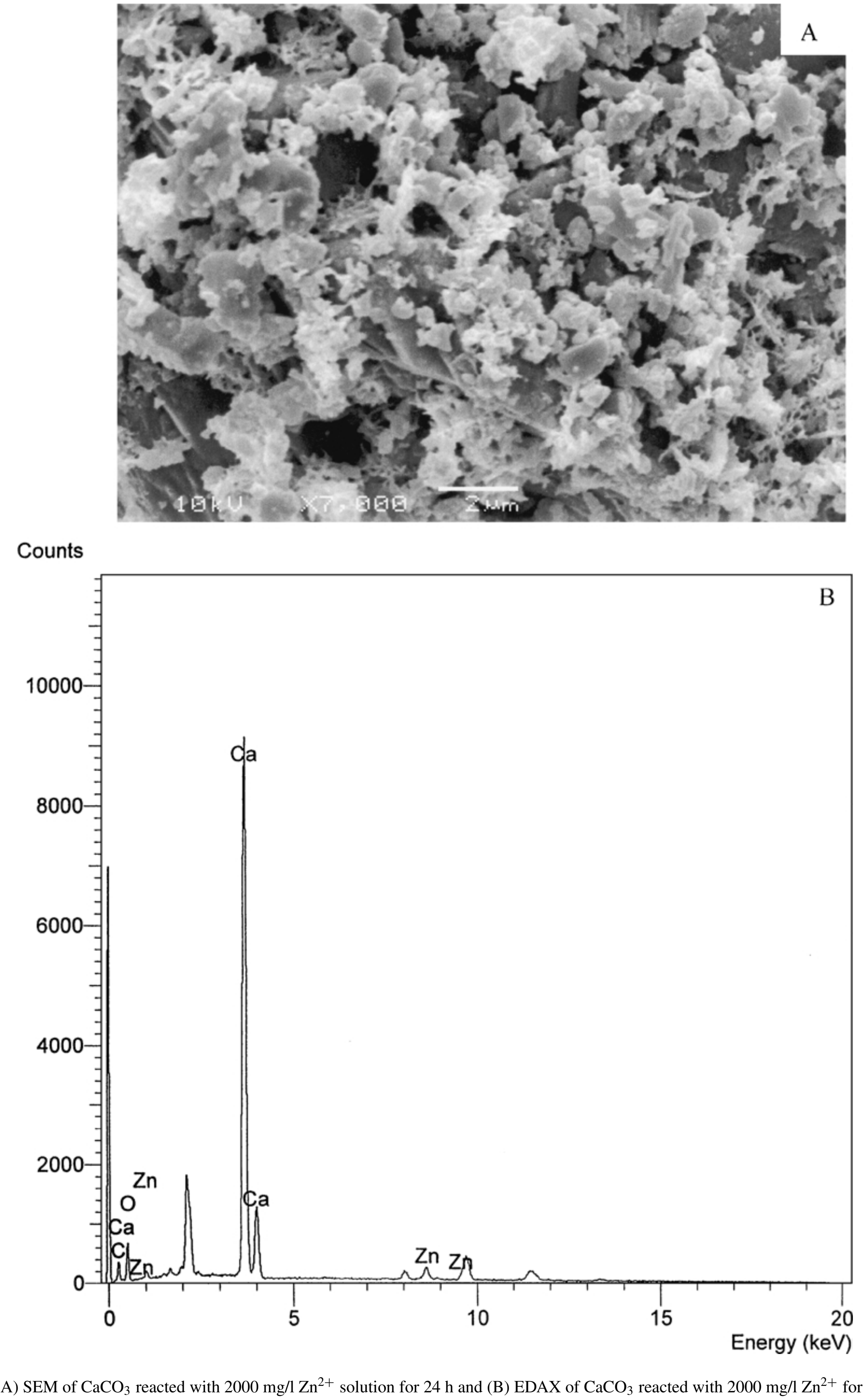

Figure 7 (A) SEM of $CaCO_3$ reacted with 2000 mg/l Zn^{2+} solution for 24 h and (B) EDAX of $CaCO_3$ reacted with 2000 mg/l Zn^{2+} for 24 h.

of iron is generally found in a subhedral habit associated with calcite crystals as shown in microstructure (Fig. 5A). The detection of Fe^{2+} with carbonate was also confirmed by EDAX (Fig. 5B). This suggested that the uptake of Fe^{2+} may take place mainly via $Fe^{2+} \Leftrightarrow Ca^{2+}$ exchange and crystallization. An this respect, it was reported [6, 7] that the uptake reaction of heavy metal captions with calcium silicate hydrate (CSH) compounds proceeds via cation exchange and crystallization together. This uptake increase with increase of the amounts of $CaCO_3$ initially present with CSH (carbonation effect). The incorporated metal ions in the lattice structure of the solids caused a considerable shift dA°-values (XRD).

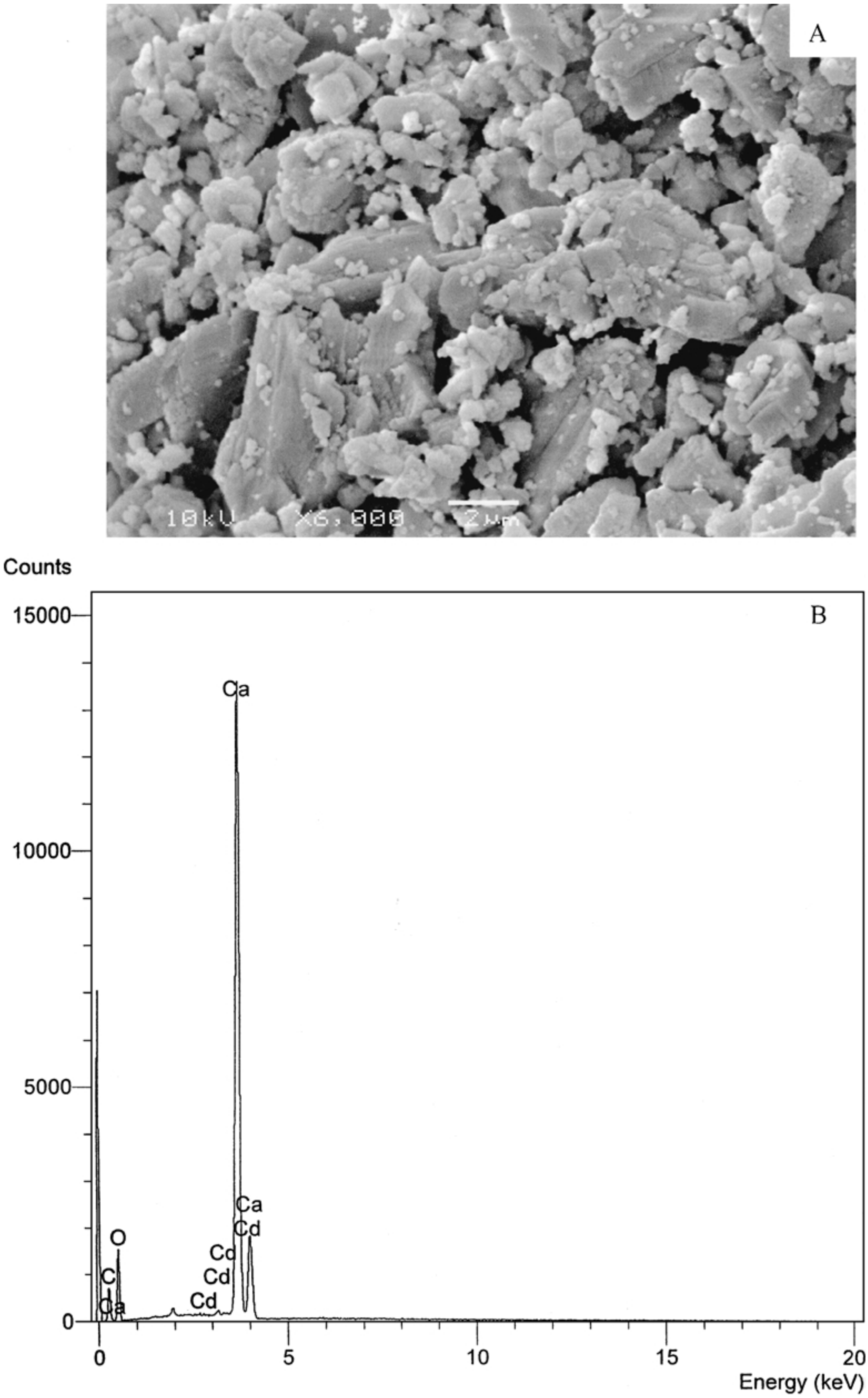

Figure 8 (A) SEM of $CaCO_3$ reacted with 2000 mg/l Cd^{2+} solution of 24 h and (B) EDAX of $CaCO_3$ reacted with 2000 mg/l Cd^{2+} for 24 h.

The uptake reactions of $CaCO_3$ with Pb^{2+}, Zn^{2+} and Cu^{2+} shows a new absorption peaks on their XRD, especially is the case of Pb^{2+} and Cu^{2+} (Fig. 1). These results are in agreement with microstructure data presented in Figs (9A and 6A) and also in EDAX (Figs 9B and 6B). Both XRD and microstructure results demonstrate the crystallization of Pb^{2+} as cerussite ($PbCO_3$) in hexagonal crystals form (Fig. 9A). While in the case of Cu^{2+} acicular in accumulation form of copper sulphate hydroxide is probably langite ($Cu_4SO_4(OH)_6 \cdot H_2O$) is detected by XRD (Fig. 1). The presence of this phase is supported by detection of sulphate peaks with examination by EDAX (Fig. 6B). Crystallization of Cu^{2+} as $CuCO_3$ is not clear from the peaks of oxygen and

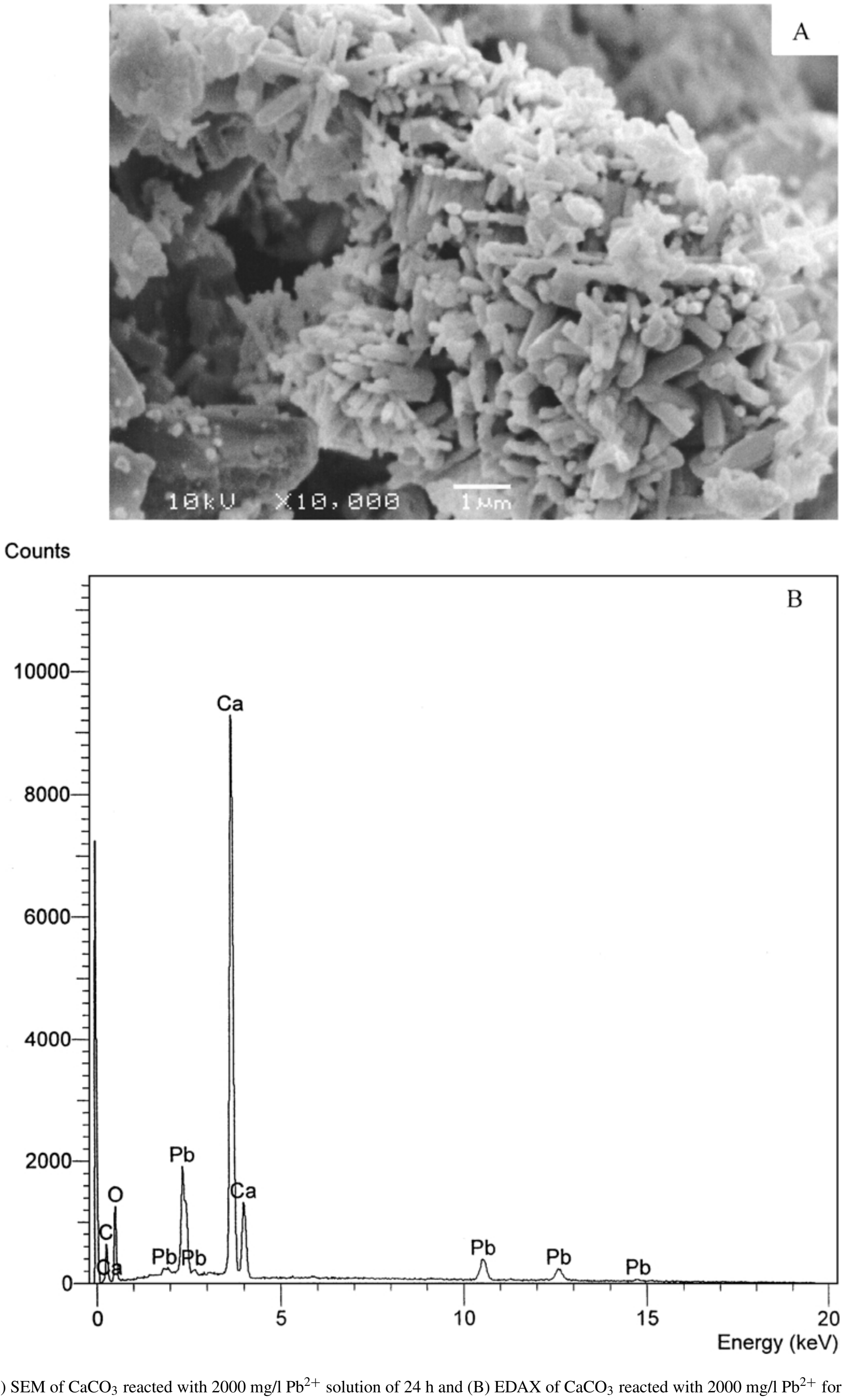

Figure 9 (A) SEM of $CaCO_3$ reacted with 2000 mg/l Pb^{2+} solution of 24 h and (B) EDAX of $CaCO_3$ reacted with 2000 mg/l Pb^{2+} for 24 h.

carbon are also the main constituent of $CaCO_3$ solid as indicated from EDAX (Fig. 6B).

Zn^{2+} on reaction with $CaCO_3$ forms a crystalline accumulation of $ZnCO_3$ (Fig. 7A). The crystallization of Zn^{2+} was also confirmed by XRD (Fig. 1) and EDAX (Fig. 7B). The formation of $ZnCO_3$ may take place through the exchange-decomposition reaction of $ZnSO_4$ solution with $CaCO_3$ according to the following equation :

$$ZnSO_4 + CaCO_3 + H_2O \rightarrow ZnCO_3 \downarrow + CaSO_4{\cdot}2H_2O$$

IR-spectra (Fig. 4) shed light on the uptake reaction of $CaCO_3$ with different metal cations, which reveals a decrease in the relative intensities of the most absorption bands of $CaCO_3$, especially those located at 1435, 875 and 715 cm^{-1}. In addition, in the presence of Pb^{2+} and Cu^{2+}-ions (Fig. 4) new absorption bands were present at 1055, 842 and 685 cm^{-1}. In the former these bands were due to the presence of $PbCO_3$ [23] which is known as a cerussite. $PbCO_3$ is characterized also by very strong doublet and broad absorption bands at 1460–1435 and 1405–1390 cm^{-1}. These bands, however, are overlapped with a very strong broad absorption band of $CaCO_3$. In the latter, new bands are found at 3400 (broad), 1140, 1120, 1070, 640 and 625 cm^{-1}. These new band are due to the presence of copper sulphate (as langite phase) [24]. Generally IR-spectra data supports and agree with the results obtained from XRD patterns.

4. Conclusion

It can be concluded from the above results and discussion, natural calcium carbonate (calcite) can be used for fixation or decontamination of different transition metal cations such as: Fe, Cu, Zn, Cd and Pb from the hazardous waste stream. The amount of uptake (meq/gm) of these cations by the solid decrease in the order: $Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+} \approx Fe^{2+}$, and increases with increasing the M^{2+} concentration and reaction time. The uptake mechanism of these ions is mainly due to the crystallization (as salts via decomposition reaction mechanism) as in the case of Pb^{2+}, Cu^{2+} and Zn^{2+}-ions and cation exchange of surface Ca^{2+}-ions of carbonate structure with metal cations, as in the case of Fe^{2+} and Cd^{2+}ions.

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