Functionalization of lambda-zirconium phosphate with ethylenediaminetetraacetic acid: Synthesis, characterization and applications

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Abstract. A new layered organic-inorganic material based on λ-Zirconium phosphate (λ-ZrP) and ethylenediaminetetraacetic acid (H_4Y) has been prepared. The thermal analyses, X-ray diffractometry and FT-IR spectrophotometry confirm the introduction of H_4Y inside the interlayer gallery of λ-ZrP. The pristine λ-ZrP and its new polyaminocarboxylic acid functionalized derivative (λ-ZrPH_2Y$) exhibit high potential for the application in the area of hard water treatment, where their Ca^{2+} uptake capacities are found to be 32.0 and 40.4 mg Ca^{2+} per gram of λ-solid, respectively.

Keywords. λ-Zirconium phosphate; ethylenediaminetetraacetic acid; functionalized λ-ZrP; layered inorganic-organic materials; metal ion uptake.

1. Introduction

Ethylenediaminetetraacetic acid (EDTA) (figure 1) is a mutidentate complexing agent, which can bind metal ions through multiple atoms. Therefore, it can wrap itself around metal ions like a claw.

EDTA is commonly added to food packaging in order to complex metal ions that catalyze reactions that can cause food spoilage and rancidity, discoloration, off-flavour or odour. It has also many other applications in medicine (treatment for lead and heavy metals poisoning), agriculture, polymerization, pulp and paper applications and textiles.

It is well-known that one of the methods used to determine the total hardness of water, caused mainly by the presence of Mg^{2+} and Ca^{2+}, is complexometric titration with EDTA. Accordingly, immobilization of EDTA inside the framework of the inorganic supports is expected to produce porous materials able to efficiently entrap those metal ions that cause water hardness.

It is noteworthy that the superficial chloride ligand of λ-zirconium phosphate (λ-ZrP), λ-ZrPO_4Cl(CH_3)_2SO$, can be topotactically exchanged by carboxylic acid compounds.[1,2] Therefore, ethylenediaminetetraacetic acid (EDTA) can be immobilized inside the interlayer of λ- ZrP through the above mentioned exchange.

Basically, λ-ZrP is structurally related to γ-ZrP (figure 2), which can be formed by bridging four different zirconium atoms with (PO_4) in a similar manner to that of γ-ZrP, then balancing the residual positive charge and completing the octahedral configuration of each zirconium atom with a monovalent anionic monodentate ligand (flouride or chloride) and neutral monodentate ligand (dimethyl sulfoxides).[3–6] The building blocks formation of this lamellar structure is shown in figure 2.

There are very few examples in the literature about the construction of porous organic- and inorganic-inorganic materials based on λ-ZrP with tailor-made properties.[2,7,8]

This study aims to immobilize EDTA inside the interlayer gallery of λ-ZrP in order to obtain organic-inorganic framework with potential applications in the area of hard water treatment.

2. Experimental

All chemicals and reagents used were of analytical grade. All of them were purchased from Aldrich Co., and used as supplied. λ-Zirconium phosphate was
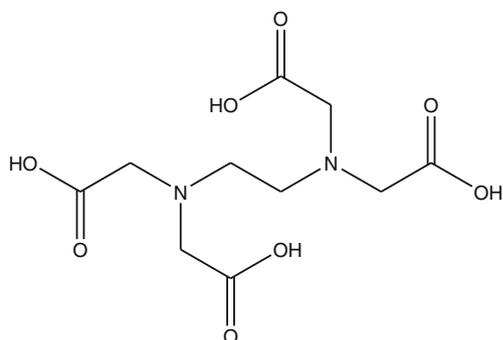
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Figure 1. Structure of EDTA (H_4Y).

prepared using a literature described procedure (inter-layer distance 1.02 nm).[8]

2.1 *Topotactic exchange of EDTA with λ-ZrP*

A 1.84 g amount of $ZrPO_4Cl(dmso)$ was contacted with 229 mL of a $6.73 \times 10^{-3}M$ H_4EDTA and $6.73 \times 10^{-3}M$ Na_4EDTA solution using a 33.4% (v/v) dmso/water mixture as solvent. The mixture was heated at 75°C for one week. The resulting white solid was separated by centrifugation and washed with 33.4% (v/v) dmso/water solution (3 × 100 mL). Finally it was dried at 80°C for 24 h to obtain 1.14 g of the product which was stored over P_2O_5.

2.2 *Hard water treatment: Ca^{2+} uptake*

A 250 mg of λ-solid (λ-ZrP or $λ$-$ZrPH_2Y$) was shaken with 12.5 mL of tap water, previously diluted to 25 mL with distilled water and adjusted to pH 10 by adding 2.5 mL of NH_3/NH_3Cl buffer solution using a polyethylene bottle with a good stopper. Several metal uptake reactions were carried out at different time intervals (0.5–72 h). The metal ion concentration was measured by flame photometer after separation of the insoluble solid by centrifuge and diluting the supernatant solution to the linear range of the calibration curve for Ca^{2+}. Each measurement was performed three times.

The metal ion uptake is calculated as mg of Ca^{2+}/g of λ-solid.

2.3 *Characterization*

X-ray powder diffraction (XRD) patterns were recorded at room temperature on Siemens D-5000 diffractometers with Cu Kα radiation ($\lambda = 0.154$ nm) and Ni filter at 40 kV, 30 mA, a scanning rate of 5°min^{-1}, and a 2θ angle ranging from 3°–70°. Infrared spectra were recorded on a FTIR-8201PC spectrometer using KBr disk in the range 4000–400 cm^{-1}. Elemental analyses were performed on a Perkin Elmer II 2400 CHN analyzer. Thermogravimetric analyses was performed on a Mettler-Toledo TGA/STDA 851e apparatus and recorded at 5°C/min. The Ca^{2+} concentration in tap water samples was measured on a Flame photometer ANA-135. Structure modelling was carried out on PC computers using the Hyperchem release 7 and the molecular mechanics method MM+.

3. Results and Discussion

The ligand exchange reaction between λ-ZrP and EDTA (H_4Y) is expected to take place in a topotactic manner, i.e., it occurs without affecting the integrity and rigidity of the inorganic layers.

The new functionalized λ-ZrP is prepared by post-synthesis modification of the surface of inorganic layers of λ-ZrP, where λ-ZrP is contacted with H_4Y/Na_4Y equimolar mixture using a 33.4% (v/v) dmso/water mixture as solvent (see section 2). The resulting solid phase material designated as $λ$-$ZrPH_2Y$ with C, H, N, S% content of 20.60, 3.25, 3.40, 7.77 (calculated: 20.53, 3.20, 3.42, 7.83), respectively. This elemental analysis is in agreement with the formula: $ZrPO_4(C_{10}H_{14}N_2O_8)_{0.5}(CH_3)_2SO$.

It is important to mention that chloride was not observed by elemental analysis, which means that the chloride anions of λ-ZrP are complete exchanged by those of carboylate groups of EDTA.
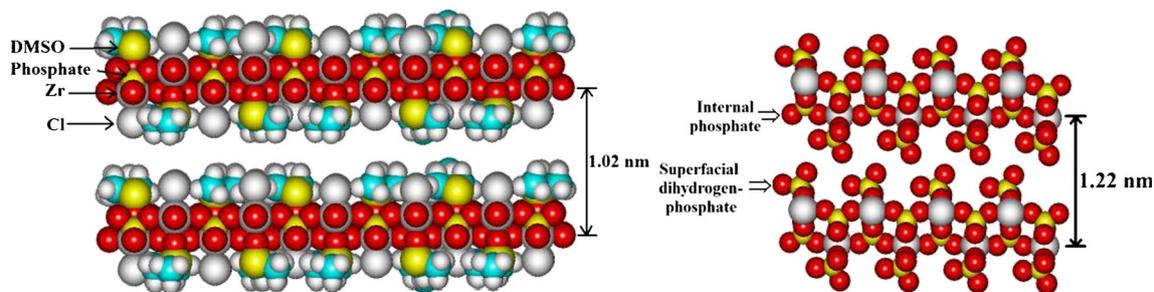

Figure 2. Space-filling models (Zr, gray; P, yellow; O, red; H, white) of two consecutive layers of λ-ZrP (left) and $γ$-ZrP (right). The experimental interlayer distances are shown.

Figure 3 shows the thermogravimetric analysis (TGA) of λ-ZrPH$_2$Y. There are two distinguishable weight loss intervals. The first one (200–375°C) is
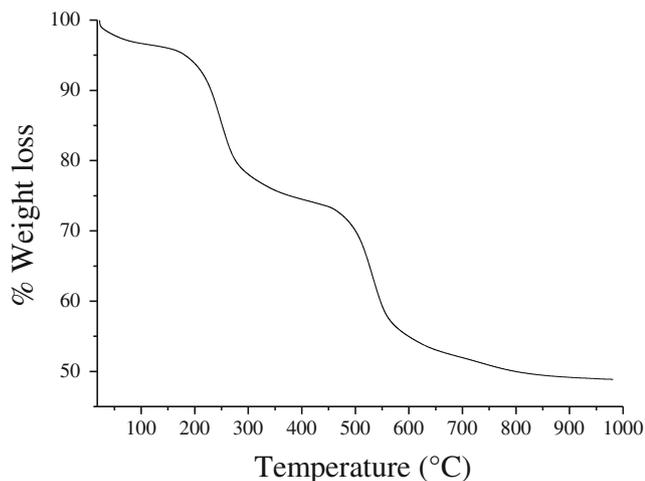

Figure 3. TGA curve of λ-ZrPH$_2$Y obtained at a heating rate 5°C/min.
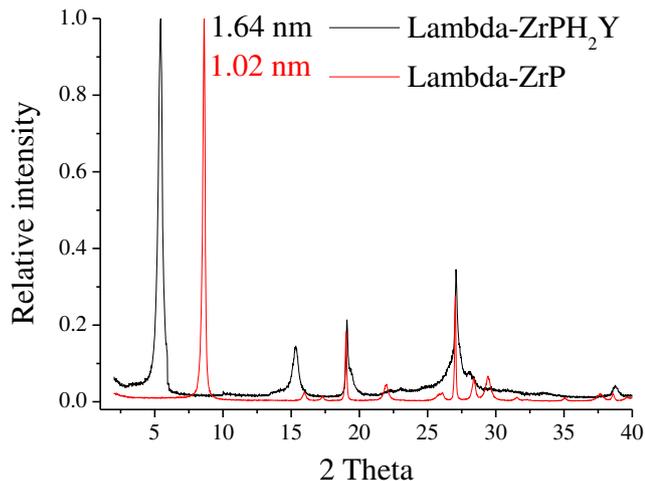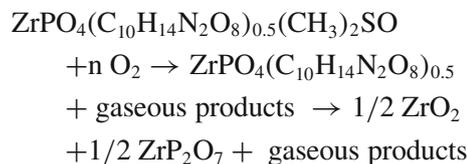

Figure 4. X-ray powder diffraction patterns of λ-ZrP and λ-ZrPY.

attributed to the loss of dmso. The second weight loss interval (375–600°C) corresponds to volatilization of EDTA moiety. The total weight loss percent at 1000°C (51.11%) is in good agreement with the calculated one (52.57%). The later percentage is calculated according the following thermal decomposition scheme.

$$ZrPO_4(C_{10}H_{14}N_2O_8)_{0.5}(CH_3)_2SO$$
$$+n\ O_2 \rightarrow ZrPO_4(C_{10}H_{14}N_2O_8)_{0.5}$$
$$+\ \text{gaseous products}\ \rightarrow 1/2\ ZrO_2$$
$$+1/2\ ZrP_2O_7 +\ \text{gaseous products}$$

To sum up, the thermal decomposition data collected from elemental analysis and TGA are in accordance and compatible with the calculated chemical formula mentioned above (ZrPO$_4$(C$_{10}$H$_{14}$N$_2$O$_8$)$_{0.5}$ (CH$_3$)$_2$SO).

Figure 4 shows the XRD pattern of λ-ZrPH$_2$Y. It allows the calculation of an interlayer distance of about 1.64 nm, much larger than that of the pristine λ-ZrP (1.02 nm; figure 2). Moreover, no reflection peaks correspond to Cl-phase (1.02 nm) or OH-phase (0.98 nm) can be observed,[2,8] which means that λ-ZrPH$_2$Y is obtained as a pure solid phase.

Figure 5 shows the structure of the most stable conformer of EDTA as calculated by MM+ molecular mechanics method. It shows also a plausible arrangement of the doubly deprotonated molecules of EDTA within λ-ZrP complying with the measured interlayer distance of λ-ZrPH$_2$Y.

Figure 6 shows the FT-IR spectrum of the pristine λ-ZrP.[7] The bands at low-frequency region are ascribed to PO$_4$ vibration bands. The bands around 3000 cm^{-1} are assigned to C-H symmetric and asymmetric stretching vibrations of dmso methyl groups and those at 1420 and 1320 cm^{-1} are attributed to symmetric and asymmetric bending vibrations of the same groups.

The FT-IR spectrum of λ-ZrPH$_2$Y (figure 6) is mostly a composite of those of λ-ZrP and free EDTA. The band at 1676 cm^{-1} (COOH) in FT-IR spectrum of EDTA is
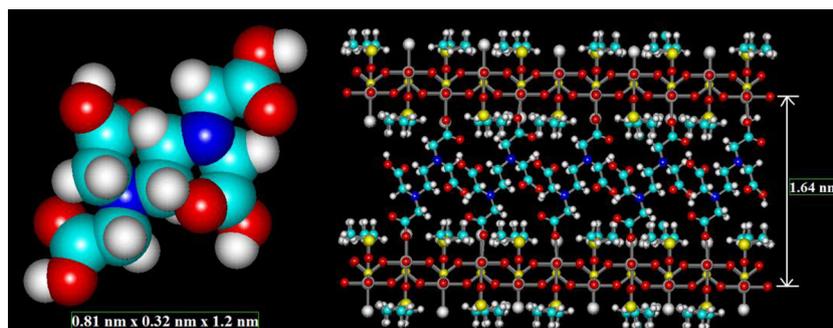

Figure 5. Calculated structures: Predicted most stable conformation of H$_4$Y (HyperChem, MM+) (left). Possible arrangement of H$_4$Y molecules in λ-ZrP complying with the observed interlayer distance of λ-ZrPH$_2$Y (right).
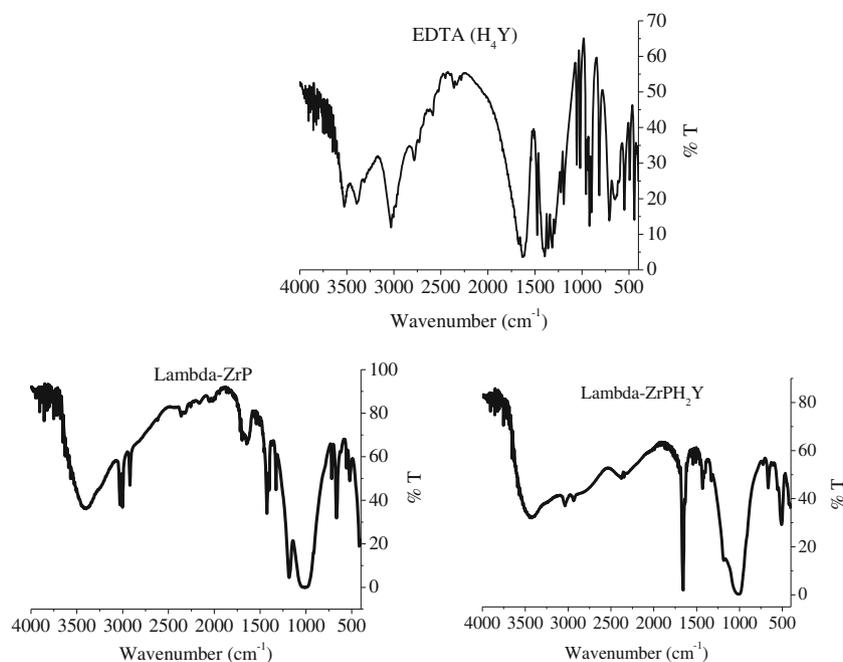
Figure 6. FT-IR spectra of the free EDTA (H_4Y), λ-ZrP and λ-ZrPH$_2$Y.

shifted to be at lower frequencies (1654 cm^{-1}) in that of λ-ZrPH$_2$Y. The very broad band within the region 2500–350 cm^{-1} belongs to the OH stretching of the free COOH groups of EDTA (two groups per moiety) (figure 5) inside the interlayer region of λ-ZrPH$_2$Y.

3.1 *Applications*

One measure of water quality is 'hardness' which is defined by the amount of Mg^{2+} and Ca^{2+} ions in a given amount of water.

It is worth mentioning that the study is conducted at Gaza strip in which the natural water suffers from very high degree of hardness. The concentration of Ca^{2+} present in the tap water has 1088 ppm. Synthesis and design of materials towards efficiently entrapping Ca^{2+} are of great industrial importance.

Actually, the metal ion uptake capacity for Ca^{2+} is determined by shaking the pristine λ-ZrP and its new polyaminocarboxylic acid functionalized derivative (λ-ZrPH$_2$Y) with buffered tap water (T.W.) at pH 10 (NH$_3$-NH$_4$Cl). At this pH, the protonation reactions of the exchanged H_4Y inside the solid matrix are not expected to compete with the complexation reaction with Ca^{2+}. Therefore, the strongest complex is formed.[9]

With regard to the shaking time dependence of Ca^{2+} uptake from tap water, two sets of measurements using flame photometer are performed. One set of measurements is performed after treating several T.W. samples (V_{sample} = 12.5 mL) with the same amount of λ-ZrP (250 mg) at different time intervals (0.5–2 h). A second

set of measurements is performed after treating another set of T.W. samples (V_{sample} = 12.5 mL) with the same amount of λ-ZrPH$_2$Y (250 mg) at the same time intervals mentioned above. The results are given in figure 7.

As an important point, all the tap water samples are taken from the same 4L polyethylene bottle, which is filled with tap water to perform the above mentioned analyses.

It is clearly seen from the kinetics curves (figure 7) that with both λ-ZrP and λ-ZrPH$_2$Y, the metal uptake reaches the equilibrium after ca. 24 hours, where the maximum Ca^{2+} uptake is obtained (32.0 and 40.4 mg Ca^{2+}/g λ-solid, respectively). These uptake values correspond to ca. 0.8 and 1.0 mmol Ca^{2+}/g λ-solid and % Ca^{2+} uptake of 60 and 74% (figure 7b), respectively. Also, figure 7 shows that the Ca^{2+} uptake takes place faster in case of λ-ZrPH$_2$Y.

As an important point to be mentioned, the amount of Ca(II) uptaken by λ-ZrPH$_2$Y (ca. 1 mmol) is very near to the number of mmol of EDTA anion present in 1 g of the solid (1.22 mmol).

The unexpected Ca^{2+} uptake capacity of the pristine λ-ZrP could be attributed to its high affinity for OH$^-$ in basic aqueous solutions.[6,8] In this respect, it is essential to mention that the Cl/OH$^-$ and dmso/H$_2$O exchange reactions proceed very fast and the OHH$_2$O-phase, ZrPO$_4$OHH$_2$O.(H$_2$O)$_3$, is obtained.[6,8] Therefore, if λ-ZrP is contacted with the buffered T.W. samples (pH = 10), then the above mentioned exchange reactions are expected to occur and be followed by
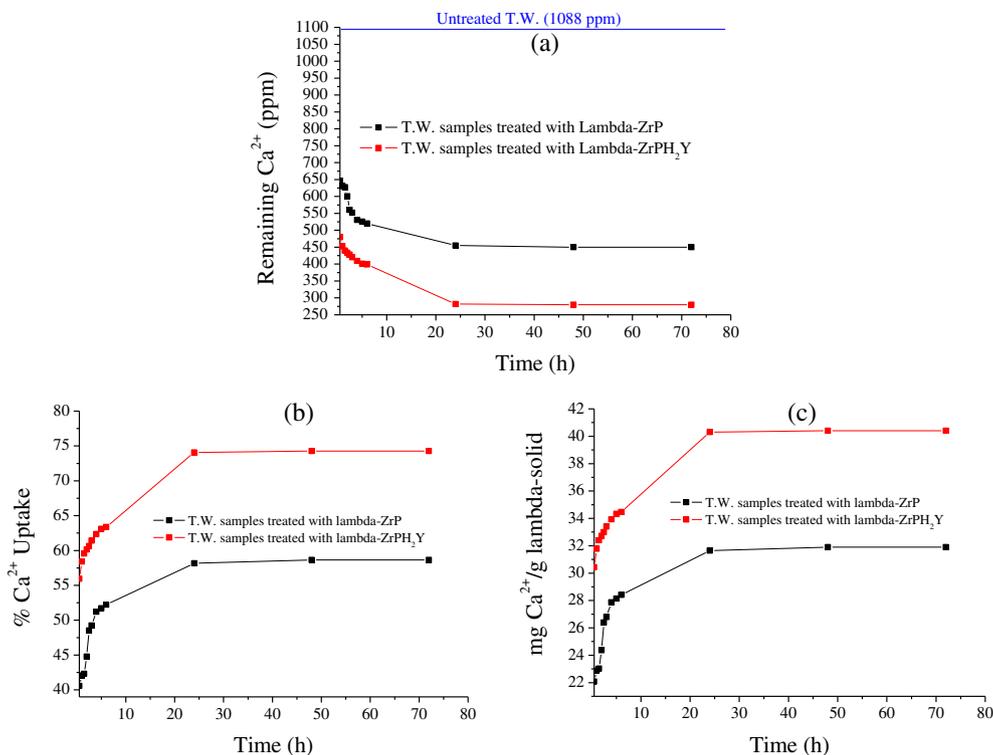
Figure 7. kinetic curves of Ca^{2+} uptake from tap water samples (T.W.). a) The remaining concentration of Ca^{2+} (ppm) in TW samples after treatment with λ-solids. b) % Ca^{2+} uptake by λ-ZrP and λ-ZrPH$_2$Y. c) Ca^{2+} uptake capacities of λ-ZrP and λ-ZrPH$_2$Y (mg g^{-1}).

another one between the OHH$_2$O-phase and Ca^{2+} ions in T.W. samples. The following scheme summarizes the three exchange reactions mentioned above.

Cldmso-phase + H$_2$O → OHH$_2$O-phase

OHH$_2$O-phase + 1/2 Ca^{2+} → O(Ca)$_{1/2}$H$_2$O-phase + H$^+$
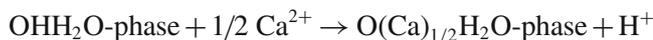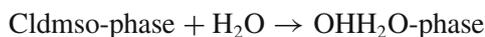
In order to be more certain with regard to the above mentioned Ca^{2+}/H^+ exchange, the separated solid, after a contact time of 24 h between λ-ZrP and buffered tap water, was re-suspended in 12.5 mL of deionized water. The mixture was then agitated and its pH adjusted at 5 over a time interval of 3 h by dropwise addition of 0.1 *M* HCl. Finally, the supernatant was separated and analyzed by flame photometer. This analysis shows that an amount of Ca^{2+} (7.0 mg) equivalent to ca. 86% of the total amount of calcium uptaken by this solid (ca. 8.2 mg) is released. This chemical test ensures that Ca^{2+}/H^+ exchange is the key step in the uptake mechanism through which OHH$_2$O-phase extracts Ca^{2+} from tap water.

Figure 8 compares the FT-IR spectra of the separated solid products after a contact time of 2, 4, 6, 24 h between the pristine λ-ZrP and buffered T.W. samples. They provide strong evidence that the hydroxyl derivative (λ-ZrPO$_4$OHH$_2$O.(H$_2$O)$_x$) is formed during the

course of the uptake process, where the symmetric and asymmetric stretching (2920, 3000 and 3020 cm^{-1}) and bending bands (1420 and 1320 cm^{-1}) of dmso disappear increasingly as the uptake duration time is gradually increased. It is obvious that a contact time of ca. 24 h is necessary to force this phase transformation to be completed. Because of that, no further change in the uptake capacity is observed over interval times longer than 24 h (figure 7).

In case of λ-ZrPH$_2$Y, the very high Ca^{2+} uptake capacity could be attributed to three main factors: (1) increasing the hydrophilicity as a result of the dmso/H$_2$O exchange, so the diffusion of Ca^{2+} into the interlayer gallery can be facilitated, (2) its higher interlayer gallery in comparison to λ-ZrP (1.64 and 1.02 nm, respectively), (3) the presence of the exchanged EDTA inside its solid matrix, therefore EDTA-Ca^{2+} complex is expected to be formed.

Figure 9 compares the FT-IR spectra of the separated solid products after a contact time of 2, 4, 6, 24 h between λ-ZrPH$_2$Y and buffered T.W. samples. As in the case λ-ZrP, dmso/H$_2$O exchange is completed at 24 h and no further change in the uptake capacity is observed over longer interval times (figure 7).

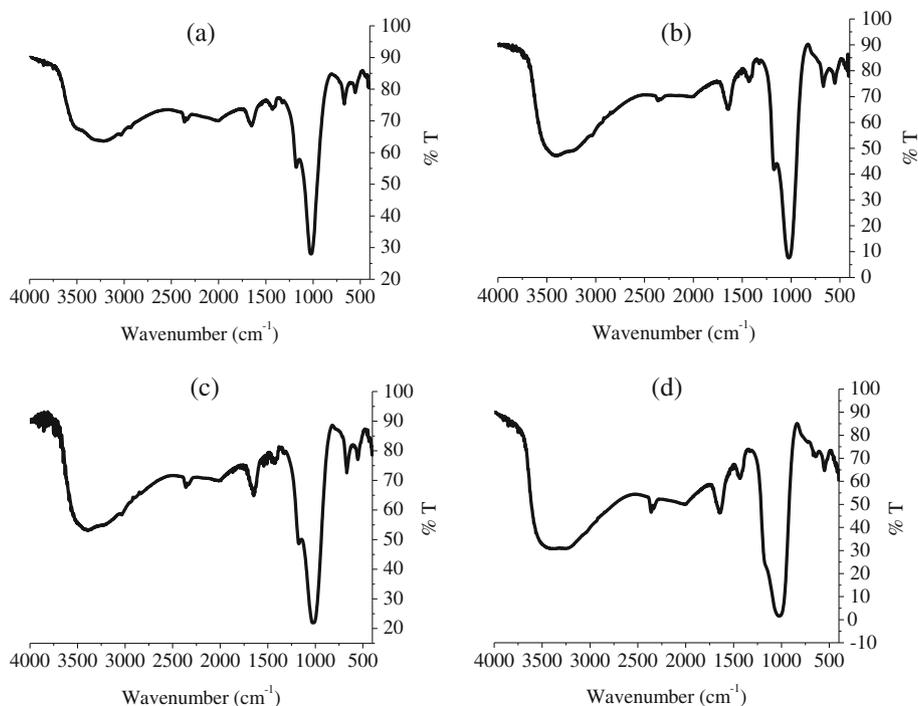In conclusion, the obtained results show that λ-ZrP and λ-ZrPH$_2$Y are highly efficient materials for the

Figure 8. FT-IR spectra of the separated solids after a contact time of (a) 2 h, (b) 4 h, (c) 6 h and (d) 24 h between the pristine λ-ZrP and buffered T.W. samples.

removal of Ca^{2+} from hard water. Moreover, equilibrium is established during a course of time of 24 h, where the maximum uptake is recorded (32.0 and 40.4 mg Ca^{2+}/g λ-solid, respectively).

3.2 *Related work*

The inorganic supports based on silica-gel that carry carboxylic groups has shown a great importance for
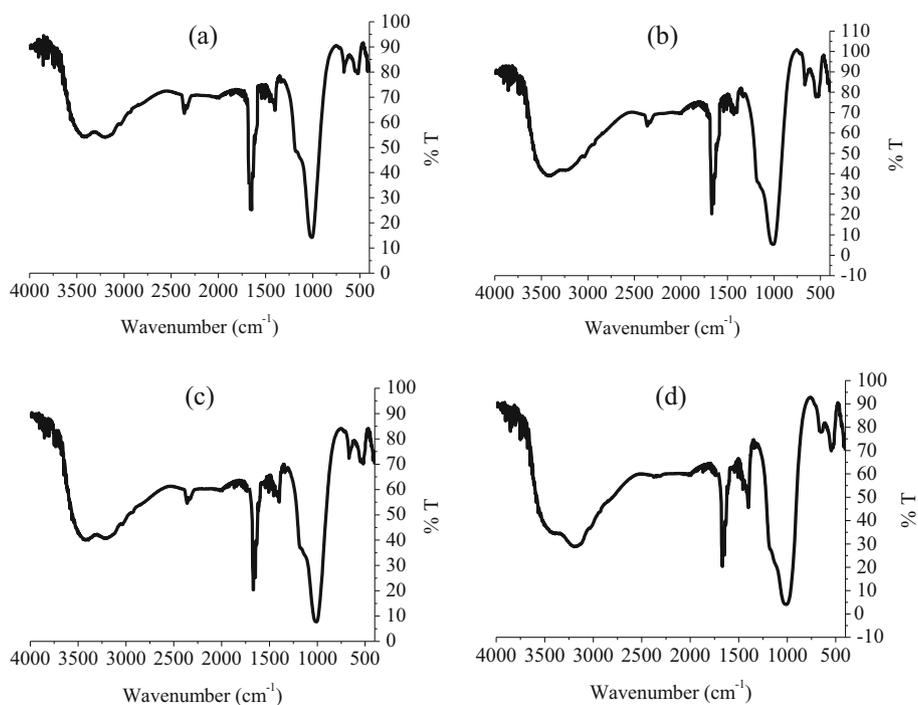

Figure 9. FT-IR spectra of the separated solids after a contact time of (a) 2 h, (b) 4 h, (c) 6 h and (d) 24 h between λ-ZrPH$_2$Y and buffered T.W. samples.

metal ions extraction.[10–13] This research sheds light on Ca^{2+} uptake capacity of two porous layered materials: the pristine λ-ZrP and its polyaminocarboxylic acid derivative with ethylenediaminetetraacetic acid (λ-ZrPH$_2$Y).

4. Conclusion

Elemental and thermogravimetric analyses, X-ray diffractometry, FT-IR spectroscopy and molecular modelling show that EDTA is successfully incorporated inside the interlayer gallery of λ-ZrP by means of topotactic carboxylate/Cl ligand exchange reaction. λ-ZrP and its new polyaminocarboxylic acid derivative (λ-ZrPY) exhibit high potential for extraction metal ions (Ca^{2+}) from hard water. Finally, it is expected that this study contributes to the related empirical studies as it attempts to fill the critical gap in the existing literature.

Acknowledgement

References

1. Alhendawi H 2014 *J. Chem. Sci.* **126**(4) 975
2. Vivani R, Masci S and Alberti G 2004 *Inorg. Chem.* **43** 368
3. Alberti G 1998 *Sc. Tech.* **80** 607
4. Alberti G, Casciola M, Costantino U and Vivani R 1996 *Adv. Mater.* **8** 291
5. Poojary D M, Zhang B and Clearfield A 1994 *J. Chem. Soc. Dalton Trans.* 2453
6. Alberti G, Bartocci M, Santarelli M and Vivani R 1997 *Inorg. Chem.* **36** 3574
7. Caneschi A, Gatteschi D, Sangregorio C, Vaz M G F, Costantino U, Nocchetti M and Vivani R 2002 *Inorg. Chim. Acta.* **338** 127
8. Alberti G, Masci S and Vivani R 2002 *Inorg. Chem.* **41** 1913
9. Skoog D A, West D M, Holler F J and Crouch S R 2004 In *Fundamentals of Analytical Chemistry* 8th edition (Canada: Thomson Learning) Chap. 17
10. El-Nasser A A and Parish R V 1999 *J. Chem. Soc., Dalton Trans.* **19** 3463
11. El-Kurd H M, El-Nahhal I M and El-Ashgar N M 2005 *Phosphorus, Sulfur Silicon Relat. Elem.* **180**(7) 1657
12. El-Ashgara N M, El-Nahhal I M, Chehimi M M, Babonneau F and Livage J 2009 *Intern. J. Environ. Anal. Chem.* **89**(14) 1057
13. El-Ashgara N M, El-Nahhal I M, Chehimi M M, Babonneau F and Livage J 2009 *J. Dispersion Sci. Technol.* **30**(5) 684