Synthesis and Characterization of α-Zirconium Phosphate Nanoparticles

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ABSTRACT

In this work, α-zirconium phosphate (α-ZrP) was prepared by hydrothermal method, Free of any hydrofluoric acid, and characterized by fourier transform infrared (FTIR), Scanning electron microscope (SEM), X-ray diffraction (XRD), and thermogravimetric analysis (TGA) techniques. FTIR shows the fingerprint peaks at 1000 and 500 cm^{-1}. SEM images of α-ZrP show a clearly layered lamellar structure of plate-like crystallites with stepped edges morphology. X-ray diffractogram showed three main peaks at 2-theta: 11.84°, 19.86°, and 25.03°, corresponding to the characteristic diffraction peaks of d (002), d (110), and d (112). Crystallinity degree was calculated from the XRD data and found to be at 21-26 nm. TGA thermogram gives two characteristic plateaus, one at about 300 °C, expressing the loss of about 4% combined water, and the other at about 600 °C representing 6.4% for the transformation of $Zr(HPO_4)_2$ to ZrP_2O_7. According to the TGA analysis the formula of α-Zirconium phosphate was proposed to be $\alpha\text{-}Zr(PO_4)_2.0.67H_2O$. Potentiometric titration for α-ZrP in the presence of Na^+, Ba^{2+}, and Al^{3+} was carried out, and accordingly the full load cation exchange capacities for Na^+, Ba^{2+}, and Al^{3+} were calculated and found to be 8.5, 10.2, and 7.1 $meq.g^{-1}$ respectively.

KEYWORDS

α-Zirconium phosphate, hydrothermal method, cation exchange capacity, lamellar structure, HF-free synthesis

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INTRODUCTION

Since the 1950s, several studies have focused on lamellar solids, namely their properties and possible applications. Precise emphasis has been paid to the development of new synthetic methods for their synthesis and subsequent use in applications across numerous technical sectors.[1] Despite this, the cation exchange properties of zirconium phosphate have been studied since the middle of the 20th century.[1] Three main techniques have been identified for the production of crystalline ZrP: The reflux, hydrothermal, and thermal complexing reagent procedures.[2] Clearfield and Stynes used the reflux process, which produced crystalline α-Zirconium bis(monohydrogen orthophosphate) monohydrate with the formula α-Zr $(HPO_4)_2.H_2O$ (α-ZrP) for the first time since 1964.[3] In 1968, Clearfield and Smith[4] described the first layered structure of zirconium phosphate with the confirmation of a more accurate structure.[5]

On the other hand, complexing agents were previously recommended for the synthesis of α-ZrP.[6] This method, called the HF approach, necessitates complexing the Zr(IV) cation with fluoride ions to produce ZeF_6^{2-} species, which then slowly degrades in the presence of phosphoric acid. The pace at which the HF is eliminated determines the degree of crystallinity. When HF is gradually removed under low nitrogen flow, the complex gradually dissociates and α-ZrP precipitates.

Furthermore, a third alternative method was proposed by Shuai et al., a hydrothermal process based on the addition of zirconyl chloride solution slowly to phosphoric acid with constant stirring followed by heating the reaction mixture at 200 °C.[7] The scientists found that the thickness and length of crystalline α-ZrP's were proportional to the amount of phosphoric acid.

The structural refinement of α-ZrP, which explained the material's behavior as a cation exchanger, was reported in two different investigations in the 1970s[7,8] after the placement of the hydrogen atoms in the crystalline phase was determined. The α-ZrP is composed of one plane of metal atoms connected by mono-hydrogen phosphate groups that alternately sit above and below each plane, comprising the α-ZrP. Three of the four oxygen atoms in each phosphate tetrahedron are shared by three zirconium atoms, and the fourth oxygen atom is joined to a hydrogen atom to produce the material's most active site. Six oxygen atoms from six distinct phosphates are coordinated with each zirconium atom. The layer packing creates six-sided holes for the water molecules, which interact with the P–OH groups in the same plane by creating hydrogen bonds (Figure 1).

The utilization of α-ZrP is supported by two important structural features: the acidic group $-HPO_4^{2-}$ and its layered structure. The first structural feature is utilized when α-ZrP is used as a cation exchanger.[9] There has been extensive research on the use of α-zirconium phosphate to remediate wastewater contaminated by heavy metals and radioactive isotopes.[10,11] In a pH > 4 medium, transition metals (Cu^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+}) were easily absorbed by semi-crystalline ZrP produced by refluxing in 6 mol/L H_3PO_4 for 6 hours. The goal of this work is to manufacture α-ZrP at low temperatures without hydrofluoric acid using a different, straightforward method.

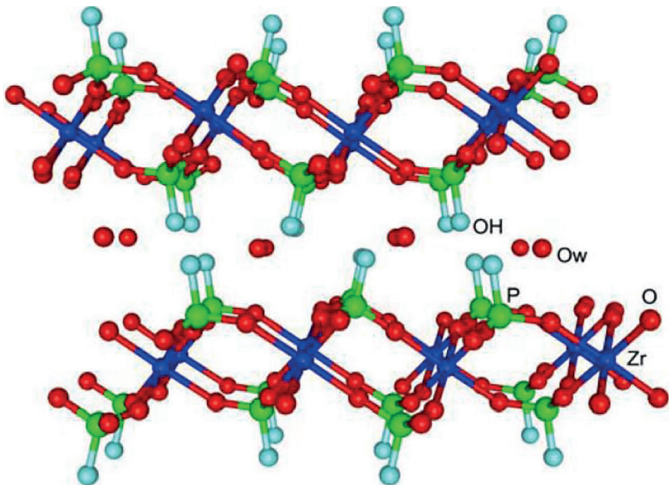


Figure 1. Structure of α-ZrP [reproduced form reference 1]

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EXPERIMENTAL

Materials

Oxalic acid (AnalaR purchased from BDH, 95.5-102%); zirconyl oxo-chloride 97% (purchased from MERCK); orthophosphoric acid 88% (purchased from Analytical Rasayan), and deionized water was used to perform all the experiments.

Preparation of α-ZrP

α-Zirconium phosphate was prepared according to a modified method.[12] 100 g of oxalic acid, $C_2H_2O_4$, was dissolved in one liter of deionized water. 10 g of zirconyl oxo-chloride, $ZrOCl_2.8H_2O$, was dissolved in an appropriate amount of deionized water and added to the oxalic acid solution. After complete dissolution of zirconyl chloride, 20 mL of orthophosphoric acid, H_3PO_4, 88%, is then added to give a 1:10 $ZrOCl:H_3PO_4$ mole ratio. The solution was diluted to about 1.5 litres with deionized water, stirred, and heated to 80 °C for 7 hours, cooled, and washed several times until pH > 3 to eliminate any residual chloride. A clear white crystalline precipitate was filtered off, air dried, characterized, and used for further applications. The oxalic acid method is a safer method compared to the HF method. Oxalic acid can control the precipitation rate of α-zirconium phosphate by forming soluble oxalate complexes, thus slowing down the formation of the amorphous phase, resulting in a crystalline product with a relatively low percent yield of 16%, which is similar to that reported by Horsley and Nowell with a yield as low as 18%. Besides oxalic acid, HF is a stronger complexing agent where the fluoride forms ZrF_6^{2-} complex with zirconium. On removal of HF gradually under low flow of nitrogen, it results gradually in the dissociation of the complex and the precipitation of α-ZrP, resulting in a very high percent yield of the product with a lower degree of crystallinity.[12, 13]

Characterization

Cation exchange capacity

The resulting material, α-Zirconium phosphate, was characterized using different techniques. Cation-exchange capacity was measured according to the added salt method.[14] Potentiometric titrations: 0.1 g of dry α-ZrP was added to 50 mL of each solution of 0.1 M NaCl, $BaCl_2$, and $AlCl_3$ shaken for about 24 h, and titrated against 0.089 M of NaOH solution at 0.5 mL intervals; the pH was measured after each addition. Then cation exchange capacity (CEC) was calculated based on the volume of sodium hydroxide solution consumed at the equivalence point.

Instruments used

The α-ZrP product was characterized using techniques, such as: FTIR (IRPrestige-21, Shimadzu) was used for a full scan from 4000 to 400 cm^{-1}. X-ray diffraction (X'Pert PRO, Cu-radiation, l=1.542 Å) was used to estimate the degree of crystallinity. A scanning electron microscope, SEM (Quanta 250 FEG - made in Holland), was used to investigate the morphology. A thermal analyzer (LINSEIS STA PT1600) was used to study the thermal stability of the exchanger and to calculate the amount of combined water.

RESULTS AND DISCUSSION

Potentiometric titration

The volume of NaOH solution was plotted against the pH change to create a potentiometric titration curve. Equation 1 was used to compute the complete load exchange capacities for Na^+, Ba^{2+}, and Al^{3+}. The results are displayed in Figure 2 and are 8.5, 10.2, and 7.1 $meq.g^{-1}$, respectively. Previous studies on the Na^+ exchange capacity of α-ZrP revealed that it was 8.8 $meq.g^{-1}$ for $Zr(HPO_4)_2.6H_2O$[15] and 6.64 $meq.g^{-1}$ for barium.[16] The ion valences indicate that the CEC for Al^{3+} should be the highest, but it appears to be lower than that of Ba^{2+} since Al^{3+} is hydrolysed from the hexahydrate $Al(H_2O)_6^{3+}$ to monomeric and polymeric hydroxyl aluminum species, including $Al(OH)^{2+}$, $Al(OH)_2^+$, and others.[17]

$$\mathrm{CEC}(\mathrm{meq/g}) = \frac{\text{No. of equivalent weight of } H^+ \times 1000}{\text{wt. of ion exchanger}(\mathrm{g})} \quad (1)$$

FTIR analysis

The α-zirconium phosphate (α-ZrP) ion-exchanger's FTIR spectrum displays bands indicative of Zr-O vibrations together with O-H stretching, H-O-H bending, and P=O stretching. The asymmetric stretching vibration of intercalated water molecules generated by the split of position asymmetry is represented by two distinct peaks in Figure 3 at 3593 cm^{-1} and 3510 cm^{-1}. The symmetric stretching vibration absorption peak of intercalated water molecules is shown by the peak at 3170 cm^{-1}.[18]

The distinctive absorption peaks between 3404 and 3385 cm^{-1} are caused by deformation vibrations of the O-H bonds in water molecules. Zr-O and/or P-O vibration is associated with the bands at 596 and 528 cm^{-1}.[19]

Deformation vibrations of the O-H bonds in water molecules produce the absorption peak at 1618 cm^{-1}. The out-of-plane bending vibration of P-OH is represented by the peak at 1247 cm^{-1}. The notable absorption peak at 1020-1120 cm^{-1} represents the stretching vibration peak of the $-PO_4$ group. The prepared α-ZrP's FTIR spectrum agrees with the traditional α-ZrP spectra.[17]

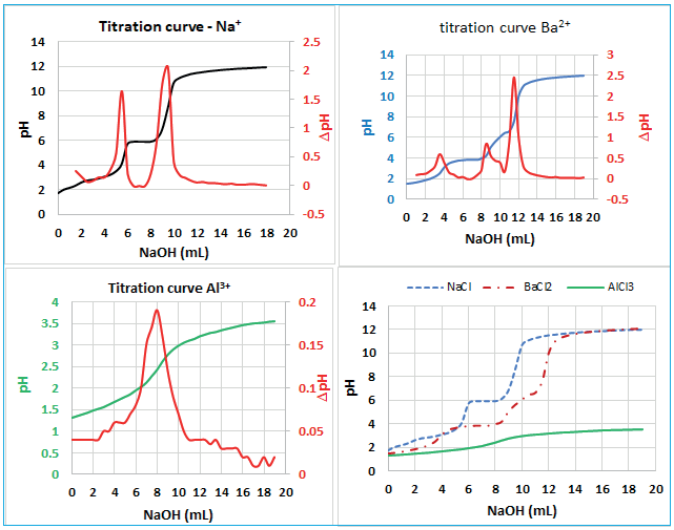


Figure 2. Investigation of exchange capacity of α-Zirconium phosphate

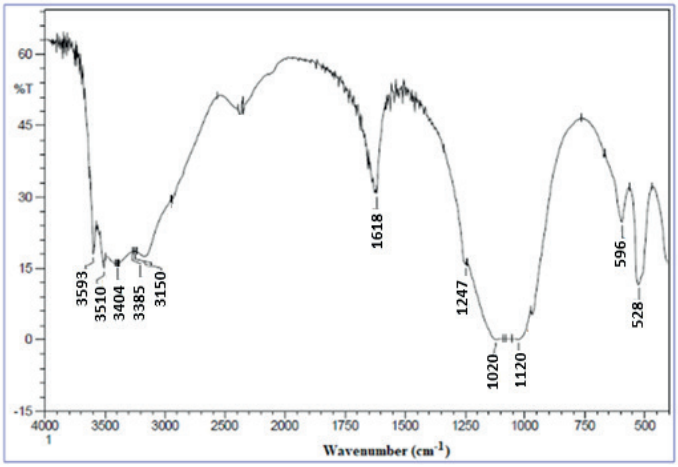


Figure 3. FTIR of α-Zirconium phosphate

Scanning electron microscope (SEM)

The SEM images of the prepared α-ZrP powder are displayed in Figure 4, Showing a layered structure morphology with discrete, plate-like crystallites with stepped edges.[20, 21]

X-ray diffraction (XRD)

The XRD patterns of α-ZrP is shown in Figure 5. There are three main strong diffraction peaks at 2q (d-spacing) equal to: 11.84° (7.48Å), 19.86° (4.47 Å), and 25.03° (3.36 Å), Corresponding to the characteristic diffraction peaks of d (002), d (110), and d (112). The x-ray pattern gives also clear peaks at 33.90° and 48.57°, corresponding to the d-spacing of 2.64Å, and 1.87Å respectively. These values are very close to that obtained previously.[18] Accordingly, the average crystal size (D, in nm) was calculated and found to be at 21-26 nm using Scheerer equation (Equation 2).

Figure 5 displays the α-ZrP XRD patterns. The characteristic diffraction peaks of d (002), d (110), and d (112) are represented by the three primary strong diffraction peaks at 2θ (d-spacing), which are equivalent to 11.84° (7.48 Å), 19.86° (4.47 Å), and 25.03° (3.36 Å). Additionally, the x-ray pattern shows distinct peaks at 33.90° and 48.57°, which correspond to the d-spacing of 2.64 Å and 1.87 Å, respectively. These figures are extremely similar to the earlier results.[18] Consequently, using the Scheerer equation (equation 2), the average crystal size (D, in nm) was determined to be 21–26 nm.

$$D = \frac{K \cdot \lambda}{\beta \cdot \cos\theta} \quad (2)$$

In equation 2, K is a constant and equals 0.9, l is the wavelength of the x-ray source (l=0.1542 nm), b is the full width at half maximum (FWHM) of the peak (rad).[18]

Thermogravimetric analysis (TGA)

Figure 6 shows the thermogram of α-Zirconium phosphate, as it is shown, the graph has two clear plateaus. The first plateau is at around 317 °C, showing 4% weight loss attributed the loss of combined water and unreacted oxalic acid, producing $Zr(HPO_4)_2$. Figure 6 shows an unexpected peak raising between ambient and 100 °C, which then decreased with a small plateau at less than 200 °C which might be due to the presence of unreacted oxalic acid. At about 596 °C, a loss of 6.4% indicating the pyrolysis of $Zr(HPO_4)_2$ to a dominant form of zirconium pyrophosphate ZrP_2O_7.[18] Therefore, the structure of the produced compound is estimated to be in the formula of $Zr(HPO_4)_2.0.67H_2O$ calculated as water loss only. On the other hand, the high decomposition temperature indicates that α-ZrP can maintain its layered structure and is thermally stable.

CONCLUSION

In this investigation, non-dangerous compounds were used to successfully and safely manufacture α-Zirconium phosphate (α-ZrP). It was estimated that the yield of α-ZrP was approximately 16%. The product was characterized using XRD, SEM, TGA including potentiometric titration revealing crystallite particle size of less than 26 nm, a layered morphology with multiple thin, angular lamellae that stack and overlap to form a loosely packed, layered texture and proposed structure of $Zr(HPO_4)_2{\cdot}0.67H_2O$. Na^+, Ba^{2+}, and Al^{3+} were found to have cation exchange capacities of 8.5, 10.2, and 7.1 meq.g^{-1} respectively.

SUPPLEMENTARY MATERIAL

There is no supplementary.

CONFLICT OF INTEREST

The authors report no financial or any other conflicts of interest in this work.

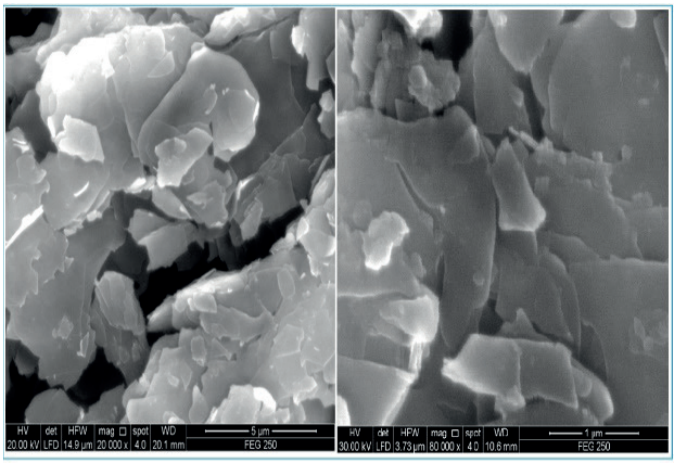


Figure 4. SEM image of α-Zirconium phosphate

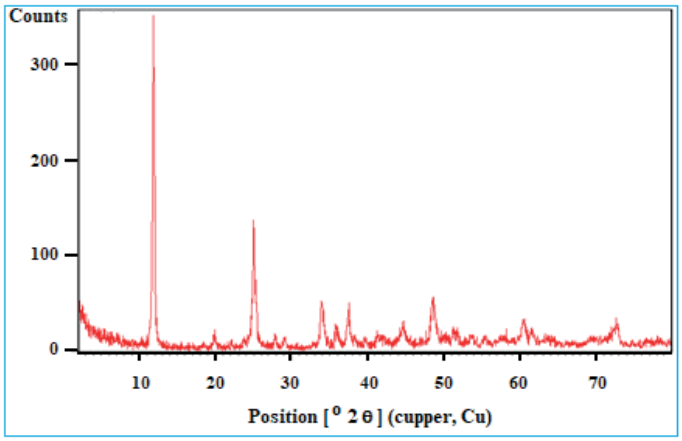


Figure 5. X-Ray diffraction pattern [° 2θ] (copper, Cu) of α-Zirconium phosphate

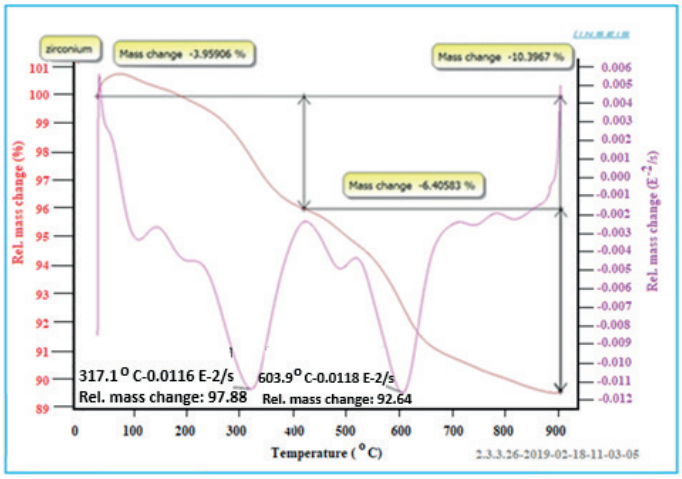


Figure 6. Thermogravimetric analysis of α-Zirconium phosphate

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CREDIT AUTHORSHIP CONTRIBUTIONS STATEMENT

Ruwaydah Ghoulah: Methodology, Ragiab Issa: Conceptualization, supervision, validation, writing draft, and editing. Abubaker Atrrog: Exchange capacity experiments. Hana AlHanash: Analysing the SEM and TGA analysis and writing the review and editing.

DECLARATION OF GENERATIVE AI AND AI-ASSISTED TECHNOLOGIES

The authors used QuillBot to proofread and check for grammatical errors and punctuation. After using QuillBot, the authors reviewed and edited the content as needed and take full responsibility for the content of the article.

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REFERENCES

1. Pica M, Donnadio A, Casciola M. From microcrystalline to nanosized α-Zirconium phosphate: synthetic approaches and applications of an old material with a bright future. Coord Chem Rev. 2018;374:218–235. https://doi.org/10.1016/j.ccr.2018.07.002.
2. Amghouz Z, García JR, Adawy A. A Review on the Synthesis and Current and Prospective Applications of Zirconium and Titanium Phosphates. Eng. 2022;3(1):161–174. https://doi.org/10.3390/eng3010013.
3. Clearfield A, Stynes JA. The preparation of crystalline zirconium phosphate and some observations on its ion exchange behavior. J Inorg Nucl Chem. 1964;26(1):117–129. https://doi.org/10.1016/0022-1902(64)80238-4.
4. Clearfield A, Smith SD. The crystal structure of zirconium phosphate and the mechanism of its ion exchange behavior. J Colloid Interface Sci. 1968;28(2):325–330. https://doi.org/10.1016/0021-9797(68)90136-7.
5. Clearfield A, Smith GD. Crystallography and structure of alphα-Zirconium bis (mono-hydrogen orthophosphate) monohydrate. Inorg Chem. 1969;8(3):431–436. https://doi.org/10.1021/ic50073a005.
6. Alberti G, Costantino U, Allulli S, Massucci M. Crystalline insoluble acid salts of tetravalent metals—XX Forward and reverse Cs+/H+ and Rb+/H+ ion exchange on crystalline zirconium phosphate. J Inorg Nucl Chem. 1975;37(7-8):1779–1786. https://doi.org/10.1016/0022-1902(75)80316-2.
7. Shuai M, Mejia AF, Chang YW, Cheng Z. Hydrothermal synthesis of layered α-zirconium phosphate disks: control of aspect ratio and polydispersity for nano-architecture. CrystEngComm. 2013;15(10):1970–1977. https://doi.org/10.1039/c2ce26402a.
8. Albertsson J, Oskarsson A, Tellgren R, Thomas JO. Inorganic ion exchangers. 10. A neutron powder diffraction study of the hydrogen bond geometry in alphα-Zirconium bis(monohydrogenorthophosphate) monohydrate. A model for the ion exchange. J Phys Chem. 1977;81(16):1574–1578. https://doi.org/10.1021/j100531a011.
9. Cheng Y, Bin Samsudin I, Jaenicke S, Chuah GK. Ion-exchange properties of γ-zirconium phosphate. Chem Asian J. 2020;15(21):3542–3550. https://doi.org/10.1002/asia.202000893.
10. Clearfield A. Inorganic ion exchanges, past, present, and future. Solvent Extr Ion Exch. 2000;18(4):655–678. https://doi.org/10.1080/07366290008934702.
11. Mu W, Chen B, Yu Q, Li X, Wei H, Yang Y, Peng S. A novel zirconium phosphonate adsorbent for highly efficient radioactive cesium removal. J Mol Liq. 2021;326:115307. https://doi.org/10.1016/j.molliq.2021.115307.
12. Horsley SE, Nowell DV. The Preparation and Characterisation of Crystalline α-Zirconium Phosphate. J Appl Chem Biotechnol. 1973;23(3):215–224. https://doi.org/10.1002/jctb.5020230309.
13. Cheng Y, Chuah GK. The synthesis and applications of *α*-zirconium phosphate. Chin Chem Lett. 2020;31(2):307–310. https://doi.org/10.1016/j.cclet.2019.04.063.
14. Kshed S M, Alhanash H B, Issa R A M. Fibrous Cerium Phosphate and its Intercalated-Urea Product as Versatile Adsorbents for Mercury (II) Removal, Scientific Journal for the Faculty of Science-Sirte University 2025;5(1):39–102. https://doi.org/10.37375/sjfssu.v5i1.3199.
15. Yinjie S, Hui Z, Qiaoling Y, Aimin Z. Preparation, characterization of crystalline zirconium phosphates and study on their acid stability and ion exchange behavior with uranyl ions. J Radioanal Nucl Chem. 1995 Dec;198(2):375–384. https://doi.org/10.1007/BF02036553.
16. Costantino U, Marmottini F, Vivani R. Ion exchange properties of zirconium phosphate phosphite with alkaline earth metal ions. Solvent Extr Ion Exch. 1990;8(4-5):713–728. https://doi.org/10.1080/07366299008918026.
17. Coskuner O. Single Ion and Dimerization Studies of the Al (III) Ion in Aqueous Solution. J Phys Chem A. 2010;114(41):10981–10987. https://doi.org/10.1021/jp102906c.
18. Han L, Chen Q, Chen H, Yu S, Xiao L, Ye Z. Synthesis and Performance of Functionalized α-Zirconium Phosphate Modified with Octadecyl Isocyanate. J Nanomater. 2018;2018:1–9. https://doi.org/10.1155/2018/5873871.
19. Pica M. Treatment of Wastewaters with Zirconium Phosphate Based Materials: A Review on Efficient Systems for the Removal of Heavy Metal and Dye Water Pollutants. Molecules. 2021;26(8):2392. https://doi.org/10.3390/molecules26082392.
20. Thakkar R, Patel H, Chudasama U. A comparative study of proton transport properties of zirconium phosphate and its metal exchanged phases. Bull Mater Sci., 2007;30(3):205–209. https://doi.org/10.1007/s12034-007-0036-3.
21. Contreras-Ramirez A, Tao S, Day GS, Bakhmutov VI, Billinge SJL, Zhou H-C. Zirconium Phosphate: The Pathway from Turbostratic Disorder to Crystallinity. Inorg Chem. 2019;58(20):14260–14274. https://doi.org/10.1021/acs.inorgchem.9b02442.