

## Research Article

# Intensification of Synthesis of Crystalline Zinc Phosphate ( $Zn_3(Po_4)_2$ ) Nanopowder: Advantage of Sonochemical Method Over Conventional Method

**Jadhav AJ, Holkar CR, Pandit AB and Pinjari DV\***

Chemical Engineering Department, Institute of Chemical Technology, Matunga, Mumbai, India

**\*Corresponding author:** Pinjari DV, Chemical Engineering Department, Institute of Chemical Technology, Matunga, Mumbai, India**Received:** April 12, 2016; **Accepted:** May 02, 2016;**Published:** May 03, 2016**Abstract**

In the present study, nano-sized zinc phosphate (ZP) powders were prepared using conventional (NUS) and sonochemically assisted (US) precipitation method, using zinc chloride and potassium dihydrogen phosphate as precursors and 25% of ammonia solution in the water as a precipitating agent. The ZP synthesized material by both the methods (NUS and US) was characterized by Fourier transform infrared (FTIR) spectra. The average particle size of synthesized ZP by US and NUS were found to be 110.3 nm and 214.9 nm, respectively. The particle size of synthesized ZP may consist of bunch of crystal structures, hence the crystal size has been checked using X-ray analysis. Crystal size of US and NUS synthesized ZP was found to be  $34.9 \pm 1.6$  nm and  $32.1 \pm 3.9$  nm respectively. It was observed that US synthesized ZP has a higher crystallinity ( $45.94 \pm 0.6\%$ ) than NUS synthesized ZP ( $36.19 \pm 1.8\%$ ) which has improved the crystallinity by almost 27%. It was also found that US method is energy efficient method and saves more than 80% of energy requirement as compared to NUS for the synthesis of ZP particles. Reaction time for US synthesis has been greatly reduced; 15 minutes from 60 minutes (NUS method), which was also a significant achievement.

**Keywords:** Zinc phosphate; Nanomaterials; Sonochemical method; Acoustic cavitation**Introduction**

Zinc phosphate (ZP), is a non-toxic and one of the most important multifunctional metal phosphate for its interesting properties and wide applications in various fields. ZP is widely used as an anticorrosive pigment because it can provide the physical barrier; can block both, anodic and cathodic corrosion reactions on metal; can inhibit anodic acidification reaction; and phosphatize the metal substrate and form complexes with the binder [1-4]. The drying property and adhesion of paint film to the metal substrate can be improved in the presence of ZP [5]. ZP is well known to have a high affinity for living organisms and is therefore expected to be useful as white pigments in cosmetics [6]. Due to its low solubility in water/biological environment and biocompatibility, ZP is widely used as dental cement [7,8]. ZP has excellent catalytic properties in hydrocarbon conversion process, such as dehydration/dehydrogenation of sec-butanol and methanol conversion [8,9]. ZP is also one kind of commonly used luminescent host material, ZP doped or co-doped with rare earth metal such as  $Eu^{3+}$ ,  $Tb^{3+}$  and  $Tm^{3+}$  shows excellent luminescent properties [10].

Several researchers have published reports on the synthesis of ZP by various techniques such as hydrothermal method [11-13], sol-gel method [14], solid-state method [15] a polyol-mediated approach etc [16]. Different precursors have also been used for the synthesis of ZP material such as Zinc phosphate tetra hydrate [8,9], zinc nitrate [17], zinc sulphate [15,18]. The sonochemical method (US) has been reported to be an advantageous technique to obtain novel materials [19-21] over other conventional methods (NUS) due to US input

specifically from a horn, is highly directional and localized as well as intensification of processes due to US generally is attributed to improved transfer coefficients as a consequence of cavity collapse. Ultrasonic irradiation produces the acoustic cavitation which can be described as sequential formation, growth and collapse of millions of microscopic vapor bubbles (voids) in the liquid. The collapse of these voids creates high localized temperatures and pressures of nearly 5000–10000 K and 1000–2000 atm. respectively [22,23]. This cavitational phenomenon can result into an activation of reactant molecules entering into it and thereby converting them into free radicals [24]. Thus, US helps in improvement of the rate of reaction, reduces particle size distribution and particle size also reduces crystallite size, increases percentage crystallinity [25].

In the present work, an attempt was made to synthesize ZP nanocrystals using NUS and US precipitation method. The synthesized ZP powders were characterized by Fourier transform infrared spectroscopy (FTIR), particle size analysis, X-ray diffraction (XRD) measurement and scanning electron microscopy (SEM) to determine functional groups, average particle size, crystallite size and % crystallinity and morphology, respectively.

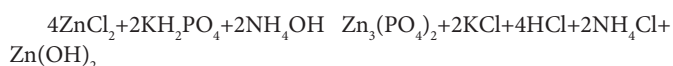
**Material and Methods****Materials**

Zinc Chloride (ZC) (analytical grade, 99%) precursor was procured from S. d. Fine Chemicals Ltd., Mumbai, India. Potassium dihydrogen phosphate (analytical grade, 99%) was purchased from

Hi-media Chemicals. Ammonia solution (AR) was obtained from Merck Ltd., Mumbai, India. Distilled water prepared using Millipore apparatus was used during all the experimental runs.

### Reaction scheme

The ion exchange reactions can take place between zinc chloride and potassium dihydrogen phosphate as given by the following equation. The formed HCl is neutralized by ammonia water ( $\text{NH}_4\text{OH}$ ), moving the reaction equilibrium to the right site.



### Ultrasound set-up

Ultrasound for sonochemical synthesis is generated with the help of ultrasonic instrument set up (horn type). The specification and details of the setup, processing parameters used during the experiments are:

Make: ACE, USA.

Operating frequency: 20 kHz

Rated output power: 750 W

Diameter of stainless steel tip of horn:  $1.3 \times 10^{-2}$  m

Surface area of ultrasound irradiating face:  $1.32 \times 10^{-4}$  m<sup>2</sup>

Ultrasound Intensity:  $3.4 \times 10^5$  W/m<sup>2</sup>

### Synthesis of ZP by conventional method

The aqueous solutions of zinc chloride 7.06g (0.05 gmol) and potassium dihydrogen phosphate 3.53g (0.026 gmol) were prepared in 25 ml distilled water, separately. The potassium dihydrogen phosphate solution was then added drop wise into the zinc chloride solution over 20 min under constant stirring using a magnetic stirrer (Model RQ1210, Remi Metals Gujarat Limited, India). The aqueous clear solutions turned into visible turbid white color as the reaction proceeds. After complete addition of potassium dihydrogen phosphate solution, the pH of the reaction mixture was adjusted to 3.0 by using ammonia solution. At pH of 3.0 the reaction mixture results into a formation of dense white precipitate of ZP. The reaction was then allowed to proceed for 60 min (this was the maximum time for the completion of reaction after which no further improvement in the reaction yield was obtained, explained in detailed in Section 4.1) under stirring at room temperature ( $35 \pm 2^\circ\text{C}$ ). After 60 min, the solution was filtered to separate the product and the solid product was washed thrice using distilled water to remove the by-products and unreacted reactant, if any. After complete washing, the product was dried at  $80^\circ\text{C}$  for 3h in a suitable oven. After complete removal of water, obtained ZP powder (whitish in nature) was cooled, checked for yield and characterized by FTIR, XRD, particle size analysis and SEM analysis.

### Synthesis of ZP by sonochemical method

Initially, aqueous solutions of zinc chloride and potassium dihydrogen phosphate were prepared separately by adding, 7.06g (0.05 gmol) of zinc chloride in 25 ml distilled water and 3.53g (0.026 gmol) of potassium dihydrogen phosphate in 25 ml distilled water. The prepared aqueous solution of potassium dihydrogen phosphate was then added drop wise to the prepared aqueous solution of

zinc chloride in the presence ultrasonic irradiation (ACE horn, 22 kHz frequency) at 40% amplitude for 5 min with a 5 s ON and 5 s OFF cycle from time  $t = 0$ h. After complete addition of potassium dihydrogen phosphate, pH of solution was adjusted by ammonia solution up to 3.0 and further reaction was continued for further 5 min with a 5 s ON and 5 s OFF cycle from time  $t = 5$ min which results into a formation of dense white precipitate of ZP nanoparticles. The solution was filtered to separate the product and the solid product was washed thrice using distilled water to remove the by-products and unreacted reactant, if any. After complete washing, the product was dried at  $80^\circ\text{C}$  for 3h in a suitable oven. After complete removal of water, obtained ZP powder (whitish in nature) was cooled, checked for yield and characterized by FTIR, XRD, particle size analysis and SEM analysis.

## Characterizations

The NUS and US synthesized ZP were characterized as follows: The FTIR spectra of ZP nanoparticles were recorded using Shimadzu FTIR spectrophotometer using ATR mode of operation and scanning of the FTIR spectrophotometer was carried out from the wavelength of 4000 to  $600 \text{ cm}^{-1}$ . Particle size was determined by a dynamic light scattering technique (DLS) which was done with Malvern Zetasizer (ZS-90). Precipitated ZP particles suspension was used for the measurement of particle size, which was analyzed by using Zetasizer. The dried ZP samples (powder form) were characterized by studying their X-ray Diffraction patterns on a Rigaku Mini-Flex X-ray Diffractometer with a copper target and X-ray wavelength  $\text{Cu K}\alpha = 1.54\text{\AA}$ . The current generated in the diffractometer was 15 mA with a voltage of 30 kV. XRD patterns were recorded at angles between  $2^\circ$  and  $80^\circ$ , with a scan rate of  $2^\circ/\text{min}$ . Crystal size was determined using the Debye-Scherrer equation. Scanning Electron Microscopy of the samples was carried out on a JOEL JSM 680LA 15 kV SEM to estimate the surface characteristics of the sample.

## Results and Discussions

### Reaction time and percentage reaction yield

The reaction time required for obtaining maximum yield of ZP by NUS and US method were found out by conducting the experiments with varying reaction time with respect to the final yield obtained. It was found that 60 min of reaction time was optimum for NUS method (Figure 1 (B)) as the further improvement in the % yield was not observed, while in case of US method 10 min was found to be an optimum reaction time to get the highest yield (Figure 1 (A)). The yield of the reaction in case of US synthesized method ( $97.50 \pm 0.43\%$ ) was marginally higher than the NUS synthesized method ( $95.50 \pm 0.58\%$ ). The acoustic cavitation can boost rapid micro mixing of reactants resulting in an increased in yield of the reaction with a saving of 50min reaction time, also reducing the average particle size (as explained in Section 4.2 and 4.4).

### Particle size

The particle size was measured using the Malvern Zetasizer (ZS-90), which utilizes a dynamic light scattering technique (DLS), transmitted through a particle suspension to measure the properties of suspended particles in water. The average particle size of ZP synthesized by the US and NUS methods were found to be 110.3 nm and 214.9 nm, respectively. The reason for this is maybe the fast

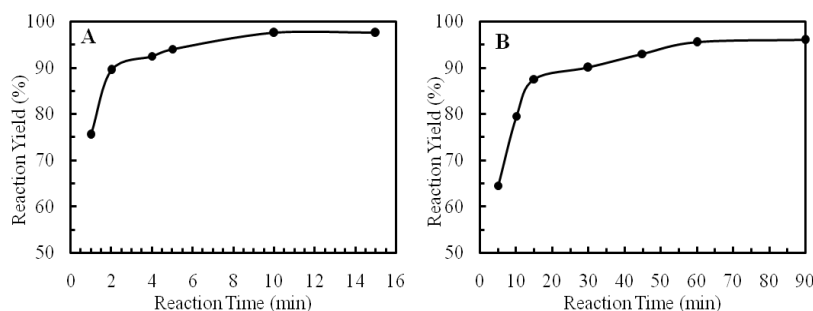


Figure 1: Reaction Yield (%) of synthesized zinc phosphate by (A) sonochemical method and (B) conventional method.

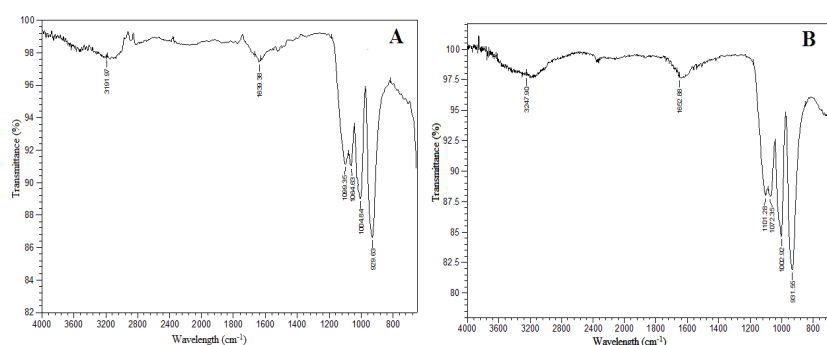


Figure 2: FTIR spectra of (A) sonochemically (B) conventionally synthesized zinc phosphate.

kinetics and efficient micro mixing of the sonochemical reaction providing not enough time for growth of particle thus a reduced average particle size. Due to the physical effects of the ultrasonic irradiation such as significantly improved micro mixing, enhanced solute diffusional transport, rapid nucleation, and formation of a large number of nuclei, as well as possibly the fast kinetics (due to increased local temperature), which does not give enough time for growth of the particles leading to a reduced particle size.

### FTIR spectrum analysis

The FTIR spectrum (Figure 2) of the NUS and US synthesized ZP was recorded. The FTIR spectrum reflects characteristic absorptions of  $\text{H}_2\text{O}$  and  $\text{PO}_4^{3-}$ . Water bonding at  $1639.38\text{ cm}^{-1}$  and O–H stretching broad band centered at  $3300\text{--}3400\text{ cm}^{-1}$  can be observed, implying the presence of crystalline hydrate [17]. Presence of several strong and sharp absorption bands from  $800$  to  $1200\text{ cm}^{-1}$ , which splits into three peaks, report a complex of stretching of  $\text{PO}_4^{3-}$  group [15]. The absorption band at  $1004.84$  and  $1099.35\text{ cm}^{-1}$  were the anti-symmetric stretching and symmetric stretching of  $\text{PO}_4^{3-}$ , respectively. A very strong peak at  $1064.63$  and  $945\text{ cm}^{-1}$  were observed due to the anti-symmetric stretching of  $\text{PO}_4^{3-}$  and P–O bending respectively [8]. From the above discussion it was confirmed that the ZP material can be synthesized successfully by both the methods.

### X-ray diffraction (XRD) analysis

The XRD pattern of US and NUS synthesized ZP was shown in Figure 3. The fifteen strong peaks have been observed at  $2\theta$  values of  $9.65^\circ$ ,  $16.68^\circ$ ,  $17.79^\circ$ ,  $18.26^\circ$ ,  $19.38^\circ$ ,  $22.17^\circ$ ,  $25.67^\circ$ ,  $31.31^\circ$ ,  $35.67^\circ$ ,  $39.88^\circ$ ,  $46.78^\circ$ ,  $47.54^\circ$ ,  $49.94^\circ$ ,  $56.41^\circ$  and  $61.07^\circ$ . The pattern matches the standard XRD data for  $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  of JC-PDS file (Numbers: 33-1474). XRD pattern of synthesized ZP for both US and NUS

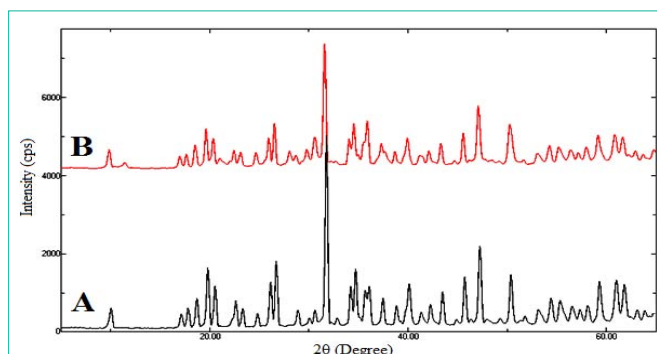
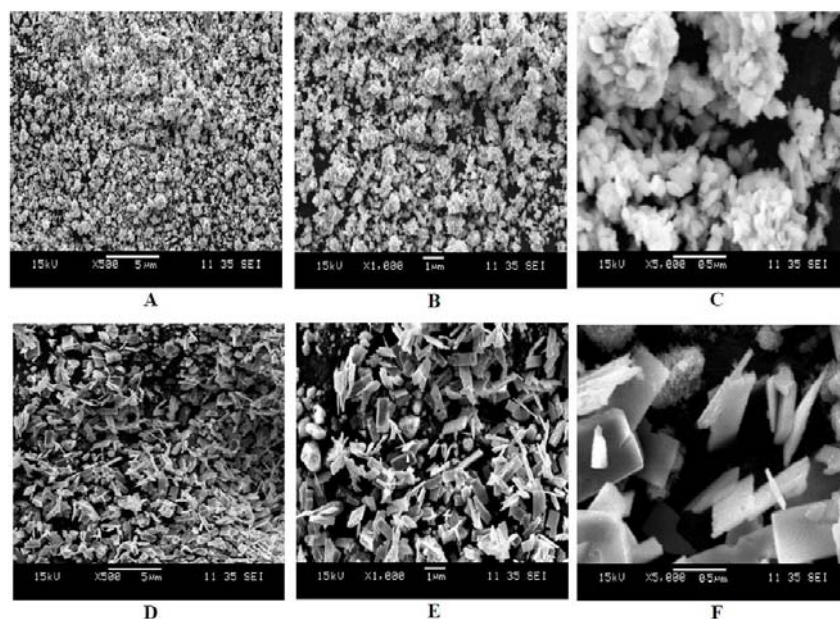


Figure 3: XRD patterns of (A) sonochemically and (B) conventionally synthesized zinc phosphate.

method exactly matches each other (Figure 3). Crystallite size and % crystallinity were calculated using XRD patterns. The crystal size for US and NUS synthesized ZP was  $34.9 \pm 1.6\text{ nm}$  and  $32.1 \pm 3.9\text{ nm}$  respectively, whereas % crystallinity was  $45.94 \pm 0.6\%$  and  $36.19 \pm 1.8\%$  respectively. It was found that US synthesized ZP shows more crystallinity (higher by 27%) than NUS synthesized ZP. Also, the crystal size of NUS synthesized ZP was found to be less than the US synthesized ZP. The crystallinity of US sample is more than that of NUS sample because of the energy dissipated by acoustic cavitation phenomenon and micro mixing may increase the randomness of the solute diffusive motion/Brownian motion of the formed ZP raw molecules (acoustic cavitation causes the micro mixing of particles and molecules which gives oscillatory motion to reactant molecules), resulting into the formation of regular crystal formation in less time and increasing overall crystallinity of synthesized ZP molecule. NUS synthesized ZP was exposed for longer time, utilizing more energy



**Figure 4:** SEM of zinc phosphate (A) at 500 ×, (B) at 1000 × (C) at 5000 × synthesized by sonochemically and (D) at 500 ×, (E) at 1000 × (F) at 5000 × synthesized by conventionally.

which may convert crystalline form of material into amorphous, resulting into a decrease in the overall crystallinity of the NUS ZP sample.

### Scanning Electron Microscopy (SEM) analysis

It can be seen from Figure 4 that NUS synthesized ZP having plate like structure while US synthesized ZP having hexagonal type of structure as clearly seen at 5000 × magnification. It was also observed from SEM images, that the particle size of ZP synthesized by US method is less than that of NUS method. The effects of cavitation on the particle size as well as shape have been clearly observed from SEM analysis.

### Energy Efficacy

The amount of energy required for the synthesis of ZP nanoparticle by NUS and US has been compared in Appendix A. The energy utilized for the synthesis of ZP nanoparticle is the total energy supplied (kJ) per unit weight of the material obtained (g). The total time required for the synthesis of ZP nanoparticle by NUS and US was 60 min and 10 min respectively as mentioned in Section 4.1. Total energy required per unit weight of the material processed to synthesize ZP is  $47.43 \times 10^{-2}$  (kJ/gm) for NUS method and  $8.6 \times 10^{-2}$  (kJ/gm) for US method. Thus, US method proved to be energy efficient which saved more than 80% of energy utilized by NUS method and also a reduction in the reaction duration.

### Conclusion

ZP nanoparticles were successfully synthesized using NUS and US method. It was concluded that the method of sonochemical synthesis can save substantial energy, give higher reaction yield, uniform particle size, material with higher crystallinity, also this technique is fast, simple, convenient, time saving, economical, and environmentally benign. Our belief that this method promises us a

future large-scale synthesis for many applications in nanotechnology field.

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