

CHEMOSYNTHESIS OF NANO-MAGNESIUM PHOSPHATES AND ITS CHARACTERIZATION

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Nano-sized magnesium phosphates have been prepared by a certain Mg/P molar ratio in the solution. Structure and morphology of magnesium phosphates were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Characterized results showed that nanostructures of magnesium phosphates were prepared by the chemical method. And thermal properties of magnesium phosphates nanoparticles were investigated by thermogravimetric-differential scanning calorimetry (TG-DSC) analysis. SEM images show that synthesized magnesium phosphates are nanoparticle clusters, and they size about in the range of 1-3 μ m. TEM photographs display that magnesium phosphates nanoparticles are irregularly in shape with size of 20-200nm.

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1. Introduction

Magnesium phosphates are an important inorganic materials, can be applied as ceramics , cement replacements in various environments, immobilisation systems for heavy metal and radioactive ash containment, sewage and wastewater treatment, etc[1, 2]. Magnesium phosphates are usually prepared by chemical precipitation[3-6], hydrothermal synthesis [7], biosynthesis[1, 2], and in the form of crystals and powders. In this paper, two types of nano-magnesium phosphates were obtained through a certain chemical technique. Structure, morphology and thermal properties of two types of nano-magnesium phosphates were characterized by Fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and differential scanning calorimetry-thermogravimetry (DSC-TG).

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2. Experimental

All the materials from commercial sources were used without further purification. And deionized water was self-made.

Syntheses of nano $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{Mg}_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$: 10mM of K_2HPO_4 and K_3PO_4 were completely dissolved in a flask bottle with 100ml deionized water, respectively. 10mM of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ was then added to the above solution. The reaction solution was also allowed to stand under static conditions at room temperature for 24 hours. The products were filtrated and washed three times with deionized water and ethanol and then dried at 66 °C for 24 h. Then, the precipitates were collected and characterized.

Fourier transform infrared spectroscopy (FTIR) spectra of the samples were recorded using a Nicolet 5700 spectrometer by KBr pellet technique in the range of 399-4000 cm^{-1} . The phase purity of products was examined by powder X-ray diffraction (XRD) with Bruker D8-Discover diffractometer using graphite-monochromatized high-intensity Cu $\text{K}\alpha$ radiation ($\lambda=1.5406\text{\AA}$). Scanning electron microscopy (SEM, FEI Company, Netherlands, operating voltage 20 kV) was used to conduct morphological studies of samples. Transmission electron microscopy (TEM) images were obtained on a FEI, G2 20 equipment. TEM grids were prepared using a few drops of nanoparticles followed by drying. Thermogravimetric-differential scanning calorimetry (TG-DSC) analysis was carried out on STA449 F3 thermogravimetric analyzer (Netzsch, Germany). The analyses were carried out simultaneously in a nitrogen atmosphere at a heating rate of 10°C / minute between room temperature and 800°C.

3. Results and discussion

The FTIR spectrum of magnesium phosphates are shown in Fig. 1. Bands at 3000-3600 and 1631.94-1654.66 cm^{-1} in magnesium phosphates are due to the presence of crystal water in the solid [7]. Magnesium phosphates show that strong transmission bands for PO_4 stretching at 1027.96-1079.22 cm^{-1} and bending at 571.19-601.16 cm^{-1} in good agreement with reported literature [8, 9]. The vibrational absorptions at 744.20-778.15 cm^{-1} are corresponding to bending bands of H-O(P) [10].

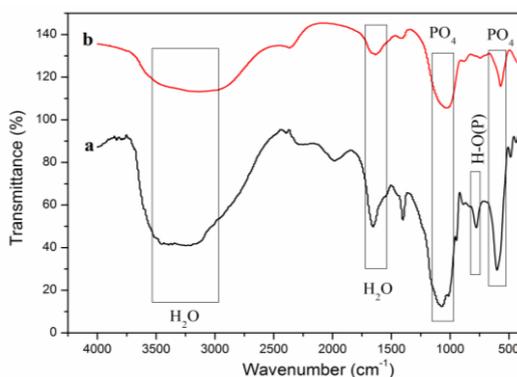


Fig. 1 FTIR spectra of magnesium phosphates: a $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, b $\text{Mg}_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$.

Fig. 2 shows powder XRD patterns. Fig. 2 (a) and (b) indicate that two samples are well crystallized, and all diffraction peaks can be readily indexed to the reported crystal structures of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (JCPDS No. 72-0023) and $\text{Mg}_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ (JCPDS No. 35-0329), and no peaks attributable to impurities are observed.

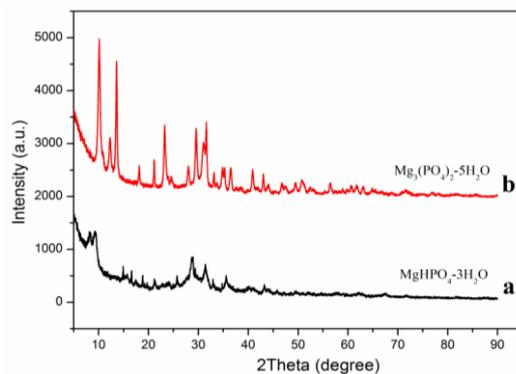


Fig. 2 XRD patterns of magnesium phosphates: a $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, b $\text{Mg}_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$.

SEM images of magnesium phosphates are shown in Fig. 3. Fig. 3 a and b and c indicate that the precipitates obtained are spere-like in shape with nonuniform size. These irregular particles length are 1 to 3 μm . TEM micrographs further confirm that magnesium phosphates are irregular sheets in shape with size about in the range of 50-200nm (Fig. 4a, c). Fig. 4 b displays that polycrystalline nature of synthesized materials.

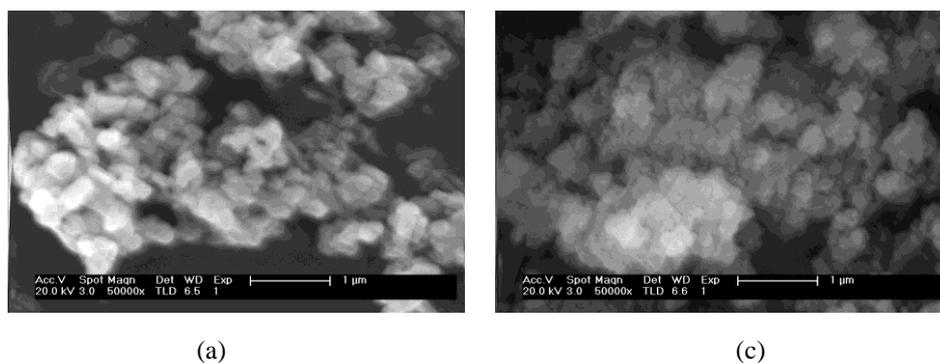


Fig. 3 SEM images of magnesium phosphates: a $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, c $\text{Mg}_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$.

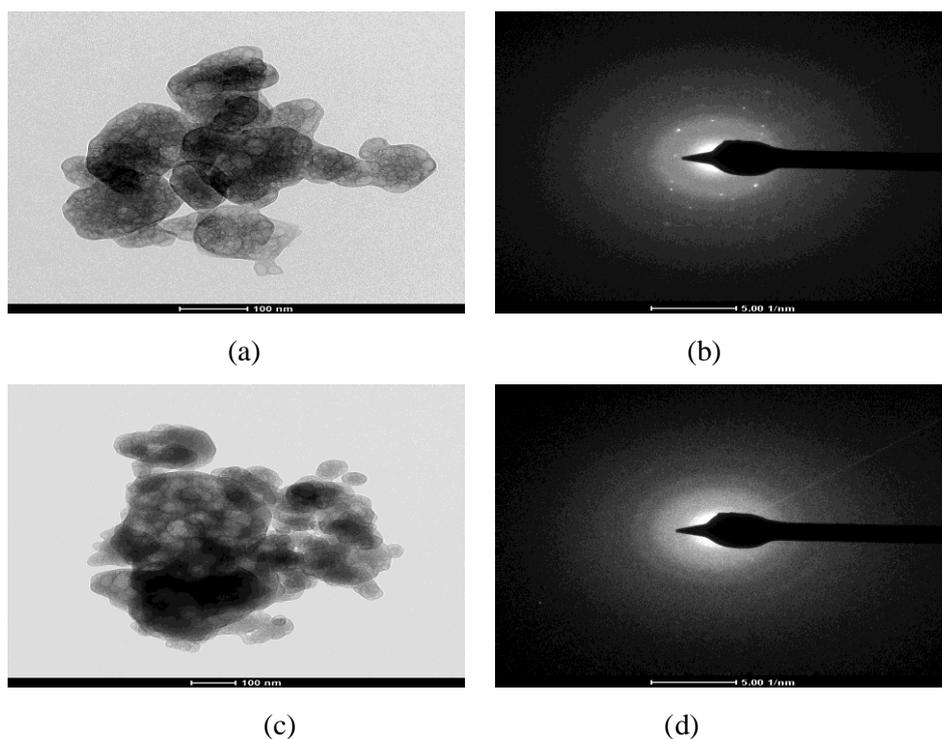


Fig. 4 TEM images (a, c, e, g) and ED pattern (b, d, f, h) of magnesium phosphates, chemical method a, b ($MgHPO_4 \cdot 3H_2O$) and e, f ($Mg_3(PO_4)_2 \cdot 5H_2O$).

The thermal stability of magnesium phosphates of all types are determined by thermogravimetric-differential scanning calorimetry (TG-DSC) analysis from room temperature to 800°C in N_2 atmosphere (Fig. 5). Over the temperature ranges, TG curves display that continuous weight-loss about 30.37 and 31.06% follow by Fig. 5 a and b. It is observed that all endothermic values less than 200 for magnesium phosphates can be considered as the elimination of crystal water of materials. Peaks around 644.9°C can correspond to crystalline temperature of $Mg_2P_2O_7$ which can be prepared by endothermic decomposition of $MgHPO_4$ (Fig. 5 a). The endothermic peaks at 670.1°C can correspond to the crystallization of $Mg_3(PO_4)_2$ (Fig. 5b). Compared with microbiological synthesis of $Mg_3(PO_4)_2 \cdot 5H_2O$, there was lower total weight-loss (31.06%) and crystallization temperature (670.1°C) of $Mg_3(PO_4)_2 \cdot 5H_2O$ of chemical precipitation. The results indicate that thermal stability of $Mg_3(PO_4)_2 \cdot 5H_2O$ of chemical precipitation is different from microbial synthesis [1].

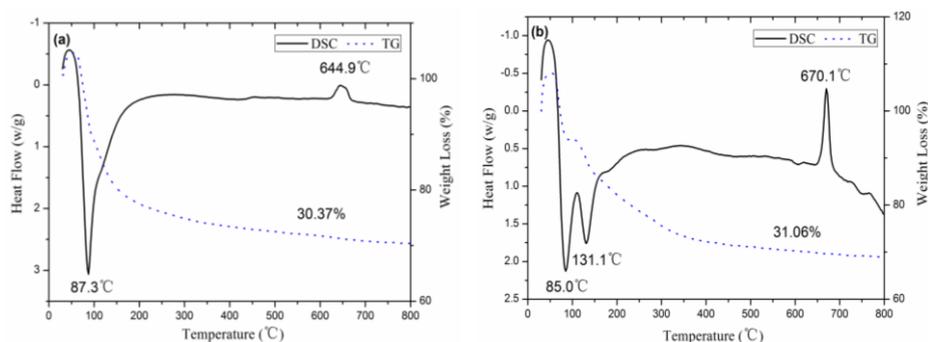


Fig. 5 DSC-TGA curves of magnesium phosphates: a $MgHPO_4 \cdot 3H_2O$, b $Mg_3(PO_4)_2 \cdot 5H_2O$

4. Conclusions

In this paper, magnesium phosphates nanoparticle were successfully prepared via a simple chemical method. The main products were a mixture of $\text{MgHPO}_4 \cdot 1.2\text{H}_2\text{O}$ and $\text{Mg}_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ when added acidic $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ to mixture solution which was reacted mixture of *Bacillus* solution with phosphate monoester. However, $\text{Mg}_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ was obtained by microbial methods when added neutral MgCl_2 to mixture solution. Above results displayed that alkaline phosphatase could hydrolyze phosphate monoester in bacterial solution and obtained PO_4^{3-} . So that, mixture of $\text{MgHPO}_4 \cdot 1.2\text{H}_2\text{O}$ and $\text{Mg}_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ was obtained via microbial methods because of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ is capable of acidification, and could make a certain percentage of PO_4^{3-} into HPO_4^{2-} . Morphology and thermal properties of magnesium phosphates of all types were systematically studied by microbiological and chemical syntheses. The results indicated that morphology and $\text{Mg}_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ of microbial precipitation differed from chemical synthesis in the thermal stability.

Acknowledgements

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