



## Synthesis and application of magnesium amorphous calcium carbonate for removal of high concentration of phosphate



Nan Xu <sup>a,\*</sup>, Yanan Li <sup>a</sup>, Lei Zheng <sup>b</sup>, Yuxi Gao <sup>c</sup>, Hongwei Yin <sup>a</sup>, Jiating Zhao <sup>c</sup>, Zhigang Chen <sup>a,\*</sup>, Jianping Chen <sup>d</sup>, Ming Chen <sup>a</sup>

<sup>a</sup>Jiangsu Key Laboratory of Environmental Functional Materials, School of Chemistry Biology and Material Engineering, Suzhou University of Science and Technology, Suzhou 215009, China

<sup>b</sup>Beijing Synchrotron Radiation Facility (BSRF), Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

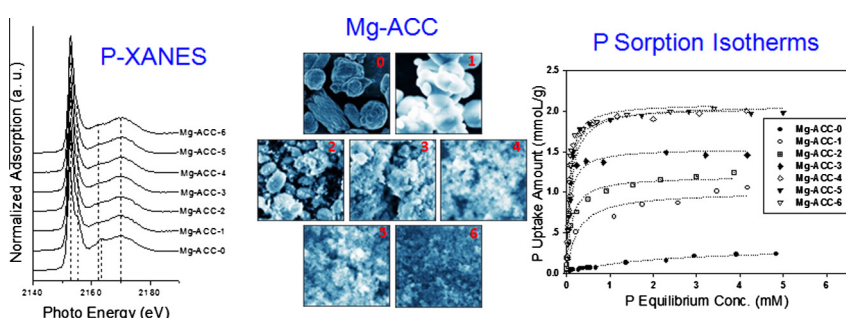
<sup>c</sup>CAS Key Laboratory of Nuclear Analytical Techniques, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

<sup>d</sup>School of Electronic & Information Engineering, Suzhou University of Science and Technology, Suzhou 215009, China

### HIGHLIGHTS

- The adsorbents of Mg-ACC series can be obtained with changing different Mg/Ca ratio.
- The uptake capacity of Mg-ACC to P is increased due to introduction of Mg species.
- XANES analysis showed that Mg provides sites for nucleation growth of Mg–P phases.
- Mg stabilizes the intermediate DCPD/DCP of Ca–P phase precursors on surface.
- ACCM material can be used as an effective adsorbent for removal of high P.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 7 February 2014

Received in revised form 9 April 2014

Accepted 10 April 2014

Available online 24 April 2014

#### Keywords:

Phosphate  
Magnesium  
ACC  
Sorption  
Removal  
Speciation

### ABSTRACT

Efforts have been made to fabricate inorganic adsorbents of magnesium amorphous calcium carbonate (Mg-ACC-X, X = 0–6) series with specific size, orientation and morphology and extend its environmental applications. The Mg species was introduced into aragonite ( $\text{CaCO}_3$ ) with varying the Mg/Ca ratio. The synthesized adsorbents before/after phosphate retention were characterized by powder X-ray diffraction, scanning electron microscopy with energy dispersive X-ray, Fourier-transform infrared spectroscopy, and X-ray Absorption Near-Edge Structure. When  $\text{Mg/Ca} < 0.5$ , Mg/aragonite material is obtained, the uptake of phosphate is raised up with increasing the surface area of solids, resulting from the introduction of Mg species. If introduced by more magnesium species ( $\text{Mg/Ca} > 0.5$ ), amorphous calcium magnesium carbonate (ACMC) is then synthesized. The monolayer uptake amount of phosphate reaches the maximum at  $\sim 2.0$  mmol/g for ACCM, which is 10 times stronger than that of calcite at 0.19 mmol/g. Further investigation suggested that the formation of various Ca–P and Mg–P phases were detected for all Mg-containing  $\text{CaCO}_3$  materials. In particular, the introduction of Mg species favor the nucleation growth of Mg–P phases, thus stabilizing the intermediate DCPD/DCP on surface and retarding the transformation from ACP to HAP. This study therefore indicated that ACCM material ( $\text{Mg/Ca} = 4:6$ ) can be used as an ideal and effective adsorbent for removal of high P from wastewater.

© 2014 Elsevier B.V. All rights reserved.

\* Corresponding authors. Tel./fax: +86 512 68083175.

E-mail addresses: [nanxu@mail.usts.edu.cn](mailto:nanxu@mail.usts.edu.cn) (N. Xu), [czg@mail.usts.edu.cn](mailto:czg@mail.usts.edu.cn) (Z. Chen).

## 1. Introduction

An excessive concentration of phosphorus (P) is a potential cause of eutrophication in water body such as lakes and reservoirs, and is a threat to ecological health, thus P should be limited to release into natural water. Currently, P has been constantly widely used in agriculture and industry. Although the factory has recovered the most of industry wastewater (the average value of phosphate concentration with 300 mg/L) before discharging for treatment, the phosphate concentration as high as 70 mg/L is commonly found [1]. Research on more effective technologies for removal and possible recovery of high concentration of phosphate from wastewater prior to discharge is required [2].

In wastewater treatment technology, conventional adsorption of phosphate onto particulate matter is an important process that affects significantly the mobility and bioavailability of phosphorus in natural environments. Extensive work has been done to investigate the various adsorbents including Fe and Fe oxides [3,4], Al and Al oxides [5,6], Mg oxides [7], soil minerals [8], modified wheat residues [9], slag [10] to facilitate the removal of phosphate from aqueous solution. Recent years, calcite as natural mineral is proposed to be used as a promising adsorbent for phosphate removal since the used calcite can then be reused as a fertilizer in acid cropland [11]. Nevertheless, calcite has the intrinsic drawback due to the limited sorption capacity to high concentration of phosphate in the wide pH range. Thus, it is a great challenge to develop simple, environmentally friendly and versatile methods for the synthesis of hierarchically structured calcium carbonate minerals with designed chemical components and textures, which could overcome this limitation and greatly facilitate their future applications.

As known, magnesium (Mg) plays a role in stabilizing amorphous calcium mineral phase [12–15]. Furthermore, Mg incorporation within amorphous calcium carbonate (ACC) significantly retards the transformation into crystalline phases [16]. Kitamura found that  $Mg^{2+}$  can be selectively included in calcite, leading to the remarkable change of the morphology of calcite [17]. The presence of  $Mg^{2+}$  and  $Ca^{2+}$  ions in seawater favors the adsorption of phosphate on calcite and aragonite [18]. In addition, the molar ratio of Ca to Mg is about 1:5 in the seawater, thermodynamically favorable for aragonite [19]. Thus the elemental composition of adsorbent, particularly calcium (Ca) and magnesium (Mg) levels, can significantly influence adsorption of phosphate. It has been demonstrated that the industrial production of  $CaCO_3$  with different polymorphs can be scaled up by varying the ratio of ethanol/water [20]. To the best of our knowledge, the synthesis of magnesium amorphous calcium carbonate (Mg-ACC) and use for removal of high concentration of phosphate are scarcely investigated. Moreover, the use of X-ray Absorption Near-Edge Structure (XANES) analysis to quantify the surface P speciation on Mg-ACC remains limited.

Accordingly, it has great importance in the design and fabrication of new functional materials for high phosphate removal based on study of adsorption behavior on solids surface. Therefore, the present research focuses on the preparation of Mg-ACC materials through the simplified biomimetic mineralization process [16,21]. Analytical techniques were used to characterize all prepared samples. As a follow-up, laboratory adsorption experiments, mathematical models and spectrum analysis using FTIR and XANES were employed in this study to determine the mechanisms of high phosphate adsorption onto the Mg-ACC minerals at molecular level.

## 2. Materials and methods

### 2.1. Material synthesis method

The inorganic calcium carbonate ( $CaCO_3$ ) series with different Mg/Ca ratios 0:6, 1:6, 2:6, 3:6, 4:6, 5:6 and 6:6, named as

Mg-ACC-X ( $X = 0-6$ ), respectively, were synthesized with the following procedure. Firstly,  $Ca(CH_3COO)_2$  mixture solution was obtained by mixing 0.3 mol/L  $Ca(CH_3COO)_2$  with  $MgCl_2$  solution to make different initial ratios of Mg/Ca. Then two solutions 1 and 2 were prepared, respectively. Solution 1 was obtained through ethylene glycol mixed by 1 mol/L  $Na_2CO_3$  solution thoroughly to reach 40% volume of total solution. Solution 2 was obtained through ethylene glycol mixed by  $Ca(CH_3COO)_2$  mixture solution thoroughly to reach 40% volume. Finally, Mg-ACC-X products were easily obtained by mixing the equal volume of solution 1 and solution 2 under controlling temperature for couple of hours. The precipitates were collected by filter and washed with anhydrous ethanol for several times, and then dried. All chemicals used in the study are analytical grade.

### 2.2. Material characterization

The crystalline phase of the products was identified by X-ray powder diffraction (XRD) using a D8 Focus X-ray diffractometer (XRD). The surface morphology of the synthesized materials was characterized by scanning electron microscopy (SEM) analysis using Quanta 400F SEM and the Mg/Ca ratio was determined by energy dispersive X-ray (EDX). The surface areas of the synthesized materials were determined by a nitrogen multi-point BET isotherm. In addition, the suspensions were prepared by the material particles suspended in the background electrolyte (0.01 M NaCl solution) at various pH values. The different pH was adjusted by adding HCl/NaOH solutions. After that, the zeta potentials of all suspensions were measured through using a Malvern Instrument Zeta-Sizer 9000. Samples were run in triplicate, and the average values of zeta potential were recorded.

### 2.3. P sorption batch experiments

Sorption experiments were performed at 25 °C room temperature in 0.01 M NaCl background electrolyte, for an equilibration time of 18 h. Sorption isotherms at  $pH 10.0 \pm 0.1$  were developed by adding the synthesized Mg-ACC-X adsorbents (5 g/L) to sodium phosphate ( $NaH_2PO_4 \cdot 2H_2O$ ) solutions (0–15.0 mM) prepared in 0.01 M NaCl solution in order to investigate the uptake ability of adsorbents to P. Sorption envelopes for Mg-ACC-X were obtained to determine sorption edge at various final solution pHs from 6.0 to 12.0. The pH in the suspension of solid adsorbents was adjusted by adding NaOH or HCl solution. The experimental details were similar as the description in our previous study [22]. At the end of equilibration, the suspensions were centrifuged and filtered through 0.45  $\mu m$  filter. Finally, P concentration in the filtrate was analyzed by colorimetry using the molybdenum blue method.

### 2.4. P Speciation characterization

At the end of sorption batch experiments, the precipitated solids were collected. In order to elucidate the possible mechanism responsible for P retention, a portion of solids were air-dried as ground powder for the subsequent chemical characterization using Fourier transforms infrared spectroscopy (FTIR) and X-ray Absorption Near-Edge Structure (XANES). K-edge XANES spectra were collected at beamline 4B7A of BSRF. The XANES spectra of sorption samples were collected by the silicon drifted detector (PGT, USA) in partial fluorescence yield (PFY) mode scanning from 2120 to 2200 eV at a step size of 0.2 eV. Multiple scans of each sample were collected and averaged together to improve the signal to noise ratio. All the data analyses of XANES spectra were performed and normalized using ATHENA Version 0.8.056 [23].

Download English Version:

<https://daneshyari.com/en/article/6586349>

Download Persian Version:

<https://daneshyari.com/article/6586349>

[Daneshyari.com](https://daneshyari.com)