Chemical Engineering Journal 351 (2018) 195–202

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Bacterial mineralization of struvite using MgO as magnesium source and its potential for nutrient recovery

Yi Luo[a], Han Li[a], Ya-Rong Huang[a], Tian-Lei Zhao[a], Qi-Zhi Yao[b,*], Sheng-Quan Fu[c], Gen-Tao Zhou[a,*]

[a] CAS Key Laboratory of Crust-Mantle Materials and Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, PR China

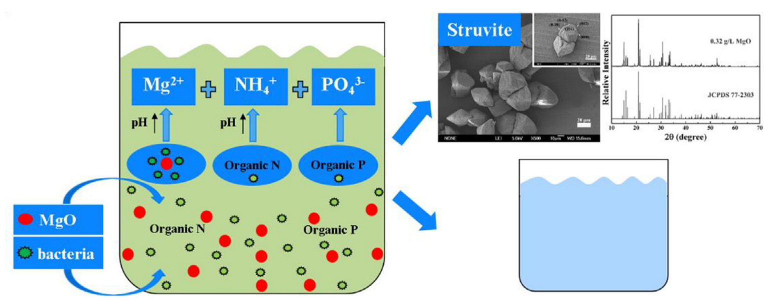
[b] School of Chemistry and Materials Science, University of Science and Technology of China, Hefei 230026, PR China

[c] Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei 230026, PR China

HIGHLIGHTS

- A new route linking MgO with bacterial mineralization of struvite was developed.
- The strain MR-1 greatly enhanced MgO dissolution and struvite mineralization.
- The bacterial mineralization transformed over 97% of Mg^{2+} from MgO into struvite.
- The operating and reagent costs for struvite production were significantly cut down.
- The route can also be applied to remove N and P as struvite from eutrophic waters.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Struvite
Bacterial mineralization
MgO
Nutrients recovery
Eutrophic waters

ABSTRACT

Bacterial mineralization of struvite is one of the novel approaches for the recovery of major nutrients nitrogen and phosphorus. However, previous studies were done by using expensive water-soluble magnesium salts, like $MgCl_2$ and $MgSO_4$, significantly limiting its large-scale application. In this context, our objective is to examine the potential of low-cost, naturally abundant MgO as Mg source in bacterial mineralization of struvite. *Shewanella oneidensis* MR-1 was selected as a model microbe to induce struvite mineralization. The structure, morphology and composition of the mineralized products were identified and characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR), thermogravimetric and differential thermal analysis (TG-DTA), and field emission scanning electron microscopy (FESEM) equipped with energy dispersive X-ray spectroscopy (EDX). Our results demonstrate that *S. oneidensis* MR-1 is able to enhance MgO dissolution, and transform organic nitrogen and organophosphorus into well-crystallized struvite. The process of bacterial mineralization not only increased the alkalinity of the culture, but also effectively transformed over 97% of Mg^{2+} from MgO into struvite, hence significantly cutting down the recovery cost of the major nutrients. Current results could provide an effective and economically feasible pathway for the nutrients removal and subsequent recovery as struvite from eutrophic waters.

* Corresponding authors.
E-mail address: gtzhou@ustc.edu.cn (G.-T. Zhou).

https://doi.org/10.1016/j.cej.2018.06.106
Received 24 March 2018; Received in revised form 19 May 2018; Accepted 16 June 2018
Available online 18 June 2018
1385-8947/

1. Introduction

Phosphorus (P) is a kind of indispensable macronutrient in living organisms, and plays a pivotal role in biological growth, development and breeding [1]. However, P is also a finite resource, and it has been reported that the existing deposits of phosphate rocks will be exhausted in 50–100 years [2]. In addition to being a diminishing resource, P would trigger hazardous eutrophication, when presented with high content in surface waters, resulting in a major environmental concern [1,3]. Over the past half century, human intervention of global phosphorus cycle has mobilized nearly half a billion tons of P from phosphate rocks into the hydrosphere [2]. Therefore, P removal combined with its recovery from nutrient-laden wastes is significantly important to ecological safety and sustainable development.

In recent years, P recovery from wastewater has gained more attention. Several kinds of wastewaters, such as municipal wastewater, industrial wastewater, and irrigation wastewater, contain a large amount of P, and offer a compelling opportunity for P recovery [4–6]. It has been reported that 15–20% of world demand for phosphate rock could theoretically be satisfied by legitimate recovery and utilization of P from domestic wastewater alone [7]. The most common method of P recovery from wastewater is through the abiotic precipitation of P-bearing minerals, such as calcium phosphates and struvite [8–10]. In particular, struvite ($MgNH_4PO_4 \cdot 6H_2O$) is attracted because it is a kind of compound containing three nutrient elements N, P, and Mg, and can be directly used as an eco-friendly slow-release fertilizer [5,11]. Thus, it has the significant potential to supplement increasingly scarce sources of P and reduce the danger of discharging wastewater into the environment, and numerous investigations have been carried out to assess the feasibility of P recovery as struvite at laboratory, pilot, and full-scale [1,5,10–14]. Moreover, struvite precipitation has also been used to remove ammonium and phosphate prior to the biological treatment of animal manures or municipal wastewater [11]. Therefore, struvite precipitation from wastewater could not only recover the nutrients as slow-release fertilizer, but also enable to eliminate the eutrophication of waters to some extent.

However, the large scale industrial production of struvite is generally limited, due to the high cost of chemical inputs [10,11,15,16]. On the one hand, the pH adjustment is required to reach the appropriate alkalinity for struvite precipitation and thus the economic feasibility of struvite is generally influenced by the cost of alkaline reagents (i.e., NaOH) [12,15]. Jaffer et al. [12] have found that the majority of chemical cost can be attributed to the addition of NaOH for struvite production at wastewater treatment. On the other hand, the addition of Mg^{2+} is indispensable to struvite production, because of the lack of adequate Mg^{2+} in majority of the wastewater [6,17]. Therefore, the economic feasibility of struvite recovery is also affected by the indispensable Mg consumption. The most common Mg sources used in struvite precipitation are expensive water-soluble Mg salts, such as $MgCl_2$ and $MgSO_4$, and they contribute up to 75% of overall production cost, limiting large scale industrial production of struvite [3]. To relieve the high input cost of Mg source, various cheap Mg compounds have been used, like $MgCO_3$ and MgO [3,11,16]. Natural abundance and low cost of MgO make it to be an important Mg source. However, MgO is sold as solid reagent, which has to be dissolved to supply Mg^{2+} for struvite formation. This unavoidable dissolution step would not only slow down the kinetics of struvite precipitation but also require excess MgO to achieve struvite precipitation [14,15]. In this context, the various alternative pre-treated methods such as MgO suspension [14], pre-mixed MgO with phosphoric acid [16], as well as milled MgO [18] were used to enhance the reagent efficiency during struvite precipitation, but additional cost of the pretreatments arises. Undoubtedly, how to use MgO as Mg source for the economical precipitation of struvite would be still a challenge.

Numerous studies indicated that bacteria have pronounced effect on mineral dissolution [19–22]. Bacterial metabolites and bacterial cell walls can act as organic ligands, which can chelate with metal ions (i.e., Mg^{2+}) both on mineral surface and in bulk solution, and thus promoting the further dissolution of minerals [19–21]. For example, Yao et al. [21] found that the enhancement of serpentine dissolution by *Bacillus mucilaginosus* is through the formation of a certain amount of Mg-complexes. Therefore, bacterially promoted Mg-complexes formation may be an ideal way to enhance MgO dissolution. Moreover, the formation of struvite is tightly related to bacteria. Many bacterial strains such as *Myxococcus xanthus* [1], *Proteus mirabilis* [23], and *Idiomarina loihiensis* [24] are able to induce struvite mineralization. In particular, the bacterial metabolic activities can provide the necessary alkaline environment for struvite precipitation, and thus alleviate the cost of alkaline reagents [16,20]. Therefore, the bacterial mineralization of struvite is regarded as a promising route to remove N, P and recover nutrients from various eutrophic wastewaters [1,13,17]. For example, Soars et al. [1] have utilized *Bacillus pumilus* and *Brevibacterium antiquum* to induce struvite mineralization in the settled wastewater and sludge dewatering centrifuge liquors. Recently, our group has investigated the effect of bacterial cells (*Shewanella oneidensis* MR-1) and different metabolites on the morphogenesis of struvite in the synthetic sludge liquor using $MgCl_2$ as Mg source [17]. Despite all that, there remains a dearth of research examining the potential of struvite precipitation for N and P removal and nutrients recovery from wastewater by combining bacterial mineralization with cheaper MgO as Mg source.

Herein, the objectives of present study are to elucidate and quantify the effect of MgO on bacterial mineralization of struvite, and assess the feasibility of using MgO as Mg source. An in situ bacterial mineralization was carried out. The cheaper MgO was used as Mg source, and *Shewanella oneidensis* MR-1 was selected as a model microbe. The growth profile of the bacterium, pH evolution of the culture medium, struvite yield and MgO transformation efficiency were tested with MgO doses of 0.16, 0.32, 0.64, and 0.96 g/L. The results obtained here may have valuable insights into N and P removal and nutrients recovery from eutrophic waters.

2. Materials and methods

2.1. Materials

Magnesium oxide (MgO), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), and sodium chloride (NaCl) were purchased from Sinopharm Chemical Reagent Co., Ltd. The tryptone and yeast extract are of biotech grade and purchased from Oxoid Ltd. All the chemicals were used as purchased without further purification. Deionized water was used in all of the experiments. The model microbe used was *Shewanella oneidensis* MR-1 (ATCC 700550) due to its metabolic versatility and sequenced and annotated genome [17]. The genus *Shewanella* is also associated with aquatic and marine environments, and has been found in wastewater and activated sludge of wastewater treatment plants (WWTPs) [17].

2.2. Methods

2.2.1. Cultivation of Shewanella oneidensis MR-1

The bacterial strain was initially maintained on sterilized solid Luria-Bertani (LB) medium: 10 g tryptone, 5 g yeast extract, 5 g NaCl and 15 g agar per liter of distilled water. Individual colonies from the plate were transferred to sterilized LB liquid medium (10 g tryptone, 5 g yeast extract and 5 g NaCl per liter of distilled water), and the inoculated medium was shaken with constant (200 rpm) for 24 h at 30 °C up to a cell density of 6×10^9 CFU per mL as seed liquid.

2.2.2. Bacterial mineralization

In a typical in situ bacterial mineralization system, 0.016 g of MgO sterilized by dry heat sterilization was added into 100 mL of sterilized