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Research article

Synthesizing slow-release fertilizers via mechanochemical processing for potentially recycling the waste ferrous sulfate from titanium dioxide production

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ABSTRACT

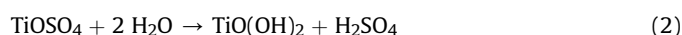
The goal of this study is aimed to develop a novel process to recycle the ferrous sulfate, the by-product of titanium dioxide industry. Zinc sulfate was added in the process of milling ferrous sulfate with calcium carbonate (CaCO₃). The sulfates were transformed into carbonates to serve as slow-release fertilizers by co-grinding the starting materials of FeSO₄·7H₂O, ZnSO₄·7H₂O, and CaCO₃ with small amounts of water in a planetary ball mill. The prepared samples were characterized by X-ray diffraction (XRD) analysis and quantitative measurements of the soluble ratios in water and 2% citric acid solution. It was found that Fe and Zn ions as sulfates were successfully combined with CaCO₃ to form the corresponding Fe and Zn carbonates respectively. After milling, the release ratios of Fe and Zn nutrients in distilled water could be controlled at 0.1% and 0.7% respectively. Meanwhile, the release ratios of them in 2% citric acid solution were almost 98% and 100%. Milling speed was the critical parameter to facilitate the transformation reaction. The proposed process, as an easy and economical route, exhibits evident advantages, namely allowing the use of widely available and low-cost CaCO₃ as well as industrial wastes of heavy metal sulfates as starting samples to prepare applicable products.

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1. Introduction

With the development of the modern agriculture, the irrigation systems have been extensively used for agricultural water management (Mahdizadeh Khasraghi et al., 2014; Valipour, 2012a,b; 2014; Valipour et al., 2015; Yannopoulos et al., 2015). However, further development of irrigation systems may lead to more environmental pollution by accelerating the migration and diffusion of heavy metal wastes. These toxic metallic species are harmful to human health, with long residence, and known as a great environmental concern (Fu and Wang, 2011; Hashim et al., 2011). Heavy metal wastes are generated from many human activities such as mining operations, paper industries, municipal solid waste, power plant batteries, fertilizer industries, pesticides, and even coking processes (Eighmy et al., 1997; Fu and Wang, 2011; Jablonska and Siedlecka, 2015; Jianguo et al., 2004; Landsberger et al., 2000; Matlock et al., 2002; Mu et al., 2012; Ward et al., 1977). In particular, mining activities and metallurgical industry generate large

amounts of wastes, which inevitably contain a lot of dissolved heavy metal sulfates (Kemper and Sommer, 2002; Kim et al., 2014; Lee et al., 2007). For example, ferrous-sulfate heptahydrate (FeSO₄·7H₂O) is the main waste generated by the TiO₂ industry (Gázquez et al., 2009; Kanari et al., 2001). The principal reactions of producing TiO₂ using the sulfuric acid process are presented by equations (1)–(3). The TiO(OH)₂ is generated by the hydrolysis of TiOSO₄ and the TiO₂ is prepared by calcining TiO(OH)₂. The irons in mineral and the required one to reduce ferric ions to ferrous ones are covered into FeSO₄·7H₂O, with six tons of FeSO₄·7H₂O generated per ton of TiO₂ produced (Gesenhues, 2001; Kanari et al., 2001, 2014). This is the major environmental disadvantage in the titanium dioxide production process.



The treatment of such waste was investigated by many

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researchers. Stabilization and recycling are the common methods to dispose the waste. The stabilization process allows these waste products to deposit in landfills. Vondruska et al. (2001) have investigated the stabilization of waste ferrous sulfate by means of fluidized bed combustion product. From the stances of environmental protection and sustainable development, the recycling of the waste would be a better choice. In this regard, Kanari et al. (2014) used the ferrous sulfate from titanium dioxide industry to synthesize sodium ferrate. Chen et al. (2011) prepared nanoparticles of ferric oxide by using the ferrous sulfate from titanium dioxide industry. Yu et al. (2013) reported the synthesis of a micro-sized hematite powder using microwave and conventional heating. However, the routes reported by the previous researchers are complex and high cost for applications. It is significant to develop an effective and low-cost method to deal with the waste.

On the other hand, the concept of controlled release or slow release fertilizers (SRFs) has been introduced for decades to improve nutrient efficiency. NPK fertilizers are universally used for improving the soil productivity. However, the balance of micro-nutrients such as Fe, Zn, Cu and Mn in the soils is also very important (Hejzman et al., 2013; Shahid et al., 2016). The effects of iron and zinc fertilizers on the growth of plants were widely reported (Hadi et al., 2014; Mooro et al., 2000; Singh and Shivay, 2016). Sánchez-Alcalá et al. (2012) reported that the ferrous carbonate (FeCO_3) could be applied as a slow-release Fe fertilizer for preventing Fe chlorosis in olive, due to its low-solubility in water and easy dissolution in dilute acid. Similar to the ferrous carbonate, zinc carbonate (ZnCO_3) also possesses these properties. Therefore, it is proposed to transform the sulfate wastes into carbonates to offer as the sources of Fe and Zn fertilizers. In other words, the by-product from the titanium dioxide industry may be used as the source of Fe fertilizer.

Na_2CO_3 or K_2CO_3 is normally used to react with sulfates to form the corresponding carbonates. Due to the strong alkalinity of these two carbonates, the pH of the solution may rise to such a high level that hydroxide precipitation occurs easily, particularly with iron ion solution. The stable iron hydroxide exhibits low solubility even in the dilute citric acid solution. A neutral source of carbonate to prevent the rise in pH of the solution from the formation of hydroxide precipitation is necessary to increase the rate for carbonate generation rather than hydroxide/oxide. CaCO_3 is the main composition of limestone, which is a cheap source around all the world and very suitable as a neutral source of CO_3^{2-} . However, the CaCO_3 is not active as Na_2CO_3 or K_2CO_3 to react easily with heavy metal sulfates and requires an activation to raise its reactivity. Recently, mechanochemical activation as a green approach has been applied in many fields, such as resource recycling (Kong et al., 2009; Yuan et al., 2012), materials syntheses (Kosova et al., 2014; Qu et al., 2016; Ye et al., 2014; Zhang et al., 2000), the degradation of hazardous materials (Di Leo et al., 2013; Ikoma et al., 2001; Tongamp et al., 2006; Wei et al., 2009) and the treatment of sludge (Kumar Jha et al., 2006). It is expected to increase the reactivity of CaCO_3 by performing mechanochemical treatment. Slow-release fertilizers are normally prepared by physically encapsulating the soluble fertilizers with polymer coating (Azeem et al., 2014; Zhan et al., 2004). However, there are some drawbacks on the common routes, such as the high costs, complex process and environmental pollution issues related to polymers. A mechanochemical process for synthesizing inorganic composites with the feature of slow-release was proposed. The methodology is simple and environment-friendly. And the raw materials are low-cost and have a wide range of sources. In addition, the synthetic materials as slow-release fertilizers will not cause any second pollution.

In this paper, a milling operation was performed for $\text{FeSO}_4\text{-CaCO}_3$, $\text{ZnSO}_4\text{-CaCO}_3$ and $\text{FeSO}_4\text{-ZnSO}_4\text{-CaCO}_3$ systems with small

amounts of water. The mechanochemical activation was introduced to activate the CaCO_3 and promote the smooth progress of the reactions, with purpose to obtain the products with low water solubility but easy dissolution in 2% citric acid solution. The fundamental results obtained by this newly developed process for Fe/Zn and Fe-Zn SRFs are reported. The process may also serve the purpose for recycling the heavy metals from the related waste samples.

2. Experimental procedure

Fe(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), Zn(II) sulfate pentahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), Fe sesquioxide (Fe_2O_3), Calcium hydroxide ($\text{Ca}(\text{OH})_2$), citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) and CaCO_3 from Sinopharm Chemical Reagent Co. Ltd., in analytical grade (purity >99%) were used as received without further purification.

With a separate case, 0.01 mol $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ or 0.01 mol $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and equimolar CaCO_3 with 1 mL distilled-water were put into a zirconia pot of 45 mL inner volume with 7 zirconia balls of 15 mm in diameter. A laboratory scale planetary mill (Pulverisette-7, Fritsch, Germany) was used to conduct the milling operation with a milling speed of 400 rpm and milling time of 60 min. With the mixed samples, 0.005 mol $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.005 mol $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.013 mol CaCO_3 (a little excess than the stoichiometric amount of 0.01 mol) were co-ground with 2.5 mL distilled-water, the milling speed was changed in the range between 200 and 700 rpm and the milling time fixed at 120 min. All the products were recovered from the pot and dried at 80 °C in an oven for 4 h for the next characterizations.

0.5 g of the prepared sample were dispersed in 100 mL distilled-water or 100 mL 2% (weight to volume) citric acid solution. Each sample was agitated for 24, 150, and 240 h, respectively at room temperature.

X-ray diffraction (XRD: RU-200B/D/MAX-RB RU-200B, Japan) analysis was performed to identify the phases in the ground samples. The concentrations of Fe and Zn ions in the water and the acid solutions were determined by inductively coupled plasma (ICP) spectrophotometry (ICP-AES: Optima-3300SYS, Perkin Elmer, USA). TG/DSC experiments were performed with a temperature-increasing rate of 10 °C/min using a simultaneous TG/DSC STA449C model analyzer in air up to 1000 °C. Particle sizes were measured using the laser diffraction method with a Mastersizer (Malvern, 2000; UK).

The release ratio of nutrient was calculated by the following formula (4):

$$R = \left(1 - \frac{A}{B}\right) \times 100\% \quad (4)$$

In the formula, R represents the release ratio of nutrient; A represents the value of the ICP measurement; B represents the original value of the sample. The unit of A and B are mg/L.

3. Results and discussion

3.1. For the $\text{FeSO}_4\text{-CaCO}_3$ and $\text{ZnSO}_4\text{-CaCO}_3$ systems

3.1.1. Characterization

The phases of the products from milling $\text{FeSO}_4\text{-CaCO}_3$ and $\text{ZnSO}_4\text{-CaCO}_3$ mixtures were identified by XRD analysis and the results are shown in Fig. 1. The starting materials of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and CaCO_3 in pattern b were found to disappear nearly, as shown in Fig. 1(A), only with some weak peaks of CaCO_3 . The FeCO_3 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ as the new components of the product were identified in the pattern b, indicating that the CaCO_3 activated by milling

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