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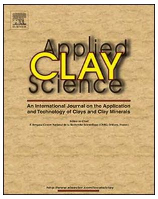

Research paper

Controlled release studies of boron and zinc from layered double hydroxides as the micronutrient hosts for agricultural application

Patsaya Songkhum[a], Tuksadon Wuttikhun[a], Narong Chanlek[b], Pongtanawat Khemthong[a], Kritapas Laohhasurayotin[a,*]

[a] *National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA), Pathum Thani 12120, Thailand*
[b] *Synchrotron Light Research Institute, 111 University Avenue, Muang, Nakhon Ratchasima 30000, Thailand*

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ABSTRACT

Two forms of zinc-aluminium layered double hydroxides (ZnAl-LDH) with borate association (iZA and cZA) were prepared by ion-exchange process and in-situ co-precipitation. The received materials were examined using several characterization techniques, e.g. x-ray diffraction (XRD), scanning- and transmission-electron microscopy (SEM and TEM). The XRD diffractograms suggested that only monoborate ions (possibly trigonal and tetrahedral forms) were involved in the intercalation and adsorption. Elemental analyses, i.e. inductive coupled plasma-optical emission and atomic absorption spectroscopies, were used to determine the starting zinc and boron compositions, and the contents after the dissolution experiment in water, soil, and plant growth study. The iZA and cZA samples were found to controlled-release Zn and B contents which can be used as micronutrient sources in agricultural application. The releases of the two nutrients are suggested to initiate from the anionic-exchange of $BO3^{3-}$ and the transformation of Zn^{2+} from LDH basal plane. The plant experiments treated with these iZA and cZA exhibit improvements in plant growth, evidently attributed to the controlled and sustainable releases of boron and zinc for assisting macronutrient uptakes when used with the NPK fertilizer.

1. Introduction

Plants need water and nutrients just like humans and animals acquire their food to survive, live, and reproduce, perhaps for the same purpose to sustain their species and biodiversity. Although some plants have shown marvelous adaptability, most of them, still, cannot cross over one big limitation—the incapability to move. As a result, they cannot reach sufficient nutrition on their own. Fertilizer is a common source of nutrients, especially nitrogen (N), potassium (K), and phosphorous (P), required in the traditional agriculture process. However, it has been noted that > 50% of the given N fertilizer is lost due to the irrigation and gas emission before reaching to the plant site (Singh et al., 2007). Most of the nutrient sources are in chemical forms, and they are water-soluble. Thus, nutrients can be washed away easily during rain and daily irrigation. Apart from the main three elements N-P-K, micronutrients such as boron (B), copper (Cu), zinc (Zn), Molybdenum (Mo), and iron (Fe), are also required for maintaining the plant quality.

B and Zn are the common micronutrients used in agricultural process because they involve extensively in the plant growth mechanisms. The important roles of these two elements in plant fertility, stem building, and seedling (Davis et al., 2003; Nikkhah et al., 2013; Salam et al., 2010) are widely known. Interestingly, their deficiencies in harvested crops are found due to the massive decrease from the industrial agriculture. Boron is an essential micronutrient based on its role in the stabilization function on cell wall (Bell and Dell, 2008). It is vital not only for building the reproductive parts such as pollen growth and seed reproduction (Asad et al., 2001), but also known to involve in the translocation of sugar and carbohydrates to balance the sugar and starch levels in plant (McIlrath et al., 1960). The lack of B critically results in short stem, poor quality of seed, and rapid ripening of fruit. Zinc is required for the synthesis mechanisms to create protein, auxin, chlorophyll, and carbohydrate (Nikkhah et al., 2013). The Zn deficiency can lead to the small leaves and therefore causes the decrease in net photosynthesis. The structure of plant membrane is thus affected, resulting in root leakiness of amino acids, phenolics, and others (Bell and Dell, 2008). The addition of B and Zn by chemicals such as $Na_2B_4O_7 \cdot 10H_2O$, H_3BO_3, $ZnNO_3$, and ZnO, aims to compensate the nutrition deficits in plant which helps user to maintain and improve the produce quality. However, the unawareness of water contamination due to the overuse of B and Zn chemicals results in accumulating pollution in natural water (Aulakh and Singh, 1996; Isaacs-Paez et al.,

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[*] Corresponding author.
E-mail address: kritapas@nanotec.or.th (K. Laohhasurayotin).

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2014), becoming the serious environmental and health issues. In fact, several remediation processes to remove Zn and B accumulation in water have been reported (Xu and Jiang, 2008). Nonetheless, those methods are expensive and inefficient. New technology that would supply nutrition to plants should be extensively studied. Slow-release technology—a process with gradual release feature of nutrients in plant fertilizer—has been developed based on several concepts of releasing mechanisms (Broschat, 2008; Hores et al., 2004; Ureña-Amate et al., 2011; Xie et al., 2011). Natural slow release processes like the use of plant (vegetables) or animal manures (cow, pig, poultry) that require microbial activity to decompose their organic ingredients to nutrients utilizable by plants is just an example. The controlled-release processes require some substance such as polymers to encapsulate the core fertilizer which will delay the release of active nutrients into soil (Morgan et al., 2009).

Layered double hydroxide (LDH), commonly called as synthetic clay, is an ionic solid referred to as hydrotalcite-like compound which consists of brucite-type—$Mg(OH)_2$—layers. Water and anions occupied within the interlayer spaces balances the positive charge established with divalent and trivalent cations of the basal plane. These anions can undergo ion-exchange process in gradual action to provide controlled release implication. The typical formula of LDH can be written as $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A^{n-}_{x/n}]\cdot mH_2O$ where the divalent cation (M^{2+}) is Mg^{2+}, Ca^{2+}, Co^{2+}, Zn^{2+}, and the trivalent cations (M^{3+}) is Al^{3+}, Fe^{3+}, Cr^{3+}. The A^{n-} abbreviation represents the anions, such as OH^-, Cl^-, and NO_3^-. The stacked layers of cationic and anionic model structures enable the ion-exchange activity which leads to advantages in many applications, for examples, adsorption (Dadwhal et al., 2009) ion-exchanger (Costantino et al., 2014), catalysis (Fan et al., 2014), and controlled-release (Gillman and Noble, 2001). The latter was first reported by Komarneni and co-workers in the introduction of NO_3^- release from LDH as N source in fertilizer (Komarneni et al., 2003). Ureña-Amate et al. also examined the controlled-release activity of nitrate from MgAl-LDH compound modified with hydroxypropyl methylcellulose, formed in two different shapes: granule and tablet (Ureña-Amate et al., 2011). Novel methods for slow releasing nitrogen could be found in some recent works (Qin et al., 2012; Wen et al., 2016a, 2016b). In fact, the release activity by ion-exchange process is not just limited to nitrate, it is applicable as well to other types of anionic species including phosphate, citrate, and fluoride (Everaert et al., 2016; Perera et al., 2015; Tammaro et al., 2014). Recent published work by Benício et al. (2017) reported the phosphate fertilization released from LDH on maize crop. This may be considered an alternative source of P in addition to available commercial fertilizers or livestock manures.

To our point of interest, two significant aspects from the LDH system should be extensively explored. First, it has been known that LDH material can be used to recover borate from wastewater via ion-exchange process, according to the research work by Delazare et al. (2014), Kameda et al. (2015), Isaacs-Paez et al. (2014) and their coworkers. Use of borate ion from LDH in controlled-release fashion by ion-exchange process for plant is expected to be a smarter way in reducing and recycling pollution caused by excessive application in boron fertilization, mostly with water-soluble chemical form. Second, the study recently conducted by Imran et al. (2016) suggested possible dissolution of divalent cation (Mg^{2+} or Zn^{2+}) from metal oxide or hydroxide of LDH form, via different reactions due to the pH of the solution. The zinc ion that is transformed from Zn atoms composed in brucite-like layer through dissolution can be released as a second micronutrient from the same LDH system for plant. This bi-micronutrient release concept gives pollution-control benefit. It saves management cost and introduces effective approach for nutrition improvement in plants.

Herein, the borate ion was associated in ZnAl-LDH via both ion-exchange process and co-precipitation to form iZA and cZA, respectively. The structures and micronutrient compositions were thoroughly examined. Best to our knowledge, the controlled release of these micronutrients exploiting the same LDH material but different mechanisms have never been reported. We show that the ion-exchange replacement of BO_3^{3-} and the dissolution of Zn^{2+} ion concomitantly occurred from LDH play significant roles in plant growth experiment.

2. Experimental

2.1. Materials

Zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) and di-sodium tetraborate decahydrate ($Na_2B_4O_7{\cdot}10H_2O$) or borax were purchased from Loba Chemie. Aluminium nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$) was purchased from Unilab. Sodium hydroxide (NaOH), 65% nitric acid (HNO_3), and 40% hydrogen peroxide (H_2O_2) were obtained from Carlo Erba. NPK fertilizer was the 16-16-16 YaraMila product purchased from Hydrothai company. Deionized (DI) water (Millipore, specific resistivity 18 MΩ) was used throughout this study. All chemicals were used as received.

2.2. Preparation of Zn-Al LDH with nitrate association (ZA)

An amount of 2 mol/L NaOH solution was added dropwise to the 100 mL mixture of $Zn(NO_3){\cdot}6H_2O$ (18 g, 60 mmol) and $Al(NO_3)_3{\cdot}9H_2O$ (8 g, 20 mmol) while vigorously stirring to adjust the mixture pH close to 9. This mixture was continued to maintain at 65 °C for 24 h. The resulting white slurry was separated by centrifugation at 8000 rpm (TOMY, MX-305), and the wet precipitate was washed with DI water until the solution pH became 7. The precipitate was then dried at 80 °C in an oven for 24 h. The retrieved chunks of ZA (8.7 g) were ground to fine powder.

2.3. Preparation of Zn-Al LDH with boron association via ion-exchange process (iZA)

One gram of ZA was added into a 50 mL of 100 mg/L boron solution prepared by which borax (8.8 g) was dissolved in 1 L DI water. The ion-exchange process was allowed to proceed for 1 h. The boron concentration that has been reduced due to the intercalation into ZA interlayer was examined through elemental analysis described in the next section. The precipitate was separated by centrifugation, washed with DI water, and dried at 80 °C for 24 h.

2.4. Preparation of Zn-Al LDH with boron association via in-situ co-precipitation (cZA)

A 2 mol/L NaOH solution (50 mL) was mixed with 0.3 mol/L boron solution (100 mL) obtained from borax (11.4 g, 30 mmol) dissolution in DI water. This mixture was added dropwise to the vigorously stirred solution of Zn^{2+} and Al^{3+} ions prepared from $Zn(NO_3)_2{\cdot}6H_2O$ (10.4 g, 35 mmol) and $Al(NO_3)_3{\cdot}9H_2O$ (6.6 g, 18 mmol), respectively, until the pH is close to 9. The resulting mixture was aged at 65 °C for 6 h and continued at room temperature for 18 h. The white slurry was washed with DI water using centrifugation until the pH value became 7. The obtained precipitate was dried at 80 °C in an oven for 24 h. The dried chunks were ground to fine powder.

2.5. Characterization methods

Powder X-ray diffraction pattern was measured with a Bruker:D8 Advance diffractometer equipped with CuKα radiation ($\lambda = 0.15406$ nm) at 40 mA, 40 kV. The scan rate was at $2\theta = 0.04^{\circ}\,s^{-1}$ within the range of 5–70°. Surface morphology was examined using a scanning electron microscope (SEM: Hitachi: S3400 N). More details in sample structure was successfully observed using a transmission electron microscope (TEM: JEOL: JEM 2100). X-