

Synthesis of zinc hydroxide nitrate complex by a sol-gel method for use as foliar fertilizers – a scale up approach

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ABSTRACT

Zinc hydroxide nitrate complex is a new class of materials with outstanding characteristics promising its application as foliar nano-fertilizers. In this study, nano crystalline zinc hydroxide nitrate powder was synthesized by a sol – gel method using NaOH and $Zn(NO_3)_2 \cdot 6H_2O$ as precursors, yielding several grams products per batch. The products were characterized by XRD, FTIR, SEM and

BET, indicating the initial molar ratio $NaOH : Zn(NO_3)_2 \cdot 6H_2O = 1.6$ and reaction time 1 hour as suitable. Under the indicated conditions, the particle size of products is in the range $50 \div 100$ nm. The characteristics of products demonstrate their potential application as foliar nano-fertilizer and the synthesis procedure might be further upgrading to production extents.

Keywords: Foliar fertilizer, nano-fertilizer, scale-up procedure, Zinc hydroxide nitrate, sol-gel method.

1. INTRODUCTION

Folia fertilizers have been applied in increasing extents and become indispensable to high-tech agriculture. Recently, zinc hydroxide nitrate $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ had been reported as a potential long-term zinc supplying foliar fertilizer owing to its appropriate characteristics, e.g. stable nano sized crystals with sheet-like morphology, positively charged surface and moderate solubility in water [1,2]. Moreover, copper could be involved to provide foliar fertilizers functioning as dual micronutrients to foliars [3]. In fact, $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ has been known for a long time as a representative

of layered hydroxide salts. Its preparation was newly patented concerning application as foliar fertilizer [4]. However, only the procedure in laboratory scale was described and boundary parameters suggested, e.g. 1 hour reaction time, concentration 0.2 M NaOH, and initial molar ratio $OH^- / Zn^{2+} = 1.6$ were suggested from the investigated ranges 1 hour \div 24 hour, 0.2 M \div 1.6 M NaOH, and 0.5 \div 1.6, respectively [1]. In order to follow this procedure, additional investigation beyond the reported ranges, e.g. stirring time shorter than 1 hour, initial $OH^- / Zn^{2+} > 1.6$ should be conducted. Moreover, the synthesis of $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ should be

scaled up towards its possible application as foliar fertilizer.

This paper describes our preliminary results of such attempts to scale up. First, both the concentrations of precursors' solutions were increased to 0.6 M and the initial molar ratio $\text{OH}^- / \text{Zn}^{2+}$ as well as aging time adjusted. Then both their volumes were increased accordingly 5- to 20-fold, resulting in its production of about 70g of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ per batch.

2. EXPERIMENTAL

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (reagent grade 98%) and NaOH (reagent grade 99%) from China were used without further purification. Ultrapure water was obtained from a reverse osmosis system. Two stock solutions 0.6 M $\text{Zn}(\text{NO}_3)_2$ and 0.6M NaOH were prepared dissolution appropriate amounts of chemicals in water and stored at ambient conditions.

Fig.1 shows the procedure scheme of a typical laboratory scale experiment: 80 ml 0.6M NaOH were gradually added to 50 ml 0.6M $\text{Zn}(\text{NO}_3)_2$ under vigorous stirring at room temperature ($28^\circ\text{C} \pm 2^\circ\text{C}$) for 1 hour. The resulting white precipitates were filtered, washed several times with ultrapure water, then dried at 50°C for 24 hours. The investigated parameters were initial $\text{OH}^- / \text{Zn}^{2+}$ molar ratio (0.5, 1.0, 1.6, 2.0 corresponding to 25 ml, 50 ml, 80 ml and 100 ml 0.6 M NaOH vs. 50 ml 0.6 M $\text{Zn}(\text{NO}_3)_2$) and stirring time (15 min., 30 min., 45 min., 1 hour).

Scale – up experiments were conducted using 5-fold and 20-fold volumes of both the stock solutions at the initial $\text{OH}^- / \text{Zn}^{2+}$ molar ratio 1.6, i.e. adding 400 ml 0.6M NaOH to 250 ml 0.6M $\text{Zn}(\text{NO}_3)_2$ or 1600 ml 0.6M NaOH to 1000 ml 0.6M $\text{Zn}(\text{NO}_3)_2$, respectively. Instead

of magnetic stirrer, a blade mixer at around 180 rpm and room temperature was applied to assure extensive mixing for 1 hour. The filtering, washing and drying steps remained similar as in laboratory scale experiments.

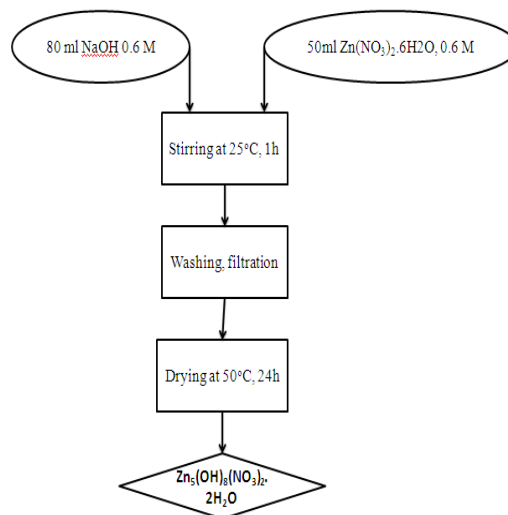


Figure 1. Procedure of the typical laboratory scale experiment

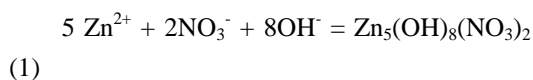
All products were characterized under the same conditions and results compared with each other. The XRD patterns were collected using a D8 Advance Diffractometer (Bruker AXS), Ni MultiFlex X – ray diffraction and Cu K(α) ($\lambda = 1.54184 \text{ \AA}$) radiation. The beam voltage and beam current are 40kV and 40mA, respectively. A two theta range of $5 - 70^\circ$ with a continuous scan rate of $3^\circ / \text{min}$ was applied and the phases identified using the Joint Committee on Powder Diffraction Society (JCPDS) database. The Fourier transform infrared (FTIR) spectra of products were obtained using the Bruker Equinox 55 (in the range $4000 - 400 \text{ cm}^{-1}$) equipped with a DTGS detector from FT – IR (Institute of Material Science – Vietnam Academy of Science and Technology). The morphology and particle size of products were

studied by a S-4800 instrument with an accelerating voltage of 10kV (Hitachi, Japan). The specific surface areas of products were recorded in a Quantachrome Instrument version 10.0.

3. RESULT AND DISCUSSIONS

3.1. Scaling-up the initial concentration of precursors

The synthesis procedure presented in Fig.1 resembles the one described by Li et al [1], except for higher concentrations of precursors (both 0.6 M instead of 0.2 M) and slightly higher ambient temperature (28 ± 2 °C instead of 25°C). Li et al [1] also tried with concentration 1.6 M NaOH but concluded the smaller one – i.e. 0.2 M – is more suitable, though the concentration of $\text{Zn}(\text{NO}_3)_2$ in the former case was not clearly specified. In fact, Newman et al. [5] synthesized the same product dropping 50 ml 0.75 M NaOH into 20 ml 3.5 M $\text{Zn}(\text{NO}_3)_2$ at room temperature, followed by an immediate filtration step. They did not recommend initial molar ratios $\text{OH}^- / \text{Zn}^{2+}$ higher than 0.5 because ZnO would appear as impurities in products [5]. However, Li et al [1] did not detect such impurities even with the initial molar ratio $\text{OH}^- / \text{Zn}^{2+} = 1.6$ using lower concentrations of both precursors (0.2 M). The main reason of this discrepancy is the rather slow kinetics of reaction:



If some local concentrations of “free” OH^- in the mixture were high enough during the reaction course, they could even attack the freshly formed $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2$, resulting in its structural changes to ZnO. Therefore, this work just scaled up the initial NaOH concentration to

0.6 M and re-checked the effect of initial molar ratio $\text{OH}^- / \text{Zn}^{2+}$.

3.1.1. Adjusting the initial molar ratio $\text{OH}^- / \text{Zn}^{2+}$

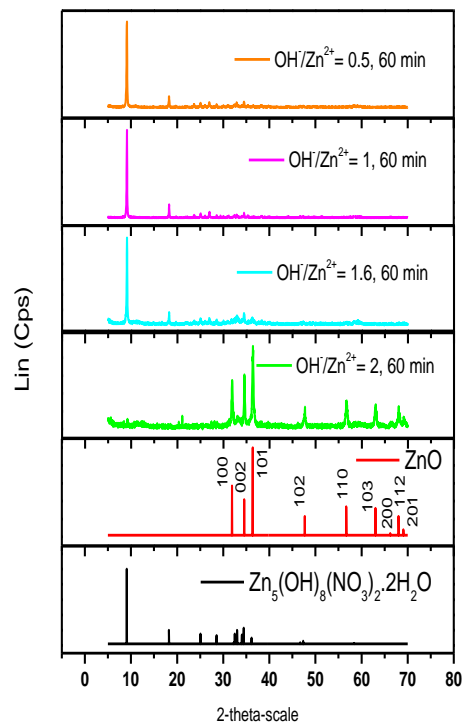


Figure 2. XRD patterns of products with different initial $\text{OH}^- / \text{Zn}^{2+}$ molar ratios

Fig.2 shows the XRD patterns of the “as synthesized” products at different initial molar ratios $\text{OH}^- / \text{Zn}^{2+} = 0.5, 1.0, 1.6$ and 2.0 , together with the reference data for ZnO (JCPDS card 36-1451) [6,7] and $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (JCPDS card 241460) [1,5,8,9]. For the initial molar ratios $\text{OH}^- / \text{Zn}^{2+} \leq 1.6$, an intense peak at $2\theta = 9.2^\circ$ demonstrating the (2 0 0) crystal planes appeared. Another peak at $2\theta = 18.40$ relevant for the (4 0 0) crystal planes is substantially less intense, but still clearly identified. However, further characteristic peaks at $2\theta = 34.6, 35.4$,

46.8, and 47.4°, corresponding to (2 2 1), (7 1 0), (10 0 0), and ($\bar{7}$ 1 2) crystal planes, respectively, are insufficiently resolved.

In our experiments, NaOH and $\text{Zn}(\text{NO}_3)_2$ solutions were simply mixed together, OH-concentrations at the beginning might reach $0.200 \text{ M} \div 0.369 \text{ M}$ ($\text{OH}^- / \text{Zn}^{2+} = 0.5 \div 1.6$) compared to about 0.123 M ($\text{OH}^- / \text{Zn}^{2+} = 1.6$) [1]. Such situations would cause some structural changes of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, resulting changes in peak intensities. Although this change in peak intensity requires more detailed investigation, all the XRD patterns of synthesized products at initial $\text{OH}^- / \text{Zn}^{2+} = 0.5 \div 1.6$ clearly show the typical peaks at $2\theta \sim 9.80$ and 18.40 as the required $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. In order to maximize the material effectiveness, the initial molar ratio $\text{OH}^- / \text{Zn}^{2+} = 1.6$ was chosen for further study. However, much attention should be paid to the mixing condition to avoid local increase of pH, as a small pH increase at the initial $\text{OH}^- / \text{Zn}^{2+} = 2.0$ resulted XRD pattern containing only characteristic peaks for ZnO.

3.1.2. Adjusting the aging time

As longer aging time than 1 hour is proved to be unsuitable [1], possible effects of shorter aging times were investigated. Fig.2 and Fig.3 compared the XRD patterns and FTIR spectra, respectively, of the as-synthesized products with aging times 15, 30, 45 and 60 minutes. For products with 15 minutes aging time, the obtained XRD pattern already shows characteristic peaks of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ at $2\theta = 9.20$ and 18.40 . For products with longer aging times than 15 minutes, this most intense peak at $2\theta = 9.20$ decreased to about $\frac{1}{2}$ while the another characteristic peaks become better

resolved. It might be interpreted that structural transformations from (2 0 0) to another characteristic diffractions of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ occurred. Li et al [1] also registered a decreasing tendency of the peak at $2\theta = 9.20$ with aging time beyond 1 hour and interpreted it as results of phase transformation from $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ towards $\text{Zn}(\text{OH})_2$. It's worth to note that this main peak intensity remained practically unchanged for aging times 30-60 minutes and no characteristic peaks for $\text{Zn}(\text{OH})_2$ (compared to JCPDS card 38-0385 [1,8]) appeared.

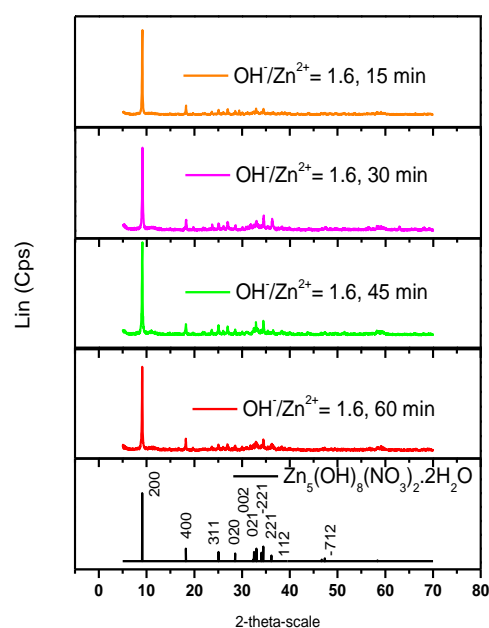


Figure 3. XRD patterns of products with different aging times

The FTIR spectra of all synthesized products with aging times up to 60 minutes resemble each other, with typical peaks of the $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ structure. e.g. the stretching vibrations of the O – H bonds resulted a sharp and a strong peak at around 3570 cm^{-1} and 3500 cm^{-1} , respectively. The presence of

H₂O molecules in the interlayer space or adsorbed in the surface resulted a shoulder and a peak at around 3300 cm⁻¹ and 1630 cm⁻¹, respectively. Also, vibrations of the nitrate groups are represented by a very strong peak at around 1380 cm⁻¹ and two weak peaks at around 1050 cm⁻¹ and 840 cm⁻¹.

Although the XRD patterns and also the FTIR spectra for products with aging times 30 ÷ 60 minutes do not significantly differ from each other, the aging time of 60 minutes was chosen for further experiments as this process should be scaled up further. It's worth to note that longer aging time is not desirable due to Zn₅(OH)₈(NO₃)₂·2H₂O transformation [1]. SEM images shown in Fig.5 reveal sheet-like product entities with thickness from ~ 20 nm to ~ 40 nm, which actually belong to the most required characteristics of our designed products.

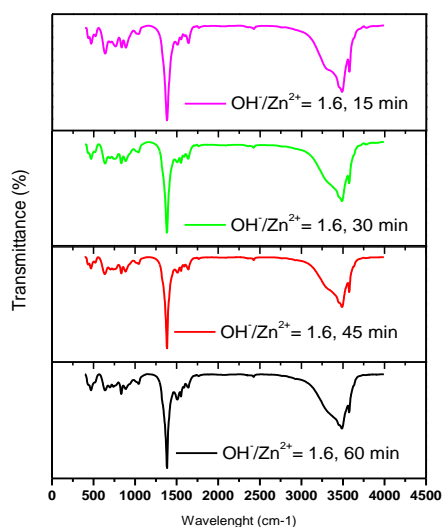


Figure 4. FTIR spectra of products with different aging times

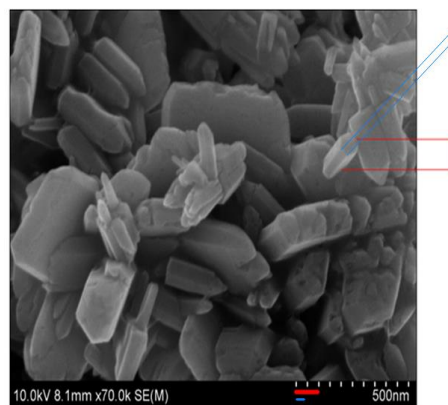


Figure 5. SEM images of products with 60 minutes aging time

3.2. Scaling-up the volumes of precursors' solutions

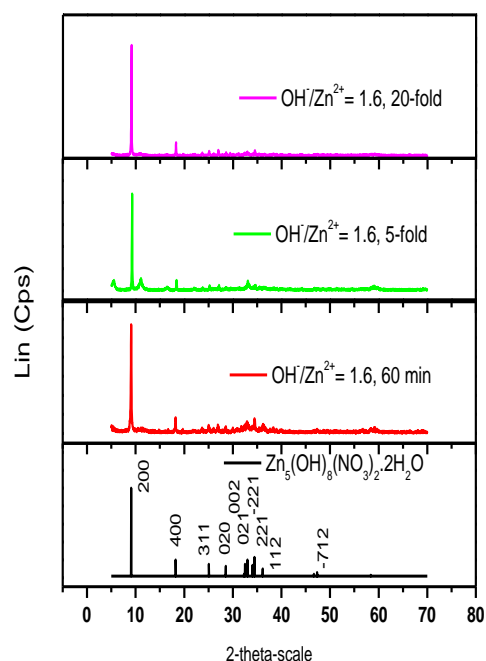


Figure 6. Comparison of XRD patterns of products at volume scaling up experiments

Towards a possible application of products, the precursors' volumes were scaled up 5-fold and 20-fold compared to those described in Fig.1. Much attention had been paid to avoid local overwhelming pH increase inside the

reaction mixture, especially the regime to mix the NaOH and $\text{Zn}(\text{NO}_3)_2$ solutions should be individually “tailor-made”. Fig.6 e.g. shows that a non-optimized mixing regime caused an additional peak at $2\theta = 100$ in the XRD pattern of products from 5-fold scaled-up approaches, while such “strange” peaks did not appear in case a good mixing regime was applied in our 20-fold scaled-up approach. The FT-IR spectra in Fig.7 also confirms that characteristic groups of the $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ structure are conserved in the products of our scaled-up approaches.

In addition, Fig.8 shows that products of our 5-fold and 20-fold volume scaled-up products conserves the desired sheet-like morphology with thickness less than about 50 nm. Comparing with Fig.5, one can see that our volume scaled-up approach did not affect the morphology of products, just increased their mass to about 70 g per batch.

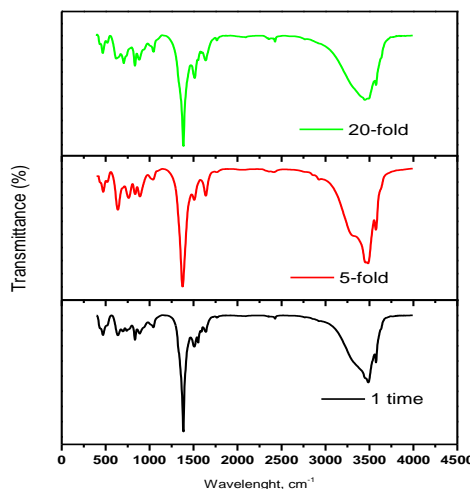


Figure 7. Comparison of FT-IR spectra of products at volume scaling up experiments

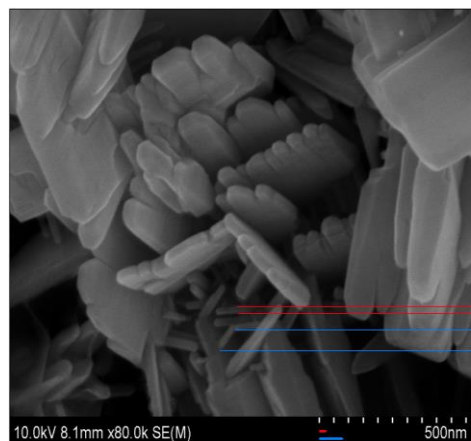


Figure 8. SEM image of products with 5-fold scaled-up volumes

4. CONCLUSIONS

A laboratory procedure reported in the literature [1] for synthesis of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ by sol-gel method was verified and scaled-up in both the initial concentrations and precursors' volumes. Under our selected conditions, the resulting products conserve the characteristic XRD patterns, FT-IR spectra and morphology as described in the literature. Comparing to the theoretical value calculated for the cited procedure [1], our product's masses could be increased about 60-fold to ~ 70g per batch. Further scaling-up the precursors' volumes and determination of the product's surface charge are required in order to verify the potential application of products as foliar nano-fertilizer.

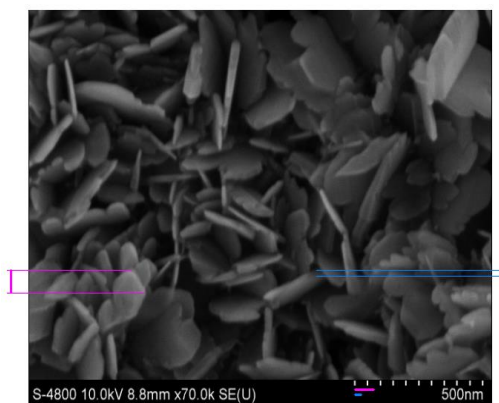


Figure 9. SEM image of products with 20-fold scaled-up volumes

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Nghiên cứu khả năng nâng cấp quy trình điều chế muối phức kẽm hydroxo-nitrat làm phân nano bón lá bằng phương pháp sol-gel lên qui mô sản xuất

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TÓM TẮT

Muối phức kẽm hydroxo-nitrat là một dòng vật liệu mới với những ưu điểm nổi trội hứa hẹn làm phân nano bón lá. Tuy nhiên, thông tin từ tài liệu tham khảo tiếp cận được giới hạn ở mức độ mg sản phẩm mỗi mẻ điều chế. Trong nghiên cứu này, muối phức kẽm hydroxo nitrat được

tổng hợp thành công ở qui mô g sản phẩm mỗi mẻ bằng phương pháp sol-gel sử dụng NaOH và $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ là tác chất. Ảnh hưởng của tỷ lệ nồng độ tác chất ban đầu và thời gian khuấy trộn đã được khảo sát. Sản phẩm dạng bột được đánh giá bằng các phương pháp XRD, FTIR,

SEM, BET, cho thấy tỷ lệ mol ban đầu NaOH : $Zn(NO_3)_2 \cdot 6H_2O = 1.6$ và thời gian khuấy trộn 1 giờ là phù hợp. Kích thước hạt của sản phẩm thu được dao động trong vùng 50÷10 nm. Kết

quả cho thấy sản phẩm thu được có thể sử dụng làm phân nano bón lá và qui trình điều chế có thể tiếp tục nâng cấp lên qui mô công nghệ.

Từ khóa: Phân bón lá, phân nano, qui trình nâng cấp, kẽm hydroxo-nitrat, phương pháp sol-gel.

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