Supporting information

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Title: Optimization and characterization of polyphosphate fertilizers by two different manufacturing processes

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2.5 Measurements of the features of APP samples

The major features of APP samples, such as polymerization degree, polymerization rate, N and P recovery rates, pH, solubility, and salt index, are assayed as following methods.

2.5.1 Polymerization degree

Polymerization degree (n) usually refers to the average polymerization degree of APP, and it was determined according to the modified end-group titration method \(^7, 34\) with an automatic potentiometric titrator (T-860, Jinan Hanon Instruments Co., Ltd, China).

Briefly, 0.5000 g APP sample was dissolved with 30 mL of Milli-Q water in a 250 mL beaker, then solution pH was adjusted to 8.5 with 4 M NaOH, afterward this solution was transferred to a 100 mL volumetric flask. Subsequently, a total of 50 mL solution was pipetted out and then passed through an ion-exchange resin (732-Na) column, after that, this resin column was washed with Milli-Q water (flow rate, 5.5-6.0 mL minutes\(^{-1}\)) until the pH of effluent was neutral. Finally, the effluent was collected and transferred to a 250 mL volumetric flask, and then fixed to the given volume of 250 mL by using Milli-Q water as the test solution.

One test solution (100 mL) was adjusted to pH 3 with 0.5M HNO\(_3\) and then titrated to pH 10 with 0.1 M NaOH using an automatic potentiometric titrator (T-860) (stirred on the ice to prevent APP hydrolysis). There were two abrupt rise points during the titration process. One abrupt rise point happened at pH 3, and another occurred pH 10. Finally, the volume of 0.1 M NaOH used was recorded between these two abrupt rise points, and it represented as \(V_1\).

Another test solution (100 mL) was transferred to a 250 mL round bottom flask, then it was mixed with 50 mL Milli-Q water and 10 mL 6M HCl, and this solution was heated for 6 h. During this procedure, poly-P was completely transformed into orthophosphate. It must ensure that all
volatile vapors were refluxed in the bottom flask through a condenser tube. After that, the solution pH was adjusted to 3 with 0.2 M HNO$_3$, then the solution was titrated to pH 10 with 0.1 M NaOH. The volume of 0.1 M NaOH used between the two abrupt rise points (at pH 4.5 and 9.5) was be referred to as $V_2$. The polymerization degree of APP fertilizer was calculated by the formula (4):

$$\text{Average polymerization degree (n) } = \frac{\text{moles of } \text{PO}_4^{3-}}{\text{moles of APP}} = \frac{2V_2}{V_1} \quad (4)$$

2.5.2 Polymerization rate (Poly-P/Total-P)

Polymerization rate referred to the percent of the polyphosphate (Poly-P) accounted for total-P in APP. It was calculated by the formula (5):

$$\text{Polymerization rate(%) } = \frac{(\text{Total } P \text{ content}) - (\text{Ortho } P \text{ content})}{(\text{Total } P \text{ content})} \quad (5)$$

Orthophosphate (Ortho-P) of APP was determined according to the method of Dick and Tabatabai (1977) 35. Briefly, 10 mL of ascorbic acid (0.1 M)-trichloroacetic acid (0.5 M) reagent was piped into a 25 mL volumetric flask and then mixed with 1 mL of sample containing 2-25 µg of orthophosphate P. Afterwards, 2 mL of 0.01 M ammonium molybdate solution and 5 mL sodium citrate (0.1 M)-sodium arsenite (0.2 M)-acetic acid (5%) mixing solution were immediately added to the samples. The solutions were thoroughly mixed in the flask and then fixed to constant volume of 25 mL with Milli-Q water. The absorbance of the molybdenum blue complex was determined after 10 minutes at a wavelength of 700 nm with a spectrophotometer (UV-vis spectrophotometry model 722, Yucheng Technologies Ltd, Beijing, China).

2.5.3 N content

N content in APP fertilizers (N %) was determined as referred to the Kjeldahl method of Tate (1994) 36. In brief, an aliquot of 1.00 g APP sample and 0.05 g anhydrous CuSO$_4$ were added to a 100 mL digest tube and wetted with 1 mL Milli-Q water, then 10 mL diluted sulfuric acid (H$_2$SO$_4$}
+ H₂O, 1+1, v/v) was added into the sample. Subsequently, the digest tube was transferred to a preheated (380°C) digest furnace for digestion reaction until the white smoke of SO₃ was produced (20 min), then the digest tube was cooled to room temperature. Afterward, the digest solution was transferred to a 100 mL volumetric flask and fixed volume with Milli-Q water. Finally, a total of 25 mL solution was pipetted to another digest tube and digested for 7 min, this solution was used for N content measurement by Kjeldahl apparatus.

2.5.4 P content

Total-P content in APP fertilizers (P₂O₅%) was measured by using the quinolone molybdophosphate gravimetric method as described by Shaver (2008) 37. In brief, an aliquot of 0.5000 g APP sample was wetted with Milli-Q water in a 150 mL beaker and then mixed with 10 mL of 1:1 HNO₃ solution. Afterward, the solution was boiled for 10 minutes on an electric furnace. Subsequently, when the solution cooled to room temperature, it was transferred to a 250 mL volumetric flask and fixed volume with Milli-Q, then 10 mL solution was pipetted into a 250 mL beaker, then 10 mL HNO₃ solution and 80 mL Milli-Q were added. The mixed solution was boiled on the electric furnace. After that, 35 mL of quinazoline solution was added to the beaker and stirred with a glass rod until yellow color precipitation was formed. The precipitation in the beaker was washed 5-6 times with Milli-Q water, then it was collected in a crucible, filtered, and then dried the precipitation to the constant weight. Finally, the precipitation was cooled and weighed.

2.5.4 N and P recovery rate

At the same time, the nitrogen (N) and phosphorus (P) recovery rates were obtained in this study. They were calculated by the formula (6) and (7):

\[
\text{N recovery rate} = \frac{C_u \cdot m_{app}}{C_N \cdot M_{\text{urea}}}
\]  

(6)
P recovery rate = \frac{C_p \cdot m_{APP}}{C_p \cdot M_{phosphate}} \tag{7}

Where \(C_n\) and \(C_N\) are the N content in Urea and APP, respectively; \(C_p\) and \(C_P\) are the P content in phosphate raw materials and APP, respectively; \(m\) is the weight of APP; \(M_{urea}\) and \(M_{phosphate}\) are the weight of urea and phosphate materials, respectively.

The pH value of APP sample was determined at APP: water ratio of 1:5 with a pH meter (PHS-2F and DDS-11A, Shanghai INESA Scientific Instrument Co., Ltd). The solubility of APP was measured according to Wu et al., (2010). Briefly, APP sample was continuously added into a 250 mL beaker and dissolved with 100 mL Milli-Q water until the solution was over-saturated (25°C), then the suspension was filtered and a total of 10 ml of the filtrate was piped in a beaker, then it was dried to constant weight at 105°C and weighted. The solubility of APP was calculated (g/100ml H\textsubscript{2}O).

2.5.6.7 Salt index (SI)

The salt index of APP was measured according to Latifian et al., (2012). Briefly, an aliquot of 1.0 g of APP fertilizer and sodium nitrate were dissolved with 200 mL of Milli-Q water in a beaker. After 24 h, the electrical conductivity of solution was measured using conductivity meter (DDS-11A, Shanghai INESA Scientific Instrument Co., Ltd).