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Mechanochemical Synthesis of Polymorphic Urea·Adipic Acid Cocrystal as a Sustained-Release Nitrogen Source

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A 2:1 urea·adipic acid cocrystal was obtained in two polymorphic forms (Form I reported earlier, and Form II synthesized in this study) using mechanochemistry as well as solution crystallization. Lower solubility and leaching study showed the newly synthesized urea·adipic acid 2:1 cocrystal to be an efficient sustained-release nitrogen fertilizer compared to commercially available urea.

Introduction

Fertilization and agriculture are closely related to each other. Fertilizers manage micro- as well as macro-nutrients required by crops. Nitrogen is a key nutrient source in biomass, food, and fiber production in plants, and urea is the most widely used plant nutrient as nitrogen source.[1] Urea has the highest nitrogen content among all commercially available solid fertilizers; however, runoff and eutrophication are two major issues of urea due to its high solubility ($\approx$110–170 g per 100 mL at 20–40 °C), volatilization, and moisture uptake properties.[2] Approximately 50–70 % of the urea used in soil is lost to the environment due to hydrolysis of urea during its use as fertilizer.[3] Nickel-containing metalloenzyme urease, present in numerous bacteria, fungi, algae, plants, as well as in soils as soil enzyme, accelerates the hydrolysis reaction of urea to a rate of 10^{15} times compared to non-enzymatic reaction.[4] The hydrolysis of urea results in formation of carbon dioxide and ammonia along with NH_4^+ and HCO_3^- ions as intermediates.[5] Due to the release of ammonia, the soil pH increases to a significant amount,[6] while also affecting the global nitrogen cycle.

In order to control stability of urea overhydrolysis, two different approaches have been used. First, by coating or encapsulating urea granules and/ or copolymerization of urea with reactive organic molecules such as formaldehyde;[7] and secondly, by addition of urease inhibitor along with urea, in order to inhibit the activity of the enzyme.[8] However, these approaches cannot minimize the solubility as well as hygroscopicity of urea, as factors that reduce leaching of urea during its application to the soil. Very recently, a third approach based on crystal engineering[9] and mechanochemistry[10] has been utilized in order to prepare cocrystals of urea (ionic as well as neutral organic) in order to reduce solubility and hygroscopicity of urea. Baltrusaitis and co-workers reported several ionic cocrystal systems of urea with inorganic acids or their metal salts in order to enhance stability of nitrogen fertilizer.[11] Among them, one of the ionic cocrystals of urea with KCl and $ZnCl_2$ in 1:1:1 has been obtained in dimorphic form based on their method of preparation.[12] In 2019, Casali et al. reported urea·catechol cocrystal that inhibits urease activity and provides improved environmental stability towards hydration compared to pure urea.[13] In another report, Aakeröy and co-workers investigated the solubility profile of a few organic cocrystals of urea and proposed urea·pimelic acid and urea·4-nitrophenol as potential multi-component solid fertilizers as alternative to urea.[14] In a very recent report, Friščić and co-workers investigated water-based autocatalysis of mechanochemically synthesized calcium urea phosphate cocrystal using in-situ Raman spectroscopy and synchrotron powder X-ray diffraction (PXRD).[15]

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