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EDITORIAL

Urea cocrystals: the fertilizer industry's next big thing

Global agriculture is being confronted with serious challenges, such as diminishing yields, shrinking cultivated areas, inefficient soil nutrient provision, poor plant absorption, and environmental damage. Nitrogen (N) is the primary nutrient used in agriculture to produce food, fiber, and biomass. Additionally, it is a crucial element in the composition of fertilizer formulations. Conventional fertilizers often lose 50 to 70 percent of their nitrogen content through processes such as leaching, volatilization, and nitrification. The loss in question presents both environmental risks and economic expenses (Schlesinger et al., 2001). Hence, there is a pressing need for eco-friendly fertilizers that can augment crop quality and optimize the efficiency of nitrogen utilization by plants (Zheng, et al., 2015). The implementation of slow-release fertilizers in recent times has successfully reduced the loss of fertilizer nutrients by regulating the rate at which plant nutrients are delivered into the soil medium. On the other hand, the rapidly progressing field of nanotechnology has played a role in developing slow release nanofertilizers that outperform conventional polymer-coated delayed-release fertilizers in terms of effectiveness. To manufacture fertilizers, plant nutrients like urea are encapsulated inside nanoporous matrices, nanoparticles, or nanoemulsions (Madusanka et al*.,* 2017).

Recently, a new crystal engineering-based strategy has come to light. In this method, the rate at which urea is released is controlled by cocrystallizing it with a suitable co-former, which should not dissolve easily in water. As the name suggests, cocrystals are solids that are made up of two or more different molecular and/or ionic compounds, usually in a stoichiometric ratio, that are neither solvates nor simple salts. Cocrystals exhibit non-covalent interactions such as Vander Waal forces, Pi bonds, and H-bonds. Mixing a coformer with an active ingredient synthesizes cocrystals, which heavily depend on the coformer for their characteristic features. They are chosen based on their pKa values, compatibility with supramolecular synthons, and capacity to form hydrogen bonds. We should classify the choice of coformers as safe or nontoxic to the entire ecosystem.

There are a few reports on urea cocrystals in the literature to date. Sandhu et al. examined the crystalline structure of urea by utilizing comprehensive interaction maps (FIMs) to create cocrystals of urea with different neutral organic coformers. Among the 60 coformers that were examined, spectroscopic investigation revealed that 49 of them (81%) formed cocrystals with urea (Sandhu et al., 2018). In 2019, Casali et al. published a study in which they described the synthesis of a cocrystal of urea and catechol (Casali et al., 2019). The cocrystal was synthesized by milling the two reactants in a 1:1 stoichiometric ratio. The choice of catechol as a conformer was based on its capacity to hinder soil urease activity. Parakatawella et al. recently published a study on a urea·adipic acid cocrystal synthesized using mechanochemistry (Parakatawella et al. 2022). This cocrystal can serve as a substitute for nitrogen. A thermodynamically stable cocrystal form (form II) was produced, which exhibited improved moisture stability, low solubility (about 77 mg per 1 mL; a 96.8% drop in solubility compared to pure urea), and sustained release properties. The investigation on urea release shown that the recently produced cocrystal required 18 days to release approximately 90% of urea, whereas commercial urea reaches its maximal release (around 85%) after 10 days. The increased strength of hydrogen bond interactions in the cocrystal enhances the resistance of the newly synthesized solid form to volatilization.

In 2023, Ragbongshi et al. published a study on urea cocrystals/salt that used substituted hydroxybenzoic acids as model humic materials (Rajbongshi et al., 2023). The aim of the study was to investigate the enhanced physicochemical features of these materials. The prepared urea cocrystals/salt exhibit enhanced hydration stability and demonstrate a substantial increase in soil nitrogen absorption. Additionally, the synthesized cocrystals/salt exhibit sustained-release behavior, allowing for prolonged nitrogen absorption by plants compared to commercial urea. Currently, numerous research endeavors are underway worldwide to assess the efficacy of urea crystals at the field level.

Mechanolochemical methods as a green manufacturing technologies for urea cocrystal production

Another significant benefit of cocrystals is their ability to be manufactured using solvent-free mechanochemical processes. Mechanochemical procedures involve reactions that take place in the solid state, triggered by the application of mechanical energy by grinding. The process of obtaining cocrystals can be categorized into two basic techniques: neat grinding and liquid assisted grinding. Neat grinding is a process where the stoichiometric components of the cocrystal are mixed together in their dry solid states, and energy is applied by friction. Liquid assisted grinding, often referred to as solvent drop grinding, kneading, or wet co-grinding, is a technique that includes adding a tiny quantity of liquid to enhance the speed of cocrystal formation in the solid state. Liquid-assisted grinding is generally more effective than neat grinding since it typically leads to increased crystallinity of the material, higher yield, and less energy consumption. Mechanochemical synthesis methods have garnered worldwide attention in the industry

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in recent years due to their economic advantages and environmentally friendly nature (Madanayaka et al., 2023).

Nanoscale cocrystals for further improvements

Cocrystals with particle size in the nanoscale range (1-100 nanometers) are considered as nanococrystals. The large surface area-to-volume ratio of nanococrystals makes them unique. It is produced similarly to cocrystals, but with far better qualities. The surface area-to-volume ratio rises as particle size approaches the nanoscale, and this can have an impact on characteristics including solubility, physical reactivity, and bioavailability of the plant nutrient formulation.

Future trends in uranium cocrystal research

The leaching, volatilization, and nitrification of urea in soil pose numerous environmental hazards and financial losses. Crystallizing urea with the right cofomers is an interesting way to change the rate at which urea is released so that you can control how much nitrogen is released from fertilizer mixtures. Although the literature has described a number of urea-based cocrystal systems, it currently lacks knowledge about their release in soil mediums or field investigations. It is also important to note that research into nanoscale cocrystals for use in fertilizers and agrochemicals is very promising, as it offers a chance to modify their characteristics, such as release rates and bioavailability, due to the improved physical and chemical qualities found in nanosized particles.

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