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REVIEW ARTICLE

Mechanochemical Synthesis of Slow-release Fertilizers: A Review

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Abstract:

Aims/Objective:

This review discusses the processes and applications associated with the mechanochemical synthesis of Slow-Release Fertilizers (SRF) from different resources.

Explanation:

The effect of mineral fertilizers on the environment and on living species will be discussed. Moreover, various aspects related to fertilizers production and applications are illustrated. It is found that solid-solid mechanical interaction initiates chemical reactions by lowering their energy of activation when compared to other thermochemical processes. Since milling is an important industrial operation, its contribution to materials processing is discussed.

Conclusion:

In general, SRFs increase the value of nutrient uptake in plants and reduces energy consumption and labor costs.

Keywords: Mechanochemical, Slow-release fertilizers, Milling, Review, Solid-solid mechanical interaction, Thermochemical.

1. INTRODUCTION

The main purpose of this review is to shed light on the processes and applications associated with the mechanochemical synthesis of Slow-Release Fertilizers (SRF). The rapidly increasing world population requires higher quantitative and qualitative agricultural productivity. Higher food crop yields have been achieved by improving soil productivity through the addition of fertilizers. This is considered to be one of the vital input materials for sustainable crop production [1 - 3]. A major drawback of conventional fertilizer is their fast dissolution in soil relative to their absorptivity by plants. Consequently, water runoff results in the loss of fertilizers material and contamination of the surrounding environment. In order to improve the efficiency of chemical fertilizers and reduce the loss of the nutrients they supply, many research has been focusing on the development of Slow-Release Fertilizers (SRF) or Controlled-Release Fertilizers (CRF) in an attempt to minimize the difference between solubility and uptake [4, 5]. Producing or synthesizing SRF and CRF include physical methods such as dispersing ordinary fertilizers throughout a matrix and chemical methods such as encapsulating ordinary fertilizers within a larger compound. Both methods aim at slowing down the release of nutrients either by diffusion or dissolution [6 - 13]. The encapsulation method that is used to produce SRF involves the formation of an organic or inorganic film as a coating on the surface of fertilizers granules [14]. The use of organic films in coated fertilizers has negative impacts on the quality of soil and hence it is avoided.

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1.1. Mechanochemistry Applications

Mechanochemistry, as a term, was introduced in 1887 by Ostwald who studied chemical reactions from an energetic point of view [15]. In 1984, Heinicke formulated a definition which has become accepted by the scientific community. He stated that mechanochemistry is a branch of chemistry in which mechanical energy is applied to materials causing chemical and physicochemical transformations regardless the state of aggregation [16]. Another definition from the IUPAC Compendium of Chemical Terminology describes mechanochemistry as the direct adsorption of mechanical energy to cause a chemical reaction [17]. In 1974, Juhasz proposed that mechanical processes are divided into primary and secondary processes [18]. The primary processes include the increase in internal and surface energies, increase of surface area and decrease of coherent energy of solids which all increase the reactivity of the mineral. The secondary processes such as aggregation, adsorption and crystallization take place spontaneously in activated systems during or after grinding has been completed [18]. This two-stage process was later verified by Molčanov *et al.* in 1988 [19]. There are two major pathways in mechanochemical applications for extractive metallurgy: dry milling (DM) and wet milling (WM) [6]. In DM processes, the milling and leaching are two distinctly separated processes, while in WM milling and leaching are performed simultaneously in one step [6]. The equipment used to achieve mechanical activation comprises retch mills, tumbling mills, stirring ball mills, vibratory mills, pin mills, rolling mills and planetary ball mills.

Mechanochemistry has been applied in a large number of different areas of engineering including chemical, materials, mineral processing, coal industry, building industry, pharmacy, agriculture and metallurgy [20]. There is a continuing and seemingly increased interest in the research field of mechanochemistry with a large number of relatively new review articles. A review giving a survey of classical works in mechanochemistry where the results are put in perspective of fundamental research of atomic force microscopy and quantum molecular dynamics simulations is given by Beyer and Clausen-Shaumann [21]. Applied extractive metallurgy was reviewed by Baláž and Dutková [22, 23]. Recent reviews on the application of mechanochemistry for metal recovery from secondary resources have been written by Ou *et al.* [24] and by Tan and Li [25].

Solid-state inorganic chemistry is typically performed using the “shake and bake” method, involving multiple grinding and calcination steps. This can be a lengthy and energy-intensive route to the synthesis of various inorganic systems, such as pyrochlores, spinals, and perovskites [26 - 28]. An alternative route to the synthesis of these materials can be achieved through mechanochemistry. Since mechanochemistry tackles ultra-fast chemical reactions. Molecular bonds are likely to undergo mechanical breakage in solids or solids and surrounding gaseous or liquid molecules that are under mechanical forces, This process can induce electronic transfer, triboelectricity (known as mechanoelectricity), and triboluminescence. Thermal expansion, piezoelectric effects, or pressure induced compression are also part of it [29, 30]. Compared to conventional processes of milling, mechanochemical processes are considered environmentally friendly. They are simpler to operate, safer as a minimum amount of solvents is used. One more advantage is that in mechanochemistry, it is easier to produce metastable state products compared to other conventional methods. Recently, the historical development of mechanochemistry and the mechanically induced self-propagating reaction (MSR) has been reviewed [31]. The authors reviewed MSR experimentally and theoretically with specific examples about the mechanism of MSR processes [31]. Tribochemistry (where tribo stands for friction) is the organic mechanochemistry and considered as a subset of mechanochemistry or generally: inorganic mechanochemistry [30].

1.2. Ball Milling and Mechanochemistry

Mechanochemical processing uses ball mills as means of powder activation during chemical reactions [32]. Many factors affect the process including: the mechanics of the mill. The thermal factor, loading conditions and pressure-torsion factor [33]. Mechanochemical synthesis uses high-energy ball milling exploiting the thermal relaxation and the vigorous motion of the milling balls. The motion and mixing processes of powders are essentially mechanical. Particle size reduction is a direct result of the powder activation due to that a major part of the energy consumption of ball mills is used in the creation of fresh surfaces [34]. Compared to other chemical processes, a mechanochemical process is more complicated than a photochemical one [32].

Mechanochemistry is a sustainable and ecological technology. Mechanical energy causes a strain in the bulk after material removal [30]. Many researchers have reviewed this topic extensively [29, 35, 36]. They tackled industrial applications of mechanochemistry and underlined the need for their sustainability [29] and the ease of manufacturing processes. Such processes in addition to new technologies help lowering the environmental demands, *e.g.* reducing the needed energy and using less harmful organic solvents.

Milling is important in the production of materials including minerals, food, medicine, chemicals and building. Being a solid state reaction, synthesis, separation and recovery of chemical products is useful, as well [37]. A combined mechanochemical method has proved to be an excellent choice for the synthesis of new compounds; it consists of co-grinding two or more elements or compounds [38]. Agriculture is a sector of the economy that plays a very crucial role in the world as a food producer and as a place of employment for millions of people. Recently, the intensification of agricultural production has become possible due to the use of high yielding varieties, irrigation and mechanization as well as to the soil feeding with mineral fertilizers and the crop protection with pesticides [38]. Consumption of these agrochemicals essentially increased during the last fifty years, resulted not only in the growth of agricultural production but also in the pollution of natural environment [39].

Mineral fertilizers are important in the agricultural industry. They provide nutrients to crops and increase their growth in addition to controlling the pH values of the soil. The production and consumption of mineral fertilizers is on the increase due to the need of more food [1].

Mechanochemical activation of layered minerals, especially clay minerals, has been studied extensively in the past and the observed effects include: increase of defects in the materials, increases in the chemical reactivity and solubility of the minerals, reduction of thermal stability and mechanochemical intercalation [40 - 47].

The rapidly increasing world population requires correspondingly higher agricultural productivity. Normally, higher food crop yields have been achieved by improving soil productivity through the addition of fertilizers, considered to be the vital input material for sustainable crop production [1, 39]. Fertilizers dissolve in soil, however, much faster than plants can absorb it, and the consequent runoff results in the loss of fertilizers and contamination of the surrounding watershed. From the environmental protection point of view, lower nutrients assimilation is a major issue [38]. It leads to the environmental dispersion of excess biogenic compounds that were not completely used up in the plant production. Thus, the migration of these compounds in the global aspect begins. In many ecosystems, the consequences of that dispersion are comparable with geological and geochemical processes lasting millions years. Mineral fertilizers compounds migrate from soil to water ecosystems along with the areal run-offs and as a result of erosion and rinsing out. It is the reason of accelerated contamination and eutrophication of surface and sea waters [48, 49].

Because of the soil microorganisms mineral nitrogen is transformed to nitrates that are soluble in soil. Nitrates leave the soil to ground and surface waters. The biggest potential danger of nitrates leaching can be met on the light soils. Higher nitrates concentration in water has many biological and health effect on humans and animals [38, 39]. For the soil, changes in nitrates concentration affect the degree of salinity and pH of the soil [50].

One of the first documents that raised the environmental concern from fertilization practices was put forth by the Clean Water Act of 1972. It dealt with phosphorous and nitrogen being the greatest risk for contamination due to its high usage [51]. Nitrogen, being the most limiting nutrient in most systems [52, 53], happens to be often discussed in relation to losses and waste during production. Several studies still focus on N because it is the primary nutrient most prone to leaching and groundwater contamination [54]. It is also important to reduce nitrogen consumption because of its high cost [55 - 57]. Depending on the crop and fertility program, a large portion of the nitrogen applied may be lost through leaching into the soil profile or disposal into sewer systems and consequently rivers and streams [58]. Nutrient leaching occurs especially under production conditions of high rainfall or heavy irrigation [59]. Nitrogen leaching can lead to groundwater contamination, and may eventually enter surface watersheds, eventually dispersing into the ocean [60]. Groundwater contamination can result in levels in excess of the maximum nitrogen concentration of 10 mg/L allowed by the EPA [60]. Phosphorous is also problematic because it has the ability to contaminate surface water and is also easily leached from the soilless substrates commonly utilized in the floriculture industry [61]. Excessive fertilization practices may also result in ammonia volatilization, nitrous oxide emission (and thus ozone destruction), degradation of soils, algal growth, eutrophication, and other related forms of pollution [62].

Preparation or synthesis of slower or controlled release fertilizers (CRF) usually takes place through physical methods such as dispersion of ordinary fertilizers in the matrix or encapsulating ordinary fertilizers, in which nutrient release is slowed down by diffusion, is widely discussed in literature [63 - 65]. In a recent studies, mechanochemical synthesis was applied to prepare complex compounds that may be excellent candidates for slow release fertilizers. Makó *et al* [66]. have reported the intercalation of urea into the kaolin structure by a mechanochemical process involving milling and compared against the aqueous suspension method. Solihin *et al*. [67] have successfully synthesized KMgPO_4 and NH_4MgPO_4 compounds by mechanochemical process.

Tongamp *et al*. [68] have reported the incorporation of the nitrate ion into the Mg -Al- NO_3 type layered double

hydroxide structure using mechanochemical process. The mechanochemical reaction process can allow the intercalation of target materials in which the crystal structure of kaolin and the layered double hydroxide are maintained. Balaž and Dutkova [69] discussed the mechanical activation of the fluoroapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) mineral that is normally used for the production of phosphorus fertilizers. Minjigmaa *et al.* [70] discussed the fine milling in applied mechanochemistry and its application in agriculture for the production fertilizers. The experimental procedures for many prepared SRF can be summarized by a few steps. The three materials are mixed at certain measured proportions. The materials are exposed to mechanochemical grinding where the collected samples are analyzed using XRD, DTA or FTIR. The samples then undergo the leaching process and finally tested for chemical composition as soil nutrients.

In order to reduce the loss of the nutrients they supply, and to improve the efficiency of chemical fertilizers, attention has focused on the development of SRF and CRF which attempt to minimize this difference between solubility and uptake [4]. A combined Mechanochemical method has proven to be an excellent choice for the synthesis of new compounds; it consists of co-grinding two or more elements or compounds [60, 61]. Recent research has successfully applied this method to the synthesis of complex compounds that are promising candidates for an effective SRF—for example, the synthesis of KMgPO_4 and NH_4MgPO_4 [65], the complex compounds kaolin- NH_2CONH_2 (or KH_2PO_4 , $\text{NH}_4\text{H}_2\text{PO}_4$) [51, 52], and the synthesis of $\text{K}/\text{NH}_4\text{-Al-P-O}$ and Mg-Al-NO_3 [66, 76]. Slow-release potassium fertilizers have also been synthesized in previous studies using a mechanochemical reaction: co-grinding KH_2PO_4 with other chemical reagents, such as $\gamma\text{-Al}_2\text{O}_3$, $\text{Mg}(\text{OH})_2$ and $\text{Al}_2\text{Si}_2\text{O}_6(\text{OH})_4$. All these studies have produced fertilizers with more than two nutrients—nitrogen, phosphorus or potassium. In the case of clay minerals, the process consists of grinding the material with a conventional, usually highly soluble, fertilizers to obtain nanostructured metastable phases that provide slow release of nutrients. The delay in the availability of nutrients for plant uptake and use after application and/or extension of their availability in the soil is the main characteristic of this type of fertilizers [71].

1.3. SRF and CRF Preparation

SRF fertilizers do retard the initial availability and extend the time of continued availability [72]. Stabilized fertilizers refer to those modified during production with a nitrification inhibitor. In all other cases, fertilizers and nitrification and urease inhibitors are separate [72]. The development of slow-release fertilizers is based on the need to improve the performance of conventional fertilizers [73 - 75] and minimize socio-environmental problems by reducing pollution caused by the excess nutrients used in agriculture [74]. Slow-release fertilizers also enhance the production of food and prevent damage from the potential loss of conventional compound-mineral fertilizers through leaching and volatilization [75]. SRFs also slowly release nutrients, but this occurs primarily due to microbial activity and/or chemical hydrolysis [56]. In order for adequate release to occur, sufficient moisture and warm temperatures (generally above 20 °C) must be present in order to initiate and encourage microbial activity [62]. SRF substances are only slightly soluble and require additional time for mineralization, thereby giving them slow-release properties. SRF materials may be organic or inorganic, and unlike CRFs are uncoated [62]. A primary example of an organic slow-release fertilizers is compost. Inorganic examples include urea-based fertilizers (such as urea formaldehyde, isobutylidenediurea, and triazone), magnesium ammonium phosphates (MagAmps) and other materials which degrade biologically and aren't easily soluble [62, 76].

Efficiency of dissolution of chemical fertilizers is very important in the plants adsorption of fertilizers [77, 78]. The limited resource requires measurement to raise the efficiency so that a concept of slow-release fertilizers (SRF) appears. The current technology to produce SRF is mainly polymer film coating of a fertilizer grain [79]. Coated slow-release fertilizers (CRF) are a new kind of fertilizers that provide nutrient release in balance with crop needs. CRF includes inorganic materials and/or organic polymers and is slightly water soluble, with the granular fertilizers at its core [80]. This coating changes the nutrient solubility characteristics and lengthens and controls nutrient release. Studies on CRF have provided new ideas for improving fertilizers use efficiency and minimizing pollution to the environment due to fertilizers losses. Scientific basis has been provided for the research and application of environment friendly, cheap, and new coated slow-release fertilizers [80]. The use of C/SRFs in crop production has demonstrated much success. There are many advantages to using C/SRFs in bedding plant production and other agricultural crops. C/SRFs have demonstrated the following advantages: i) Nutrients are better utilized when slowly released throughout a season rather than applied in “bursts” or instantly soluble applications such as is the case in WSF (water-soluble fertilizers) application, thus increasing nutrient use efficiency and perhaps more closely synchronizing release rates with plant demand [51, 53, 56], ii) The quantity of fertilizers used is also reduced, leading to less of a risk for plant injury through high soluble salt levels [54]. C/SRFs are used primarily in specialty markets such as nursery (woody- plant) production

and compose only 0.15% of the current fertilizers market with demand rising by approximately 5% annually [56, 81]. These fertilizers are often utilized in a nursery setting in order to reduce nutrient losses due to high irrigation or rainfall and a wide variability in temperature [58]. In contrast, such conditions are not likely to be encountered in a greenhouse setting, which is under constant environmental control [51]. In this context, it may be more difficult for greenhouse growers to recognize the potential advantages of fertilization with CRFs. Zhong *et al.* integrated water-retaining and controlled-release fertilizers. The results showed that CRF possessed excellent sustained-release property of plant nutrient and could improve the phosphorous release greatly [82]. Rashidzadeh and Olad studied a novel slow-release NPK fertilizers encapsulated by superabsorbent nanocomposite involving the mineral clay montmorillonite. The results indicated that the presence of the montmorillonite caused the system to liberate the nutrient in a more controlled manner than that with the neat superabsorbent. The good slow-release fertilizers property as well as good water retention capacity is important for application in agriculture as a fertilizers carrier [83]. Du *et al.* studied the effect of several slow-release fertilizers on decreasing ammonia volatilization and nitrogen leaching. The results indicated that

CRF development is a green technology that improves the kinetics of nitrogen release [84]. Zhang *et al.* studied slow-release fertilizers encapsulated by graphene oxide films, and the results showed that new coating technology is promising for developing environmentally benign CRFs for crop production [85, 86]. Muldera *et al.* developed an economically feasible and biodegradable slow-release coating for urea. The results showed that lignin provides high potential as a coating material [87]. Du *et al.* studied the waterborne silicone-acrylate emulsions with excellent performance of nutrient controlled release, which provided novel and improved materials for coated CRF industry [88]. Wenyi Yuan *et al.* developed and synthesized a slow-release K-Si-Ca-O compound fertilizers through a mechanochemical process, with starting materials of KOH, SiO₂ and CaO. The results indicated that the decrease in the K⁺ release rate from the synthesized compound can be attributed to the formation of a K-Si-Ca-O glass phase. The leaching test showed that the prepared sample had with a low nutrient release level, at approximately 25%, suggesting that this mechanochemical method is an easy and economical route for the synthesis of slow-release potassium fertilizers, using simple hydroxides or oxides as the starting materials [14]. Qiwu Zhan *et al.* synthesized a glass phase of K/NH₄-Al-P-O through the mechanochemical reaction of KH₂PO₄/NH₄H₂PO₄-Al₂O₃-AlPO₄. Leaching tests proved that the new fertilizer is a slow release with the dissolution of fertilizers nutrients of phosphate nutrient of 10% [89]. Sahnoun *et al.* investigated the effects of the addition of KH₂PO₄, K₂HPO₄ and K₃PO₄ to kaolin by mechanochemical treatment for the synthesis of new complex compounds. These compounds are offered as slow-release fertilizers. After, the characterization of the ground kaolin, the authors concluded that two hours of milling are sufficient to achieve the distortion of the crystalline network of kaolin in order to insert additives [90].

CONCLUSION

Slow-release fertilizers are quite numerous and diverse group of materials are involved in the improvement of the effectiveness of fertilization, mitigation of the negative impact of fertilizers on the environment and the reduction of labor and energy consumption connected with the application of conventional fertilizers. Slow-release fertilizers comprises materials with complex structure and little solubility in water such as the urea-kaolin products. Various synthetic organic products, matrix-based formulations, with the nutrients dispersed in the polymeric or inorganic matrices and polyphosphate-based micronutrient fertilizers. Many fertilizers are commercially important and are shown to be excellent in the area of environmental protection, as well. A mechanochemical process only needs very simple equipment. It is a fast, economic and ecological. Thus, this technology does significantly and positively contribute to the fertilizers industry. However, it should be noted that the majority of research in this field is still in the experimental stage, and there needs some work to do in order to reach better product commercialization. The efficiency of mechanochemical treatment and the properties of materials obtained or treated by mechanochemical processes needs further improvement. This review highlights the prospective future of mechanochemistry in the slow-release fertilizers area.

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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