

Controlled-Release Fertilizers: Advances and Challenges

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Abstract: Controlled-release fertilizers (CRFs) offer an excellent option to improve nutrients uptake by plants and reduce the environmental hazards due to excess release of chemicals. Polymer-coated fertilizers, compared to the other types of CRF, are by far the most intensively researched topic because of their great characteristics. Polymer-coated fertilizers, which are less sensitive to the soil and environmental factors, offer superior control over nutrients release for plants uptake. In recent years, the art has mainly focused on the design of biodegradable polymer-based coating for fertilizers considering the effective control on nutrient release. This review covers the basic information about CRFs with an emphasis on the development of polymer-coated fertilizers. Topics that are discussed herewith include materials and methods utilized for coated fertilizer, particularly polymer-coated fertilizers, manufacturing and related issues. The large market potential for fertilizer using necessitates more studies for development and commercial production of polymer-coated fertilizers.

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1. Introduction

The growth of plants and its quality are mainly a function of the fertilizer quantity and water used (Wu, 2008). Depending on application methods and soil condition, some amount of the nutrients from the conventional fertilizers cannot be absorbed by plants and is lost to the environment (Fan, 2004; Chien 2009). This phenomenon not only causes large economic and resource losses, but also causes serious environmental pollution (Wu, 2008; Jarosiewicz, 2003, Hafshejani, 2013). One alternative route to effectively reduce the loss of fertilizer nutrients is utilizing of controlled-release fertilizers (CRF) (Wu, 2008; Akelah, 1996; Shaviv, 2000; Jin, 2011; Dave, 1999). CRFs are commonly defined as products or materials in which the release of nutrients to the soil for plant uptake takes place at a pre-determined time and rate (Jain, 2007). The release of nutrients is controlled through special chemical and/or physical characteristics, such as hydrolysis, degradation or diffusion (Bhattacharya, 2000) and the rate of nutrient dissolution is synchronized to the plant needs. Compared to the conventional fertilizers, the advantages of CRFs are numerous. The most important one is increasing the efficiency of nutrients uptake by gradual release of the nutrients that may better coincide with the plant needs and consequently increase the grain yield (Carreres, 2003; Munoz, 2005; Cong, 2010). As the nutrients are released at a slower rate throughout the season, the nutrients supply can be sustained for a prolonged time, and consequently lower the labour cost by eliminating

the need for labour associated with repeated fertilizer application (Cong, 2010; Jacobs, 2004). Another imperative advantage of using CRF is reducing the rate of nutrient removal from soil by rain or irrigation water (Cong, 2010). The other benefits of using CRFs over conventional fertilizers mentioned in the literatures (Jain, 2007; Cong, 2010; Tomaszewska, 2004) can be addressed as:

- No problem on fertilizer burn even at high rates of application,
- Reduction of seed or seedling damage from high local concentrations of salts,
- Reduction of leaf burn from heavy rates of surface-applied fertilizers,
- Improved storage and handling properties of fertilizer materials,
- Reduction of the eutrophication of natural waters caused by excessive concentration of nitrogen and phosphorus compounds, and
- Minimal negative toxic effects associated with overdose of fertilizers.
- Reduction of urea decomposition due to higher temperatures and bright sunlight (Dave, 1999).

Besides all the listed benefits, Rudjak et al. (2010) indicated that coating of ammonium nitrate leads to higher thermal stability of this fertilizer. Thermal instability of ammonium nitrate makes its handling and storage unpredictable, which has led to several catastrophic explosions (Dechy, 2004; Oxley, 2002). Numerous researchers have investigated the

thermal behaviours and the possibilities of increasing the thermal stability of ammonium nitrate (Sun, 2005; Wu, 2008; Skordilis, 1993; Simoes, 1998).

2. Typical routes for manufacturing of CRF

A few important manufacturing routes for CRFs are listed as follows

Complex fertilizers: The nutrients release is chemically controlled. These products are slightly soluble materials because of the complex or high molecular weight chemical structure. Examples of such fertilizers are urea-formaldehyde, polyphosphate, isobutylidene, diurea, and crotonylidene diurea (Chien 2009; Jarosiewicz, 2003; Liang, 2006; Al-Zahrani, 2000; Bandyopadhyay, 2008).

Urea-formaldehyde products are commercially known as Nitroform, Ureaform, Methylene Urea, Blue Chip, Nutralene or Methex (Jain, 2007; Wang, 2001).

Coated fertilizers: A fertilizer core is given a protective cover (water insoluble, semipermeable or impermeable with pores) and the release of nutrients is generally controlled by diffusion through the coating. The conventional materials applied as fertilizer coatings can be classified as inorganic materials, such as sulfur, phosphates, and silicates; or organic materials, like polyethylene, poly(vinyl chloride), poly(lactic acid) and wax (Chien 2009; Jarosiewicz, 2003; Trenkel, 1997; Wu, 2007).

1. **Encapsulated fertilizers:** Materials releasing nutrients through a membrane which may or may not itself be soluble (Trenkel, 1997). In most of the references, this type is not distinguished from coated fertilizers.

2. **Matrix-Based CRFs:** Nutrients are incorporated into a matrix, which itself may be coated. Different materials are used for fabricating the matrix phase, in which the fertilizer is dispersed. The materials used for preparation of matrices are subdivided into hydrophobic materials, such as polyolefin and rubber, and hydrophilic materials which are gel-forming polymers (sometimes called "hydrogels"). These materials, which are hydrophilic in nature, reduce dissolution of the soluble fertilizer due to their high water retention (swelling) (Jarosiewicz, 2003; Shavit, 2003). In general, the matrices are less common in practice than the coated fertilizers (Jarosiewicz, 2003).

3. **Other types of CRF:** like super-granules (Kapoor, 2008) briquettes (Savant, 1998).

The majority of CRFs developed to date are grouped in the second category, which is a coated fertilizer. The focus of this paper will then be on this type of CRF.

3. Coated Fertilizers

Conventional soluble fertilizer materials, after granulation, prilling or crystallization, are given a protective coating to control the water penetration and thus the rate of nutrient release. Nutrient release from

coated fertilizers basically occurs by diffusion through a coating material, which is permeable or semi-permeable. The mechanism of nutrient release is accomplished in two stages; soon after application and exposure to moisture, water vapour infiltrates into the coated fertilizer and condenses on the soluble fertilizer salt, creating an internal osmotic pressure gradient. The elevated pressure within the product then allows the fertilizer salts to leak into surrounding media (Jacobs, 2004). The pattern of nutrient release from coated fertilizers is directly influenced by several factors, such as type of coating, coating agents, coating process and coating quality, for example thickness and surface characteristics (Tzika, 2003; Hanafi, 2000). In general, porous and thin coatings result in high nutrient release rates, whereas smooth, uniform and thick coatings indicate well-controlled and substantially retarded nutrient release rates (Hanafi, 2000). It is obvious that cracks in the coatings cause immediate release of nutrients when the fertilizer is brought in contact with water (Chien 2009). Accordingly, the longevity of the coated fertilizers, i.e. the rate of nutrient release can be, to a certain extent, controlled by manipulating the properties of the coating, either its thickness or chemical composition (Jain, 2007; Jacobs, 2004; Trenkel, 1997; Shaviv, 2005; Shoji, 2001; Wen, 2001).

It is worth mentioning that, the physical characteristics of the substrate on which the coating is applied, such as particle size, shape and surface, also affect the pattern of nutrient release (Hanafi, 2000; Trenkel, 1997). A suitable pre-treatment of the fertilizer to produce more uniform and regularly shaped granules does significantly improve the quality of the coating and therefore release characteristics of the coated fertilizer (Hanafi, 2000). Other factors influencing nutrient release from coated fertilizers can be addressed as soil type, humus content in the soil, soil acidity, temperature, moisture (irrigation), and microbial activity in the soil (Jacobs, 2004). The quantity of the coating material used conventional soluble fertilizers depends on the geometric parameters of the core, such as granules to surface area and roundness as well as the target of longevity (Trenkel, 1997). Materials that ensure a controlled-release of nutrients to the soil by diffusion through the pores or by erosion and degradation of the coatings are generally applied as a coating on fertilizers. Materials currently used for fertilizer coating can be classified into two main categories namely non-organic and organic.

3.1 Fertilizers Coated with Non-Organic Coatings

Non-organic materials commonly utilized for fertilizer coating includes sulfur, silicate and phosphate compounds, such as phosphogypsum and attapulgite. Vermiculite or cement have been also applied (Chien 2009; Zhang, 2006; Hua, 2009; Ni, 2010; Wu, 2008).

Among these compounds, sulfur is by far the most common coating material used. Sulfur-coated urea (SCU) probably was the first coated fertilizer developed by the Tennessee Valley Authority (TVA) (Rindt, 1968). Its preparation is based on coating preheated urea granules with molten sulfur followed by spraying a wax layer that acts as a sealant and covers fissures or cracks in the sulfur coating. Finally, a conditioner layer is added. There are several reasons favoring the combination of urea and sulfur. Urea contains high amount of nitrogen concentration, therefore coating with sulfur results in a product with lower amount of nitrogen release. Urea is likely to volatilize and leach easily; consequently covering the urea granules significantly reduces the losses of ammonia. On the basis of economy and efficiency point of view, sulfur is selected as a coating material since it has low cost and is a valuable secondary plant nutrient. Besides that, sulfur coating gradually degrades through microbial, chemical and physical processes (Trenkel, 1997). The SCU dominated the market for years; however, agriculture markets required more control in longevity and efficiency of the nutrient delivery for plants uptake. In consequence, a new and modified coating method using organic polymers has been introduced and developed.

3.2 Polymer coating of Sulfur-coated fertilizers

Due to relatively poor performance of the SCU, a polymer-coated SCU (PSCU) was introduced into the market. In general, polymer-coated sulfur-coated fertilizers are called PSCFs. These products have a primary coating of sulfur and a secondary coating of a polymeric material. Sulfur-coated fertilizers are not attrition-resistant due to the nature of the sulphur, and additional layer of polymer improves the attrition resistance of the coated granules resulting more control on the release rate of the nutrients. The polymeric layer also provides a continuous membrane through which water and nutrients must diffuse (Jain, 2007). Consequently, this hybrid coating (polymer-sulfur coating) offers better control release of nutrients accompanied with a positive cost value over singular coatings of only sulfur or polymer. Another obstacle for application of large amount of SCU is that it may increase the acidity of the soil, since both sulfur and urea contribute to an increase in the soil acidity (Trenkel, 1997).

3.3 Fertilizers coated with organic polymer

In an effort to minimize the nutrients losses from fertilizer, polymer-coated fertilizers (PCFs) have been extensively considered. A wide variety of natural and synthetic polymers have been investigated for fertilizer coating. These polymers include Polyvinylidene chloride (PVDC)-based co-polymers, polyolefin, polyurethane, polyethylene, polyesters, polystyrene, alkyl resins, kraft pine lignin, polyacrylamide,

polysulfone, ethyl-cellulose, fatty acid salts (e.g. Castereate in Multicote which is stearic acid and calcium hydroxide), latex, rubber, guar gum, petroleum derived anti-caking agents and wax. Though all are classified under the general category of PCF, the coating technology differs greatly among producers, depending on the type of coating material and the coating process utilized.

Basically, there are two types of polymer coating namely thermoset resin and thermoplastic polymer (Jain, 2007; Jacobs, 2004; Salman, 1988).

The other types of PCF utilizes thermoplastic resins such as low-density polythene, polypropylene, ethylene/carbon monoxide copolymer, and poly(vinylacetate) (Ge, 2002). The commercial types of PCF are produced using thermoplastic resins like polyolefin, polyvinylidene chloride, and copolymers as coating materials. Thermoplastic resins are highly impermeable to water, and thus release controlling agents like ethylene-vinyl acetate and/or surfactants must be added to the coating to attain desired diffusion character (Jacobs, 2004). For the products of the same thickness, the amount of added release controlling agents determines the rate of nutrients release. For better control over nutrients release, a novel idea that is using nanoparticles in the coating has been recently presented (Teodorescu, 2009; Corradini, 2010). However a study on incorporation of the fertilizer into the nanoparticles is still new and novel, thus, more investigations are needed to strengthen the technology.

The profile of nutrients release from PCF is basically described in three stages: lag period, linear stage and decay period (Du, 2006 a). The nutrients release from PCFs is mainly controlled by diffusion mechanism and is dependent on the type of medium. The pattern of temporal release from PCFs is generally sigmoidal indicating that the release is complex and "non-Fickian" (nonlinear process) (Shaviv, 2003a; Shavit, 1995). For a certain PCF, the main controlled-release factors are the diffusion coefficient, thickness of coating, temperature, nutrient saturation concentration and granule radius (Du, 2005). The release of each nutrient also depends on its own solubility in solution, permeability through the polymer coating, water content, medium types and the interaction among nutrients that could be demonstrated by the saturated concentration (Du, 2005; Du, 2006 b).

The surroundings temperature and coating thickness are the most imperative factors since they influence the diffusion coefficient significantly. Lower temperature and thicker coating reduce the diffusion coefficient of the interface that the nutrients need to diffuse to, and therefore slow the release rate of the nutrients (Du, 2006 a). Huett and Gogel (2000) demonstrated that PCFs are resilient to high pot media temperatures with an about 20% increase in the rate of

nutrients release for a temperature increase of 30°C to 40°C for Nutricote and Osmocote formulations. Manufacturers attempt to minimize the effect of temperature on the pattern of nutrients release by dispersing mineral fillers into the coating (Jacobs, 2004). Detailed information on mechanisms, modelling and quantitative descriptions of nutrient release for PCF have been reported in elsewhere (Shaviv, 2003a; Du, 2006 b ; Shaviv, 2003 b; Du, 2008; Basu, 2008; Basu, 2010; Fujinuma, 2009).

The main important issue of the polymer-coated fertilizers is remaining of the coating materials in soil after nutrients release, since most of the polymers are very difficult to degrade. With the continuous usage of the fertilizers, the remaining coating materials will accumulate over time to become a new type of white pollution. Accordingly, many researches have focused on development of new polymeric coatings, which are environmentally safe and biodegradable (Tomaszewska, 2004; Wu, 2008; Mathews, 2010; Peng, 2011; Peng, 2010; Pe' rez-Garci'a, 2007; Wu, 2008; Sakai, 2003; Luckachan, 2011 Ibrahim, 2013; Rudnik, 2011). One example of this environmental-friendly coating material is photodegradable polyethylene that comprises ethylene-carbon monoxide copolymer and polyethylene with an iron additive (Sakai, 2003). In other cases, natural polymers such as lignin, lignocelluloses and corn starch, have been used as polyols in the preparation of biodegradable polymers. However, biodegradability is not the only issue and researchers encounter a principal difficulty, which is selection of the proper polymer for fertilizer coating. In order to guarantee the longevity of the PCF, no biodegradation, chemical degradation or mechanical destruction of the coating should occur during the active time of the fertilizer. In other words, it is desired that after the function of fertilization, microbial attack and/or mechanical destruction of the empty shell occur to decompose the coating over time (Trenkel, 1997). Water vapour permeability of the coating may help in this choice, as water permeability characteristic of the polymers control the rate of water diffusion into the particle (Devassine, 2002). Devassine et al.(2002) investigated the water vapour and liquid diffusion of several polymers and classified these polymers as a function of two properties, water vapour and liquid barrier, to select the best polymer(s) for coating. It was indicated that the crystallinity of the polymer affects the permeability and diffusion characteristics of the polymers. Crystallites interrupt the flow lines, leading to increase tortuosity of the diffusion path and consequently act as a crosslink, restraining the mobility of the chains. It was also indicated that polymers crystallinity reduces the water vapor permeability. However, very crystalline polymers have a low

solubility and then selection must be performed based on balance of these two parameters (Devassine,2002).

3.3.1 Hydrogels

Hydrogels, water-swollen polymer materials with a distinct three-dimensional structure, have been extensively applied in different fields such as bioengineering, biomedicine and agriculture (Shavit, 2003; Shaviv, 2003 a; Peng, 2010; Peng, 2011; Berger, 2004; Garcia, 1996; Vazquez-Duhalt, 2001). Hydrogel-based natural polymers like chitosan, lignin and cellulose attract a great interest because of their unique advantages, e.g., abundance, non-toxicity, biocompatibility and biodegradability. These polymers have been also applied in coating materials for slow release of agrochemicals and nutrients in agricultural applications. Release rate in hydrogel-based coating is controlled by wetting and swelling of the hydrophilic polymer and dissolution rate of the active ingredient (Shavit, 2003). It is influenced by the formation of the hydrogel matrix (i.e., wetting and confined swelling), the internal dissolution of the fertilizer and the advective-diffusive transport of the dissolved fertilizer (Shavit, 2003). Loading of a hydrogel is typically performed by two methods (Ward, 2001). In the first method, the compound, which needs to be loaded in gel, is added to the reaction mixture and polymerized in situ whereby the compound is entrapped within the gel matrix. In the second approach, the dry gel is allowed to swell in the compound solution. When swelling equilibrium is achieved, the gel is dried and the final product is obtained. There are several advantages and disadvantages for each technique (Liu, 2007). In the former technology, the entrapped compound may influence the polymerization process and the polymer network structure whereas for the latter approach, the loaded compound accumulates on the surface during the hydrogel drying, which consequently leads to a 'burst effect'. Besides that, the loading amount may be low if the compound affects the water absorbency strongly.

3.3.2 Superabsorbents

Fabrication of highly water-swallowable polymers using superabsorbents is now extensively considered for controlled-release of nutrients in agricultural applications. Superabsorbents are three-dimensional polymeric networks that can absorb and retain large volumes of water. Because of the unique characteristics of the superabsorbents, they are broadly applied in various fields, such as agriculture and horticulture, hygienic products, wastewater treatment, bio-medical area as antibacterial materials, and drug delivery. Incorporating fertilizers into a superabsorbent polymeric network was indicated as an effective method for enhancing the utilization efficiency of water and fertilizers (Wu, 2008a; Liang, 2006; Hua, 2009; Ni, 2010; Liu, 2007; Guo, 2005a; Guo, 2005b;

Liang, 2007; Zhang, 2006; Ni, 2009; Ni, 2010; Liu, 2006 a; Liu, 2006 b; Wang, 2012; Wu, 2003; Wu, 2008b; Zhan, 2004; Lee, 2005). These studies emphasize that using superabsorbent in synthesis of coated fertilizers can be tailored to enhance the water-holding capacity of the soil and properties of the coated fertilizer. The superabsorbents help to reduce irrigation water consumption, lowers the death rate of plants, improves fertilizer retention in soil, and increases plant growth rate (Liang, 2006; Zhang, 2006; Bakass, 2002; Li, 2005). The key properties of the superabsorbent polymers are the water absorbency and the elastic modulus of the swollen crosslinked gel, both of which are related to the crosslinking density of the network (Wu, 2008a). Crosslinker is essential for the formation of three dimensional network structures in the polymerization process. The greater the amount of the crosslinker is the higher crosslinking density of the hydrogel (Ni, 2009). However, the application of superabsorbents in the field of CRF production has met some problems since most of the superabsorbents are based on pure poly(sodium acrylate), and they are too expensive and not suitable for saline-containing water and soils (Kohls, 1999). To overcome these problems, several researches have focused on reducing the production costs of superabsorbents and improving their salt resistance (Zhang, 2006). Introducing inorganic clays, such as kaolin (Liang, 2007), bentonite, montmorillonite (Wu, 2003), attapulgite (Zhang, 2006) and mica (Lee, 2005) into pure polymeric superabsorbents have improved the swelling properties, increased the hydrogel strengths, and reduced the production costs.

3.4 Partly polymer-coated fertilizers or mixtures of coated and uncoated fertilizers

Another alternative in order to combine the advantage of CRF with the lower cost of conventional fertilizers is to mix coated fertilizers with uncoated fertilizer. For example, commercial fertilizers (N-P-K type), of which only 50% or 25% of the granules are polymer-coated, were registered under the German fertilizer law. It is believed that using partly polymer coated fertilizers not only offer a greater flexibility of usage but also further improved economy of using coated fertilizer (Trenke, 1997).

4. Coating process

The process of fertilizers coating has been studied widely applying various techniques such as rotating drum, fluidized bed and spouted bed and using different kinds of material. Tennessee Valley Authority (TVA) first used continuous coating process of urea with sulfur in a rotating drum (Blouin, 1971). Later on, a process for manufacturing of the sulfur-coated urea (SCU) was developed using a spouted bed (Meisen, 1978) and in further study, Salman (1982, 1988) conducted the coating of urea with polyethylene in a

modified fluidized bed. Weiss and Meisen (1983) developed a process to produce SCU in a two dimensional spouted bed. The use of each process, either rotating drum, spouted bed and/or fluidized bed for coating of fertilizers has been further studied by other researchers (Wu, 2008a; Tzika, 2003; Devassine, 2002; Tao, 2011; Donida, 2002). Whatever the process of coating, several parameters were found to affect the quality of the fertilizer coating and hence time release of the nutrients. These parameters include type of fertilizer, granule radius, particle size distribution of the uncoated or initial fertilizers, binder properties, moisture content, contact area, pH, and temperature (Basu, 2010; Adetayo, 1993).

Currently, various types of materials have been discovered to be suitable for polymer coatings of fertilizers; however, most polymeric compounds should be dissolved in organic solvents during the coating process. The problem is organic solvents are relatively expensive, and most of them are toxic or pollutant. Accordingly, more attention is now paid to waterborne coating, which has the advantage of non-toxicity, non-flammability, low price, and good quality in comparison with the traditional organic coating (Ahmad, 2008; Tang, 2004). Besides that, the substitution of organic solvent by water is the current trend for the following reasons: simplification the operations in relation to safety and equipment, reduction the operating costs and minimization the environmental contamination (Donida, 2002). For the waterborne coating materials, reacted layer technology has been widely used to improve the water resistance of coatings, and cross-linker is commonly used to modify this property (Pfeffer, 2001). Basically, any cross-linker employed must first be compatible with the polymer to produce a homogeneous membrane with desirable properties (Cong, 2010).

However, using water-born process is under discussion and dry coating process is proposed as a practical technique for polymer coating of the fertilizers. Pfeffer et al. (2001) stated that wet coating process is now less desirable over dry coating methods owing to the environmental concerns over the resulting waste streams and possible volatile organic carbon (VOC) emissions. Dry particle coating creates new-generation materials by combining different powders having different physical and chemical properties. The new composites formed illustrate new functionality or improve the characteristics of the known materials Pfeffer et al. (2001). In dry coating process tiny and fine particles, called guest, can directly attach onto relatively larger particles, host or core, without using any solvents, binders or even water Pfeffer et al. (2001). Another obstacle of using waterborne coating is the coating process requires more heat for water evaporation (Ito, 2003) and the polymer coating

obtained using this method is fairly unstable during long storage. Ito et al. (Ito, 2003; Ito, 2002) proposed a dry-based coating of core particle with the impermeable wax dispersing fine permeable particles to extend the release time of the urea core. The authors claimed that this process requires much less heat for the formation of a stable wax layer than the conventional spraying method with polymer solution. Pfeffer et al. (2001) reviewed a number of different devices with different conditions used to achieve dry particle coating.

5. Coating of N-P-K fertilizers

Fertilizer usage can be more effective, if the rate of nutrients release can match the plant requirements throughout the growth period (Jin, 2011). However, if the fertilizer not only consists of just one nutrient, particularly when containing secondary and micronutrients such as N-P-K type fertilizers, it is very difficult to determine the mechanism and the rate of the nutrients release accurately (Trenke, 1997). This complexity is due to differences in the solubility, mass transfer characteristics and chemical properties of the nutrients that cause each nutrient to be diffused and released differently. However, there are some inconsistencies in the observations made by those researchers who studied the rate of nutrients release from the compound fertilizers. Du et al. (2006) investigated the effects of temperature and water content on the release rates and release patterns of nitrate, ammonium, potassium and phosphate. It was indicated that activation energy of the nutrient release varies in different media. With regard to the nutrient release, nitrate release was the fastest, followed by ammonium and potassium whereas phosphate was significantly the slowest. The lag period of phosphate was significantly longer than others, which implies strong interactions exist among nutrients in the fertilizer granule, especially on the nutrient solubility. Shaviv (2000) also mentioned such a common trend for PCF emphasizing on the significantly lower rates of phosphate release compared to potassium and nitrate. These observations are in contrast with Huett and Gogel (2000) who reported an inconsistent trend in nutrient release periods for potassium and nitrate, i.e., nutrient release periods for potassium was higher than nitrate.

The release phenomenon and release characteristics of fertilizers coated using paraffin and polyethylene waxes were studied by Al-Zahrani (2000). It appears that the efficient release of nutrients

is governed by the principles of mass diffusion models. The release kinetics of these coated fertilizers fitted well the Sinclair formula, modified hyperbola formula and modified Schwartz18 formula, which can be applied to describe the diffusion phenomena for releasing of the nutrients. However, the modified hyperbola formula indicated the best fit in describing the release data for different types of the fertilizers studied in this study Al-Zahrani (2000). Detailed information that relates to the materials and methods utilized for production of the coated fertilizers are summarized in Table 1. The characteristics of the final product, and observations made by the researchers are also presented.

6. Coated fertilizers quality assessment

Two terms, the rate and the pattern of nutrient release, are fundamentally considered and investigated to characterize the releasing of nutrients from the coated fertilizers. The rate refers to the total quantity of nutrients released over the entire time period, whereas pattern refers to the periodic distribution of nutrient release at specified time intervals throughout the designated release period (Jacobs, 2004). Several analysis methods conducted in assessing the quality of coated fertilizer can be listed as below:

- Structure analysis of the coated fertilizer (mass ratio of the coating material to the whole product, measurement of coating percentage)
- Measurement of water absorbency of the product
- Characterization of the coating material by Fourier Transform Infrared (FTIR)
- Measurement of water retention for the coated fertilizer in soil (largest water-holding ratio of the soil with the product (Jin, 2011))
- Release behaviour of the coated fertilizer in soil (Jin, 2011)
- Rate of release of active components in water
- Morphology of the coated fertilizer using Scanning electron microscopy (SEM)
- Effect of the coated fertilizers on the concentration of ions in soil (Jin, 2011)
- Measurement of the coating thickness (Tomaszewska, 2002)
- Ions release of fertilizers immersed in water (Devassine, 2002)
- Measurement of the coated fertilizer bulk density, sphericity and grain size Donida, 2002.

Table 1: A summary of process information and the results achieved in several studies

Core	Coating	Method	Ref.	Remark
Compound fertilizer	Polysulfone, Cellulose acetate and Polyacrylonitrile	phase inversion technique	Tomaszewska 2002	The concentration of the polymer in a casting solution affects the physical properties of the coating. The coating formed from polysulfone showed the most advantageous properties for all coatings tested. The salt addition causes faster polymer precipitation during the coating formation, hence a more porous coating is formed.
Compound fertilizer	Polysulfone	phase inversion technique	Tomaszewska 2002	The concentration of polysulfone in the film-forming solution influences the coating structure. The temperature affected the release rate of ingredients from coated fertilizer. The increase of temperature caused an increase release rate of NPK.
Compound fertilizer	Polysulfone, Polyacrylonitrile, and cellulose acetate	phase inversion technique	Jarosiewicz 2003	It was observed that the release rate of components from the fertilizer coated with biodegradable coating (cellulose acetate) was the highest. In the case of coatings prepared from two other polymers, the release rate of nutrients was much lower. The type of polymer and its concentration influences the porosity of the prepared coating.
Compound fertilizer	Latex of poly (vinylidene-chloride)	Wurster chamber of a fluidized-bed	Tzika, 2003	Depending on the selected process conditions, the coating thickness varies, while the surface of the coated granules changed from completely smooth to rough and porous. It was shown that by suitable selection of the coating conditions in the Wurster process, controlled-release fertilizers exhibiting prolonged release profiles could be produced.
Ammonium sulfate	Polyurethane foams consisting of diisocyanate, polyester, Acacia mearnsi bark, and corn starch	As described in the reference	Ge, 2002	The release ratio of the fertilizer decreased with an increasing amount of biomass in PUFs and increasing the sizes of sample particles. The ratio increased with increasing doses of foaming agent, water, in the preparation of polyurethane, regardless of the amount of coating material. The PUFs were degradable, to some extent, by soil microorganisms.
Compound Fertilizer	Chitosan, Poly(acrylic acid-co-acrylamide) superabsorbent polymer	Rotary drum	Wu, 2008	The coated fertilizer indicated controlled-release property and the ability to absorb water and preserve the soil moisture at the same time. The outer coating is not harmful to the soil material as it can be degraded in soil.
Urea	Polyethylene, poly (acrylic acid-co-acrylamide) superabsorbent, and poly (butyl methacrylate)	Fluidized bed	Tao., 2011	The first layer possesses controlled release property, the middle layer has water absorbent characteristic, and the thin outer layer aims to protect the fragile layer of the superabsorbent. The results showed that the coated fertilizer not only performed as a good controlled-release fertilizer but also had excellent water retention capacity.

Compound Fertilizer	Polysulphone, Starch	As described in the reference	Tomaszewska, 2004	As the polysulfone coatings are not biodegradable, the starch was added to facilitate the destruction of the coating in soil. The addition of starch to the polymer solution influenced the release rate of NPK from coated fertilizer. The release rates of macro-elements rose when the starch concentration in coating was higher.
Urea	Polymeric film (as described in the reference)	Two-dimensional spouted bed	Donida, 2002	Coating of the polymeric suspension of Eudragit improved up to four times the moisture holding capacity of coated urea in relation to uncoated urea. The bulk density, grain size and sphericity were found to be independent of operational conditions. The increase of air temperature and atomizing air pressure favors the formation of uniform and smooth films.
Compound Fertilizer	Paraffin and polyethylene waxes	based on the technique illustrated in U.S. patent 5,137,563,19	Al-Zahrani, 2000	The amount of the fertilizer released from the matrix in a given time was affected by the type of wax used. The released times were at least doubled for all of the coated fertilizers. The polyethylene wax gives a longer release time than the paraffin wax; however, the paraffin wax has the advantage of total degradation in the soil.
Urea	Low-density polyethylene	Fluidized-bed	Salman 1989	
Urea	Pine lignin	As described in the reference	Garcia 1996	The most efficient are was for those coating embodies a mixture of dimerized, esterified, and natural rosins, as well as lignin. The efficiency of the products noticeably increases by adding linseed oil as a sealing agent.
Urea	Cross-linked poly(acrylic acid)/organo-attapulgite, urea-formaldehyde	Rotary drum	Liang 2006 a	The product not only had the slow release property, but also could absorb water and preserve soil moisture.
Urea	Various types of polymers were tested.	Fluidized-bed	Salman 1988	Except for LDPE-coated urea, very high dissolution was observed (95%), even at a high coating percentage (15%).
Compound fertilizer	Cellulose acetate, Poly(acrylic acid-co-acrylamide)/unexpanded vermiculite (P(AA-co-AM)/UVMT) superabsorbent composite. vermiculite (P(AA-co-AM)/UVMT) superabsorbent polymer.	Phase inversion	Wu 2008 b	The product not only had a controlled-release property but also could absorb a large amount of water and preserve the soil moisture at the same time.
Urea	Copolymers of AA and AM (the second layer) and cross-linked starch (the first layer)	As described in the reference	Guo., 2005 a	The product not only had good slow-release property but also excellent water retention capacity. The slow-release and water retention experiments showed that it not only had good slow-release property but also had excellent moisture preservation capacity in soil, and could efficiently improve the utilization of fertilizer and water resources at the same time.

Compound Fertilizer	Acrylate latex	As described in the reference	Cong., 2010	The amount of cross-linker in the coating latex played an important role in the structure and property of fertilizer coating.
Compound Fertilizer	poly(acrylic acid-co-acrylamide)/kaolin superabsorbent polymer	As described in the reference	Wu, 2007	The product, which possessed the core/shell structure, showed good slow-release and water-retention capacity, being nontoxic in soil and environmentally friendly
-	Polylactic acid	Fluidized bed and pan coating	Devassine, 2002	The spongy structure of wall strongly depends on the rate of drying. A drying in air current and an annealing could be done to avoid this problem. Fluidized bed is superior to pan coating. The fertilizer granules coated with the same polymer, using the coating pan present a quicker release
Compound Fertilizer	acrylic acid, acrylamide, and active carbon	As described in the reference	Jin, 2011	The product not only had good slow-release property and excellent water retention capacity but also higher adsorption capacities of cations in saline soil.
Compound Fertilizer	Chitosan nanoparticle	As described in the reference	Corradini, 2010	The stability of the prepared suspension was higher with the addition of nitrogen and potassium than with the addition of phosphorus, due to the higher anion charge from the calcium phosphate than the anion charges from the potassium chloride and urea.
Urea	poly(acrylic acid)-containing urea (PAAU) (the outer coating), polystyrene (PS) (the inner coating)	As described in the reference	Liang, 2006 b	The outer coating (PAAU) regulated the nitrogen release rate and protected the inner coating from damage. PS coating percentage, temperature, and water absorbency had a significant influence on the release of nitrogen. However, the pH had no effect. The product not only had a good slow release property but also excellent water-retention capacity, which could effectively improve the utilization of fertilizer and water resources.

7. Conclusion

Controlled-release fertilizers improve the efficiency of the fertilizer usage in terms of increasing the plants production as well as the efficiency and quality of nutrients uptake while the cost of fertilizer application is reduced. Using CRFs also decrease plants toxicity and stress as well as soil, water reservoirs and atmosphere pollution. Among different types of CRFs, coated fertilizers in particular polymer-coated fertilizers attract great attentions since they provide a gradual and consistent nutrient release pattern. Coating of fertilizers also leads to improvement of handling properties, and the crushing strength of the product. However, there are some challenges and complexities in production of coated fertilizers. It is desired to make a product that begins to release the nutrients soon after application, and provides a consistent flow of nutrients through the duration of the designated release period. The release of each nutrient is expected to depend on its own solubility in solution, diffusivity/permeability through the coating, interactions between elements as well as temperature, water content and medium type. In

general, temperature and sometimes moisture are the main factors affecting the nutrient release from the CRF. The type of coating is also responsible for the mechanism of nutrients release from the coated fertilizers. The coating structure controls the diffusion of the elements from the interior of the CRF granule. The release rate of nutrients from CRF decreases with the decrease of the coating porosity. In coated fertilizers, the release rate of nutrients also depends on the thickness of the coating. Taking into account, the coating materials should be inexpensive and exhibit a good coating property. In addition, they should undergo nontoxic degradation in soil, which is safe for plants and environment.

Polymer-coated fertilizers comprise the majority of coated-fertilizers used in plant production and have gained the greatest important. Polymer-coated fertilizers offer a better control over release characteristics, as they are less sensitive to the soil and environmental factors. Among various types of polymers, hydrogel-based natural polymers are extensively applied in the synthesis of coated fertilizers. The reason is these types of polymeric

coating have unique advantages, such as abundance, non-toxicity, biocompatibility and biodegradability.

Consequently, it is envisaged that proper selection of coating material is an important aspect of creating efficient coated fertilizers. The profound influence of the coating properties on the effective function of coated fertilizers was noted. The cost of coating is considered to be a major impediment in commercialization and utilization of the coated fertilizers. Besides that, using degradable polymers are of immense practical importance for pollution abatement. One alternative can be using of the end-products of recycled polymers, for example degradable polyurethane produced from PET recycling.

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References

1. Abdel-Aal, S.E.; Hegazy, E.A.; Abdel-Rehim, H.A.; Khalifa, N.A.; El-Hosseiny, E.M. Radiation copolymerization of (PVA/4-VP) hydrogel for treatment of industrial waste dyes, *Int. J. Polym. Mater.* 2003, 52, 901.
2. Adetayo, A. A.; Litster, J. D.; Desai M. The Effect of Process Parameters on Drum Granulation of fertilizers with Broad Size Distributions, *Chemical Eng. Sci.* 1993, 48(23), 3951.
3. Ahmad, S.; Ashraf, S. M.; Riaz, U.; Zafar, S. Development of novel waterborne poly(1-naphthylamine)/poly(vinylalcohol)-resorcinol formaldehyde-cured corrosion resistant composite coatings. *Prog. Org. Coat.* 2008, 62, 32.
4. Akelah, A. Novel utilizations of conventional agrochemicals by controlled release formulations. *Mat. Sci. Eng.* 1996, C4, 83.
5. Al-Zahrani, S. M. Utilization of Polyethylene and Paraffin Waxes as Controlled Delivery Systems for Different Fertilizers, *Ind. Eng. Chem. Res.* 2000, 39, 367.
6. Bajpai, A. J.; Giri, A. Water sorption behaviour of highly swelling (carboxy methylcellulose-g-polyacrylamide) hydrogels and release of potassium nitrate as agrochemical. *Carbohydr. Polym.* 2003, 53, 271.
7. Bakass, M.; Mokhlisse, A.; Lallemand, M. Absorption and desorption of liquid water by a superabsorbent polymer: Effect of polymer in the drying of the soil and the quality of certain plants. *J. Appl. Polym. Sci.* 2002, 83, 234.
8. Bandyopadhyay, S.; Bhattacharya, I.; Ghosh, K.; Varadachari, C. New slow-releasing molybdenum fertilizer. *J. Agric. Food Chem.* 2008, 56, 1343.
9. Basu, S. K.; Kumar, N. Mathematical model and computer simulation for release of nutrients from coated fertilizer granules. *Math. Comput. Simul.* 2008, 79, 634.
10. Basu, S.K.; Kumar, N.; Srivastava, J.P. Modeling NPK release from spherically coated fertilizer granules. *Simul. Model. Prac. Theory* 2010,18, 820.
11. Berger, J.; Reist, M.; Mayer, J. M.; Felt, O.; Peppas, N. A.; Gurny, R. Structure and interactions in covalently and ionically cross-linked chitosan hydrogels for biomedical applications. *Eur. J. Pharm. Biopharm.* 2004, 57 (1), 19.
12. Bhattacharya I; Bandyopadhyay S.; Varadachari Ch; Ghosh K. Development of a Novel Slow-Releasing Iron-Manganese Fertilizer Compound. *Ind. Eng. Chem. Res.* 2007, 46, 2870.
13. Blouin, G.M.; Rindt, D. W.; Moore, O. E. Sulfur-Coated Fertilizers for Controlled Release: Pilot Plant Production. *J. Agr. Food Chem.* 1971, 19(5), 801.
14. Carreres, R.; Sendra, J.; Ballesteros, R.; Valiente, E. F.; Quesada, A.; Carrasco, D.; Legane's, F.; de La Cuadra, J. G. Assessment of slow release fertilizers and nitrification inhibitors in flooded rice. *Biol. Fertil. Soils.* 2003, 39, 80.
15. Chatzoudis, G.K.; Rigas, F.; Macroreticular hydrogel effects on dissolution rate of controlled-release fertilizers, *J. Agric. Food Chem.* 1998, 46, 2830.
16. Chien S. H.; Prochnow L; Cantarella H. Recent Developments of Fertilizer production and Use to Improve Nutrient Efficiency and Minimize Environmental Impacts, *Adv. Agr.* 2009, Chapter 8,102.
17. Cong, Z.; Yazhen, Sh.; Changwen, D.; Jianmin, Zh.; Huoyan, W.; Xiaoqin, Ch.; Evaluation of Waterborne Coating for Controlled-Release Fertilizer Using Wurster Fluidized Bed. *Ind. Eng. Chem. Res.* 2010, 49, 9644.
18. Corradini, E.; De oura, M. R.; Mattoso, L. H. A preliminary study of the incorporation of NPK fertilizer into chitosan nanoparticles, *eXPRESS Polym. Lett.* 2010, 49(8), 509.
19. Dave, A. M.; Mehta, M. H.; Aminabhavi, T. M.; Kulkarni, A. R.; Soppimath, K. S. A review on controlled release of nitrogen fertilizers through polymeric membrane devices. *Polym. Plast. Technol. Eng.* 1999, 38, 675.
20. Dechy, N; Bourdeaux, T; Ayrault, N; Kordek, M-A; Le Coze, J-C. First lessons of the Toulouse ammonium nitrate disaster, *J. Hazard Mater.* 2004, 111,131.
21. Devassine, M.; Henry, F.; Guerin, P.; Briand, X. Coating of fertilizers by degradable polymers, *International Journal of Pharmaceutics* 2002, 242, 399.
22. Donida, M. W.; Rocha, S.C.S. Coating of Urea with an Aqueous Polymeric Suspension in a Two-Dimensional Spouted Bed, *Dry Technol.* 2002, 20(3), 685.
23. Du, C.; Tang, D.; Zhou, J.; Wang, H.; Shaviv, A. Prediction of nitrate release from polymer-coated fertilizers using an artificial neural network model. *Biosys. Eng.* 2008, 99, 478.

24. Du, C; Zhou, J; Shaviv, A. Characteristics of potassium release from polymer-coated controlled release fertilizer and its modelling. *Trans. CSAE*, 2006, 22, 18. (b).
25. Du, C; Zhou, J; Shaviv, A. Lag period of nutrient release from polymer 2 coated NPK Compound fertilizers. *J. Plant Nut. Fert. Sci.* 2005, 2, 179.
26. Du, Ch.; Zhou, I.M.; Shaviv, A. Release Characteristics of Nutrients from Polymer-coated Compound Controlled Release Fertilizers, *J Polym Environ.* 2006, 14, 223. (a).
27. Dusek, K.; Duskova-Smrckova, M. Network structure formation during crosslinking of organic coating systems. *Prog. Polym. Sci.* 2000, 25, 1215.
28. El-Sherbiny, I.M.; Harding, D.R.K.; Abdel-Bary, E.M. Preparation and swelling study of a pH-dependent interpolymeric hydrogel based on chitosan for controlled drug release *Int. J. Polym. Mater.* 2006, 55, 789.
29. Fan, X.; Li, F.; Liu, F.; Kumar, D. Fertilization with a new type of coated urea: Evaluation for nitrogen efficiency and yield in winter wheat. *J. Plant Nutr.* 2004, 27, 853.
30. Fujinuma, R.; Balster, N. J.; Norman, J. M. An improved model of nitrogen release for surface-applied controlled-release fertilizer. *Soil Sci. Soc. Am. J.* 2009, 73, 2043.
31. Garcia, M. C.; Diez, J. A.; Vallejo, A.; Garcia, L.; Cartagena, M. C. Use of kraft pine lignin in controlled-release fertilizer formulation. *Ind. Eng. Chem. Res.* 1996, 35, 245.
32. Ge, J.; Wu, R.; Shi, X.; Yu, H.; Wang, M.; Li, W. Biodegradable Polyurethane Materials from Bark and Starch. II. Coating Material for Controlled-Release Fertilizer. *J. Appl. Polym. Sci.*, 2002, 86, 2948.
33. Guo, M. Y.; Liu, M. Z.; Zhan, F. L.; Wu, L. Preparation and properties of a slow-release membrane-encapsulated urea fertilizer with superabsorbent and moisture preservation. *Indust. Eng. Chem. Res.* 2005, 44, 4206(a).
34. Guo, M.; Liu, M.; Hu, Z.; Zhan, F.; Wu, L. Preparation and Properties of a Slow Release NP Compound Fertilizer with Superabsorbent and moisture Preservation, *J. Appl. Polym. Sci.*, 2005, 96, 2132 (b).
35. HafShejani, M.K.; Khandani, F.; Heidarpour, R.; Arad, A.; Choopani, S., Study the sources of mercury vapor in atmosphere as a threatening factor for human health and bio-filtering methods for removal of toxic pollution, *Life Science Journal* 2013;10(1).
36. Hanafi, M. M.; Eltaib, S. M.; Ahmad, M. B. Physical and chemical characteristics of controlled release compound fertilizer. *European Polymer Journal* 2000, 36, 2081.
37. Hua, Sh.; Wang A. Synthesis, characterization and swelling behaviors of sodium alginate-g-poly(acrylic acid)/sodium humate superabsorbent, *Carbohydrate Polymers*, 2009, 75(1), 79.
38. Huett, D. O.; Gogel, B. J. Longevities and nitrogen, phosphorus, and potassium release patterns of polymer coated controlled release fertilizers at 30°C and 40°C. *Communi. Soil Sci. Plant Anal.* 2000, 31,959.
39. Ibrahim, G. E.; Abdel-motaleb A.F and Mahmoud, E.RE., Achieving Optimum Scientific Standards for Producing Fabrics Suitable for Protecting Against Hazardous, *Chemical Liquids Life Science Journal* 2013;10(1).
40. Ito, R.; Golman, B.; Shinohara, K. Controlled release of core particle coated with soluble particles in impermeable layer, *J. Chem. Eng. Jpn.* 2002, 35, 40.
41. Ito, R.; Golman, B.; Shinohara, K. Controlled release with coating layer of permeable particles, *J. Control. Release.* 2003, 92, 361.
42. Jacobs, D. F. Variation in Nutrient Release of Polymer-Coated Fertilizers, Source: Dumroese, R. K.; Riley, L. E.; Landis, T. D., tech. coords. 2005. National proceedings: Forest and Conservation Nursery Associations—2004; 2004 July 12–15; Charleston, NC; and 2004 July 26–29; Medford, OR. Proc. RMRS-P-35. Fort Collins, CO: U.S. Department of Agriculture, Forest Service, Rocky Mountain Research Station. p. 113-118.
43. Jain S. K. Controlled Release Fertilizers: Trends and Technologies. 2007 www.Pharmainfo.net.
44. Jarosiewicz A. and Tomaszewska M. Controlled-Release NPK Fertilizer Encapsulated by Polymeric Membranes, *J. Agric. Food Chem.* 2003, 51, 413.
45. Jin Sh.; Yue G.; Feng L.; Han Y.; Yu X; Zhang Z. Preparation and Properties of a Coated Slow-Release and Water-Retention Biuret Phosphoramidate Fertilizer with Superabsorbent, *J. Agric. Food Chem.* 2011, 59, 322.
46. Kapoor, V.; Singh, U.; Patel, S. K.; Magre, H.; Shrivastva, L. K.; Mishra, V. N.; Das, R. O.; Samadhiya, V. K.; Sanabria, J.; Diamond, R. Rice growth, grain yield, and floodwater dynamics as affected by nutrient placement and rate. *Agron. J.* 2008, 100, 526.
47. Kohls, S. J.; Baker, D. D.; Kremer, D. A.; Dawson, J. O. Water retentive polymers increase nodulation of actinorhizal plants inoculated with Frankia. *Plant Soil* 1999, 214, 105.
48. Kopecek, J.; Yang, Hydrogels as smart materials. *J. Polym. Int.* 2007, 56, 1078.
49. Lee, W. F.; Chen, Y. C. Effect of intercalated reactive mica on water absorbency for poly (sodium acrylate) composite superabsorbents. *Eur. Polym. J.* 2005, 41, 1605.
50. Li, A; Zhang, J. P.; Wang, A. Q. Synthesis, characterization and water absorbency properties of poly(acrylic acid)/sodium humate superabsorbent composite. *Polym Adv Technol.* 2005, 16,675.
51. Liang, R.; Liu, M.; Wu, L. Controlled release NPK compound fertilizer with the function of water retention, *Reactive and Functional Polymers* 2007, 67(9), 769.
52. Liang, R; Liu M. Preparation and Properties of Coated Nitrogen Fertilizer with Slow Release and Water Retention, *Ind. Eng. Chem. Res.* 2006, 45, 8610. (a).
53. Liu, M. Z.; Liang, R.; Zhan, F. L.; Liu, Z.; Niu, A. Z. Preparation of superabsorbent slow release nitrogen fertilizer by inverse suspension polymerization. *Polym. Int.* 2007, 56, 729-737.

54. Liu, M.; Liang, R.; Niu, A. Granular Urea-Formaldehyde Slow-Release Fertilizer with Superabsorbent and Moisture Preservation. *J. Appl. Polym. Sci.* 2006, 99, 3230 (a).
55. Liu, M.; Liang, R.; Zhan, F.; Liu, Z.; Niu, A. Synthesis of a slow-release and superabsorbent nitrogen fertilizer and its properties. *Polym. Adv. Technol.* 2006, 17, 430 (b).
56. Luckachan, G. E.; Pillai, C. K. S. (2011) *J Polym Environ* 19:637.
57. Mathews, A. Narine S. Poly[N-Isopropyl acrylamide]-co-Polyurethane Copolymers for Controlled Release of Urea, *J. Polym. Sci.: Part A: Polymer Chemistry*, 2010, 48, 3236.
58. Meisen, A.; Mathur, K.B. Production of Sulphur-Coated Urea by the Spouted Bed Process, *Proceedings of the British Sulphur Corporation*, 1978, 2.
59. Mikkelsen, R. L. Using hydrophilic polymers to control nutrient release, *Fertil. Res.* 1994, 38(1), 53.
60. Mulder, W. J.; Gosselink, R. J. A.; Vingerhoeds, M. H.; Harmsen, P. F. H.; Eastham, D. Lignin based controlled release coatings. *Ind. Crops Prod.* 2011, 34, 915.
61. Munoz, F.; Mylavarapu, R. S.; Hutchinson, C. M. Environmental potato production: A review. *J. Plant Nutr.* 2005, 28, 1287.
62. Ni, B. L.; Liu, M. Z.; Liu, S. Y. Multifunctional slow-release urea fertilizer from ethylcellulose and superabsorbent coated formulations. *Chem. Eng. J.* 2009, 155, 892.
63. Ni, B.; Liu, M.; Lu, Sh.; Xie, L.; Zhang, X.; Wang, Y. Novel Slow-Release Multielement Compound Fertilizer with Hydroscopicity and Moisture Preservation, *Ind. Eng. Chem. Res.* 2010, 49, 4546. (a).
64. Ni, B.; Liu, M.; Lu, Sh.; Xie, L.; Wang, Y. Multifunctional Slow-Release Organic-Inorganic Compound Fertilizer, *J. Agric. Food Chem.* 2010, 58, 12373. (b).
65. Oxley, J. C.; Smith, J. L.; Rogers, E.; Yu, M. Ammonium nitrate: thermal stability and explosivity modifiers. *Thermochim Acta.* 2002, 384, 23.
66. Pe'rez-García, S.; Fernández-Pe'rez, M.; Villafranca-Sánchez, M.; González-Pradas, E.; Flores-Céspedes, F. Controlled release of ammonium nitrate from ethylcellulose coated formulation. *Ind. Eng. Chem. Res.* 2007, 46, 3304.
67. Peng, Z.; Chen, F. Synthesis and Properties of Lignin-Based Polyurethane Hydrogels, *Inter. J. Polym. Mater.* 2011, 60, 674.
68. Peng, Z.Y.; Chen, F.G. Synthesis and Properties of Temperature-Sensitive Hydrogel Based on Hydroxyethyl Cellulose *Int. J. Polym. Mater.* 2010, 59(6), 450.
69. Pfeffer, R.; Dave, R. N.; Wei, D.; Ramlakhan, M. Synthesis of engineered particulates with tailored properties using dry particle coating. *Powd. Technol.* 2001, 117, 40.
70. Rindt, D. W.; Blouin, G. M.; Getsinger, J. G. Sulfur Coating on Nitrogen Fertilizer to Reduce Dissolution Rate. *J. Agr. Food Chem.* 1968, 16(5), 773.
71. Rudjak, I.; Kaljuvee, T.; Mikli, T.V.; Thermal behaviour of ammonium nitrate prills coated with limestone and dolomite powder. *J. Therm Anal Calorim.* 2010, 99,749.
72. Rudnik, D. Briassoulis (2011) *J Polym Environ* 19, 18.
73. Sakai, M.; Saeki, M.; Sakamoto, A.; Kanazawa, Sh. Biodegradability of Photodegradable Coating Materials Used for Coated Fertilizers in Agricultural Soils. *Soil Sci. Plant Nutr.* 2003, 49 (4), 647.
74. Salman, O. A. Polyethylene-coated urea. 1. Improved storage and handling properties. *Ind. Eng. Chem. Res.* 1989, 28, 630.
75. Salman, O. A. Polymer Coating on Urea Prills To Reduce Dissolution Rate, *J. Agric. Food Chem.* 1988, 36, 616.
76. Sannino, A.; Nicolais, L. Concurrent effect of microporosity and chemical structure on the equilibrium sorption properties of cellulose-based hydrogels. *Polymer* 2005, 46, 4676.
77. Savant, N. K.; Stangel, P. J. Urea briquettes containing diammonium phosphate: A potential NP fertilizer for transplanted rice. *Fertil. Res.* 1998, 51, 85.
78. Shavit, U.; Reiss, M.; Shaviv, A. Wetting mechanisms of gel-based controlled-release fertilizers, *J. Control. Rel.* 2003, 88, 71.
79. Shavit, U.; Shaviv, A.; Zaslavsky, D. Solute diffusion coefficient in the internal medium of a new gel based controlled-release fertilizer, *J. Control. Release* 1995, 37, 21.
80. Shaviv, A. *Advances in Controlled Release Fertilizers*, *Adv. Agr.* 2000, 71,1.
81. Shaviv, A. (2005). *Controlled release fertilizers*. In "IFA International Workshop on Enhanced-Efficiency Fertilizers", Frankfurt, Germany, 2830. June 2005.
82. Shaviv, A.; Smadar, R.; Zaidel, E. Model of diffusion release from polymer coated granular fertilizers. *Environ. Sci. Technol.* 2003, 37, 2251. (a).
83. Shaviv, A.; Smadar, R.; Zaidel, E. Statistically based model for diffusion release from a population of polymer coated controlled release fertilizers. *Environ. Sci. Technol.* 2003, 37, 2257. (b).
84. Shoji, S., Delgado, J., Mosier, A., and Miura, Y. (2001). Use of controlled release fertilizers and nitrification inhibitors to increase nitrogen use efficiency and to conserve air and water quality. *Commun. Soil Sci. Plant Anal.* 32, 1051.
85. Simoes, P. N.; Pedroso, L. M.; Portugal, A. A. Campos JL. Study of the decomposition of phase stabilized ammonium nitrate (PSAN) by simultaneous thermal analysis: determination of kinetic parameters. *Thermochim Acta.* 1998, 319, 55.
86. Skordilis, C. S.; Pomonis, P. J. The influence of Mn, Co and Cu cations on the thermal decomposition of NH₄NO₃ in pure form and supported on alumina. *Thermochim Acta.* 1993, 216, 137.
87. Smith, J. D.; Hellen, C.H. Evaluation of polymers for controlled-release properties when incorporated with nitrogen fertilizer solutions, *Commun. Soil Sci. Plant Anal.* 1991, 22, 559.
88. Sun, J.; Sun, Z.; Wang, Q.; Ding, H.; Wang, T.; Jiang, C. Catalytic effects of inorganic acids on the decomposition of ammonium nitrate. *J. Hazard Mater.* 2005, 127, 204.

89. Tang, L. S.; Zhang, M.; Zhang, S. F.; Yang, J. Z. High performance waterborne aminoacrylic coatings from the blends of hydrosols and latexes. *Prog. Org. Coat.* 2004, 49, 54.
90. Tao, Sh.; Liu, J.; Jin, K.; Qiu, X.; Zhang, Y.; Ren, X.; Hu, Sh. Preparation and Characterization of Triple Polymer-Coated Controlled-Release Urea With Water-Retention Property and Enhanced Durability, *J Appl Polyme Sci.* 2011, 120, 2103.
91. Teixeira, M.A.; William, J. P.; Edward, J. D.; Qiangliang, L.; Brian, K. H. ; Mattheus, F. A. Assessment of chitosan gels for the controlled release of agrochemicals, *Ind. Eng. Chem. Res.* 1990, 29, 1205.
92. Teodorescu, M.; Lungu, A.; Stanescu, P. O.; Neamtu, C.; Preparation and properties of novel slow-release NPK agrochemical formulations based on poly(acrylic acid) hydrogels and liquid fertilizer. *Indust. Eng. Chem. Res.* 2009, 48, 6527.
93. Tomaszewska, M.; Jarosiewicz, A. Polysulfone coating with starch addition in CRF formulation. *Desalination.* 2004, 163, 247.
94. Tomaszewska, M.; Jarosiewicz, A.; Karakulski, K.; Physical and chemical characteristics of polymer coatings in CRF formulation, *Desalination* 2002,146 (3), 19.
95. Trenkel M. E. *Controlled-Release and Stabilized Fertilizers in Agriculture.* Published by the International Fertilizer Industry Association, Paris, Source: <http://www.fertilizer.org>, 1997.
96. Tzika, M.; Alexandridou, S.; Kiparissides, C. Evaluation of the morphological and release characteristics of coated fertilizer granules produced in a Wurster fluidized bed, *Powd. Technol.* 2003, 132, 16.
97. Vazquez-Duhalt, R.; Tinoco, R.; D'Antonio, P.; Topoleski, L. D. T.; Payne, G. F. Enzyme conjugation to the polysaccharide chitosan: Smart biocatalysts and biocatalytic hydrogels. *Bioconjugate Chem.* 2001, 12 (2), 301.
98. Wang, Y.; Liu, M.; Ni, B.; Xie, L. A κ-carrageenan-sodium alginate beads and superabsorbent coated nitrogen fertilizer with slow-release, water-retention and anti-compaction properties, *Ind. Eng. Chem. Res.*, 2012,51 (3), 1413–1422.
99. Wang, Y.; Wan, T. Synthesis of polyurea formaldehydesan environmental protection and controlled release chemical fertilizer. *Chin. J. Soil Sci.* 2001, 32, 73.
100. Ward, J. H.; Peppas N. A. Preparation of controlled release systems by free-radical UV polymerizations in the presence of a drug. *J Control Release* 2001, 71,183.
101. Weiss, P.J.; Meisen, A. Laboratory Studies on Sulphur-Coating Urea by the Spouted Bed Process. *Canad. J. Chemical Eng.* 1983, 61(3), 440.
102. Wen, G. T.; Mori, T.; Yamamoto, J.; Chikushi, J.; Inoue, M. Nitrogen recovery of coated fertilizers and influence on peanut seed quality for peanut plants grown in sandy soil. *Commun. Soil Sci. Plant Anal.* 2001, 32, 3121.
103. Wu L. and Liu M. Preparation and properties of chitosan-coated NPK compound fertilizer with controlled-release and water-retention, *Carbohydrate Polymers* 2008, 72, 240.
104. Wu, Ch. Controlled release evaluation of bacterial fertilizer using polymer composites as matrix. *J. Control. Release.* 2008, 132, 42.
105. Wu, H. B.; Chan, C. K. Effects of potassium nitrate on the solid phase transitions of ammonium nitrate particles. *Atm Environ.* 2008, 42, 313. (c).
106. Wu, J.; Wei, Y.; Lin, J.; Lin, S. Study on starch-graft-acrylamide/ mineral powder superabsorbent composite. *Polymer* 2003, 44, 6513.
107. Wu, L.; Liu, M. Preparation and characterization of cellulose acetate-coated compound fertilizer with controlled-release and water-retention, *Polym. Adv. Technol.* 2008; 19, 785. (b).
108. Wu, L.; Liu, M. Slow-Release Potassium Silicate Fertilizer with the Function of Superabsorbent and Water Retention. *Ind. Eng. Chem. Res.* 2007, 46, 6494.
109. Wu, L.; Liu, M. Z.; Liang, R. Preparation and properties of a double coated slow-release NPK compound fertilizer with superabsorbent and water-retention. *Bioresour. Technol.* 2008, 99, 547.
110. Zhan, F. L.; Liu, M. Z., M. Y., Wu, L. Preparation of superabsorbent polymer with slow-release phosphate fertilizer. *J. Appl. Polym. Sci.* 2004, 92, 3417.
111. Zhang, J. P.; Chen, H.; Wang, A. Q. Study on superabsorbent composite. IV. Effects of organification degree of attapulgit on swelling behaviors of polyacrylamide/org-attapulgit composite. *Eur. Polym. J.* 2006, 42, 101 (a).
112. Zhang, J.; Liu, R.; Li, A.; Wang, A. Preparation, Swelling Behaviors, and Slow-Release Properties of a Poly(acrylic acid-co-acrylamide)/Sodium Humate Superabsorbent Composite. *Ind. Eng. Chem. Res.* 2006, 45, 48. (b).

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