

ChemTech

International Journal of ChemTech Research CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555 Vol.10 No.15, pp 01-08, 2017

Revision of Optimized Hydrogel Design for the Covering of NPK Fertilizers as a Strategy for Sustainable Development

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Abstract : The agricultural sector has been forced to use large quantities of fertilizers to increase food supply, which consequently increases production costs with the exponential growth of the world's population. Fertilizersare vulnerable to losses by volatilization and leaching, causing environmental pollution as well as eutrophication in different water bodies when they have been applied to crops. One approach that compensates for this environmental problem is the design of hydrogels for which several methods and polymeric materials have been reported used as a coating of controlled release fertilizers. In this way, both sustainable development and the economy has forced the global fertilizer industry to develop new nutrient recovery methods and strategies from alternative sources. Controlled Release Fertilizers on the environment, reducing the loss of nitrogen caused by volatilization and leaching, and alters nitrogen release kinetics, which provides nutrients to plants at a rate that is more compatible with their metabolic needs. This article reviews recent studies on the latest methods of NPK fertilizer coating, as well as its properties and release mechanisms, having a critical analysis of this alternative for crops, followed by suggestions for future research.

Keywords : Hydrogel, Slow-Release Fertilizers, Sustainable Development, Environmental Impact. Polymer.

Introduction

The global use of fertilizers containing nitrogen, phosphorus and potassium (NPK) is approximately 200 Mt (Malingreau et al., 2012) and due to the increase in food demand, it is estimated that the application of these inputs will triple with the growth of the human population on the planet, which is believed to exceed 9 billion individuals by 2050 (Zlotnik, 2009).

Although fertilizer implementation is necessary to support agricultural production and meet food demand, its use is inefficient, since the crop (Stewart, 2007) absorbs not all applied nutrients. This not only

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causes reductions in the production of plant biomass and in the loss of soil fertility, also causes environmental pollution since the excess nutrients that are not absorbed reach leachate water bodies or the atmosphere by volatilization (Ongley, 1997). For example the potato, Colombia's second largest agricultural product with greater demand of inorganic fertilizers after the coffee, consumes 1,000 to 2,000 kg ha -1 year -1 of a compound fertilizer with high doses of phosphorus (P), nitrogen (N) and potassium (K) (Martínez et al., 2006; CCB, 2015). These nutrients account for more than 20% of production costs. However, the percentage of nutrients absorbed is less than 50% of nitrogen, less than 10% of phosphorus and about 40% of potassium (Baligar et al., 2001).

In addition to the low efficiency of fertilizer use, another problem in the agricultural industry is the reduction of soil moisture. Water deficits can be the result of tillage activities, as they promote moisture losses through evaporation (Altieri et al., 2000) and may also be the result of the decrease in precipitation produced by the phenomenon of the child, which generates low water potential in the soil (Valladares et al., 2004). In either case, the consequence is the decrease in productivity.

Today, a key strategy is to develop management practices that increase nutrient use efficiency and soil moisture retention, to be reflect in increases in productivity, an increase in the benefit/cost ratio for the farmer, and in reducing the negative impact at the environmental level. The adoption of slow release fertilizers has been considered as a promising strategy, since they allow the release of nutrients gradually (Trenkel, 1997). When these slow-release fertilizers are coat with hydrogels, they also help to retain moisture in the soil (Hurtado et al., 2007).

For example, in Colombia, Rozo&Rozo (2008) developed a superabsorbent hydrogel based on the linear sulfated polysaccharide Kappa carrageenan, isolated from the red alga Hypneamusciformis. This hydrogel has been evaluated for the production of different species of seedlings in seedbedsand has demonstrated a high absorption capacity and good gel strength. This makes it a good candidate to be evaluated as a fertilizer coating to control the release of nutrients and as a soil conditioner to improve its moisture retention.

This review analyzes the different designs of hydrogels with polymeric materials for the coating of NPK fertilizer, analyzing formulations, synthesizes and physicochemical evaluation of hydrogels characterized by high water retention capacity to analyze their slow and continuous release of nutrients to the environment, having the potential to increase the efficiency of fertilizer use.

Method

The bibliography review was done using the ScienceDirect and Scopus databases on the impact of (FLC). In relation to sustainable development, the consultation was only carried out for articles between 2010 and 2017, but in some articles there was important information of lower years, which were used. About 120 articles were consulted, of which 60 were used for the revision of this article. The importance of this issue is due to population growth, agroindustrial development and the daily activities that develop as a society involving alterations on the environment.

Development of the Topic

General aspects of fertilizers

A fertilizer is a chemical compound, natural or synthetic, used to enrich the soil with nutrients that favor plant growth. Fertilizers are supplied directly or indirectly, incorporated into the soil or applied to the plants so that they can be absorbed, helping to stimulate growth, increasing productivity or improving the quality of production (Arevalo et al., 2009). The most important characteristic of any fertilizer is the solubility in water, due to the contact with the irrigation water the fertilizer enters solution with the soil and the nutrients can be absorbed by the plant (FAO, 2002).

Fertilizers must contain primary nutrients required for crop growth, such as nitrogen, phosphorus, and potassium. Nitrogen is essential for plant growth since it forms part of the molecular structure of key biomolecules in the process of photosynthesis. Phosphorus participates in energy storage and generation processes that allow growth to occur and potassium helps to avoid invading organisms that attack the plant (Chun et al., 2015). Fertilizers should also contain secondary nutrients such as sulfur, calcium and

magnesium. Some fertilizers may contain micronutrients and these are applied when the soil presents deficits in these elements, which include Manganese, Zinc, Copper, among others.

One of the most common practices in agriculture is the application of granules of NPK fertilizers to provide nutrients to the plant through the roots (Garcia, 2003). This is done because most soils are not fertile enough so they require periods of treatment with primary nutrients. This type of fertilizer is easy to apply, since its granular presentation makes it manageable due to its size and texture.

One of the problems associated with fertilizers is that not all the nutrients added to the soil are absorbed by the crop. The literature reports that the efficiency of nutrient use in plants can range from 20 to 80% (Robinson et al., 2012). This implies that through irrigation water or rainfall events, up to 80% of the nutrients contributed to the soil through fertilizers can be lost through runoff or leaching.

Environmental problems of fertilizer use.

The excess of nutrients in a soil produced by the application of fertilizers can have two destinations. In the first, these nutrients escape to bodies of groundwater by leaching or to lakes, reservoirs and ponds by runoff. The consequence is the eutrophication problems that occur in these bodies of water that end in the proliferation of algae that suppress other plants and animals (Ongley, 1997). In the second, nutrients go into the atmosphere because the metabolic activity of denitrifying bacteria, which use nitrogen in the form of nitrite as an electron acceptor, convert it to molecular nitrogen or nitrogen oxides like NO and N_2O , which are greenhouse gases (Snyder et al., 2005).

Another problem associated with the use of fertilizers is the increase of soil salinity (Rodríguez et al., 2009), which inhibits plant growth due to the low osmotic potential of the soil solution, reducing the absorption of nutrients, generating degradation and decline in agricultural production (Meena et al., 2016).

Controlled or slow release fertilizers

In response to the low efficiency of the use of nutrients contained in fertilizers by plants, slow-release or controlled fertilizers have been developed, characterized by slowly releasing the nutrients contained in the fertilizer granules to the soil, in compared to normal fertilizer granules, avoiding nutrient losses and ensuring a continuous source of nutrients for plants (Senna et al., 2015). The release of nutrients from this type of fertilizer will depend on the level of soil moisture, microbiological activity and temperature (Trenkel, 2010).

Controlled-release fertilizers can be classified into three groups. The first, organic fertilizers are all those natural residues of animal and plant origin from which the plant can obtain nutrients.Examples of these fertilizers include animal manure, sludge, compost, worm humus among others (Azeem et al., 2014). The second, slow-solubility nitrogen fertilizers are based on nitrogen and are created from chemical reactions of a nitrogen component that is soluble in water and aldehydes (Rose et al., 2004). This fertilizer when introduced into the soil is released and slowly transformed into chemical form making it available to the plant. An example of this fertilizer is "urea-form", which are composed of large polymers that are obtained from urea and formaldehyde. Its solubility regulates the microbiological activity in the soil and the release of nutrients will depend on the temperature, humidity, pH and oxygen concentration (Ewen et al., 2000). Finally, coated fertilizers are those that are wrap in a water-insoluble layer under normal environmental conditions (Fujinuma, et al., 2009); whose composition and thickness will depend on the speed at which they are desired to be the release of nutrients (Hanafi et al., 2000). In the present work it was chosen to design a coated fertilizer due to the great diversity of materials that can be used as coating and to the advantages that their use in an agricultural production system offers. These advantages are described in the next section.

Coated Fertilizers

Coated fertilizers have been shown to improve nutrient availability throughout the productive cycle, avoiding nutrient deficiencies or excesses (Azeem et al., 2014), allowing labor savings by not having to fractionate the applications (Geng et al. (Rashidzadeh et al., 2014), reducing nutrient losses by washing, favoring an increase in the efficiency of plant nutrients and decreasing salt accumulation in soils. These advantages are given because the coating slows down the speed at which the nutrients contained in the fertilizer

granule migrate towards the medium and come into contact with the soil solution, compared to fertilizers that do not have coatings.

The speed at which the nutrients contained in the fertilizer grain migrate towards the medium depends on the material with which the wrapping is made, its thickness, humidity, temperature, pH and microbial activity. The coating has been made using different materials including minerals, oils, waxes, sulfur, plastics, resins and polymers (Fujinuma et al., 2009).

In the market there are fertilizers coated with minerals such as sulfur and phosphoric acid, with organic polymers such as starch, polyethylene and PVC or with low solubility substances such as urea formaldehyde (Yang et al., 2008). The disadvantage of these coatings is that some of them are not biodegradable or are toxic substances.

One coating used is carrageenan, a polymer extracted from different red algae of the Rhodophyceae class, with the genus Eucheuma, Chondrus and Gigartina being the main sources of raw material for the commercial production of carrageenan. Within this group is the algae of tropical waters belonging to the family Solieraceae known as the cottoni, is one of the red algae most used as raw material for production. Carrageenan is readily biodegradable, non-toxic and with it can be constructed super-absorbent hydrogels that do not solubilize in water under normal conditions of temperature, salinity and pH. Today carrageenan is widely used in food, medical and pharmaceutical industry. Although laboratory trials have been reported (Wang et al., 2012), carrageenan has not yet been reported as a raw material for a roof construction to commercial fertilizer.

Synthesis of hydrogels with polymeric materials

The presence of polysaccharides allows the formation of hydrogels. In the hydrogel state, the polysaccharides are physically cross-linked and form three-dimensional networks that swell in water. These gels can absorb up to ten thousand times their weight in water without dissolving or losing their integrity.

The formation of the hydrogel goes through different phases involving several stereochemical changes within the molecule. In solution state, the polymer molecules are presented as simple and random chains, which subsequently due to the conditions of temperature change form an energetically more favorable structure, where the molecules adopt an ordered conformation of double helix, which then added, to form a three-dimensional network that will give rise to a stable and firm gel. The concentration favors the condition of low solubility and therefore a gel is formed. The texture of the gel can be modified by adding cations (Shewan, 2013).

In the synthesis of the hydrogel it requires a cross linking agent, which generates free radicals that will allow the polymerization, forming a reticulated structure that allows the solvent to enter and subsequently the swelling of the hydrogel (figure 1). It has been proved that both the degree and nature of the polymer crosslinking are responsible for the swelling characteristics of the hydrogel and the ability to absorb water in addition to the ions which give it special characteristics with respect to the degree of swelling and properties related to the Cohesion strength (Rhim et al., 2013).

The use in the industry of these hydrogels basically depends on two properties, the gel strength, which represents the total amount of force required to perform the hydrogel cutting process, and the water holding capacity, which refers to the amount of water the hydrogel can store in its structure under equilibrium conditions. Therefore, when designing a hydrogel, it is essential to determine the preparation technique that will produce a hydrogel with the properties required in the different types of industrial uses of these gels (Ullah et al., 2015).



Figure 1. Scheme of behavior of the hydrogel. a. Polymer and b. Polymer with the plasticizer (glycerol, blue color).

Work hydrogels with different polymeric materials

The fertilizers coated by polymerscan be prepared by coating conventional fertilizer granules with various polymeric materials such as polyolefins (Du, 2002), polyvinyl chloride (Liang, 2006; Salman, 1989), polysulfone (Posey, 1994), and Polyacrylamide (Rajsekharan, 1996, Tomaszewska, 2002). The coating process requires a volatile organic solvent that is polluting to the environment and produces negative effects on human health evidencing different types of cancer (Abraham, 1998; Yang, 2008).

Han et al. (2009) evaluated starch-polyvinyl alcohol (PVA) as a coating of a granular fertilizer and found that the absorption and water permeability of the films increased the PVA content while it could biodegrade in the soil environment.

Rashidzadeh and Olad (2014) developed a slow release fertilizer NPK (10-5-5) encapsulated in sodium alginate, acrylic acid, acrylamide and montmorillonite; it shows that the coating had good release property as well as good water retention ability, reducing the loss of fertilizers and improving irrigation activity in agricultural applications.

Rozo and rozo (2008) synthesized a superabsorbent gel by copolymerizing polyacrylamide and kcarrageenan isolated from red algae (*Hypneamusciformis*), evaluating in combination with mixture of peat and natural fibers (rice hulls). It was found that the water retention of this gel was higher in substrates in which it was incorporated in higher concentrations, being able to absorb sixty times its volume in water and retaining up to twice as much water as peat. As for its physicochemical properties, the gel showed good strength, high capacity of absorption, reason why it was classified as a potential waterproof gel with great environmental and biodegradable advantages.

Finally, in another experiment, k-carrageenan and sodium alginate were used as the inner coating and polyacrylic acid as the outer coating of a granular fertilizer with 22% of urea, giving as a result that the incorporation of this product into the soil could prevent in a effectively way the compaction. Besides having good slow release properties and water retention presenting optimal potential applications for agriculture (Wang *et al.*, 2012).

Discussion

Anthropic activity has effects on the environment that can imply a wide range of environmental impacts, from imperceptible to large magnitudes. The dimension of the consequences of human activity on the environment will be determine by the responsible management of productive activity.

In the particular case of agricultural activity, the eutrophication of bodies of water and the escape of greenhouse gases into the atmosphere are large environmental impacts caused by the excessive use of fertilizers and the low efficiency of use of the nutrients contained in fertilizers by plants. These problems are compounded by the loss of soil structure caused by tillage which is reflected in a low moisture retention capacity of some soils and which decreases even more when there are dry seasons. Fertilization and tillage are not only having negative impacts on the environment, they are also compromising the sustainable productivity of the agroecosystem. Therefore, it is necessary to design management strategies that help to reduce the negative impact at the environmental level and that promote the sustainable productivity of agricultural systems.

Through the design of hydrogels with polymeric material as coating of slow release fertilizer NPK is intended to provide an option for the generation of responsible strategies for agricultural systems, because with this management will not only depend the impact dimension at environmental level but also productivity. Since the different works take advantage of the properties of naturally occurring polymers in the design of controlled release fertilizers, can first reduce the flow of nutrients applied through the fertilizers to the environment and second they have the potential to improve retention of soil moisture.

Conclusions

Sustainability is practically an obligation in any human activity, understanding it as economically viable, environmentally friendly and socially responsible. In industry, including the fertilizer industry, the cost /

benefit ratio for assessing the attractiveness of a project will shift increasingly towards cost / sustainability, which will apply in the agricultural sector when selecting a fertilizer or fertilization technique.

Production processes should be oriented towards those that do not generate (residues) or emissions that contribute to the greenhouse effect. Fertilizer efficiency should be oriented to fertilizers and fertilization techniques that optimize water, preservation of the physical-chemical quality of soils and greater efficiency of nutrient recovery (in plants) provided by fertilizers.

Based on the review of works, a sustainable fertilizer production strategy has been proposed to responds to these orientations in a simple and at the same time consistent and efficient way, using natural materials such as polymers that are friendly to the environment. In addition, its physicochemical properties allow an optimum coating, reducing the risks of environmental contamination, guaranteeing the availability of nutrients, continuous throughout the whole crop cycle, through a single initial contribution, saving labor, being an environmentally friendly green technology sustainable.

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