New Trends in Improved Nitrogen Fertilizers

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Abstract— *The Technology Roadmapping (TRM) method is a decision-making tool that allows aligning market, product and technology within a defined time horizon through the mapping of scientific and technological trends. The present study aimed to identify possible research lines for implantation of a fertilizer development laboratory. The study focused on controlled or slow-release fertilizers, due to their improved performance in the gradual nutrient release in the soil and their lower environment damage ability than conventional fertilizers. The development of TRM was based on the mapping of the state of the art and the main technological advances reported in sources such as patent documents, patent applications and scientific articles. The construction of roadmaps allowed identifying the most important technological innovations in a short, medium and long-term timeframe. In the long-term, the trend is in the use of coating from biopolymers, mostly from chitin, starch and cellulose. In matrix case, the analysis pointed to the use of solids such as clay and zeolite, materials considered superabsorbent. In the short term, the concern about the environment indicates the search for less aggressive products, besides easy to handle and of low cost. In the mid-term, the use of biomass as support was evidenced.*

I. INTRODUCTION

In order to increase sustainable agricultural productivity, the fertilizer industry continuously improves the use and production of nutrients from plant varieties in an efficient and responsible manner, benefiting the soil and preserving the environment. This avoids pollution of soil, surface and groundwater. In this scenario, improved efficiency fertilizers appear, capable of releasing nutrients more efficiently and minimizing adverse environmental impacts (TRENKEL, 2010). This group of improved fertilizers includes slow-release fertilizers (SRF) or controlled-release fertilizers (CRF) and stabilized fertilizers. The first group releases nutrients according to the needs of plants with a single application, as they are less water-soluble and more nutrient-rich materials. This characteristic reduces losses by leaching, immobilization and volatilization (nitrogen fertilizers' case), achieved by preparation techniques for improving conventional fertilizers or through new types of specific fertilizers (TRENKEL, 2010).

Within the context of a globalized world, the chemical industries are driven to produce more diversified and innovative materials due to the new extremely competitive environment. This demand generates investments in research and development (R&D) as a source of innovation (WONGTSCHOWSKI, 2012). In this sense, competitive information is a fundamental and valuable tool in a digital age for helping to use knowledge in a systematic and targeted way (TAVARES et al., 2015). The main challenge of information management is to connect technological planning with business planning. One of the tools developed to address this issue is Technology Roadmapping (TRM). It integrates and communicates the market, product and technology development strategies with the business goal in a time horizon, in which the planning procedures depend on the technical expertise of

professionals in the area (ALBRIGHT & KAPPEL, 2003). Moreover, it is a simple methodology whose script is detailed in the literature.

1.1. Basic and fundamental concept

Roadmapping or Tecnology Roadmapping is a decision-making tool used mainly in the industry for the development of planning strategies in order to align the market, product and technology in three distinct layers within a defined time horizon (GARCIA and BRAY, 1997 A; LIZASO and REGER, 2004). Roadmapping must be driven by needs (needs-driven) or driven by a mission / objective (mission-pull). In addition, the method must:

• Integrate problem holders and solution providers in an integrated and cooperative team consensus.

• Be embracing in order to provide the means to identify, evaluate and select technological alternatives that can be used to meet short, medium and long term needs and objectives.

• Be reliable, defensible, and the reasons for decisions must be documented. This stage of the process will lead to a new stage, namely: extraction of control indicators.

1.2. Roadmap architecture, types and formats.

The most common architecture of the roadmap is a representation based on the time dimension and the relevant aspects of the business (market, product and technology), as shown in Figure 1.
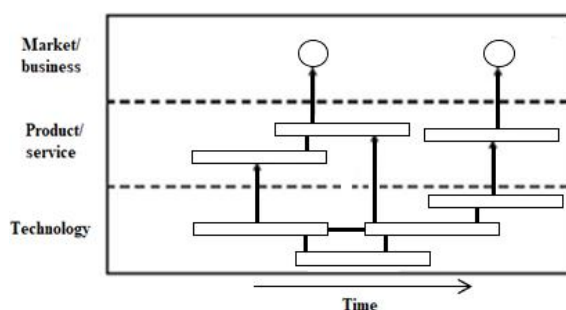

Fig.1: Common architecture of a roadmap.

Source: Adapted of Phaal *et al.* (2003).

The most common types and formats are: product roadmap, emerging technology roadmap, subject-oriented roadmap, corporate roadmap, industrial roadmap. According to Albright (2007), roadmappings define a future goal and answer a set of essential questions in order to develop an action plan to achieve the objective set. The first step is known as the "why" of a roadmapping. The second part is defined as the "what" stage of the roadmapping, where action plans are outlined. The third stage deals with the evolution of the technologies that will be used to achieve the objectives, being the "how" of a roadmapping. The fourth part, known as the "tasks" stage of the roadmapping, defines the action plan and risks.

1.2.1. Methodology adopted by Garcia and Bray (1997)

This application consists of three phases. In the first one, preliminary activities are defined. It is during this phase that strategic objectives are explicitly outlined and relevant stakeholders are identified and management of the technological roadmapping is created. The second phase is a development in itself of the TRM divided into seven steps that can be applied both at the corporate level and at the industrial level. And the last phase is about continuity activities that also include their review and update. In this phase, there is the criticism, validation and approval of the roadmap elaborated through three steps.

1.2.2. Methodology adopted by Suzana Borschiver and Andrezza Rangel (2016)

This method consists in three steps, they are: pre-prospective, prospective and post-prospective. The pre-prospective stage is divided in four phases, they are: (1) identification of the theme to be studied, (2) bibliographic survey of the theme (state of the art/ technique), (3) establishment of goals and, (4) strategies outlined for the elaboration of the desired product roadmap. The prospective stage is divided in two phases: (1) driven research (for example, search on the basis of patents, patent applications and scientific articles) and, (2) analysis of the results generated by the search. The post-prospective stage is divided in two phases: (1) elaboration and analysis of the roadmap and, (2) conclusion.

In face of the scenario presented in this work, the present study aims to identify, through a decision-making tool, R&D investment opportunities for the next ten years, prioritizing possible lines of research for the implantation of a laboratory for the development of fertilizers. In this sense, this work was structured as follows: initially, the technology roadmapping (TRM) decision-making tool id presented. Subsequently, the tool is applied in the treatment of information related to the state of the art / art referring to improved efficiency fertilizers. Only supported controlled or slow-release fertilizers are focused, thus portraying an overview of the existing product, technology and market found in the literature review. At the end, the main possible lines to be covered for research and development in the segment of matrix slow or controlled release fertilizers are shown and pointed out.

II.   MATERIALS AND METHODS

The phases of the TRM method adopted in the organization of this work are an adaptation of the roadmap method made by Garcia and Bray (1997), which can be conducted in three phases: preliminary activities, development of the roadmap and continuity activities. In the present adaptation, the teaching used in the methodology developed by Suzana Borschiver and Andrezza Rangel (2016) was also considered, which can be conducted in three phases as can be seen in the Figure 2
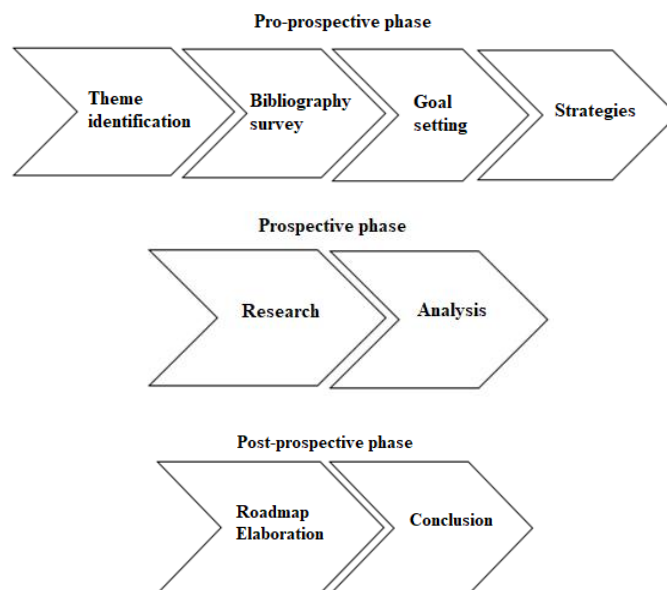
below. The Pre-prospective phase mentioned by Borschiver and Rangel (2016) is similar to the preliminary phase mentioned by Garcia and Bray (1997).

2.1.   Strategy adopted for the construction of the Roadmap

Figure 2 illustrates the scheme applied in the research, from the identification of the theme to the conclusion, in which a proposal was developed to adopt measures / actions to be carried out.

Fig.2: Methodology adopted at work.

Source: the authors.

2.2.   Methodology applied to use the roadmap in the analysis of bibliography research

a) Search on the basis of granted patent documents (short term) was carried out by consulting the free online database of the United States Patent Trademark Office (USPTO) and Espacenet, of the European Union.

b) Search in the patent application documents database (mid-term) was carried out by consulting the USPTO and ESPACENET's free online database.

Both searches carried out in the patent databases adopted the search criteria: (i) keywords "fertilizer and release and (slow or controlled) and (matrix or coat) and (encapsulate or impregnate or entrap)"; (ii) the international patent classification codes specifically related to nitrogen fertilizers, which fall under the C05C code and its ramifications and; (iii) year of grant, in the case of patents granted, or year of publication, in the case of patent applications. For both cases, the period between 2008 and 2018 was adopted.

c) Research in the scientific articles database (long term) was carried out in the SCOPUS databases adopting the search criteria: (i) year of publication of the article in the period between 2008-2018 and, (ii) keywords "fertilizer and release and (slow or controlled) and (matrix or coat) and (encapsulate or impregnate or entrap)".

In the three surveys carried out above, only documents with the following technical characteristics were selected: matrix or coated controlled or slow release nitrogen fertilizers.

2.3.   Taxonomies identification

The key parameters found for the taxonomies were identified through a careful analysis of all documents considered relevant in the stages of gathering technical and scientific data. These key parameters were interpreted as relevant aspects that define the object of the study: nitrogen fertilizers matrix or coated with controlled or slow release.

III.   RESULTS

3.1 Improved efficiency or intelligent fertilizers

US patent application 2,016,340,265 reveals that different approaches have been proposed to reduce nitrogen loss. Among them, the encapsulation of the fertilizer delaying the release of fertilizer, so that the plants have more time for assimilation of nutrients. The use of the urease inhibitor and / or nitrification was also evidenced to delay the activity of the particular enzyme or microorganism. According to the depositor, both approaches have been extensively explored to develop improved efficiency fertilizers. However, the application of inhibitors is limited due to its instability in the soil under various conditions, such as pH, temperature, precipitation, among others.

In controlled release fertilizer (CRF), dominant parameters of nutrient release, such as, release rate, pattern and duration are known over a certain period of time (BORSARI, 2013; SHAVIV, 2005) and are a consequence of the CRF preparation step (SHAVIV, 2005). The release pattern of slow-release fertilizers (SRF), in turn, is dependent on the soil and climatic conditions. Therefore, it cannot be predicted over time (BORSARI, 2013). For Shaviv (2005), SRF involves the release of nutrients at reduced rates. But the nutrient release parameters (rate, pattern and duration) cannot be controlled.

Shaviv (2000) classifies SRF or CRF into three groups: (1) organic compounds with low solubility; (2) fertilizers with physical barrier control; and (3) inorganic compounds with low solubility. Inside the group 2, there are the coating and matrix fertilizers. Regarding matrices, they are divided into two subgroups of materials for their preparation: hydrophobic materials, such as polyolefins and rubber; hydrophilic materials, such as hydrogels. As examples of inorganic compounds with low solubility, metallic ammonium phosphates and partially acidulated phosphate rocks stand out (SHAVIV, 2000). Trenkel (2010) highlights three main groups of materials for preparing coated / encapsulated fertilizer coatings: (1) sulfur; (2) sulfur together with polymers, including waxy polymeric materials; and; (3) polymeric materials / polyolefin.

According to Borsari (2013), the main products manufactured in the current market with their different mechanisms are: (i) low solubility fertilizers with a complex chemical structure, dependent on microbial action, such as urea-formaldehyde; (ii) fertilizers with physical barriers, such as fertilizers coated with sulfur, minerals or organic polymers and; (iii) gel-based matrix fertilizers or organic matter with or without coating.

3.2 Guiding taxonomies identified in the patent and scientific literature survey

Table 1 shows the identified guiding taxonomies of the referred trinomial (Market / Product and Technology):

Table.1: Adopted taxonomy.

Section	Key parameters	
	NUE (nutrient use efficiency)	
	Less aggressive to the environment	
	Water retention capacity	
	Water absorption capacity	
Market	Swelling capacity	
	Degradation capacity	
	Mechanical properties and/or improved elastic ones	
	Good quality in storage and transportation	
	Cost reduction	
	Easy handling	
Polymer and/or resin		Biopolymers
		Synthetics
	Mixture of polymers and sulfur	
	Mixture of polymers, biomass and others	
	Biomass	

Product		Mixture of biomass and others
		Sulfur
		Mixture of polymers and sulfur
		Mixture of sulfur and others
	Others	Clays
		Silica
		Zeolites
		Varied materials
	Polymers and/or resins	Single
		Combination
	Biomass	Single
		Combination
Technology	Coating	1 layer
		2 layers
		Multiple layers
	Matrix	Impregnation
		Mixture/combination
	Polymer matrix	Impregnation
		Mixture/combination

Source: the authors.

I. DISCUSSION

In this topic, roadmap analysis is presented and discussed.

4.1 Market-related aspects

Analyzing the results of surveys carried out in the short, medium and long terms (Figure 3) in relation to market aspects, it appears that the trend continues with the focus on the nutrient use efficiency (NUE), on the environmental issue and on the water retention capacity. In other words, the researchers aim products with improved NUE, less aggressive to the environment, with good degradation and swelling capacity, as well as good water retention and absorption capacity, being this profile shown in Table 2.

Table.2: Market analysis. Source: the authors.

Sections	Key parameters	Mid-term	Long term
Market	Nutrient use efficiency	USPTO (21)/ESPACENT (36)	SCOPUS (61)
	Less aggressive to the environment	USPTO (18)/ESPACENET (36)	SCOPUS (61)
	Water retention capacity	USPTO (14)/ESPACENET (18)	SCOPUS (51)
	Water absorption capacity	Not found	SCOPUS (49)
	Swelling capacity	Not found	SCOPUS (21)
	Degradation capacity	Not found	SCOPUS (37)
	Mechanical properties or improved elastic ones	Not found	SCOPUS (49)
	Good quality in storage and in transportation	Not found	Not found
	Cost reduction	USPTO (20)/ESPACENET (33)	SCOPUS (50)
	Easy handling	Not found	Not found

4.2 Aspects related to product

According to Table 3, in the long term, there is an increase in the interest of researchers in biodegradable natural polymers, relatively non-toxic to the environment. For instance, the articles reveal an interest in superabsorbent hydrogel based on natural polymers. Duquette and Dumont (2018) define superabsorbent hydrogels as polymeric materials known for their ability to absorb and retain a large amount of water or aqueous solution. Sannino and co-authors (2009) show that hydrogels are capable of absorbing and releasing aqueous solutions in a reversible manner, in response to specific stimuli in the environment.

Some hydrogels mentioned in the articles are based on alginate, cellulose, among others. Alginate, a polysaccharide (natural polymer) derived from seaweed, was mentioned in some of these articles as a biodegradable material applied as a raw material for coatings and polymer matrix (NI et al, 2010). Cellulose, a natural polymer, was mentioned as an abundant material in nature because it is the largest constituent of plants and natural fiber, besides being biodegradable and having low cost (SANNINO et al, 2009). Some researchers have focused their research on biopolymers derived from starch, which is abundantly available from renewable plant sources (Niu and Li, 2012).

The survey reveals that the researchers aimed at applying polymers or combining them with other materials. Or, even, a combination of polymers with biomass and other materials. To be more specific, many authors have combined polymers with materials, such as silica, clay, zeolite, biomass etc.

Table.3: Product analysis.

Sections		Key parameters	Short term	Mid-term	Long term
	Polymers or resins	Biopolymers	USPTO (2)	ESPACENT (4)	SCOPUS (18)
		Synthetics	USPTO (24)/ESPACENT (34)	USPTO (5)/ESPACENET (4)	SCOPUS (8)
		Mixture of polymers and others	Not found	Not found	SCOPUS (20)
		Mixture of polymers, biomass and others	Not found	Not found	Not found
		Biomass	USPTO(9)/ESPACENET (4)	USPTO (12)/ESPACENET (12)	Not found
		Mixture of biomass and others	Not found	Not found	Not found
Product		Sulfur	Not found	Not found	Not found
		Mixture of polymers and sulfur	USPTO(6)/ESPACENET (22)	Not found	Not found
		Mixture of sulfur and others	Not found	Not found	Not found
		Clays			
		Silica	USPTO(10)/ESPACENET (7)	ESPACENET (13)	SCOPUS (10)
		Zeolites			
		Varied materials			
		Single	USPTO (25)	ESPACENET (8)	SCOPUS (31)
		Combination	ESPACENET (48)	USPTO (3)	Not found
		Single	Not found	Not found	SCOPUS (7)
		Combination	USPTO (8)	USPTO(11)/SPA	Not found

CENET (7)

4.3 Aspects related to the technology

For technology analysis, it was regarded three taxonomies, they are: coating, matrix and polymeric matrix. Within coating category, are the coating fertilizers and the mixed-type ones. The last ones involve the use of a coating around the matrix holding the fertilizer; therefore, it is characterized by a combination of two types of physical barrier. The analysis in long term identified the number of layers the coating fertilizer has of raw material (resin and /or polymer) (Table 4). In the articles, it is reported that this fertilizer type has one or more layers of protection formed through the encapsulation or covering step of the fertilizer.

As well as reported in the search for patents and patent applications, the articles took to the understanding that the majority number of studies about coated fertilizers is based on encapsulation having a single layer. In the short and mid-term, patents and patent applications indicated that the predominant quantity of coating fertilizers are the ones encapsulated with a single layer. This is due to the increase in production costs when applying larger quantities of high-value raw materials (in general, polymers) to obtain two or more layers. Coatings are obtained by immersion, emulsion, spraying, precipitation, etc.

Regarding the form of holding the fertilizer in the solid raw material (biomass, silica, clays, zeolites), in the case of the non-polymeric matrix type and mixed systems, the articles revealed the authors' preference for physical mixing/combining technique. In general, they reported physical mixing through granulation, melting, extrusion, among others. Some articles reported the use of binders or additives in this mixing stage. Regarding the polymeric matrix, all the cases found had used the mixing method as a preferred technique, such as, extrusion, emulsion and fusion and the raw material may be composed only of polymers (single or combination of two or more); combination of polymer and biomass; combination of polymer and others (for example, silica, clays and zeolites) and; still, combination of polymer, dry biomass and others. The predominant fertilizer used in all studies was urea.

Sections		Key parameters	Short term	Mid-term	Long term
Technology	Coating	1 layer	USPTO (32)	USPTO (3)/ ESPACENET (14)	SCOPUS (18)
		2 layers	Not found	Not found	Not found
		multiple layers	ESPACENET (40)	Not found	Not found
	Matrix	Impregnation		USPTO (12)	Not found
		Mixture/combination	ESPACENET (4)	ESPACENET (11)	SCOPUS (8)
	Polymeric matrix	Impregnation	Not found	Not found	Not found
		Mixture/combination	Not found	Not found	SCOPUS (24)

Table.4: Technology analysis.

IV.   CONCLUSION

Roadmaps, mainly of medium and long term, showed a tendency towards slow or controlled release fertilizers, using mainly materials such as clays, silica, zeolite, biomass, biopolymers or combinations of these. Regarding the mixed materials, the documents showed that multiple layers form more efficient slow or controlled release fertilizers. In the matrices, the mixture of the supports with the fertilizers is more common than the impregnation of the fertilizers in the supports. Thus, research lines exploring different solid types and/or combination of them, besides the application of biopolymers in the synthesis of new SRF and CRF seem to be promising lines for a fertilizer development laboratory.

The market analysis points to the interest in products that are less aggressive to the environment, as well as products with low cost. These two aspects, in addition to nutrient use efficiency (NUE), are the aspects most addressed in patents and scientific articles. Roadmapping technology, although widely used in the corporate sector, proved to be an interesting tool for prospecting ideas and strategic planning also in the area of Research and Development. It therefore becomes useful in gathering information to foster entrepreneurship at the academic level.

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