

The Future of Fertilizer: Formulations and Usage

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Abstract

The development of modern fertilizers has sustained an ever-growing world population. This development has been strongly facilitated by the discovery of deposits of phosphate rock in various parts of the world and the implementation of the Haber-Bosch process for the production of ammonia. Plant nutrients from both sources are now facing challenges. The sources of phosphate rock are being depleted in many areas and the Haber-Bosch process is energy intensive, expensive and exacerbates negative climate change. Further, overuse of these materials has contributed to environmental pollution, clogged waterways, and dead zones in various parts of the oceans. The development of better methods for applying and using fertilizers is becoming increasingly important. Significant progress is being made in the development of new technology to replace nitrogen fixation by conventional techniques, the recovery of fertilizer components, particularly phosphorus and nitrogen, from wastewater, and new formulations to permit controlled release of plant nutrients to facilitate more efficient utilization by plants and reduce polluting runoff.

Keywords: Plant Nutrients, Plant Growth, Food Production, Efficient Fertilizer Utilization, Agricultural Runoff, New Fertilizer Sources, Polymeric Fertilizers.

Introduction

Almost from the time that homosapiens began to organize into groups to settle into communities and to domesticate plants and animals, there has been a need for nutrients to support plant growth and development [1]. These were first supplied by animal manure. Manure is an excellent fertilizer. It contains both phosphates and urea, which provide the essential elements, phosphorus and nitrogen. These two elements, along with potassium (potash; potassium chloride) constitute the principal components of modern commercial fertilizers [2,3]. Manure does contain some potassium, depending on source, but generally not in large amount. These three along with several elements required in lesser amounts and present in most soils are essential for rigorous plant growth. In addition, the use of manure improves soil quality and health to facilitate plant growth. However, there was never enough manure available to meet the demand for crop production, principally cereal grains and legumes. Further, the transport of bulky material over long distances often incurs prohibitive cost. As agriculture was developed in Europe, the guano islands in the Atlantic were discovered [4]. Within a few years, these precious resources were exhausted.

The next great advance was the exploitation of Chilean nitrate deposits [5,6]. This continued to the early twentieth century and advent of the Haber-Bosch process for the generation of ammonia from nitrogen [7]. Although the Haber-Bosch process was developed to support the production of munitions in Germany,

its impact on the fertilizer industry and food production has been far greater. Ammonia can be readily converted to nitrate or urea for use in solid fertilizer formulations or, using modern equipment, applied directly as a fertilizer in crop fields. The ready availability of ammonia along with the mining of phosphate and potash deposits made possible the modern fertilizer industry and the consequent vast improvements in agricultural productivity that occurred throughout the last half of the last century. It should be noted, that while fertilizer development has had a dramatic impact, it is not the only development that has contributed to the dramatic improvement in agricultural productivity.

The enhancement of plant characteristics has strongly influenced productivity. A prime example is provided by the domestication and exploitation of teosinte (maize; corn) as a food crop [8]. When the cultivation of this plant began, it had the appearance and characteristics of a typical small grain. However, within a few generations, this plant began to take on the appearance of a modern corn plant-central strong stalk, single seed pod. How did this happen? The people growing this plant were not chemists or geneticists but rather subsistence farmers. How were they able to develop a superior plant? The answer, of course, is selection. These people were dependent on good crop yields for existence. At the end of each growing season, they selected seeds from the best plants to be planted the following season. The genetic traits of the plant improved with every cycle. This approach, selection coupled with plant breeding techniques (natural genetic

modification), was heavily utilized by major seed companies to generate ever-improved crop plant varieties long before there was a sufficient understanding of genetic chemistry to permit direct manipulation of the DNA polymer to insert desired traits. Another prominent example of plant improvement through natural genetic modification is the Borlong development of rust-resistant short-stemmed wheat [9,10]. This was accomplished through selection and painstaking cross-breeding and had a dramatic impact on world food production. It led to the green revolution, which saved countless lives worldwide [11]. The ability to directly manipulate DNA has permitted the rapid introduction of desirable features into crop plants. Perhaps, the most impactful advance has been the development of herbicide-resistant crops [12,13]. The development of effective pesticides has also strongly contributed to more efficient crop production [14].

Challenges in Fertilizer Use

With the world's population projected to approach ten billion people by 2050, the requirement for efficient food production will become paramount. The production of food will face significant hurdles, by no means all related to the availability of high-quality fertilizers. However, the challenges facing the availability and effective utilization of fertilizers are large and increasing. The necessity to close the loop on resource procurement/utilization is becoming ever more apparent as the impacts of human activity, induced climate change and degradation of the natural environment are increasingly felt [15-21]. "Sustainability" may be required for survivability.

Innovative Fertilizer Technologies

Deposits of phosphate rock are limited (produced in only six countries) and being consumed at an ever-increasing rate (those in the southeastern United States have largely been exhausted). Phosphate from other sources is highly desirable [22-24]. Huge quantities of phosphorus are discarded annually in wastewater treatment facilities. Residue from the treatment process is rich in phosphorus and other nutrient elements. Recovery of phosphorus from sewage residue is beginning to receive serious consideration [25-30]. Initially, sewage was applied directly to agricultural fields. This is effective in providing nutrients, promotes the growth of soil organisms, and adds organic matter to the soil, all beneficial to plant growth.

However, many wastewater treatment facilities accept industrial effluent that may contain heavy metals and other contaminants. These concentrate in the residue. When it is used on crop fields, these may be taken-up by plants and enter the human food chain. Many methods for the recovery of phosphorus from sludge have been explored. One of the most promising is the conversion of sludge to biochar [31,32]. During the conversion the nature of phosphorus species may be changed and some contaminants volatilized [33]. The precipitation of struvite has also been widely explored as a recovery method [34-37]. The potential for recovery of phosphorus from sludge and its impact on agricultural production is huge. However, infrastructure and regulatory changes to prevent industrial discharge from contaminating wastewater streams may be necessary.

The Haber-Bosch process for the production of ammonia has made nitrogen fertilizers widely available and has supported major increases in food production. However, it suffers from several significant shortcomings. It is energy intensive, expensive, and generates huge amounts of carbon dioxide, a major greenhouse

gas. In the main, it relies on hydrogen production from fossil sources (most hydrogen is produced from steam reforming of methane) as a feedstock. Use of hydrogen from water splitting using electricity from wind power would strongly improve the process but it is not yet available on a huge scale [38,39]. Other innovations could reduce the energy consumption required by the process. These may include electrochemical processes for generating (again, dependent on the availability of non-fossil electricity) ammonia directly from air and water, laser-induced fixation or utilization of new catalytic processes [40-51]. Smaller units capable of utilizing green methods may be attractive for single farms or clusters of farms [52]. This might be particularly appropriate where non-fossil hydrogen is readily available or where transport costs make up a substantial portion of fertilizer prices. As noted, the increasing demand for nitrogen fertilizers and the deficiencies of the Haber-Bosch process for ammonia production has stimulated efforts to generate ammonia using innovative approaches that feature milder conditions with far smaller environmental impact [53]. An unusually intriguing approach suggests the production of ammonia underground in the presence of mineral catalysts naturally present [54].

Environmental Impact of Current Fertilizer Usage

Two features of modern fertilizer use represent major difficulties. First, fertilizer applications normally occur as a single event at the beginning of the growing season. Second, plant uptake of nutrients occurs over the length of the growing season and is inefficient. As a consequence, much of the applied fertilizer is leached away and enters streams and waterways. Ultimately, it is dumped into the world's oceans where it promotes excessive plant growth which consumes aquatic oxygen such that animal life is not possible. So-called dead zones now exist in several parts of the world [55-57]. Perhaps, the most notorious is that in the Gulf of Mexico at the mouth of the Mississippi River [58]. Runoff from the agricultural midwest of the United States carries large amounts of both nitrogen and phosphorus to the gulf each year. Efforts to mitigate both problems are underway. Although, it is in its infancy, the development of microbes capable of fixing nitrogen directly from air is being pursued by several commercial entities [59, 60]. Biostimulants to facilitate the uptake of nutrients by plants are also being developed [61,62]. These include microbes, plant extracts, protein hydrolysates, and others.

Sustained Release Fertilizer Formulations

Perhaps, the approach with the greatest potential is the formulation of sustained-release fertilizer compositions [63-77]. This approach can make nutrients available to plants throughout the growing season at a rate that will permit maximum uptake efficiency. This reduces the potential for excess application with consequent detrimental runoff and the cost to farmers.

Nanocellulose has been prominently proposed as an environmentally attractive carrier in sustained-release fertilizer formulations [78-80]. Traditional polymers have also been used for this purpose [81,82]. With the advent of new technology which permits the generation of hyperbranched poly(ester)s of any desired molecular weight, controlled branching and single identity (either hydroxyl or carboxyl) endgroups while avoiding gelation, a new approach for the formulation of sustained release fertilizers has become available [83-85]. These materials may be utilized to encapsulate solid fertilizers, e.g., urea. More importantly, fertilizer moieties may be attached covalently. For example, an oligomer with hydroxyl endgroups may be readily converted to phosphorus esters

to provide a material suitable for phosphate release. Similarly, polymers containing carboxyl endgroups may be converted to amide, or similar, groups to release nitrogen species. Release of the active species occurs readily at ambient conditions under enzyme (soil organisms) catalysis [86]. An attractive hyperbranched poly(ester) is that derived from the readily available, inexpensive, nontoxic biomonomers, glycerol and adipic acid. The polymer undergoes hydrolytic degradation to regenerate the innocuous monomers under the same mild conditions required for release of the active agent. Thus, no unwanted or toxic material remains after release of the nutrient species (it is likely that these biomonomers will be rapidly consumed by soil organisms) [85]. Perhaps even greater potential rests with hyperbranched poly(ester)s using core entities containing phosphorus, boron, nitrogen or other important nutrient elements. A simple example might be the hyperbranched poly(ester) obtained from trimethyl phosphate and ethylene glycol.

Sustainability and Future Directions

The development of the modern fertilizer industry has been a boon to society permitting ever-increasing population growth. However, it is facing serious limitations and must undergo significant change in coming years. The two most pressing problems faced by the industry (and society) are the high cost and the negative impacts of the Haber-Bosch process for the production of ammonia and the depletion of phosphate rock deposits. Fortunately, an awareness of these problems is increasingly present, and efforts are being made to address them. However, most of these are in very early stages of development. The rate of progress needs to be accelerated. Public and governmental support for these efforts is essential. Increased funding for research and development in both areas can be hugely beneficial. The fundamental question remains, "How can a population of ten billion by 2050 be sustained?"

The electrochemical production of ammonia from water and air, using renewable electricity, would seem to be the most favorable alternative to Haber-Bosch. This has been proposed in several variants. One needs to be selected and pushed forward, perhaps by a farmer's cooperative with governmental support, to a demonstration facility. In the coming years, the recovery of phosphorus from wastewater will become imperative. Currently, huge amounts of recoverable phosphorus is wasted annually. An impediment to progress is the comingling of industrial and household waste. Recovery efforts can be strongly enhanced by enlightened governmental regulation and support. Governments worldwide need to be more attentive to alternative sources of both nitrogen and phosphorus fertilizers.

The utilization of fertilizers must be made more effective and sustainable. Currently, fertilizers are applied in far greater quantities than can be efficiently taken up by plants. The excess is leached away as runoff leading to great environmental damage to waterways. This situation may be alleviated through the use of sustained release fertilizer formulations. Several methodologies for doing this are being pursued. The most promising would seem to be the incorporation of fertilizer components into biocompatible, biodegradable polymers derived from readily-available, low-cost, nontoxic biomonomers.

Conclusions

To feed the growing world population in the face of finite supplies of phosphate rock, the inadequacies of the Haber-Bosch process for the production of ammonia, the increasing encroachment of urban areas onto farmland, the loss of soil fertility because of poor

conservation practices, and the negative impacts of climate change on agricultural production, changes in the formulation and use of fertilizers will be needed. Fortunately, this is now widely recognized and various efforts to address the situation are underway. Clearly, the waste of large amounts of nutrients, particularly phosphorus, from wastewater treatment cannot continue. In the future, this will inevitably become a base for phosphorus fertilizer production. More efficient production of ammonia using improved methods and hydrogen from water produced using renewable energy sources will be needed. Fertilizers will need to be more efficiently used in crop production both to contain demand and prevent nutrient runoff and consequent pollution. Controlled or sustained release fertilizer systems can make significant contributions in this area. Plant nutrients contained in appropriate polymeric matrices, either by encapsulation or covalent attachment, represent agents for the slow release of species necessary for plant growth over the growing season. Several requirements need to be met by polymers to be used in such formulations. They must be available from abundant, renewable, inexpensive, nontoxic monomers. Ideally, these should be biobased. The polymer must be readily degradable in the presence of soil moisture and organisms both to release the active agent and avoid the accumulation of undesirable residue. Hyperbranched poly(ester)s derived from nontoxic, environmentally-friendly biomonomers are well-suited for this application. Using newly developed technology, the Martin-Smith model for predicting appropriate monomer ratios, these materials may be produced using a simple process that avoids gelation and affords a polymer with a single endgroup identity (either hydroxyl or carboxyl). The plethora of reactive endgroups permits the ready attachment of nutrient entities.

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