[1.]Vasilica ȘTEFAN, [1.]Iuliana GĂGEANU, [1.]Radu CIUPERCĂ, [1.]Ana ZAICA, [2.]Oana Elena MILEA, [1.]Melania CISMARU

PHOSPHORUS EXTRACTION TECHNOLOGIES

[1.]National Institute of Research – Development for Machines and Installations Designed to Agriculture and Food Industry Bucharest, ROMANIA;
[2.]National University of Science and Technology Politehnica Bucharest, Faculty of Biotechnical Systems Engineering, ROMANIA

Abstract: Inadequate global management of fertilizers leads to areas with severe nutrient deficiencies in agricultural lands, linked to insufficient access to fertilizers, thereby limiting food production. On the other hand, there are areas that are over–fertilized, leading to subsequent environmental pollution issues that affect human health. Therefore, a more efficient use of nitrogen (N), phosphorus (P), and potassium (K) fertilizers is necessary for food security while maintaining an environmental balance. The technological study regarding the methods and sources of phosphorus extraction encompasses numerous modern and complex approaches to obtaining and supplying new phosphorus resources. Essential for the daily processes of living organisms and crucial for the growth and development of plants, phosphorus stands as one of the most important chemical elements. As an essential limited resource, the creation of new sources, recycling, and phosphorus recovery are crucial strategies for maintaining environmental balance and reducing dependence on finite phosphorus resources. The different economic and geopolitical characteristics of these three main macronutrient fertilizers need to be taken into account. Phosphorus has the fewest reserves, depending largely on mining efforts, with the majority of reserves concentrated in very few countries. Thus, sources derived from organic or inorganic waste, animal excreta, bone ash, expired food products, wastewater, are exploited through phosphating technologies, thermal treatments, composting, anaerobic biodigestion, adsorption, chemical precipitation, etc

Keywords: phosphorus, fertilizer, agriculture, extraction, pyrolysis, combustion, poultry

INTRODUCTION

The massive use of fertilizers in recent decades has allowed for a significant increase in global food production capacity. However, in recent years, several studies have highlighted the inefficiency and country–level asymmetries in the use of these fertilizers, which have generated environmental problems, soil nutrient imbalances, and suboptimal food production.

Inadequate global management of fertilizers leads to areas with severe nutrient deficiencies in agricultural lands, linked to insufficient access to fertilizers, thereby limiting food production. On the other hand, there are areas that are over–fertilized, leading to subsequent environmental pollution issues that affect human health. Therefore, a more efficient use of nitrogen (N), phosphorus (P), and potassium (K) fertilizers is necessary for food security while maintaining an environmental balance. Nutritional imbalances, especially the imbalance in the N:P ratio caused by the unbalanced release of N and P from anthropogenic activities, primarily through crop fertilization and the expansion of nitrogen–fixing crops that continuously increase the soil's N:P ratio, represent another problem to be addressed. This imbalance has already affected several terrestrial and aquatic ecosystems, altering the composition and functionality of species and threatening global biodiversity. The different economic and geopolitical characteristics of these three main macronutrient fertilizers need to be taken into account. Phosphorus has the fewest reserves, depending largely on mining efforts, with the majority of reserves concentrated in very few countries (85% in Morocco). This issue is a major concern for current and future access to phosphorus, especially in low–income countries. On the other hand, nitrogen is readily available due to the well–established and relatively inexpensive Haber–Bosch synthesis of ammonia from atmospheric N_2, which is increasingly used even in some low–income countries, leading to an increasing imbalance in nutrient ratios with the application of P and K fertilizers.

Phosphate rock is unevenly distributed worldwide, with control over the remaining reserves being limited to a small number of countries. According to the US Geological Survey's 2015 study, Morocco, China, Algeria, Syria, and South Africa together control 88% of the world's phosphate. Morocco alone controls 75% of the world's high–quality reserves, and it is expected that the Kingdom's share will increase to 80–90% in the coming decades.

The United States used to be the largest producer, consumer, importer, and exporter globally, but it is now estimated to have only about 20 years of reserves remaining. China recently imposed a 135% export tariff to ensure domestic fertilizer supply, leading to a halt in the majority of exports. This means that all importing countries, from India to Australia and Europe, are vulnerable to price fluctuations and supply disruptions in the producing countries. Phosphorus fertilization has increased much less compared to nitrogen fertilization in recent decades (*Romero E. et al., 2021*). However, the demand for phosphorus fertilizers is expected to increase in the coming decades, with the global peak of phosphorus production projected to occur around 2030 (*Cordell D. et al., 2009*).

Estimates regarding the depletion of existing P reserves, however, vary widely, for the next 40–400 years *(Cordell D. et al., 2018; Obersteiner M. et al., 2013; US 2016)*. The exact timing of the peak of P production is disputed, but it is widely recognized that the quality of the remaining phosphate rock is continuously decreasing (*Desmidt E. et al., 2014; Herrera–Estrella and López–Arredondo,* 2016), leading to increased production costs and, implicitly, to difficulties in low–income countries' access to P fertilizers.

The situation may become more problematic, as some sources forecast that the global need for P fertilizers will double by 2050 *(Nedelciu et al, 2020)* and also predict increased loss of P from soil, including agricultural land, as a result of climate change–related soil erosion, which will increase the need for P fertilizers to support agricultural production *(Alewell C. et al , 2020)*.

MATERIALS AND METHODS

Phosphorus is one of the 17 essential nutrients for plant growth, being a catalyst for many biochemical reactions that take place in plants. It is essential for growth, development and reproduction, being required by plants in the process of photosynthesis and important for plant development throughout the life cycle, from germination to senescence. Its functions cannot be fulfilled by any other nutrient, and an adequate supply of P is necessary for optimal growth and reproduction.

Phosphorus is classified as a major nutrient, meaning that it is often deficient for agricultural production and is required by crops in relatively large quantities. Total P concentration in agricultural crops generally varies between 0.1 and 0.5 percent (*Armstrong, 1999*). This is due to a number of factors such as pH value, moisture, organic matter concentration and soil texture.

Identifying other sources of phosphorus, other than natural rock, is a global priority, as the global population is expected to reach over 9 billion by 2050 and the demand for food will be greater with 60% by that date, seen in the NPK Prospective Study carried out by *JRC, 2012*. Therefore, it is imperative to find other ways to solve the PHOSPHORUS problem both globally and at the level of Romania

The technological study of phosphorus extraction methods and sources is a complex and vast subject because there are different ways to obtain phosphorus and the sources may vary depending on the method used.

Determining the precise amount of phosphorus that is currently accessible worldwide due to the recycling of wastes such as sludge, manure, and sanitation is a challenging task. There is currently opportunity for improvement at every stage of the process, with a 20% efficiency of P use along the mine–to–fork pathway being calculated *(Schroeder et al., 2010)*. Though it won't have an immediate influence on lowering reliance on P imports, it is important to emphasise that "recycling of waste" should be prioritised in order to minimise the negative effects on the ecosystem.

Global fertiliser demand estimates, based on regional analyses of i) future food consumption (*Bruinsma, 2011); ii)* known relationships between crop use and Gross Domestic Product GDP (*Tilman et al., 2011); or* iii) other relationships between application rates and crop output *(Tenkorang and Lowenberg–Deboer, 2009)* are shown in Figure 1.

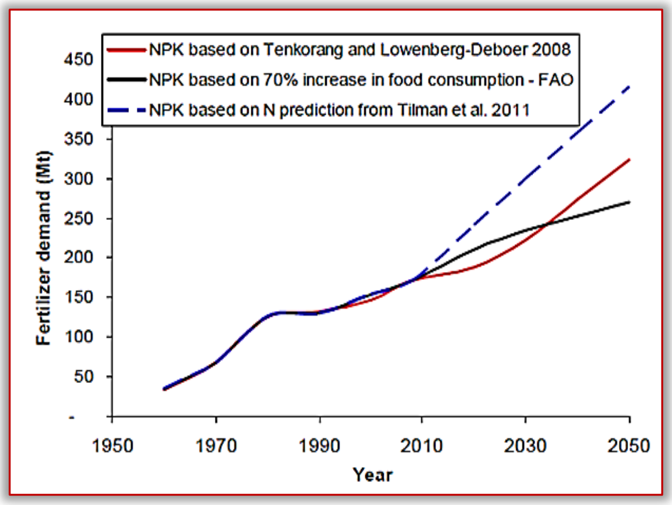

Figure 1 – Future fertilizer demand projections obtained through multiple estimations (JRC, 2012)

RESULTS

Phosphate rock

One of the major sources of phosphorus is phosphate minerals. Phosphate ore such as apatite contains phosphorus in the form of calcium phosphate. These minerals are mined and then processed to obtain the necessary calcium phosphate.

Figure 2 – Phosphate rock (or phosphorite) (https://khetkidawai.com/nurturing–triumph–revealing–natures–gem–eco–friendly–rock–phosphate–in–agriculture/)

The processing of phosphate ore involved complex steps to obtain the necessary calcium phosphate. Process steps:

- *Mining*: Phosphate ore is mined by underground or surface mining. Phosphate deposits are identified and ore is extracted according to the specific method used in each mine;
- *Crushing and grinding*: The raw ore is crushed and ground into small pieces to increase the contact surface and facilitate the subsequent extraction process. This process helps to release the phosphate from the mineral matrix and achieve a uniform particle size;
- *Beneficiation*: Next, the phosphate ore is subjected to beneficiation steps in order to beneficiate your phosphate and remove unwanted impurities. This may include the use of various separation techniques, such as flotation or magnetic separation, to separate the phosphate particles from the other mineral *components;*
- *Phosphate* reactivation: After beneficiation, the phosphate particles are subjected to a reactivation process. This involves treatment with water or dilute acids to break down the calcium phosphate and convert it to a more soluble form such as phosphoric acid or other phosphate salts;
- *Purification and concentration*: After reactivation, the solution containing calcium phosphate is subjected to further purification and concentration steps. This may involve the removal of impurities and other unwanted elements by the process of precipitation or other separation methods;
- *Conversion into fertilizer*: The calcium phosphate obtained from the processing process is used for the production of fertilizers. This can be further treated with other chemicals to obtain specific forms of fertilizers such as ammonium phosphate or potassium phosphate;

The processing of phosphate ore involved a combination of physical, chemical and separation methods to obtain the necessary calcium phosphate. It is important to note that the process may vary depending on the type of ore and the technology used in each processing unit.

Phosphorus recovery from poultry manures

The phosphorus content in poultry manure is 2 to 4 times higher than in other manures and ranges from 13.6 to 25.4 g $P2O5$ kg−1dm. Since in cereals and others (barley, wheat bran, soybeans, rapeseed meal), phosphorus occurs in the form of phytin, therefore the phytic form is present in significant amounts in poultry droppings.

Available sources of phosphorus for birds are mineral supplements added to the feed. Inorganic phosphorus in poultry manure is in the range of 32–84% by weight and organic in the range of 14–68% by weight, with the potential to be mineralized in a plant–available form.

The solid phase of phosphorus is not entirely organic, but is a combination of minerals and organic compounds. The inorganic phosphate fraction includes calcium phosphate, dibasic calcium phosphate, and weakly bound water–soluble phosphorus. Both fractions of total phosphorus (orthophosphates and organic phosphorus) are essentially easily modified. Phytates are an exception.

Compared to other animal manures, poultry manure contains proportionally more of the stable form of phosphorus, which ranges from 22 to 58% of total phosphorus

Between 12 and 20% of the phosphorus in poultry manure is in a water–soluble form and is washed away in precipitation after it has been applied to the soil. Burning poultry manure to produce nutrient–rich ash for agricultural applications is the most environmentally friendly method. The phosphorus content of the ash ranges from 8.3 to 13% and is comparable to that of some natural phosphate rocks.

The amorphous phase of phosphorus in bird ash is a source of a bioavailable form of phosphorus and depends on the combustion temperature. The main mineral phase of ash is potassium–sodium–calcium phosphate (K,Na)Ca2(PO4)2 and in the form of calcium phosphates (hydroxyapatite and whitlockite) – from 8.8 to

14.8% P2O5. Bioavailable forms in ash can reach up to 31% P2O5 of the total content.

Conversion of poultry litter to biochar by slow pyrolysis at ≥ 350 °C was shown to reduce the proportion of water–soluble phosphorus from 19.5% to less than 6.9%. This will help maintain a constant and long–term supply of nutrients to the soil, preventing rapid nutrient loss during rainfall.

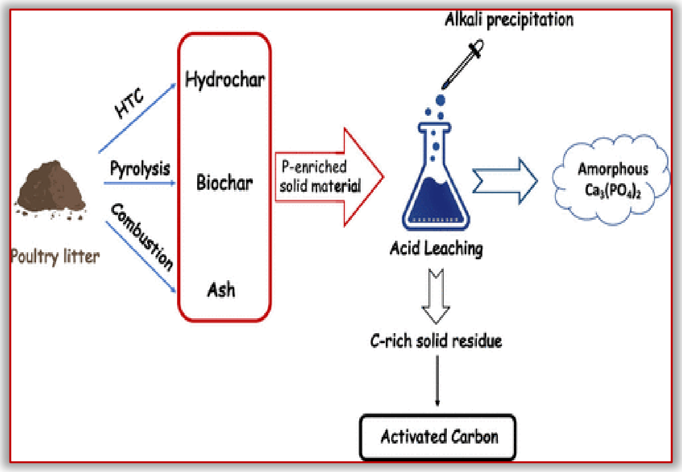

Figure 3 – Poultry manure processing possibilities
(https://pubs.acs.org/doi/10.1021/acsomega.2c00975)

Direct land application of fresh poultry manure or in its composted form as organic amendments can lead to various problems: the spread of pathogens, air pollution due to emissions of greenhouse gases and phytotoxic substances, and possible eutrophication of surface water resources and groundwater pollution from nitrogen and phosphorus leaching.

One of the main potential methods used to reduce nutrient losses from poultry manure is the thermal conversion by pyrolysis (in the absence of oxygen) to biogas and bio–oil that could have an important added energy value and a solid residue, called biochar.

Biochars are highly porous carbonaceous materials that could be exploited for agricultural purposes as soil amendments, for mitigating climate change by sequestering carbon and reducing greenhouse gas emissions, and for environmental protection, as they have high capacities for removing various pollutants from liquid and gaseous effluents.

RECYCLING AND RECOVERY OF PHOSPHORUS FROM DIFFERENT SOURCES

Another important approach is the recycling and recovery of phosphorus from different sources, such as wastewater or food waste. Wastewater treatment processes may include precipitation or filtration steps to separate phosphorus from wastewater.

Also, modern technologies allow the recovery of phosphorus from organic materials, such as compost or expired food products. Phosphorus recycling and recovery methods:

Waste water treatment:

- *Chemical precipitation*: In the wastewater treatment process, chemical precipitation can be used to separate phosphorus from water. By adding chemicals such as aluminum salts or iron salts, insoluble phosphate compounds are formed, which precipitate and can be removed by sedimentation or filtration;
- *Adsorption*: Some adsorbent materials can be used to absorb phosphorus from wastewater. For example, materials with high adsorption capacity, such as iron oxide or zeolites, can be used to capture phosphorus in an adsorption process. The adsorbent material can then be regenerated and the phosphorus can be recovered in a concentrated form.

Recovery of phosphorus from food waste:

- *Composting*: Food waste and other organic materials can be composted to produce phosphorus–rich compost. During the composting process, the phosphorus in the waste is decomposed by microorganisms and can later be used as an organic fertilizer in agriculture;
- *Anaerobic biodigestion*: Another process used to recover phosphorus from food waste is anaerobic biodigestion. In this process, organic materials are broken down in an anaerobic environment by bacteria that produce biogas. After the biodigestion process, the resulting residues, called digestate, contain phosphorus and other nutrients and can be used as fertilizer.

Bone ash extraction technology

Ash from burning bones can contain phosphorus and other minerals. Chemical or thermal extraction methods can be used to recover phosphorus from this source. Methods of extraction from bone ash:

- **Chemical extraction:**
  - *Preparation of bone ash:* The bones are assed in a controlled process and the resulting ash is collected and prepared for extraction. This may include grinding the ash to achieve uniform particle size and increase extraction efficiency;
  - *Extraction process:* The bone ash is mixed with a suitable chemical solvent such as hydrochloric acid or dilute sulfuric acid. The acid will react with the calcium phosphate in the bone ash, forming soluble phosphate salts and producing phosphorus in solution;

- *Filtration and separation*: After the reaction, the resulting solution is filtered to remove impurities and unwanted particles. The filtered solution contains the phosphorus extracted from the bone ash in the form of phosphate salts;
- *Phosphorus recovery:* The filtered solution, containing the extracted phosphorus, can later be subjected to purification and concentration steps to obtain a purer and more concentrated form of phosphorus. This may involve solvent evaporation or other separation processes.

— **Thermal extraction**

- *Preparation of bone ash:* The process of burning bones is carried out at high temperatures to convert the bones into an ash. The resulting ash contains phosphorus and other minerals;
- *Thermal extraction process*: The bone ash is subjected to an additional heat treatment at high temperatures, in an oven or other suitable system. This heat treatment may involve calcination or other thermal decomposition processes;
- *Phosphorus recovery*: During the thermal process, phosphorus from bone ash is released as volatile compounds or as gases. These gases can be collected and further treated to obtain the phosphorus in a purified form or to be converted into other usable forms.

Both chemical and thermal extractions are methods for extracting phosphorus from bone ash. Selection of the appropriate method may depend on aspects such as extraction efficiency, costs and available resources. Research and technological developments in this area are still evolving, and new methods and sources of measurement may appear as the technology advances.

The processing of phosphate ore involve a combination of physical, chemical and separation methods to obtain the necessary calcium phosphate. It is important to note that the process may vary depending on the type of ore and the technology used in each processing unit.

CONCLUSIONS

The recycling and recovery of phosphorus from diverse sources are essential methods for the effective management of this critical nutrient and for reducing dependence on finite phosphorus resources. They contribute to the conservation of natural resources and to reducing the impact on the environment.

Research and technological developments in this area are still evolving, and new measurement methods and sources may emerge as the technology advances.

The processing of phosphate ore involved a combination of physical, chemical and separation methods to obtain the necessary calcium phosphate. It is important to note that the process may vary depending on the type of ore and the technology used in each processing unit.

Acknowledgement

This paper was financed by MINISTRY OF AGRICULTURE AND RURAL DEVELOPMENT – ROMANIA – MADR – Sectorial Project ADER 25.3.1 Contract no.: ADER 25.3.1 /20.07.2023 Technology for valorification poultry manure by obtaining biofertilizers rich in phosphorus and NUCLEU Programme, carried out with the support of ANCSI, Project 9N/ 01.01.2023 "Technology for the valuation of vegetable residues in the form of biochar for the improvement of soil quality.

Note: This paper was presented at ISB–INMA TEH' 2023 – International Symposium on Technologies and Technical Systems in Agriculture, Food Industry and Environment, organized by University "POLITEHNICA" of Bucuresti, Faculty of Biotechnical Systems Engineering, National Institute for Research–Development of Machines and Installations designed for Agriculture and Food Industry (INMA Bucuresti), National Research & Development Institute for Food Bioresources (IBA Bucuresti), University of Agronomic Sciences and Veterinary Medicine of Bucuresti (UASVMB), Research–Development Institute for Plant Protection – (ICDPP Bucuresti), Research and Development Institute for Processing and Marketing of the Horticultural Products (HORTING), Hydraulics and Pneumatics Research Institute (INOE 2000 IHP) and Romanian Agricultural Mechanical Engineers Society (SIMAR), in Bucuresti, ROMANIA, in 5–6 October, 2023.

References

[1] Alewell C, Ringeval B, Ballabio C, Robinson DA, Panagos P, Borrelli P (2020).Global phosphorus shortage will be aggravated by soil erosion. Nature Com.; 11:4546.
[2] Armstrong, D. L., (1999). Functions of Phosphorus in Plants, Better Crops With Plant Food, Vol. 83 (No. 1).
[3] Bruinsma, J.,(2011). The resources outlook: by how much do land, water and crop yields need to increase by 2050? In: Conforti, P. (ed.) Looking Ahead in World Food and Agriculture – Perspectives to 2050, (pp.233–278). Food and Agriculture Organization of the United Nations, Rome.
[4] Cordell D, Drangert JO, White S. (2009) The story of phosphorus: global food security and food for thought. Glob Env Change.;19:292–305.
[5] Cordell D, White S. (2011), Peak phosphorus: clarifying the key issues of a vigorous debate about long–term phosphorus security. Sustainability.;3:2027–49.
[6] Obersteiner M, Peñuelas J, Ciais P, van der Velde M, Janssens IA.(2013) The phosphorus trilemma. Nature Geosci.;6:897–8.
[7] Romero E, Ludwig W, Sadaoui M, Lassaletta L, Bouwman AF, Beusen AHW, van Apeldoorn D, Sardans J, Janssens IA, Ciais P, Obersteiner M, Peñuelas J.(2021), The mediterranean region as a paradigm of the global decoupling of N and P between soils and freshwaters. Glob Biogeochem Cycl.; 35:2020GB006874.
[8] Schröder, J.J., Cordell, D., Smit, A.L, Rosemarin, A., (2010). Sustainable Use of Phosphorus (European Union tender project ENV.B.1/ETU/2009/0025). Report 357, Plant Research International, Wageningen University and Research Centre, Wageningen, The Netherlands, 122 pp.

[9] Tenkorang, F., Lowenberg–DeBoer, J., (2009). Forecasting long–term global fertilizer demand. Nutr. Cycl. Agroecosyst. 83: 233–247.

[10] Tilman, D., Balzer, C., Hill, J., Befort, B. L., (2011). Global food demand and the sustainable intensification of agriculture. Proceedings of the National Academy of Sciences, 108 (50) 20260– 20264.

[11] ***JRC SCIENCE AND POLICY REPORTS, (2012), NPK: Will there be enough plant nutrients to feed a world of 9 billion in 2050?, Foresight and Horizon Scanning Series, ISSN 1831–9424 (online).

[12] ***US. Geological Survey. Mineral commodity summaries 2016, p. 202, U.S. Geological Survey. 2016.

[13] ***https://khetkidawai.com/nurturing–triumph–revealing–natures–gem–eco–friendly–rock–phosphate–in–agriculture/

[14] ***https://pubs.acs.org/doi/10.1021/acsomega.2c00975

ISSN: 2067-3809
copyright © University POLITEHNICA Timisoara,
Faculty of Engineering Hunedoara,
5, Revolutiei, 331128, Hunedoara, ROMANIA
http://acta.fih.upt.ro