

Review

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**Bio-based fertilizers: a practical approach towards circular economy**

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**Abstract**

Although for the past 100 years, fertilizer technologies have increasingly used renewable resources, the majority of manufactured products are still based on mineral deposits and fossil fuels. The European Commission has set a goal of 30% reduction of non-renewable resources in fertilizer production. This can only be accomplished if there are incentives for wastes valorization and fines for making use of non-renewable raw materials. This will enable the reduction of eutrophication of surface waters due to the presence of nitrogen and phosphorus, originating from agricultural fields fertilizers. The use of biological waste is a practical solution to recover valuable fertilizer components. In order to effectively implement technologies based on biological resources, it is necessary to construct small wastes solubilization or fertilizer installations at the site of waste generation, which will solve the problem of waste transport or sanitary hazards.

**Keywords:** nutrients recovery, nutrients cycle, fertilizer industry, biomass, preservation of deposits

## 1. Introduction

The rapid growth of human population determines a rising demand for food and water (Nizami et al., 2017), which leads to increased consumption of energy and the use of non-renewable resources. Today's economy follows a linear pattern, with copious amounts of perishable produce. The extensive exploitation of raw materials depletes their global resources at a rather rapid pace, which pushes up their price. The number of pollutants and the amount of waste discharged into the environment increases (Sarsaiya et al., 2019). The concept of the Circular Economy (CE) – that is a system that is based on the recovery of materials – was introduced by the European Commission as a response to environmental and social problems (Ritzén and Sandström, 2017).

The human population is growing exponentially due to the elimination of widespread famine and outbreaks of epidemics. Food production can either be increased by enlarging cultivable areas or by increasing fertilizer doses, with both having their limits. Ultimately, when in 2067 the population reaches 10.4 billion with 81% residing in Africa or Asia (Britt et al., 2018), it will exceed the capacity of the planet to feed it. By 2050 the demand for crops will have increased by 100-110% from 2005 (Tilman et al., 2011). This has to be remedied.

The global generation of wastes is estimated at 3.5 million Mg per day. This value will have doubled by 2050 and tripled by 2100 (Hoornweg et al., 2013). While in Europe the annual amount of waste remains stable, in sub-Saharan Africa and South Asia, it is growing fast (Hoornweg et al., 2013). Since waste is a reservoir of valuable and renewable substances, it ought to be recycled as much as possible. Apart from obvious benefits, we have a chance of the footprint of industrial processes. To this end, we need innovative technologies. Waste sorting plays a very important role (Boas Berg et al., 2018) because of the materials that were previously extracted from non-renewable

deposits. The effective implementation of material recycling is essential just as leakage of nutrients into the environment poses a greater threat to food security than depletion of resources (Stiles et al., 2018).

## **2. Fertilizer industry and recovery of phosphorus and nitrogen**

Circular economy – which prescribes that the production of fertilizers should be closed in a loop – is not only recommended by the EU but also the European Industrial Organization of Fertilizers. Some of the raw materials should be substituted with residual biomass, e.g. post-harvest residues, residues from livestock production and slaughter or food processing. Closing the loop will prevent fertilizing nutrients from being dissipated in the environment and becoming pollutants (Scholtz, 2017). The idea of circularity includes the use of by-products from one production process as secondary raw materials in another (Hansen, 2018).

The fertilizer regulation was the first in the EU's circular economy package. The mineral fertilizer industry is linked to several important value chains (Hansen, 2018). Ammonia was first produced as a by-product 150 years ago. Sulfur from oil and gas refineries was used to produce sulfur-containing fertilizers or was the basis for the production of phosphate fertilizers (Hansen, 2018). The technical concept of 'by-product use' is, in fact, nothing but an implementation of CE. However, the EU Parliament suggests allowing the use of by-products on the condition that they are compliant with REACH obligations (Hansen, 2018). The EU expects that bio-waste will replace up to 30% of the inorganic fertilizers currently used (Hansen, 2018).

The transition from a fossil-based to a bio-based economy requires the recovery of nutrients from waste streams (Christel et al., 2014). The substitution of mineral fertilizers with bio-based alternatives is an important direction in materials and energy

recovery (Christel et al., 2014). The production of fertilizers is highly energy consuming (Svanbäck et al., 2019), they are based on fossil fuels (N-fertilizers on Haber–Bosch process) or fossil ore deposits (phosphate rock) (Sigurnjak et al., 2016). Chemical fertilizer use in the EU in 2010 was 10.4 Mt of nitrogen, 2.4 Mt of  $P_2O_5$ , and 2.7 Mt of  $K_2O$ . By 2019/2020 it should reach 10.8 Mt, 2.7 Mt, and 3.2 Mt, for those fertilizers.

The fertilizer industry has never been involved in the valorization of renewable resources to fertilizers because it had no clear interest. The fertilizer sector has been based on proven technologies using non-renewable raw materials for over a hundred years. A modification of the wet process phosphoric acid involving the replacement of a non-renewable raw material (e.g. phosphorites or apatites) with a renewable raw material (e.g. animal bones) would cause new technological problems due to the lower mineralization of the raw material, the presence of organic matter (in particular fat), difficulties in the accessibility, collection, storage and introduction of the raw material (sealing reactors). Because using the introduction of a renewable raw material involves the need to build completely new production installations adapted to the specifics of the renewable raw material, without a clear incentive in the form of subsidies or tax breaks, fertilizer producers will not shift to renewable resource base.

Technological progress in fertilizer industry bases mainly on process, not product innovations, in particular on increasing efficiency of existing technologies (higher yields, lower use of raw materials, lower energy consumption, higher profitability of the process). This is related with low expectations of farmers that are final customers of fertilizer products. Due to the constant demand for fertilizers, demand still exceeds supply. Process innovations relying on controlled or slow-release products cause lower consumption of fertilizer products (lower application rates). It is not in the interest of fertilizer producers to reduce fertilizer doses but to produce high tonnage

products that will be sold in large quantities. Farmers are still underestimating the added value of fertilizers, being accustomed to perceiving the quality of fertilizers through the prism of their content of fertilizer components, not application doses that could be smaller.

The push of fertilizer industry to use valorization of the biomass in fertilizer technologies could be direct subsidies – R&D grants for elaboration of new bio-based technologies, building production installation and commercialization, tax benefits for using renewable raw materials and on the other hand - tax charges for the use of non-renewable resources, support in products commercialization through building awareness among farmers and recipients of food produced on the basis of eco-raw materials. It is probable that building small scale fertilizer installations on the site of wastes generation, managed by fertilizer producers would be the practical solution towards the implementation of technologies basing on bio-based raw materials. On-site utilization of biomass wastes would solve the problem of collection and sanitation, difficulties with transport. Bio-based wastes are noxious in collection and transport because they undergo biological transformations mainly anaerobic decay that causes odours emission and sanitary danger. This is another argument for elaboration of fertilizer technologies that are located on-the-site of bio-wastes generation. Another solution would be to partially conduct the process at wastes generation site – for instance acidic solubilization and the formed by-product could be collected by fertilizer producers and used in composing fertilizers.

Clarification and harmonization of the legislation should be of prime concern. A very important stage will be EU-wide acknowledgment of recycled fertilizers, revision of the fertilizers regulation, quality control of the fertilizers obtained from recycled fertilizers (Hukari et al., 2016). The P recovery sector is heterogeneous with its small

production scale as compared to fossil-based fertilizers. Recovered nutrients from new fertilizers should be made increasingly available to plants. Public perception of the recovery and recycling of phosphorus from human waste should soon become a social norm (Roy, 2017), supported by ecological engineering and sanitation. Funding initiatives and policy actions contributing to recovery of nutrients are important steps towards circular economy. All this is included in the European Commission's "Towards a Circular Economy: A Zero Waste Programme for Europe" – part of the Europe 2020 strategy (Roy, 2017).

CE phosphorus approach means the optimization of P fertilization, collection, and recycling of P-rich wastes, improvement of household sewer systems, and the application of biogenic wastewater treatment (van Dijk et al., 2016). The recovery of mineral P from wastewater is technologically possible but not executed because the process is not profitable (Hukari et al., 2016). In order to be able to implement the CE directives/guidelines in the fertilizer sector, it is necessary to improve selected areas (Table 1).

TAB. 1.

The intense use of chemical fertilizers causes water contamination, loss of nutrients, and deterioration of soil. It is estimated that 30-50% of fertilizer nutrients are either leached to groundwater or volatilizes to air. The number of chemical fertilizers can be reduced their composition is tailored to the type of soil, their controlled release rate, and crops rotation (Wang et al., 2018).

Particular attention is paid to closing nutrient loops. An example is the decentralized anaerobic digestion of agricultural residues and the utilization of digestate in the agricultural sector (Vaneckhaute et al., 2018). Some of the nutrients are lost from the field to the environment. These are a nitrous oxide ( $N_2O$ ) (50% of the total

global emission) and methane (CH<sub>4</sub>) (40% of emission). N<sub>2</sub>O originates from conversion of nitrogen fertilizers by ammonia volatilization and nitrate leaching, and also denitrification, and CH<sub>4</sub> from fermentation and manure management. What makes the problem even more serious is that those are greenhouse gases that may affect global warming 25 and 298 times higher than carbon dioxide, respectively (Vaneckhaute et al., 2018). Life Cycle Analysis (LCA) can be useful in the determination of environmental and economic advantages and disadvantages related to the modification of fertilizer production and use, in particular nutrients recovery (Ubando et al., 2019). Both aspects should be taken into consideration: not only energy recovery but first of all nutrient recycling (Vaneckhaute et al., 2018).

## 2.1. Phosphorus

Phosphate rock was listed as a critical raw material in May 2014 (European Commission, 2014) that should be a push for P recovery from wastewater and other renewable sources. Phosphorus resources are expected to deplete by the end of the 21<sup>st</sup> century (Christel et al., 2014). The use of mineral fertilizers influences biogeochemical cycles of nutrients, particularly N and P, which greatly influence eutrophication. Phosphorus becomes spread in the environment while its non-renewable deposits become scarce (Svanbäck et al., 2019). The most burdensome barrier for phosphorus recovery is legislation for P as a resource in fertilizer production or as a pollutant in wastewater treatment. Recovered phosphorus can also be put on the market to compete with fossil fertilizers (Hukari et al., 2016).

In the European Union, 25% of soils have a low level of available phosphorus. Fertilization might, therefore, include bio-fertilizers – microflora that would solubilize phosphorus that is present in soil but is not readily bioavailable to plants. This could be achieved by e.g. inoculation of soil with *Bacillus megaterium* or *Acidithiobacillus*



*ferrooxidans*, which produce acids and can thus solubilize phosphates that become dissolved in soil solution (Vaneeckhaute et al., 2016).

The use of P is still inefficient, non-circular and dissipative, and only 10% of the applied P reaches the consumer due to losses during use (e.g. excretion, erosion, and leaching) (Ott and Rechberger, 2012). At present, the phosphorus value chain is half-circular, since 80% of the element obtained from non-renewable resources is not reused. The majority is lost in waste food, leaks to ground and surface waters (causing algal blooms), and becomes accumulated in soils, sediments or unharvested biomass. More efficient use of phosphorus and its recycling can be improved through reuse of animal, food and human wastes (Chen and Graedel, 2016).

Phosphorus is a non-renewable resource, essential to life and food production. Imbalanced global distribution of P is a geopolitical problem for Europe. The reserves of P are estimated to be exhausted within 50–400 years (van Dijk et al., 2016). Morocco holds more than 77% of the resources in the world, moreover, together with China and the USA holds two-thirds of global production. Long-term indicators include higher demand, lower quality, and higher production costs. Therefore it is predicted that the price of P fertilizers will increase (Cooper and Carliell-Marquet, 2013). Europe uses imported mineral phosphates because it does not have its resources. Deliveries of non-EU mineral fertilizers can affect food safety in Europe. The EU should move towards a circular, resource-efficient economy that uses the processing of nutrients from waste materials and prevents their losses (Cooper and Carliell-Marquet, 2013). On the other hand, there is P excess in nature that causes eutrophication.

Van Dijk et al. (2016) carried out P flow analysis (PFA) to identify how human population uses P and how much of it is lost into the environment. P-management should be implemented in agriculture, in terms of recovery, bioavailability, and

nutrients use efficiency (Ott and Rechberger, 2012). Phosphorus is adsorbed on clay, Al and Fe oxides, carbonates, and organic matter. The majority of nutrient pools are not available to plants. In the past, fertilization with organic manure was the basis for the cultivation of plants. Because of higher food demand, mineral P fertilizers in the 20<sup>th</sup> and 21<sup>st</sup> centuries became the most important source of soil P.

At each node of the value chain of fertilizers production and application, it is necessary to assure high productivity. Phosphorus fertilizers industry requires improvement of the P extraction efficiency from phosphate rock. Production of fertilizers that makes it possible to apply nutrients optimally and precisely is important (Chen and Graedel, 2016).

Bioavailability is an important aspect of phosphorus fertilizers technology. Some limitations of wastes valorization into fertilizers are related to legal constraints, e.g., slaughter wastes. Phosphorus fertilizers can be produced from different types of bio-wastes: municipal, agricultural, and food wastes. Phosphorus recovery can also be achieved through controlled struvite precipitation ( $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ ) (Vaneeckhaute et al., 2016).

Nutrient recovery provides many side streams that can be useful in fertilizers production (Sigurnjak et al., 2016). Animal waste can be the source of both energy and fermentation digestate as alternatives to synthetic fertilizers (Sigurnjak et al., 2016). Sigurnjak et al. (2016) valorized derivatives from nutrient recovery processes as fertilizer for *Lactuca sativa* L. by using a liquid fraction of digestate, air scrubber water, and struvite.

Christel et al. (2014) investigated P availability from the solid fraction of pig slurry after composting and thermal treatment. For instance, wastewater from acidic air scrubbers for ammonia removal can be used as N-S (nitrogen-sulfur) fertilizer.

Concentrates from membrane filtration of liquid digestate can be applied as N-K fertilizer (nitrogen-potassium) (Christel et al., 2014). It would be beneficial to couple recovery of nutrients with simultaneous generation of energy, which can be achieved by the use of anaerobic digestion of animal manure – bio-energy production and anaerobic mineralization of fertilizer nutrient present in digestate (Vaneckhaute et al., 2016). Bio-digestion can close the cycle of nutrients to produce substitutes of fertilizers (Vaneckhaute et al., 2013). It is worth to determine biogas production potential of post-harvest residues. Improvement of crop yield and soil fertility is expected (Vaneckhaute et al., 2013).

Sewage sludge and sewage sludge ashes can be a good source of fertilizer phosphorus in composing fertilizer formulations. In particular, ashes have the properties of neutralization of post-solubilization digestates and are the source of phosphorus, as well. However, recently phosphorus has been withdrawn from detergents. This posed the problem with hindering growth of activated sludge and interferes phosphorus content of sewage sludge from tertiary treatment that bases of biological enhanced phosphorus removal.

## 2.2. Nitrogen

Nitrogen – a building block of proteins and genetic material – is one of those nutrients that are necessary for the proper growth and development of living organisms. It is obtained from the atmosphere using the Haber-Bosch process for the production of ammonia. One kilogram of nitrogen fertilizer consumes almost 60MJ of energy (Huo and Wernick, 2012).

Nitrogen fertilizers make plants produce proteins and nucleic acids. However, these components do not enter the closed nitrogen cycle: they are not processed by biofuel production. They can be used to feed farm animals, which results in the production of a

large amount of nitrous oxide and nitrogen dissipation (Huo and Wernick, 2012). Scientists have succeeded in developing the bacterial strain *Escherichia coli*, which can metabolize proteins for the production of alcohols C4-C5 (Huo et al., 2011). The use of such modified microorganisms that can convert proteins into fuel and ammonia can enable nitrogen recycling and reduce the amount of fertilizers (Wernick and Liao, 2013).

The production of nitrogen fertilizers is energy-consuming, although nitrogen compounds are found in nature widely. Nitrogen recovery from waste biomass can, therefore, affect the environment, even leading to mitigation of climate change (Cobo et al., 2018). Large amounts of chemical fertilizers containing nitrogen are lost, some evaporate, a part is washed out or drained to surface waters, causing its eutrophication. The remaining small amount is often insufficient for plants, and so re-fertilization is necessary (Yan et al., 2014).

Almost all the nitrogen content from waste biomass can be recovered during anaerobic digestion, with the small losses being caused by the release of gaseous  $\text{NH}_3$ . The digestate contains both mineralized and organic nitrogen (in the ratio of 1:1). Over 60% of nitrogen digestate moves to the liquid fraction, which is a fertilizer easily available to plants. The insoluble fraction is rich in organic nitrogen, characterized by slower release into the environment (Zabaleta and Rodic, 2015). Composting causes a much higher loss of nitrogen, mainly due to the discharge of gaseous products (ammonia, nitrogen or nitrogen oxides) and as a result of leachate formation (de Guardia et al., 2010). Incineration brings about the total emission of nitrogen to the gaseous phase, mainly in the form of  $\text{N}_2$  and  $\text{NO}$ . Nitrogen residue in the ash is low, the magnitude of several hundredths of a gram per kg of biomass (Godbout et al., 2012).

Energy production from waste biomass increases the accumulation of some compounds in the final products of these processes and also affects the increased emission of gaseous products, including nitrogen compounds (mainly  $N_2O$ ), whose annual growth of atmospheric concentration is estimated at 0.7 mg/L (Montzka et al., 2011). The nitrogen cycle has increased significantly due to the application of chemical fertilizers, and the  $N_2O$  emission has also increased through microbiological processes. It is estimated that the emission of nitrogen compounds associated with human activity accounts for about 40% of the total emission (almost 2 Gt  $CO_2$ -eq per year) (Montzka et al., 2011).

### **3. Biomass valorization methods**

The most popular method of biomass valorization is composting (Bian et al., 2019). Compost can be directly applied to fields. The increased concentration of nutrients (N, P, K) during composting can be achieved by reducing biomass particles (Haynes et al., 2015). The obvious disadvantage of this process is the loss of nitrogen in the form of volatile  $NH_3$ . The valorization of materials of pharmaceutical origin enables their use for agricultural purposes, as evidenced by studies on composting waste from daptomycin production (Cucina et al., 2018). The type of composting is vermicomposting, where the transformation of organic matter is achieved by earthworms (Lee et al., 2018). In contrast to composting, vermicomposting does not require mixing because the natural movement of earthworms increases the availability of oxygen.

Anaerobic digestion (AD) is a three-stage process made up of hydrolysis, acetogenesis, and methanogenesis, and its main products are methane, carbon dioxide and digestate (Daza Serna et al., 2016). Anaerobic digestion is used to produce energy from organic waste materials (of animal and plant origin) (Zhang et al., 2019). The

production of biogas in the anaerobic digestion depends primarily on the type of raw material, its chemical composition, temperature (Liu et al., 2019) and the ease of biodegradation. Research shows that the application of one type of biomass for the AD process limits the production capacity, the additional biomass differentiates the composition of the mixture as well as the bacterial flora, which has a beneficial effect on fermentation (Hagos et al., 2017). The use of AD is not possible where a large amount of organic waste (including food waste and green waste) is produced, e.g. in large agglomerations. The main problem is the distance from cultivable fields and the high cost of transport, storage, and processing (Takemura et al., 2019).

From the sanitary point of view, digestate is a microbiologically stable product that has a reduced number of pathogenic bacteria (Riva et al., 2016). Since it contains nitrogen in inorganic form (over 60% of total nitrogen), phosphorus, and potassium, it has a great potential as organic fertilizer with high bioavailability (Kataki et al., 2017). Apart from providing important nutrients, digestate also improves soil quality, which results in a better yield (Kataki et al., 2017). Two-year AD field trials showed similar yield efficiency as chemical fertilizers. The digestate was applied in the form of a sub-surface injection to avoid emission of nitrogen compounds (ammonia) into the atmosphere, which also contributed to the reduction of odors (Riva et al., 2016). In some countries, such as Germany, anaerobic digestion is one of the key techniques of turning waste biomass into energy (De Meester et al., 2012). Anaerobic digestion can utilize most of the waste biomass. As a result of a series of microbiological changes, biogas and digestate are produced, which is suitable for fertilizing purposes. Polish scientists proposed the concept of a production line, processing two types of waste from biomass conversion (digestate and ash), which are raw materials for the production of fertilizer. The mixture of waste with the addition of *Trichoderma* strains is to serve as a

multi-component fertilizer, the production of which is designed as waste-free. The presence of *Trichoderma* fungi will affect the absorption of nitrogen by plants (Jewiarz et al., 2018).

The most popular procedure for waste thermal biomass processing is incineration. Other thermal methods, including gasification and pyrolysis, also have great potential (Haddad et al., 2017). Biomass after combustion contains several valuable components, including P, K, Ca, and at the same time constitutes waste, which is then stored in landfills. It is estimated that each year globally about 500 million Mg of ash from the incineration of biomass is generated (Silva et al., 2019). Ash from biomass is a potential fertilizer for crops and forests. Due to the basic nature of ash, its use could be justified in particular on acidic soils, e.g. mining areas (Silva et al., 2019). Field studies have shown that the addition of ash and organic waste to conventional chemical fertilizers increases the agricultural production, improves soil pH and provides the available form of nutrients (Rautaray et al., 2003).

One of the by-products of biomass incineration is ash, which is collected in a non-selective manner and, combined with other waste, is deposited in landfills. The composition of the ash depends on the type of biomass. If a separate collection of ash from households fired with charcoal could be applied, it would be possible to obtain a homogeneous waste that could be used for agricultural purposes. The return of valuable ingredients to the environment is the greenest method of waste management, allowing for closing the circulation of micronutrients and macroelements (Zajac et al., 2018). Wood ash is rich in nutrients necessary for plant growth excluding nitrogen, which during the combustion of biomass reaches the gaseous phase. Nitrogen supplementation is therefore necessary before the ash is applied in agriculture. Also, the possibility of using other waste materials containing large amounts of nitrogen, including sewage

sludge, is examined (Pesonen et al., 2016). However, ashes from coal combustion may contain heavy metals that are toxic and undesirable in products intended for the agricultural sector. That is why the selective collection of ashes from biomass combustion is so important. Research on 35 different plant biomasses, including woody, agricultural biomass, forest residues, and agri-food residues uncovered the chemical composition of ashes from various sources, thus enabling the analysis of toxic compounds (Pb, As) (Zajac et al., 2018). In the ash, high content of macroelements (P, K, Ca, S), micronutrients (Zn, Cu, Mg) and a very small amount of toxic substances was determined, which suggests the possibility of direct use of ashes for fertilizing purposes (Zajac et al., 2018). Wood ashes are useful as neutralizing agent (Kurola et al., 2011). In order to achieve a complete nutritional composition, they can be added to other biological residues that have been solubilized with acid, e.g. high-protein waste such as feathers.

The result of pyrolysis is three fractions with various physical states, which are valuable products used as fuels (gas, bio-oil) or as adsorbents or soil additives (Haddad et al., 2017). Biochar is a carbon resulting from biomass pyrolysis. For many years it has been used to improve the quality of soils (Intani et al., 2018). Biochar formed from lignocellulosic materials has a relatively low content of minerals, while the one from marine and freshwater algae has a high content of nutrients (Roberts et al., 2015). Biochar applied to the soil brings several benefits such as the improvement of soil quality, removal of soil contaminants (large sorption surface), and release of nutrients (Zhao et al., 2016). The co-pyrolysis of biomass with phosphate fertilizers causes the formation of composite biochar, increasing its functionality by slowing down the release of phosphorus compounds (Zhao et al., 2016). The biochar obtained from pyrolysis on the fermentative biomass of *Escherichia coli* was analyzed as a



phosphorus-rich fertilizer. Just over 50% of the soluble phosphorus fraction was released in the first five days of the test (Kim et al., 2018).

#### **4. Bio-based wastes for fertilizer production**

Over 120 million Mg of bio-waste is produced annually in Europe. Bio-waste is landfilled, and a small part of it is incinerated without its wealth of valuable nutrients being recovered (Zabaleta and Rodic, 2015). The global generation of municipal solid waste is around 1.3 billion Mg per year and is expected to double over the next few years (De Medina-Salas et al., 2019). Organic waste, which is food waste, green and garden waste (grass, leaves), is a large part of municipal waste which can be managed with a few scenarios depending on its composition and humidity (De Medina-Salas et al., 2019). Bio-waste management can contribute to the recovery of energy and materials as well as to the production of new chemicals. These residues are also a source of many valuable bioactive compounds, including phenolic compounds (Talekar et al., 2018), vitamins, carotenoids (Akao, 2018), proteins (Contreras et al., 2019).

TAB. 2.

Several bio wastes could be used as a part of raw materials input, among them the three largest and ubiquitously available materials: agricultural waste, food waste, and sewage sludge.

##### **4.1. Agricultural waste**

Agricultural waste is a group of organic substances, which are derived from agricultural production. This group includes forest residues, plant, and cereal biomass and animal manure.

Agricultural and forestry biomass wastes are lignocellulose materials composed of cellulose, hemicellulose, and lignin. So far, the most popular way of utilization was fermentation and thermochemical conversions (Cao et al., 2017). Large amounts of

wood ash are generated by energy plants in Europe, especially in Sweden and Finland. Ashes from incineration are varying in composition, depending on the feedstock, type of incinerator, and process parameters. Wood ash has useful properties for fertilization, as a strong alkali. It is a neutralizing agent for acidic soils (Väätäinen et al., 2011).

Wood ash, apart from nitrogen, contains the nutrients, especially phosphorus that plants need for growth (Górecka et al., 2006). Application of wood ash to fertilize peatland forests seems to be a promising and cost-effective method of waste management after wood combustion (Väätäinen et al., 2011). Co-granulation of plant ash with sewage sludge is a fertilizer containing all the nutrients that plants need, including nitrogen (Pesonen et al., 2016). Co-incineration of fossil fuels and biomass can prevent the use in fertilization due to the presence of many undesirable substances, like an excessive content of heavy metals in fly ashes made from fossil fuels.

Agricultural waste can also be used as a source of biodegradable polymers such as polylactic acid (PLA). Various PLA biocomposites have also been tested with other wastes, including celery root fibers and pomace (Spiridon et al., 2018). Agricultural residues with low water content (cereal straw, maize stalks) are a useful combustion input (Menardo and Balsari, 2012).

New opportunities for a circular economy are created by the utilization of waste biomass, e.g. post-extraction residues that could be enriched with micronutrient ions, such as ions of Cu, Mn, and Zn to produce bio-based micronutrient fertilizers (Samoraj et al., 2019). The concept of new bio-based micronutrient fertilizers also includes other agricultural residues enriched with microelements necessary for proper plant growth (Michalak et al., 2015; Tuhy et al., 2015).

Global annual production of nitrogen from animal manure is 100 Tg N. 60-80% of this amount is dissipated into the environment; the rest is recovered and used as

fertilizer (Oenema et al., 2007). Livestock manure (mostly from pigs, cattle, and poultry) is a resource of organic material and useful microorganisms, which is an unexploited source of N fertilizer, also improving the soil properties and crop yields (Xia et al., 2017).

Poultry litter is a waste in poultry farms contains, apart from the excrement, also feathers and residues of spilled animal feed (Turan, 2008). Due to the dynamic development of the poultry sector, the amount of waste is rapidly increasing and needs to be managed. The poultry litter contains many valuable macro and microelements, which after pre-processing (due to the odor and presence of pathogens) can be used in agriculture (Ma and You, 2019). For the processing of poultry litter for fertilizer production, biological and thermal methods are proposed, of which thermal methods seem to be worth considering on a larger scale (Ma and You, 2019). Similarly, manure from pigs and cattle husbandry is the source of many valuable ingredients that can be recovered, e.g. through microbiological methods. Anaerobic co-digestion of cattle manure with sweet potatoes has shown that the addition of sweet potatoes significantly increases the production of biogas and bio-fertilizer compared to mono-digestion (Montoro et al., 2019). Mixing manure with plant materials in a ratio of 1:1 to 1:3 affects the structure, hydration, aeration of compost and also diversifies the consortia of microorganisms (Leconte et al., 2011). Europe imports most of its chemical fertilizers, while there are many concentrated livestock production facilities which cope with manure disposal, which is a noxious waste product (Tur-Cardona et al., 2018).

There are several technologies available for the production of inorganic/organic liquid/solid fertilizers from manure. The final products include  $\text{NH}_4\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$ , as well as N and K concentrate (Klop et al., 2012), K fertilizer, struvite, Ca/Mg-phosphate, P-rich ashes. They can be manufactured by liquid/solid separation followed by

evaporation/filtration, ammonia stripping, liming, biological treatment, phosphorus precipitation or by anaerobic digestion followed by drying, pelletizing, incineration, composting, liming, and P-precipitation. Currently several membrane processes (nanofiltration, reverse osmosis, membrane distillation) are applied for ammonium fertilizer recovery from manure (Zarebska et al., 2015). However, there are still challenges related to the production of more concentrated and marketable products, storage, and handling as well as diminishing losses of nutrients (Ippersiel et al., 2012).

#### **4.2. Food waste**

The production of food waste in North America and Europe is on average 95-115 kg/year per person. Annually 1.3 billion Mg of food is wasted in the world, which is approximately one-third of the edibles produced globally (Gustavsson et al., n.d.). Food waste includes residues from households and restaurants, waste streams from processing, and crop cultivation residues (Du et al., 2018). Such waste contains carbohydrates (starch, cellulose, and hemicelluloses), proteins, lignin, fat and a high amount of moisture (Uçkun Kiran et al., 2014).

Prevention of food loss and waste – through theoretically well discussed – has been implemented by 20% of the 50 largest global food companies. The losses occur mainly at cultivation and consumption, around 30% on the stage of food supply chain (Principato et al., 2019). Various organizations (e.g. UN – Sustainable Development Goal) urge that a 50% reduction of food waste be reached by the year 2030, for which goal the support of policymakers is required (Principato et al., 2019).

Food waste – a useful resource of valuable compounds – is incinerated with other combustible municipal wastes or landfilled (Uçkun Kiran et al., 2014). The effect of orange waste as an organic fertilizer on the growth of durum wheat in field

investigations was assessed. The yield was similar to that brought about by chemical fertilization when the dose of organic fertilizer was well selected (Tuttobene et al., 2009). Biofertilizers can be produced from food waste by anaerobic digestion, aerobic composting, and chemical hydrolysis; various agricultural wastes (i.e. wheat straw) can be directly returned to soil (Du et al., 2018). Spent coffee grounds could be valorized through appropriate management (i.e. composting, anaerobic digestion, pyrolysis) and reused, bringing valuable products for agriculture and improving soil structure and fertility (Stylianou et al., 2018). A fertilizer made from used coffee grounds mixed with ash from biomass combustion was tested on four plant species. No toxic effect on germination of the tested plants was observed, except for cress (Ciesielczuk et al., 2018). The use of an organic fertilizer resulting from mixing organic and mineral waste as possible and will bring the expected results provided that the composition of the mixture is adjusted to the needs of the plant. It was observed that a given fertilizer mixture might adversely affect root development in some plants and stimulate their growth in others (Ciesielczuk et al., 2018). High-temperature dynamic aerobic fermentation of food residues can be a suitable method for the quick production of organic fertilizers (Jiang et al., 2015). Nutrient-rich digestate for agriculture produced by aerobic digestion can be treated to remove water excess and concentrate nutrients i.e. in reversed osmosis (Tampio et al., 2016). Potassium-rich banana waste combined with sewage sludge containing a large amount of phosphorus was used to produce biochar in thermal processes such as slow pyrolysis and thermal plasma treatment. Both methods are perfectly suited for the production of biochar with nutrients available for plants. The only disturbing aspect is the presence of arsenic, which must be removed before the process because its presence precludes the use of biochar as a fertilizer for edible plants (Karim et al., 2019).

In the processing of animal products, only 40-60% of materials are used for food production. Partially, skin and fat are recovered, to a lesser extent protein, mainly in the form of blood, meat and bone meal. They can be used as ingredients for animal feed production. (Mekonnen et al., 2016). These meals can also serve as the basis for the production of thermoplastic and thermosetting materials as well as coagulating and flocculating agents used in wastewater treatment (Mekonnen et al., 2016).

Bones are a valuable and concentrated source of phosphorus (Wyciszkiewicz et al., 2017). Of course, the substitution of a part of phosphate rock with bones will generate new technological problems, e.g., higher consumption of sulfuric acid required for hydroxyapatite solubilization in wet-process phosphoric acid. In the case of bones as a feedstock, some of the acids would be necessary for solubilization of the organic matrix of bones. Phosphate fertilizers can be obtained by pyrolysis of slaughter waste, also with the participation of other biomass like meat residue, wood, and corn (Zwetsloot et al., 2015). Fish meat and fish waste, in particular after composting with an addition of a bulking agent, is a valuable fertilizer material rich in nitrogen, phosphorus, and calcium (Radziemska et al., 2018). Waste keratin materials, including feathers, after hydrolysis is a cocktail of amino acids, which digested with sulfuric acid is a source of nitrogen and can be given directly to plants as foliar fertilizers (Chojnacka et al., 2011). Similarly, wool, which even without treatment is introduced into the soil, releases valuable nutrients and absorbs moisture. Employing hydrolysis with superheated water, wool can be transformed into a fertilizer material without the need for pre-treatment (Zoccola et al., 2015). On the other hand, a renewable source of potassium could be ashes from power plants, especially from those that use biomass as the feedstock. The ash from the combustion of animal waste is rich in phosphorus and calcium, applicable

as agricultural fertilizers. The mixture of hydrolysates from animal residues with ashes composes a complete set of nutrients for plants.

In many cases, microorganisms transform different biowastes. It is estimated that annually on the global basis  $3.7 \times 10^9$  Mg of agricultural residues and  $1.3 \times 10^9$  Mg of food residues are generated. This vast amount can be processed by incineration, anaerobic fermentation or composting to generate heat, electricity or fertilizers. A biotechnological process can transform these wastes and use them as source of nutrients. The idea relies on the preliminary hydrolysis of organic residues (wastes from food processing) to monomers such as glucose and amino acids to obtain substrates for the production of various industrially important chemicals, e.g. lactic acid, succinic acid, fatty acids, and food supplements (Pleissner et al., 2016). It is possible to valorize different organic residues to different chemicals with an added value. This is the concept of bio-based economy, it includes the multifunctional integrated method of wastes valorization that is an optimized sequence of processes aiming to make different products (chemicals (polyhydroxyalkanoates, sorbents, polyols, polyurethane foam, carotenoids, phenolic antioxidants) and bioenergy (biodiesel, bio-oil, biogas) (Zabaniotou and Kamaterou, 2019). The valorization of food waste as the resource for bio-based products and energy in waste biorefineries is of great importance.

#### **4.3. Sewage sludge**

In the course of biological wastewater treatment, huge amounts of residues are generated in the form of sludge (biosolids): in the EU alone about 10 million Mg annually (Gil et al., 2018), which is expected to rise to 13 million by 2020 (Kominko et al., 2018). Sewage sludge can be used in agriculture after stabilization, removal of toxic compounds, pathogens and undesirable odor. Algae biomass from wastewater algal systems can be used to recover up to 44% of nitrogen (as ammonium sulfate) and

91% of the phosphorus content of the struvite form. Valorization of waste algae biomass can be carried out through thermal and chemical processes, with the estimated value of the recovered nutrients standing at \$500 per 1 kg of biomass (Li et al., 2018).

Nutrients and carbon can be used for fertilization and energy production. The most popular method of waste management – mainly due to the low cost – is its storage on sediment plots. Sewage sludge must be dehydrated and stabilized before agricultural use. Draining is carried out with centrifuges, drying or filter presses. Stabilization can be done by anaerobic digestion, combustion or composting (Wang et al., 2008).

Anaerobic digestion appears to be a more efficient method of recovering valuable nutrient components than incineration (Wang et al., 2008). The use of sewage sludge for land applications will enable complete utilization of nutrients with a low financial output. In the case of compost as a substitute for mineral fertilizers, it is the composition of the composting mixture that is important. Compost from sewage sludge and anaerobic digestion performed very well in a 112-day pot test, being a full alternative to chemical fertilizers. In the same test, compost from green waste showed a much worse composition (Grigatti et al., 2019).

Sewage sludge can be treated by biological (composting, anaerobic digestion, stabilization using earthworms), chemical, and thermal methods (drying, incineration, pyrolysis) (Cieřlik et al., 2015). Anaerobic digestion and pyrolysis are renewable energy production methods (energy recovery), therefore meet the requirements of circular economy only if residues after the process are reused as raw materials in other areas (e.g., fertilizer applications). Sewage sludge is rich in phosphorus that can be recovered (Kominko et al., 2018). The most popular method of sewage sludge processing is anaerobic digestion that can be followed by removal of phosphate by enhanced biological phosphorus removal or precipitation with the formation of struvite.



The biggest threat is the presence of micro-pollutants, including heavy metals and pathogenic bacteria, which must be removed before application (Johansson et al., 2008). Due to the presence of undesirable substances, thermal processes seem to be the proper way of sludge management. Dried sewage sludge has a similar composition as brown coal; its heating value is lower by 50% (around 10 MJ /kg) (Lundin et al., 2004). Fly ash from sludge can be used as a soil amendment, rich in potassium and phosphorus, and as a carrier of essential nutrients for plants. Fly ash, due to its high pH, can be applied as a liming agent added to acidic soils (Ferreira et al., 2003).

The successive use of sewage sludge on pastures did not show a negative impact on the yield quality or soil quality. To avoid the accumulation of heavy metals in the soil, it is recommended to apply fertilization with sewage sludge for three years and then cease for the next two years (Sigua et al., 2005). The use of sewage sludge in biomass valorization brings the risk of an increased concentration of non-biodegradable organic substances and heavy metals in the soil. Their presence may cause phytotoxic effect (Ma et al., 2018). Still, sewage sludge after proper stabilization and hygienization can be successfully applied for fertilization, which has been proved by experiments in the energetic willow plantation in Poland, where no increased concentration of heavy metals in the soil was found (Wójcik et al., 2018).

## **5. Assessment of properties of fertilizers from bio-resources**

Large amounts of generated waste are a continuous source of important components. Waste containing valuable materials, going to landfill, mixed up, is an irreparable loss to the industry while being a significant burden to the environment. Since waste biomass is varied, it must be processed with different methods (Cobo et al., 2018). Waste ought to be collected selectively for appropriate fractions and biodegradable groups, starting with households, which is necessary to manage waste in

terms of valorization. This will enable its proper management to obtain energy or materials, including good quality fertilizers (Ciesielczuk et al., 2018). In the elaboration of new fertilizers, it is important to investigate in real system (on the field) their effect on soil quality and crop yield (Sigurnjak et al., 2016). When developing a new fertilizer technology through valorization of waste, it is important to maintain the balance of nutrients, economic and environmental assessment. Crop yield and soil quality should be considered, similarly as NPK use efficiency and compared with the commercial reference products. The performance of fertilizers can be investigated by chemical soil analysis, plant response to fertilizer determination and P-fractionation – P-release patterns (Vaneeckhaute et al., 2016). The large scale of fertilizer production facilities is a barrier to the implementation of technologies that use a renewable raw material base. Hence, there is a demand for a large amount of raw material that is repeatable and qualitatively standardized. For example, the ammonia plant produces 1500-1800 tons/day from air. Phosphoric acid plants process 60 tonnes of raw material per hour. This calls for the availability of high tonnage of standardized raw materials. Farmers prefer the use of chemical rather than bio-based fertilizers because the application of the latter involves more labor. Therefore some additional factors are required to convince farmers to use fertilizers produced from the renewable resource base, such as national policies, subsidies, creating infrastructure for collection, handling, storage, distribution and sanitation (Wang et al., 2018). Wang et al. (2018) investigated what factors influence the promotion of the replacement of chemical fertilizers with their organic counterparts. Several parameters were analyzed, including prospect utility, risk, and environmental aspects. It was found that membership in farmer associations, subsidies and the size of farm influences the selection of the type of fertilizers. It is important to assess whether fertilizers containing valorized nutrients are marketable. Tur-Cardona et

al. (2018) carried out such an investigation in various European countries and found that the said replacement can be carried out if farmers' preferences are taken into account and these are the price (should be 65% lower than that of chemical fertilizers).

Additional characteristics should include high nutrients bioavailability, organic carbon content, and hygienization of biological fertilizers. If those criteria were fulfilled, there would be a chance for replacement of chemical fertilizers with their bio-based counterparts (Tur-Cardona et al., 2018).

## **6. Practical applications and future research perspectives**

The fertilizer industry did not have pressure to improve its products. Everything that has happened in the fertilizer industry has been process, not product innovation, which is related to the fact that all produced fertilizers were sold. Ammonia technology was implemented in 1913 at BASF (Haber-Bosch process). This technology has not changed for 100 years. Technological modifications including higher gas consumption efficiency rates and lower process energy use were developed. However, no significant modifications were made. A similar situation as in the nitrogen fertilizer industry was in phosphorus fertilizers sector. In 1846, the first superphosphate factory was founded in Liverpool. In the 1920s, a continuous method of obtaining phosphoric acid (V) was developed. In 1942, in England, a patent was approved for the treatment of phosphorites with sulfuric acid (VI). Since then, the technology of wet process phosphoric acid has not been changed.

There has been virtually no pressure so far to change in the phosphorus industry. Fertilizers are produced in very large installations, so there must be a large and repeatable raw material base. At this time, we cannot count on the fertilizer industry to solve the problem of wastes utilization. The fertilizer industry is not particularly interested in renewable resources, because there are no economic arguments. However,

the fertilizer industry has several environmental problems, which creates a certain perspective of technological changes, for instance CO<sub>2</sub> emission in ammonia production. Nitrogen fertilizer plants must pay fees for CO<sub>2</sub> emission allowances. Even if a part of CO<sub>2</sub> is used in the production of urea, soil urea would release some of the CO<sub>2</sub>. In turn, the phosphorus industry has two major problems. The first are depleting non-renewable natural resources and the second is phosphogypsum, which is produced in the quantity twice as high as consumption of raw material. Additionally increasing problem is phosphogypsum storage, e.g. in Florida, where rock formation occurs.

The concept of a circular economy is based on reuse, valorization, recycling, and exploitation of natural cycles. Although this concept is widely discussed scientifically and politically, it has only been fragmentarily applied in practice. In elaboration of bio-based fertilizer technologies, the following aspects are important: environmental impact should be minimized, resources should be used in a regenerative way with the consideration of resource scarcity issue, technologies should assure profitability and economic benefits to industrial enterprises. Limitations of natural resources and environmental protection should be a priority, but with sustaining business requirements for economic benefits.

The fertilizer industry underestimates the benefits of these technologies. For example, the utilization of feathers that contain 11% nitrogen can be a source of not only macronutrient N, but also if the process is skilfully designed – this can be a source of amino acids, which are a chelating agent for micronutrient ions and a biostimulator of plant growth. At the same time, the technology is emission-free and not energy-consuming. In the phosphate fertilizer industry, bone meal can be converted to hydroxyapatite and then broken down in the same way as in the wet phosphoric acid

process. Consequently, bio-based raw materials can be used to compose very modern products.

The obligation to dispose of waste is the responsibility of agri-food producers, i.e. processing plants that generate biological waste. Large agri-food processing plants send commercial grocery products to the recipients, without wastes, e.g. chickens are carcasses. Slaughter waste remains in place and should be utilized. Therefore facilities producing fertilizers from biological waste should be located very close, so that transport is not required. There is also a problem of sanitization. Bio-waste in landfills causes rotting and, as a result, emissions. Another barrier to the implementation of renewable raw materials in the production of fertilizers is the variability of the raw material. Technologies should take this into account.

Recovery of phosphorus from wastewater is no longer so attractive because the wastewater is no longer as rich in phosphates. Only a few years ago it was an interesting direction. However, phosphates have been eliminated from washing powders and are no longer an attractive source of phosphorus. In addition to struvite, dicalcium and tricalcium phosphate can be secreted. Exemplary technologies operate in the Netherlands and Japan. Urine recovery is also possible - if it is separated in the sewage system (Karak et al., 2015). The dishwasher effluents also contains phosphates because they are found in washing powders and tablets. Crystallization of struvite is not an attractive direction anymore, because sewage does not have as much phosphorus as it used to be. An interesting direction is the mobilization of phosphorus in soil through the use of phosphorus-solubilizing bacteria (Wei et al., 2018).

## **7. Conclusions**

In implementing CE assumptions in the production of fertilizers, logistics and production organization are important. Bio-based wastes can be delivered to fertilizer

plants in the form of by-products to add value to fertilizer formulations. There is a lot of room for action, but it requires taking into account the specificity of waste. In the future of fertilizer industry, innovation should be both process and product, but mainly product. In implementation of such technologies, priority directions and political determinants are important.

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Table 1. Barriers limiting the implementation of CE guidelines

Table 2. Elemental composition of potential fertilizers from waste biomass

Table 1.

Section	Improvement
Level of technology readiness	Using each renewable feedstock requires conduction of R&D studies for technology elaboration and product development



Legislation	<ul style="list-style-type: none"> <li>• standardization</li> <li>• registration</li> <li>• compatibility with REACH</li> </ul>
A biological wastes collection system	<ul style="list-style-type: none"> <li>• ensure the availability of secondary raw materials</li> </ul>
Market stimulants	<ul style="list-style-type: none"> <li>• direct payments</li> <li>• tax reduction</li> </ul>
Penalties	<ul style="list-style-type: none"> <li>• tax on the use of higher doses of fertilizers</li> <li>• prohibition of/increase in charges for storage and non-selective waste incineration</li> <li>• the tax on the leakage of nutrients</li> <li>• tax on the use of non-renewable resources</li> </ul>

Table 2.

Waste biomass	Fertilizer type	N	K	P	Cu	Mn	Zn	References
		(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	
chicken manure incineration ash	ash	n.a.	120000	84500	270	n.a.	1600	(Kaikake et al., 2009)

Sewage sludge ash	ash	n.a.	19100	88800	2510	n.a.	6460	(Kaikake et al., 2009)
banana peduncle + sewage sludge	biochar	n.a.	n.a.	5600	21.5	294.7	186.2	(Karim et al., 2019)
<i>E. coli</i>	biochar	n.a.	3739	84700	131.6	n.a.	62.0	(Kim et al., 2018)
sugarcane waste straw	biochar	4000	16000	7930	n.a.	n.a.	n.a.	(Riaz et al., 2018)
anaerobically digested bio- waste	compost	26700	n.a.	6970	97	n.a.	179	(Grigatti et al., 2019)
sewage sludge	compost	27000	n.a.	8850	162	n.a.	309	(Grigatti et al., 2019)
chicken manure with mixture of plant biomass	compost	19650	28500	12090	n.a.	489	471	(Vandecasteele et al., 2014)
fish waste	compost	11400	3070	2610	19.3	n.a.	159.9	(Radziemska et al., 2018)
manure from beef cattle fed 60% wheat or 40% corn dried distillers' grain with solubles	compost	23200	n.a.	10600	n.a.	n.a.	n.a.	(Thomas et al., 2017)
slaughterhouse waste + source- separated organic household waste	digestate	7900	1600	900	69.7	201	474	(Abubaker et al., 2015)
distiller's waste from ethanol production + cereals	digestate	5900	2800	700	69.4	266	465	(Abubaker et al., 2015)
pharmaceutical	digestate	94200	6700	5600	n.a.	n.a.	n.a.	(Cucina et al.,

organic waste co-digested								2017)
pig slurry	slurry	5300	2500	1400	218	426	801	(Abubaker et al., 2015)
dairy manure	algal turf scrubber biomass	45100	9100	7300	84	250	270	(Mulbry et al., 2005)

N – nitrogen, K – potassium, P – phosphorus, Cu – copper, Mn – manganese, Zn - zinc

n.a. - not available

122.

### Highlights:

- The use of biological waste is a solution that recovers valuable fertilizer components
- Nutrients recycling in accordance with the circular economy assumption is suggested
- Bio-waste management can improve valuable materials recovery
- There is a chance to replace chemical fertilizers with bio-based products
- Practical solutions are needed for the implementation of biomass valorization to fertilizers

123.