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BIODEGRADATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN THE COMPOSTING PROCESS AS A REMOVAL STRATEGY OF ORGANIC POLLUTANTS

Summary

Aroused in recent time fears for environmental with petroleum compounds, such as polycyclic aromatic hydrocarbons (PAHs) resulted in development of many technological strategies aimed at remediation of degraded and devastated areas. Composting, as ex situ bioremediation strategy can be useful not only in production of natural fertilizers, but also in effective removal of xenobiotics from the environment. In the case of remediation of soils containing organic compounds such as polycyclic aromatic hydrocarbons it is important to distinguish strategy of using already mature compost as an additive to contaminated soil, and the strategy of composting contaminated soil, which results in producing compost.
Keywords*: composting, PAHs, bioremediation, biodegradation*

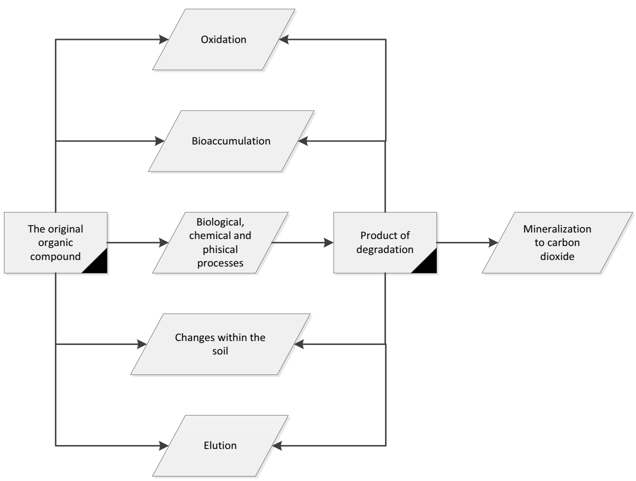
BIODEGRADACJA WIELOPIERŚCIENIOWYCH WĘGLOWODORÓW AROMATYCZNYCH W PROCESIE KOMPOSTOWANIA JAKO STRATEGIA USUWANIA ZANIECZYSZCZEŃ ORGANICZNYCH

Streszczenie

Zwiększone w ostatnim czasie obawy związane z zanieczyszczeniem środowiska związkami ropopochodnymi, w tym wielopierścieniowymi węglowodorami aromatycznymi (WWA), doprowadziły do rozwoju wielu strategii technologicznych mających na celu rekultywację obszarów zdegradowanych i zdewastowanych. Kompostowanie, jako strategia ex situ bioremediacji może spełniać nie tylko dobrze znaną rolę produkcji naturalnego nawozu, ale również prowadzić do efektywnego usuwanie ksenobiotyków ze środowiska. W przypadku oczyszczania gleb zawierających związki organiczne, takie jak np. wielopierścieniowe węglowodory aromatyczne istotne jest rozróżnienie strategii zakładającej wykorzystanie dojrzałego już kompostu jako dodatku do zanieczyszczonej gleby, od strategii kompostowania zanieczyszczonej gleby, w wyniku której powstaje kompost/stabilizat.
Słowa kluczowe*: kompostowanie, WWA, bioremediacja, biodegradacja*

1. Characteristics of polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons are a group of organic compounds consisting of at least two aromatic rings, which are the most common organic pollutants in soils, water and sediments. PAHs containing up to six aromatic rings in a molecule are often called small PAHs, while those containing more than six rings – large PAHs and they are characterized by higher stability and toxicity compared to the first group [4]. Although PAHs in the environment are generated both from natural (forest fires, volcanic activity) and anthropogenic (industrial combustion of fossil fuels, vehicular emissions, residential wood burning, etc.) sources, the great majority of them are produced by human activity [5, 20]. Transformations of polycyclic aromatic hydrocarbons in the environment, as well as other organic compounds, are very complex and could be simplified as shown in Fig. 1. Soil is the most common environment of PAHs pollution. The accumulation of PAHs in soils leads to their transfer via food chains, and eventually threatens human life. PAHs leak into the atmosphere and groundwater as a result of steaming, leaching, migration etc. [20]. Despite the partial susceptibility of PAHs to photolysis or chemical degradation, biodegradation is still the main process of their degradation [7].



Source: own work based on [13] / Źródło: opracowanie własne na podstawie [13]

Fig. 1. Transformation of PAHs in the environment
Rys. 1. Przemiany WWA w środowisku

2. Remediation strategies of organic pollutants removing

There are both physical, chemical (sometimes also called physicochemical) and biological removal methods of organic pollutants. Physical and chemical methods are not a subject of this publication, but have been included in Fig. 2. summing up remediation techniques used in organic pollutants removal. Bioremediation methods can be conducted *in situ* - directly at the place of contamination, and *ex situ*, by its transfer to the storage.

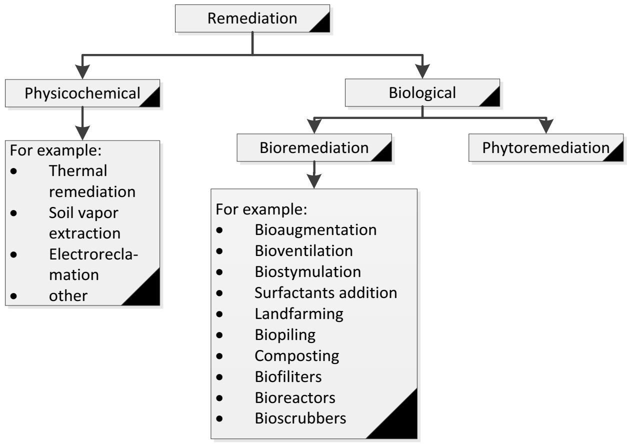


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Fig. 2. Strategies of bioremediation/supporting bioremediation
Rys. 2. Strategie bioremediacji/wspomagania bioremediacji

3. Composting of organic pollutants

Composting is a method of waste recovery and is based on the decomposition of organic substances by microorganisms under aerobic conditions. It is assumed that during composting about 75% of the organic matter is mineralized and the remaining 25% is converted into humus compounds [14]. The decomposition of organic matter during composting undergoes as follows: organic matter ($C_aH_bO_cN_dS_e$) + O_2 from air + P + N + aerobic microorganisms = H_2O + CO_2 + NH_3 + heat + compost (humus + minerals) [14].

In the case of composting, heat generated during process leads to a characteristic increase in temperature. This enables the division of the composting process on stages characterized by different activation of various groups of microorganisms. Literature reports distinguish two [10], or four phases of the process [14]. Regarding the two-stage process generally 1) thermophilic phase (intensive composting) and 2) mesophilic phase (maturation) are distinguished. However, most researchers prefer a model dividing the process into four phases; 1) the phase of low temperature (mesophilic, temperature rising) associated with the start of the composting process; the intense proliferation of microorganisms and the decomposition of easily degradable organic matter (mainly amino acids and sugars); which lasts a few days; 2) high-temperature phase (thermophilic), characterized by increasing temperature of compost material (up to 70°C), resulting in reduction of the number of mesophilic microorganisms and increase in thermophilic microorganisms. During this stage most of the microbial decomposition and production of biomass is observed and it lasts from few days to few weeks; 3) mesophilic phase (actual composting), characterized by a decrease of temperature due to a decrease in metabolic activity of microorganisms associated with depletion of the organic carbon source in the form of organic pollutants. An increase in the number of mesophilic microorganisms is observed and this phase lasts about 20-35 days; 4) the phase of maturation of compost, characterized by the drop of temperature to ambient temperature [14, 17].

4. The main aim of composting

According to the Polish Ministry of the Environment (Department of Waste Management), compost production is the primary objective of composting process. Compost is a product meeting criteria for organic fertilizers or plant conditioners and is not dangerous for the environment in the form of waste [13]. When the compost does not meet requirements, it cannot be called compost and it is treated as a waste with code: 19 05 03. Such waste is not suitable for use as a product (compost).

5. Methods of composting

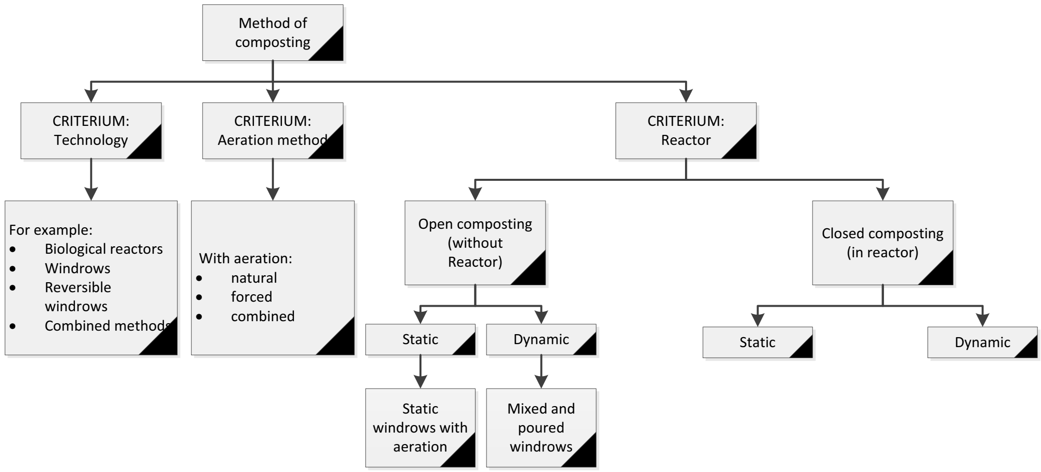
There are many classifications of composting methods. Different methods can be classified into different categories depending on the chosen criterion. They can be distinguished by the criterion of technology used during process (composting in the bioreactor, in windrows, in reversible windrows, combined methods), criterion of aerating the compost material (natural aeration, forced aeration, combined aeration), and, criterion considering reactor type used in process [10]. The division depends on the type of reactor or its absence (open / closed composting) in association with the used operation mode (static / dynamic process). Dynamic methods, in opposite to static methods, require the mixing of composting biomass. In the case of the open aerated static method in windrows, biomass is placed over the network of aeration canals, while height of windrows can reach up to 2 meters. Systems of windrows in a dynamic process are based on similar principles as a static process, with periodically pouring and mixing of windrows, usually more than five times, while the temperature at least 55°C is maintained. During the composting in reactors, it is possible to monitor and adjust parameters such as temperature, oxygen content, airflow and others [9, 10]. Review of the main classifications of composting methods according to the mentioned criteria is shown in Fig. 3.

6. Factors influencing the composting process

Composting process is influenced by factors related both to the structure of the composted material and to microbial activity.

In the case of composted material, the chemical (susceptibility to biodegradation), and physical properties, as well as the structure of material (the optimal crumbling material leads to increase in microbial activity surface) are crucial. Furthermore, the addition of structural material (for example straw, wood chips, etc.) prevents the formation of anaerobic conditions, and provides an additional source of carbon for microorganisms.

On the other hand, the optimization of pH, temperature, humidity, content of nutrients and an appropriate proportion of biogenic elements is essential for maintaining the proper activity of microorganisms. It should be noted that the changes in conditions are associated especially with temperature variations in the different phases, resulting in a significant diversity of microorganisms prevalent in subsequent stages, which can also be described as a succession of microbes (subsequent dominance of a particular species of microorganisms).



Source: own work based on [2, 17] / Źródło: opracowanie własne na podstawie [2, 17]

Fig. 3. Review of classification of composting methods
Rys. 3. Przegląd klasyfikacji metod kompostowania

The changes mainly concern the number of meso- and thermophilic bacteria, actinomycetes and fungi. It is generally accepted that bacteria are able to assimilate 5-10% of organic carbon, actinomycetes 15-30%, and fungi 30-40%. It means that the highest metabolic activity is exhibited by fungi. This may be related to their ability to decompose cellulose [2].

7. Composting/use of a mature compost during the bioremediation of contaminated soils

In the case of the use of composting / mature compost during the biodegradation of organic xenobiotics, two main strategies can be distinguished; 1) the strategy of using already matured compost as an additive to the contaminated soil, and 2) the strategy of composting, which results in compost production [17].

Composting of soil contaminated with organic compounds is initiated by mixing the structural materials, which are also treated as sources of nitrogen and carbon, with the contaminated soil. The first reports of composting of soil contaminated with PAHs appeared in the late eighties and early nineties [1]. Crawford et al. (1993) demonstrated the differences in PAHs degradation depending on the used compound – in the experiment, the naphthalene, pyrene and benzo[a]anthracene were used. During composting process the most biodegradable PAH was naphthalene (total biodegradation within 7 days), less biodegradable was benzo[a]anthracene (25% removal within 7 days), while the pyrene was non-biodegradable [3]. A comprehensive review of achievements at the beginning of this century was made by Antizar-Ladislao et al. [1]. Recent research in the field of PAH-contaminated soils composting clearly demonstrates the much higher efficiency of five studied types of PAHs removal (naphthalene, phenanthrene, pyrene, benzo[a]pyrene, benzo[ghi]perylene) in the composting process, than during anaerobic degradation [18]. A research on comparison of the sorption and mineralization of fluoranthene and other organic compounds (two surfactants sodium linear dodecylbenzene sulfonate - LAS and 4-n-nonylphenol - NP as well as a herbicide glyphosate) during the various composting phases was made by Lashermes et al. [11]. The highest degree of fluoranthene mineralization was observed at the end phase of maturation, in contrast to the other compounds (for LAS and glyphosate thermophilic phase; for NP the beginning of maturation phase). The authors explained this by the fact that in the biodegradation of fluoranthene specific microflora was involved, while the degradation of the remaining compounds were probably related to the total activity of all microorganisms. Furthermore, in the case of fluoranthene as highly hydrophobic compound, the highest sorption was observed, although it decreased with maturation of the compost. Zhang et al. studied the composting with fresh organic waste. The results clearly confirmed the optimization of the organic composition as a proper strategy during the composting process [21]. On the other hand, Hubalek et al. [8] studied the ecotoxicity of soil contaminated with PAHs during composting using toxicity tests with indicator organisms *Vibrio fisheri*, *Sinapis alba*, *Lemna minor*, *Eisenia fetida* and *Heterocypris incongruens*. The highest toxicity was observed during the first phase of composting. A decrease in the concentration of PAHs during composting was correlated with the lowering of the ecotoxicity, although the results varied depending on the model organism [8]. Sayara et al. [15] determined the effect of biostimulation and bioaugmentation on the process of biodegradation during composting of soil contaminated with seven PAHs (fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene and chrysene). Bioaugmentation with *T. versicolor* did not affect the biodegradation of PAHs, as opposed to biostimulation, which significantly increased the efficiency of degradation [15].

The application of mature compost (product of composting process) to contaminated areas is another method. Mature compost has a high biodegradation potential due to the high biodiversity of microorganisms capable of degrading the various types of pollution. In addition, the compost can contribute to changes in pH, moisture, soil structure and consequently optimal oxygenation, but also can be treated as a source of valuable nutrients for microorganisms. However, a proper homogenization of compost and contaminated soil is the main drawback and problem of this strategy [17]. The first reports related to the addition of compost to soil contaminated with PAHs appeared in the early 80s, when the changes in concentration of PAHs in fresh and mature compost were examined [12]. The mineralization reached 19% and 62% for anthracene, 8% and 58% for benzo[a]anthracene, 0.5% and 19% for benzo[a]pyrene and 1.4% and 21% for benzo[a,h]anthracene for fresh and mature compost respectively after 70 days of the experiment. These results clearly demonstrated the greater efficiency of the mature compost compared to fresh one during mineralization of PAHs. Moreover, literature reports after 2010 indicate the addition of compost as a suitable strategy for bioremediation process. Gandolfi et al. [6] using a high-quality compost as an additive to soil contaminated with tetracyclic PAHs noted both the upward trend in degradation and reduction of ecotoxicity [6]. On the other hand, Saraya et al. [16] emphasized the importance of optimizing the process parameters. Authors studied the effect of concentration of pyrene (0.1-2 g kg^{-1}), the ratio of soil : compost (1 : 0.5-1.2), and the stability of compost (0.78; 2.69; 4.52 mgO_2 / (g of organic matter • h) on the biodegradation of PAHs. The optimum conditions turned to be as follows – 1.4, 1:1.4, 0.78 (after 10 days); 1.4, 1:1.3, 2.18 (after 20 days); and 1.3, 1:1.3, 2.18 (after 30 days) for respective parameters. It should be noted that authors indicate the stability of the compost as a key parameter of effective process [16]. Wu et al. [19] in the 8-month studies determined the effect of the addition of mature compost on degradation and bioavailability of PAHs in soil contaminated with: 1) diesel oil, 2) ash obtained after coal combustion, and, 3) coal tar. Analyses were conducted for 0, 3, 6, 8 months of the experiment. Studies have shown that the bioavailability of PAHs was inversely proportional to the amount of aromatic rings, and octanol-water partition coefficient. Furthermore, the addition of compost resulted in more than 90% reduction of PAHs content after 8 months regardless of the type of contamination in the soil [21].

8. Conclusions

Contamination of the environment with carcinogenic, teratogenic and mutagenic polycyclic aromatic hydrocarbons, results from incomplete combustion of organic matter both from natural and anthropogenic sources. In order to reduce their content in soils, both physicochemical remediation and bioremediation, including composting can be used. Numerous composting technologies are designed to conduct the process in open and closed systems, but the characteristic temperature increase (up to 70°C) being a result of exothermic reactions and thermal energy production, remains constant regardless of the applied method. Available literature reports indicated usefulness of PAHs removal both with the addition of already matured compost, and during conventional composting of contaminated soil.

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