



Biodegradation of high-molecular-weight polycyclic aromatic hydrocarbons under anaerobic conditions: Overview of studies, proposed pathways and future perspectives[☆]



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ABSTRACT

The biodegradation of low- and high-molecular-weight polycyclic aromatic hydrocarbons (PAHs) (LWM-PAHs and HMW-PAHs, respectively) has been studied extensively under aerobic conditions. Molecular O₂ plays 2 critical roles in this biodegradation process. O₂ activates the aromatic rings through hydroxylation prior to ring opening and serves as a terminal electron acceptor (TEA). However, several microorganisms have devised ways of activating aromatic rings, leading to ring opening (and thus biodegradation) when TEAs other than O₂ are used (under anoxic conditions). These microorganisms belong to the sulfate-, nitrate-, and metal-ion-reducing bacteria and the methanogens. Although the anaerobic biodegradation of monocyclic aromatic hydrocarbons and LWM-PAH naphthalene have been studied, little information is available about the biodegradation of HMW-PAHs. This manuscript reviews studies of the anaerobic biodegradation of HMW-PAHs and identifies gaps that limit both our understanding and the efficiency of this biodegradation process. Strategies that can be employed to overcome these limitations are also discussed.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds consisting of carbon and hydrogen, forming aromatic cycles with 2 or more rings. These molecules are all solid and stable, and therefore, they have high melting and boiling points and low solubility in aqueous solutions (Masih et al., 2012). As the number of rings increases, the aqueous solubility of PAHs decreases, leading to their persistence in the environment; thus, these compounds represent an important class of environmental pollutants (Abdel-Shafy and Mansour, 2016).

PAHs comprise low-molecular-weight PAHs (LMW-PAHs) with two rings, such as naphthalene (NAPH), and three-ring fluorene (FLR), anthracene (ANT), and phenanthrene (PHEN); and high-molecular-weight PAHs (HMW-PAHs) with four or more rings. The HMW-PAHs include pyrene (PYR), chrysene, and fluoranthene (FLT) [four rings] as well as benzo[a]pyrene (BZP) and benzo[a]anthracene [five rings] (Fig. 1) (Abdel-Shafy and Mansour, 2016).

The negative effects of these compounds on various organisms

have been well documented. PAHs display moderate to high levels of acute toxicity in aquatic life and birds, including toxic effects on the development of the reproductive system, immunity and a risk of tumour development (Abdel-Shafy and Mansour, 2016; Kim et al., 2013). In humans in particular, and in mammals in general, PAHs have been shown to be carcinogenic and teratogenic (Abdel-Shafy and Mansour, 2016; Ohura et al., 2004), and compelling evidence indicates that humans who are exposed to PAHs develop lung cancer (Abdel-Shafy and Mansour, 2016; Kim et al., 2013). In addition, a growing body of evidence also indicates a possible role for PAHs as endocrine disruptors (Zhang et al., 2016).

The environment is contaminated with PAHs primarily derived from pyrogenic and petrogenic sources. In general, PAH production from pyrogenic processes originates from the exposure of organic molecules to high temperatures under low levels of or in the absence of oxygen. These situations include the transformation of coal into coke and coal tar, the thermal cracking of petroleum products into lighter hydrocarbons, the incomplete combustion of fuels in motor vehicles and the combustion of wood in forest fires and fireplaces (Abdel-Shafy and Mansour, 2016). Additionally, PAHs originating from petrogenic sources are produced by petroleum product spills and leakage during transport, storage and refinery

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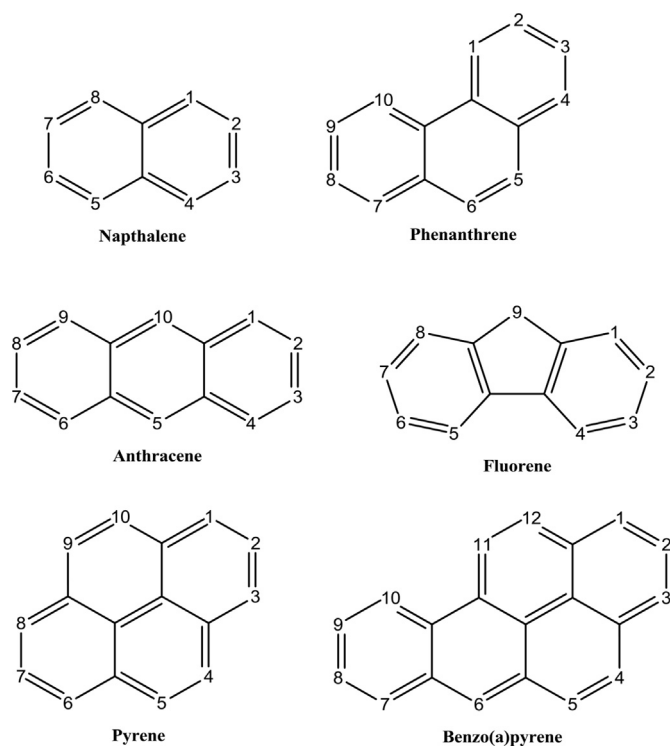


Fig. 1. Chemical structures of the polycyclic aromatic hydrocarbons along with the ring numbering.

processes. In addition, PAHs (primarily those derived from petroleum products) have various industrial uses, such as in the lubrication of photographic products and thermosetting plastics (Abdel-Shafy and Mansour, 2016). The waste generated by these industrial activities further increases PAH contamination in the environment.

In natural settings, these pollutants are removed by biodegradation, a process based on the ability of microorganisms to use these pollutants as their carbon and energy sources. PAH biodegradation have been extensively examined under aerobic conditions, as shown by the substantial number of papers on this topic. This form of biodegradation has been evaluated in various environments (soil, sea, and sediments); PAH-degrading microorganisms have been characterised, and the PAH biochemical pathways have been elucidated (Haritash and Kaushik, 2009; Nzila, 2013; Seo et al., 2009). Comparatively, little is known about the anaerobic biodegradation of these compounds.

As discussed earlier, PAHs are not soluble in aqueous solutions; therefore, they tend to accumulate in the environment. For example, they accumulate in the lower soil layer, where the O_2 concentration is reduced or even zero (Li et al., 2009). Because O_2 is required for both ring opening and terminal electron acceptor (TEA) activity, aromatic compounds may not undergo biodegradation in anoxic environments. However, naturally occurring anaerobic microorganisms with unique biochemical characteristics that are present within these environments would likely degrade these compounds. This concept was supported in the 1980s, when the first evidence of mono- and dicyclic aromatic hydrocarbon biodegradation was provided (Evans and Fuchs, 1988; Mihelcic and Luthy, 1988). Since then, more studies have been dedicated to examining the biodegradation of aromatic compounds and understanding the mechanisms underlying this process. However, a careful examination of the studies published to date shows a primary focus on the monocyclic aromatic hydrocarbon (MAH) benzene and its derivatives as well as the LMW-PAH NAPH and its

derivatives. Readers are referred to several excellent reviews that summarise this work (Ghattas et al., 2017; Heider and Fuchs, 1997; Meckenstock and Mouttaki, 2011; Meckenstock et al., 2004).

However, the anaerobic biodegradation of HMW-PAHs (PYR and BZP) and, to some extent, the LMW-PAHs PHEN and ANT, have received little attention compared with that of MAH and NAPH. The reason is that the high complexity of these PAHs makes them less amenable to anaerobic biodegradation. Nevertheless, few reports have investigated their biodegradation, and the current review attempts to summarise this work. The anaerobic degradation of MAH and NAPH are excluded from this review, except in terms of a broader overview. This review identifies important knowledge gaps that limit our understanding of the anaerobic biodegradation of PAHs, and it also proposes future research strategies to overcome these limitations. Overall, this review suggests new avenues for research on the anaerobic biodegradation of complex PAHs.

2. Reduction conditions, TEAs and ATP formation

Respiration is a process in which the cell converts the energy stored in organic compounds to ATP (adenosine triphosphate). This process is initiated by the breakdown of organic compounds into smaller compounds and eventually to CO_2 , releasing electrons that will drive the conversion of ADP (adenosine diphosphate) to ATP (Fig. 2). For this process to continue, these electrons must be captured *in fine* by TEAs. Oxygen is the TEA under aerobic conditions, whereas in an anaerobic (or anoxic) milieu, these TEAs include i) sulfate, which is converted into sulfide by sulfate-reducing bacteria; ii) nitrate, which is transformed into N_2 by denitrifying bacteria; iii) CO_2 , which becomes biomethane through reactions mediated by methanogens; and iv) ions such as Fe^{3+} and Mn^{4+} , which are reduced to Fe^{2+} and Mn^{3+} by metal-ion-reducing bacteria (Figs. 2 and 3) (Muyzer and Stams, 2008; Nzila, 2017; Zumft, 1997). To a lesser extent, molecules such as chlorate, perchlorate, trimethylamine oxide and fumarate can also be used as TEAs by bacteria (Barrett and Kwan, 1985; Coates and Achenbach, 2004; Tomasiak et al., 2007).

The ability of TEAs to receive electrons is based on the TEA potential. Molecular oxygen, O_2 , has the highest TEA potential (+818 mV), followed by nitrate (+433 mV), ferric iron or Mn^{4+} (ca. +200 mV), and sulfate (ca. -200 mV), whereas CO_2 has the lowest value (-380 mV) (Heider and Fuchs, 1997). Thus, in the presence of O_2 , none of the abovementioned TEAs will be predominantly reduced, and likewise, CO_2 will be preferentially reduced only in the absence of all other TEAs.

In culture media, reducing conditions are achieved by increasing the sulfate and nitrate concentrations, generally from 0.1 to 20 mM (Table 1). As stated earlier, methanogenic conditions are achieved in the absence of any other reducing agents. However, bicarbonate (up to 20 mM) may also be added to the medium, leading to an increase in CO_2 concentrations and thus favouring the methanogenesis process.

3. Anaerobic biodegradation of HMW-PAHs

The anaerobic biodegradation of PHEN, ANT, PYR and BZP has been investigated using single PAHs and mixtures of various PAH compounds. Thus, the author summarised studies in which single substrates were used to obtain a better understanding of this process.

3.1. Biodegradation of single PAHs

The first evidence for the anaerobic biodegradation of PHEN (the conversion of PHEN to CO_2) was provided in the 1990s. Using

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