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Review

Using Low Molecular Weight Organic Acids to Enhance Microbial Degradation of Polycyclic Aromatic Hydrocarbons: Current Understanding and Future Perspectives

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Abstract: Polycyclic aromatic hydrocarbons (PAHs), an organic pollutant with persistence and carcinogenicity, are universally present in the environment and food processing. Biological approaches toward remediating PAHs-contaminated sites are a viable, economical, and environmentally friendly alternative compared to conventional physical and/or chemical remediation methods. Recently, various strategies relating to low molecular weight organic acids (LMWOAs) have been developed to enhance the microbial degradation of PAHs. However, the remaining challenge is to reveal the role of LMWOAs in the PAHs biodegradation process, and the latter limits researchers from expanding the application scope of biodegradation. In this mini-review, we summarized the current understanding of the impact of LMWOAs on (1) the physicochemical behavior of PAHs in the extracellular environment; (2) the interactions between PAHs and the microbial cell surface; and (3) the intracellular metabolization of PAHs. Future perspectives for this field are discussed in this review as well.

Keywords: low molecular weight organic acids; polycyclic aromatic hydrocarbons; bioremediation; extracellular environment; cell surface; intracellular metabolization

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), persistent organic pollutants, are widely distributed in the environment and food processing [1]. Over the past decades, increasing amounts of PAHs have been generated from the incomplete combustion of organic substances, such as coal, oil, wood, and tobacco [2,3]. The strong genotoxic, mutagenic, and carcinogenic properties of PAHs pose a severe threat to human health and, therefore, raise global concerns [4–6]. In total, 16 widespread PAHs compounds were listed as priority pollutants by the US EPA (United States Environmental Protection Agency) [7,8]. The majority of PAHs are chemically stable with low solubility in water and worse adsorption towards solid particles [9]. Hence, universal and transferable approaches to degrading the PAHs are still demanded.

Conventional methods, including physical or chemical remediation approaches, have already been developed to overcome the PAHs pollution challenge. However, physical or chemical remediation approaches are often costly and may cause secondary environmental pollution [10–12]. Bioremediation provides a cost-effective and environmentally sustainable alternative [13,14]. Generally, soil organic matters, such as humins, low molecular weight organic acids, amino acids, are favorable for the biodegradation of pollutants [15–17]. For

instance, electrochemically-reduced humins were able to enhance microbial denitrification. Solid-phase humins improve all reducing reactions from nitrate to nitrogen gas [18,19]. In addition, the degrading rate of petroleum hydrocarbons was significantly affected by soil organic content [20].

Among various dissolved soil organic matters, low molecular weight organic acids (LMWOAs, MW < 500 Da) also facilitate the degradation of pollutants by plants or microbes. LMWOAs can be discovered in the root exudates and the microbial decomposition of plant litter [21–24]. LMWOAs include mono-, di-, and tricarboxylic acids containing hydroxyl groups as well as unsaturated carbon and often exist as the dissociated anions (carboxylates) [25,26]. The release of LMWOAs from root exudates could be influenced through different factors, such as the acidity of the soil, the absence/presence of insoluble minerals, type of soil microorganisms, and plant developmental stage [17,27]. These produced soluble elements which are easily available for microbial growth [26,28,29]. The synthesis and/or secretion of LMWOAs by microbes play essential roles in the process of biotic or abiotic stress responses [30]. Furthermore, the root exudate organic acids are crucial for the rhizoremediation of heavy metals and PAHs. To date, although some excellent reviews thoroughly elucidate the importance of the root exudate in heavy metals and PAHs bioremediation [26,31–33], few focused on investigating the role that individual compounds (such as carboxylates, amino acids) of root exudate in PAHs bioremediation [26].

Recently, the addition of LMWOAs has been an attractive and promising strategy to enhance the capacity of microbes to degrade organic pollutants, especially PAHs (Table 1). LMWOAs showed a powerful ability to chelate multivalent cations (e.g., Fe^{3+}, Al^{3+}) and thus significantly influenced the mobility, solubility, and fate of pollutants in nature [34]. In addition, glutaric acid and citric acid improve the growth rates and the vital enzymatic activities of microorganisms in the degradation process, resulting in increased organic pollutants biodegradation [25,35]. PAHs degradation research undoubtedly benefits from the occurrence of various LMWOAs towards microorganisms. Meanwhile, an in-depth understanding of how LMWOAs affect microbial bioremediation at the molecular level is in demand to view the comprehensive biodegradation landscape and inspire us to develop additional bio stimulation techniques for engineering the efficiency of bioremediation systems.

In this review, we explored different LMWOAs, introduced factors for degrading PAHs, classified them according to the process of biodegradation (Figure 1). The latter include (1) the behavior of PAHs and other chemicals in the extracellular environment, (2) interactions between PAHs and the microbial cell surface, and (3) the intracellular metabolization of PAHs. We discuss each approach in a dedicated section and highlight examples in which LMWOAs have found their way into improving efficiency as stepping-stones for future developments. We critically discuss the current status of LMWOAs in the bioremediation of PAHs. Finally, we propose promising directions from the understanding of the regulated mechanism in microorganisms by LMWOAs to microbe modification based on genetically edited for further development of the field.

Table 1. The predominant low molecular weight organic acids (LMWOAs) applied to enhance microbial degradation of pollutants.

LMWOAs	Microorganism	Pollutants	Main Function	Reference
Citric, succinic, and aconitic acid	-	PAHs contaminated soil	Enhance PAHs degradation	[36]
Citric and malic acid	-	Phenanthrene	Enhance desorption	[37]
Oxalic acid	Microbial community	Agricultural field contaminated with PAHs	Promote PAHs dissipation, enhanced the microbial biomass and activity	[38]
Citric, lactic, malic, oxalic, and succinic acids mixture	*Stenotrophomonas sp.*, *Microbacterium sp.*, and *Arthrobacter sp.*	Benzo(a)pyrene and pyrene	Enhance biodegradation	[39]
Eight organic acids mixed: oxalic, formic, tartaric, lactic, acetic, malic, maleic, and citric acid	Microbial populations	Phenanthrene and pyrene	Influence the bioavailability of PAHs and microbial activity	[40]
Root exudates were prepared by mixing glucose, oxalic acid, malic acid, and serine	Soil microbial community	Pyrene	Enhance biodegradation	[41]
Glutaric acid	*Pseudomonas aeruginosa* NY3	Hexadecanol	Increase strain growth rates, hexadecane monooxygenase activities, and enhance biodegradation	[35]
Citric and malonate acid	Microbial community	Petroleum hydrocarbons	Stimulate heterotrophic microbial activity	[25]
Citric acid, oxalic acid, malic acid	-	Phenanthrene and pyrene	Enhance bioavailability	[42]
Oxalic and malic acids	-	Phenanthrene	Favor photodegradation on Fe(III)–clay	[43]
Citric acid, oxalic acid, and malic acid	-	Naphthalene, acenaphthene, fluorene, phenanthrene, fluoranthrene, pyrene, benzo(a) anthrancene, and benzo fluoranthrene	Promote bound PAH residues release, and enhance the PAH availability in soils	[44]
Citric and malic acids	-	Phenanthrene and pyrene	Promote the release and enhanced the availability of PAHs in soil	[45]
Malic acid	-	Phenanthrene	Enhance desorption	[46]
Acetic acid, oxalic acid, tartaric acid, and citric acid	-	Phenanthrene	Enhance desorption	[47]
Citric and oxalic acid	-	Phenanthrene and pyrene	Enhance desorption	[48]
Citric, oxalic, and malic acid	-	Phenanthrene	Enhance desorption	[49]
Citric and oxalic acid	-	Phenanthrene and pyrene	Increase phenanthrene and pyrene availability	[50]
Succinic, tartaric, malic, malonic, oxalic, citric, or ethylenediaminetetraacetic acid		p,p′-DDE	Enhance desorption	[34]

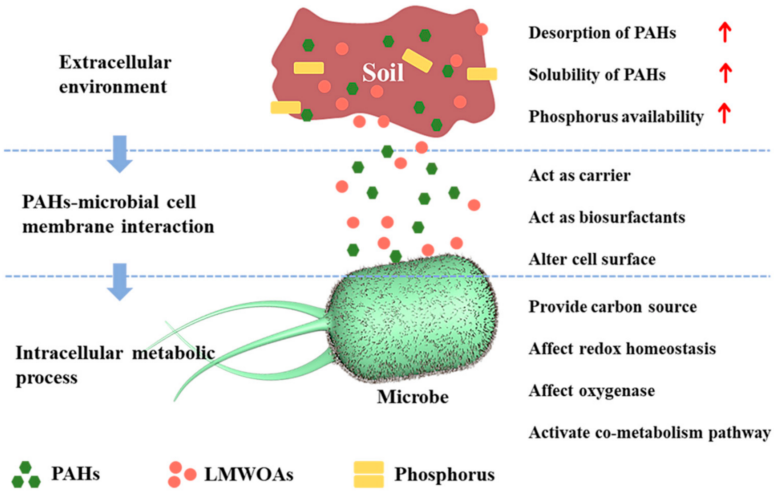

Figure 1. The influence of low molecular weight organic acids (LMWOAs) on the microbial degradation process of polycyclic aromatic hydrocarbons (PAHs).

2. Effects of LMWOAs in the PAHs Biodegradation Process

2.1. Physicochemical Behavior Changes in PAHs and Other Chemicals in the Extracellular Environment

2.1.1. Effects on the Desorption of PAHs

Desorption is a key property applied to evaluate the bioavailability of PAHs [51], and LMWOAs have been reported to enhance the bioavailability of PAHs by improving their desorption from the soil [46–49,52]. Ling et al. found that citric, oxalic, and malic acid might promote the desorption of PAHs from the soil, which is most likely mediated by the organic acid anions derived from LMWOAs [53]. Gao et al. found that LMWOAs (such as citric and oxalic acid) in the artificial root exudates significantly increased the desorption of phenanthrene and pyrene in soils [48,49]. These phenomena may explain why the LMWOAs might disrupt the linkages among the soil organic matter, metal cations, and minerals, causing the release of additional soil organic matters [53]. These resulting dissolved organic matter (DOM) in the soil would further strengthen the desorption of PAHs [50]. Interestingly, the enhancement magnitude of PAHs desorption also depends on several determinants, such as pH, the type of soil, the time of exposure to the contaminant, and the concentrations of the LMWOAs [49,52]. Generally, high LMWOAs concentrations (up to 500 mM) and pH approaching neutral can promote better desorption of PAHs [49,52]. Furthermore, different LMWOAs presented different influences on PAHs desorption regarding their chemical structures [52].

2.1.2. Effects on the Solubility of PAHs

The rate of microbial uptake and biodegradation of PAHs is also highly dependent on the solubility of the compounds in water [54]. Thus, enhancement of the PAHs solubility is essential for achieving higher microbial degradation [55]. The presence of LMWOAs can change the solubility of PAHs in the solution. Zhou et al. found with the increase in LMWOAs concentration, the solubility of naphthalene from water to mixtures (water and LMWOAs) was increased [21,56]. However, the increasing tendency did not show a linear relationship with the organic acid concentration, while the sudden change exhibited when the concentration of organic acid was over a specific value. Meanwhile, the naphthalene solubility was increased with the carbon chain length of LMWOAs. The increased solubility of naphthalene by LMWOAs was ascribe to a clathrate structure of LMWOAs in the water-rich region.

2.1.3. Effects on the Bioavailability of Phosphorus

Applying LMWOAs into the soil affects not only the bioavailability of PAHs but also phosphorus availability in soil [26,57]. Microbes usually play a pivotal role in mobilizing various forms of phosphorus, which is mediated by the microbes' exudates, such as LMWOAs [58,59]. The carboxylate moiety of LMWOAs has the capacity to compete with phosphorus for anion exchange sites and chelate metal cations and then be released into the soil solution [60]. The ability of LMWOAs in mobilizing phosphate is associated with the number of carboxyl groups and structural arrangement with the following trend: tricarboxylic acid > dicarboxylic acid > monocarboxylic acid [31]. The increased phosphorus release can facilitate microbial growth and activity that may provide an avenue to accelerate PAHs biodegradation. Besides phosphorus, LMWOAs can also chelate nutrient elements (such as Fe and Mn) in soil, thus better accelerating plant growth in low-nutrient soils [61] that may also benefit for PAHs removal by plants.

2.2. Effects on PAHs-Microbial Cell Surface Interactions

Basically, there are two ways for microbes to internalize PAHs: (1) passive diffusion [62,63] and (2) an inducible active transport system when microbes are grown on PAHs as the sole carbon source [64]. Some insights have been gained on how DOM, e.g., humic acids (HAs), is involved in the interaction between PAHs and microbes REF. Most DOM shows micellar properties and acts as carriers and/or biosurfactants in the aqueous solution. PAHs dissolved with micellar surfactants and directly interacted with the bacterial surface accompanying better bioavailability [65]. While DOM hardly changes cell wall permeability, it might facilitate the active transport ability during the PAHs internalization [66]. In addition, DOM may alter the unstirred boundary layer near the bacterial surface [67]. Therefore, bacteria can internalize dissolved PAHs through diffusion and then degrade hydrophobic substances [68]. HA is bound to the cell surface mainly via hydrophilic moiety, and thus the hydrophobic part is directed outward into the environment. In this context, the microbial surface yielded heterogeneous hydrophobic binding sites obtaining a larger interfacial area for attracting PAHs, which introduces the highly enhanced sorption capacity [69]. Although there is no direct demonstration of how LMWOAs facilitate the cellular uptake of PAHs on the cell surface, it is plausible to assume that LMWOAs act similarly to DOM since LMWOAs are essential components of DOM and show similar properties with biosurfactants as well [26].

2.3. Effects of LMWOAs on the Intracellular Metabolization of PAHs

2.3.1. Serving as an Additional Carbon Source for Microbes

LMWOAs can serve as an easily degradable and direct energy source for microbes. Mostly, LMWOAs increase the total number of PAHs degrading bacteria and these microbe activities, which in turn improves the PAHs degradation efficiency [25,38,40]. For example, Li et al. reported that oxalic acid facilitates the desorption of PAHs from soil (Figure 2a) and acts as a carbon resource for microbes in the soil. The latter stimulated the microbial biomass and activity, accompanied by the increased abundances of PAH degradation related genera and genes (Figure 2b–d) [38]. However, the high inputs of energy and nutrients into polluted soils would decrease the PAHs degradation rate due to catabolite repression [70]. Catabolite repression refers to the inhibition of the transport and/or metabolism of certain carbon sources in the presence of preferred metabolized carbon sources [71]. Nonetheless, the decreased PAHs degradation could be compensated by the overall increased bacteria number and the metabolic activity [72].

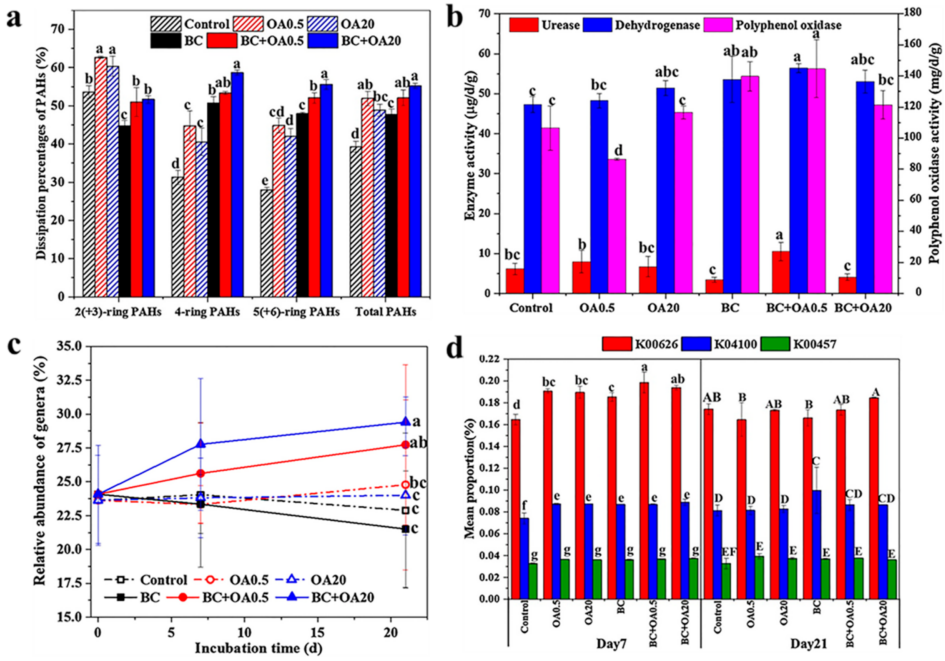

Figure 2. (**a**) Dissipation percentages of PAHs; (**b**) The regulation of urease, dehydrogenase, and polyphenol oxidase enzyme activity; (**c**) The genus-level community structure, after 21 days of incubation; and (**d**) Mean proportions of three functional genes associated with PAH degradation, BC: maize straw biochar, OA: oxalic acid. (Reproduced from ref. [38] with permission from Elsevier, copyright 2019).

2.3.2. Effects of LMWOAs on Intracellular Redox Homeostasis

Readers can find more information regarding the metabolic processes by which microbes degrade PAHs in wonderful reviews [73,74]. Generally, PAHs are first transformed into smaller ring molecules and finally turned into Krebs cycle intermediates. In these metabolization pathways, several oxidative steps are involved in reducing NAD^+ to NADH that influences intracellular redox homeostasis [75] and finally may affect the biodegradation of PAHs. Interestingly, intracellular redox homeostasis and oxygenase status can be perturbed by the supplementation of LMWOAs. For instance, previous studies utilized *Pseudomonas aeruginosa* NY3 to degrade n-hexadecane with the addition of glutaric acid. The latter demonstrated that the ratio of NAD^+ to NADH increased significantly by inserting glutaric acid. Moreover, both the gene expression level and enzyme activity of alkane monooxygenase can be induced by supplementing glutaric acid [35]. The reason might be that the synchronous metabolism of glutaric acid leads to the accumulation of oxidized NAD^+, which might increase the intercellular oxidation potential. And the respiration rates were accelerated by reducing one NADH dehydrogenase at the start of the respiratory chain, which ultimately transfers the electrons to oxygen under aerobic conditions [76].

2.3.3. Activation of Co-Metabolism Pathways

PAHs are degraded to catechols under the action of dioxygenases in bacteria after undergoing ring-opening by symmetrical or asymmetrical pathways. The produced organic acids are further transformed into LMWOAs (e.g., pyruvic, succinic, and oxaloacetic acid) and subsequently enter the tricarboxylic acid cycle with finally converting into CO_2 and H_2O [77]. The toxicity and sparingly solubility of PAHs indeed limited PAHs' biodegradation efficiency and resulted in slow microorganism growth and worse PAHs uptake [78,79]. However, PAHs may partly or even completely be degraded via microbial metabolic processes when certain ancillary carbon sources are supplemented. Such a phenomenon is usually termed microbial co-metabolic biodegradation [80]. For example, Ambrosoil et al. showed that the degradation of PAHs in the presence of glucose or acetate

is more efficient than without an ancillary carbon source [81]. In our previous study, we pointed out that glutaric acid can effectively promote the degradation of hexadecane by *Pseudomonas aeruginosa* NY3 via a co-metabolic process [35]. The co-metabolism approaches were applied to the bioremediation of PAHs contamination [82,83]. Generally, the ancillary carbon sources affect the co-metabolic process mostly in two ways: (1) by promoting cell growth and enhancing the biodegradation of the non-growth substrate, and (2) by acting as a co-substrate in co-metabolism with inducing specific enzymatic reactions [84]. The probability of co-metabolism would be higher under the similar chemical structures of the (non-)growth-substrates [79]. This observation implies that LMWOAs with a PAHs-similar structure might effectively increase biodegradation efficiency.

2.3.4. The role of LMWOA in Aerobic Degradation and Anaerobic Degradation

The degradation of PAHs also can be divided into aerobic degradation and anaerobic degradation. Preliminary work in this field focused primarily on investigating the influence of LMWOAs on PAHs' intracellular metabolization in terms of aerobic processes, but few are studied in anaerobic processes. Sivaram et al. found that LMWOAs promoted benzo(a)pyrene and pyrene degradation in soil by rhizosphere bacteria under aerobic conditions, and some essential dioxygenase genes (such as nidA, phnAc) were detected in bacteria during the degradation process [39]. Nie et al. pointed out that in aerobic processes, the addition with LMWOAs can perturb intracellular redox homeostasis and oxygenase status in microbe [35].

3. The Application of LMWOAs in PAHs-Contamination Remediation

3.1. In Situ Remediation

In situ remediation is an approach to break down and purify contaminants by activating microorganisms present in the soil. Few studies have been reported about applying the LMWOAs toward in situ remediation of PAH. Through investigating the influence of LMWOAs on the in situ distribution of PAHs adsorption, Li et al. found that LMWOAs lead to the homogeneity of the PAHs in the mangrove sediment but also contribute to the enhancement of the particulate organic matter content [85]. Zhao et al. discovered that combining the nonionic surfactant (e.g., Tween80) with LMWOAs (e.g., citric acid) has improved performance compared to single surfactant in terms of in situ cleaning the PAHs contaminated soils [86]. Moreover, many LMWOAs, including citric acid, oxalic acid, and malic acid, are favorable for directly releasing the PAH-bound residues from soils [44].

3.2. Soil Flushing/Washing

Soil flushing/washing, as an in situ chemical method of soil remediation, involves the extraction of PAHs via a fluid that was injected into the contaminated soil. LMWOAs as additives have been employed to remediate PAHs polluted soils through integrating into the soil flushing/washing technology [42,47,87]. For instance, Jia et al. observed that LMWOAs markedly promoted the release of phenanthrene and pyrene from sediment columns and, therefore, led to bioavailability enhancement (Figure 3). In detail, citric acid showed the best elution strength. With the increase in the concentration of citric acid from 0 to 160 mmol/L, the phenanthrene and pyrene in leachates enhanced from 0.045 and 0.039 mg to 0.125 and 0.087 mg, respectively [42]. Moreover, LMWOAs (e.g., acetic acid, oxalic acid, tartaric acid, and citric acid) promoted phenanthrene desorption in the soil–water system. Falciglia et al. applied citric acid as enhancers to break up calcium carbonate on the surface and thus accelerate the washing step to remove PAHs from seabed sediments [87]. These studies stressed the importance of LMWOAs involved in soil washing technologies to deal with the PAH-contaminated sites [47].

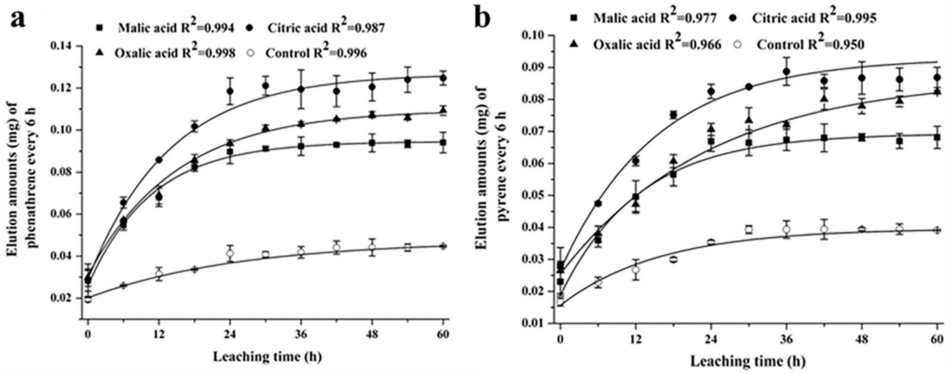

Figure 3. The concentration of (**a**) phenanthrene and (**b**) pyrene in leachate solutions from contaminated sediment (160 mmol/L root exudates). Error bars represent the standard error (SD). (Reproduced from reference [42] with permission from Springer, 2019).

3.3. Others

In addition, LMWOAs have markedly influenced PAHs photolysis. Jia et al. pointed out that oxalic and malic acids favor the phenanthrene photodegradation on the photocatalytic material Fe(III)–smectite [43]. Applying LMWOAs oxalic acid with maize straw biochar also amended the dissipation of PAHs in soil, accompanying enhanced PAH degradation related to genera and functional genes [38,88]. The latter suggested that combining biochar with LMWOAs might be a feasible strategy for promoting PAHs biodegradation.

4. Conclusions and Future Perspectives

In the previous section, we critically discussed the knowledge and challenges of the effects of LMWOAs on the PAHs degradation capability in general and revealed the underlying mechanisms in detail (Figure 1). In brief, the strategy to apply LMWOAs in PAHs bioremediation is a cost-effective and environmentally sustainable approach, which is supported by considerable evidence. To improve LMWOAs' performance and make them more competitive for industrial applications, we believe that more exciting results will be obtained if more efforts are made in the following directions:

(1) More detailed and direct evidence about how humic acids influence the apparent solubility and PAHs-microorganisms interactions are still required to investigate whether all LMWOAs have a similar function with humic acids.

(2) At present, since few research pieces have examined the mechanism of LMWOAs playing in PAHs' intracellular metabolism within the anaerobic process, it is necessary to explore such direction to improve the application of LMWOAs in the actual PAHs pollution treatment process with a better understanding.

(3) Proteomics and metabolomics technologies are potential tools for elucidating PAHs degradation process mechanisms with microbes at the molecular level [89]. High throughput "omics" technologies would help researchers reveal the complicated effect of LMWOAs in detail, from gene expression to whole-cell metabolic pathways.

(4) Advanced genetic tools, especially CRISPR/Cas9, can be employed to modify and optimize the target microbes' PAH degradation capacity. Better microbial remediation strategies are required to be developed by integrating genetically edited microbial cells with optimal LMWOAs.

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