Review

Bioremediation mechanisms of combined pollution of PAHs and heavy metals by bacteria and fungi: A mini review

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H I G H L I G H T S

- Species of bacteria and fungi that dealt with PAHs and heavy metals were reviewed.
- Factors affecting bioremediation of PAHs and heavy metals were discussed.
- Bioremediation mechanisms of PAHs and heavy metals were elucidated.
- Potential research needs for this field were discussed.

A B S T R A C T

In recent years, knowledge in regard to bioremediation of combined pollution of polycyclic aromatic hydrocarbons (PAHs) and heavy metals by bacteria and fungi has been widely developed. This paper reviews the species of bacteria and fungi which can tackle with various types of PAHs and heavy metals entering into environment simultaneously or successively. Microbial activity, pollutants bioavailability and environmental factors (e.g. pH, temperature, low molecular weight organic acids and humic acids) can all affect the bioremediation of PAHs and heavy metals. Moreover, this paper summarizes the remediation mechanisms of PAHs and heavy metals by microbes via elucidating the interaction mechanisms of heavy metals with heavy metals, PAHs/PAHs metabolites with PAHs and PAHs with heavy metals. Based on the above reviews, this paper also discusses the potential research needs for this field.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental pollutants which include benzene rings arranged in linear, angular or cluster ways (Li et al., 2014; Chen et al., 2015). PAHs have teratogenic, carcinogenic, and mutagenic properties and can pose a huge threat to human health through food-chain bioaccumulation (Moscoso et al., 2012). They usually occurred in industrial sites resulted from the incomplete combustion of organic materials such as coal, petroleum and wood. Most of PAHs are recalcitrant in environment owing to the high resistance to nucleophilic attack (Zhang et al., 2006) and the properties of low bioavailability (Cheng et al., 2016). Compared with physical and chemical remediation technologies, bioremediation is considered as feasible remedial technology because it is more effective and less costly, and will not bring other pollutants while degrading PAHs.

Heavy metals together with various pollutants can cause numerous hazards to both human health and environment even at low concentration because of gradual accumulation (Zeng et al., 2013a,b; Zhang et al., 2014; Nouha et al., 2016). Among heavy metals, Cd (II), Cr (VI), Cu (II), Pb (II) and Zn (II) have attracted lots of attention of researchers because they are widely spread in environment, and some of them are necessary to plants in small amount but turn out to be hazardous in slightly larger amount than the required consistence (Zhang et al., 2016). Heavy metals are usually released by industrial operations such as electroplating, steel manufacturing and chemical processing (Chaturvedi et al., 2015; Zhou et al., 2016). Even though heavy metals are indestructible, they will become less toxic to environment either by chelating with chelators via chemical or physical remediation or by shifting the valence by redox reaction (Fan et al., 2008), which is the main mechanism of metal-removing-methods such as phytoremediation and microbial remediation (Wu et al., 2010). Phytoremediation and microbial remediation (bioremediation) are emerging as environmentally friendly and cost-effective technologies (Ma et al., 2016b).

Since PAHs are often occurred together with heavy metals in industrial spots caused by anthropogenic activities such as fossil fuel combustion, automotive emission and waste incineration, the combined pollution of PAHs and heavy metals has caused increasing concerns. A large number of researches highlighted the benefit of bioremediation of the combined pollution (Fig. 1), because it is economical, environmental compatible and of high disposal ability for combined contaminants of organics and inorganics (Zhang et al., 2007; Chen et al., 2014; Ma et al., 2016a). The effect of the co-exposure of PAHs and heavy metals to environment is complicated. Lu et al. (2014) found that the addition of a moderate dosage of pyrene could alter the microbial population and promote the microbial prosperity in soils, thus relieving metal stress and favoring the phytomass yield. While Gauthier et al. (2014) summarized that the more-than-additive deleterious effects of PAHs-metal mixtures to microbes were common in metal-PAHs mixtures. Most of the studies have paid attention to the effect of the combined pollutions. However, mechanisms of interaction effect were still not deeply understood. The objectives of this review are to (1) discuss the factors affecting biodegradation of PAHs and heavy metals; (2) outline the bioremediation mechanisms of PAHs and heavy metals by bacteria and fungi; (3) stimulate further exploration into the co-exposure of PAHs and heavy metals.
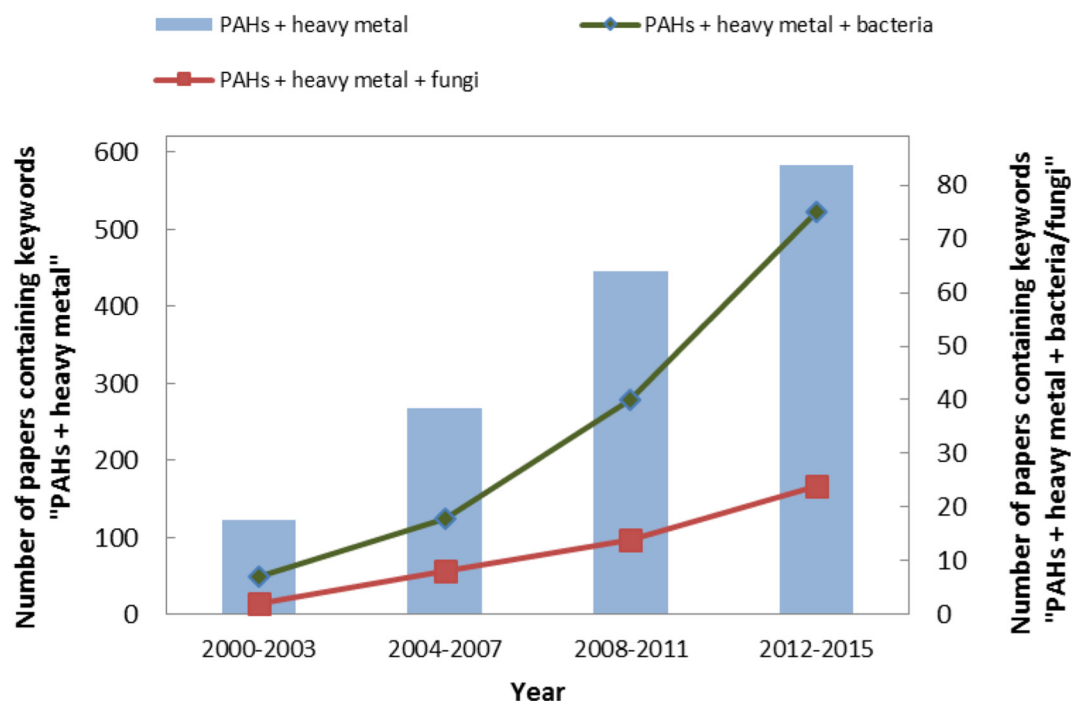

Fig. 1. Variation trend of the number of papers on index journals (according to ISI Web of Science™) containing keywords "PAHs + heavy metal" and "PAHs + heavy metal + bacteria/fungi" from 2000 to 2015.

2. Applications of bacteria and fungi for bioremediation

2.1. Bacteria and fungi

A number of microbes are known to treat co-contaminates of PAHs and heavy metals, including bacteria and fungi species. Most of them are isolated from contaminated sediments or soils. Long-term waste discharge enables microbes to tackle with the combined pollution of PAHs and heavy metals to a considerable extent. Jiang et al. (2015) found that with the addition of *Bacillus thuringiensis* FQ1, the accumulation of Cd increased with 14.29–97.67%, and 95.07% of phenanthrene was removed in the bacteria-fungi treatment with the spike of 500 mg/kg phenanthrene. Summaries of various microbes dealing with PAHs and heavy metals are presented in Table 1. *Bacillus*, *Escherichia* and *Mycobacterium* are the commonly found bacteria for PAHs and heavy metals bioremediation. They can break down PAHs such as anthracene, naphthalene, phenanthrene, pyrene and benzo[a]pyrene in the presence of heavy metals, and can relieve the suppression brought by heavy metals such as Cd, Cu, Cr and Pb occurred together with PAHs. These pollutants can also be remediated by fugal communities, such as *Acremonium*, *Pleurotus* and *Fusarium*. Microbial consortia associated with plants are also effective for the remediation of PAHs and heavy metals (Li et al., 2016). Some techniques such as immobilization (Huang et al., 2015) and compost (Poulsen and Bester, 2010; Tang et al., 2008) can either protect the microbes from heavy metals and PAHs or enhance the activity of microorganisms, thus enhancing the remediation effect.

2.2. Type of contaminants

PAHs such as naphthalene, phenanthrene and pyrene are widely studied in the presence of Cd and Pb, which are the typical represents of heavy metals (Baldrian et al., 2000; Ma et al., 2014; Xiao et al., 2010). Generally, the PAHs which possess more aromatic rings and more complicated molecular structures are tend to be stable in environment due to their high hydrophobicity and low bioavailability. Niederer et al. (1995) found that the concentration of 4-ring pyrene was much higher than those of 2-ring naphthalene and 3-ring phenanthrene in soil samples of Basel (Switzerland). Kuppusamy et al. (2016) figured out that both low molecular weight PAHs (LMW PAHs) (two or three ring groups such as phenanthrene) and high molecular weight PAHs (HMW PAHs) (more than three rings such as pyrene) could be degraded into undetectable levels by bacterial consortia, which showed high biodegradation rate constants. However, the time needs for pyrene degradation was 4 times longer than phenanthrene.

Different kinds of heavy metals showed various toxic effects to microbes and environment because of the bonding degree divergence of potential ligands for each metal ion and the mobility variance of each metal ion (Huang et al., 2008; Feng et al., 2010). Liu et al. (2015) found that both Pb and Cd could affect the degrading ability of *Bacillus* sp. P1 by impacting the content, the component and activities of enzymes during phenanthrene degradation process, but Cd was much more toxic to *Bacillus* sp. P1 than Pb. Wiatrowska et al. (2015) found that the sensitivity of dehydrogenases, phosphatases and urease of soils towards metal ions turned out to be Cd > Pb.

2.3. Factors affecting bioremediation efficiency

2.3.1. Environmental factors

Environmental factors such as pH, temperature, low molecular weight organic acids and humic acids will alter the transformation,

Table 1
Application of bacteria and fungi species tackling with PAHs and heavy metals.

Species	PAHs	Initial concentration	Removal efficiency	Heavy metals	Initial content	Remediation efficiency	Data source	References
Bacteria								
Bacillus thuringiensis FQ1, *Pleurotus cornucopiae*	Phenanthrene	500 mg/kg	95.07%	Cd	5 mg/kg	97.67%	Lab	Jiang et al. (2015)
Pseudomonas	Naphthalene, acenaphthene, fluorene, anthracene, phenanthrene, pyrene, fluoranthene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a, h]anthracene, benzo[ghi]perylene, indeno[1, 2, 3-cd]pyrene	1000 mg/kg	10%–60%	Pb, Cu, Zn, Cd, Cd, Ni, Co, Sn	100 mg/kg	20%–45%	Lab	Gałązka and Gałązka (2015)
Stenotropho monasmaltophilia	Benzo[a]pyrene	1 mg/L	76.9%	Cu	10 mg/L	94%	Lab	Chen et al. (2014)
Achromobacte, Pseudomonas, Enterobacter	Naphthalene	1000 ppm	29%–99.8%	Pb, Cr, Cd	0.1–10 mM	–	Lab	Patel et al. (2012)
Alcaligenesfaecalis, Brevundimonas	Phenanthrene	50 mg/L	90.62%–95.4%	Cd	0.01–0.5 mM	–	Lab	Xiao et al. (2010)
Mycobacterium, Pseudomonas	Naphthalene, pyrene, fluoranthene	2935–28,430 µg/kg	92% naphthalene, 72% pyrene, 52% fluoranthene	Cd, Cu	9.6 µg/kg Cd, 246 µg/kg Cu	–	Lab	Brito et al. (2015)
Fungi								
Acremonium	Naphthalene, fluorene, phenanthrene, anthracene, fluoranthene	25 mg/L	64.9%–96.9%	Mn, Fe, Zn, Cu, Al, Pb	50 mg/L	–	Lab	Ma et al. (2014)
Pleurotusostreatus	Pyrene, benzo[a]anthracene, chrysene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[ghi]perylene	10 ppm	0.5%–52.2%	Cd, Hg	10–500 ppm	–	Lab	Baldrian et al. (2000)
Fusarium flocciferum, Trichoderma, Trametesversicolor, Pleurotus	Benzo[a]anthracene, benzo[a]fluoranthene, benzo[a]pyrene, chrysene, phenanthrene	150–250 mg/kg	21%–93%	Cd, Ni	50–500 mg/kg	–	Lab	Atagana (2009)

transportation, valance state of heavy metal and the bioavailability of PAHs, thus causing complete changes in the toxic manifestations of PAHs and heavy metals towards microbes.

It is generally accepted that pH is a predominant variable in bioremediation efficiency of PAHs and heavy metals. Microorganisms will be affected by pH since the optimal pH for different species is varying. Therefore, PAHs and heavy metals can strongly influence bacteria community structure and enzyme activity by altering pH, oxygen condition and other environmental elements, meanwhile conversely influence the bioremediation of PAHs and heavy metals (Brito et al., 2015). Moreover, pH has impacts on the redox and solubility of heavy metals. Discrepancy valence states and forms of heavy metals pose different toxic effects on microbes, which influence heavy metal remediation efficiency in return. Some in situ microbes are severely inhibited under acidic or alkaline conditions and cannot degrade PAHs or transform heavy metals, but they are more tolerant to extreme conditions and still have the potential to tackle with PAHs and heavy metals in sub-optimal conditions. Therefore, adjusting pH at polluted sites may be a great attempt (Bamforth and Singleton, 2005).

Temperature has a crucial effect on the bioremediation system of PAHs and heavy metals. The solubility of PAHs and heavy metals increases with the rise of temperature, which improves the bioavailability of PAHs and heavy metals (Bandowe et al., 2014). Besides, the activities of microbes increase with the increase of temperature in the appropriate range, because it can enhance the microbial metabolism as well as the enzyme activity, which will accelerate the bioremediation process of PAHs and heavy metals. For example, the magnitude of cumulative O_2 at 43 °C, which is a main index of microbial activity during composting, is remarkably higher than that at 22, 29 and 36 °C (Liang et al., 2003). Additionally, temperature can directly influence the adsorption and desorption process of PAHs and heavy metals on microorganisms or particles. The adsorption capacity and adsorption intensity will increase with the increase of temperature (Chung et al., 2007). The increased adsorption of heavy metals (PAHs) may restrain the adsorption of PAHs (heavy metals) because the adsorption sites on the microorganisms or particles are comparatively unvarying. Interestingly, the co-existing PAHs may promote heavy metals adsorption because both of the pollutants can redistribute between weakly bound and strongly bound fractions (Zhang et al., 2015).

Low molecular weight organic acids and humic acids are widely distributed in soils and ground water, which play notable roles in the bioremediation fate of PAHs and heavy metals. Low molecular weight organic acids and humic acids can affect the migration, transformation and bioavailability of heavy metals by ion exchange, surface adsorption and coordinate complexation (Wu et al., 2003; Qin et al., 2004). Particularly, the functional groups such as phenolic groups, carboxylic groups, quinine groups, amino and sulfhydryl of humic acids can bond with heavy metal ions as heterogeneous ligands (Wang et al., 2009). And electrostatic interactions and other proton competition will affect the binding strength (Benedetti et al., 1995; Wang and Chen, 2009). Low molecular weight organic acids and humic acids can also adsorb PAHs, compete with soil minerals, directly decrease the adsorption or indirectly increase the release of bound PAH residues in soil particles, thus improving the mobility and availability of PAHs, and enhancing the degradation rate of PAHs by microbes (van de Kreeke et al., 2010). Gao et al. (2015) found that with the addition of 10–100 mmol/kg low molecular weight organic acids, the concentration of butanol-extractable ΣPAH and each PAH in soils were 54–75% larger after 40 days compared with control groups without addition of low molecular weight organic acids.

2.3.2. Microbial activity

The species of microbes, screening conditions and genes of organisms can all affect microbial activity. The occurrence of PAHs and heavy metals can impact microbial communities. And new microbial communities are forced to form in order to adapt to the hazardous environment. The strains screened from these contaminated areas usually show high capacity to tackle with the pollution of PAHs and heavy metals. They can be intensified and used as exogenous strains in other contaminated conditions, but the competition with indigenous microorganisms is still noteworthy (Momose et al., 2008). Besides, the DNA located in the strains with high capacity of repairing PAHs and heavy metal pollution, usually contains resistance genes or degradation genes, which can be separated and recombined by genomic approaches for the purpose of enhancing the remediation efficiency (Farmer et al., 2003; Haritash and Kaushik, 2009; Mahmoudi et al., 2011). For example, the ring-hydroxylating dioxygenase (RHDase) coding for the RHDase, and the 1-hydroxyl-2-naphthoate dioxygenase (1H2Nase) genes coding for the 1H2Nase enzymes play important roles in decomposing the intermediates of PAHs, which can be separated from Arthrobacte sp. SA02 and have a high capacity of degrading phenanthrene (Li et al., 2015). This genomic technology improves the remediation possibilities of PAHs and heavy metals by talentless microbes.

2.3.3. Matrix effect

The matrix effect is concentrated on the impact of concentration, structure, solubility and adsorption of PAHs and heavy metals on their bioavailability. Surfactants are widely used in PAHs and heavy metals restoration. Li et al. (2015) found out that the addition of sodium dodecyl benzenesulfonate (SDBS) could increase the Δ9 fatty acid desaturase level, which would increase the content of unsaturated fatty acid, augment membrane fluidity and promote the transmembrane transport. The surfactants could also enhance cell surface hydrophobicity and intracellular degradation of microbes for PAHs by upregulating other genes such as RHDase and 1H2Nase. Surfactants, especially biosurfactants, have been proposed for the remediation of heavy metals in recent years because they can act as metal complexing agents. Luna et al. (2016) observed that the biosurfactants produced by Candida sphaerica could remove 95%, 90% and 79% of Fe, Zn and Pb, respectively. Surfactants can form complexes with metal ions, and directly contact with sorbed heavy metals before detachment from the soil. They reduce surface properties by lowering interfacial tension and fluid forces, undermining the adhesion between metal and soils (Hu et al., 2011), lifting the metal from soils and enhancing the complexation of metal with surfactants (Mulligan et al., 1999).

3. Bioremediation mechanisms of combined pollution

The bioremediation of PAHs and heavy metals can be affected by each kind of contaminants or the interaction of these two kinds of pollutants. This section focuses on the interaction mechanisms of heavy metals to heavy metals, PAHs/PAHs metabolites to PAHs and PAHs to heavy metals, thus elucidating the bioremediation mechanisms of PAHs and heavy metals by microbes, which are exhibited in Fig. 2.

3.1. Heavy metal-heavy metal

Some heavy metals are fundamental for the biological processes of the microbes (e.g. Cu and Zn), whereas others bringing no biological benefit but only inducing oxidative damages, denaturing organisms and weakening the bioremediation ability of microbes to heavy metals (e.g. Cr and Cd). All metals become toxic when

they present in excess concentration. The redundant of concentrations of trace metals will pose deleterious effect to microbes (Xu et al., 2012). Heavy metals will alter the physiological and biochemical properties of microbes, even when organisms are associated with plant roots. Besides, the co-existing heavy metals will impact on each other or organisms' habitats. For example, Manzano et al. (2014) found that the treatment with Fe^{2+} could decrease extractable As, but enhanced the extractable Cu, Mn and Zn concentrations in soil obtained from an arsenopyrite mine, which still did harm to some soil enzymatic activities.

Heavy metals can pose deleterious effect to microorganisms through several key mechanisms, i.e., reacting as redox catalysts in the production of reactive oxygen species (ROS), breaking fatal enzymatic functions, destructing ion regulation, and directly affecting the formation of DNA and protein adducts (Hildebrandt et al., 2007; Gauthier et al., 2014). Heavy metals such as Cu(I) and Cu(II) can catalyze the production of ROS through the Fenton and Haber-Weis reactions, acting as soluble electron carries to donate or accept electrons, which lead to severe injury to cytoplasmic molecules, DNA, lipids, and other proteins (Osman and Cavet, 2008; Giner-Lamia et al., 2014). Besides, heavy metals can break vital enzymatic functions by competitive or non-competitive interactions with substrates, which will cause configurational changes in enzymes, alter enzyme gene expression, and form ROS which could lead to enzyme oxidation by generating carbonyl (Gauthier et al., 2014). Heavy metals can also cause ion imbalance by adhering to the cell surface, and entering into cells via ion channels, or transmembrane carriers, or self-defusion (Chen et al., 2014). Furthermore, heavy metals can directly cause DNA damage or affect enzyme formation. Booth et al. (2015) demonstrated that Al could stabilize superoxide radicals, which was responsible for DNA damage. Moreover, the *P. pseudoalcaligenes* KF707 used in this research possessed a phosphoglycolic acid phosphatase, and no genes encoding for any subunits of glycolate oxidase were found based on a BLAST (basic local alignment search tool) search. The glycolic acid was only generated from oxidative DNA damage, which indicated that oxidative stress caused DNA damage because of Al.

Heavy metals will in return stimulate the antioxidant defensive system of microbes to facilitate the efflux of heavy metals and reduce their presence within cells (Williams and Silver, 1984; Ehrlich, 1997; Zeng et al., 2012). For example, siderophores such as desferrioxamine E (DFOE), desferrioxamine B (DFOB) and coelichelin (Cch), which are commonly used for Fe transportation and have the capability to chelate heavy metals such as Cd^{2+}, may be responsible for maintaining metal homeostasis (Złoch et al., 2016). Dimkpa et al. (2008) demonstrated that siderophores significantly up-regulated when Cd^{2+} was added and the accumulation of Cd^{2+} in the cells was decreased, which indicated that bacteria could sequestrate toxic metals by influencing their diffusion through porins and accelerating their transportation out of bacterial cells (Saha et al., 2013). Besides, metallothionein (MT), a thiol-containing, cysteine-rich protein, induced by heavy metals and served to transport and reduce toxic metals, is of great help in the sequestration of metal ions. Thiol groups of cysteine residues in metallothionein can bind Cd^{2+} to form metal-thiolate complexes, thus rendering Cd unavailable to exert toxicity (Khan et al., 2015).

Microbes still have other detoxification methods such as glutathione (GSH) system, except for the facilitating efflux of heavy metals. GSH system contains GSH, glutathione S-transferase (GST), oxidized glutathione (GSSG) and glutathione reductase (GR). The detoxification mechanism is shown in Fig. 3 according to some researches (Wang and Wang, 2010; Barmo et al., 2011; Won et al., 2011; Cirillo et al., 2012).

3.2. PAHs/PAHs metabolites-PAHs

PAHs or PAHs metabolites can impact the degradation of PAHs. For example, co-metabolism enables microbes utilize poorly available PAHs in the presence of some easily available ones as carbon
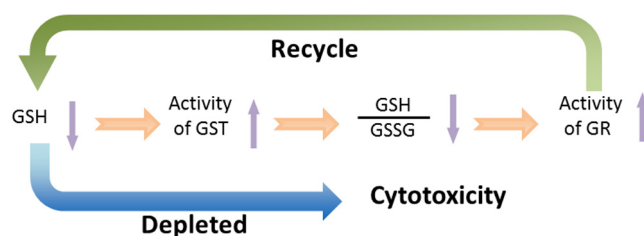
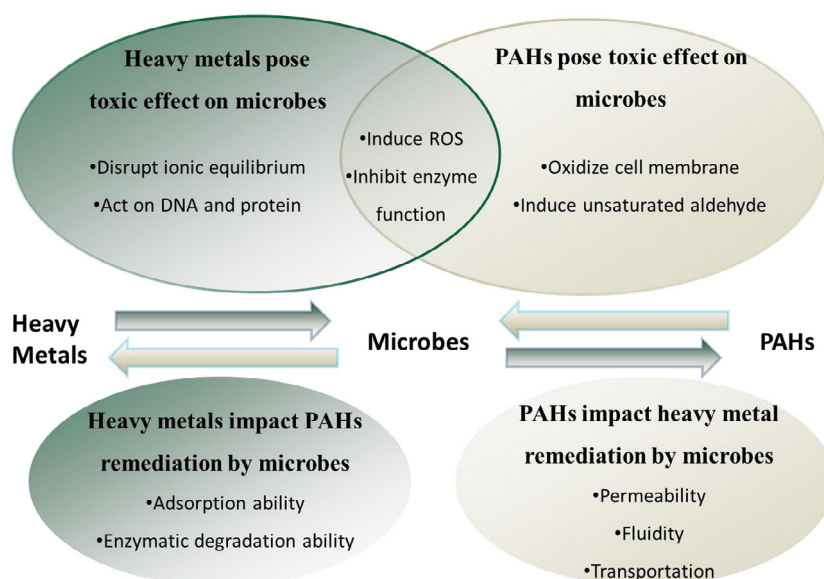**Fig. 3.** Detoxification mechanism of GSH system.

Fig. 2. Interaction mechanism of PAHs and heavy metals with bacteria and fungi.

and energy source. Zhang et al. (2013) found out that anthracene, fluoranthene and pyrene could not be degraded by *Micrococcus* sp. PHE3 as sole carbon and energy source, but with the addition of naphthalene and phenanthrene, all of them could be degraded with the degradation rates of more than 90% over ten month incubation. Monoculture replaced by co-culture can entail poorly available pollutants consumed by microbes due to the key enzymes induced by easily available pollutants. With these enzymes, strains can convert poorly available ones (Gupta et al., 2015).

The intermediates of PAHs can also have an effect on the degradation of PAHs. Wen et al. (2011) indicated that the accumulation of metabolites such as phthalic acid and salicylic acid restrained pyrene degradation, and the degradation efficiency was lower than that without co-substrates by 6.69% and 2.42%, respectively. The intermediates may be unsuitable or the concentrations are too high for the growth of microbes and pose a toxic effect on microbes, thus suppressing the PAHs degradation. With an appropriate concentration of the metabolites, the degradation of PAHs may be enhanced (Meng et al., 2014).

3.3. PAHs-heavy metals

The combined effects of PAHs and heavy metals on bacteria or fungi in environment are much more complex than the separate exposures. The remediation of PAHs can be challenging in the presence of heavy metal because heavy metal can adversely compromise microbial activities by affecting ATP production, C-mineralization, community shift and enzymatic function (Biswas et al., 2015). Whilst PAHs may be metabolized by the cytochrome P450 to generate ROS, rendering the decrease of microbial activity and the capability of tackling with heavy metals (Kuang et al., 2013). Besides, the intermediates of PAHs such as salicylic acid can also impact the microbial cell metabolism, thus affecting the adsorption capacity of heavy metals (Gong et al., 2009; Guo et al., 2015). Additionally, long-term contaminants of PAHs and heavy metals can alter the indigenous microbial communities by bringing about certain compression but leave others intact (Thavamani et al., 2012).

3.3.1. Influence of heavy metals on PAHs biodegradation

Heavy metals can affect PAHs degradation by (a) changing the surface properties of microbes and (b) interfering with enzymes of microbes.

Heavy metal can affect the adsorption of PAHs by microbes via changing the surface properties of microbes (Fig. 4), especially for microbes which have a lagre surface area. With the addition of heavy metals ions, the negatively charged microbes are tend to attract metal cations (Yan and Viraraghavan, 2003). This can be attribute to that the electrostatic attraction between the surface of microbes and heavy metal ions are much stronger than the van der walls interaction between the surface and PAHs (Zouboulis et al., 2004). So firstly, heavy metals occupy adsorption areas of PAHs on the surface of microbes. As an increase of metal cation concentrate on the surface, microbes are gradually neutralized. Then the surfaces become less hydrophilic, which promotes PAHs adsorption (Weissenfels et al., 1992; Al-Turki, 2009). In addition, PAHs are inclined to be attracted on the aggregation heavy metals because of the cation-π interaction, which also facilitates PAHs adsorption by microbes (Zhu et al., 2004; Zhang et al., 2011).

Heavy metals stress will cause oxidation process by ROS, which will impair membrane and stimulate the development of antioxidant enzymatic defense system produced by the microbes in response to the attack of ROS (Ke et al., 2010). Moreover, heavy metals exert a cytostatic effect on microorganisms, which can be attributed to that the motor function of the cytoskeletons is hindered and this prevention may consequently retard cytokinesis (Su et al., 2009). Furthermore, heavy metals can disturb the cell homeostasis by penetrating through the cell wall and oxidizing the surface proteins on membrane (Wang and Chen, 2009; Gauthier et al., 2014). Since PAHs will exhibit a narcotic effect to the lipophilic compound, which may affect the perviousness and configuration of microbes, heavy metals may permeate into microbial cells more facily and influence their functions (Shen et al., 2005; Michalec et al., 2016).

Enzymes generated by microbes will catalyze the PAHs degradation due to the formulation of enzyme-substrate complexes (Fig. 5). It is possible that some species of low concentration heavy metals will enhance the PAHs enzymatic degradation due to the formulation of enzyme-metal-substrate complexes. These heavy metals may work as cofactors of proteins and are in charge of proteins' biological activities. Nevertheless, excessive heavy metals will compete with macronutrient (e.g. Mg^{2+}, Ca^{2+}), which are extensively existed in environment and are generally used for enzyme-metal-substrate complexes (Karaca et al., 2010). Heavy metals are considered deleterious because they can mask as catalytically active groups or denature protein structures, thus
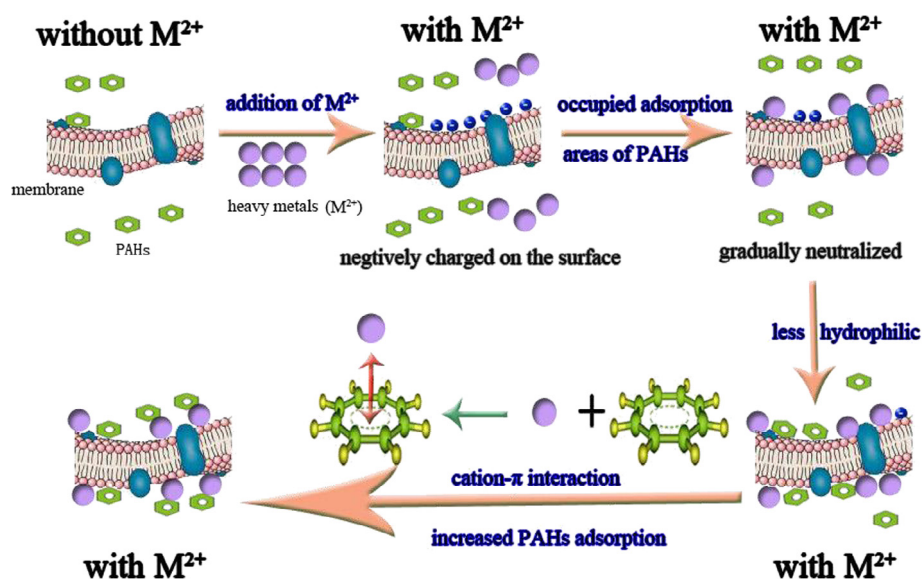

Fig. 4. Mechanism of heavy metals enhancing PAHs adsorption by microbes.
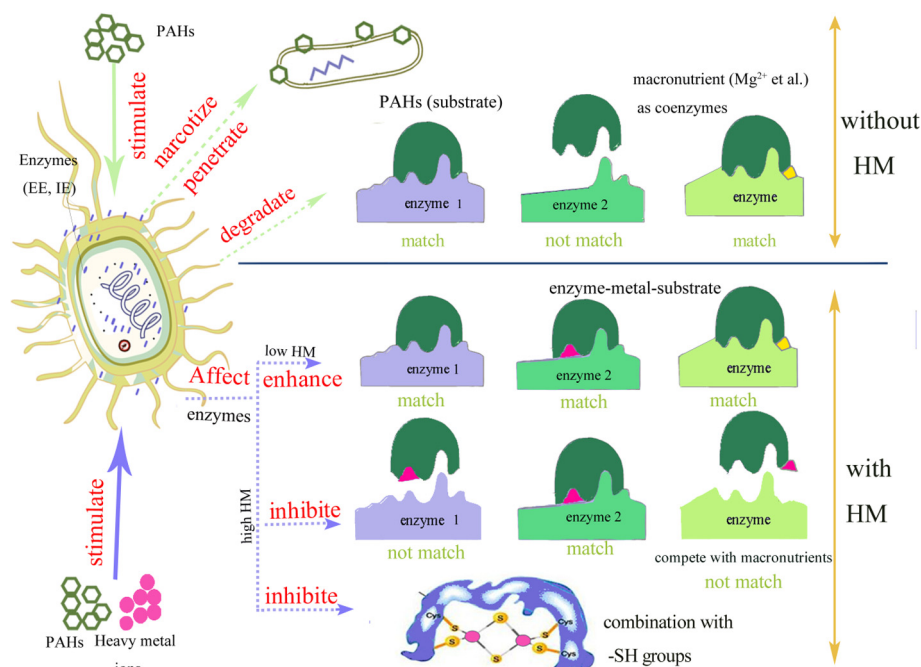
Fig. 5. Mechanism of heavy metals affecting PAHs enzymatic degradation process (Liu et al., 2015).

inhibiting the activities of enzymes or proteins. Additionally, they can also associate with sulfhydryl groups of proteins and pose a noxious effect on proteins or enzymes (Guo et al., 2010).

3.3.2. Influence of PAHs on heavy metal bioremediation

Bioadsorption is the most effective and common pattern for microbes to tackle with heavy metals. When PAHs pose a deleterious effect on microbial membranes, it can alter the transport of heavy metals on the biomembrane. PAHs may narcotize microbes and interact with lipophilic components of biomembranes, thus altering permeability of biomembranes and enabling heavy metals penetrate easily into microbial cells (Shen et al., 2006). Hence, the toxic effects of pollutants to microbes are magnified and the remediation effects of heavy metals by microbes are therefore diminished. Besides, PAHs can alter membrane fluidity and change the electrical potential, thus inhibiting the adsorption of heavy metals by microbes (Gorria et al., 2006). Additionally, membrane enzymes impacted by PAHs can cause ionoregulation disruption, which will decrease the metal-ATPase activity, thus influencing the transportation of heavy metals (Gauthier et al., 2015).

4. Future perspectives

The present approaches for bioremediation of PAHs and heavy metals still have potential needs for future research.

(1) Screened bacteria and fungi which are highly-efficient for PAHs and heavy metals bioremediation will compete with aborigines organisms and weaken the ability of reducing pollution. Thus, finding out an appropriate way to increase the competitiveness and aggrandize activity of the screened strains in reality is very essential.
(2) The bioavailability of pollutants influences the utilization for microorganisms. Using suitable methods to enlarge the bioavailability may increase the remediation effect.
(3) The deleterious effect that the pollutants pose on bacteria and fungi severely damaged the cells' structure and function, which in turns affect the remediation efficiency. Microbial

detoxification mechanisms as well as the retarding methods of biotoxicity caused by the pollutants still need further research especially for bacteria.
(4) There are some other methods or substances valid for the remediation of PAHs and heavy metals. It will be promising to enhance the remediation efficiency by combing biremediation with other means or materials.
(5) The function of enzymes secreted by microbes still needs further annotation since enzymes are very vital in the remediation of PAHs and heavy metals.

5. Conclusions

Overall, this paper reviews species of the microbes and pollutants, summarizes factors affecting the bioremediation efficiency and elucidates the remediation mechanisms of the combined pollutants by bacteria and fungi by elaborating the interaction mechanisms of heavy metals to heavy metals, PAHs/PAHs metabolites to PAHs and PAHs to heavy metals. In order to promote bioremediation efficiency of PAHs and heavy metals, future studies should concentrate on improving bioavailability of pollutants, enhancing competitiveness of dominant strains and exploring novel technologies to increase detoxification of microbes.

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