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Insights into biofilm carriers for biological wastewater treatment processes: Current state-of-the-art, challenges, and opportunities

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Abstract

Biofilm carriers play an important role in attached growth systems for wastewater treatment. This study summarizes the traditional and novel biofilm carriers utilized in biofilm-based wastewater treatment technology. The advantages and disadvantages of traditional biofilm carriers are evaluated and discussed in light of basic property, biocompatibility and applicability. The characteristics, applications performance, and mechanism of novel carriers (including slow-release carriers, hydrophilic/electrophilic modified carriers, magnetic carriers and redox mediator carriers) in wastewater biological treatment were deeply discussed. Slow release biofilm carriers are used to provide a solid substrate and electron donor for the growth of microorganisms and denitrification for anoxic and/or anaerobic bioreactors. Carriers with hydrophilic/electrophilic modified surface are applied for promoting biofilm formation. Magnetic materials-based carriers are employed to shorten the start-up time of bioreactor. Biofilm carriers acting as redox mediators are used to accelerate biotransformation of recalcitrant pollutants in industrial wastewater.

Key words: Biofilm carrier; biofilm reactors; hydrophilic/electrophilic modified carriers; magnetic biofilm carrier; redox mediator carrier.

1. Introduction

Wastewater treatment plants are designed to eliminate both chemical and microbial pollutants from municipal/industrial wastewater (Tran et al., 2015). Biological wastewater treatment process is still the most widely used method to remove organic pollutants and nutrients due to its cost effectiveness and high treatment efficiency (Kikuchi and Tanaka, 2012; Zhang et al., 2015; Xu et al., 2018). Until now, wastewater treatment systems based on suspended growth, such as conventional activated sludge (CAS), are frequently employed to treat municipal and industrial wastewater (Radjenovic et al., 2009; Tran and Gin, 2017; Tran et al., 2018). However, the use of CAS for wastewater reclamation usually shows drawbacks, such as high sludge production and low removal efficiency for many organic and inorganic pollutants, especially in terms of recalcitrant contaminants (Petrovic et al., 2009; Tran and Gin, 2017).

To overcome the challenges of CAS systems, the use of membrane bioreactors (MBRs) has been deemed as a promising treatment technology to reduce microbial and chemical pollutants in wastewater due to its high removal efficiencies, especially for suspended solids, nutrients, fecal coliforms, pathogens, and organic micropollutants (Kimura et al., 2005; Petrovic et al., 2009; Luo et al., 2014c; Le et al., 2018). However, a major drawback of MBRs is membrane fouling, which directly affects membrane performance (i.e., permeability). In recent years, the use of biofilm systems, such as fixed bed biofilm reactors (FBBRs) or moving bed biofilm reactors (MBBRs), has emerged as promising alternative to eliminate nutrients and organic micropollutants, such as pharmaceuticals and personal care products (Kunkel and Radke, 2008; Ilse Forrez, 2009; Guo et al., 2010; Casas et al., 2015; Deng et al., 2016b). Generally, biofilm-based wastewater treatment systems have several advantages over conventional activated sludge processes, such as their high active biomass concentration, low space requirements, reduced hydraulic retention time, more stable performance and low sludge production. Especially, microbial communities in biofilms tend to be more diverse than those in activated sludge system, which allow degrading a wide range of organic pollutants, such as pharmaceuticals and personal care products (Table 1). Indeed, Ilse Forrez (2009) found that the removal of the synthetic estrogen 17α-ethinylestradiol (EE2) by aerated nitrifying fixed bed reactor was more than 96%, which seemed to better than that by activated sludge process (Urase et al., 2005). Similarly, other studies also claimed that MBBRs showed similar or even better removal efficiency for a large number of organic micropollutants (Falås et al., 2012; Hapeshi et al., 2013; Casas et al., 2015; Tang et al., 2017). However, it was found that there were variations in the removal efficiencies of micropollutants between biofilm systems (Falås et al., 2012; Hapeshi et al., 2013; Casas et al., 2015; Tang et al., 2017). One of the factors affecting the fluctuation in removal efficiencies is assumed to be due to the difference in carriers employed in those biofilm reactors.

Till now, it is widely accepted that performance of biofilm systems seem to largely depend upon biofilm formation. The biofilm formation is known as a function of biotic and abiotic factors, including (i) diversity of microbial community; (ii) physical properties of carrier surfaces, which are related to electrostatic interactions and surface energy on bacterial adhesion to surfaces of carriers; (iii) topographic properties of carrier surfaces (surface roughness); (iv) chemical properties of carrier surfaces (i.e. desired functional groups); and (v) environmental factors, i.e. pH and temperature (Renner and Weibel 2011). Of these factors, physical/chemical properties of surfaces, surface roughness, pore structure, specific area, and material types of carriers play a decisive in biofilm formation (Guo et al., 2010; Huang et al., 2011; Müller-Renno et al., 2013; Tarjányi-Szikora et al., 2013; Ahmad et al., 2017). For example, it was reported that traditional carriers based on inorganic materials often exhibited their poor permeability, large flow resistance, and slow biofilm formation compared to modified carriers, e.g., light porous ceramic carriers or surface-modified zeolites (Zhang et al., 2010; Li et al., 2013; Wang et al., 2016; Reeve and Fallowfield, 2018). Similarly, other studies found that organic material-based carriers appeared to be better for the biofilm formation; especially those carriers could also serve as electron donor for microbes in promoting their growth (Feng et al., 2015b; Feng et al., 2017; Reyes-Alvarado et al., 2018). In recent studies, hydrophilicity and electronegativity of carrier surface are assumed to play a significant role in the biofilm formation and treatment efficiency (Chu et al., 2014; Deng et al., 2016b; Mao et al., 2017). Hitherto, the knowledge on the removal efficiency of pollutants by biofilm-based systems has been well documented. However, very little information about carriers is reviewed. Therefore, the objective of this review was to systematic summarize current knowledge on different biofilm carriers, e.g. inorganic/organic materials-based biofilm carriers, biofilm carriers with hydrophilic/electrophilic modified surface, biofilm carriers with magnetic property, and biofilm carriers as redox mediators. In this review, the performance of both traditional and novel carriers was evaluated in terms of biofilm formation and treatment efficiency.

2. Traditional biofilm carriers

Based on the nature of materials, traditional carriers in biological wastewater treatment can be categorized into three groups: inorganic, inert organic and reactive organic materials-based carriers.

2.1. Inorganic materials-based microbial carriers

Inorganic materials such as zeolite, volcanic rock, ceramics, and activated carbon are often used as biofilm carriers in biological wastewater treatment processes (Lameiras et al., 2008; Dong et al., 2011; El-Shafai and Zahid, 2013; Zhang et al., 2017a; Zhang et al., 2017b). For example, El-Shafai and Zahid (2013) used local scoria (i.e. volcanic rock) as microbial carrier in aerated submerged biofilm reactor to treat nitrogen and carbon in municipal wastewater. In another study, Dong et al. (2011) used ceramics as carriers in moving bed biofilm reactor (MBBR) to treat oilfield wastewater. In general, inorganic materials-based biofilm carriers are found to be omnipresent and exhibit excellent mechanical strength. These carriers also possess stable chemical properties (Wang et al., 2016). In addition, inorganic materials-based carriers tend to have a large specific surface area (Müller-Renno et al., 2013; Wang et al., 2016). For example, the specific surface areas of ceramsite and zeolites often vary from 500 to 1200 m^2/m^3 and from 300 to 1000 m^2/m^3, respectively (Zhang et al., 2016b; Ahmad et al., 2017). Moreover, the rough surface and wide pore structure of inorganic materials-based carriers allow protecting microorganisms from shock loads, meanwhile also provide an excellent environment for biofilm attachment (Zhang et al., 2010). To date, it has been reported that inorganic materials-based biofilm carriers appear to be effective in treatment of nutrients and organic pollutants (Lameiras et al., 2008; Dong et al., 2011; El-Shafai and Zahid, 2013; Zhang et al., 2016b; Ahmad et al., 2017).

Among inorganic materials-based biofilm carriers, zeolite has been frequently used to eliminate ammonia-nitrogen containing wastewater/water since this carrier shows high selectivity to NH_4^+ (Eldyasti et al., 2012; Tarjányi-Szikora et al., 2013), since natural zeolites have extremely negative charge surface. In earlier studies, it was observed that the adsorptive removal efficiencies of NH_4-N in water were greater than 90% or even up to 99% using zeolite as carriers (Foglar and Gašparac, 2013; Huang et al., 2013). Zeolite was proven to have better adsorptive removal efficiency than other inorganic carriers (i.e. ceramics and activated carbon) for nitrogen containing wastewater (Chang et al., 2009; Huang et al., 2011). For example, Huang et al. (2011) found that removal efficiency of nitrogen by zeolite-based carriers could be 89.6%, while it was only 65.1 and 35.6% by ceramsite and light porous media, respectively. Higher removal of ammonium-nitrogen observed in zeolite-based carriers compared to other inorganic materials-based carriers (i.e. ceramsite and light porous media) could be attributed to the ion-exchange property of zeolite allowing removing ammonium-nitrogen via adsorption mechanism (Hedström, 2001).

In an earlier study, Chang et al. (2009) reported that nitrification rate in granular activated carbon based biofilm reactor tended to be significantly lower than that of zeolite-based biofilm reactor by a factor of 2. In a recent study, however, Zhang et al (2016b) claimed that COD removal efficiency by ceremsite-based biofilm carriers seemed to be far superior to zeolite-based biofilm carriers. Indeed, ceramsite shows more advantages over zeolite in promoting the growth of nitrifying bacteria.

Inorganic materials-based carriers, such as zeolite and activated carbon, exhibit good sorption properties. As such, these carriers are often used to remove heavy metals in wastewater treatment, but removal efficiencies of heavy metals by these carriers seem to be relatively low. For example, Lameiras et al. (2008) observed that removal efficiencies of Cr(VI) by granular activated carbon/zeolite were less than 20%.

Apart from the aforementioned advantages, inorganic materials-based biofilm carriers also have some disadvantages related to slow biofilm formation, poor permeability, large flow resistance, and easy clogging (Inam et al., 2011; Misaelides, 2011; Kvetková et al., 2012; Zhang et al., 2016b). To tackle these drawbacks, numerous studies were conducted to modify inorganic materials to have desired characteristics, such as reticulated porous ceramics (Wang et al., 2016), light porous ceramic carriers (Zhang et al., 2010), or surface-modified zeolites (Li et al., 2013; Reeve and Fallowfield, 2018).

2.2. Organic materials-based microbial carriers

To date, organic materials-based carriers are widely used as microbial carriers in wastewater treatment (Zhang et al., 2008; Xiao and Chu, 2014; Zhu et al., 2015). For example, Zhang et al. (2008) used polyvinyl alcohol (PVA)-gel beads as a biomass carrier in UASB reactor to enhance the removal of organic nutrients in wastewater. Zhu et al. (2015) used polybutylene succinate as carbon source and biofilm carrier to increase biological denitrification in recirculating aquaculture system. Organic materials-based microbial carriers can be categorized into two types: (i) reactive organic materials-based carriers and (ii) inert organic materials-based carriers.

2.2.1. Reactive organic materials-based biofilm carriers

For reactive organic materials-based carriers, such as alginate and bamboo fiber (Behera et al., 2010; Xiao and Chu, 2014; Liu et al., 2017), they have good biocompatibility and hydrophilicity, meanwhile these materials such as bamboo are relatively cheap for practical application (Xiao and Chu, 2014; Yang et al., 2015). In a recent study, Yang et al. (2015) evaluated the suitability of agriculture wastes (i.e. corncob, peanut shell, retinervus luffae fructus, wheat straw, cotton stalk, rice straw, rice husk and reed) as solid carbon sources and biofilm carriers in membrane bioreactor (MBR) and found that retinervus luffae fructus, corncob and rice straw were suitable materials to use as biofilm carriers, especially was demonstrated to be most effective in enhancing denitrification and controlling the effluent COD.

In general, the surface structure of natural organic materials-based carriers facilitates to adhere to microorganisms, especially this type of biofilm carriers is not toxic to cells and easy to handles after use, and do not cause environmental pollution (Fan et al., 2012; Yang et al., 2015). In addition to role acting as biofilm carriers, natural organic materials-based biofilm carriers are known to be a solid carbon source to promote the growth of microorganisms or serve as an electron donor for biological denitrification in wastewater treatment (Feng et al., 2015b; Yang et al., 2015; Feng et al., 2017; Liu et al., 2017; Reyes-Alvarado et al., 2018). For example, Li et al. (2012) and Yang et al. (2015) found that denitrification and removal efficiency of total nitrogen increased by 20–40% when agricultural waste was used as solid carbon source and biofilm carrier in the MBR system.

However, natural organic materials-based biofilm carriers often exhibit low mechanical strength, poor mass transfer performance and rapid degradation by microorganisms. For these reasons, the reuse of these biofilm carriers is relatively limited. In addition, the unstable release of soluble carbon source for denitrification during wastewater treatment is considered as another drawback of this type of carriers (Zhao et al., 2017).

2.2.2. Inert organic materials-based biofilm carriers

Aforementioned, reactive organic materials-based biofilm carriers have several drawbacks. As such, their application in wastewater treatment seems to be considerably limited. In recent decades, numerous efforts have been made to develop inert organic materials for biofilm carriers, e.g., polyethylene (Chen et al., 2012; Shore et al., 2012; Tang et al., 2017; Ooi et al., 2018), polyester (Guo et al., 2010; Lim et al., 2011), polyolefin (Makarevich et al., 2000) and other materials (Müller-Renno et al., 2013), which are expected to overcome the limitation of reactive organic materials to be used as biofilm carriers. For example, Sato et al. (2004) reported that high nitrification efficiency (>90%) in wastewater was observed by using polyurethane (PU) as porous hydrogel carrier for microorganisms in wastewater treatment. Shore et al. (2012) also observed that removal efficiency of NH_4-N in wastewater was about 90% by MBBR using high-density PE as biofilm carrier. In recent years, commercial carriers made from durable high-density PE (i.e. AnoxKaldnes™K5 or AnoxKaldnes™ BAS™) have widely used in MMBR systems to enhance the removal of both common macropollutants and organic micropollutants in wastewater (Ooi et al., 2017; Tang et al., 2017; Torresi et al., 2017; Ooi et al., 2018; Tang et al., 2019).

Normally, inert organic materials-based biofilm carriers (e.g. polypropylene, polyethylene, polystyrene, and polyurethane) are known to have low density, stability, resistance to biodegradation and aging, and strong mechanical strength, but their large specific surface area is still limited (460–900 m^2/m^3) (Quan et al., 2015; Deng et al., 2016b). However, in recent efforts, it is reported that polyurethane sponge (PUS)-based biofilm carriers with high porosity (98%) and specific surface area up to 3000 m^2/m^3 are considered as an ideal one for the formation of biofilm (Chu and Wang, 2011; Feng et al., 2012; Chu et al., 2014; Zhang et al., 2017c; Nguyen et al., 2019; Song et al., 2019). For instance, Chu and Wang (2011) revealed that removal efficiencies of TOC and NH_4-N in wastewater by MBBR with PUS-based biofilm carriers were better than poly-ε-caprolactone-based biofilm carriers. This might be due to the better biofilm formation onto PUS compared to that of poly-ε-caprolactone (PCL). In addition, they also found that a large number of microorganisms were trapped into the pores of PUS-based carriers (Chu and Wang, 2011; Zhang et al., 2016a). Especially, biomass found in PUS-based biofilm carrier was much higher than that in PCL based biofilm carriers (Chu and Wang, 2011). Recently, PUS-based carriers are widely used in MBBR system to improve the elimination of nutrients as well as organic micropollutants (Luo et al., 2014b; Deng et al., 2016a; Zhang et al., 2016a; Zhang et al., 2017c; Song et al., 2019)

Regarding the bio-affinity of biofilm carriers, inert organic materials-based biofilm carriers, such as polypropylene (PP), polyethylene (PE), polystyrene (PS), and polyvinyl chloride (PVC) are known to have the lower bio-affinity and hydrophilicity. This is considered as one of the drawbacks of these materials in the use as biofilm carriers. In light of water contact angle, it has been revealed that water contact angles of biofilm carriers based on polyurethane (PU), pure polypropylene (PPP), polyethylene (PE), and high-density polyethylene carrier (HDPE) were 90, 88.7, 92/77 and 94.3°, respectively (Chen et al., 2012; Chu et al., 2014; Liu et al., 2018; Mao et al., 2017; Zhu, 2017). It is noteworthy that the measurement of the water contact angle is widely used as a method to evaluate the hydrophilic surface of materials. For example, materials with contact angle <90° exhibit their hydrophilic surface. In contrast, the materials with water contact angle >90° indicate their hydrophobic surface (Cerca et al., 2005; Liu and Zhao, 2005; Chu et al., 2014; Feng et al., 2015a). Nguyen et al. (2016) also reported that water contact angles of PE, PP, PVC, polyvinylidene fluoride (PVDF), polyethylene terephthalate (PET) and polytetrafluoroethylene (PTFE) seemed to be related to their hydrophobicity. For example, PTFE has the lowest total surface free energy and the most hydrophobic surface with a high water contact angle of 116°. In contrast, PVC possessed the highest surface free energy and was the most hydrophilic surface with a relatively lower water contact angle (72°). In general, the water contact angle of inert organic materials-based biofilm carriers are higher than that of microorganisms (<60°)(Cerca et al., 2005; Nguyen et al., 2016). For this reason, these inert organic materials-based carriers may be not good for biofilm formation (Chavant et al., 2002; Cerca et al., 2005; Müller-Renno et al., 2013; Mao et al., 2017). Chavant et al. (2002) reported that the formation of biofilm was faster on the hydrophilic surface of stainless steel than that on hydrophobic surface of PTFE. Other studies also suggest that highly hydrophic surfaces (i.e. water contact angles >90°) appear to have lower microbial attachment and biofouling (Feng et al., 2015a; Yuan et al., 2017b).

Taken together, traditional organic materials-based biofilm carriers exhibit several drawbacks related to biofilm formation and removal efficiency of pollutants. For these reasons, many efforts have been made to develop novel biofilm carriers with superior functions including: (i) slowly releasing nutrients (i.e. carbon source) to promote microbial growth, (ii) enhanced hydrophilicity/electrophilicity to improve microbial adhesion; (iii) increased electron transfer rate to boost removal performance, or (iv) promoted cell metabolism with magnetism. This is discussed in more detail in the following sections.

3. Novel biofilm carriers

3.1. Slow release carriers

Slow release carriers known as controlled release carriers are often used to stably provide nutrient sources/electron donors at a specific rate during a specific period of time (Davidson and Gu, 2012; Yusoff et al., 2016; Maincent and Williams, 2018). To date, slow release carriers are widely utilized in the fields of medicine, food and agriculture (Davidson and Gu, 2012; Yusoff et al., 2016; Maincent and Williams, 2018). In the field of wastewater treatment, slow release carriers have increasingly gained attention due to its superior functions compared to other traditional biofilm carriers (Magalhães et al., 2007; Wu et al., 2012; Luo et al., 2014a; Yang et al., 2015; Liu et al., 2018a; Reyes-Alvarado et al., 2018; Zhang et al., 2018a). For example, in an earlier study, Madalhaes et al. (2007) prepared slow release carriers by adding bioavailable substances, such as trace elements and biodegradable compounds to biofilm carriers. Luo et al. (2014a) found that polybutylene succinate [PBS] were suitable as biofilm carrier and the carbon source for denitrification, especially the use of PBS as the carbon source allowed reducing the cost of denitrification.

In a recent study, Liu et al. (2018a) also revealed that the use of polybutylene succinate/bamboo powder (PBS/BP) as a biofilm carrier and solid carbon source helped to enhance denitrification and reduce startup time in reactors for nitrate removal in wastewater. In another study, Reyes-Alvarado et al. (2018) suggested that lignocellulosic materials from natural scourer and cork were suitable as both biofilm carrier and slow release electron donors (SRED) for biological sulfate reduction during wastewater treatment.

Generally speaking, a slow release carrier should play at least two roles as a biofilm carrier and the solid-phase carbon source/electron donor, depending on the purpose of application. Until now, insoluble biodegradable polymers (BDPs) such as polycaprolactone [PCL], polyacetic acid [PLA], poly(3-hydroxybutyrate-co-3-hydroxyvalerate) [PHBV], and polybutylene succinate [PBS] are widely used as the solid-phase carbon source in slow release carriers (Khan et al., 2007; Luo et al., 2014a; Yang et al., 2015; Zhu et al., 2015; Liu et al., 2018a; Zhang et al., 2018a). In particular, PHBV is the best suitable BDP compared to other polymers as it is produced by microorganisms. However, one of the hindrances for wide deployment of these BDPs as slow release carriers in wastewater treatment process is their high cost.

To reduce the cost, several natural biopolymers such as crab-shell chitin, starch, and lignocellulose were used as alternatives to expensive BDPs (Annadurai et al., 2000; Robinson-Lora and Brennan, 2009; Zhang et al., 2009; Shen and Wang, 2011; Reyes-Alvarado et al., 2018). However, the use of these natural biopolymers as the carbon source can result in high ammonia formation, dissolved organic carbon (DOC) and color problems in effluent (Robinson-Lora and Brennan, 2009). For these reasons, the key issue of slow release carrier is to develop a solid substrates with low cost and without deterioration of effluent water quality.

Hitherto, blending aliphatic polymers (PCL, PBS, PHBV, and PLA) with some cheap natural biopolymers (i.e. starch) is deemed to be a most potential method to lower the price of slow release carrier. Indeed, comparing to other biodegradable thermoplastic polymers, starch is an abundant renewable polysaccharide with superior biodegradability and low cost. Aliphatic polyesters (e.g., PCL, PBS, and PHBV) are biodegradable thermoplastic polymers with good processability, thermal stability, excellent mechanical strenght, good Water Res.istance, and dimensional stability (Shen et al., 2013). As such, the blending aliphatic polyesters with starch is expected to lower the cost of biofilm carrier and minimize pollution of effluent water quality due to rapid starch in the surfaces of granules. In an earlier study, Shen and Wang (2011) found that more than 90% total nitrogen was removed in a fixed-bed bioreactor once the cross-linked starch/polycaprolactone blends (SPCL11) was used as a slow release carrier. Apart from advantages of slow release carrier mentioned above, this type of biofilm carriers also have some disadvantages such as low bio-affinity, which readily cause biofilm detachment.

3.2. Biofilm carriers with desired functional groups

Biofilm formation onto carrier plays a key role in determining efficiency of wastewater treatment systems based on biofilm process (Chu et al., 2014; Mao et al., 2017; Liu et al., 2018b; Zhang et al., 2018b), because it is associated with biomass retention and synergistic function of microbial community. Microorganisms tend to adhere to carrier surface and form structures known as biofilm. As such, the selection of the desired carrier is considered as a determing factor affecting bacteria adhesion and biofilm formation (Liu and Zhao, 2005; Zhang et al., 2018b). In particular, it was reported that functional groups (i.e. hydrophilic and electrophilic groups) on a carrier surface play a significant role in biofilm formation (Lee et al., 2000; Khorasani et al., 2006; Chu et al., 2014; Zhang et al., 2018b). Roles of hydrophilic and electrophilic groups in materials used for biofilm carriers is discussed in more details in the following sections.

3.2.1. Biofilm carriers with hydrophilic modified surface

As aforementioned, an ideal biofilm carrier should possess the following features: low cost, excellent mechanical strength, large specific surface area, low density, stability, high bio-affinity, resistance to biodegradation and aging (Liu et al., 2017; Xu and Jiang, 2018; Zhang et al., 2018b). To date, biofilm carriers used in wastewater treatment are generally inorganic materials, e.g. activated carbon (van der Zee et al., 2003; Olivo-Alanis et al., 2018), ceramic (Zhang et al., 2010; Dong et al., 2011; Wang et al., 2016), carbon fiber (Xu and Jiang, 2018) and organic materials such as PCL (Chu and Wang, 2011), PBS (Luo et al., 2014a; Zhu et al., 2015), PHBV (Wu et al., 2012; Shen et al., 2013; Liu et al., 2018a), PLA (Accinelli et al., 2012; Wu et al., 2012), or natural macromolecular biopolymers (Xiao and Chu, 2014; Yang et al., 2015). For inorganic materials-base biofilm carriers have advantages in cost and mechanical strength (Wang et al., 2016), but have disadvantages in mass transfer due to low porosity and easy blockage (Zhang et al., 2018b). Similarly, organic materials appear to have large specific surface area (Feng et al., 2012; Chu et al., 2014), but have low bio-affinity caused by the smooth surface (Liu et al., 2017). For this reason, the surface modifications of biofilm carrier, such as hydrophilically modified surface or electrophilically modified surface, are expected to enhance bio-affinity of biofilm carriers.

Fig. 1 depicts the action mechanism of biofilm formation between a biofilm carrier with hydrophically modified surface and microrganisms. The biofilm formation on carriers is related to the physical interactions (i.e. electrostatic interactions and surface energy on bacterial adhesion to surfaces (Renner and Doughlas, 2011). The interactions between bacterial cell wall and carrier surfaces are mainly affected by interfacial interactions, such as repulsions/attractions and van der Waals forces. It is widely accepted that bacterial cells secrete DNA, proteins, lipids, and lipopolysaccharides, known as extracellular polymer substances (EPS), indicating that cell wall surfaces of bacteria contain functional groups (e.g. –OH, –COOH, –CHO, or –C=O). Therefore, there is the formation of hydrogen bonds between functional groups on carrier surfaces and bacterial cell wall (Kang and Choi, 2005; Renner and Doughlas, 2011). In addition, the energy surface of hydrophilic carriers is always higher than that of hydrophobic carriers (Nguyen et al., 2016), indicating that microbes in water are easier to adsorb and grow on the biofilm carrier with hydrophilic modified surface (Renner and Doughlas, 2011). In earlier studies, it was found that superhydrophobic surfaces with water contact angle >130° reduce significantly bacterial adhesion on the surface (Chavant et al., 2002; Feng et al., 2015a; Yuan et al., 2017b).

Table 2 summarizes the changes of water contact angle, biofilm growth and treatment efficiency of carriers with hydrophilic modified surfaces. It can be seen that biofilm carriers with surface modifications via grafting hydrophilic groups, such as –COOH,–CHO, and –C=O exhibited a lower water contact angles compared with the biofilm carrier without surface modification (Elshahat et al., 2003; Shen et al., 2007; Chu et al., 2014; Zhu, 2017; Zhang et al., 2018b). For example, Zhu et al. (2017) found that modified polyurethane sponge (MPUS) exhibited a significantly lower water contact angle (60°) compared to that of unmodified PU sponge (90°). Similarly, Zhang et al. (2018b) observed that modified basalt fiber (MBF) had an extremely water contact angle (1.59°) compared to unmodified basalt fiber (BF), as shown in Table 2. In addition, the attached biomass on the biofilm carriers with hydrophilic-modified surfaces was also higher than that in the carriers without surface modification (Deng et al., 2016b). In a recent study, Zhu (2017) found that the growth of microbes onto the surface of a novel hydrophilic and biocompatible magnetic polypropylene (HBM-PP) carrier was better than that of unmodified polypropylene (PP) carrier, as summarized in Table 2. For example, adsorption capacity of HBM-PP carrier to microorganisms (9.8×10^5 CFU/g.h) was significantly higher than that of unmodified PP carrier (8.4×10^4 CFU/g.h). In addition, the time required to for complete biofilm formation in HBM-PP carrier (12 h) was also shorter than that in unmodified PP carrier (15 h).

So far, there are two main methods that are often used to modify surface, including grafting and blending hydrophilic groups. For example, Shen et al. (2007) modified the surface of polysulfone hollow fiber (PSF) membrane by grafting hydrophilic acrylamide chain. They found that the water contact angle of the modified PSF membrane segments was decreased considerably, from 70° to

48°. In addition, the attached biomass on the modified PSF was largely increased (Table 2), indicating that modified PSF membrane segments could provide more ideal living environment for microbes than the unmodified ones due to the improvement of surface hydrophilicity. Regarding the treatment efficiency, the modified carriers showed higher removal efficiencies for both COD and NH_4-N than unmodified carrier. In a recent study, Zhang et al. (2018b) found that the bio-affinity of modified basalt fiber (MBF) was significantly improved because of introduction of many hydrophilic groups (e.g., –CONH and –OH) onto BF surfaces, which were subsequently demonstrated to facilitate biofilm formation. Apart from grafting method, blending a surface active substance such as N-methyl diethanolamine (N-MDA) into the carrier materials is considered as another method of surface modification (Chu et al., 2014).

3.2.2. Biofilm carriers with electrophilic modified surface

In addition to hydrophilicity, the electrophilic property of the biofilm carrier also affects the adhesion of microorganisms and biofilm formation (van Merode et al., 2006). It is reported that the surface of microorganisms possess negative charge due to the presence of carboxylic acid and phosphoric acid groups in the cell membrane of microbes (Terada et al., 2012; Tarjányi-Szikora et al., 2013). As aforementioned, PP or PE is widely used as the main material for biofilm carriers. However, pure PE, PP, and high-density polyethylene (HDPE) have negatively charged surfaces (Mao et al., 2017) same as the surface charge of bacteria. Thus, the biofilm formation on these carriers is hampered by the repulsions between microbes and surfaces of carriers.

To overcome this limitation, surface modification of the materials for biofilm carriers is often used to generate surface positive charge content or change surface electronegativity of the biofilm carriers (Chen et al., 2012; Mao et al., 2017; Liu et al., 2018b). The water contact angle of modified carriers with positively charged surfaces are significantly lower than that of unmodified carriers with negatively charged surfaces (Mao et. Al, 2017, Liu et al., 2018b). For example, Mao et al. (2017) reported that modified HDPE carriers with positively charged surfaces have water contact angle (58.8°), which is substantially lower than that of unmodified HDPE (94.3°). In addition to enhancing hydrophilic properties of carrier surfaces, surface modification helps to enhance the biofilm formation onto the carriers. Mao et al. (2017) found that biofilm formation (i.e. biofilm growth) on HDPE carriers were enhanced significantly when HDPE carriers were modified by two kinds of positively charge polymers (e.g. polyquaternium-10 [PQAS-10] and cationic polyacrylamides [CPAM]). As summarized in Table 3, the biomass yield and attached biomass on modified HDPE carriers with PQAS-10 and CPAM were higher than those on unmodified HDPE carriers (Mao et al., 2017). In addition, start-up time of bioreactor with modified HDPE carriers was shorter than in the bioreactor with unmodified HDPE carriers (Mao et al., 2017).

Fig. 2 shows the interaction mechanism between microorganisms and unmodified carriers or electrophilic modified biofilm carriers. In a previous study, Abbasnezhad et al. (2008) showed that the addition of cationic surfactant can promote bacterial adhesion on the surface of the carrier material. Electrophilic modified carriers possess positively charged surface have lower water contact angle compared to unmodified carriers. In addition, the concentrations of extracellular polymer substances (e.g. polysaccharide or protein) and attached biomass on modified carriers are substantially increased, indicating that electrophilic modified carriers enhance the adhesion of microbes.

In addition to enhanced biofilm formation, the removal efficiencies of target pollutants (i.e. COD, NH_4-N, and total nitrogen) in the biofilm reactor with electrophilic modified carriers are assumed to be better than those with unmodified carriers (Mao et al., 2017; Liu et al., 2018b). For example, Liu et al. (2018b) found that that a higher amount of attached biomass was observed on modified carriers (PQAS-10 and Fe_2O_3 modified PE) compared to unmodified carriers (pure PE). As a result, the removal efficiency of TN, COD, and NH_4-N in biofilm reactor with modified carriers was superior to that with unmodified carriers.

3.3. Magnetic biofilm carriers

Over the past few decades, effect of magnetic field on microbial activities has increasingly gained attention due to the changes in permeability of microbial cell membrane, which can promote metabolism, growth and degradation of microbes (Tomska and Wolny, 2008; Kriklavova et al., 2014; Zaidi et al., 2014; Pospisilova et al., 2015; Quan et al., 2017; Liu et al., 2018c; Quan et al., 2018). For example, Tomska and Wolny (2008) found that the transformation of nitrogen compounds in activated sludge system exposed to magnetic field tended to be more effective than the system without magnetic field exposure, especially the oxygen uptake rate of second nitrification phase once being exposed to magnetic field was higher than that without magnetic field by a factor of 1.6–2. Kriklavova et al. (2014) also observed that the magnetic field could stimulate the oxidation of phenol and promote microbial growth. In recent studies, Quan et al. (2017) and Quan et al. (2018) revealed that magnetic field directly affected trichloroethylene removal in biotricking filter systems. They found that biotricking filter systems exhibited a better removal under magnetic field intensity (MFI) of 20 mT. In general, magnetic field shows many advantages in wastewater treatment, but it is challenging to install an external magnetic field for bioreactors.

To tackle this issue, the use of magnetic materials as biofilm carriers has been widely employed to replace the installation of external magnetic field (Yavuz and Celebi, 2003; Yao et al., 2013; Cheng et al., 2014; Cheng and Guo, 2014). To date, Fe_3O_4 or ores containing Fe_3O_4 has been commonly used to prepare biofilm carriers (Yao et al., 2013; Cheng and Guo, 2014; Liu et al., 2015). For example, Yao et al. (2013) developed a novel magnetic carrier with surface magnetic field of 4 mT to investigate the effect of magnetic field on nitrification in sequencing batch biofilm reactors. They also found that oxidation activities of NO_2-N and NH_4-N in biofilm reactor with magnetic carrier were considerably enhanced compared to biofilm reactor with non-magnetic carrier. In another study, Liu et al. (2015) used a new type of magnetic carrier that was prepared by combining air stone with ferrofluid (Fe_3O_4) nanoparticles to enhance biofilm formation and oxygen dissolution in municipal wastewater treatment. As expected, Liu et al. (2015) found that dissolved oxygen content, attached biomass, and biofilm adhesion were substantially increased. As depicted in Table 4, magnetic biofilm carriers promoted biofilm formation, increased biomass, shortened the startup time, and improved biodegradation.

Presently, magnetic carriers are extensively used in wastewater treatment technologies to remove heavy metals, organic compounds, nitrogen and phosphorous compounds (Yavuz and Celebi, 2001; Yavuz and Celebi, 2003; Yao et al., 2013; Cheng et al., 2014; Cheng and Guo, 2014; Xu and Jiang, 2018). For instance, Cheng et al. (2014) found that a higher removal efficiency of COD and NH_4-N was observed in the biofilm reactor with magnetic ceramsite carriers compared to that in the biofilm reactor with nonmagnetic ceramsite carriers. Similarly, in a recent study, Xu and Jiang (2018) found that the load of Fe_3O_4 on the surface of carbon fiber (CF) to form a magnetic carrier CF-FeC_2O_4 could enhance biofilm formation and improve wastewater treatment efficiency, especially the growth/metabolism of microbes and enzymatic activity of microbes were enhanced considerably. For example, dry weight of biofilm per unit for CF-FeC_2O_4 was 3.6 g/g, which is significantly higher than that of nonmagnetic CF (1.1 g/g). This is interpreted is due to the increase of hydrophilic functional groups on CF-FeC_2O_4. Indeed, the water contact angle of CF-FeC_2O_4 (74.15°) was considerably lower than that of CF (107.67°). In addition to enhancing biofilm formation, magnetic carriers (CF-FeC_2O_4) tend to have a higher removal efficiency for COD, NH_4-N and total phosphorous (TP) compared to nonmagnetic carriers (Yavuz and Celebi, 2001; Yavuz and Celebi, 2003; Yao et al., 2013; Xu and Jiang, 2018). Recently, Xu and Jiang (2018) found that removal efficiency of COD, NH_4-N and TP when using magnetic carriers (CF-FeC_2O_4) increased by 7.18%, 10.30% and 9.40% compared to that of nonmagnetic carriers (CF).

Another advantage of magnetic biofilm carriers is to allow preventing the washout of biomass in continuously stirred tank reactors (CSTR), subsequently which helps to increase solid retention time (SRT) and reduce hydraulic retention time (HRT).

So far, the use of magnetic biofilm carriers has successfully employed in lab-scale wastewater treatment systems, while no information on the application of these carriers for full-scale wastewater treatment plants is reported. For large-scale applications, the particles used as magnetic biofilm carrier must be available at a reasonable cost. Therefore, further studies to reduce the cost of magnetic carriers are critically needed.

3.4 Biofilm carriers acting as redox mediators

It is reported that biotransformation of many organic pollutants (i.e. azo dyes) takes place very slowly, especially for compounds with high polarity and/or electron-withdrawing functional groups such as some sulfonated reactive azo dyes, nitroaromatics, halogenated aliphatics, halogenated aromatics and metalloids (Tran et al., 2009; Lu et al., 2010; Pereira et al., 2010; Tran et al., 2010; Yuan et al., 2017a; Olivo-Alanis et al., 2018). These recalcitrant compounds usually remain unaffected during aerobic wastewater treatment, but can undergo reductive transformation under anaerobic conditions at a very low rate (van der Zee and Cervantes, 2009). This limits for the application of high-rate anaerobic bioreactors since long HRT would be needed to reach a satisfactory extent of dye reduction (Rau et al., 2002; van der Zee et al., 2003; Lu et al., 2010). To overcome this problem, the use of redox mediating compounds (i.e. redox mediators) to enhance reductive transformation rate of recalcitrant pollutants by shutting electrons from microbes or chemical electron donors to electron accepting pollutants is deemed as a potential solution in improving biotransformation rate (Rau et al., 2002; van der Zee et al., 2003; Lu et al., 2010; Tran et al., 2010; Tran et al., 2013).

Fig. 3 shows the biotransformation mechanisms of pollutants in the presence of redox mediator, which serves as electron shuttle [ES] as reported by (Watanabe et al., 2009; Brutinel and Gralnick, 2012). As depicted in Fig. 3a, in the presence of electron donor, the redox mediator is first reduced by quinone reductase on the inner membrane of the cell, and then reduced mediator chemically reduces extracellular pollutants and regenerates the mediator. In another case, electron donor (i.e. sulfide) can chemically reduce the mediator to hydroquinone. Such reduced mediator provides electrons to the microorganisms as an electron donor in reducing pollutants (Fig. 3b). The pathway of reaction involving microorganisms is described in Fig. 3c, in which microorganisms obtains electrons from electron donors and secrete electron shuttles, and then transfer the electrons to the quinone mediator.

In fact, redox mediators are electron shuttles, which can be reversibly oxidized and reduced. Redox mediators accelerate reactions by lowering the activation energy of the total reaction (van der Zee and Cervantes, 2009). To date, redox mediators have been known to be able to transfer electrons in redox reactions between a broad-spectrum of both inorganic and organic compounds (van der Zee and Cervantes, 2009). In earlier studies, soluble quinone compounds, such as anthraquinone-2-sulfonic acid ester (AQS), 2-hydroxy-1,4-naphthalene quinone, anthraquinone disulfonate (AQDS), lawsone, juglone, and menadione, are widely used as redox mediators to accelerate transformation (decolorization) of azo dyes (van der Zee et al., 2003; Guo et al., 2007; Pereira et al., 2010; Yuan et al., 2012; Zhang et al., 2014a; Olivo-Alanis et al., 2018). Fig. 4 shows the role of quinone mediator in redox reactions of a variety of pollutants (inorganic/organic compounds).

However, the main drawback limiting their application in wastewater treatment processes is that continuous dosing implies continuous expenses of mediators as well as continuous discharge of this kind of biologically recalcitrant compound into the environment. To tackle this issue, the immobilization of active redox mediators onto the surface of insoluble materials (e.g., polyethylene terephthalate fiber cloth [PETFC], polyurethane [PU] sponge, graphene oxide [GO], reduced graphene oxide [RGO], ceramsites, calcium alginate [CA], etc.,) or the use of activated carbon/ biochar is considered as attractive alternatives to soluble redox mediators (Guo et al., 2007; van der Zee and Cervantes, 2009; Lu et al., 2010; Pereira et al., 2010; Yuan et al., 2012; Zhang et al., 2014a; Zhang et al., 2014b; Wu et al., 2019). For example, Van der Zee et al. (2003) found that a significantly higher decolorization capacity of azo dye RR2 (>90%) was observed in an activated carbon-amended bioreactor compared to the bioreactor without adding activated carbon (<40%).

Van der Zee et al. (2003) also revealed that activated carbon in bioreactor could act as a redox mediator and terminal electron acceptor during anaerobic transformation of azo dyes. In another study, Pereira et al. (2010) also found that reduction rates of azo dyes increased up to 9 times in a bioreactor with adding activated carbon (0.1 g/L) as a redox mediator compared to the bioreactor without activated carbon. In recent studies, it was reported that the addition of activated carbon in anaerobic digester accelerated the decomposition of edible oil in food waste and enhanced the methane production from food waste (Zhang et al., 2017a; Zhang et al., 2017b). More recently, Wu et al. (2019) have reported that biochar can act as an electron shuttle and stimulator of denitrification.

In comparison to soluble redox mediators, insoluble redox mediators are retained in bioreactor for prolonged time. In addition, activated carbon or other insoluble materials can be physically and chemically modified to associate or entrap redox-active functional groups onto its surface. The introduction of functional groups allows increasing the surface wettability of biofilm carriers, which promote the biofilm formation (Li et al., 2014).

In an earlier study, Guo et al. (2007) reported that anthraquinone (a soluble redox mediator) was easily immobilized by entrapment in calcium alginate [CA] to form an insoluble redox mediator. They found that the decolorization rate of CA immobilized anthraquinone retained over 90% of their original value. In a recent study, Zhang et al. (2014a) immobilized anthraquinone-2-sulfonate (AQS) onto the surface of polyethylene terephthalate fiber cloth (PETFC) and found that AQS-PETFC resulted in the increased anaerobic transformation rates of various azo dyes and nitroaromatics. In addition, the decolorization efficiencies of azo dyes could remain over 93.7% of their original value during 5 runs. Table 5 summarizes the characteristics of several immobilized redox mediators.

4. Future perspectives

To date, there is no gold standard to select ideal biofilm carriers for biological wastewater treatment systems. The selection of the best suitable biofilm carriers for the biofilm reactors can be challenging and is largely dependent on how much is known about the characteristics of wastewater and the degree of treatment required to meet the applicable discharge limits or reuse requirements. The purpose of this section is to underline several important topics that should be considered in the future studies, including:

[1] Develop novel slow release carriers for anaerobic treatment of nutrients and organic pollutants in municipal wastewater.

[2] Evaluate biofilm carriers with desired functional groups (i.e. hydrophilic and/or electrophilic-modified surface) in removal of emerging organic contaminants.

[3] Investigate the roles of activated carbon, biochars, and graphene oxides as insoluble redox mediators in biotransformation of recalcitrant micropollutants, such as endocrine-disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in wastewater.

5. Conclusions

This review provides comprehensive information on the characteristics of different types of biological carriers. An in-depth analysis on advantages and disadvantages of biofilm carriers was evaluated. Slow-release biofilm carriers can provide a carbon source and electron donor for the microbial growth and denitrification in anoxic/anaerobic wastewater treatment. Biofilm carriers with hydrophilic/electrophilic modified surface allow promoting biofilm formation. Magnetic materials-based carriers help to shorten the start-up time of bioreactor and improve enzymatic activity of microorganisms. Biofilm carriers acting as redox mediators allow accelerating the biotransformation of recalcitrant pollutants in industrial wastewater and food waste treatment processes. Further studies on the use of novel biofilm carriers in removing emerging contaminants are recommended.

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Table 1. The application of biofilm-based systems for removal of macro- and micropollutants.

Biofilm-based systems	Biofilm carrier type	Target pollutants	Reference
Airlift reactors	Granular activated carbon	Organic micropollutants (i.e. PPCPs)	(Shen et al., 2010)
Anaerobic sequencing batch biofilm reactor	Granular activated carbon	Macropollutants (i.e. COD)	(Dutta et al., 2014)
	Zeolite	Macropollutants (i.e. COD)	(Dutta et al., 2014)
Modified packed bed biofilm reactor	PP	Heavy metals (Zn, Cu, Cd and Ni)	(Azizi et al., 2016)
Moving bed biofilm reactors (MBBRs)	PE (AnoxKaldnes Z-MBBR™)	Organic micropollutants (i.e. PPCPs)	(Torresi et al., 2017)
	PE (AnoxKaldnes™ K1 or AnoxKaldnes™ K5)	Organic micropollutants (i.e. PPCPs)	(Falås et al., 2012; Ooi et al., 2017; Ooi et al., 2018; Tang et al., 2019)
	PE (AnoxKaldnes™ K1, AnoxKaldnes™ K2, and Mutag Biochip™).	Organic micropollutants (i.e. PPCPs)	(Zupanc et al., 2013)
	PU sponge	Organic micropollutants (i.e. PPCPs)	(Luo et al., 2014a; Luo et al., 2014b; Nguyen et al., 2019)
	Sepiolite-modified suspended ceramic	Macro- and micropollutants (COD, NH_4-N, and PAHs)	(Dong et al., 2011)
	Zeolite powder-based PU sponges	Macropollutants (i.e. TN)	(Song et al., 2019)
Natural ventilation trickling filters	Ceramsite	Macropollutants (COD, NO_3-N, NH_4-N, and TN)	(Zhang et al., 2016b)
	Polyurethane sponge	Macropollutants (COD, NO_3-N, NH_4-N, and TN)	(Zhang et al., 2016b)
	Zeolite	Macropollutants (COD, NO_3-N, NH_4-N, and TN)	(Zhang et al., 2016b)

PE: polyethylene; PP: Polypropylene; PU: polyurethane: PAHs: polycyclic aromatic hydrocarbons; PPCPs: pharmaceuticals and personal care products; TN: total nitrogen. .

Table 2. Characteristics of biofilm carriers with hydrophilic modified surface.

Carrier type	Modified substance	Surface property	Water contact angle	Biofilm growth	COD removal efficiency	NH$_4$-N removal efficiency	Reference
Hollow fiber membrane	None	Poor hydrophilic surface	70°	• Biomass: 2264–4552 mg TSS/L	Higher removal of COD was observed by biofilm carrier with hydrophilic modified surface	Higher removal of NH$_4$-N was observed by biofilm carrier with hydrophilic modified surface	(Shen et al., 2007)
Polysulfone hollow fiber membrane	Hydrophilic acrylamide	Hydrophilic surface	48°	• Biomass:3310–5653 mg TSS/L			(Shen et al., 2007)
Basalt fiber (BF)	None	Superhydrophobic surface	155°	• IRM:149% • k:0.92×10^{-9} mL/cell·h	–	–	(Zhang et al., 2018b)
Modified basalt fiber (MBF)	Polyacrylamide/epoxy/nano-SiO$_2$	Superhydrophilic surface	1.59°	• IRM:218% • k:1.33×10^{-9} mL/cell·h	–	–	(Zhang et al., 2018b)
Unmodified polyurethane (PU)	None	Hydrophobic surface	90°	• The amount of attached biofilm to MPU was 1.3 times higher than that of unmodified PU carriers.	80–86%	77–91%	(Chu et al., 2014)
Modified polyurethane (MPU)	N-MDA	Hydrophilic surface	66°				
Unmodified polypropylene (PP)	None	Poor hydrophilic surface	88.7°	• Adsorption capacity: 8.4×10^4 (CFU/g h) • Sludge concentration: 7.9×10^4 (CFU/mL) • Time required for successful biofilm culture: 15 d	＞80%	63.70%	(Zhu, 2017)
Hydrophilic and biocompatible magnetic polypropylene (HBM-PP)	Barium ferrite or diatomite	Hydrophilic surface	58.5°	• Adsorption capacity: 9.8×10^5 (CFU/g h) • Sludge concentration: 7.9×10^4 (CFU/mL) • Time required for successful biofilm culture：12d	＞90%	85.40%	(Zhu, 2017)

IRM: the immobilization ratio of microorganisms indicated the capacity of microorganism immobilization.

k: the adhesion rate constant.

Table 3. Characteristics of biofilm carriers with electrophilic modified surface.

Biofilm carrier type	Modified substance	Water contact angle	Zeta potential (mV)	Biofilm growth			Startup time	COD removal efficiency	NH_4-N removal efficiency	TN removal efficiency	References
				Biomass	Polysaccharide concentration	Protein content					
Unmodified HDPE	None	94.3°	-39.4 at (pH 6.8)	• Y: 0.457 • X: 2030	46.5 mgCOD/L	168.7 mg COD/L	NH_4-N : 32 d COD: 22 d	Similar with PQAS-10 carrier	51%	49%	(Mao et al., 2017)
Modified HDPE with PQAS-10	PQAS-10	59.8°	+12.9 at (pH 6.8)	• Y: 0.747 • X: 2350	↑14%	↑11%	NH_4 -N: 18 d COD:7 d	93%	92%	72%	Mao et al., 2017)
Modified HDPE with CPAM	CPAM	58.8°	+10.8 (pH 6.8)	• Y: 0.649 • X: 2160	↑9%	↑5%	NH_4 -N: 24d COD: 9 d	Similar with PQAS-10 carrier	67%	63%	Mao et al., 2017)
PE	None	92°	-38.6 at (pH 7.0)	• TSS on carriers:179 g/m^2	35 mg/L	86 mg/L	25 d	81.3%	92.9%	77.6%	(Liu et al., 2018b)
Modified PE with PQAS-10 and Fe_2O_3	PQAS-10 and Fe_2O_3	60.2°	+11.7 at (pH 7.0)	• TSS on carriers: 192 g/m^2	40 mg/L	97 mg/L	42 d	83.8%	93.3%	80.2%	(Liu et al., 2018b)
PE	None	77°	n.r	＞2000 mg/L	~ 40 mg/gSS	<80 mg/gSS	~ 20 d	~ 85%	n.r	n.r	(Chen et al., 2012)
Chemical oxidation-surface covering with ferric ion (CO-SCFe)	Ferric ion	65°	n.r	↑54.8 %	↑63%	↑43%	↓37.5%	↑10.63%	n.r	n.r	(Chen et al., 2012)
Chemical oxidation-surface grafting with gelatin (CO-SGG)	Gelatin	41.5°	n.r	↑76.1 %	↑18.5%	↑15.4%	↓60%	↑8.64%	n.r	n.r	(Chen et al., 2012)

Y: Biomass yield (mgVSS/mgCOD); X: attached biomass (mg/L); ↑ increase; ↓ decrease; n.r: not reported; PE: polyethylene; PQAS-10: Polyquaternium-10; CPAM: Cationic polyacrylamides; HDPE: high-density polyethylene.

Table 4. Characteristics of biofilm carriers with and without magnetic property.

Carrier type	Modified substance	Process	Biofilm characteristics		Pollutants	Removal efficiency	Comparison	Reference
Magnetic polystyrene particles (without magnetic field)	Fe_3O4	Fluidized bed	Biofilm Thickness Attached biomass	173 µm 8.6 g/L BV	Glucose	n.r	n.r	(Yavuz and Celebi, 2001; Yavuz and Celebi, 2003)
Magnetic polystyrene particles (continuous: DC 17.8mT)	Fe_3O4	Fluidized bed	Biofilm thickness Attached biomass	155 µm 10.2 g/L BV	Glucose	n.r	Removal efficiency increased 8–12%	(Yavuz and Celebi, 2001; Yavuz and Celebi, 2003)
Magnetic polystyrene particles (pulsed: 2 sec on/2 sec off, 17.8mT)	Fe_3O4	Fluidized bed	Biofilm thickness Attached biomass	157 µm 10.8 g/L BV	Glucose	n.r	Removal efficiency increased 18–26%	(Yavuz and Celebi, 2001; Yavuz and Celebi, 2003)
Non-magnetic PET	None	Cylindrical sequencing batch biofilm reactor (CSBBR)	Time required for biofilm formation	25 d	NH_4-N and NO_2-N	n.r	Higher specific oxygen uptake rates was observed at biofilm reactor with magnetic PET carriers compared to nonmagnetic PET carriers	(Yao et al., 2013)
Magnetic PET	Ba ferric powder		Time required for biofilm formation	18 d	NH_4-N and NO_2-N	n.r		
Porous ceramsite	None	Biofilm reactor	Biomass (g) MLSS (g/L) SV (%) Zoogloea	42.11 31.27 73 Limited and small	COD NH_4-N	n.r n.r	A higher removal efficiency of NH_4-N and COD was observed at the biofilm reactor with magnetic carriers compared to non-magnetic carriers	(Cheng et al., 2014)
Magnetic ceramsite	Fe_3O4	Biofilm reactor	Biomass (g) MLSS (g/L) SV (%) Zoogloea	35.34 28.36 64 Copious and large	COD NH_4-N	10–20% 20–30%		

BV: bed volume; SV: sludge volume; PET: Polyethylene terephthalate

Table 4. Continued.

Carrier type	Modified substance	Process	Biofilm characteristics		Pollutants	Removal efficiency	Comparison	Reference
Porous ceramsite	None	Biofilm reactor	Biomass (g) MLSS (g/L) SV (%)	43.91 31.19 65	Cr(VI)	n.r	Better quality of effluent was observed at biofilm reactor with magnetic ceramsite compared to porous ceramsite	(Cheng and Guo, 2014)
Magnetic ceramsite	Fe_3O_4	Biofilm reactor	Biomass (g) MLSS (g/L) SV (%)	33.86 28.72 60	Cr(VI)	5–10%		(Cheng and Guo, 2014)
Air stone (AS)	None	Biofilm reactor	Biofilm weight (g) Absorbance value Glucose concentration (mg/L)	1.4 3.01 3.09	n.r	n.r	High biomass concentration was observed at biofilm reactor with MAS compared to AS	(Liu et al., 2015)
Magnetic air stone (MAS)	Fe_3O_4 nanoparticle	Biofilm reactor	Biofilm weight (g) Absorbance value Glucose concentration (mg/L)	1.9 3.63 3.73	n.r	n.r		(Liu et al., 2015)

n.r: not reported.

Table 5. Characteristics of biofilm carriers acting as redox mediators.

Carrier type	Modified substance	Pollutants	Performance efficiency of unmodified carrier	Performance efficiency of modified carrier	Higher performance of modified carrier compared to unmodified carrier	Reference
AQS-modified poly(ethylene terephthalate) fiber cloth (AQS-PETFC)	Anthraquinone-2-sulfonic acid (AQS)	Nitrobenzene	<60%	n.r	↑1.8-fold	(Zhang et al., 2014a)
		Acid Red 73			↑1.6-fold	
		Reactive Red 2			↑1.7-fold	
		Acid Yellow 36			↑3.7-fold	
		Acid Red 27			↑2.4-fold	
AQS-modified polyurethane sponge (AQS-PUS)	AQS	Reactive Red 141	3.7 mM/g·h	12.3 mM/g · h	n.r	(Lu et al., 2010)
		Acid Red 73	6.5 mM/g·h	32.3 mM/g · h	n.r	
		Direct Black 22	3.0 mM/g·h	11.1 mM/g · h	n.r	
AQS-ceramsites	AQS	Acid Yellow 36	n.r	n.r	↑ 8.0-fold	(Yuan et al., 2012)
		Reactive Red 2	n.r	n.r	↑ 2.3-fold	
		Acid Red 27	n.r	n.r	↑2.7-fold	
		Acid Orange 7	n.r	n.r	↑2.5-fold	
AQS-modified reduced graphene oxide (AQS-RGO)	AQS	Acid Yellow 36	k=0.0364/h	k=0.8827 h^{-1}	n.r	Lu et al. 2014)
NH_2-RGO	Diethylenetriamine	Acid Yellow 36	n.r	k=0.131 h^{-1}		
NQ-GO	2-Amino-3-chloro-1,4-naphthoquinone (NQ)	Cr (VI)	n.r	increased from 9.5 to 100% within 11 h	n.r	(Zhang et al., 2014b)
AQ-GO	2-Aminoanthraquinone (AQ)	Cr (VI)	n.r	increased from 17.5 to 29.3% within 24 h		

The k is rate constant; ↑ increase; n.r: not reported.

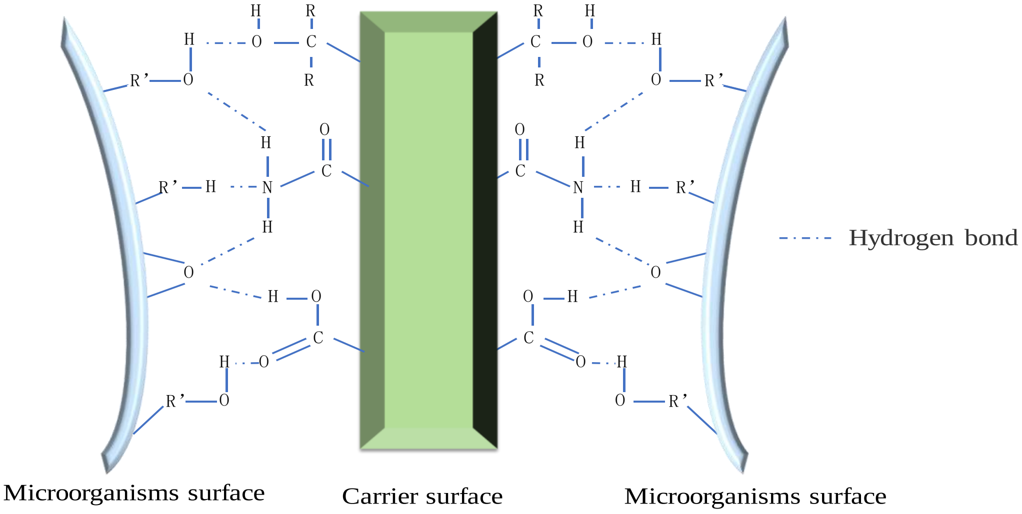

Fig. 1. Mechanism of hydrophilic carriers.

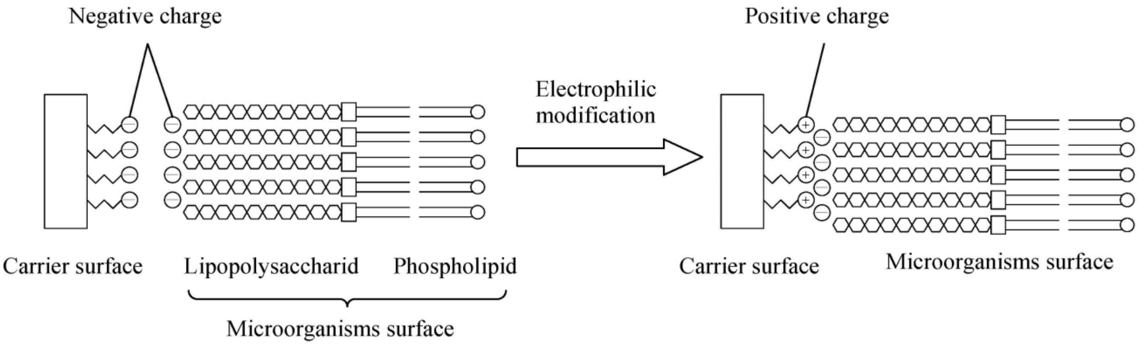

Fig. 2. Interaction between microorganisms and unmodified/modified biofilm carriers.

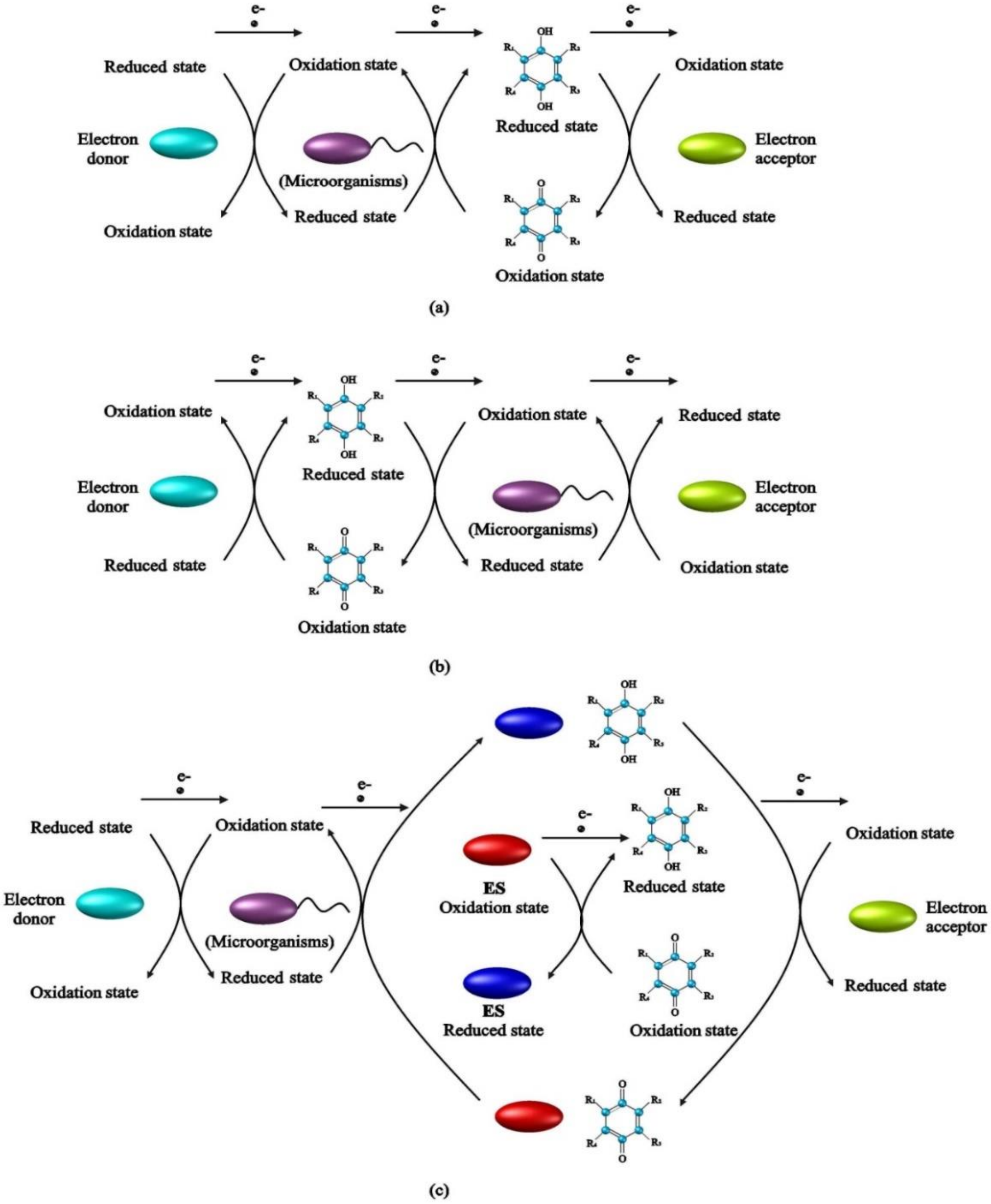

Fig. 3. Biotransformation mechanism in the presence of redox mediator (i.e. electron shuttle [ES]) as reported by (Watanabe et al., 2009; Brutinel and Gralnick, 2012).

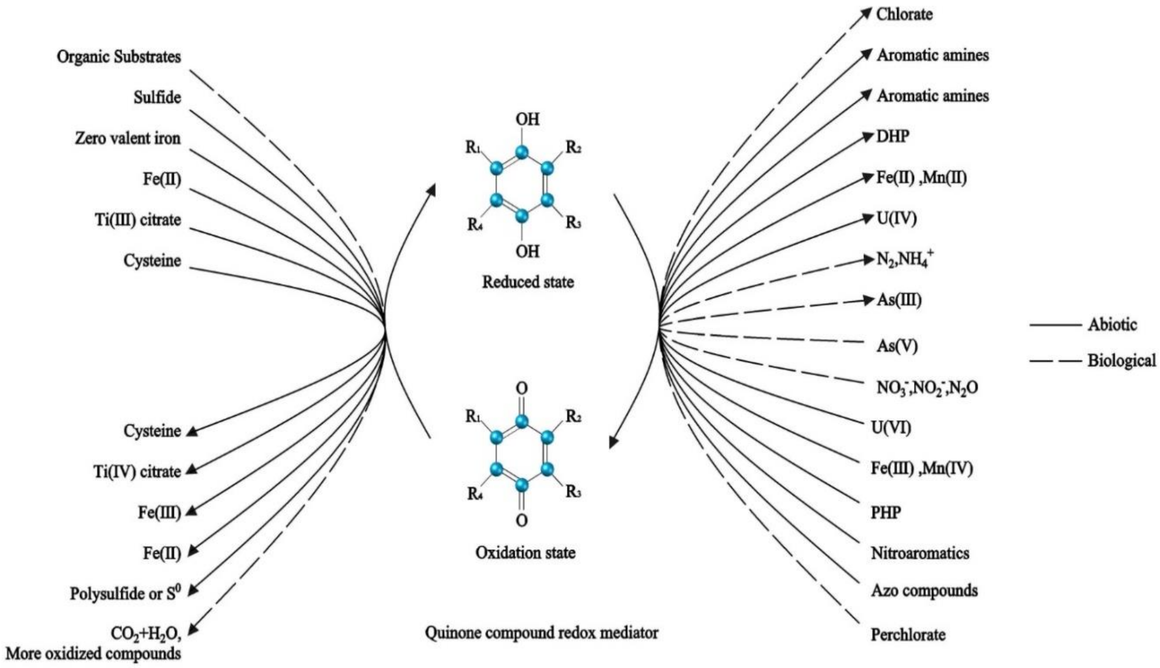

Fig. 4. Role of quinones as a redox mediator in reduction-oxidation of a variety of pollutants (Stolz, 2001).