Environmental Applications of Immobilized and Bio-Resourced Redox Mediators: A Review

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Redox mediators (RMs), also known as electron shuttles, have been widely reported to promote both biotic and abiotic reductions of oxidized pollutants in water, soil, biogeochemical cycles, and wastewater treatment systems. However, the continuous addition of dissolved RMs is unaffordable and the potential environmental risks remain unknown because most applied RMs are synthetic chemicals. Immobilization technology enables RMs to be attached on non-dissolved supports, avoiding wash-out from the treatment systems. This realizes the reuse of RMs in scaled-up engineering applications and the *in-situ* remediation. Moreover, renewable natural biomass and their derivatives, such as biochar, have also aroused increased interest because they provide an economical and feasible way to solve the shortcomings of applying soluble RMs. This review presents different RM immobilization methods, which include entrapment, adsorption, and surface modification, as well as the use of bio-resourced RMs. The immobilization procedures and reaction mechanisms of the immobilized RMs and bio-resourced RMs in environmental applications are critically compared and summarized.

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INTRODUCTION

In recent decades, the global environment has been challenged by serious pollution caused by synthetic chemicals, which are often recalcitrant, biorefractory, and carcinogenic. These contaminants include but are not limited to nitroaromatic compounds (NACs), azo dyes, nitrate, perchlorate, sulfate, halogenated compounds, polyhalogenated pollutants, hexavalent chromium (Cr(VI)), persistent organic pollutants, and so on. Because of the electron-withdrawing features of special groups associated with these oxidized pollutants, aerobic conditions usually fail to treat them (van der Zee and Cervantes 2009; Zhang *et al*. 2020). However, they can be moderately reduced under anaerobic conditions when electron donors are available, whereupon they can be readily removed aerobically. Thus, combined anaerobic-aerobic processes are typically applied to treat oxidized pollutants or concerned substances. In such approaches, the anaerobic reduction is the rate-limiting step and the bottleneck part of the process.

Redox mediators (RMs) are vital important compounds capable of accelerating redox reactions by shuttling electrons between their reduced and oxidized forms, as well as of lowering the activation energy for redox reactions. Within this catalytic process, the electrons from the primary electron donors would be quickly transferred to the final electron acceptors (Olivo-Alanis *et al*. 2018; Li *et al*. 2022a). They have been widely applied in the oxidation of H_2, alcohols, biomass, cellulose, and so on (Anson and Stahl 2020; Chen *et al*. 2022). To promote the reductive transformation of oxidized pollutants, the use of RMs has also been extensively reported for both biotic and abiotic reduction of oxidized pollutants in water, soil, biogeochemical cycles, and wastewater treatment systems (Rau *et al*. 2002; O'Loughlin 2008; Uchimiya and Stone 2009; Song *et al*. 2021). Currently, the most frequently applied RMs consist of flavin-based compounds and quinone-based compounds. Flavin-based compounds are those such as flavin adenine dinucleotide, flavin mononucleotide, and riboflavin; quinone-based compounds include, among others, anthraquinone-2,6-disulfonate (AQDS), anthraquinone-2-sulfonate (AQS), juglone, lawsone, and natural organic matters (NOM), such as humic acids (HA). Besides, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) is another commercially available RM by the TEMPO/TEMPOH redox cycle (Zhan *et al*. 2019; Sun *et al*. 2022; Zhang *et al*. 2021). The chemical structure of three typical RMs and the conversion between their oxidized and reduced forms are shown in Fig. 1 (Buckel and Thauer 2018; Zhang *et al*. 2021).

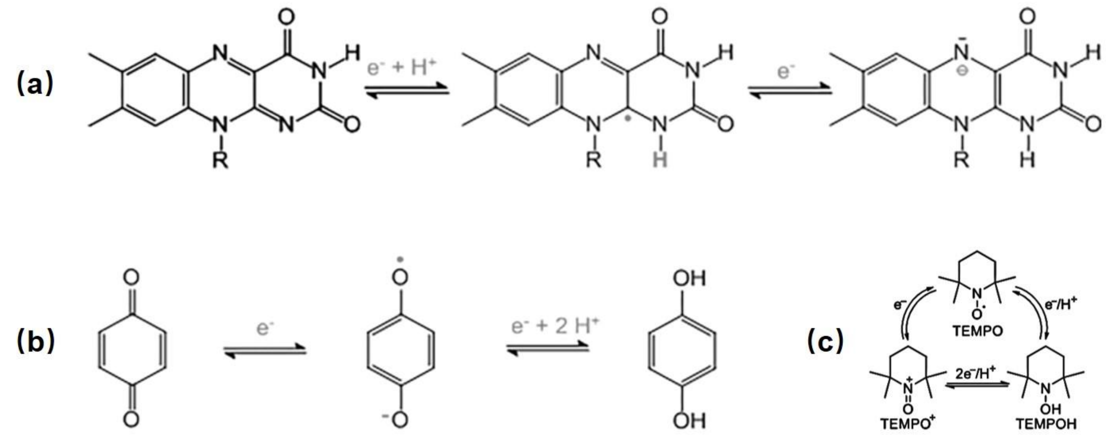

Fig. 1. The chemical structure and conversion cycle of flavin-based (a), quinone-based (b) and TEMPO (c) RMs

The RMs have been extensively reported to accelerate biological/chemical reduction of oxidized pollutants in various bioreactors and further prevent the toxic inhibition of them to the biological processes (van der Zee *et al*. 2001; Liu *et al*. 2009; Costa *et al*. 2010; Saratale *et al*. 2011; Mani *et al*. 2018). In these processes, RMs could speed up the electron transferring from the electron donors - carbohydrate, protein, volatile fatty acids, alcohol, hydrogen, (biogenic)sulfide, zero valent iron and ferrous iron, nicotinamide adenine dinucleotide phosphate hydrate, and electrical power - to the acceptors of oxidized contaminants, increasing the reduction rates by several folds or even dozens. Mixed cultures of microorganisms (such as activated sludge) as well as pure strains have been reported to contribute to the above mediated processes (Borch *et al*. 2005; dos Santos *et al*. 2005; Bhushan *et al*. 2006; Kwon and Finneran 2006, 2008; Bibi *et al*. 2019; Liu *et al*. 2021; Ren *et al*. 2022). Moreover, TEMPO-mediated decolorization, cellulose oxidation, photocatalysis and electroreduction have also been reported in the literature, implying the electron shuttling role of TEMPO/TEMPOH couple (Gharehkhani *et al*. 2019; Wen *et al*. 2019; Lukyanov *et al*. 2022).

In practical applications, the continuous addition of soluble RMs has been unaffordable because of their washout from the treatment systems. Moreover, most applied RMs are synthetic chemicals, for which the potential environmental and health risks are still unknown. Thus, urgent ways are needed for avoiding or mitigating the loss of soluble RMs (Zhou *et al*. 2012; Zhang *et al*. 2020). These methods include decreasing the soluble RM dosage, immobilizing RMs on special materials, and/or utilizing economical and naturally available alternatives. The RM immobilization enables soluble RMs to be attached to non-dissolved and inert carriers that fulfill the electron shuttling role in the redox process. This technology has aroused the most interest because it provides an economical and feasible way to solve the shortcomings of applying soluble RMs in continuously operating reactors. The abundance of target pollutants followed the order: azo compounds (52%) > polyhalogenated pollutants (15%) > NACs (13%) > nitrate and/or nitrite (12%) > Fe (4%) and Cr(VI) (3%) (Dai *et al*. 2016). Furthermore, some natural biomass or their derivatives, such as activated carbon, biochar, and natural humic substance (HS) are also capable of shuttling electrons during the redox reactions, providing cost-saving alternatives in the future. However, the direct use of natural biomass as RM would bring problems such as the release of unwanted organic compounds, which might increase secondary pollution.

The immobilization of soluble RMs is a complex process, depending on the physical-chemical features of both RMs and solid carriers. Thus, the selection of immobilization methods for specific chemical RMs has always been challenging. To guide the future applications of RMs in the environmental field, it is necessary to summarize different RM immobilization methods, focusing on immobilization procedures, and further prospects; in addition, natural and bio-resourced RMs are also proposed because of their economical and eco-friendly advantages. This review paper attempts to (1) summarize different RM immobilization methods (procedures and mechanisms) such as entrapment, adsorption, and surface modification, (2) investigate the catalytic effect and bottlenecks of various immobilized RMs in environmental applications, and (3) select bio-resourced RMs to speed up the bioredox processes for pollutants the removal.

IMMOBILIZATION METHODS AND APPLICATIONS

Entrapment-type Immobilization

In biological systems, entrapment has been traditionally considered for the physical retention or fixation of microorganisms and/or enzymes by polymeric carriers such as alginate, nanomaterials, silica gel, polyacrylamide, gelatin, polyion complex, and so on (Moyo *et al.* 2012; Romero-Soto *et al.* 2021). This method keeps the suspended cells and/or enzymes trapped in a porous solid matrix and thus condenses them, preventing their wash-out or loss from environmental systems or developing enzyme electrodes/biosensors for bioelectrochemical systems (Sakurada *et al*. 2017). Therefore, immobilization using polymeric materials as carriers of bioactive components can improve the efficiency and stability of microorganisms compared to that with free cells and/or enzymes, thus providing a promising technology to mitigate the pollutants in the environment (Fernández-Fernández *et al.* 2013; Somu *et al*. 2022).

The RMs, like microorganisms and enzymes, also can be non-covalently entrapped in different porous polymeric substances. The reported entrapmental immobilization methods of RMs and their applications in the reductive biotransformation of oxidized pollutants and bioelectrocatalysis capability are listed in Table 1. It indicates that the entrapmental immobilization is quite simple and the operating conditions are relatively moderate, meaning that high temperature and/or high pressure are not required during the redox reaction. Calcium alginate (CA), polyvinyl alcohol (PVA), and agar gel are the popularly used polymer supports for RMs entrapment because of their relatively easy procedures and low costs (Guo *et al*. 2007). The RMs entrapped on CA/PVA beads have been used in the bio-decolorization and denitrification processes. In these RM-assisted systems, the adsorption of pollutants by CA and PVA polymer beads only accounted for 0.2% to 2.0% of the total removal, indicating that the main removal pathways were *via* bio-reduction. Under the electron-shuttling assistance of polymer-trapped RMs, the removal of azo dyes and nitrate would be promoted to some extent with yeast extract, peptone, acetate, and glucose as electron donors (Liu *et al*. 2012b). Additionally, silica-entrapped TEMPO is an efficient heterogeneous catalyst and is more environmental-friendly and less tedious during immobilization, attracting attentions on the selective oxidation of cellulose, glucoside, and alcohols (Palmisano *et al*. 2006; Chen *et al*. 2022).

Table 1. Entrapment-type Immobilization of RMs and Their Applications

RMs	Carriers	Processes	Targeting Pollutants	Results	References
AQ	CA	Bio-decolorization	Single-azo, diazo and triazo dyes (0 to 200 mg L^{-1})	Immobilized AQ increased 1.5 to 2 fold of decolorization rates	Guo *et al*. 2007
AQ, 1,5-DCAQ	CA	Bio-denitrification	NO_3^-–N and NO_2^-–N (300 to 350 mg N L^{-1})	The denitrification rates increased 1.5 to 2.1 fold of that in the control.	Liu *et al*. 2012b; Guo *et al.* 2010
AQ	CA	Bio-decolorization	AR3R (180 mg L^{-1})	AR3R removal reached ~ 100%	Su *et al*. 2009
AQDS	PVA, SA, kaolin, chitosan	Bio-decolorization	MR (100 mg L^{-1}), azo dye wastewater (2849 mg COD/L)	Higher or comparable decolorization with soluble RMs	Sharma *et al*. 2016; Zhou *et al.* 2021
PES	Polyelectrolyte complex	Bio-electrocatalysis	--	MR removal achieved 100%	Romero-Soto *et al*. 2021
TEMPO	Sol–gel	Selective oxidation	Methyl α-D-glucopyranoside	Rapid selective-oxidation of Dimethylglucose	Ciriminna *et al*. 2000
TEMPO	Sol–gel	Selective oxidation	Cellulose	Widely used	Ciriminna *et al.* 2018
TEMPO	MIP	Selective oxidation	Cholesterol	70% oxidation within 15 min	Viveiros *et al.* 2022

Note: 1,5-DCAQ: 1,5-dichloroanthraquinone; AQDS: Anthraquinone-2,6-disulfonate; AR3R: Acid red 3R; AQ: Anthraquinone; CA: Calcium alginate; MIP: Molecularly imprinted polymeric (MIP); MR: Methyl red; PES: Phenazine ethosulfate; PVA: Polyvinyl alcohol; SA: Sodium alginate

Although entrapment presents advantages in immobilizing RMs, it would wrap the selected RM groups into the the polymer matrix. This means that the substrates, including electron donors and acceptors, must pass through the porous matrix to reach active RM groups and react with them, thereby limiting the electron-transferal during the bio-reduction process. Previous studies indicated that the RMs immobilized by entrapment are only capable of increasing the bio-decolorization/bio-denitrification rates up to two-fold compared to rates in the control systems (Guo *et al*. 2007, 2010; Liu *et al*. 2012b). In contrast, the RM polymer matrix might be disrupted because of the weakening mechanical strength of CA/PVA/Sol-gel beads after the long operation, resulting in the blockage of the matrix pores. To maintain the effective entrapment of soluble RMs on a more durable polymeric matrix than CA and PVA, hydrophobic RMs, such as anthraquinone, AQS, and 1,5-dichloroanthraquinone are preferred. Feng *et al.* (2017) developed a "foldable" but strengthened RM, *i.e.*, AQSA-Na (anthraquinone-2-sulfonic acid sodium salt)-doped PVA-H_2SO_4 robust gel film electrolyte, and suggested a great contribution of loaded RMs to the outstanding electron-transferring capability. This advance enabled the fabrication of smarter bio-electrochemical systems for the continuous removal of oxidized pollutants.

For the future application of RM entrapment as a technique to enhance pollutants removal, the mechanical strength of the polymer matrix and the diffusion rates of soluble substrates must be improved. To solve these problems, the co-entrapment of RMs and microorganism/enzymes seems promising, as this approach provides a better electron/mass transferring condition between microbial cells and entrapped RMs, thereby stably accelerating the reductive transformation of oxidized pollutants. Su *et al*. (2009) reported that the co-entrapment of RMs and microorganisms in a polymer matrix achieved better decolorization performance than was achieved with mono-immobilization of only RMs or microorganisms. Repeated decolorization batch experiments using co-entrapment systems showed that the RMs were reusable after several operating batch cycles (Su *et al*. 2009; Sharma *et al*. 2016).

Adsorptive Immobilization

Adsorption is another frequently employed RM immobilization method (Dai *et al*. 2016). After adsorption of soluble RMs into the surface of solid adsorbents, the electron-shuttling groups can be concentrated, enabling their reutilization during the redox reaction of oxidized pollutants. The adsorptive types by which soluble RMs are incorporated into special adsorbents include physical and chemical pathways. Physical adsorption is governed by the van der Waals intermolecular force, which weakly binds the soluble RMs with the adsorbent's surface and the adsorption was even reversible (Wang *et al*. 2010). Thus, physically adsorbed RMs can be easily detached from their carrier. For a wastewater treatment system as an example, a fluctuating influent can easily wash off physically immobilized RMs from the adsorbents. However, chemically adsorbed RMs are co-joined by chemical bonds, such as covalent bonds and hydrogen bonds, which are much stronger and more stable than physical force. Consequently, chemical-adsorptive RM immobilization has been widely used, depending on the linked functional groups (hydrophilicity/hydrophobicity) and/or charges (positive/negative) between adsorbents and RMs (Cervantes *et al*. 2010). As indicated in recent reports, ceramsite-based products, anion exchange resin, cellulose acetate, activated carbon (AC), polyurethane foam, porous silica beads, and metal-oxides nanoparticles are typically used as the potential adsorbents to immobilize different soluble RMs (Table 2).

These above immobilization procedures are relatively easy, but in some cases they are costly due to the usage of some advanced adsorptive materials such as nanoparticles or metal-organic frameworks (Li *et al*. 2017; Lou *et al*. 2023). The adsorption performance of an adsorbent to immobilize RMs is usually determined by adsorption isotherms modeling, the result of which provides proper guidance to maximize the electron-transferring capacity. Functional groups of chemical-adsorptive immobilized RMs are tightly attached to the adsorbent's surface. This leads to much better mass/electron transferal capability as compared with entrapmental immobilized RMs, which was inside the polymer matrix (Dai *et al*. 2016). Thus, the pollutant removal rates achieved using adsorptive immobilized RMs (maximally 10.4-fold) are much higher than that achieved using entrapped immobilization RMs (maximally 2.1-fold). Furthermore, benefitted by immobilized RMs, an anaerobic consortium can even utilize toxic substrates (such as phenol) as the sole energy source (electron donor) (Martínez *et al*. 2013).

Surface modification could potentially improve the adsorption capacity, enabling RMs to be immobilized as designed. Yuan *et al.* (2012) produced organic–inorganic hybrid materials using adsorption/covalence coupling methods. With OH-ceramsite and NH_2-ceramsite as a base, the sulfonic acid group associated in AQS can covalently bind with the -OH and $-NH_2$ bonds to form AQS-ceramsite. The grafted AQS on ceramsite has been shown to effectively catalyze the bio-decolorization process in a high salt environment. Furthermore, Fe_3O_4-quinone/TEMPO nanocomposites have also been identified as a promising RM complex because they can be easily and quickly separated from the mixed liquor with the assistance of a magnetic field; once separated, they can then be reused. Zhang and Hu (2017) introduced nano-scale Fe_3O_4 as an adsorbent to immobilize quinone-based RMs, achieving efficient and stable bio-reduction of NACs during multiple use cycles. Gao *et al.* (2018) used amino-functionalized magnetic Fe_3O_4 nanoparticles as a support to develop a co-immobilize TEMPO/laccase complex to remove acid fuchsin, and 50% residual activity was retained after eight cycles of operation.

Table 2. Adsorptive Immobilization of RMs and Their Applications

Functional RMs	Supports	Procedures	Catalyzed Processes	Target Pollutants	Results	References
AQS	Ceramsites, PUF	Adsorption/covalence coupling method	Decolorization, Biological nitro-reduction	AY36, RR2, AR27, AO7, Amaranth, NB	Reduction rates increased 6.4-fold for azo dyes and 5-fold for NB, respectively	Lu *et al*. 2010; Yuan *et al*. 2012; Wang *et al*. 2013
NQS	AER with amine type 1	Continuous shaking until equiblium	Decolorization	RR2 (0.3 mM)	Decolorization rates increased 8.8-fold	Cervantes *et al*. 2010
AQDS	MONPs, GAC	Continuous shaking until equiblium	Decolorization	RR2 (0.3 mM), CR (150 mg L^{-1})	Decolorization rates increased up to 7.5-fold	Alvarez *et al*. 2010; Del Ángel *et al*. 2021
COOHQ, NH_2Q	Nano Fe_3O_4	Modified nano Fe_3O_4 react with COOHQ and NH_2Q under sonication	Biological nitro-reduction	NACs (0.1 mM)	Reduction rates were 2.2- to 6.5-fold higher than controls	Zhang and Hu 2017
AQ, CAQ, DCAQ, TCAQ	CA	RMs were mixed with CA and acetone, and then were stirred under ultrasonication until equilibrium	Bio-reduction and denitrification	Cr(VI), NO_2^-–N (110 mg L^{-1})	Cr(VI) and NO_2^-–N reduction rates increased 4.5- and 2.3-fold, respectively	Lian *et al.* 2016; Li *et al*. 2014
Lawsone	GAC	Chemical adsorption until equilibrium	Decolorization	CR (175 mg L^{-1})	Decolorization rate increased 4.6-fold	Olivo-Alanis *et al*. 2018

RF	MC	MC was firstly thermal/chemical modified and then used to adsorb RF	Decolorization	RNL (50 $mg\ L^{-1}$)	Zero order decolorization rate was 56% higher than the control	Martins *et al.* 2015
(i)-leonardite HS	AER amine type 1, resin	HS with sulfonate groups serving as linking functional groups between quinones and the carrier	Decolorization and dehalonation	CT (40.7 μM) and RR2 (0.3 mM)	Reduction rates of CT and RR2 increased 4-fold and 2-fold, respectively	Cervantes *et al.* 2011, 2013; Martínez *et al*. 2013
FA	Alumina particles	Chemical adsorption until equilibrium	Dechlorination	CT (50 μM)	Dechlorination rate increased 10.4-fold	Alvarez *et al*. 2012
ABTS	MOF	Co-immobilized laccase and mediator based on MOFs membrane	Dechlorination	MG, AG, MO	Decolorization rate increased up to 62%	Lou *et al*. 2023
TEMPO	Magnetic Fe_3O_4 nanoparticles	Co-immobilization of laccase and TEMPO on Fe_3O_4 nanoparticles	Decolorization	AF	Decolorization rate was up to 77.41%	Gao *et al*. 2018
TEMPO	PSB	Adsorptive immobilization	Selective oxidation	Alcohols	Complete conversions and reused for more than 10 times	Di and Hua *et al.* 2011
TEMPO	PVAm	Grafting	Oxidization of C6 hydroxyl to aldehyde groups	Cellulose	High oxidation activity	Pelton *et al*. 2011

Note: AER: Anion exchange resins; ABTS: 2,2-Azino-bis-3-ethylbenzothiazoline-6-sulfonic acid; AF: Acid Fuchsin; AG: Alizarin green; AO7: Acid orange 7; AQ: Anthraquinone; AQDS: Anthraquinone-2,6-disulfonate; AQS: Anthraquinone-2-sulfonate; AR 27: Acid red 27; AY 36: Acid yellow 36; CA: Calcium alginate; CAQ: Chloroanthraquinone; COOHQ: 2-carboxyl-anthraquinone; CR: Congo red; CT: Carbon tetrachloride; DCAQ: Dichloroanthraquinone; FA: Fulvic acid; GAC: Granular activated carbon; HS: Humic substances; MC: Microcrystalline cellulose; MG: malachite green; MO: Methyl orange; MOF: metal–organic framework; MONPs: Metal-oxides nanoparticles; NACs: Nitroaromatic compounds; NB: Nitrobenzene; NH_2Q: 1,4-diaminoanthraquinone; NQS: 1,2-naphthoquinone-4-sulfonate; PSB: porous silica beads; PUF: Polyurethane foam; PVAm: Polyvinylamine; RF: Riboflavin; RNL: Remazol golden yellow; RR2: Reactive red 2; TCAQ: Tetrachloroanthraquinone

Solid Carbon Materials and their Modification

Solid carbon-based materials can be derived from carbon-enriched substances including coal, petcoke, resin, and agricultural/forestry residues. The commercially available carbon materials include powdered activated carbon, activated carbon felt, carbon paper, carbon nanotubes, graphene oxide (GO), graphite electrodes, and so on. These carbon materials were associated with functional groups of carboxyl, quinone, carbonyl, lactone, hydroxyl, and carboxylic anhydride in their surface, enhancing the reductive biotransformation of various oxidized pollutants by improving electron shuttling ability (van der Zee *et al*. 2003; Pereira *et al*. 2014; Colunga *et al*. 2015; Amezquita-Garcia *et al*. 2016). However, the density of these active groups of solid carbon materials is at a relatively low level, limiting the electron-shuttling rates during the pollutant removal processes. Thus, carbon materials can slightly enhance pollutant removal (maximally 3.7-fold over the control) in chemical and/or biological decolorization, denitrification, anammox, and NAC reduction processes. Although GO and reduced graphene oxide (rGO), with proper size distribution, unique spatial structure, and better redox potential, lead to a higher redox conversion of oxidized pollutant (up to 10-fold), they are costly for full-scale applications (Yin *et al*. 2015; Colunga *et al*. 2015; Li *et al.* 2016b).

In consideration of the above drawbacks, researchers have attempted to selectively modify the surface chemistry of carbon materials to promote the richness of desired groups and thereby develop the electron-transferal capacity for contaminants removal (Li *et al*. 2016a). Thermal (heat), chemical (acidic and alkaline/basic treatments), electrochemical, and biological (bio-adsorption) modification methods are typically used to change the surface characteristics of carbon materials, depending on their group features (acidic, basic, and/or neutral) (Yin *et al*. 2007). Research studies regarding different modification methods to fix RMs are briefly summarized in Table 3. For example, Pereira *et al*. (2010) compared chemical oxidation (with HNO_3 and O_2) and thermal treatments (in an H_2/N_2 atmosphere) in modifying the surface chemistry of commercial AC, suggesting that chemical modification introduced more quinone groups than did thermal treatments. In this case, the first-order reduction rate constants of azo dyes increased by 9.0-fold compared with the control treatment. Further, a two-step procedure consisting of amination and the Buchwald–Hartwig reaction was also developed to immobilize quinone-based RMs, efficiently mediating the reductive removal of azo dyes, nitrate, and NACs (Zhang *et al*. 2014b; Xu *et al*. 2015).

Table 3. Immobilization of RMs by Surface Modification and Their Applications

Functional RMs	Supports	Procedures	Catalyzed Processes	Target Pollutants	Results	References
AQS	PETFC	Two-step modification procedure consisting amination and cross-linking	Biological decolorization and NACs-reduction	AR, RR2, AY36, CNB, NB (0.7 to 1.0 mM), NO_3^--N	Removal rates were about 1.6 to 3.7-fold higher	Zhang *et al*. 2014b
AQS	ACF/PPy	PPy composites with AQS were prepared by galvanostatic polymerization at ACF electrode	Denitrification, decolorization, NACs-reduction	NO_3^--N (200 to 700 mg N L^{-1}) ,KE-3B (100 mg L^{-1}), NB, DNT	The denitrification and decolorization rates increased 1.5-fold and 3-fold, respectively; NAC reduction rate increased by one order of magnitude	Li *et al*. 2008; Jing *et al*. 2009; Li *et al.* 2009; Liu *et al*. 2012a
AQDS	Graphite/ PPy	As above but doped with graphite	Electro-Fenton decolorization; Denitrification	Amaranth azo dye (80 mg L^{-1}); NO_3^--N (20 mg N L^{-1})	Dye removal (complete mineralization) achieved 80.3%; stable NO_3^--N removal (＞90%)	Zhang *et al*. 2008; Zhai *et al*. 2022
AQDS	ACF/PPy	AQDS/electropolymerization-modified anode in an MFC system	Bioelectricity generation and RR2 decolorization	RR2 (0.3 mM)	High power density (816 to 1303 mW m^{-2}) and RR2 decolorization (92 ± 1.5%)	Feng *et al*. 2010; Martinez *et al*. 2017;
AQDS	PEI-modified GF anode	GF were dipped in PEI methanol solution to form PEI-coated GF, and then was	Bioelectricity generation	Modified GF	Stable and high energy output (2000 to 4000 mW cm^{-2})	Adachi *et al*. 2008

		subjected to cross-linking with AQDS				
RF and AQDS	CP cathode	CP was used for PNT/RMs modification by a layer-by-layer assembly method	Electrocatalytic reduction	AO7 (100 mg L^{-1})	Decolorization rates increased 1.3-fold; power density increased 4.7-fold	Xu *et al*. 2017
RF	GE	GE was modified by immersing it into a pH 6.1 buffer containing 0.1 mM RF until equilibrium	Reduction of hemoglobin (Hb)	Hemoglobin (HbFe^{3+})	The immobilized RF shuttled electrons between HbFe^{3+} and graphite electrode	Sun *et al.* 1997
RF and HA	GF	Electrodepositing with RF and HA on the surface of MFC anodes	Decolorization	CR (300 mg L^{-1})	High CR decolorization (86%) in 16 h	Huang *et al*. 2017
CAs	PET	Two-step modification procedure consisting amination and cross-linking	Heterotrophic denitrification	NO_3^--N (200 mg N L^{-1})	High denitrification rate constant (175.64 h^{-1})	Xu *et al*. 2015
PD	GRE	Dropping PD on GRE to be covered by GOx, and the modified PDs/ GOx/ GRE was stored in glutaraldehyde solution	Glucose biosensor	Electrode (--)	Immobilized PDs can efficiently shuttle electrons between the active center of GOx and the GRE	Zor *et al*. 2016
CNTs	CP/PPy	CP anode was prepared by spraying PPy-coated CNT, which was synthesized by *in-situ* polymerization	Bioelectricity generation in MFC	Cathode: potassium hexacyanoferrate (100 mM)	The maximum power density (228 mW m^{-2}) was several times higher than control	Zou *et al.* 2008
NR, MV	PANI	RMs-modified electrodes were prepared by electropolymerization	Electro-synthesis	CO_2	Biofuel production from CO_2 increased 18%	Anwer *et al*. 2021

Note: ACF: Activated carbon fiber; AR: Acid red; AQDS: Anthraquinone-2,6-disulfonate; AQS: Anthraquinone-2-sulfonate; AY 36: Acid yellow 36; CAs: Chloroanthraquinones; CF: Carbon fiber; CNB: chloronitrobenzene; CNT: Multiwall carbon nanotubes; CP: Carbon paper; CR: Congo red; DNT: 2,4- and 2,6-dinitrotoluene; GE: Graphite electrode; GF: Graphite felt; GOx: Glucose oxidase; GRE: Graphite rod electrode; HA: Humic acid; Hb: Hemoglobin; KE-3B: Reactive red 120; MV: Methyl viologen; NB: Nitrobenzene; NR: Neutral red; PANI: polyaniline PD: 1,10-phenanthroline-5,6-dione; PEI: Polyetherimide; PET: Polyethylene terephthalate; PETFC: Poly(ethyleneterephthalate) fiber cloth; RF: Riboflavin; PNT: Peptide nanotube; PPy: Polypyrrole; RR2: Reactive red 2

In (bio)electrochemical systems, electrodeposition, adsorption, and crossing-linking have been successfully applied to prepare RM-modified electrodes for use in MFC and microbial electrolysis cell (MEC) systems; which in turn benefit the electron-transferal during redox reactions, enhancing the bioelectricity generation, pollutant removal, and energy storage (Table 3). In addition, electropolymerization has been used to increase the required density of electron shuttling groups on the surface of carbon materials or functional composites. This method is usually a coating procedure to enable a conducting polymer to be fixed or deposited into a conducting material from a solution, which was previously used in the enzyme immobilization (such as encapsulating glucose oxidase electrochemical biosensors) by choosing a defined electrical potential and current (Chiorcea-Paquim *et al.* 2008). When applying the electropolymerization to immobilize RMs on an electrode, attempts have been made to coat polymer materials, such as polypyrrole and pyrrole, on a carbon electrode by doping designed RMs. This polymer/RMs composite film has a vast surface area and pseudo-capacitance, which has aroused great interest in its application in electricity-assisted or electricity-produced systems (Lang *et al.* 2010; Anwer *et al.* 2021). Regarding the interest in RMs to enhance pollutant removal, this composite film can also promote the functional group density and prevent the wash-out of RMs from systems. Compared to the entrapped AQDS/PVA particles, AQDS/electropolymerization-modified anode in an MFC system shows better performance in both electricity generation and pollutants removal (Martinez *et al*. 2017).

Natural and Bio-resourced Redox Mediator

The previously mentioned RM immobilization technology has enabled the separation of RM retention time from hydraulic retention time in environmental applications. However, the complex procedures of these immobilization processes, the time-consuming lab work to select suitable process conditions and unaffordable carriers always limited their wide applications (Rocha-Martín *et al*. 2021; Wang *et al*. 2021). To overcome these raised issues, data-driven approaches such as machine learning algorithms have been attempted to predict and optimize those complex procedures and to obtain feasible immobilization conditions (Shi *et al*. 2022). Moreover, some natural biomass and/or their derivatives such as biochar would be expected to be good and low-cost alternatives because of the renewable raw materials. The reported uses of these materials, i.e., natural biomass and bio-resourced derivates in facilitating pollutant removal are shown in Tables 4 and 5, respectively.

Henna plant (*Lawsonia inermis*) biomass (HPB) has been reported to be a natural source of lawsone (an effective RM), with lawsone comprising up to 1.8% of the plant’s dry weight (Almeida *et al*. 2012). Previous studies indicated that natural HPB, including stem, leaf, flower, and seed, could serve as both an electron donor and RM source to improve the bio-reduction of azo dyes and Cr(VI) in batch and continuous bioreactors, all showing positive effects of HPB on pollutants removal (Huang *et al*. 2014, 2015, 2016a 2021; Tang *et al.* 2016; Rau *et al.* 2002). Moreover, HPB could be co-fermented with waste sludge in municipal wastewater treatment plants and enhance the production of VFAs (Huang *et al*. 2016b). As a protein-rich biomass, waste sludge could be firstly hydrolyzed to amino acid, and then converted to carboxylic acid and NH_4^+-N by the Stickland redox reaction (Huang *et al*. 2019). The associated RM of lawsone in HPB could speed up the transfer of electron from one amino acid to another, resulting in higher VFAs production. Moreover, another waste biomass of *Punica granatum* peal was also approved as a natural RM to efficiently degrade orange G dye (Bibi *et al*. 2019). In contrast, some extractions from plant biomass or algae, such as chlorophyll, laccase, syringaldehyde, and acetosyringone, were also reported to serve as natural RMs for enhanced denitrification, decolorization, and electricity generation (Ma *et al.* 2017; Mani *et al.* 2018; Lu *et al.* 2020; Song *et al.* 2021). Furthermore, a novel biomass-derived lignin with electron transfer 3D networks was developed to act as cathode interlayer, achieving high-efficient performance of solar cells (Hu *et al.* 2020). However, raw plant biomass or its extractions without proper treatment can cause problems such as secondary pollutants (*e.g.*, organic substances lost from biomass as well as wash-out of associated RMs). To address these problems in engineering applications, researchers have suggested that natural biomass could be prepared as biochar to retain or modify most of the active electron transferral groups.

Table 4. Natural Biomass Acting as Redox Mediator

RMs Sources	Funtional Group	Reaction	Target Pollutants	Results	References
HPB	Associated lawsone	Decolorization	AO7 (0.69 to 1.9 mM)	AO7 reduction rate enhanced ~6-fold in batch reactors, and AO7 reduction rate constant increased ~7-fold in UAF	Rau *et al.* 2002; Huang *et al.* 2014, 2015; Tang *et al*. 2016
HPB	Associated lawsone	Bio-reduction	Cr(VI) (90 ± 10 mg L^{-1})	Average Cr(VI) removal rate achieved 2.04 mg L^{-1} h^{-1}	Huang *et al*. 2016a, 2021
HPB	Associated lawsone	Stickland redox reaction	Amino acids	VFAs production in (co-)fermentation system increased to 2.6-fold	Huang *et al*. 2016b, 2020
Punica granatum	*P. granatum* peel extracts	Decolorization	Orange G (100 mg/L)	Orange G removal increased from 61% to 97%	Bibi *et al.* 2019

Note: AO7: Acid orange 7; HPB: Henna plant biomass

Biomass-resourced derivatives including biochar and natural HS are listed in Table 5. Biochar is a porous bio-resourced carbon material that has rich functional groups and can be widely obtained from natural biomass, especially cellulosic, hemicellulosic, and lignin agricultural and forestry residues. The biochar is usually prepared *via* pyrolysis, forming graphitized structure and redox active sites (functional groups such as quinone groups) in its surface, and is functioned as extracellular electron mediation for pollutant removal, contamination transformation, and *in-situ* remediation (Chen *et al*. 2019; Zhang *et al*. 2020; Fang *et al*. 2020; Yuan *et al.* 2022). Pyrolytic temperature, heating rate, and holding time are the effective impactors for shaping surface properties of biochar. The electron transfer/exchange capacity (EEC) and hydrophilicity of biochars prepared under different conditions were significantly varied. Although higher pyrolytic temperature (700 to 800 °C) can improve the hydrophobicity, the density of electron transfer groups, such as quinone groups, on the biochar surface decreased, resulting in weakened EEC for redox process (Oliveira *et al.* 2017; Yuan *et al.* 2017). In contrast, lower pyrolytic temperature (300 to 600 °C) could enrich the functional mediating groups for the reduction of hydrophilic contaminants (Zhao *et al.* 2018; Zhang *et al.* 2022); however, the surface hydrophobicity decreased, which is unfavorable for the removal of hydrophobic contaminants (Xu *et al.* 2020). Therefore, optimizing the pyrolytic temperature is an effective method to regulate the surface hydrophilic/hydrophobicity and electron transfer capability of the designed biochar, targeting the fast and efficient transformation of specific contaminants.

Natural humic substances (HS), derived from dead biomass underground through thousands of years, is another bio-resourced RM usually containing redox functional groups (carboxylic or phenolic groups) that facilitate the electron transfer process (Guo *et al.* 2018). Natural HS is vastly present in the soil, sedimentation, and natural water environment (Yang *et al*. 2021), implying an inexpensive but promising method for *in-situ* remediation and elimination of biorefractory pollutants (Table 5).

Table 5. Bio-resourced Derivatives Acting as Redox Mediator

RMs Sources	Funtional Group	Reaction	Target Pollutants	Results	References
Biochar derived from peanut shell, corn straw, modeling cellulose/hemicellulose/lignin	Carboxylic, phenolic, and quinone groups	Cr(VI) reduction	Cr(VI)	Reduction rates increased up to 345 times	Zhao *et al*. 2018; Xu *et al*. 2020; Zhang *et al*. 2022
Bamboo and sawdust biochar	Superficial quinone group	Anammox, denitrification	NH_3-N, NO_3^--N	Increased the nitrogen removal and anammox bacteria up to 16.4% and 82.6%, respectively	Li *et al*. 2022b; Wang *et al*. 2022
Bamboo biochar	Superficial quinone group	Decolorization	MO	Decolorization increased by 93%	Ren *et al*. 2022
HS from Soil	Carboxylic or phenolic groups	Dechlorinating, denitrification	PCB_{153}, NO_3^--N	Enhanced the reduction rates	Guo *et al*. 2018
HS-metal	Carboxylic or phenolic groups	Biological deiodination	Iopromide (400 μg L^{-1})	UASB metal–HS achieved 80% removal of iopromide, as compared with 31.6% in the control.	Cruz-Zavala *et al*. 2016

Note: HS: Humic substance; UASB: Up-flow anaerobic sludge bed reactor; UAF: Up-flow anaerobic filter; MO: Methyl orange; PCB_{153}: 2,2′,4,4′,5,5′-hexachlorobiphenyl

Moreover, HS has even been reported to accelerate the acidification step during the fermentation process and to decrease (or even halt) the activities of acetotrophic methanogens by inhibiting the key bio-reaction of acetyl-CoA → 5-methyl-THMPT (Liu *et al*. 2015), preventing the electron sink to methane (CH_4). Thus, the presence of HS in anaerobic condition potentially mitigates the release of greenhouse gases, such as CH_4, contributing to the carbon neutralization society (Zhang *et al.* 2020). However, as a typical NOM, HS is a precursor of carcinogenic disinfection byproducts, limiting its application in aquatic systems (Krasner *et al*. 2009). This provides motivation for the immobilization of them on insoluble carriers, which has been mentioned earlier (Table 2). Moreover, insoluble humic-mineral complexes have also been demonstrated to be effective solid-phase RMs that fulfill the electron-mediating function during the reductive transformation of poly-halogenated contaminants (Zhang *et al*. 2014a; Cruz-Zavala *et al.* 2016).

CONCLUSIONS AND FUTURE PERSPECTIVES

The immobilization of soluble redox mediators (RMs) on inert carriers is a promising environmental technology to promote biorefractory pollutant removal and bioelectricity generation by speeding up the electron transfer. The RMs have been found to enable the reuse of redox mediators in scaled-up engineering applications and *in-situ* remediation. This article reviewed the currently reported RM-immobilizing technologies such as entrapment, adsorption, and surface modification. Entrapment entails the physical fixation of soluble RMs into a polymeric matrix; adsorption concentrates soluble RMs into special solid materials; and surface modification involves chemical, thermal, and electro-chemical modification of specific materials to enhance functional groups that are responsible for electron shuttling. Furthermore, renewable natural and biomass-derived RMs, such as biochar, containing functional groups that transfer electrons, were also included in this review.

However, the immobilization procedure of RMs is still complex and expensive, requiring the process optimization and techno-economic analysis when using specific immobilizing methods and carriers. Although the use of natural RMs or some biomass derivatives, such as biochar, could reduce the operational costs, the densities of functional groups are at a low level. Moreover, properties of natural RM or biochar are varied from different areas, requiring extensive experiments to select suitable ones and their optimal preparation conditions for the effective transformation of specific contaminants. At present, data-driven approaches, such as machine learning algorithms, have been widely applied to assist research results towards engineering applications. In future work, to reduce the labor-consuming and repeated experiments, powerful machine learning algorithms are suggested to aid the design/selection of RM immobilization procedures, feasible carriers, and optimal operating parameters.

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