Journal of Hazardous Materials 168 (2009) 1098–1104

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Enhanced biodecolorization of azo dyes by electropolymerization-immobilized redox mediator

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ARTICLE INFO

Article history:
Received 18 November 2008
Received in revised form 25 February 2009
Accepted 27 February 2009
Available online 13 March 2009

Keywords:
Azo dyes
Biodecolorization
Electropolymerization
Solid redox mediator
Activated carbon felt
Polypyrrole

ABSTRACT

The biodecolorization rate of azo dyes can be improved by the addition of some soluble quinoid redox mediators, but continuous dosing and discharge of these mediators will result in the secondary contamination due to their recalcitrant trait. In this study, the effect of anthraquinone-2,6-disulfonate (AQDS) bound into polypyrrole (PPy) on activated carbon felt (ACF) on anaerobic biodecolorization of azo dyes was investigated and compared with that immobilized on platinum (Pt). The results showed that in the presence of AQDS/PPy/ACF, the biodecolorization efficiency of azo dye RR15 reached over 80% at the optimal pH 7 in 8 h and kept stable during successive 10 times repeated experiments. In contrast, in the presence of AQDS/PPy/Pt biodecolorization efficiency of RR15 was less than 60% under the above conditions, and the PPy doped by AQDS desquamated from the substrate material Pt at the third biodecolorization experiment. In addition, in the presence of AQDS/PPy/ACF biodecolorization efficiencies of 5 reactive dyes, 4 acid dyes and 2 direct dyes increased more than 3-fold than that without AQDS. This indicates that electropolymerization-immobilized AQDS (AQDS/PPy/ACF) has potential applications in accelerating the anaerobic biodecolorization of azo dyes.

1. Introduction

Dyes were widely used in a number of industries such as textile, food, cosmetics and paper printing. It was reported that approximately 10–15% of the dyes are released into the environment during manufacturing and usage [1]. Among these dyes, azo dyes account for more than 50% of dyes, and they generally resist biodegradation in conventional activated sludge treatment due to their xenobiotic nature [2]. One effective strategy for the biological treatment of azo dyes is the anaerobic/aerobic sequential treatment. Under anaerobic or anoxic conditions, azo dyes are initially reduced to corresponding colorless aromatic amines, which are further mineralized aerobically [2]. The anaerobic decolorization of azo dyes is usually the rate-limiting step, especially for highly polar sulfonated and/or polymeric azo dyes having limited membrane permeability [3]. It has been demonstrated that humus and some quinone compounds such as anthraquinone-2,6-disulfonate(AQDS) can function as redox mediator and significantly accelerate anaerobic biotransformation of many biologically recalcitrant organic compounds (e.g. azo dyes, nitroaromatics, chlorinated aromatics). In this system the quinones are reduced by the quinone reductase located in the cell membrane and the hydroquinones formed reduce azo dyes in a purely chemical redox reaction [3,4].

However, continuous dosing of the redox mediators implies continuous expenses related to procurement of the chemical as well as continuous discharge of the biologically recalcitrant redox mediators, resulting in the secondary contamination. Thus, it is expected that redox mediator such as AQDS can be effectively immobilized and used in bioreactor. It was reported that activated carbon as a possible solid redox mediator containing surface quinone structures can accelerate azo dye reduction in lab-scale upflow anaerobic sludge bed reactors (UASB) and upflow packed-bed reactors (UPBR) [5,6]. Aside from activated carbon, Guo et al. [7] used entrapment-immobilized anthraquinone as redox mediators. A 0.5–1-fold increase in azo dye decolorization rate by salt-tolerant bacteria was observed.

Recently, it has been demonstrated that the electrodes modified with polypyrrole (PPy) doped by quinones exhibit excellent electrocatalytic activities as well as remarkable stability compared with those modified with spontaneously adsorbed monolayer of quinones [8]. Therefore, the PPy matrix with the characteristics of harmlessness and good environmental stability could be used as a good carrier for immobilizing AQDS. Activated carbon felt (ACF) consists of randomly dispersed fibers with three-dimensional structure, moderate hydrophilic character and high porosity. Moreover, ACF has a good affinity for biological film, and is an excellent

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doi:10.1016/j.jhazmat.2009.02.152

carrier of microorganism's growth [9]. Thus, active carbon felt (ACF) was chosen as the substrate material of AQDS-doped PPy, and AQDS/PPy/ACF prepared using the electrochemical polymerization-doping method was proposed as a novel immobilized redox mediator for the anaerobic reduction of recalcitrant pollutants. Our previous study indicated that AQDS/PPy/ACF can effectively accelerate the anaerobic biotransformation of the nitroaromatic compounds, such as nitrobenzene, 2,4- and 2,6-dinitrotoluene, to corresponding aromatic amines with over 4-fold increases in rate constants [10].

In this study, the effect of AQDS/PPy/ACF on the biological decolorization of azo dyes was investigated and compared with that of AQDS/PPy/Pt.

2. Materials and methods

2.1. Chemicals

The chemical structures of azo dyes used in this study were shown in Table 1. All the dyes were purchased from Tianjin Tianshun Chemical Co., Ltd. Anthraquinone-2,6-disulfonic disodium salt (AQDS) was purchased from Sigma Co., Ltd. Pyrrole (Py) monomer (Aldrich, 99%) was used after twice distilled. All solutions were prepared using deionized water and purged with nitrogen before use.

2.2. Activated sludge, media and culture conditions

Three kinds of original sludge were taken from Dalian Chunliu river wastewater treatment plant, Dalian petrochemical company wastewater treatment plant and black sediment derived from Dalian Xishan reservior, respectively. The mixture (1:1:1) of three kinds of sludges was used as seed inoculum for the enrichment of AQDS-reducing community, which was then maintained at 4 °C under anaerobic conditions before use.

The growth medium consisted of (g L^{-1}): $NaHCO_3$, 0.71; NH_4Cl, 1.0; KH_2PO_4, 0.5; K_2HPO_4, 0.6; $MgCl_2{\cdot}6H_2O$, 0.2; $CaCl_2{\cdot}2H_2O$, 0.05; $Na_2S{\cdot}9H_2O$, 0.037; glucose, 0.5; AQDS, 0.15. The decolorization medium contained the same compositions as the growth medium without the addition of AQDS. The pH of both mediums, respectively, was adjusted to pH 7.0 unless otherwise stated.

2.3. The preparation of AQDS/PPy/ACF

Adhesive-base ACF (800 m^2 g^{-1}, 4 mm thick) was kindly provided by Anshan Senxin Activated Carbon Fiber Plant, China. The electropolymerization of Py was performed in a conventional three-electrode system with three-compartment electrochemical cell. The central one was working electrode compartment, in which there were 100 mL of aqueous solution containing 0.1 M Py and 0.24 M AQDS, and a sheet of activated carbon fiber (2 cm × 2 cm) as working electrode. Auxiliary electrode compartment was connected and separated by cation selective membrane with working electrode compartment, in which there were 100 mL 0.1 M H_2SO_4 solution and a platinum plate (1 cm × 1 cm) used as counter electrode. The reference electrode, a KCl-saturated calomel electrode (SCE) was placed in the third compartment and was connected with working electrode compartment by salt bridge. All the composites used in batch anaerobic biological experiments were prepared under galvanostatic mode (1.79 mA cm^{-2}) with the reaction time of 1 h unless otherwise stated, and controlled by a 263A potentiostat-galvanostat (Princeton, NJ, USA). The composites were twice cleaned using distilled water and kept in distilled water saturated with high purity N_2 gas before use.

2.4. Enrichment of AQDS-reducing community

A homogeneous sample (50 mL) of the sludge suspension was smashed by glass beads (diameter of 0.6–0.8 mm). Then the homogeneous sample (5 mL) of the smashed suspended sludge was added into 135-mL serum bottles containing 130 mL sterilized growth medium and sealed with butyl rubber stoppers. After 5 days of cultivation at 30 °C in anaerobic incubator, complete reduction of AQDS occurred. And then the cell suspension was further transferred several times to fresh growth medium. After 1 month of enrichment and screening, the efficient AQDS-reducing community was obtained for this study. Cells were harvested by centrifugation (10 min, 8000 rpm) and resuspended in 0.1 M phosphate buffer (pH 7.0). Then the cells were washed with the same buffer twice and finally suspended in the buffer to obtain condensed cell suspensions with a final concentration of 120 g L^{-1} (wet weight).

2.5. Batch decolorization experiments

All batch decolorization experiments were conducted in 135 mL glass serum bottles. The different azo dyes (initial concentration of 100 mg L^{-1}) and cell suspensions were added using sterilized syringe under anaerobic conditions with a final cell concentration of OD_{660} = 0.4. Then the serum bottles were filled with the decolorization medium, and sealed with butyl rubber stoppers, and then statically cultured at 30 °C. In the presence of a sheet of AQDS/PPy/ACF, Na_2SO_4/PPy/ACF and AQDS/PPy/Pt, respectively, which was immerged in the medium, azo dye reduction was monitored. Control experiments without microorganism were performed. Successive repeated experiments were conducted to evaluate the catalytic stability of AQDS/PPy/ACF. Decolorization efficiency (r) was expressed as the percentage of azo dye reduction (%) = $(A_0 - A_t)/A_0 \times 100\%$, where A_0 and A_t are the dye concentrations at time zero and time t (h) respectively. In this study, the time t was set as 8 h. A pseudo first-order model could be applied to describe the kinetics of azo dye biodecolorization. The equation was as followed $A_t = A_0 e^{-kt}$. The first-order rate constant k (h^{-1}) was determined.

All experiments were performed in triplicate and the mean values of data were presented.

2.6. Analytical methods

The morphology of the PPy composites was observed using a Philips XL-30 scanning electron microscope.

Cell concentration was determined by optical density (OD) at 660 nm, and cell wet weight (g L^{-1}) = 2.8005OD_{660} + 0.029 (R^2 = 0.9978). The concentrations of azo dyes were also determined by monitoring changes at the corresponding maximum visible absorption wavelength using a UV–visible spectrophotometer (V-560, JASCO, Japan).

3. Results and discussion

3.1. Effect of substrate materials on morphology of AQDS/PPy

It has been demonstrated that AQDS was incorporated into PPy as doping species according to the characteristic absorption band (1669 cm^{-1}) of highly conjugated C=O groups in the infrared spectroscopy spectra of both AQDS/PPy and pure AQDS [10]. In this study, the morphology of PPy electropolymerized on ACF and Pt for 1 h, respectively, was observed using SEM (Fig. 1). It is evident that some microballs and cluster of grains appeared on the randomly dispersed netting fibers which became thicker and coarser as the increase of the amount of PPy deposited on. With the decrease of space between the fibers, the specific surface area of PPy/ACF would

Table 1
The chemical structures of azo dyes.

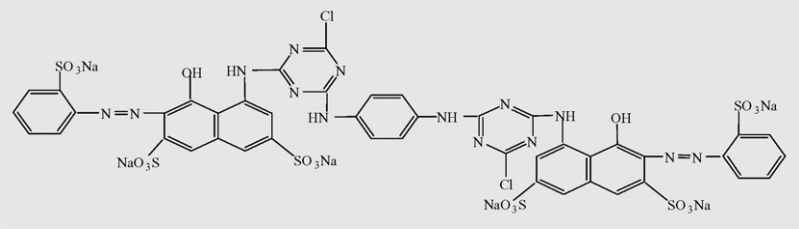
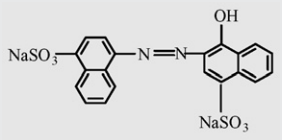
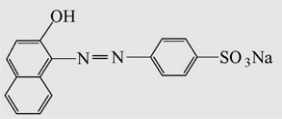
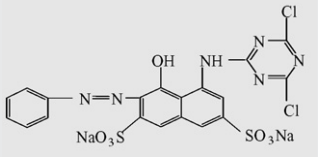
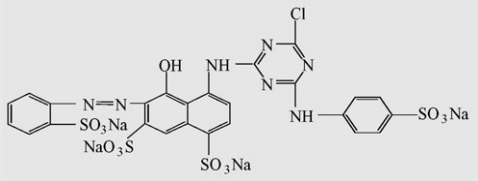
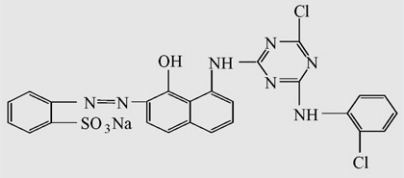
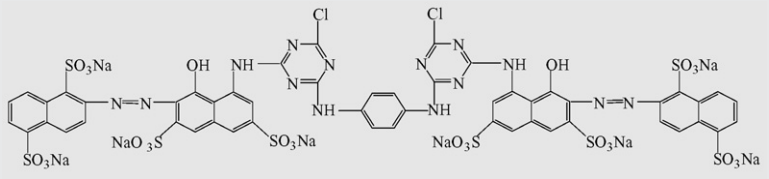
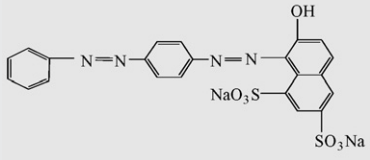
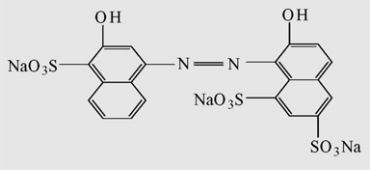
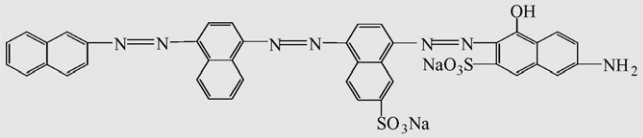
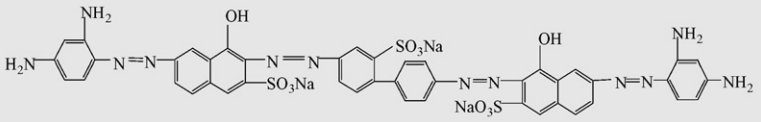
Azo dyes	Structures	λ_{max} (nm)
Reactive Red 120 (RR120)		513
Acid Red 14 (AR14)		522
Acid Orange 7 (AO7)		484
Reactive Red 2 (RR2)		538
Reactive Red 15 (RR15)		535
Reactive Red 24 (RR24)		535
Reactive Red 141 (RR141)		545
Acid Red 73 (AR73)		512
Acid Red 18 (AR18)		507

Table 1 (*Continued*)

Azo dyes	Structures	λ_{max} (nm)
Direct Blue 71 (DB71)		582
Direct Black 22 (DB22)		589

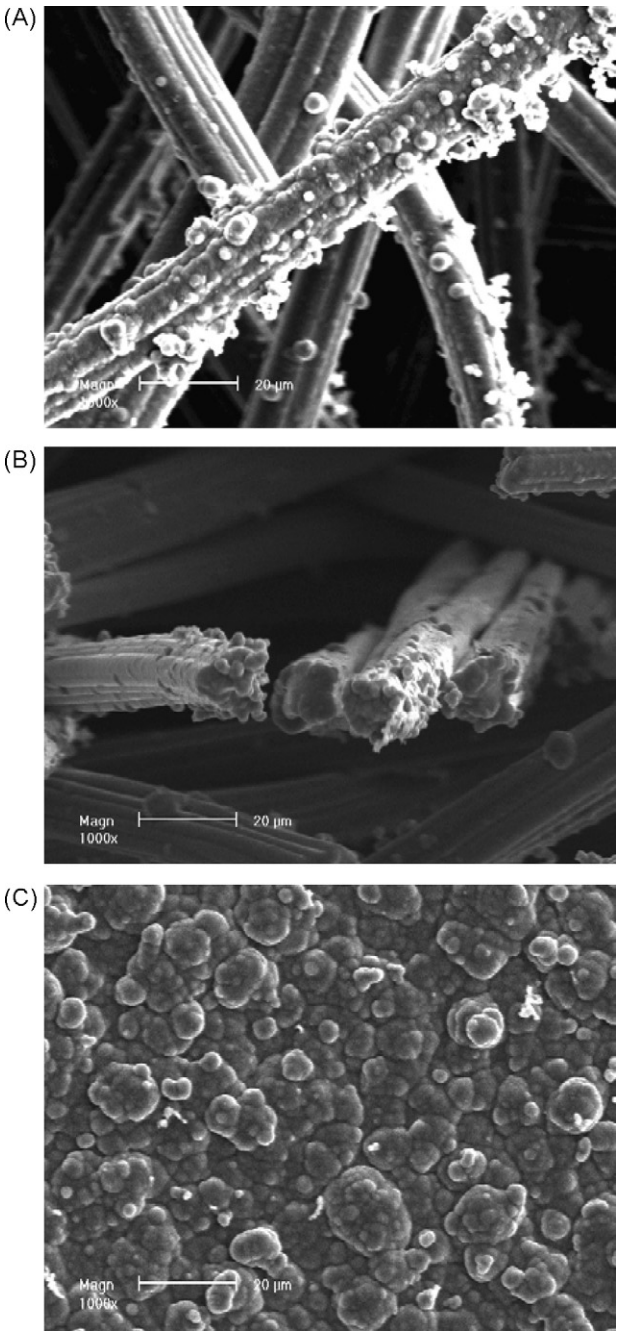


Fig. 1. SEM photos of PPy deposits on different substrate materials. (A) ACF, (B) ACF (transects) and (C) Pt.

reduce. Fig. 1(A) indicates that PPy deposited on ACF are not uniform since branches are observed at different location away from the surface. This may be due to the rough surface of the ACF. The PPy also deposited on the transects of ACF was shown in Fig. 1(B), which increased the amount of PPy exposed to outer circumstances.

In contrast, the PPy deposited on Pt are homogeneous, thick, compact and their surfaces are characterized by a cauliflower-like structure as shown in Fig. 1(C). Based on the above results, it was concluded that the morphology of the PPy mainly depended on the surface texture of substrate materials.

3.2. Performance of AQDS/PPy/ACF for RR15 biodecolorization

The anaerobic decolorization of 100 mg L^{-1} RR15 in the presence of AQDS/PPy/ACF was shown in Fig. 2. Only less than 0.5% decolorization occurred in microorganism-free controls. This indicated that the effect of RR15 adsorption to AQDS/PPy/ACF was negligible. RR15 reduction by the AQDS-reducing community without redox mediator followed a first-order reaction with respect to the dye concentration, and its decolorization rate was very low ($k = 0.075\ h^{-1}$). The addition of AQDS greatly accelerated RR15 biodecolorization. For instance, when supplied with 0.1 mM AQDS, the decolorization rate ($k = 0.26\ h^{-1}$) was about 2.5-fold higher than that without AQDS. It is consistent with the previous reports that AQDS as an excellent redox mediator can significantly accelerate anaerobic biotransformations of azo dyes [5,11]. In this process, AQDS is reduced by microorganism and hydroquinone formed (AH_2QDS) reduce the azo dyes in a chemical redox reaction [3,4].

Meanwhile, enhanced decolorization rates were also observed in the presence of AQDS/PPy/ACF electropolymerized for 0.5 h

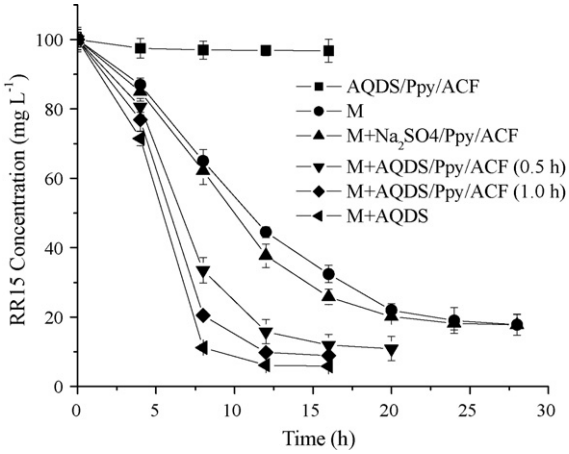


Fig. 2. Decolorization of RR15 in the presence of different electropolymerized materials at 30 °C under anaerobic conditions. M: AQDS-reducing community.

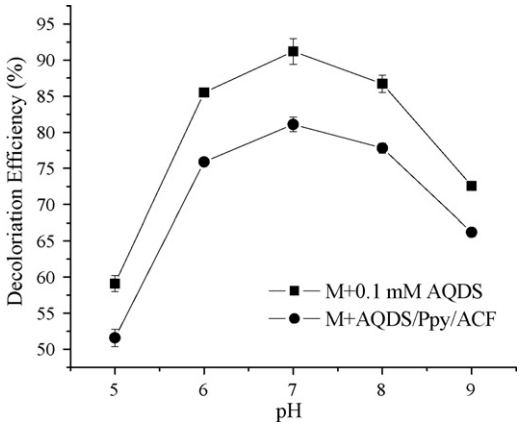


Fig. 3. Effects of pH on biodecolorization efficiency of RR15 in the presence of redox mediators in 8 h under anaerobic conditions. M: AQDS-reducing community. Initial RR15 concentration 100 mg L^{-1}, temperature 30 °C.

($k = 0.15\ h^{-1}$) and 1.0 h ($k = 0.21\ h^{-1}$), which represent increments of 1-fold and 1.8-fold, respectively. But the addition of Na_2SO_4/PPy/ACF ($k = 0.078\ h^{-1}$) had a negligible effect on the k value. These results suggested that AQDS is the active component in AQDS/PPy/ACF and AQDS-immobilizing method is effective in enhancing the decolorization rate of RR15. Moreover, the higher decolorization rates can be attributed to the larger amount of AQDS deposited on AQDS/PPy/ACF (1.0 h), as demonstrated in previous studies that the biodecolorization rate of azo dyes was enhanced with the increase of the concentration of redox mediator AQDS [5,11].

3.3. Effect of pH on RR15 biodecolorization in the presence of AQDS/PPy/ACF

The pH presents significant effects on both microbial activity and polypyrrole structure, thus the effect of pH on RR15 biodecolorization in the presence of AQDS/PPy/ACF was investigated.

The results showed that the efficiencies of RR15 biodecolorization in the presence of AQDS dissolved in solution and immobilized on ACF are both pH dependent (Fig. 3). This phenomenon is mainly related with the activities of AQDS-reducing community. In the presence of AQDS dissolved in solution, it was observed that the activities of the community exhibited better at pH 6–8 than that at over pH 8 or below pH 6, and its optimal pH was 7. Thus, in the presence of AQDS/PPy/ACF, it was also observed that at pH 6–8 biodecolorization efficiencies of RR15 reached over 75% in 8 h. Especially, at pH 7 it reached the highest (over 80%).

During in situ the electrochemical polymerization of Py, the positively charged chains of PPy are formed in general [12]. AQDS dissolved in the solution as counterion is irreversibly and covalently inserted into Py units at the N position in PPy chain [8]. Polypyrrole generally exists with oxidized state under acidic and neutral conditions (Fig. 4). This indicates that AQDS immobilized on ACF

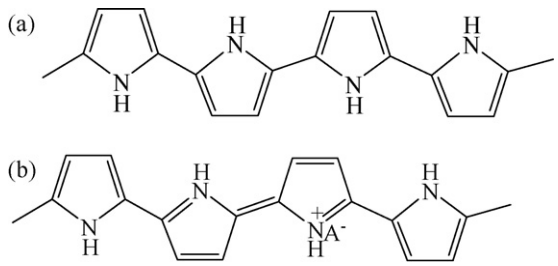


Fig. 4. Structures of reduced polypyrrole (a) and oxidized polypyrrole (b).

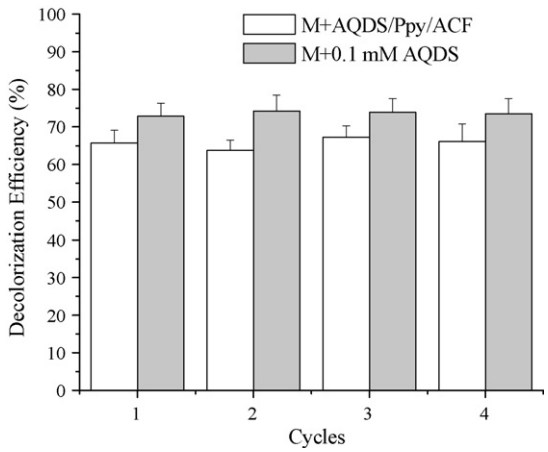


Fig. 5. Decolorization efficiencies of RR15 during repeated biological experiments under anaerobic conditions. Initial RR15 concentration 100 mg L^{-1}, temperature 30 °C, pH 9.

was stable and could not be released from PPy matrix under these conditions.

But under alkaline conditions polypyrrole exists with reduced state (Fig. 4). Especially, under stronger alkaline conditions it is possible that partial counterions (i.e. AQDS) could be released from PPy matrix, resulting in dedoping [13,14]. However, AQDS/PPy/ACF was found to exhibit reproducible biodecolorization efficiencies of RR15 during successive 4-times repeated biological experiments under pH 9 (Fig. 5). This indicated AQDS/PPy/ACF has stronger resistance for OH^- attack. It is beneficial for practical wastewater treatment with sharp pH fluctuation.

3.4. Effect of AQDS/PPy/ACF on the biodecolorization of different azo dyes

Fig. 6 showed biodecolorization of 5 reactive dyes, 4 acid dyes and 2 direct dyes after 8 h incubation (30 °C, pH 7.0) in the presence of AQDS/PPy/ACF as redox mediator. It is obvious that biodecolorization efficiencies of all tested dyes increased about 3-fold in the presence of AQDS/PPy/ACF than that without AQDS, and shortened the time reaching their maximal decolorization efficiencies by 1–3-fold (data not shown). Among these dyes, in AQDS/PPy/ACF systems, decolorization efficiencies of mono-azo and di-azo dyes reached around 80%. Moreover, for multi-sulfonic azo dyes with

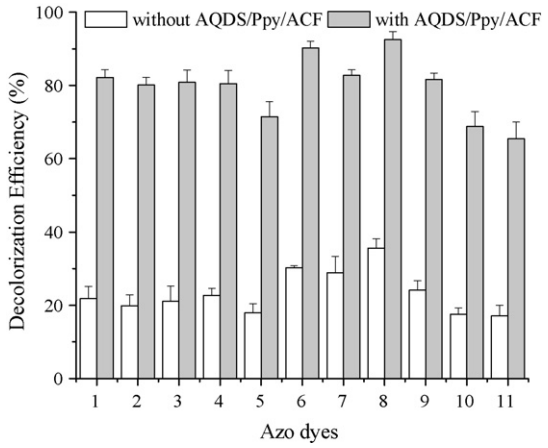


Fig. 6. Catalytic effects of AQDS/PPy/ACF on decolorization of different azo dyes in 8 h under anaerobic conditions. 1, RR2; 2, RR15; 3, RR24; 4, RR120; 5, RR141; 6, AR18; 7, AR73; 8, AR14; 9, AO7; 10, DB71; 11, DB22. Initial dye concentration 100 mg L^{-1}, temperature 30 °C, pH 7.

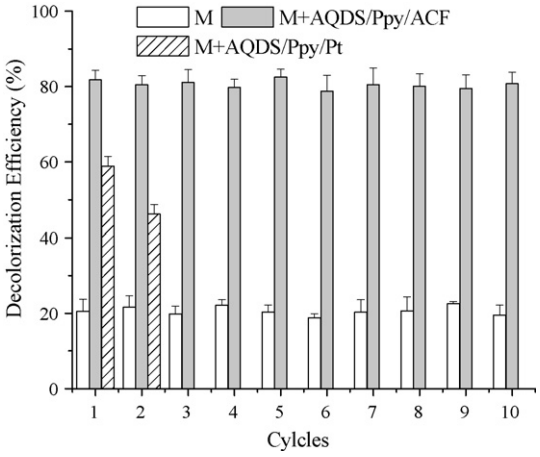


Fig. 7. Decolorization efficiencies of RR15 in the presence of AQDS/PPy on different materials during the repeated biological experiments under anaerobic conditions. M: AQDS-reducing community. Initial RR15 concentration 100 mg L^{-1}, temperature 30 °C, pH 7.

high-molecular weight, the decolorization of Reactive Red 141 (RR141), Direct Blue 71 (DB71), and Direct Black 22 (DB22) also reached over 65% in 8 h. As these azo dyes are unlikely to pass through the cell membrane, it was suggested that their bioreduction occurs extracellularly. Thus, in the presence of AQDS/PPy/ACF biodecolorization of a broad range of azo dyes could be greatly enhanced.

Recently, some intracellular azo reductases have been discovered [3,15]. However, intracellular azo reduction cannot be used for the conversation of all types of azo dyes, especially highly polar sulfonated azo dyes, as well as polymeric azo dyes with high-molecular weight, which have limited membrane permeability [3]. The extracellular reduction process of azo dyes is usually slow, but it could be significantly enhanced by redox mediators such as lawsone, riboflavin, and anthraquinone-2,6-disulphonate(AQDS)[16–18].

Fig. 6 illustrated PPy-bound AQDS can also act as redox mediator for accelerating the biodecolorization of azo dyes. It was reported that in the case of the bacterial respiration of insoluble metal oxides or anode in microbial fuel cells, two distinct pathways have been proposed, namely, the direct transfer of electrons from the cell surface and the use of low-molecular weight soluble redox mediators or "electron shuttles" to promote extracellular electron transfer [19–22]. Based on the mechanism, AQDS as the active component in AQDS/PPy/ACF is probably reduced by the redox components on the cell surface or those released from AQDS-reducing community into bulk solution, Then bioreduced AQDS (AH_2QDS) chemically reduce azo dyes.

3.5. The stability of catalytic activity

The anaerobic biodecolorization efficiency of RR15 with the AQDS/PPy deposited on different materials during the repeated experiments was investigated. Fig. 7 showed that AQDS/PPy deposited on three-dimensional ACF showed higher catalytic activity than that deposited on platinum. Moreover, it was found that the PPy desquamated from the substrate material Pt at the third experiment. Thus, it showed that substrate materials have considerable effects on the catalytic activity of AQDS/PPy and its adherence to different substrate material. As shown in Fig. 1, the more firmly PPy was adhered to the ACF, the more stable decolorization efficiencies would be obtained in terms of durability. For practical application of PPy composites, a high specific surface area is usually of the most importance as it can improve the reaction kinetics. In addition, the size (diameter) of bacteria is usually larger than 0.2 μm, thus whether bacteria can directly contact with PPy-bound AQDS and how much bound AQDS can directly contact with bacteria are the decisive factors for the decolorization rate of azo dyes. The void space between the polymers determined the amount of bound AQDS, which could be utilized by bacteria. ACF consists of randomly dispersed fibers. As there is a large and homogeneously distributed void space between the fibers (Fig. 1), the void space of the polymers deposited on the fibers of ACF was larger than that of the polymers deposited on the Pt. Obviously, a larger specific surface area and void space between the polymers of ACF would be much more beneficial to the biological reduction of AQDS.

4. Conclusions

In this study, AQDS was incorporated into polypyrrole as doping species onto ACF and Pt. The results clearly demonstrate that biodecolorization of a broad range of azo dyes was effectively improved in the presence of AQDS/PPy/ACF. Moreover, the performance of AQDS/PPy/ACF was better in terms of decolorization efficiency and catalytic stability than that of the AQDS/PPy/Pt. The morphologies shown on the micrograph of SEM were correlated with the above results. All results showed that AQDS/PPy/ACF has potential applications in accelerating the anaerobic biodecolorization of azo dyes.

Acknowledgment

The authors gratefully acknowledge the financial support from the Chinese National Nature Science Foundation (No. 50578022).

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