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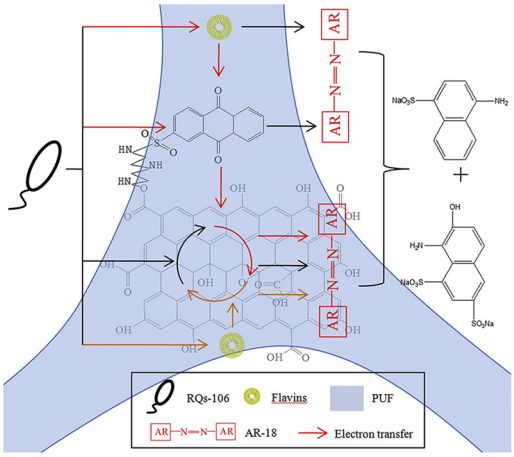
Catalytic performance of quinone and graphene-modified polyurethane foam on the decolorization of azo dye Acid Red 18 by *Shewanella* sp. RQs-106

Yang Zhou, Hong Lu*, Jing Wang, Jiti Zhou, Xueying Leng, Guangfei Liu

Key Laboratory of Industrial Ecology and Environmental Engineering, Ministry of Education, School of Environmental Science and Technology, Dalian University of Technology, Dalian, 116024, China

GRAPHICAL ABSTRACT



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ABSTRACT

Quinone-modified graphene powder is not reusable in bio-treatment systems, and the roles of quinone and graphene during extracellular electron-transfer processes remain unclear. In this study, we prepared anthraquinone-2-sulfonate and reduced graphene-oxide-modified polyurethane foam (AQS-rGO-PUF) and found that AQS-rGO-PUF exhibited higher catalytic performance on Acid Red 18 (AR 18) bio-decolorization compared with AQS-PUF and rGO-PUF. We observed a significant synergistic effect between AQS and rGO in AQS-rGO-PUF-mediated system in the presence of 50 μM AQS and 1.63 mg/L rGO. The synergistic effect was mainly attributed to electron transfer from AQS to rGO either directly or via flavins secreted by strain RQs-106, and ultimately to AR 18, accounting for ~33.47% of AR 18 removal during AQS-rGO-PUF-mediated decolorization. Additionally, AQS-rGO-PUF exhibited good mechanical properties and maintained its macroporous structure. Furthermore, after eight rounds of experiments using AQS-rGO-PUF, the bio-decolorization efficiency of AR 18 retained > 98.18% of its original value. These results indicate that the combination of AQS-rGO-PUF and *Shewanella* strains show potential efficacy for enhancing the treatment of azo-dye-containing wastewater.

* Corresponding author.
E-mail address: lvhonghj@163.com (H. Lu).

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1. Introduction

Quinone compounds (QCs) can be used as redox mediators to enhance anaerobic biotransformation of various refractory pollutants, including azo dyes, nitroaromatics, and chlorinated compounds [1–4]. To avoid continuous addition of QCs in practical application, various carriers, such as calcium alginate [5], exchange resins [6], polyurethane foam (PUF) [7], metal-oxide nanoparticles, and graphene oxide (GO) [8,9], have been used to immobilize QCs. Among these carriers, GO has high specific surface area and strong adsorption ability. Moreover, GO can be reduced by chemical reductants or microorganisms [10], after which reduced GO (rGO) can be used as an electron-transfer mediator to improve the bioreduction or chemical reduction rates of environmental contaminants [4,11–13]. Previous studies show that GO is superior to other carriers. However, quinone-modified graphene powder is not reusable in bio-treatment systems, because composites of quinone-modified graphene powder and microorganisms easily formed, and it is difficult to separate quinone-modified graphene powder from the composite. PUF with macropores exhibits good mechanical strength and low toxicity [14–16], and quinone-modified PUF-mediated decolorization can retain > 98.7% of its original value after 10 rounds of experimentation [7]. Based on these results, we hypothesized that a composite material comprising PUF and GO (or rGO) would be an effective carrier for immobilizing QCs.

Many bacteria, including *Clostridium* sp., *Geobacter* sp., and *Shewanella* sp., capable of reducing QCs have been isolated and studied [1,3,17]. Among these bacteria, *Shewanella* strains exhibit good quinone-reducing ability and can secrete more flavins in the presence of QCs than in the absence of QCs [1,18]. Flavins can also be used as redox mediators to accelerate the reduction of refractory pollutants [19]. Therefore, the combination of *Shewanella* strains and QCs is beneficial for removing refractory pollutants. However, when QCs are immobilized on PUF and GO (or rGO) composite material, the extracellular electron-transfer process in the simultaneous presence of QCs, rGO, and flavins secreted by *Shewanella* strains remains unclear. Moreover, the roles of QCs and rGO in QC-rGO-supplemented systems have not been elucidated [9,20].

In this study, we prepared a novel rGO-modified PUF (rGO-PUF) carrier and immobilized anthraquinone-2-sulfonic sodium (AQS) on the carrier using a chemical method. The azo dye Acid Red 18 (AR 18) was selected as a model substrate, and the catalytic performance of AQS-modified rGO-PUF (AQS-rGO-PUF) on AR 18 decolorization by the newly isolated exo-electrogenic bacterium *Shewanella* sp. RQs-106 was investigated in detail. During this process, we also investigated the reaction kinetics and extracellular electron-transfer pathways associated with this process.

2. Materials and methods

2.1. Chemicals and materials

AR 18 (> 99% purity) was purchased from Taixing Zhongcheng Chemical Co., (Taixing, China). AQS was purchased from Sigma-Aldrich (Shanghai, China). All other reagents used were of analytical grade. GO was purchased from Beijing Nanoon Technology Co., Ltd. (Beijing, China). PUF cubes were obtained from Dalian-Landa Bio-environment & Tech. Co. Ltd. (Dalian, China), with the cubes having a specific surface area ranging from 1.6×10^5 m^2 m^{-3} to 2.2×10^5 m^2 m^{-3} and a pore size ranging from ~300 μm to 600 μm.

2.2. Isolation, identification and cultivation of a quinone-reducing strain

A quinone-reducing strain was isolated from anaerobic activated sludge from a Dalian Chunliu River wastewater-treatment plant (Dalian, China). The isolated strain (RQs-106) was identified by 16S rRNA gene-sequencing analysis, with the sequence accession number subsequently deposited in GenBank (accession no. MF168410).

The basal medium (BS) used in this study was modified according to previous work [15], and which contained 6.71 g/L $K_2HPO_4{\cdot}3H_2O$, 2.80 g/L KH_2PO_4, 0.20 g/L $MgCl_2{\cdot}6H_2O$, 0.02 g/L $CaCl_2$, 1.00 g/L NH_4Cl and 10 mL/L trace-element solution (pH = 7.5). The trace-element solution contained (g/L) 1.50 nitrilotriacetic acid, 3.00 $MgSO_4{\cdot}7H_2O$, 0.50 $MnSO_4{\cdot}H_2O$, 1.00 NaCl, 0.10 $FeSO_4{\cdot}7H_2O$ 0.18 $CoSO_4{\cdot}2H_2O$, 0.10 $CaCl_2{\cdot}2H_2O$, 0.18 $ZnSO_4{\cdot}7H_2O$, 0.01 $CuSO_4{\cdot}5H_2O$, 0.02 $KAl(SO_4)_2{\cdot}12H_2O$, 0.01 H_3BO_3, 0.01 $Na_2MoO_4{\cdot}2H_2O$, 0.03 $NiCl_2{\cdot}6H_2O$, 0.30 $Na_2SeO_3{\cdot}5H_2O$, and 0.40 $Na_2WO_4{\cdot}2H_2O$.

2.3. Preparation of AQS-rGO-PUF

GO was ultrasonically dispersed in deionized water to a final concentration of 1.00 mg/mL. PUF cubes (1.50 × 1.50 × 0.50 cm) were dipped into GO solution for 5 min, followed by a drying process at 50 °C and rinsing with deionized water. The dipping-drying-rinsing process was repeated three times to enable GO to be uniformly adsorbed on the surface of PUF for GO-PUF preparation. Afterward, 0.70 g GO-PUF cubes were placed into 2 M NaOH solution (100 mL) and reacted with 5 g diethylenetriamine in a 500 mL round-bottomed flask, which was then placed in a water bath at 90 °C and stirred for 1 h. During this process, the oxygenated groups (e.g., hydroxy and carboxyl) in GO-PUF reacted with diethylenetriamine, resulting in the formation of amino-modified GO-PUF. After the reaction system was cooled to room temperature, amino-modified GO-PUF cubes were taken out, washed with deionized water, and dried at 50 °C. The total concentrations of GO and amino-modified GO on PUF were quantified according to weight.

Anthraquinone-2-sulfonyl chloride (ASC) was synthesized using AQS, as described by Feng et al. [21]. The amino-modified GO-PUF cubes (rGO-PUF; ~0.70 g) reacted with three concentrations of ASC (0.18 g/L, 0.24 g/L, and 0.30 g/L), respectively, in 2 M NaOH solution (100 mL) for 1 h at 30 °C. The AQS-modified rGO-PUF (AQS-rGO-PUF) cubes were then taken out, washed with deionized water, and dried at 50 °C, resulting in synthesis of three types of AQS-rGO-PUF (i.e., AQS-rGO-PUF-1, -2, and -3). Under the same conditions, PUF cubes reacted with ASC (0.3 g/L) for AQS-PUF preparation, as described by Lu et al. [7]. GO-PUF and rGO-PUF cubes (~0.70 g each) also reacted with ASC (0.3 g/L) and AQS (0.3 g/L) respectively, for 1 h at 30 °C as controls.

2.4. Batch decolorization experiments

Strain RQs-106 was aerobically cultivated in 100 mL of Luria – Bertani medium with 150 rpm for 12 h at 30 °C. The culture was then centrifuged at 10,000*g* for 10 min and washed twice with BS medium, after which the cell pellets were resuspended in BS medium. Batch decolorization experiments were performed in 135-mL serum bottles containing 100 mL BS medium using 20 mM sodium formate as an electron donor. AQS-rGO-PUF, rGO-PUF, and AQS-PUF cubes were added into these bottles, respectively. After the bottles were purged with N_2 for 30 min, they were tightly sealed with rubber stoppers and aluminum caps. All of the bottles were autoclaved at 121 °C for 20 min prior to use. The described cell suspensions [0.05 *g* cells (dry weight)/L] and AR 18 (0.20 mM) were added into the bottles in an anaerobic incubator, followed by incubation at 30 °C.

The catalytic effect of AQS-rGO-PUF-3 (50 μM AQS; 1.63 mg/L rGO) on AR 18 decolorization was evaluated and compared with those of rGO-PUF (1.63 mg/L rGO) and AQS-PUF (50 μM AQS). Moreover, the effects of rGO (~0–8.98 mg/L) and immobilized AQS (~10–100 μM) concentrations on AR 18 decolorization were also investigated by changing the masses of rGO-PUF and the three types of AQS-rGO-PUF, with PUF and AQS-PUF cubes as controls. All treatments and controls were performed in triplicate. A pseudo-first-order model ($C_t = C_0e^{-kt}$) was used to describe the kinetics of AR 18 decolorization, where C_t (mM) and C_0 (mM) represented the residual dye concentrations at times t and zero, respectively. Additionally, we determined the decolorization