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Improving the biodecolorization of reactive blue 13 by sodium anthraquinone-2-sulfonate immobilized on modified polyvinyl alcohol beads☆

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ABSTRACT

In order to enhance the biodecolorization rate and avoid the wash-out problems of redox mediators in continuous systems such as a fluidized bed reactor, polyvinyl alcohol (PVA) beads modified with N-containing function groups were investigated and employed as a new sodium anthraquinone-2-sulfonate (AQS) carrier material. Elementary and XPS analyses confirm the existence of AQS on modified PVA bead. The modified PVA beads suit with immobilizing AQS better in adsorption capability and stability. AQS supported on modified PVA beads shows high catalytic activity for biodecolorization of reactive blue 13 in a long process (>10 runs).

1. Introduction

Effluents from dye manufacturing industries exist in water and sediments for a long time [1]. Their disposal into environment is harmful and will cause death of aquatic life [2–4]. On account of the low energy cost and environmental compatibility, biodegradation of electron-accepting pollutants, such as dyes, under anaerobic condition has been widely applied for wastewater treatment [5,6]. However, its long-time cost and the low efficiency limit its applications [7].

Recently, many redox mediators (RMs) have been investigated for reductive biotransformation of electron-accepting priority pollutants, such as humic substances [8,9] and quinones [10,11]. RMs can accelerate the electron transfer between pollutants and microorganisms, enhancing the removal rate of pollutants. Soluble RMs are usually used, but they will be washed-out with the wastewater, so continuous addition of RMs is needed. This will increase running costs. Moreover, the RMs in effluent water will cause secondary contamination [12]. To avoid these problems, RMs immobilized on suitable carriers have been investigated. Guo *et al.* [13] prepared calcium alginate beads immobilized with anthraquinone, where beads were 3.0–4.0 mm in diameter and the loading of anthraquinone was about 0.00047 g. Their results showed about 2-fold denitrification rate and good reusability. Cervantes *et al.* [14] used anion exchange resins (AER) to adsorb RMs, including 1,2-naphthoquinone-4-sulfonate and anthraquinone-2,6-disulfonate, and obtained 8.8-fold decolorization rate for azo dyes compared with the control group. The desorption tests of immobilized quinones on AER showed that the RM detached from AER was negligible at 25 °C, but quinone desorption occurred above 25 °C. Moreover, the competition of other anions with quinones also limited the utilization of AER.

With the advantage of uniform particle distribution and sludge reduction, fluidized bed reactors are widely used for degradation of pollutants [15,16]. However, the decolorization is time consuming and is not effective, so immobilized RMs are needed [17,18]. In an anaerobic fluidized bed system, polyvinyl alcohol (PVA) beads are suitable carriers for microorganism immobilization due to their superior mechanical strength and chemical stability [19]. The density of PVA beads (1.02–1.05 $g \cdot ml^{-1}$) is nearly the same as that of water, so they are easily fluidized in the reactor. For this reason, PVA beads are suitable as the carrier for RMs. Taking into account its high redox ability and good water solubility, sodium anthraquinone-2-sulfonate (AQS), a typical RM, is employed in this study.

Here AQS is immobilized on modified PVA beads to improve biodecolorization efficiency. The catalytic activity and stability of biodecolorization of reactive blue 13 (RB13), a representative of sulfonated reactive azo dyes, are investigated in an anaerobic batch system.

2. Methods

2.1. Chemicals and PVA beads

All chemical reagents used in this study were of analytical grade and were purchased from Hangzhou Huipu Co. Ltd., China. AQS and PVA

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beads were obtained from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China) and Kuraray Co. (Japan), respectively. The PVA beads contain 80%–95% water, are 3 mm in diameter and 4 mg in dried mass, and could endure the highest temperature about 200 °C.

2.2. Preparation of modified PVA beads

PVA beads were first dried at 80 °C for 8 h as raw material, then 2 g beads were added into mixture solution of 5 ml *N*-3-(trimethoxysilyl) propyl ethylenediamine (AEAPS, 95% purity) and 95 ml toluene. The solution was heated to 110 °C under reflux condition for 24 h with argon atmosphere (Ar). The amine-functioned PVA beads were obtained after washing with excessive toluene three times and dried at 80 °C for another 8 h.

In the protonated process, 1 g dried amine-functioned PVA beads were protonated with 100 ml 0.1 mol·L^{-1} H_2SO_4 solution for 24 h, and washed with abundant deionized water until the pH of wash solution was near neutral, then dried for further use.

2.3. Immobilization of AQS on PVA beads

Immobilization of AQS on modified PVA beads was quantified by adsorption isotherms. Various concentrations (100, 150, 200, 250 and 300 mg·L^{-1}) of AQS were used with 0.04 g PVA beads in 40 ml of deionized water for the adsorption process at a constant temperature of 33 °C with continuous shaking (200 r·min^{-1}). The loading of adsorbed AQS on PVA beads is calculated with

$$q_{e=V(C_0-C_e)/M} \quad (1)$$

where q_e is the loading of AQS on PVA (μmol·g^{-1}), C_0 is the initial AQS concentration in the solution (μmol·L^{-1}), C_e is the liquid phase concentration of AQS at equilibrium (μmol·L^{-1}), V is the volume of solution (L), and M is the mass of PVA beads (g).

2.4. Desorption of immobilized AQS on modified PVA beads

To evaluate the adsorption of AQS on PVA beads, AQS immobilization beads were exposed to different temperatures and bacteria growth solutions (NH_4Cl, KH_2PO_4 and their mixture). 0.04 g AQS-saturated PVA beads were put in 50 ml vials containing 40 ml basal medium, which was the same as the inoculum given in the inoculum part. For the effect of growth medium, the basal medium only contained the same concentration of NH_4Cl, KH_2PO_4 and their mixture without other nutrients.

Initial and final concentrations of AQS were measured to evaluate AQS immobilization ability. The desorption rate of the AQS–PVA bead is calculated with

$$r_{desorption} = V_w\left(C_{desorption} - C_{initial}\right)/C_{adsorption} \quad (2)$$

where $r_{desorption}$ is the AQS desorption rate from PVA beads (%), $C_{desorption}$ is the liquid phase AQS concentration at desorption equilibrium (μmol·L^{-1}), $C_{initial}$ is the initial AQS concentration in the solution (μmol·L^{-1}), V_w is the volume of solution (L), and $C_{adsorption}$ is the total concentration of AQS on the PVA beads in the solution (μmol·L^{-1}).

2.5. Inoculum

Bacteria (*Pseudomonas* sp. isolate) used in all batch experiments were cultivated in serum bottles (115 ml) and the medium used for bacterial growth had the following composition [16]: glucose 500 mg·L^{-1}, NH_4Cl 191 mg·L^{-1}, KH_2PO_4 15 mg·L^{-1}, K_2HPO_4 10 mg·L^{-1}, $MgSO_4$ 12.5 mg·L^{-1}, $FeSO_4$ 12.5 mg·L^{-1}, and phosphate buffer with 6.8 g·L^{-1} KH_2PO_4 and 1.135 g·L^{-1} NaOH, with the pH value of solution maintaining at 7. The serum bottles were sealed with a rubber septum by a screw cap and N_2 was aerated at the beginning to maintain anaerobic condition. Glucose was used as co-substrate (carbon source) and electron donor. 1 mol·L^{-1} NaOH and 1 mol·L^{-1} HCl were needed for adjusting pH whenever necessary. All incubations were carried out in a temperature controlled incubator at 33 °C and pH 7 [16].

2.6. Batch biodecolorization of azo dye RB13

The degradation experiments were performed in serum bottles (115 ml) with a 99 ml inoculum, and 1 ml bacteria culture (original $OD_{600} = 0.35$) was added into the bottles and sealed with a rubber septum by a screw cap. After bacteria grew for 24 h, RB13 was injected into these bottles at an initial concentration of 25 mg·L^{-1}, and different amounts of AQS/PVA beads were added into the bottles whenever necessary. The controls without bacteria or AQS/PVA beads were also used. All the experiments were carried out in triplicate.

2.7. Analytical methods

Samples were periodically collected and centrifuged at 10000 r·min^{-1} for 10 min, and the filtrate was analyzed with a UV–Vis spectrophotometer. The concentrations of RB13 and AQS were characterized at a maximum wavelength λ_{max} of 570 and 330 nm, respectively. The elementary analysis was performed by Elementar Analysensysteme GmbH (Vario Micro, Germany). The XPS analysis were performed using an X-ray photoelectron spectrometer (Escalab 250Xi, UK), and the morphologies of unmodified and modified PVA beads were examined by using scanning electron microscopy (SU8010, Japan).

3. Results and Discussion

3.1. Characterization of AQS/PVA beads

The composition of modified PVA and AQS/PVA samples obtained by an elementary analysis instrument is summarized in Table 1. The PVA beads are mainly composed of elements C and O, consistent with the chemical structure of PVA (Fig. 1). In the AEAPS modified PVA sample, elements N and Si are present. Since only –NH_2 groups contain element N in AEAPS, the presence of N confirms that –NH_2 groups are introduced on the surface of PVA beads. Since AQS is soluble in water as anion, more –NH_2 groups lead to better AQS adsorption. With the protonated process for increasing adsorption capacity of AQS, due to the utilization of H_2SO_4, element S also appears in protonated amine-functioned PVA beads. Comparing with the initial protonated amine-functioned PVA beads, the percentage of S increases when AQS adsorbs on these beads. The elementary analysis identifies that AQS is immobilized on the modified PVA beads.

Fig. 2 depicts the XPS analysis of elements O and C in PVA beads. For element O, C–O is the main function group in PVA beads and amine-functioned PVA beads, and the S–O function group appears in AQS/PVA beads as expected. The same as element O, there is little difference in element C between PVA beads and amine-functioned PVA beads, and AQS/PVA beads have the C–S function group. Elements N, Si and S are also analyzed by XPS, and the results agree with the elementary analysis.

The surface morphologies of PVA beads did not change much in the preparation of AQS/PVA beads [Fig. 3(b) and (c)]. However, when PVA beads were dried at 80 °C, their microstructures were destroyed [Fig. 3(a) and (b)]. In a preliminary test, the PVA beads could not adsorb AQS regardless of whether they were dried or not, so their modification is necessary. In Fig. 3(d), bacteria are clearly found on the AQS/PVA beads, attaching in the decolorization process.