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Mechanism of anaerobic bio-reduction of azo dye assisted with lawsone-immobilized activated carbon

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ABSTRACT

Lawsone redox (LQ) mediator was covalently bound to granular activated carbon (GAC) by Fischer esterification. A high LQ adsorption capacity on GAC was achieved (~230 mg/g), and desorption studies showed strong chemical stability. Furthermore, kinetic experiments with solid-phase redox mediator (RM) and their controls (soluble RM, GAC and anaerobic sludge) were tested for decolorization of congo red dye at initial concentration of 175 mg/L. Benzidine, a by-product of complete congo red reduction, was also measured by HPLC analysis along the kinetic experiments. The highest percentage of decolorization after 24 h of incubation was achieved in cultures with soluble (77%) and immobilized (70%) LQ. In contrast, low decolorization efficiency was reached in anaerobic bio-reduction assays with unmodified GAC (47%) and anaerobic sludge (28%) after 24 h. Removal of congo red by adsorption onto LQ-GAC was negligible. The rate of benzidine production was slower than decolorization rate, suggesting that one azo bond of congo red is selectively broke and followed by a slower breaking of the second azo bond, consequently, appearance of benzidine in solution. These issues could be attributed to the steric rearrangement and the inhibitory effects of the produced aromatic amines in the biotransformation process.

1. Introduction

Azo dyes represent the largest class of organic dyes employed on textile-processing industries [1], and about 50% of dyes are discharged into the wastewater. It represents an eco-toxic hazard and a potential danger of bioaccumulation, which can significantly damage the flora, fauna, and the human health.

Redox mediators (RM) have been implemented on anaerobic treatment for accelerating biotransformation of azo dyes, but continuous addition of these chemicals increases the cost of the process [2–5]. To overcome these shortcomings, in the recent years, immobilization of RM by different techniques has been employed for bio-reduction process. For example, anthraquinone-2, 6-disulfonate (AQDS) has been immobilized by entrapment on calcium alginate, crosslinking with poly-pyrrole composite, adsorption in metal oxides and ion exchange in polymeric resins, reaching high reduction percentage (100, 95, 90 and 90% respectively) [6–9]. Nevertheless, detachment of AQDS was observed during bio-reduction process.

To enhance immobilization stability, different methods of covalent immobilization have been tested [10–12]; for instance, it was purposed a novel modification of poly (ethylene terephthalate) for the immobilization of anthraquinone-2-sulfonate (AQS), increasing the rate of reduction of different azo dyes and nitroaromatics, about 1.6–3.7 fold higher than those lacking RM. Alternatively, henna leaves were applied as co-substrate and electron shuttle on anaerobic processes, because it contains 1% of LQ glucosides, a redox mediator with good catalytic potential on the decolorization of amaranth, reaching about 75% of decolorization compared with the soluble control (95%) at same LQ concentration (0.25 mmol/L) [3]. Additionally, previous reports showed that LQ is an excellent redox mediator for anaerobic chromate reduction [13]. Direct bacterial reduction of Cr(VI) can require days or even weeks for complete reduction of less than 50 mg/L, LQ-mediated reduction of 100 mg/L of Cr(VI) was completed in hours. Recently, henna plant biomass was applied as electron shuttle on continuous reactor for the anaerobic reduction of acid orange 7 [14]. Henna leaves played a multiple role on the anaerobic process, acting as electron donor due to cellulose presented on the leaves and redox mediator due to the quantity of LQ contained on henna plant (1.8%). Nevertheless, release of LQ along the time, decreased its catalytic activity due to cumulative redox mediator in the medium, causing inhibition of microorganism [15] being unsuitable for its usage on anaerobic bio-reduction processes.

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On the other hand, LQ high reactivity may facilitate its immobilization due hydroxyl reaction with other functional groups [16]. In addition, carbon materials are demonstrated to be a suitable option for solid-phase RM, but adsorption process can play a major role on the global removal of pollutants [17–20]. Taking into account that activated carbon exhibits adsorption and redox properties, surface functional groups can promote interactions with other molecules that make it a good candidate as support for immobilization. To the best of our knowledge, there is no evidence of immobilization of LQ on activated carbon materials.

Moreover, just a few researchers have reported complete anaerobic azo dye reduction mechanism with redox mediator [4,9,10], but there is no studies of anaerobic poly-azo dye reduction mechanisms. The aims of this research are to immobilize LQ on activated carbon and to evaluate its catalytic potential during the anaerobic decolorization of congo red (a di-azo dye), elucidating the bio-reduction mechanism.

2. Methodology

2.1. Materials

Granular activated carbon (GAC) for supporting the redox mediator was obtained from a mineral source (CLARIMEX) and particle diameter was in the range of 0.5–1 mm. Congo red dye, benzidine, LQ, and AQDS were obtained from Sigma Aldrich.

Anaerobic granular sludge was obtained from an UASB anaerobic digester from a brewery industry (Cd. Obregón, Sonora, México). Granular sludge was activated before batch experiments with 1 g/L of glucose as energy source. The basal medium for the activation of anaerobic sludge was prepared as follows: $NaHCO_3$ (1.68 g/L), NH_4Cl (0.3 g/L), KH_2PO_4 (0.2 g/L), $MgCl_2{\cdot}6H_2O$ (0.03 g/L), $CaCl_2$ (0.1 g/L), and 1 mL/L of trace elements solution. This solution contained (mg/L): $FeCl_2{\cdot}4H_2O$ (2000); H_3BO_3 (50); $ZnCl_2$ (50); $CuCl_2{\cdot}2H_2O$ (38); $MnCl_2{\cdot}4H_2O$ (500); $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, (50); $AlCl_3{\cdot}6H_2O$, (90); $CoCl_2{\cdot}6H_2O$ (2000); $NiCl_2{\cdot}6H_2O$ (92); $Na_2SeO_3{\cdot}5H_2O$ (162); EDTA (1000); and 1 mL/L of HCl (36%). The pH was buffered with the quantity of bicarbonate added in the basal medium and inert atmosphere was provided by flushing head space with nitrogen gas.

2.2. Adsorption and desorption tests of redox mediator on activated carbon

Redox mediator (LQ) was immobilized on activated carbon by adsorption until the equilibrium was reached and, subsequently, LQ-loaded adsorbent was dried at 100 °C in a conventional oven. Adsorption experiments were carried out in triplicate at various pH values (3, 4, 5 and 7) and the average values are presented. These experiments were conducted as follows: a mass of 30 mg of GAC was added to 30 mL of LQ solutions with concentrations varying from 50 to 200 mg/L. These suspensions were continuously stirred at 150 rpm and 30 °C for 24 h. The pH of solution was initially adjusted by adding 1.0 M HCl or NaOH as required. Aliquots of 3 mL were taken from the suspension to measure the initial and final LQ concentration by UV–vis spectrophotometry at 450 nm to determine the adsorption capacity by mass balance relationship using Eq. (1):

$$Q_e = \frac{V(C_0 - C_e)}{W} \quad (1)$$

Where Q_e is the adsorption capacity (mg/g); V is the volume of LQ solution (L); C_0 and C_e are the initial and equilibrium concentration of LQ (mg/L), respectively; and W the mass (g) of granular activated carbon. Additionally, to covalently bind LQ to GAC, the lawsone-loaded GAC (LQ/GAC) was separated from solution by filtration and heated at 100 °C for 24 h to enhance the Fischer esterification reaction. Next, to evaluate desorption of redox mediator, 30 mg of LQ/GAC were added to 30 mL of basal medium solutions and these suspensions were continuously stirred at 150 rpm at 30 °C for 24 h. After that period, 3 mL aliquots were taken to measure LQ concentration in solution (C_d, mg/L) and this results were used to quantify the desorption capacity (Q_d, mg/g) from the mass of granular activated carbon (W, g) because of the basal medium (Eq. (2)).

$$Q_d = \frac{VC_d}{W} \quad (2)$$

2.3. Immobilization of lawsone on activated carbon

Lawsone was covalently immobilized on granular activated carbon (LQ-GAC) based on the maximum adsorption capacity from previous adsorption/desorption experiments. First, 1 L of solution with a LQ concentration of 250 mg/L was prepared with deionized water in an Erlenmeyer flask, a few drops of 1.0 M sodium bicarbonate into the flask to solubilize LQ. Next, pH of solution was adjusted to 3.0 adding 0.1 N HCl. Then, 1 g of GAC was added to LQ solution and it was continuously stirred at 150 rpm and 30 °C for 24 h. Finally, LQ-GAC material was separated from solution by filtration, heated at 100 °C for 24 h to promote Fischer esterification, and washed with deionized water until no LQ was observed in solution. Initial and final (at the equilibrium) concentration of LQ was measured by an UV–vis spectrophotometer at 450 nm to quantify LQ immobilized in the activated carbon.

2.4. Characterization by Boehm titrations

Boehm tests were conducted in 50 mL conical tubes mixing 30 mL of 0.1 N NaOH, 0.1 N $NaOC_2H_5$, 0.1 N Na_2CO_3, 0.1 N $NaHCO_3$ or 0.1 N HCl solutions each one with 300 mg of activated carbon. These suspensions were stirred at 150 rpm and 30 °C during 3 days. Afterwards, the solution was separated by filtration and 10 mL aliquots were potentiometric titrated with the corresponding solution for neutralization (0.1 N HCl or 0.1 N NaOH) to calculate acidic and basic functional groups on the activated carbon [21,22].

2.5. Adsorption of azo dyes

The adsorption capacity (Qe) of congo red dye onto GAC was determined at pH 7 in triplicate and the average values are presented. Samples of 30 mg of GAC or LQ-GAC were added separately to 30 mL of congo red concentrations of 50–200 mg/L. These experiments were continuously stirred at 150 at 30 °C until equilibrium was achieved. Aliquots of 3 mL were taken to measure the initial and final congo red concentration by UV–vis spectrophotometer at 485 nm.

2.6. Electron transferring capacity of GAC and RM immobilized on GAC

The electron transfer capacity (ETC) of all solid-phase redox mediators were determined by biological methods using a mass to liquid ratio of 1 g/L of each material (GAC or LQ/GAC). Incubations were prepared with 0.1 g VSS/L at different temperatures (30 and 37 °C) with 2 g/L of glucose as electron donor. All ETC measurements were conducted by the ferrozine technique following the protocol previously described [23]. Briefly, Fe (III) citrate was mixed with incubation samples to obtain a final concentration of 20 mM, and allowed to react for 30 min. Then, equal volume of 0.5 M HCl was added to the sample and an aliquot was mixed with ferrozine solution for spectrophotometric (562 nm) determination of Fe (II). The Fe (II) concentration was used to calculate the ETC from each material under all experimental conditions. All ETC measurements were corrected for intrinsic inoculum transfer capacity.

2.7. Kinetics of congo red reduction

Decolorization kinetic experiments were conducted in 100 mL