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Activated carbon fibers with redox-active functionalities improves the continuous anaerobic biotransformation of 4-nitrophenol

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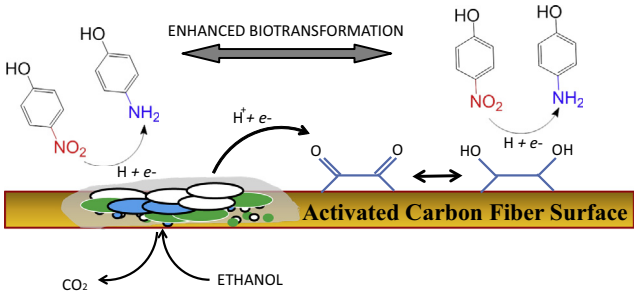
HIGHLIGHTS

- Novel UASB reactors packed with activated carbon fibers (ACFs) reduced 4-nitrophenol.
- Redox-active groups in ACFs improved by 2.11-fold the nitroaromatic biotransformation.
- Carbon source restrictions allowed the function of ACFs as redox mediators (RMs).
- First report under continuous conditions reducing 4-nitrophenol with ACFs as RMs.

GRAPHICAL ABSTRACT



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ABSTRACT

The number of studies dealing with the use of activated carbons as redox mediators in biological systems has grown rapidly in recent years. However, evidence explaining the role of the surface chemistry of activated carbons in the biotransformation of recalcitrant pollutants under continuous conditions is rather meager at present. This study offers a discussion about the role of the chemistry of activated carbon fibers (ACFs) on the increased reduction of a model nitroaromatic compound 4-nitrophenol (NP), under continuous conditions and using novel UASB-packed reactors. ACFs with different physicochemical properties and different levels of redox-active groups were studied, including un-modified (AW), HNO_3 treated (OX) and modified with anthraquinone-2,6-disulfonate (AQDS) ACFs. The results indicate that biofilm formation could cover up the effect of the different ACFs studied during the first days of the continuous experiment. However, with modifications in the concentration of ethanol (exogenous carbon source) the interaction bacteria-ACF surface was enhanced and resulted in increased biotransformation efficiencies of 1.47-, 1.97- and 2.11-fold for the reactors packed with AW, AQDS and OX materials, respectively, as compared with the control reactor, which lacked any carbonaceous support. We correlated the observed NP biotransformation efficiencies in the order OX > AQDS > AW with the content or redox-active groups such as carbonyl groups (quinone moieties) on the ACF surface in the order 1.3 > 1.0 > 0.78 milliequivalents/g, respectively. The present work proposes a novel treatment concept to enhance the reductive biotransformation of contaminants and provides a deep understanding on the complex subject of using activated carbons as redox mediators in biological systems.

1. Introduction

Xenobiotic compounds usually contain molecular arrangements that are not normally found in nature and therefore they are hard

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to metabolize by microorganisms. For some anthropogenic pollutants with strong electronegative groups, like azo dyes or nitroaromatic compounds, anaerobic conditions foster biotransformation into less harmful compounds [1] or products that could be detoxified in a secondary treatment with air [2]. Several studies have improved the kinetics of anaerobic (biotic and abiotic) transformation of recalcitrant compounds with the use of electron shuttles (redox mediators, RM) that could accept electrons (RM becomes reduced) from chemical substances or the fortuitous metabolism of a carbon source by microorganisms and donate them (RM becomes oxidized) to the pollutant of interest. Heretofore most of the research in RM as catalyst for biological applications has focused in anaerobic environments were the consumption of a carbon source (e.g. ethanol, glucose, volatile fatty acids) by pure or mixed microbial populations generate the energy necessary to reduce the soluble (e.g. anthraquinone-2,6-disulfonate (AQDS)) or immobilized RM (e.g. graphene, graphite carbon nanotubes, black carbon, granular activated carbon, and activated carbon fibers), and subsequently, shuttle that energy to the targeted electron withdrawing compounds in aqueous solutions (e.g. nitroaromatic, azo, and polychlorinated compounds) [3–6]. Among the recent advances in the use of RM, the immobilization of redox functionalities (i.e. quinone moieties) is regarded as a promising strategy to reduce costs and accelerate biotransformation of xenobiotic compounds [7].

Activated carbons are widely known to have versatile applications due to the possibility of tailoring their chemical and physical properties, including the quantity of carbonyl (quinone) groups on their surface. In biotechnology, the role of activated carbons in its granular [8] and powder [9] forms has often been limited to support bacteria and to adsorb toxic compounds that could hinder biological degradation/transformation of xenobiotic pollutants [10,11]. However, recent studies have taken advantage of the presence or introduction of quinone groups on the surface of activated carbons towards an improvement in the rate of anaerobic biotransformation of recalcitrant compounds. For instance, quinone groups have been hypothesized to act as redox mediators in the anaerobic azo dye reduction over granular activated carbons [3,5,12,13], activated carbon fibers (ACFs) [14], and active carbon felt [4]. On the other hand, nitroaromatic compounds also have been reduced to their amino derivatives with the use of graphene [15], carbon cloth [16], and active carbon felt [17]. From the above studies, only some have been carried out under continuous conditions in the biotransformation of azo dyes [3,13], and none (to the author's knowledge) in the biotransformation of nitroaromatic compounds.

The goal of this study was to demonstrate that activated carbon fibers (ACFs) could serve not only as a support media for the growing of anaerobic microorganisms, but also as RM in the continuous biotransformation of the model nitroaromatic compound, 4-nitrophenol (NP). The amount of redox active functionalities (carbonyl structures) onto ACFs were increased by HNO_3 treatment and by anchoring AQDS molecules on the ACF surface as described in previous studies [18,19]. The contribution of the physicochemical properties of ACFs on the reduction of NP is also discussed to fully disclose the role of ACFs as RM in continuous systems.

2. Experimental

2.1. Chemicals and mineral medium

4-Nitrophenol (NP) and 4-aminophenol (AP) were purchased (>99% purity) from Sigma–Aldrich (Mexico City, Mexico) and Riedel-de-Haën (Seelze, Germany), respectively. Ethanol (absolute grade) was purchased from Fermont (Monterrey N.L., Mexico). The aqueous mineral media had the following composition (g/L): $NaHCO_3$ (5.0), NH_4Cl (0.28), KH_2PO_4 (0.25), $MgSO_4{\cdot}7H_2O$ (0.1), $CaCl_2{\cdot}2H_2O$ (0.01), and trace elements (1 mL/L).

2.2. Characterization of activated carbons

Polyacrilonitrile ACFs (AW) purchased from KoTHmex (Taichung, Taiwan) were oxidized with HNO_3 8 M (OX) or pretreated with $SOCl_2$ prior to AQDS anchorage on ACF surface (AQDS) as described in previous studies [18,19]. The surface area (m^2/g) was determined by nitrogen adsorption/desorption at 77 K (BET method) using a Micromeritics ASAP 2020 surface analyzer. Specific surface functional groups on ACFs were measured by potentiometric titrations as described by Boehm [20], and the point of zero charge (PZC) was obtained by the procedure reported by Rangel and Streat [21].

2.3. Bioreactor design and operational conditions

Novel lab scale up-flow anaerobic sludge bed (UASB)-packed reactors were inoculated with anaerobic granular sludge (AGS) with10.6% of volatile suspended solids (VSS) from a UASB reactor treating wastewater from a brewery factory (Cd. Obregon, Sonora, Mexico). The polyacrylate UASB reactors (5:22 cm of internal diameter:height) were packed with polyvinyl chloride (PVC) disks of 5:4:1 cm (external diameter:internal diameter:height) as showed in Fig. 1. The top of PVC disks was designed to have a space of 1 mm where the ACFs were fixed as follows: (a) squares of 5 × 5 cm of ACFs were cut and placed on top of PVC disks, (b) the ACFs were fastened tightly with a nylon cord on top of PVC disks, (c) the excess of ACF was removed with a blade in order to obtain a 4 cm in diameter ACF disk. Two holes of 0.5 cm in diameter were cut in order to facilitate the flow of biogas and liquid to the top of the reactor. The holes created in the ACF disks were intercalated from disk-to-disk to promote the complete mixture of the fluid passing through the UASB reactor.

Four UASB reactors (working volume of 400 mL) were inoculated at the bottom with 25 g VSS/L (94.3 g of AGS per reactor). A total of 12 disks were inserted to different UASB reactors: (1) control reactor with only AGS (un-packed), (2) reactor packed with AGS and 2.87 g of AW, (3) reactor packed with AGS and 3.37 g of OX, and (4) reactor packed with AGS and 3.34 g of AQDS-anchored ACF (AQDS). The difference in the mass of AW,

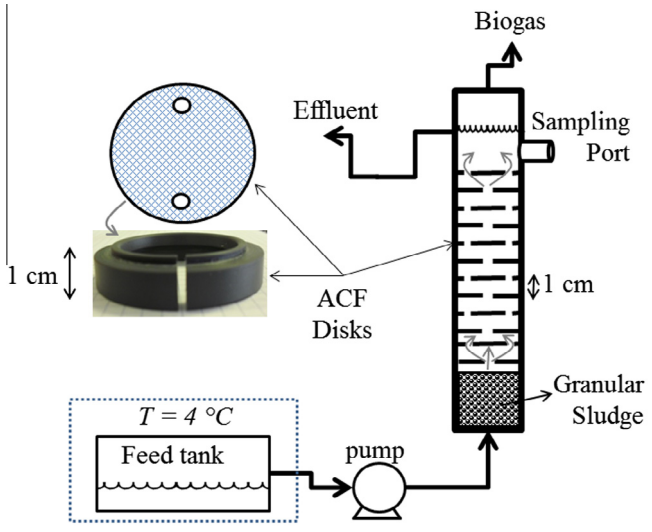

Fig. 1. Bioreactor design for the anaerobic reduction of 4NF with and without the presence of ACFs. Room temperature 25–32 °C.