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Perspectives on carbon materials as powerful catalysts in continuous anaerobic bioreactors

R.A. Pereira [a], A.F. Salvador [a], P. Dias [a], M.F.R. Pereira [b], M.M. Alves [a], L. Pereira [a, *]

[a] Centro de Engenharia Biológica, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal
[b] Laboratório de Catálise e Materiais (LCM), Laboratório Associado LSRE/LCM, Departamento de Engenharia Química, Faculdade Engenharia da Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

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ABSTRACT

The catalytic effect of commercial microporous activated carbon (AC) and macroporous carbon nanotubes (CNT) is investigated in reductive bioreactions in continuous high rate anaerobic reactors, using the azo dye Acid Orange 10 (AO10) as model compound as electron acceptor and a mixture of VFA as electron donor. Size and concentration of carbon materials (CM) and hydraulic retention time (HRT) are assessed. CM increased the biological reduction rate of AO10, resulting in significantly higher colour removal, as compared to the control reactors. The highest efficiency, 98%, was achieved with a CNT diameter (d) lower than 0.25 mm, at a CNT concentration of 0.12 g per g of volatile solids (VS), a HRT of 10 h and resulted in a chemical oxygen demand (COD) removal of 85%. Reducing the HRT to 5 h, colour and COD removal in CM-mediated bioreactors were above 90% and 80%, respectively. In the control reactor, thought similar COD removal was achieved, AO10 decolourisation was just approximately 20%, demonstrating the ability of CM to significantly accelerate the reduction reactions in continuous bioreactors. AO10 reduction to the correspondent aromatic amines was proved by high performance liquid chromatography (HPLC). Colour decrease in the reactor treating a real effluent with CNT was the double comparatively to the reactor operated without CNT. The presence of AC in the reactor did not affect the microbial diversity, as compared to the control reactor, evidencing that the efficient reduction of AO10 was mainly due to AC rather than attributed to changes in the composition of the microbial communities.

1. Introduction

Carbon materials have a versatile and powerful role in the field of environmental biotechnology. Activated carbon is available in granular and powder forms, but also as felts, fibres, clothes, or monoliths. It has been widespread applied as pollutant adsorbent (Marsh and Rodríguez-Reinoso, 2006), as support for biofilm formation (Herzberg et al., 2004), in activated sludge processes (Shaul et al., 1983; Specchia and Gianetto, 1984), and also inducing microbial shifts in anaerobic processes, apparently by promoting the growth of electroactive bacteria (Liu et al., 2012). The use of tailored CM in electrodes of bioelectrical systems is also an emerging field where these materials influence the rate of current production (Xie et al., 2015).

The use of CM as redox mediator (RM) in biological and chemical reactions has been deserved growing importance in the field of environmental bio/technology. RM are soluble compounds or insoluble materials that accelerate the electron transfer from an electron donor to an electron acceptor in multiple redox reactions (Van der Zee and Cervantes, 2009). RM have the capacity to minimize the steric hindrance of the molecules and to decrease the activation energy of the reduction reaction, thus acting as catalysts (Bragger et al., 1997; Moir et al., 2001). Compared with soluble RM, insoluble materials such as CM have the advantage of being retained inside the reactors, avoiding the need to be fed continuously, and thus decreasing the operating costs. Being continuously reduced and oxidised, these materials are self-regenerated and only a small amount is necessary to achieve a significant improvement in process performance.

The use of CM as RM has been reported in several studies of dyes decolourisation (e.g. Van der Zee et al., 2003; Pereira et al., 2010; 2014; Mezohegyi et al., 2007, 2008, 2010), and reduction of nitrocompounds (Amezquita-Garcia et al., 2013, 2016; Colunga et al., 2015; Pereira et al., 2016).

* Corresponding author.
E-mail address: lucianapereira@deb.uminho.pt (L. Pereira).

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In previous batch experiments at our laboratory, the capacity of different CM as RM on chemical (using sodium sulfide) and biological reduction of azo dyes (Pereira et al., 2010, 2014) and of nitroanilines (Pereira et al., 2016) was demonstrated, increasing the reduction rates of azo dyes up to 9-fold and of nitroanilines up to 8-fold. Among the tested materials, the best results for azo dyes were obtained with the macroporous CNT, due to the easier access of the azo dye molecules to the internal surface. For nitroanilines, smaller molecules, AC was preferential.

The purpose of the present work is to evaluate the performance of different CM as RM on the biological reduction reactions in continuous Upflow Anaerobic Sludge Blanket (UASB) reactors. These reactors are able to retain high concentrations of settling granular biomass with high specific activity and thereby can achieve good COD removal efficiency at high organic loading rates (Lettinga et al., 1980). When treating compounds with electrophilic groups such as azo-dyes or nitrocompounds, the rate of reduction can be increased by amending the sludge blanket with small concentrations of insoluble RM. AO10 was chosen as model compound due to its recalcitrant nature as previously found in batch assays (Pereira et al., 2014). In order to optimize the process, different parameters were studied: type of CM (AC and CNT), concentration of CM (0.6 and 1.2 g L^{-1}), size of CM (from 0.6 to 0.25 mm) and HRT (20, 10 and 5 h). CNT were also tested in a bioreactor treating an industrial textile effluent. This is the first report on the application of CNT as RM for the biological reduction of azo dyes and industrial effluents, in continuous reactors. The amount of CM used is circa 8 to 80 times lower than the quantity used by other authors. Because the presence of AC was suggested to induce changes in the microbial diversity of anaerobic sludge (Liu et al., 2012), the effect of the presence of CM on the microbial community present in the UASB reactors was also investigated.

2. Materials and methods

2.1. Carbon materials and chemicals

The CM tested were a commercial AC (NORIT ROX0.8, pellets of 0.8 mm diameter and 5 mm length) and a commercial CNT (Nanocyl 3100, with an average diameter of 9.5 nm, an average length of 1.5 mm with carbon purity higher than 95%). The characteristics of those materials were previously reported (Pereira et al., 2010, 2014, 2016; Tessonnier et al., 2009) and are given in supplementary information (Tables S1 and S2). In order to prepare AC with different sizes, granular ($0.3 < d < 0.6$ mm) or powder AC (<0.25 mm), the pellets were crushed and sieved. AO10 (dye content of 90%) and aniline (99%) were purchased from Sigma and used without additional purification. The real effluent was collect after the dyeing process from a textile company located in the north of Portugal, Valintece SA. The effluent was composed of the reactive azo dyes Remazol Blue RR, Remazol Brilliant Yellow and Remazol Yellow RR. Salts and detergents, softeners, surfactants and sizing, coating and finishing additives were also present. The exact composition of the effluent was not provided. This effluent was previously characterized in terms of colour, pH, COD, SO_4^{2-}, NO_3^{2-}, NO_2^- and conductivity (Da Motta et al., 2014). The chemicals used to prepare the nutrients and substrate solutions were purchase from Sigma or Fluka at highest analytic grade purity commercially available. The solvent acetonitrile (ACN) and ammonium acetate for HPLC analysis were purchased from Acros and Panreac, respectively.

2.2. UASB reactors operation

The lab scale UASB reactors, made of acrylic glass and having a work volume of 400 mL (L = 98 cm; d = 2 cm). The reactors were seeded with 10 g L^{-1} of VS of anaerobic granular sludge obtained from a full-scale UASB reactor treating brewery wastes (Central de Cervejas, Portugal). Three reactors were operated: one with AC (RAC), other with CNT (RCNT) and a third without CM (R0). The reactors were feed with a synthetic wastewater containing 0.50 mmol L^{-1} of AO10 and basal nutrients. The solution of micronutrients was composed of 2 g L^{-1} $FeCl_2 \cdot 6H_2O$; 0.05 g L^{-1} H_3BO_3; 0.05 g L^{-1} $ZnCl_2$; 0.038 g L^{-1} $CuCl_2 \cdot 2H_2O$; 0.5 g L^{-1} $MnCl_2 \cdot 4H_2O$; 0.05 g L^{-1} $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$; 0.09 g L^{-1} $AlCl_3 \cdot 6H_2O$; 2 g L^{-1} $CoCl_2 \cdot 6H_2O$; 0.092 g L^{-1} $NiCl_2 \cdot 6H_2O$ and 0.164 g L^{-1} $Na_2SeO_3 \cdot 5H_2O$ (Zehnder et al., 1980) and the solution of macronutrients of 30 g L^{-1} $MgSO_4 \cdot 7H_2O$; 28.3 g L^{-1} KH_2PO_4 and 170 g L^{-1} NH_4Cl. Micronutrients were supplemented to the influent feed by addition of 1 mL per litre of feed and macronutrients by addition of 0.6 mL of the solution per gram of COD fed.

A mixture of 2 g L^{-1} of VFA at 1:10:10 COD ratio of acetate, propionate and butyrate, was added as the primary electron donor in order to provide the reducing equivalents for the reduction and the cleavage of the azo chromophore. This solution was refrigerated at 4 °C and fed to the reactor with a peristaltic pump. An internal recycle was made by a second peristaltic pump with a constant flow rate of 100 mL min^{-1}. Operating temperature was set at (37 ± 2) °C by circulating water through an external water jacket. The variables under study were CM concentrations (0.06 or 0.12 g per g VS − 0.6 and 1.2 g L^{-1}, respectively), CM size (granular or powder) and reactor HRT (5, 10 or 20 h) (Table 1). RAC was operated at phases I to VI and RCNT at phases V and VI, with AO10, and at phase I' with the real effluent. R0 was operated at all phases (Table 1). Aniline was also feed to RAC at the concentration of 0.5 mmol L^{-1} in the conditions of phase V (RAC_{AN}) aiming at evaluating if the aniline formed from AO10 reduction, could be further bio reduced.

In order to replace the various CM, the UASB was stopped and the medium removed, so the previous material was separated from the medium with a sieve. As granular biomass has higher size than AC or CNT, remains in the sieve and the CM pass through it. UASB reactor was then filled again with the biomass and the new CM was added. In order to verify if the amount of CM was maintained constant, when AC was added in pellets, it was confirmed by counting the few number of pellets; when CM were added in powder, it was verified by visual inspection of the effluent collected and, additionally, by separating and weighing the possible fraction of CM that was washed out. With this procedure, it was verified that no CM were washed out from the reactor during the operation.

2.3. Routine analysis

Samples were withdrawn from the bioreactors every 24 h, centrifuged and diluted up to an absorbance of less than 1, with a freshly solution of ascorbic acid (200 mg L^{-1}) to prevent aromatic amines oxidation. AO10 decolourisation was followed by measuring the absorbance at the dye wavelength of maximum absorbance, 480 nm, in a 96-well plate reader (ELISA BIO-TEK, Izasa) and converted to concentration with the molar extinction coefficient of the dye (ε_{480nm} = 24.56 mmol L^{-1} cm^{-1}). Dye reduction was confirmed by HPLC in an Ultra HPLC (Shimadzu Nexera XZ) equipped with a diode array detector (SPD-M20A), autosampler (SIL-30AC), degassing (DGU-20A5R) and LC -30AD, and a Labsolutions software. A RP-18 endcapped Purospher Star column (250 mm × 4 mm, 5 μm particle size, from MERCK, Germany) was used. Mobile phase was composed of two solvents: 10 mM ammonium acetate solution and ACN. Compounds were eluted at a flow rate of 0.8 mL min^{-1} at room temperature, with an increase from 0% to 95% of ACN over 25 min and followed by an isocratic gradient during 10 min. Samples were monitored at