Carbon nanotubes as novel redox mediators for dyed wastewaters biodegradation

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Abstract

Due to their large-scale production and extensive application, dyes have turned serious pollutants as when improperly handled and disposed, they may create serious public health and environmental problems. One of the problems that textile industry is facing is related with the incomplete exhaustion of dyes onto textile fibre from an aqueous dyeing process and the need to implement innovative and sustainable effluent treatment methods to remove colour. Biological treatment systems were shown to be promising technologies. The main limiting factor of the reductive transformations by anaerobic sludge is the electron transfer, a slow process. This limitation can be overcome by making use of redox mediators, compounds that accelerate the electron transfer from a primary electron donor to a terminal electron acceptor, to speed up the process. Activated carbon (AC) has been shown as a feasible redox mediator. Samples of microporous thermal treated AC (AC_{H2}) and mesoporous carbons: Xerogels (XA, XB) and Carbon nanotubes (CNT) were tested on azo dye and textile wastewater biodegradation. ~80 % Mordant Yellow 10 (MY10) and 70 % of Reactive Red 120 (RR120) colour removal was obtained with all the carbon materials. Acid Orange 10 (AO10) is not biodegraded in the absence of Carbon Materials, but with XB a 98 % of colour removal at 4.48 ± 0.74 d^{-1} of reduction rate was achieved. For MY10 and RR120, rates increased in the order: control < AC_{H2} < XA < XB < CNT. HPLC analysis confirmed the reduction of dyes with the corresponding aromatic amines formation. Biological treatments of real wastewater lead to 65 % of colour removal with rate improvement in the presence of CNT.

Keywords
Activated carbon, nanotubes, carbon xerogels, azo dyes, anaerobic biodegradation

INTRODUCTION

One of the main problems associated with the treatment of textile wastewater is the removal of dyes. Most of the dyes applied in textile-processing industries are azo compounds, i.e. molecules with one or more azo (-N=N-) bridges linking substituted aromatic structures [1]. Discharge of azo dyes is undesirable because some of them, and specially their breakdown products, are toxic toward aquatic life and mutagenic for humans [2]. Biological treatment technologies for textile wastewater treatment are economical alternative and have shown greater efficiency with remarkable results over physico-chemical methods [3,4]. Recently advanced biological reactors have been developed for efficient removal of dyes [5]. However, reductive transformation of many recalcitrant compounds proceeds very slowly due to limitations in the rate of electrons transfer. Redox mediators are compounds that can be reversibly oxidized and reduced, thereby conferring the capacity to serve as an electron carrier in multiple redox reactions, increasing the reactions rates by one or more orders of magnitude [6,7]. Activated Carbon has been proved as an effective redox mediator; additionally it can be tailored in order to improve its capacities [7]. In the present study, the effect of different carbon materials (AC_{H2}, XA, XB and CNT) as redox mediators in the

anaerobic biodegradation of three azo dyes (MY10, AO10 and RR120) and of a real wastewater, was investigated for the first time.

MATERIALS & METHODS

The biological dye decolourisation assays were conducted in 70 mL serum bottles, sealed with a butyl rubber stopper, containing 25 mL of medium. The primary electron donating substrate was composed of 2 g L^{-1} chemical oxygen demand (COD) of a NaOH-neutralised volatile fatty acids (VFA) mixture, containing acetate, propionate and butyrate in a COD based ratio of 1:10:10. Basal nutrients were also added: NH_4Cl (2.8 g L^{-1}), $CaCl_2$ (0.06 g L^{-1}), KH_2PO_4 (2.5 g L^{-1}), $MgSO_4 \cdot 7H_2O$ (1 g L^{-1}). Medium was buffered at a pH of 7.3 ± 0.2 with $NaHCO_3$ (2.5 g L^{-1}). Non-adapted anaerobic granular sludge was added to the medium at a concentration of 2.5 ± 0.5 g L^{-1} volatile suspended solids (VSS). Biological azo dye reduction was conducted in the presence and absence of different carbon materials such as a modified activated carbon (AC_{H2}), carbon nanotubes (CNT) and two different carbon xerogel (CXA, CXB) at concentration of 0.1 g L^{-1}. After a pre-incubation period, overnight, at 37 ºC, 120 rpm, dye and VFA´s (2 g_{COD} L^{-1}) were added with a syringe from the stock solution to the desired concentration. Controls without carbon material and without biomass were also conducted in order to distinguish adsorption from biological conversion. All experiments were prepared in triplicate. All experiments were prepared in triplicate. Different classes of dyes, acid (AO10), mordant (MY10) and reactive (RR120), were tested (Figure 1).
Color decrease was monitored spectrophotometricaly in a 96-well plate reader (ELISA BIO-TEK, Izasa). At select intervals, samples were withdrawn (300 µL), centrifuged at 5000 rpm for 10 min to remove the biomass and/or CM and diluted, to obtain less than one absorbance unit (AU). Ascorbic acid was also added, to prevent autooxidation of the products. The visible spectra (300–900 nm) were recorded and dye concentration calculated at λ_{max}. Molar extinction coefficients were calcultated for each dye at λ_{max}: $\varepsilon_{350\ nm}$= 15,52 mM^{-1} cm^{-1} for MY10; $\varepsilon_{510\ nm}$= 28.59 mM^{-1} cm^{-1} for RR120; $\varepsilon_{480\ nm}$= 24.59 mM^{-1} cm^{-1} for AO10. Color removal (CR) was calculated according to equation CR (%) = ((A0-At)/A0)*100, where A0, is the absorbance at λ_{max} at the beginning of incubation and At, the absorbance at λ_{max} at a selected time (t). First-order reduction rate constants were calculated in OriginPro 6.1 software, applying the equation $Ct = C_0 + Ci*e^{-kt}$, where C_t is the concentration at time t; C_0, the offset; C_i, the concentration at time initial time; k, the first-order rate constant (d^{-1}) and t is the accumulated time of the experiment. HPLC analyses were performed in a HPLC (JASCOAS-2057 Plus) equipped with a DAD (Diode Array Detector) detector. A C18 reverse phase Nucleodur MNC18 column (250 9 4.0 mm, 5 µM particle size and pore of 100 Å from Machenerey-Nagel, Switzerland) was used. The following solvent systems were used as mobile phase: solvent A (10% of Acetic acid) and solvent B (Acetonitrile). Compounds were eluted at a flow rate of 0.5 mL min^{-1} and at room temperature, with isocratic condition with 0 % of solvent B over 10 min, 0% to 80 % of solvent B during 20 min and remaining in these conditions during 6 min. Compounds elution was monitored at λ_{max} of MY10, 350 nm, and at 250 nm and 300 nm, corresponding to the standards (Sulfanilic acid, SA, and 5-aminosalicilic acid, 5-ASA,respectively).

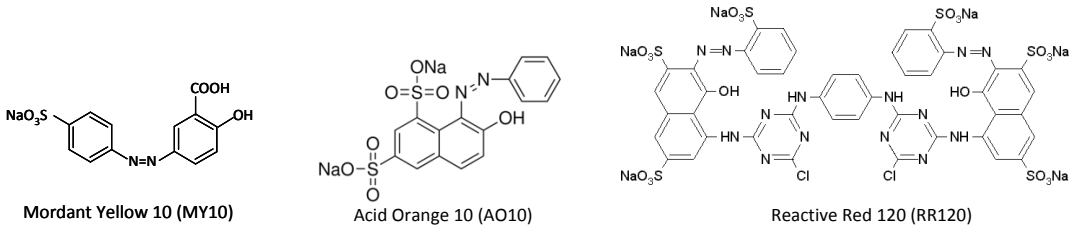

Figure 1. Chemical structure from the azo dyes and aromatic amines used in this study.

RESULTS & DISCUSSION

All the reactions followed a first-order kinetic model and the apparent rate constants and degrees of colour removal were calculated from the initial slope of the dye concentration vs time. In the absence of carbon materials, MY10 and RR120 were, although at different extents, 83 ± 1 % and 67 ± 3, respectively, decolorized by anaerobic biomass (Table 1). Rate of MY10 decolourisation was also higher, 9.50 ± 0.88 d^{-1}, than that of RR120, 3.09 ± 0.30 d^{-1}. AO10 was not decolorized in the absence of CM. These results show that the chemicals structures of the dyes influence their degradation process. However, when the biological assays were amended with the 0.1 gL^{-1} of different carbon materials, the decolourisation rate increased for all dyes tested proving the effect of redox mediation. For MY10 and RR120, rates increased in the order: *control* < AC_{H2} < *XA* < *XB* < *CNT* (Table 1). In the case of the most resistant to biodegradation, AO10, total of colour removal was achieved was obtained with XB and CNT at reduction rate of 4.48 ± 0.74 d^{-1} and 3.16 ± 0.65 d^{-1}, respectively. With the other materials, although at lower extent and rates, decolourisation was also evident. In the abiotic controls, no colour removal was obtained indicating that any adorption to the materials occurred. It is worth noting that the amount of the materials is very low, once the objective of their presence in the reaction medium is to accelerate the electron transfer from a primary electron donor to a terminal electron acceptor, to speed up the process. This is of utmost importance since the costs are reduced. Besides, those insoluble materials can be retained within the sludge been re-used for many cycles. Results have shown that the reuse of them was possible with very low decrease on their catalytic properties. Additionally, they can also be easily recovered from the reaction medium and reused in other reactions. HPLC chromatograms of MY10 show the decrease in the intensity of the peak at retention time (R_t) of 21 min, corresponding to the dye, and the emergence of two new peaks at Rt of 6.9 and 8.3 min, attributed to the correspondent aromatic mines (SA and 5-ASA), was observed (Fig. 3). These results indicate the cleavage of the azo bound, proving that reduction reactions occurred. Biological treatments of real wastewater lead to 65 % of colour removal and 1.5-fold higher rate was obtained with CNT (Data not shown).

Table 1. Extent (%) and rates (d^{-1}) of the anaerobic biodegradation of dyes (1 mM) in the absence and presence of the different carbon materials (0.1 g L^{-1}).

	MY10		**RR120**		**AO10**	
	%	**d^{-1}**	**%**	**d^{-1}**	**%**	**d^{-1}**
Biom	83 ± 1	9.50 ± 0.88	67 ± 3	3.09 ± 0.30	0	0
Biom+AC_{H2}	85 ± 1	11.02 ± 0.68	68 ± 3	3.15 ± 0.04	46 ± 5	2.07 ± 0.24
Biom+CNT	86 ± 1	16.84 ± 1.14	75 ± 2	4.01 ± 0.28	98 ± 2	3.16 ± 0.65
Biom+CXA	85 ± 1	11.11 ± 0.44	73 ± 1	3.78 ± 0.19	67 ± 1	2.72 ± 0.13
Biom+CXB	85 ± 1	14.99 ± 0.18	75 ± 2	4.54 ± 0.67	98 ± 2	4.48 ± 0.74

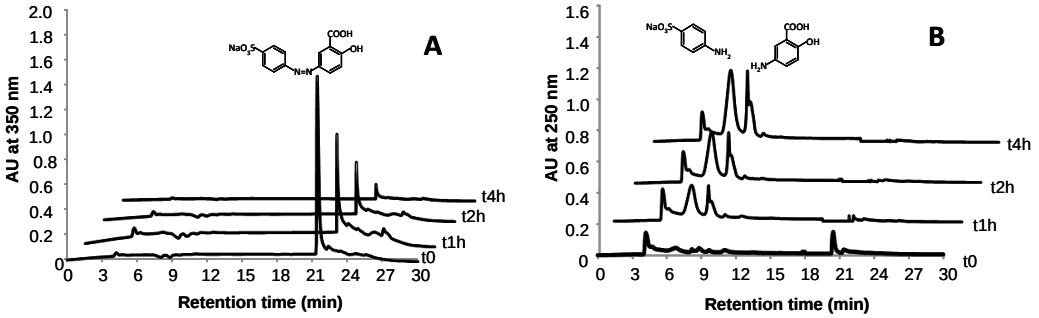

Figure 2. HPLC chromatograms of MY10 biological reduction. Monitorization at the λmax of the dye, 350 nm (A) and at 250 nm (B). Rt_{MY10} = 21 min, Rt_{SA} = 6.9 min and $Rt_{5\text{-}ASA}$ = 8.3 min.

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