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Carbon based materials as novel redox mediators for dye wastewater biodegradation

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ABSTRACT

Due to their large-scale production and extensive application, dyes have turned serious pollutants when improperly handled and disposed, creating grave public health and environmental problems. One of the problems that textile industry is facing is related with the incomplete exhaustion of dyes onto textile fibres from an aqueous dyeing process, and the need to implement innovative and sustainable effluent treatment methods to remove colour. Additionally, legislation on the limits of colour discharge has turn increasingly rigid. Biological treatment systems have been shown as 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, which are 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 (CXA, CXB) and carbon nanotubes (CNT) were tested on azo dye and textile wastewater biodegradation. ~85% 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 CXB and CNT a 98% of colour removal was achieved. For MY10 and RR120, rates increased in the order: control < AC_{H2} < CXA < CXB < CNT. HPLC analysis confirmed the reduction of dyes with the formation of corresponding aromatic amines. The effect of CNT was also observed in the biological treatment of real textile wastewaters.

1. Introduction

Textile industry faces a problem related to the incomplete exhaustion of dyes onto textile fibres, during the aqueous dyeing process, and needs to implement innovative and sustainable effluent treatment processes to remove colour. Azo compounds are molecules with one or more azo (—N=N—) bridges, linking substituted aromatic structures, and constitute the largest and most diverse group of dyes and pigments used in commercial applications [1,2]. Discharge of azo dyes is undesirable because, apart from the aesthetic point of view, some of them and their breakdown products are toxic towards aquatic life and mutagenic for humans [1,3,4]. Conventional physical and chemical techniques can be used efficiently to remove dyes from textile wastewater. However, these methods are quite expensive, have operational problems and generate huge quantities of sludge [5–7]. Biological treatment of textile wastewater is an economic alternative and has shown better efficiency than physico-chemical methods, with remarkable results [9–11]. Mixed culture activated sludge processes and, more recently, other biological processes involving anaerobic transformations, have been developed for efficient removal of dyes [12]. However, reductive transformation of many recalcitrant compounds proceeds very slowly, leading to poor performance of bioreactors (need of long retention times to reach a satisfactory extent) [13]. Redox mediators are compounds that can be reversibly oxidised and reduced, thereby conferring the capacity to serve as electron carriers in multiple redox reactions, increasing the reaction rates by one or more orders of magnitude [14]. Activated carbon (AC) has been shown to be a feasible redox mediator presenting advantages in comparison with soluble ones (ex. anthraquinone-disulphonate and anthraquinone-2-sulphonate) [15–17]. In addition, those carbon materials have the possibility of being modified in order to take advantages of their unique specific proprieties. Recently, Pereira et al. [16] have demonstrated the role of surface chemistry of activated carbon in the catalysis of chemical and biological reduction of dyes, by

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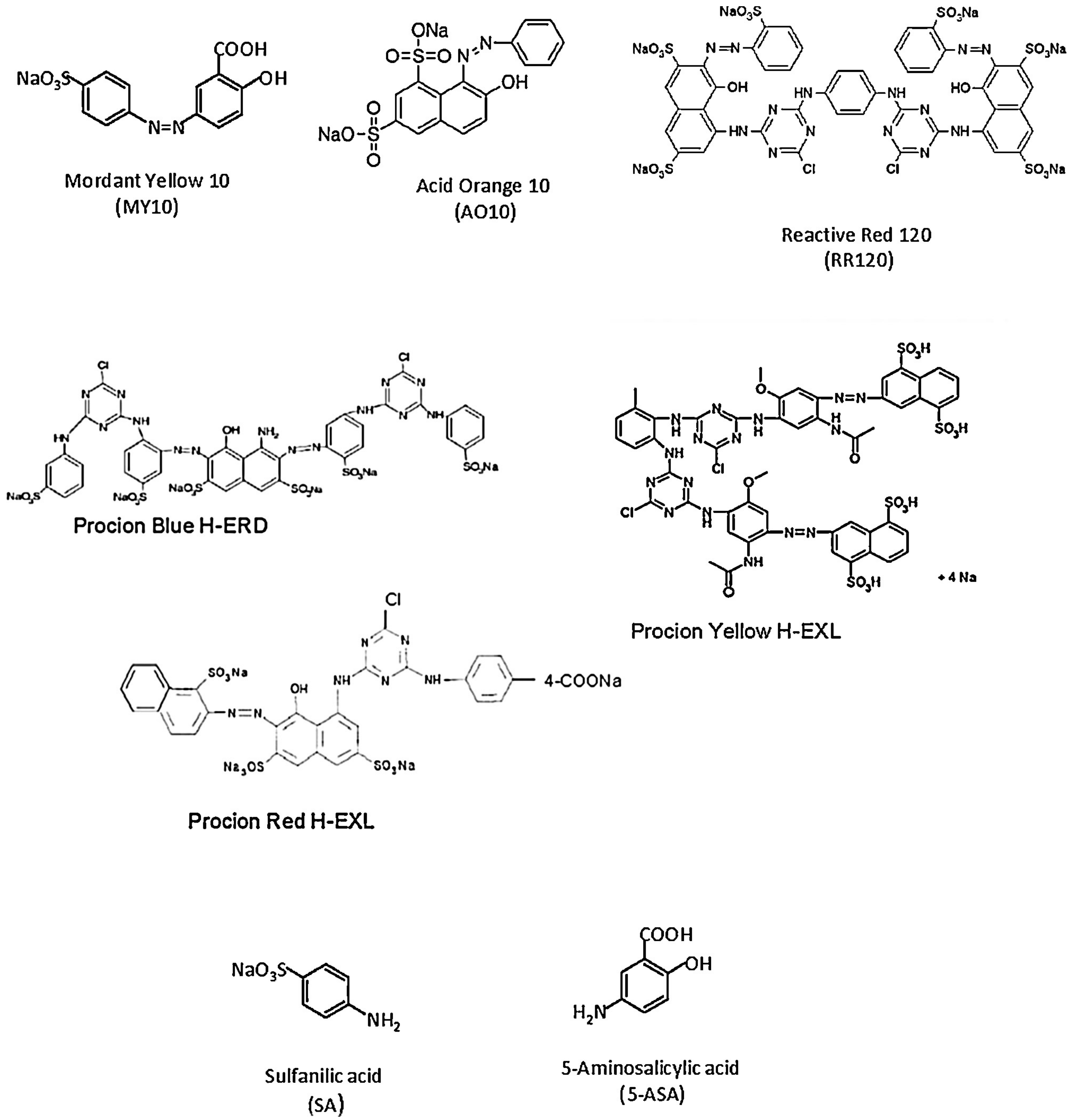

Fig. 1. Molecular structure of azo dyes and aromatic amines.

testing a set of carbon samples which were prepared by chemical and thermal modifications of the same commercial activated carbon. However, activated carbons are generally microporous, with low macropore or mesopore volumes, which can induce diffusion limitations during the catalytic and adsorptive processes. The use of carbon xerogels (CX) and carbon nanotubes (CNT) as catalysts for organic pollutants degradation has been demonstrated before [18,19]. These new mesoporous materials may present technological advantages as new shape catalyst mainly for large molecules (e.g. azo dyes) degradation. Carbon xerogels present excellent properties, such as high specific surface area, porosity and conductivity and controllable average pore size, which can be customised for the final applications.

In the present study, the mesoporous materials, CX and CNT, were studied for the first time as redox mediators on anaerobic dye reduction and compared with the microporous thermal modified activated carbon, AC_{H2}. Three azo dyes from different classes (mordant, reactive and acid) were tested: Mordant Yellow 10, Reactive Red 120 and Acid Orange 10. Biodegradation of real textile wastewaters was also investigated.

2. Experimental

2.1. Chemicals

Mordant Yellow 10 (MY10, dye content 85%), Reactive Red 120 (RR120, dye content 50%) and Acid Orange 10 (AO10, dye content 90%) were purchased from Sigma and used without additional purification. Stock solutions of 15 mM were prepared in deionised water. Aromatic amines were also purchased from Sigma at the