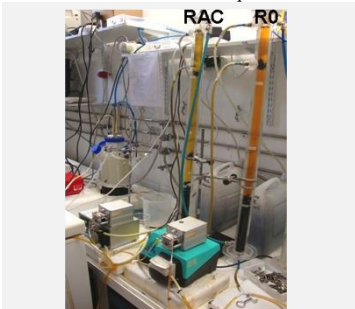


## Improvement of the Upflow Anaerobic Sludge Blanket reactor performance for azo dye reduction by the presence of low amounts of Activated Carbon

P-BE46

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**Figure 1.** Picture of the UASB reactors treating Acid Orange 10. RAC-reactor with activated carbon; R0-reactor without activated carbon.

Activated carbon (AC) was investigated as redox mediator of the azo dye Acid Orange 10 (AO10) anaerobic biodegradation in a laboratory scale Upflow Anaerobic Sludge Blanket (UASB). During reactor operation, the effect of AC concentration and the hydraulic retention time (HRT) were investigated and better results were obtained with 0.15 g of AC per g of Volatile Suspended Solids (VSS) and 10 h, respectively. In the mediated reactor, with an HRT of 10 h, high colour and COD removal was obtained, ~70% and ~85%, respectively. In the control, thought similar COD removal, AO10 decolourisation was only 20%, evidencing the ability of AC to accelerate the reduction reactions in continuous reactors.

### Introduction

Textile wastewaters generate considerable amounts of non fixed dyes lost during the dyeing or printing process in textile industries, which are concerned sources of environmental contamination. Therefore, in recent years, decolourisation and detoxification of dye wastewater have taken an increasingly important environmental significance [1]. Generally, dye wastewater is characterized by strong colour, high pH, high chemical oxygen demand (COD) and low biodegradability [2]. Physical-chemical techniques such as membrane filtration, coagulation/flocculation, precipitation, flotation, adsorption, ion exchange, ion pair extraction, ultrasonic mineralisation, electrolysis, advanced oxidation, can be employed to remove colour from dye containing wastewaters [3]. However, colour removal using these methods are not always as effective as expected. Some of these methods are nondestructive, consisting in a transfer of organic compounds from water to another phase thus causing secondary pollution. In addition, the high cost, the requirement for expensive equipment and high reagent or energy requirement, limits their use [4]. Treatment of textile wastewaters by applying biological methods, such as activated sludge process and anaerobic treatment have been shown as cost-effective, efficient and environmental benign alternatives.

In 1970s, the Upflow Anaerobic Sludge Blanket reactor system developed by Lettinga and co-workers [5] was a major breakthrough for the treatment of a variety of biodegradable industrial wastewaters. Compared with other advanced

anaerobic systems such as anaerobic filter and fluidized bed reactors, the UASB process is able to retain a high concentration of biomass with high specific activity and, thereby, it can handle high organic loading rates and achieve good COD removal efficiency. However, colour removal efficiency is dependent of high hydraulic retention time, given the slow rates of reduction [6]. The use of redox mediators to significantly accelerate the electron transfer and, thus, the rate of azo dye reduction, can surpass this limitation [7]. Recently, Pereira et al. [8,9] have studied different carbon materials as redox mediators on anaerobic dye reduction in batch assays. Mesoporous carbon xerogels (CX), carbon nanotubes (CNT), and different samples of modified microporous activated carbon (AC), were tested on azo dyes reduction and high colour removal was obtained in all cases. Additionally, AO10 was only decolourised in the presence of the carbon materials. Due to the size of dye molecules, better results were obtained with mesoporous carbons. However, as the purpose of the present work was to scale-up the process, the commercial microporous AC was tested in a continuous process. Two UASB reactors, one with AC and other without, were therefore operated for treating a synthetic wastewater containing the azo dye AO10. The choice for this dye was due to its recalcitrance, in the batch assays, in the absence of carbons.

### Materials and Methods

Two UASB reactors, made of acrylic glass, with 400 mL of work volume ( $L = 98$  cm;  $d = 2$  cm)

were maintained at  $37 \pm 2$  °C (Fig. 1). The reactors were seeded with  $10 \text{ gVSS L}^{-1}$  of anaerobic sludge obtained from a full-scale UASB reactor treating brewery wastes (Central de Cervejas, Portugal). One reactor contained a commercial AC (NORIT ROX, pellets of 0.8 mm diameter and 5 mm length) partially crushed (RAC) and the other reactor, without AC, was used as control (R0). Characterization of AC was previously reported [9]. Both reactors were feed with synthetic wastewater containing  $0.50 \text{ mM}$  of AO10 and basal nutrients ( $0.23 \text{ g L}^{-1} \text{ ZnCl}_2$ ;  $0.29 \text{ g L}^{-1} \text{ CuSO}_4 \cdot 5\text{H}_2\text{O}$ ;  $0.29 \text{ g L}^{-1} (\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ;  $0.26 \text{ g L}^{-1} \text{ CoCl}_2 \cdot 6\text{H}_2\text{O}$ ;  $0.16 \text{ g L}^{-1} \text{ MnSO}_4 \cdot \text{H}_2\text{O}$ ;  $90.41 \text{ g L}^{-1} \text{ MgSO}_4 \cdot 7\text{H}_2\text{O}$ ;  $6.74 \text{ g L}^{-1} \text{ CaCl}_2 \cdot 2\text{H}_2\text{O}$ ;  $14.53 \text{ g L}^{-1} \text{ FeCl}_3 \cdot 6\text{H}_2\text{O}$ ;  $190.90 \text{ g L}^{-1} \text{ NH}_4\text{Cl}$ ;  $33.40 \text{ g L}^{-1} \text{ Na}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ ;  $28.50 \text{ g L}^{-1} \text{ K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ ;  $8.50 \text{ g L}^{-1} \text{ KH}_2\text{PO}_4$ ). A mixture of  $2 \text{ gCOD L}^{-1}$  of VFA at 1:10:10 COD ratio of acetate, propionate and butyrate, was added as the primary electron donor. This solution was refrigerated at  $4$  °C and feed to reactor with a peristaltic pump. The reactors recycle was made by a second peristaltic pump with a constant flow rate of  $100 \text{ mL min}^{-1}$ . The AC concentration and HRT were changed during the experiment according to table 1.

**Table 1.** Experimental conditions for the different phases of reactor operation.

Phase	HRT(h)	gAC gVSS <sup>-1</sup>	Time (d)
I	10	0.06	0-5
II	10	0.12	6-30
III	10	0.15	31-38
IV	20	0.15	39-63
V	10	0.15	64-74

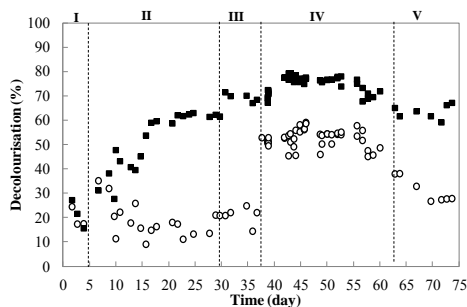
**Analysis.** AO10 colour was measured spectrophotometrically with in a 96-well plate reader (ELISA BIO-TEK, Izasa) at dye wavelength of maximum absorbance, 480 nm, and the concentration was converted using the calculated molar extinction coefficients ( $\epsilon_{480\text{nm}} = 24.56 \text{ mM}^{-1} \text{ cm}^{-1}$ ). Liquid samples were analyzed every day, centrifuged and diluted up to an absorbance of less than 1, with a freshly solution of ascorbic acid ( $200 \text{ mg L}^{-1}$ ), to prevent autoxidation. The pH was measured with HANNA HI 83141 pH meter (Germany) and VSS were determined according to standard methods [10]. COD were determined using standard kits (Hach Lange, Düsseldorf, Germany). HPLC analyses were performed in a HPLC (JASCO AS-2057 Plus) equipped with two pumps JASCO PU 2085, UV-Detector UV-2075 Plus, autosampler JASCO AS-2057 Plus and LC Net II/ADC with Crompass software. A RP-18

endcapped Purospher Star column (250mm x 4 mm,  $5\mu\text{m}$  particle size, from MERK, Germany) was used. Mobile phase was composed of two solvents: A ( $10 \text{ mM}$  ammonium acetate solution) and B (acetonitrile, ACN). Compounds were eluted at a flow rate of  $0.8 \text{ mL min}^{-1}$  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 230 nm.

The methanogenic activity assays were performed as described by Pereira *et al.* [9]. All chemicals and solvents used were purchase from Sigma Aldrich or Acros, at the highest analytic grade purity commercially available.

## Results and Discussion

The AO10 decolourisation in the reactors continuous operation are presented in figure 2.



**Figure 2.** Colour removal of AO10 in UASB reactors. ■- RAC; ○-R0.

In phase I, with an initial HRT of 10 h and  $0.06 \text{ gAC gVSS}^{-1}$ , the colour removal was  $\sim 20\%$  in both reactors. In previous batch assays with AC as redox mediators [9], AO10 reduction in the presence of  $0.05 \text{ gAC gVSS}^{-1}$ , lead to 50% of colour removal. In order to improve the reactor performance, the amount of activated carbon was duplicated (phase II). Whereas AO10 decolourisation in reactor control remained  $\sim 20\%$ , in reactor AC it increased to 40% and, after 6 days, additional increase to 60% was observed, remaining constant during the entire period of operation under those conditions. A slight AC concentration increase to  $0.15 \text{ gAC gVSS}^{-1}$  (phase III) lead also to a little improvement of the colour removal ( $\sim 70\%$ ). In phase IV of reactor operation, the HRT was upped to 20 h. To achieve this modification, the feed pump worked at periods of 15 min (continuous mode) and stopped for 15 min (batch mode). In this phase, samples were analyzed at each period, but decolourisation results were similar in both. Nevertheless, the increase of HRT to 20 h leads to an increased of AO10

decolourisation in both reactors: 80% in RAC and 50% in R0. The increase of AO10 decolourisation from  $21 \pm 4\%$  to  $53 \pm 3\%$  in the reactor control at higher HRT is in accordance with studies from Van der Zee *et al.* [7]. In phase V, the conditions of phase III were retaken and, consequently, the percentage of AO10 decolourisation decreased to similar values of this phase in both reactors. These results suggest that the higher decolourisation obtained in R0 at HRT of 20h was due to the higher HRT rather than biomass adaptation to the dye.

Regarding to the COD removal, good removal efficiency was obtained in all phases:  $\sim 70$  in phase I and II, and  $\sim 85\%$  in phases III and V. These results show that the COD removal yields obtained are not significantly altered by the change of HRT along the reactors operations and also that it corresponds mainly to the VFAs consumption. Indeed, the amount of VFAs added, as carbon source, contributed for the main COD in the medium, while the dye contributed to a small portion ( $0.33 \text{ gCOD L}^{-1}$ ) and similarly their expected reduction products (aromatic amines). In fact, samples from influent and effluent of both reactors were analysed by HPLC in order to prove dye reduction to the correspondent aromatic amines. The peak of AO10 with a retention time ( $R_t$ ) at 10 min was observed in the influent sample and, in the effluent it was at lower intensity (30% in RAC and 80% in R0, similarly to the results obtained with UV-vis analysis), but two new peaks at  $R_t$  of 4 and 12.6 min were present. As compared with the standards, peak at 12.6 min corresponds

to the expected aniline, proving the reduction of the dye (data not shown).

pH was constant over the entire reactor operation,  $\sim 7.5 \pm 0.2$ , indicating a good stability of anaerobic reactor conditions.

According to the specific methanogenic activity tests with anaerobic granular sludge, in the presence of 0.50 mM of AO10 75% of activity was obtained, as compared with the control without dye. However, this does not justify the low colour removal in R0, which, according to the results obtained at higher HRT or with the addition of AC, appears to be more related with electron transfer. On the other hand, in the case of RAC, it can be the reason for no total colour removal achievement.

## Conclusions

Decolourisation of AO10 in a continuous process was significantly improved in the presence of low amount of AC. Circa 70% of colour and 85% of COD removal were obtained in the UASB reactor amended with  $0.15 \text{ gAC gVSS}^{-1}$ . Contrarily, colour removal was just 20% in the reactor control (though the similar COD removal obtained). The efficiency of AC as redox mediator added at very low concentration has great significance in terms of low costs for this treatment process. In addition, compared with soluble redox mediators, insoluble materials have the advantage of being retained within the sludge, which allows their easier removal after the operation and no need to feed the reactor continuously with the mediator.

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