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The testing of several biological and chemical coupled treatments for Cibacron Red FN-R azo dye removal

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Abstract

Several biological and chemical coupled treatments for Cibacron Red FN-R reactive azo dye degradation have been evaluated. Initially, a two-stage anaerobic–aerobic biotreatment has been assessed for different dye concentrations (250, 1250 and 3135 mg l^{-1}). 92–97% decolourisation was attained during the anaerobic digestion operating in batch mode. However, no dissolved organic carbon (DOC) removal neither biogas production was observed during the process, indicating that no methanogenesis occurred. Additionally, according to Biotox® and Zahn–Wellens assays, the anaerobically generated colourless solutions (presumably containing the resulting aromatic amines from azo bond cleavage) were found to be more toxic than the initial dye as well as aerobically non-biodegradable, thus impeding the anaerobic–aerobic biological treatment. In a second part, the use of an advanced oxidation process (AOP) like photo-Fenton or ozonation as a chemical post-treatments of the anaerobic process has been considered for the complete dye by-products mineralisation. The best results were obtained by means of ozonation at pH 10.5, achieving a global 83% mineralisation and giving place to a final harmless effluent. On the contrary, the tested photo-Fenton conditions were not efficient enough to complete oxidation.

Keywords: Aerobic biodegradation; Anaerobic digestion; AOPs post-treatment; Reactive azo dye

1. Introduction

Azo dyes are the most widely used class of industrial dyes, constituting 60–70% of all produced dyestuffs [1]. During the dyeing process, the degree of exhaustion of dyes is never complete resulting in dye-containing effluents [2]. Not only aesthetic problems occur, but also biotoxicity and the possible mutagenic and carcinogenic effects of azo dyes or their metabolites have been reported [3]. Their degradation by conventional wastewater treatment technologies is difficult due to their complex structure and synthetic nature; they are non-biodegradable by standard aerobic activated sludge methods, and systems based on physical and chemical methods are quite inefficient and require further treatment or disposal of the pollutant. Therefore, the development of effective and economic methods for textile wastewaters treatment should deserve particular attention. Not only colour removal but organic degradation of dyes and their intermediates must also be the pursued goals.

Among the emerging technologies for wastewater decontamination, advanced oxidation processes (AOPs) are capable to mineralise almost all toxic and non-biodegradable organic compounds [4]. These processes are principally based on the in situ generation of highly reactive hydroxyl radicals ($HO^{\bullet}$, $E^{\circ} = 2.8$ V versus NHE). The most widely studied AOPs include: heterogeneous photocatalytic oxidation with TiO_2 [5,6], treatment with ozone (often combined with H_2O_2 and/or UV) [7,8], UV/H_2O_2 systems [9], and Fenton and photo-Fenton reactions [10–12], which generate $HO^{\bullet}$ by interaction of H_2O_2 with a ferrous salt in aqueous media. Nevertheless, the operational costs associated are a common problem of all AOPs and they often are too expensive to be applied as exclusive treatment. In this sense, several earlier studies focus on the combination of an AOP with

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conventional aerobic biological treatment in an attempt to avoid the drawbacks of each of them. A minimum oxidation is performed as a pre-treatment to just increase the biodegradability and generate a new effluent more amenable to biodegradation [13–15].

On the other hand, since azo dyes are potentially reduced under anaerobic conditions, and biological processes are the preferred choice for wastewater treatment, biotreatments based on anaerobic–aerobic sequences are currently under investigation [16–18]. Azo bonds (R_1–N=N–R_2) can be anaerobically reduced basically leading to the corresponding aromatic amines (dye solution decolourisation), compounds that are recalcitrant and toxic under reducing atmosphere but theoretically susceptible to further aerobic biodegradation [19].

In a previous work, the coupling of photo-Fenton reaction and an aerobic biological process for the degradation of a representative reactive azo dye employed for cellulosic fibres dyeing (250 mg l^{-1} hydrolysed Cibacron Red FN-R, DOC = 80 mg l^{-1} C) was carried out [15]. At the studied concentration, the dye was neither aerobically biodegradable nor toxic (EC_{50} > 80 mg l^{-1} C) as seen by Zahn–Wellens and Biotox® assays, respectively. With the application of the photo-Fenton catalytic process as a biological pre-treatment, a complete decolourisation and 80% mineralisation was accomplished in the combined oxidation system.

In this paper, several biological and chemical coupled treatments for Cibacron Red FN-R azo dye removal were evaluated as alternatives to the chemical–biological (aerobic) strategy. In a first part, the possibility of Cibacron Red FN-R anaerobic digestion coupled to an ensuing aerobic degradation was tested. Anaerobic assays were carried out in batch mode. Biogas production, % decolourisation, DOC reduction and toxicity evolution after digestion were monitored in order to evaluate the success of the anaerobic stage. The Zahn–Wellens test was carried out for the aerobic biodegradability assessment of the resulting anaerobic effluent. In a second part, the application of an AOP as a chemical post-treatment of the anaerobic process has also been considered to complete reactive azo dye and by-products mineralisation. Ozonation and photo-Fenton processes have been chosen to play this role.

2. Materials and methods

2.1. Synthetic dye solution

A commercial reactive azo dye, Cibacron Red FN-R bireactive vinylsulphone fluorotriazine dye (CI Reactive Red 238, empirical formula $C_{29}H_{15}O_{13}S_4ClFN_7Na_4$, 944.2 g mol^{-1}) was purchased from CIBA and used as received without further purification (80% purity approx.). Its chemical structure was not disclosed by the manufacturer. The different Cibacron Red FN-R concentrations were prepared by diluting an initial concentrated stock solution of 4180 mg l^{-1} (DOC = 1213 mg l^{-1} C; chemical oxygen demand (COD) = 3433 mg l^{-1} O_2). The initial solution of Cibacron Red FN-R was hydrolysed to convert it to the form in which it is normally found in industrial effluents. The hydrolysis was done by adjusting the pH to 10.6, followed by heating to 60 °C for 1 h. Finally, the pH of the hydrolysed stock solution was adjusted to 7.0 ± 0.2 before storage at 4 °C.

2.2. Anaerobic biodegradation set-up and operation conditions

The anaerobic experiments were conducted in batch mode and under static conditions in 600 ml thermostated aluminium bottles. The test sample volume was 500 ml and the headspace was 100 ml. The anaerobic sludge seed was a methanogenic culture obtained from a mesophilic municipal anaerobic digester (Manresa, Spain), containing an initial total suspended solids (TSS) and a volatile suspended solids (VSS) of 30 and 12 g l^{-1}, respectively. All bottles were seeded with the same volume of original sludge to finally obtain an initial 1.5 g l^{-1} VSS and 3.8 g l^{-1} TSS concentration.

0.2 g of yeast extract and 2 ml of the following solutions were added per litter of sample [20]: 100 mg l^{-1} $Na_2S{\cdot}9H_2O$ solution; a macronutrients solution composed of 170 g l^{-1} NH_4Cl, 37 g l^{-1} KH_2PO_4, 8 g l^{-1} $CaCl_2{\cdot}2H_2O$ and 9 g l^{-1} $MgSO_4{\cdot}4H_2O$; a micronutrients solution composed of 2000 mg l^{-1} $FeCl_3{\cdot}4H_2O$, 2000 mg l^{-1} $CoCl_2{\cdot}6H_2O$, 500 mg l^{-1} $MnCl_2{\cdot}4H_2O$, 30 mg l^{-1} $CuCl_2{\cdot}2H_2O$, 50 mg l^{-1} $ZnCl_2$, 50 mg l^{-1} H_3BO_3, 90 mg l^{-1} $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, 100 mg l^{-1} $Na_2SeO_3{\cdot}5H_2O$, 50 mg l^{-1} $NiCl_2{\cdot}6H_2O$, 1000 mg l^{-1} EDTA, 1 ml l^{-1} HCl 36% and 500 mg l^{-1} resazurin. Additionally, 1 g of $NaHCO_3$ per g COD was added to the solution in order to maintain the pH and reduce the negative effects to methanogenesis due to the possible acidification caused by volatile fatty acids (VFA) generation. Before incubation, nitrogen gas was bubbled into the bottles to ensure anaerobic conditions during the biodegradation process. Temperature was maintained under mesophilic conditions at 37 ± 1 °C. Each experiment was extended to 50 days.

Biogas production was measured at regular intervals by monitoring pressure changes in the bottles headspace with a digital manometer (SMC Pressure Switch 10 bars) connected to the bottles by a valve. The methane composition was determined using a HP 5890 gas chromatograph equipped with a thermal conductivity detector and a Porapak Q, 3 m × 1/8 in. column (Supelco). The temperature of the injector was 130 °C. The oven temperature was initially maintained at 30 °C for 3 min. Then, it was increased to 70 °C at a 10 °C min^{-1} rate and finally maintained at 70 °C for 5 min. The temperature of the detector was 180 °C.

The methanogenic activity of the anaerobic sludge was ensured by the assessment of the specific methanogenic activity (SMA) of a VFA standard solution composed of acetic, propionic and butyric acids (73:21:4 weight proportion, total COD = 4500 mg l^{-1} O_2) [20]. From the maximum biogas generation slope (60–70% in CH_4), a SMA value of 0.084 $gCOD_{CH_4}$ g^{-1}VSS day^{-1} was obtained (typical SMA values of anaerobic biomass from a municipal anaerobic digester range between 0.02 and 0.2 $gCOD_{CH_4}$ g^{-1}VSS day^{-1} [20]).

To analyse dye solutions, samples were centrifuged and the supernatant was filtered through 0.45 μm pore size filters. Prior toxicity testing, samples were gassed with nitrogen to strip out