

## **Overcoming barriers in the treatment of textile wastewaters using advanced oxidation processes**

### ABSTRACT

Currently, the textile industry is one of the most important economic sectors in many countries. Besides, it is known as a major consumer of water and consequently one of the largest groups of industries causing intense water pollution. Chemicals, including surfactants, dyes, resins, dispersants agents, inorganic salts, etc., play a variety of functions during the textile processing and are present as a by-product in large volumes of toxic wastewater. As a consequence, textile industry has been challenged for colour removal, salt content reduction and elimination of the non-biodegradable organic fraction from the generated wastewaters. Biological processes are the preferred choice for textile wastewater treatment because they are less costly, and the by-products resulting from complete degradation are not toxic. However, conventional biological processes do not always provide satisfactory results, since many of the organic substances used in the textile industry are toxic or recalcitrant. Advanced oxidation processes (AOPs) have been considered a promising wastewater treatment technology for the elimination of recalcitrant/toxic organic pollutants, as those present in textile wastewaters. The main aim of this thesis was the study of alternative processes for the treatment of textile wastewaters, combining AOPs and biological oxidation. The treatment strategy was applied to four different textile wastewater, two real textile wastewaters and two synthetic ones. Firstly, for two textile wastewaters, both with high percentage of recalcitrant organic matter, a treatment strategy including AOPs and biological oxidation was proposed. The efficiency of different AOPs (UVA-Vis; UVA-Vis/TiO<sub>2</sub>; UVA-Vis/H<sub>2</sub>O<sub>2</sub>; UVA-Vis/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> and UVA-Vis/Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>) was compared in the treatment of a real cotton-textile dyeing wastewater using a pilot plant under natural sunlight. The obtained results demonstrated that solar-photo-Fenton treatment was the most efficient of all solar AOPs studied, enhancing the biodegradability of the wastewater and making possible its combination with a downstream biological oxidation process. The photo-Fenton reaction rate was also assessed at different iron concentrations, pH, temperature and light intensity, in a lab-scale prototype under controlled conditions using artificial solar radiation. Thus, considering the combination of a photo-Fenton reaction with a biological oxidation process, the energy dose required for the phototreatment was 0.5 kJUV L<sup>-1</sup> (T= 30°C; pH = 2.8), while consuming 7.5 mM of hydrogen peroxide and leading to 58.4% mineralisation (DOC<sub>f</sub> = 62.9 mg C L<sup>-1</sup>). Afterwards, the enhancement of a solar photo-Fenton reaction by using different ferric-organic ligands (oxalic acid, citrate acid and EDDS-Ethylenediamine-N,N'-disuccinic acid), applied to the treatment of a simulated acrylic-textile dyeing wastewater to increase its biodegradability, was evaluated. The catalytic activity of the organic ligands toward the ferrous-catalysed systems followed this order: Fe(III)-Oxalate > Fe(III)-Citrate > Fe(III)-EDDS, and all were better than the traditional photo-Fenton reaction. The influence of the main ferrioxalate-solar-photo-Fenton reaction variables, such as iron concentration, pH, temperature, UV irradiance and H<sub>2</sub>O<sub>2</sub> concentration and dosage strategy was also investigated. Thus, the ferrioxalate induced photo-Fenton process presented the best results, achieving 87% mineralisation after 9.3 kJUV L<sup>-1</sup> and allowing working until pH 5.0. As expected, the

biodegradability of the textile wastewater was significantly enhanced during the photo-Fenton treatment, achieving a value of 73%, while consuming 32.4 mM of H<sub>2</sub>O<sub>2</sub> and 5.7 kJUV L<sup>-1</sup>. For the other two textile wastewaters, both with high percentage of biodegradable organic matter, a biological oxidation treatment followed by AOPs was proposed. A synthetic polyester-cotton dyeing wastewater was firstly subjected to biological oxidation, achieving a DOC removal of 76%, resulting in a bio-treated wastewater with 84 mg L<sup>-1</sup> of DOC. The colour reduction was less than 5% (Pt-Co scale), 9% (DFZ436nm), 3% (DFZ525nm) and 0% (DFZ620nm). Thus, UVC/H<sub>2</sub>O<sub>2</sub> and photo-Fenton oxidation processes were used as a polishing step for the decolourisation of bio-treated textile wastewater. The photo-Fenton reaction did not promote the decolourisation. Moreover, the addition of oxalic acid did not result in an enhancement of the photo-Fenton reaction. On the other hand, the photolysis of hydrogen peroxide using UVC radiation led to decolourisation efficiencies of 71% (Pt-Co scale), 86% (DFZ436 nm) and 97% (DFZ525 nm) and more than 40% of mineralisation, consuming 14.1 mM H<sub>2</sub>O<sub>2</sub> and 2.5 kJUV L<sup>-1</sup> of energy (time = 95 min; 6W UVC lamp; natural pH = 8.4; T = 30°C). The influence of hydrogen peroxide dosage, lamp power, solution pH and temperature on the UVC/H<sub>2</sub>O<sub>2</sub> system was evaluated. It was shown that the UVC/H<sub>2</sub>O<sub>2</sub> reaction efficiency is mostly affected by the relation between H<sub>2</sub>O<sub>2</sub> dosage and lamp power. The integrated treatment strategy was able to achieve a wastewater quality in agreement with the discharge limits imposed by legislation. Finally, UVC/H<sub>2</sub>O<sub>2</sub> and photo-Fenton oxidation processes were used as a polishing step in the decolourisation of a bio-treated real textile wastewater. The photolysis of hydrogen peroxide using UVC radiation achieved decolourisation efficiencies of 86% (Pt-Co scale) and 96% (DFZ436nm), consuming 1.6 mM H<sub>2</sub>O<sub>2</sub> after 0.9 kJUV L<sup>-1</sup> (time = 35 min; UVC lamp power = 6 W; natural pH = 7.8; T = 30°C). The photo-Fenton reaction was promoted by different radiation sources (UVC, UVA or UVA-Visible), showing best results under UVC light. The efficiency of the UVC/Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> system was also studied for different iron concentrations, H<sub>2</sub>O<sub>2</sub> availability and pH values. Decolourisation efficiencies of 78% (Pt-Co scale) and 93% (DFZ436nm) were achieved applying the UVC/Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> system at pH = 2.8 and T = 30°C, consuming 3.6 mM H<sub>2</sub>O<sub>2</sub> after 0.6 kJUV L<sup>-1</sup> (time = 25 min; UV lamp power = 6 W). To further investigate the use of solar energy, additional photo-Fenton assays mediated by ferric-organic ligands under UVA-Visible radiation were also performed, considering the effect of the type of ferric-organic ligand as well as the iron/ferric-organic ligand molar ratio, iron concentration and pH. Maximum values for the decolourisation with UVA-Vis/Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub>/oxalic acid were 84% (Pt-Co scale) and 94% (DFZ436nm), consuming 1.9 mM H<sub>2</sub>O<sub>2</sub> after 2.9 kJUV L<sup>-1</sup> (pH = 2.8). In addition, the costs associated with the processes studied were estimated. For the optimal conditions, aiming at achieving the legal wastewater discharge requirements, the total unit costs were: a) 0.25 € m<sup>-3</sup> (UVC/H<sub>2</sub>O<sub>2</sub> at pH 2.8); b) 0.16 € m<sup>-3</sup> (UVC/H<sub>2</sub>O<sub>2</sub> at natural pH); c) 0.24 € m<sup>-3</sup> (UVC/Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> at pH 2.8); d) 0.61 € m<sup>-3</sup> (UVA-Vis/Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> at pH 2.8); e) 0.79 € m<sup>-3</sup> (UVA-Vis/Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub>/Oxalic acid at pH 2.8) and; f) 0.83 € m<sup>-3</sup> (UVA-Vis/Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub>/oxalic acid at pH 5.0).