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Comparative efficiencies of the decolourisation of leather dyes by enzymatic and electrochemical treatments

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ABSTRACT

Leather dyes are important chemical pollutants of industrial origin. The society demand for colour-free waste discharge to receiving waters has made decolourisation of industrial wastes a top priority. Due to their complex chemical structures, the decolourisation of these wastes is a challenging task. In this study, the decolourisation and degradation efficiency of six leather dyes by enzymatic and electrochemical treatments were studied. In the presence of salts, all dyes were totally decolourised by electrochemical treatment in 4 h. Though it has showed appreciable ability of enzymatic degradation, it was observed that the salts present in tannery effluents cause inhibition problems that significantly affected the dye degradation. In addition, enzymatic and electrochemical treatments with a mixture of the six dyes were carried out. Once again, the electrochemical treatment shows better results and after 4 h the obtained decolourisation was total which is squared with a complete total organic carbon (TOC) reduction. Besides, the degradation of this mixture was carried out successfully in a continuous electrochemical bubble reactor. Therefore, the results provide fundamental knowledge for the treatment of a leather wastewater stream.

1. Introduction

Dyes are widely used in textile, rubber, paper, plastic and cosmetic industries for colouring process [1]. Two percent of the dyes produced are discharged directly in aqueous effluent, with a further 10% subsequently lost during the textile colouration process [2]. Dye wastewater is commonly characterized as high in salt and organic content and low in biodegradation potential [3]. Direct discharge of dye effluents can cause serious problems to the environment due to the contribution of high organic loading, toxicity and aesthetic pollution related to colour. Contaminated dye can absorb and reflect sunlight entering the water stream causing interference with the growth of bacteria to levels such that the biological degradation of impurities is impeded and an ecological imbalance results [4].

The industrial use of leather dyes is increasing rapidly and presents significant problems for the treatment and decolourisation of wastewater containing dyes. In addition, high salt concentration used in dyebaths (up to 50 kg/m^3 sodium chloride) results wastewaters with high-salt content [5]. A variety of pH values and complex chemical structures may add to the complications.

In general, the decolourisation of industrial wastewater can be achieved by chemical (ozonisation, alkalinisation with calcium hydrosulphate…) [6], physical (adsorption, flocculation-filtration…) [7] and biological treatments [8]. Dye effluents are poorly decolourised by conventional biological wastewater treatment and may be toxic to the microorganisms used in the treatment plants.

There is a need to determine technologies that achieve technically and economically efficient reduction of colour in textile industry discharges. Among these technologies the electrochemical treatment can be consider as good solution to decolourise and degrade dye molecules [9]. The electric current induces redox reactions resulting in the transformation and destruction of the organic compounds and almost complete oxidation to CO_2 and H_2O. The oxidation of pollutants in an electrolytic cell can occur through the anodic oxidation, cathodic reduction or indirect oxidation. The main advantages of using these electrochemical methods include that they do not consume a significant amount of chemicals, nor do they produce sludge. Additionally, the processes are commonly performed at room temperature and atmospheric pressure, thus avoiding the undesirable volatilization and discharge of untreated residues [10].

On the other hand, bioremediation with oxidative enzymes is seen as a very promising alternative. Among them, laccase (benzenediol: oxygen oxidoreductase; EC 1.10.3.2) is particularly interesting since it only needs molecular oxygen (air) as a co-substrate. Laccases are multicopper oxidases that are able to oxidise a wide variety of xenobiotics compounds such as synthetic dyes, chlorinated phenolics and polycyclic aromatic hydrocarbons. Previous studies by our research group have shown the ability of the crude laccase from the white-rot fungus *Trametes hirsuta* to decolourise synthetic dyes from the leather industry [11]. However, total decolourisation of the dyes was not achieved despite the high potential for dye decolourisation showed by *T. hirsuta* laccase [12].

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Despite an extensive literature concerning the application of electrochemical technologies and enzymatic treatment for removing dyes from water [8], [13–16] and [17], there are no reports concerning comparative studies between both methodologies. For this reason, to determine the more efficient technology for leather dye wastewater, in this study the decolourisation and degradation efficiency of enzymatic and electrochemical treatments with several leather dyes Derma Carbon (DC NBS), Derma Burdeaux (DB V), Derma Pardo 5 GL (DP 5GL), Derma Blue (DB DBN), Sella Solid Yellow 4GL (SSY 4GL) and Sella Solid Blue 4GL (SSB 4GL) were studied.

2. Materials and methods

2.1. Dye solutions

In this work several dye solutions were used to evaluate the enzymatic and electrochemical treatments. The chosen dyes were Derma Carbon (DC NBS), Derma Burdeaux (DB V), Derma Pardo 5 GL (DP 5GL) and Derma Blue DBN (DB DBN) manufactured by Clariant Iberica, SA (Spain) and Sella Solid Yellow 4GL (SSY 4GL) and Sella Solid Blue 4GL (SSB 4GL) manufactured by TFL (Germany). The purity of these commercial dyes is around 90–95%. The dye characteristics and their concentrations are described in Table 1. When the six leather dyes are used together, their concentrations are reduced by 25%. Furthermore, in several experiments a salt mixture of NaCl (5 g/L) and Na_2SO_4 (2 g/L) was added to simulate the real wastewater of dyeing process [3,18].

2.2. Laccase

Commercial *Trametes versicolor* laccase was obtained from Sigma. Laccase activity was determined spectrophotometrically by the method of Niku-Paavola et al. [19] with ABTS (2, 2′-azino-di-[3-ethyl-benzothiazoline-(6)-sulphonic acid], Boehringer) as substrate. The laccase reaction mixture (in a total volume of 3 mL) contained 2.3 mL enzyme diluted to buffer (25 mM succinic acid, pH 3.0) and 0.7 mL 20 mM ABTS. The reaction was monitored at room temperature by measuring the change in A_{436} for 2 min. One activity unit was defined as the amount of enzyme that oxidised 1 μmol of ABTS per minute and the activities were reported as U/L.

2.3. Enzymatic treatment

During the enzymatic experiments, the reaction mixture (final volume 1.5 mL) consisted of an aqueous solution of dye, laccase (final concentration 500 U/L) in citrate phosphate buffer at pH 5.0 (stock solutions are 0.2 M dibasic sodium phosphate; 0.1 M citric acid). Dye concentrations are shown in Table 1, the initial dye concentrations were selected around 2.0 absorbance units, at the maximum wavelength, in order to operate below the spectrophotometer saturation measure. All the reactions were incubated at room temperature (22 °C), in static conditions and in complete darkness, to avoid the possible photodegradation. The reaction mixture was analysed for dye concentration before and after the enzymatic treatment. Control test mixture in enzymatic treatment containing the same amount of a heat-denatured laccase was conducted in parallel.

Table 1
Dye characteristics description.

Dye	Conc. (g/L)	Type	λ_{max} (nm)
Derma Carbon — DC NBS (Direct black 168)	0.15	Mixture of both direct and acid, anionic	637
Derma Burdeaux — DB V (Acid red 119)	0.07	Acid, anionic	521
Sella Solid Blue 4 GL — SSB 4GL (Direct blue 78)	0.07	Direct	559
Derma Pardo 5 GL — DP 5GL (Acid brown 98)	0.10	Acid, metal complex (Fe), anionic	439
Derma Blue DBN — DB DBN (Acid blue 312)	0.05	Acid, anionic	580
Sella Solid Yellow 4 GL — SSY 4GL (Acid yellow 166)	0.10	Acid, anionic	403

2.4. Electrochemical treatment

2.4.1. Batch treatment: electrochemical rectangular cell

Experiments were carried out in a reaction cell with a rectangular body with a working volume of 0.1 L, by using graphite electrodes with an immersed area of 19 cm^2, and an electrode gap of 6.5 cm (Fig. 1a). A constant potential difference (5 V) [5] was applied with a power supply (HP model 3662), and the process was monitored with a multimeter (Fluke 175). Graphite electrodes were fixed in caps, which can be mounted on the ends of the cell body and magnetic stirring was used to avoid concentration gradients. Samples of reaction mixtures were taken from the electrochemical cell in order to be analysed for residual dye concentration. A control test with no electric current was conducted in parallel. The experiments were performed at room temperature (22 °C).

2.4.2. Continuous treatment: electrochemical bubble reactor

A glass cylindrical reactor with two electrode bars connected to a direct current (DC) power supply was used (Fig. 1b). The electrochemical bubble reactor had working volume of 0.1 L, an air flow was introduced at the reactor bottom as turbulence promoter in order to avoid concentration gradients and was operated in continuous mode (flow rate 0.0667 L/h). Graphite bars were employed as electrode. Each bar was 60 mm high with a diameter of 6.35 mm for graphite, resulting in a total contact surface area of 1.90 cm^2. The cathode and anode bars were placed 350 mm and 700 mm above the bottom of the cell, respectively. A constant potential difference (5 V) was applied with a power supply (HP model 3662). Samples of reaction mixtures were taken from the electrochemical reactor in order to be analysed for residual dye concentration. A control test with no electric current was conducted in parallel. The experiments were performed at room temperature (22 °C).

2.5. Dye decolourisation

The absorption spectrum showed in all cases a single peak with a strong absorption in the visible region at the wavelength indicated in Table 1. Therefore, the initial and residual dye concentrations were measured spectrophotometrically (Unicam Helios β, Thermo Electron Corp.) from the area under the curve between λ = 300 and 750 nm. Dye decolourisation was expressed in terms of percentage.

$$D = \frac{A_i - A_t}{A_i} \cdot 100 \quad (1)$$

where D, decolourisation (in %); A_i and A_t, area under the curve of each dye at the initial and through time, respectively. The assays were done twice, the experimental error was calculated as standard deviation (SD) and in all cases the SD was below 3%.

2.6. Total organic carbon determination

Total organic carbon content (TOC) was determined by difference method using a Lange cuvette test (LCK 380) in a Hach Lange DR 2800. The sample was introduced in the Lange cuvette. Under the conditions of the test, the carbon forms carbon dioxide, which diffuses through a membrane into an indicator solution. The change of colour of the indicator solution is evaluated photometrically.