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Decolourisation of dye solutions by oxidation with H_2O_2 in the presence of modified activated carbons

V.P. Santos, M.F.R. Pereira, P.C.C. Faria, J.J.M. Órfão*

Laboratório de Catálise e Materiais (LCM), Laboratório Associado LSRE/LCM, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

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ABSTRACT

The decolourisation of dye solutions by oxidation with H_2O_2, using activated carbon as catalyst, is studied. For this purpose, three different samples, mainly differing in the respective surface chemistries, were prepared and characterized. Moreover, this work involved three pH levels, corresponding to acid, neutral and alkaline solutions, and six dyes belonging to several classes. The catalytic decolourisation tests were performed in a laboratorial batch reactor. Adsorption on activated carbon and non-catalytic peroxidation kinetic experiments were also carried out in the same reactor, in order to compare the efficiencies of the three processes. The non-catalytic reaction is usually inefficient and, typically, adsorption presents a low level of decolourisation. In these cases, the combination of activated carbon with hydrogen peroxide may significantly enhance the process, since the activated carbon catalyses the decomposition of H_2O_2 into hydroxyl radicals, which are very reactive. Based on the experiments with the different activated carbon samples, which have similar physical properties, it is proved that the surface chemistry of the catalyst plays a key role, being the basic sample the most active. This is discussed considering the involvement of the free electrons on the graphene basal planes of activated carbon as active centres for the catalytic reaction. Additionally, it is shown that the decolourisation is enhanced at high pH values, and a possible explanation for this observation, based on the proposed mechanism, is given.

1. Introduction

One of the main problems found in the decontamination of textile effluents is the removal of colour. When introduced in water courses, the highly coloured components resulting from the incomplete fixation of dyestuffs on textile substrates may cause significant disturbance in the ecological systems, beyond the undesirable aspect of the receiving waters [1]. Furthermore, several studies have shown that some of those compounds are highly carcinogenic [2,3]. Hence, degradation of organic dyes is necessary from a point of view of public health and safety.

Due to the variability of the organic dyes used and the corresponding effluents, there is a wide range of treatment techniques for this type of wastewater. Most of them include an initial step of activated sludge treatment to partially remove the organic matter, followed by oxidation (usually with ozone [4], Fenton's reactant [5] or H_2O_2/UV [6]), or by membrane separation [7], or by adsorption on activated carbon [8,9]. Despite this variety, there is no single process capable of adequate treatment, due to the complex nature of these effluents [10]. Hence, the better solution for textile wastewater treatment is a combination of different techniques.

Environmentally, H_2O_2 is a friendly oxidant. Recent studies [11–13] indicate that the combination of H_2O_2 and activated carbon into a single process could offer an attractive alternative for coloured wastewater treatment. This type of procedure combines adsorption and catalysis in a single step, taking advantage of the performance of activated carbon as adsorbent and catalyst (mainly resulting from its large surface area and flexibility, i.e. the possibility of tailoring the porous structure and the surface chemical properties for a specific application). One disadvantage of the process is the risk of saturation and/or deactivation of the catalyst, which would require regeneration or complete replacement. The studies in this area proposed reaction mechanisms that involve the formation of $HO^\bullet$ radicals, justifying the inclusion of this type of treatment in the group of advanced oxidation processes.

In this work, the decolourisation kinetics of different dye solutions was studied in a laboratory scale batch reactor by three different processes: adsorption on activated carbon, non-catalytic oxidation with H_2O_2 and oxidation with H_2O_2 in the presence of activated carbon. The main goal of this study is to evaluate the synergic effect between H_2O_2 and activated carbon in the oxidation of

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* Corresponding author. Tel.: +351 22 508 1665; fax: +351 22 508 1449.
E-mail addresses: santos.vera@fe.up.pt (V.P. Santos), fpereira@fe.up.pt (M.F.R. Pereira), pfaria@fe.up.pt (P.C.C. Faria), jjmo@fe.up.pt (J.J.M. Órfão).

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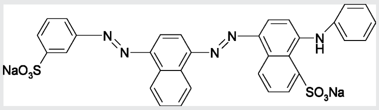
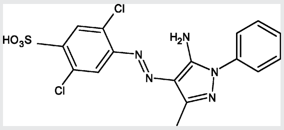
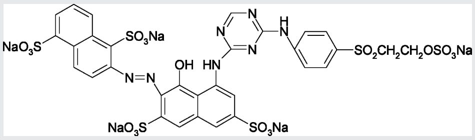
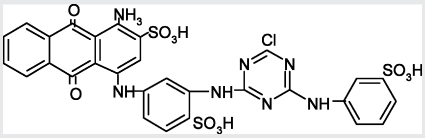
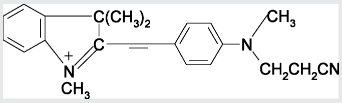
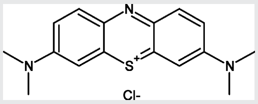
Table 1
Main characteristics of the selected dyes

Class	Commercial and generic name	Molecular structure	Chemical class	λ_{max} (nm)
Acid	Erionyl Navy R, CI Acid Blue 113		Diazo	566
Acid	Telon Light Yellow FG, CI Acid Yellow 49		Monoazo	402
Reactive	Rifafix Red 3BN, CI Reactive Red 241		Monoazo	540
Reactive	Cibacron Blue BR, CI Reactive Blue 5		Anthraquinone	597
Basic	Astrazon Brilliant Red 4G, CI Basic Red 14		Cyanine	513
Basic	Methylene blue, CI Basic Blue 9		Thiazine	664

organic dyes, considering in the analysis both the initial solution pH and the surface chemistry of the carbon material.

2. Materials and methods

2.1. Preparation of modified activated carbons

The starting material used in this work is the activated carbon Norit GAC 1240 PLUS (granulates with diameters between 0.42 and 2.0 mm). This material was submitted to different modifications, using well-established procedures such as the oxidation with HNO_3 and the thermal treatment with H_2, in order to produce samples with different surface chemistries, while maintaining the original textural properties as far as possible. The samples are labelled as follows: ACo: activated carbon Norit GAC 1240 PLUS; ACa: sample ACo oxidized in the liquid phase with HNO_3 6 M at boiling temperature for 3 h, using a Soxhlet extraction apparatus; ACb: sample ACa thermally treated under H_2 flow at 700 °C for 3 h plus 1 h under dry air flow at room temperature. A detailed description of these treatments can be found in Pereira et al. [8].

2.2. Characterization of the activated carbon samples

The textural and surface chemical properties of the activated carbon samples were obtained by the following techniques, as described elsewhere [9]: N_2 adsorption at 77 K, determination of acidity, basicity and pH_{pzc}, and temperature programmed desorption (TPD). XPS analyses of sample ACo before and after reaction were also performed, in order to evaluate the possible effect of the prolonged contact with hydrogen peroxide during reaction on the surface chemistry of the catalyst.

2.3. Chemicals

The coloured effluents were simulated considering various dyes belonging to different classes: CI Acid Blue 113, CI Acid Yellow 49, CI Reactive Red 241, CI Reactive Blue 5, CI Basic Red 14 and methylene blue. Their main characteristics are shown in Table 1. The textile anionic dyes CI Acid Blue 113 and CI Reactive Red 241 were analysed with particular detail. The respective stock solutions were prepared by dissolving a selected amount of each dye in deionised water.

Hydrogen peroxide (30%, w/w) was obtained from Fluka. Other chemicals were of analytical reagent grade and were used without further purification.

2.4. Decolourisation experiments

All the experiments were carried out at room temperature in a laboratorial stirred reactor (800 mL). The influence of both the initial pH (3 and 7 for CI Acid Blue 113 and 3, 7 and 10 for CI Reactive Red 241) and the surface chemistry of activated carbon on the decolourisation of the dye aqueous solutions were assessed. In order to analyse the magnitude of external and internal mass transfer resistances, preliminary experiments were carried out at different agitation rates and carbon particle sizes ($0.42\ mm < \phi < 2.0\ mm$ and $0.1\ mm < \phi < 0.3\ mm$). According to this study, a particle size between 0.1 and 0.3 mm was selected, in order to reduce internal mass transfer resistances. The agitation level used was high enough to maintain the system perfectly mixed and without external mass transfer resistances.

The typical reaction tests were performed introducing into the reactor 300 mL of H_2O_2 3 M, 300 mL of a 100-mg L^{-1} dye solution and 1.3 g of activated carbon ($0.1\ mm < \phi < 0.3\ mm$), at the desired pH (adjusted with HCl or NaOH solutions). The effect of the carbon