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Kinetic modelling of the hematin catalysed decolourization of Orange II solutions

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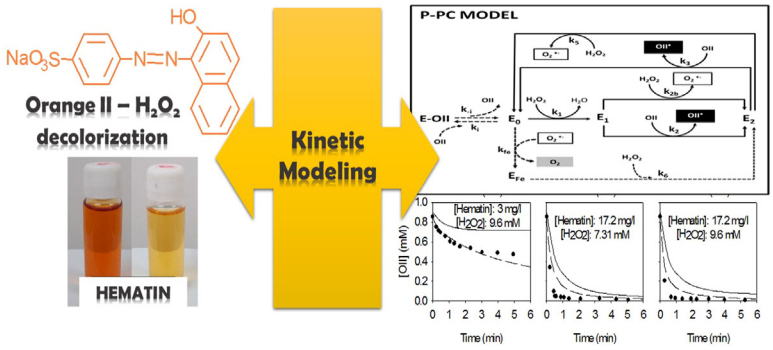
HIGHLIGHTS

- Mechanistic models for hematin-catalysed decolourization of Orange II were validated.
- Ineffective hematin-catalysed H_2O_2 dismutation was detected and simulated.
- High Orange II levels caused rates depletion probable by blocking hematin activation.
- Hematin inactivation by superoxide explained biphasic profiles during H_2O_2 dismutation.

GRAPHICAL ABSTRACT



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ABSTRACT

A mathematical description of the kinetics of the hematin catalysed decolourization reaction of Orange II alkaline solutions was constructed and validated under the assumption that hematin mimics the action of peroxidases. The clean oxidant H_2O_2 was applied, however, hematin dismutated it, as catalases do, under reaction conditions. Thus, special attention was cared to the understanding of this ineffective side-reaction by the proposal of straightforward pathways concerning the catalatic or the pseudo-catalatic cycles. Model validations were implemented by a parametrization procedure of relevant rate constants under dynamic simulation fitting to selected experimental time-courses data. The peroxidatic coupled to pseudo-catalatic mechanism gave predictions closer to experimental findings in a wide range of conditions. The initial rate method for data processing was successfully applied for providing reliable initial rate constant guesses but also for the detection of unexpected rate depletion at high dye concentrations. This was considered in the model as unproductive dye coordination to hematin native state prior to H_2O_2 activation. The pseudo-catalatic pathway involves the production of superoxide and its coordination to hematin native state to afford inactive but regenerable ferrous porphyrin. Model underestimations of experimental data were interpreted as cooperative oxidation of Orange II molecules by superoxide whereas model deviations at high dye concentration (>400 mg/l) was assigned to further hematin catalysed oxidation of Orange II degraded products.

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1. Introduction

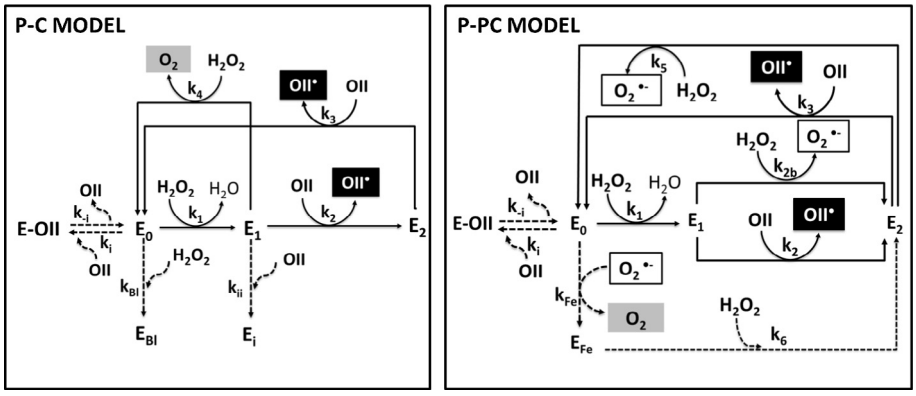
Textile wastewaters have different composition depending on the kind of fabrics produced at the particular industry. Nevertheless, all of them are characterized by high values of pH, chemical oxygen demand (COD) and biochemical oxygen demand (BOD) (Centro Panamericano de Ingeniería Sanitaria y Ciencias del Ambiente, 1994, 1997). The effluents generated during the dyeing step reach 65% of the total wastewater (Lachheb et al., 2002). Different technologies focusing on synthetic dyes degradation have been developed based on model studies. Orange II (OII, C.I. 15510) is one of the most used azoic dyes (Hunger, 2003) and it has been extensively studied as model compound (Cardona et al., 2009; Gong et al., 2010; Hai et al., 2009; Lodha and Chaudhari, 2007).

Chemicals methods named as Advanced Oxidation Processes (AOPs) include the generation of hydroxyl radical ($OH^{\cdot}$), able to degrade the organic matter. The most studied AOPs methods are Fenton and Fenton-like. Iron salts catalyse hydroxyl radical formation (Babuponnusami and Muthukumar, 2014; Chen and Zhu, 2010; Liang et al., 2010; MacKay and Pignatello, 2001). However, those systems required acidic pH to achieve high yields. Biological treatments use bacteria or fungi to degrade organic contaminants. Mono and di-oxygenases of these organisms can catalyse oxygen incorporation at double bonds in aromatic compounds (Saratale et al., 2011). Synthetic dyes with azo or sulfonic groups are recalcitrant because of their resistance to oxygenases (Saratale et al., 2011). In order to improve the efficiencies of biological treatments, enzymatic methods have been successfully developed. Excellent results of peroxidase-mediated OII decolourization have been published (López et al., 2004a,b; Yousefi and Kariminia, 2010). The removal of phenolic pollutants from aqueous solutions catalysed by Horseradish Peroxidase (HRP) has been extensively studied (Bhunia et al., 2001; Hamid and Khalilur, 2009; Nicell et al., 1995; Ulson de Souza et al., 2007; Wagner and Nicell, 2002). However, spite of high performance in phenolics oxidation using peroxidases, several drawbacks arose including: (1) enzyme's high cost, (2) H_2O_2-mediated inactivation and (3) organic radicals-mediated inactivation, among others.

Biomimetic systems based on synthetic or natural, porphyrinic or nonporphyrinic metal complexes have been studied as replacement of enzymes in synthetic dyes degradation (Ambrosio et al., 2004; Hodges et al., 1997; Pirillo et al., 2010a,b; Zucca et al., 2008). Our research group published promising results about the use of hematin as a HRP biomimetic (Córdoba et al., 2012a,b, 2015). Hematin is a natural IX-ferry-protoporphyrin analogous to the active site of HRP and catalases (Sheldon, 1994). At least 92% conversion of OII (75 mg L^{-1}) after 1 h -hematin/H_2O_2 treatment- was obtained corresponding to azo bond cleavage followed by degradation into aromatic and aliphatic carboxylic acids (Córdoba et al., 2012a). Indeed, response surface analysis was implemented to determine the effects of operational conditions (temperature, pH, oxidant and catalyst concentration). Temperature (in the range 30–50 °C) was a statistically insignificant factor on conversion as well as on catalytic efficiency (defined as mmol of converted OII per gram of catalyst, per mmol of oxidant) according the experimental design results analysis. This was not an expected result and it was interpreted as typical for reaction mechanisms involving radicals.

HRP oxidation mechanism (i.e. peroxidatic mechanism) and its inactivation routes have been studied by different authors (Dunford, 1999, 2002; Hernández-Ruiz et al., 2001; Hiner et al., 2001; Loew et al., 1997; Nicell and Wright, 1997; Reihmann and Ritter, 2006; Rich and Iwaki, 2007; Veitch, 2004; Vlasits et al., 2010; Vojinovic et al., 2004). HRP-catalysed hydrogen abstraction from reducing substrates has been confirmed (Buchanan and Nicell, 1997; Dunford, 1999; Reihmann and Ritter, 2006). Different metalloporphyrin oxidation mechanisms have been deeply discussed (Bruice et al., 1988; Hodges et al., 1997; Rebelo et al., 2005; Stephenson and Bell, 2007a; Traylor and Xu, 1987). Nam, Bell and coworkers proposed a Fenton-based mechanism with Fe (II) intermediates species and homolytic cleavage of the peroxidic bond (O—O) of H_2O_2 (Bell et al., 1991; Nam et al., 2000, 2001; Stephenson and Bell, 2005). However, heterolytic O—O cleavage with formation of an oxoperferryl π-cation radical (as the analogous to HRP species E_1) is widely accepted (Nam et al., 2000; Stephenson and Bell, 2005; Traylor and Xu, 1990).

In a previous work by our group a peroxidatic model for phenol oxidation based on the HRP reaction mechanism was proposed for hematin. UV–visible analysis and kinetic modeling results were in line with formation of Compound I and II (E_1 and E_2) (Córdoba et al., 2015). On the other hand, O_2 production was observed in phenol/H_2O_2 systems only with hematin, in line with the existence of an effective "catalatic-pathway", i.e. catalytic H_2O_2 dismutation ($2\ H_2O_2 \rightarrow 2\ H_2O + O_2$). Hernández-Ruiz, Hiner and coworkers modelled the HRP catalatic-like activity as a single coordination reaction between E_1 and H_2O_2 to E_0, analogous to catalases (Hernández-Ruiz et al., 2001; Hiner et al., 2001). Besides, Vlasits and coworkers reviewed the mechanism of catalase activity of heme peroxidases and postulated a pseudo-catalatic mechanism involving hydroperoxyl radical formation ($HOO^{\cdot}$) (Vlasits et al., 2010). During the study of phenol polymerization, Akkara et al. suggested an hematin oxidation mechanism with E_1 and E_2 formation and a catalatic pathway (Akkara et al., 2000). Based on this scenario, the peroxidatic mechanism was proposed for decolourization of Orange II solution catalysed by hematin but coupled to



Scheme 1. Peroxidatic and Catalatic Mechanisms. P-C MODEL: Peroxidatic coupled to catalatic pathway; P-PC MODEL: Peroxidatic coupled to pseudo-catalatic pathway. Dash lines denote added routes to original pathways in order to interpret experimental data.