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Heterogeneous Fenton's oxidation using Fe/ZSM-5 as catalyst in a continuous stirred tank reactor

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ABSTRACT

This work is the first known report dealing with the heterogeneous Fenton-like process in a continuous stirred tank reactor. A Fe/ZSM-5 zeolite was used as catalyst for degradation of an azo dye (Orange II, OII)-containing solution.

A parametric study was carried out to evaluate the effect of the main operating conditions in the basket reactor performance, namely temperature (in the range 10–70 °C), pH (1.5–4.0), feed hydrogen peroxide concentration – $[H_2O_2]_{feed}$ (1.75–20.0 mM), contact time – W/Q (10–200 mg min/mL), residence time – t_{resid} (30–180 min) and the size of the catalyst particles ($0.25 < dp_1 < 0.60$, $0.60 < dp_2 < 0.80$ mm and as pellets, $dp_3 > 5$ mm), for a OII feed concentration of 0.1 mM. Under the best operating conditions found (pH = 3.0, T = 70 °C, $[H_2O_2]_{feed}$ = 6 mM, W/Q = 200 mg min/mL, dp_2 and t_{resid} = 90 min), it was achieved 91% of discoloration and 36% of mineralization, at steady-state. Moreover, it was found a removal of 29% in terms of the chemical oxygen demand (COD), being worth noting the improvement in the effluent biodegradability (k' – oxygen uptake rate – increased from 9.3 to 23.2 $mgO_2/(g_{VSS}\ h)$) and the fact that the final effluent is non-toxic (0.0% of *Vibrio fischeri* inhibition).

The stability of the catalyst performance was checked during five consecutive runs. The crucial factor for the catalyst long-term use is the leaching of iron, which in all runs reached very low levels (e.g. only 0.173 mg/L of iron for the run in the optimized conditions, corresponding to only 0.13% of leaching). The catalyst was characterized by different techniques before and after the reactions (namely SEM/EDS and N_2 adsorption); textural and chemical transformations during its use can be considered negligible (except for very acidic conditions of pH = 1.5) favoring the catalytic stability of the Fe–zeolite.

1. Introduction

Water pollution, caused by the discharge of effluents into the environment without prior treatment, is a serious problem worldwide. The chemical industry is one of the biggest polluting entities, where the industry of organic dyes is a non-negligible part contributing to the total pollution by ca. 3–4% [1]. It is estimated that for every ton of dyes used are produced between 25 and 250 m^3 of dye-containing effluents [2].

In textiles manufacturing, a large amount of dyes is lost during the dyeing step, because the fixation rate is sometimes only as low as 50% [3]. Thus, high volumes of colored effluents are generated, which are often difficult to degrade, although typically they contain low concentrations of dyes (approximately 0.1 mM) [4]. These compounds, and due to their complex structure, can hardly be removed by biological or physical–chemical processes such as coagulation/flocculation, sedimentation, flotation, filtration and adsorption. Moreover, in most of such processes there is only transfer of the dyes from one phase to another, rather than their destruction [5].

In recent decades, the advanced oxidation processes (AOPs) have gained importance in this area, namely the Fenton's process due to its effectiveness in degrading organic compounds at room temperature and atmospheric pressure [6]. AOPs are based on the high oxidation power of the hydroxyl radicals ($HO^{\cdot}$) generated, as compared to other existing oxidants, being capable of oxidizing most organic compounds, sometimes with total mineralization, that is, with complete oxidation until the final products as CO_2 and H_2O.

The Fenton's process is an AOP based on a catalytic reaction involving hydrogen peroxide where there is an exchange of

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electrons between the oxidant and a transition metal, usually iron, which acts as a catalyst, to yield, among other products, the said hydroxyl radicals, as described by the simplified Eqs. (1)–(3) [7]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^{\cdot} \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^+ \quad (2)$$

$$HO^{\cdot} + \text{organic matter} \rightarrow \text{oxidation products} \quad (3)$$

Despite its proven efficacy, the homogeneous Fenton process has some disadvantages, including the need for a high amount of iron ions (about 50–80 ppm) in solution, which subsequently implies downstream processes for their removal/recovery. This removal requires the inclusion of another stage in the treatment process, thus making it more expensive and complex [7]. To minimize these disadvantages, different forms to attach the iron species to a porous solid matrix (such as a zeolite, clay or activated carbon support) were studied – so-called heterogeneous Fenton-like process [5,8,9–15].

The principles of the heterogeneous Fenton-like reaction are the same of the homogeneous one, however, owing to the phenomena of adsorption and catalysis, the process becomes more complex. Eqs. (4) and (5) present the main reactions involved:

$$X - Fe^{3+} + H_2O_2 \rightarrow X - Fe^{2+} + HO_2^{\cdot} + H^+ \quad (4)$$

$$X - Fe^{2+} + H_2O_2 \rightarrow X - Fe^{3+} + OH^- + HO^{\cdot} \quad (5)$$

where X represents the surface of the catalyst; reaction (4) describes the reduction of Fe^{3+} to Fe^{2+} yielding HO_2 radicals (which are less oxidative than $HO^{\cdot}$ species), and then the resultant Fe^{2+} is responsible for the production of hydroxyl radicals, described in Eq. (5) [7].

Zeolites are hydrated aluminosilicates that can accommodate a variety of different positive ions such as iron, sodium, calcium, barium or potassium. They have a highly regular three-dimensional structure, with high porosity and, consequently, high surface area [16,17]. Zeolites are of particular interest as catalysts in this topic; in fact, their catalytic and adsorptive potential are well known in various reactions such as the reduction of nitrous oxides, oxidation of benzene to phenol, as well as in heterogeneous AOPs, namely ozonation [18,19], photo-Fenton [20–22] and Fenton [17,23–26] processes.

It should be noted that the overwhelming majority of the works that are available in the literature make use of closed (or batch) reactors, which brings disadvantages of industrial applicability because they operate discontinuously. In the field of continuous packed-bed reactors, the work by Mesquita et al. [14] and Duarte et al. [8] proved the ability of iron-containing activated carbon to act as heterogeneous catalyst in the Fenton's process. In particular, Duarte et al. [8] achieved 97% of dye degradation and 74% of total organic carbon (TOC) removal from an effluent containing 0.01 mM of alcian blue dye, while Mesquita et al. [14], for a 0.01 mM solution of chicago blue, reached removals of 88% and 47% for dye and TOC, respectively. Although there are some (but little) studies with packed-bed (or column) reactors, these reactors present problems of mass transfer due to the formation of bubbles (O_2 and/or CO_2) that are caught in the catalyst particles; such problems should not occur in a configuration like a continuous stirred tank reactor (CSTR).

The CSTR is a configuration widely used in the chemical and biological industry. Recently, it was investigated the applicability of the homogeneous Fenton process in a CSTR, where a detailed parametric study was carried out, resulting in a very good degradation of the dye, which reached 95%, proving that the concept of applying a homogeneous Fenton CSTR is plausible [27]. Other authors achieved high performances (97% for organic matter and 99% for phenolic compounds removal) when treating an olive-oil mill wastewater by the homogeneous Fenton's process using a CSTR [28]. Zhang et al. [29] applied the homogeneous Fenton oxidation in a CSTR for treating a landfill leachate effluent and also reached good efficiencies of COD removal (in the range 76.6–94.3% when initial COD varied between 1000 and 3000 mg/L).

The industrial wastewater processing using batch vessels (closed reactors) by the homogeneous Fenton's reagent implies a further separation of the iron in solution, presenting itself as a time consuming and with little future alternative; indeed, a secondary treatment of the effluent is required. The application of the treatment process in a heterogeneous CSTR presents itself as a promising approach, allowing operating continuously and without the disadvantages of the homogeneous process. Moreover, and up to the author's knowledge, it was never tested before. In this work it is therefore intended to proof the concept of applying the Fenton's process in a continuous heterogeneous perfectly stirred tank reactor, and evaluate the influence of some parameters on the degradation of the dye Orange II (OII).

2. Materials and methods

2.1. Catalyst and its characterization

The catalyst selected for this work was a zeolite in pellets form ($d_p > 5$ mm), with trade name Alsi-Penta Fe/ZSM-5 (ref. FE-SH-27). These pellets were milled and sieved to obtain different fractions ($0.25 < dp_1 < 0.60$, $0.60 < dp_2 < 0.80$ mm and as pellets, $dp_3 > 5$ mm). The fresh and used zeolite samples were morphologically characterized by scanning electron microscopy (SEM) using a GEMINI (Carl Zeiss SMT) microscope equipped with EDS microanalysis; the iron distribution was analyzed by mapping before and after the catalytic reactions.

The porous texture of the materials was analyzed by N_2 adsorption at −196 °C using an Autosorb 1 equipment from Quantachrome. Prior to measuring the N_2 adsorption isotherms, samples were outgassed overnight at 110 °C and under high vacuum (10^{-6} mbar). N_2 adsorption isotherms were analyzed by the BET equation (bellow $P/P_0 = 0.10$) from which the surface area, S_{BET}, was obtained. To characterize the microporosity of the samples, the Dubinin–Radushkevich (DR) equation was applied to N_2 adsorption data [30]:

$$W = W_0 \exp\left[\left(-\frac{A}{\beta E_0}\right)^2\right] \quad (6)$$

where W is the amount adsorbed at relative pressure P/P_0, W_0 is the limiting value filling the micropores (micropore volume), A is the differential molar work given by $A = RT \ln(P_0/P)$, β is the affinity coefficient, taken to be 0.33 for N_2, and E_0 is the characteristic adsorption energy. Then the mean micropore width, L_0, was obtained by applying the Stoeckli equation [31]:

$$L_0\,(\text{nm}) = \frac{10.8}{E_0\left(\frac{\text{kJ}}{\text{mol}}\right) - 11.4} \quad (7)$$

The pore size distributions (PSD) were determined by applying the Quenched Solid Density Functional Theory (QSDFT), assuming slit-shaped pores and BJH derived methods [32,33] to the N_2 adsorption isotherms. The total pore volume is considered as the volume of adsorbed nitrogen at a relative pressure of $P/P_0 = 0.95$ ($V_{0.95}$) according to Gurvitch's rule. Thus, mesopore volume, V_{meso}, was obtained from the difference between the total pore volume ($V_{0.95}$) and the micropore volume (W_0 (N_2)) [34].