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Using central composite experimental design to optimize the degradation of black liquor by Fenton reagent

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ABSTRACT

We investigated the advanced oxidation of the black liquor effluent from the pulp and paper industry using the dark Fenton reaction in a lab-scale experiment based on central composite experimental statistical design. The independent variables considered for the optimization of the oxidative process were temperature, H_2O_2 and Fe(II) concentrations, for a black liquor with a chemical oxygen demand (COD) of 628 $mg \cdot L^{-1}$ O_2 at pH = 3. The response functions were the decrease in COD, aromatic content (UV_{254}) and lignin content (UV_{280}). The methodology lets us identify and statistically evaluate the effects and interactions of the study variables and their roles in the efficiency of the treatment process. In the optimization, the correlation coefficients for the model (R^2) were 0.954 for COD, 0.936 for UV_{254} and 0.945 for UV_{280}. Optimum reaction conditions at pH = 3 and temperature = 298 K were $[H_2O_2]$ = 44.1 mM and [Fe(II)] = 4.655 mM. At these optimal conditions, the molar ratio H_2O_2/Fe(II) was 9.5. Under these conditions, 90 min of treatment resulted in a 94.8% decrease in COD, an 80.9% decrease in UV_{254} and an 85.6% decrease in UV_{280}.
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1. Introduction

The environmental pollution caused by small- and medium-scale pulp and paper facilities is multidimensional and causes serious problems not only for the fertility of soils and bodies of water but also for natural flora and fauna.

Black liquor, an intermediate product produced during various pulp production processes that use, wood and non-wood raw materials, is an important industrial fuel [1]. The black liquor produced from wood raw materials is generally burned in recovery boilers in the form of small drops, with the objective of simultaneous recovery of heat and chemicals. However, small- and medium-scale pulp and paper facilities are not always equipped with recovery units. Consequently, these facilities produce high amounts of residual black liquor, which is difficult to dispose of and therefore represents an environmental problem. Moreover, black liquor contains valuable chemical compounds, such as lignin, that could be recovered [2]. As a consequence, the final effluent is a serious pollutant that must be treated, and high treatment costs can make the production process uncompetitive. Specially polluted are black liquors generated when using non-wood raw materials for the production of pulp [3].

Different physical–chemical processes, including chemical oxidation, have been used to treat this kind of effluent [4,5]. These treatments include both aerobic and anaerobic biological treatment schemes [4,5]. However, in the presence of toxic or recalcitrant compounds, biological treatments may be inhibited or the microorganisms may be destroyed.

Increasing public concern and the application of stringent international environmental standards such as ISO 14001 for environmental management systems (http://www.iso.org/iso/iso 14000 essentials) have created the need for novel treatment methods capable of converting organic and inorganic contaminants into harmless final products.

Advanced Oxidation Processes (AOPs) are powerful remediation technologies that generate highly reactive *hydroxyl radicals* ($HO^{\bullet} + H^+ + e^- \rightarrow H_2O$, $E^0 = 2.8$ V *vs* NHE), and because of their nonselective character, these radicals can oxidize and mineralize most organic compounds to produce CO_2 and inorganic ions. However, the lifetime of $OH^{\bullet}$ is extremely short lived ($t \leq 10^{-3}$ s) and once the radicals have formed, they can give rise to several elementary reactions, such as hydrogen abstraction, electrophilic addition, and one-electron oxidation, before they are regenerated [6]. When hydroxyl radicals are present, all other slower routes (i.e., direct photolysis, electron-transfer reactions, auto-oxidation, and pyrolysis) are shunted or even bypassed [7]. Hydroxyl radicals are generated by a variety of chemical, photochemical, photocatalytic, radiolytic and sonolytic methods [8,9]. Light energy can also be an integral component of AOP processes [8]. Depending on the type of AOP employed, the ultraviolet (UV) of λs reaching 200–300 nm, near-UV (λ = 300–400 nm) or visible light radiation (λ = 400–700 nm) can be used to produce the $OH^{\bullet}$ radical.

Fenton reactions are AOPs in which oxidant species are generated from hydrogen peroxide and Fe(II)/Fe(III) as a catalytic couple. In dark

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Fenton reaction [10], Fe(II) salts react with hydrogen peroxide to generate hydroxyl radicals (reaction 1):

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + HO^{\bullet} + HO^{-} \quad k = 76.5\ l \cdot mol^{-1} \cdot s^{-1} \quad (1)$$

A Fenton type reaction can successfully remove pollutants with relatively low operating costs [11] and with the possibility of the efficient exploitation of solar radiation [12]. Consequently, the Fenton reagent has been used for the treatment of different industrial wastewaters [13,14]. However, there is little knowledge of the effects of these reactions or other AOPs on industrial black liquors. Some studies have been performed on black liquor produced by the Kraft pulping process [2,15–19], on alfalfa black liquor [20] and on wheat straw black liquor [21].

The oxidation efficiency of the Fenton reagents depends on several variables: pH, temperature, and the H_2O_2 and Fe(II) concentrations. In most published studies, the effect of each variable was studied independently, with the others variables held constant. This approach is a time-consuming and inefficient method because the interactions between variables and the effects of these interactions on the overall reaction rates are not determined. This problem can be solved using an important tool, i.e., statistical design of experiments, which can provide valuable and statistically significant models of a phenomenon by performing the minimum number of well-chosen experiments. With this smaller number of experiments, the importance of each variable and of their interaction effects can be determined. Several such study designs exist, including the central composite design (CCD), Doehlert matrices, Box–Behnken designs and three-level full-factorial designs [22].

Several previous studies investigated the use of statistical design of experiments to develop optimal AOPs for wastewater treatment. For example, researchers have studied the degradation of pulp and paper effluents [23,24], of dyes [25–27] and of other synthetic materials [28,29] and industrial effluents [30]. However, until now, no study has used the central composite design to analyze the optimal conditions for the Fenton reaction to obtain efficient degradation of the organic compounds present in wheat straw black liquor.

The goal of the present work has been to identify reaction conditions that would efficiently degrade the organic compounds present in this black liquor obtained from the pulping of wheat straw, using the dark Fenton reaction in a lab-scale experiment based on the central composite experimental design To do so, we evaluated the roles of the key parameters in the reactions and their interactions. Our results suggest that this kind of effluent can be successfully treated using the dark Fenton reaction.

2. Materials and methods

2.1. Black liquor

We obtained black liquor from the pulping of wheat straw in a laboratory reactor under optimal conditions for the preparation of the corresponding pulp. We mixed 950 g of wheat straw, 114 g of NaOH and 6600 g of H_2O. This mixing was introduced in a reactor and heated until 150 °C for 1 h. This temperature was maintained 1 h 30 min. Afterwards, when the temperature lowed until 105 °C, the solution was filtered and we obtained the black liquor. The resulting effluent had a distinctive dark coloration and was characterized by high alkalinity (pH = 12), high organic content (COD > 60000 $mg \cdot L^{-1}$ O_2) and a high solid content (87 $g \cdot L^{-1}$), determined as the total suspended solids (TSS), according to the TAPPI test method (TAPPI T650, 1989). In order to be treated with the Fenton reaction the pH was adjusted to 3 by using concentrated H_2SO_4. This process implies the precipitation of an important part of the lignin that the effluent contains. The black liquor was filtered and finally diluted 100 times so that the initial COD was 628 $mg \cdot L^{-1}O_2$. The final characteristics of the black liquor after dilution and acidification were: COD = 628 $mg \cdot L^{-1}$ O_2, UV_{254} (aromatic content) = 2.018 absorbance units and UV_{280} (lignin content) = 1.978 absorbance units.

2.2. Chemicals for pH adjustment

For the pH adjustment, we used concentrated reagent-grade H_2SO_4 and NaOH solutions (Panreac). All solutions were prepared with deionized water prepared using a Millipore Milli-Q system.

2.3. Fenton reagent

The hydroxyl radical, HO·, was generated *in situ* by adding the following reagents in aqueous media: hydrogen peroxide, H_2O_2, Panreac, 33% w/v and ferrous sulphate, $FeSO_4 \cdot 7H_2O$, Merck, 99.5%.

2.4. Chemical assays

We measured COD ($mg \cdot L^{-1}$ O_2) using the closed-reflux colorimetric method [31] with a DR-700 colorimeter (HACH).

We measured the H_2O_2 consumption using the KI titration method [32]. Accordingly, correction was made in the COD measurement for residual hydrogen peroxide [33].

UV absorption at 254 and 280 nm was used to estimate the contents of aromatics and lignin, respectively, using a UV-1603 double-beam spectrophotometer (Shimatzu) and cells with a10-mm light path. To avoid interferences from Fe(III) and H_2O_2 when measuring UV_{254} and UV_{280}, we raised the pH of the sample to 10 by adding NaOH and then centrifugated the samples, an aliquot of the liquid was taken and its absorbance was measured [21].

3. Results and discussion

When working with the Fenton reaction, at least four variables must be considered: the pH, the temperature and the H_2O_2 and Fe(II) concentrations. Ordinarily, defining the optimal levels of all four variables would require many experiments. Before we can simplify the experimental analysis, we must understand the roles of these variables.

First, it is well known that the Fenton reaction depends strongly on the medium's pH [9]. The catalytic activity of the Fenton reaction is optimum at pH 3. This activity diminishes drastically with an increase or reduction of pH. At pH higher than 3 the formation and precipitation of $Fe(OH)_3$ impedes the development of the Fenton reaction. Also, H_2O_2 breaks down into O_2 and H_2O [34]. Moreover, the formation of Fe(II) complexes at high pH values leads to a drop of the Fe(II) concentration [35]. On the other hand, the low activity at pH values more acidic than the optimal level results from Fe(III) forming different complex species in solution.

Although several authors [11,36–38] have recommended a pH around 3 to obtain good degradation performance when applying the Fenton reaction to different samples, each sample could exhibit optimal performance at different pH values. Based on these recommendations and previous work that we performed on a wheat straw black liquor [21], we chose to test pH values between 2.0 and 4.0 at room temperature ($T = 298 \pm 1$ K) and with a treatment time of 90 min. The H_2O_2 and Fe(II) concentrations in these preliminary experiments were 1500 $mg \cdot L^{-1}$ (44.1 mM) and 200 $mg \cdot L^{-1}$ (3.58 mM), respectively. These doses are in accordance with previous work [21] and the stoichiometric requirements for COD removal [36].

Fig. 1 shows that the highest COD removal was obtained at a pH between 2.5 and 3.0. At pH values lower than 2.5 or higher than 3, the COD removal levels decrease. Consequently, we performed all subsequent experiments at pH = 3.

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