Degradation of phenol in mine waters using hydrogen peroxide and commercial steel wool

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ABSTRACT

The present work describes the use of zero-valent Fe in the form of commercial steel wool as a possible catalyst in the hydrogen peroxide oxidation of phenol in waters. The process was studied as a set of batch experiments on a bench scale, simulating the treatment of a contaminated mine water or wastewater from a coal beneficiation operation with an initial phenol concentration extended to 200 mg/L. The effects of the following variables were studied: pH (5 to 9); steel wool mass ratio per volume of effluent (1 g/L to 7 g/L); hydrogen peroxide concentration (1 g/L to 3 g/L) and temperature (25 °C to 45 °C). The best experimental conditions studied led to a reduction of phenol concentration from 200 mg/L to less than 0.5 mg/L in 120 min reaction time.

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1. Introduction

Phenol is a significant contaminant in mining drainage waters and in wastewaters of coal beneficiation processes (Toomik and Liblik, 1998; Jablonska, 2012). It is also commonly present in the effluents from some metal processing operations, such as iron and steel works that either use charcoal as a reducing agent or process coal in coking operations, and also in the mining and beneficiation of oil shale and tar sands (Benton, 1992). Although phenol concentrations do not usually exceed 10 mg/L in coal mine drainage waters, phenol concentrations in effluents from iron and steelmaking works and in the dewatering of brown coal may reach higher values (Allardice et al., 2004).

As phenol is a harmful substance which can also be regarded as an indicator or precursor of other toxic compounds containing phenol rings, in particular the highly toxic pentachlorophenol, the concentration limit of this compound in waters and effluents for discharge into the environment must be low. The World Health Organization (apud Daviá and Gnudi, 1999) classifies phenolic compounds in a class of substances noxious to human health with a maximum permissible concentration in drinking water of 0.2 mg/L for 2,4,6-trichlorophenol, 0.009 mg/L for pentachlorophenol, 0.01 mg/L for 2-chlorophenol and 0.04 mg/L for 2,4-dichlorophenol. Due to their toxicity phenolic

compounds have been included in the list of priority pollutants by the U.S. Environmental Protection Agency (Zhou et al., 2011).

The degradation of phenolic and related compounds in waters and wastewaters has been well studied on a laboratory scale (Eisenhauer, 1964; Kochany and Bolton, 1992; Lipczynska-Kochany et al., 1995; Zhu et al., 1996; Miller et al., 1996; Esplugas et al., 2002); a comprehensive review of the subject has been published by Busca et al. (2008). The treatment of effluents from industrial operations uses mainly biological processes for the attenuation of phenol contamination. However, these are limited to handling low phenol concentration levels (few mg/L) due to the fact that phenol can have an inhibitory action, even at low concentrations and upset the conventional activated sludge process (Maszenan et al., 2011). The treatment of effluents containing higher phenol concentrations usually requires strong chemical oxidation. In this case one of the current options for the efficient degradation of phenol to permitted levels for effluent discharge is the use of ferrous ion activated hydrogen peroxide to generate powerful oxidative OH* radicals, an advanced oxidation process known as the Fenton process.

Eisenhauer (1964) was the first to investigate the treatment of phenolic wastes using the Fenton reaction. Although the conventional aqueous Fe^{2+} catalyzed Fenton process used in the treatment of effluents with high phenol concentrations is an advanced oxidation process that does not require special equipment, such as UV photo-reactors or ozone generators, it has the limitation of generating $Fe(OH)_3$ sludge and requiring a specific pH range (3 to 4) (Walling, 1998) to effectively degrade the organic contaminants.

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For this reason there has been interest in developing variations of the Fenton process for the degradation of phenolic compounds in waters and wastewaters that employ the $Fe^{2+/3+}$ catalyst in solid form rather than as dissolved aqueous species, as reported by Guélou et al. (2003) and Moura et al. (2005). These variations have been referred to as heterogeneous Fenton processes. By activating the H_2O_2 molecule to yield OH* radicals using an iron-supported solid catalyst it was hoped to avoid the generation of solid waste $(OH)_3$ and the limitation of having to operate in a narrow pH range of 3 to 4.

The catalytical activity of mineral iron oxide compounds such as Fe_2O_3 and Fe_3O_4 for the generation of OH* radicals in surface reactions with aqueous H_2O_2 has been investigated for the degradation of azo dyes in wastewaters (Araujo et al., 2011). Results showed that the heterogeneous Fenton reaction was effective only in acidic medium, suggesting that acid was required to dissolve Fe ions from the mineral surface to allow the reaction to proceed as a conventional homogeneous aqueous Fenton reaction. Hence the solid Fe minerals were not efficiently providing surface active sites for OH* generation from H_2O_2 decomposition.

However, the possibility of using other solid Fe species sparked the interest of various authors. Lu et al. (2002) studied the role of goethite in the oxidation of 2-chlorophenol with hydrogen peroxide. A more recent publication (Bremner et al., 2006) reported the degradation of phenol using OH* radicals generated from zero-valent Fe (iron cuttings) and H_2O_2. That investigation focused on the reaction mechanism with HPLC identification of the intermediates. The authors used a 1000 mg phenol/L test solution and a sub-stoichiometric H_2O_2:phenol molar ratio of 9:1 instead of the 14:1 ratio which would be required for total mineralization according to reaction (1).

$$C_6H_5OH + 14\ H_2O_2 \rightarrow 6\ CO_2 + 17\ H_2O \qquad (1)$$

The main conclusions from that study were that the reaction proceeds via hydroxylation/oxidation to yield initially catechol and hydroquinone, which become further degraded, and an unidentified compound believed to be an iron-catechol complex which proved to be refractory to further oxidation. The kinetic information relevant to the use of this process in mining or industrial wastewater treatment plants shows that the phenol concentration can be almost totally reduced from an initial concentration of 1000 mg/L in 25 min in a batch reaction under the best conditions of H_2O_2 concentration of 9.5 mol/L, zero-valent Fe surface supplied as a bar dipped in the solution and acid pH due to the addition of H_2SO_4 at T = 25 °C.

The promising results of Bremner's investigation led the present authors to study this system further using a process-oriented approach of the heterogeneous Fe^0-catalyzed H_2O_2 oxidative degradation of phenol in water. The aim was to find suitable reaction conditions that would allow a simple operation employing steel wool (or other sources of iron such as carbon steel scrap) as elemental Fe material suitable for mining, mineral beneficiation and extraction plant processes. We also intended to study the reaction at stoichiometric and higher concentrations of H_2O_2 and investigate the effect of the pH of the initial solution and the steel wool (Fe^0 surface) mass ratio per solution volume. Steel wool was chosen as a catalytic material because of its wide commercial availability at fairly low cost and its high surface area with little resistance to fluid flow, which makes it suitable for use in packed columns.

More specifically the aim of this work has been to conduct an experimental study on the kinetics of the oxidation of aqueous phenol with Fe^0-catalyzed H_2O_2 at the fixed initial phenol concentration [phenol] = 200 mg/L, at room temperature (and up to 45 °C) by controlling the effect of variables H_2O_2/phenol ratio, Fe^0 catalyst concentration (mass/solution volume) and pH. The control variables, units and concentration ranges were chosen to cover those that might be found in actual mining and mineral beneficiation processes and industrial plants requiring phenol detoxification operations.

2. Materials and methods

The effect of reaction conditions (experiments carried out with H_2O_2 only; Fe^0 only; and with $H_2O_2 + Fe^0$) on the rate and efficiency of phenol breakdown was investigated for an initial phenol composition of 200 mg/L and an initial pH in the range 5 to 9.

Experiments were carried out as batch reactions in a glass beaker with mechanical stirring using 500 mL of distilled water made up with phenol to the chosen initial [phenol] = 200 mg/L. Temperature for the main set of runs was room temperature (25 °C +/− 1 °C). Initial pH was adjusted by the addition of NaOH. The NaOH and phenol used were of analytical grade supplied by Vetec (Brazil). H_2O_2 (50% weight) was supplied by Peróxidos do Brasil. Limpano steel wool (Brazil) of composition 99.8% Fe and 0.1% C with a surface area of 0.00325 m^2/g was used; this was degreased with water and household detergent and dried with acetone prior to use. The pH was monitored with a glass electrode/pH meter (Hanna Brazil Ltd., model pH 21).

Each run started at time zero with the addition of a single amount of H_2O_2 calculated to give the required concentration, to the previously pH-adjusted aqueous phenol solution in contact with the set amount of steel wool with vigorous stirring using a magnetic bar. Runs were carried out for a maximum time of 300 min and samples were taken at intervals for immediate phenol concentration photometric determination with a Merck Spectroquant kit (number 1008560001) using a Merck Nova 60 spectrophotometer.

For each experiment the concentration of oxidant was defined by the oxidant/phenol molar ratio. An oxidant/phenol molar ratio of 14:1 corresponded to the stoichiometric oxidant requirement for the complete mineralization of phenol, based on the reaction stoichiometry (Eq. (1)).

The 1.0 g/L concentration of H_2O_2 used in most runs corresponded to the stoichiometric requirement for the complete mineralization of 200 mg/L of phenol according to Eq. (1).

The equilibrium constant for the above reaction was calculated using Outotec's HSC 6.0 program and is $K = 1 \times 10^{308}$ (at 25 °C), which confirms its thermodynamic feasibility.

All experiments were conducted with replicates and the maximum experimental error in the measurement of the initial rates was calculated to be 0.2 $mg \cdot L^{-1} \cdot min^{-1}$. All the kinetic curves shown below are the average values obtained from the replicated runs.

3. Results and discussion

3.1. Preliminary blank trials: possible degradation of phenol with uncatalyzed H_2O_2

Fig. 1 shows the lack of reactivity of H_2O_2 on its own towards phenol oxidation under conditions similar to those adopted in the subsequent
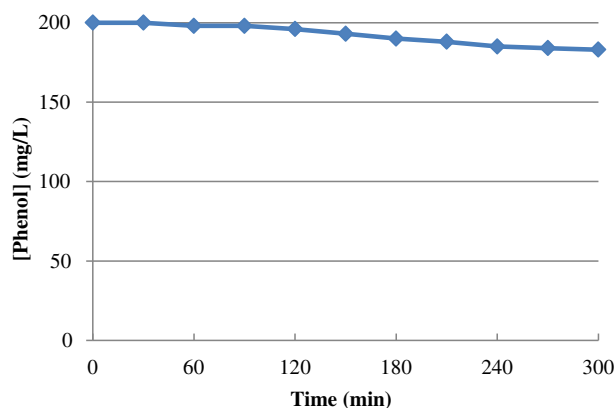

Fig. 1. Degradation of phenol by hydrogen peroxide only. Initial [phenol] = 200 mg/L; [H_2O_2] = 1 g/L; initial pH = 5; Temperature = 25 °C.