OPTIMAL CONDITIONS FOR OXIDIZING PHENOL IN WATER BY FENTON AND PHOTO-FENTON PROCESSES

H. A. Blas López\textsuperscript{a}, G. H. Lopes\textsuperscript{a}, A. C. Silva Costa Teixeira\textsuperscript{a}, C. E. Flores Barreda\textsuperscript{a}, P. A. Pantoja\textsuperscript{a}

ABSTRACT

Phenol can be degraded to almost 100 % within a few minutes via Fenton and photo-Fenton processes. Its degradation and the ratio of initial molar concentrations of oxidant and catalyst increase in inverse senses, and a ratio of 38.4 was optimal for aqueous solutions contaminated with 20 ppm of phenol. In addition to this, the use of ultraviolet-A light enhanced degradation when compared to shorter wavelengths.

Key words: Advanced oxidation, Fenton, photocatalysis, organic pollutants, wastewater, phenol.

CONDICIONES ÓPTIMAS PARA OXIDAR FENOL EN AGUA VÍA LOS PROCESOS FENTON Y FOTO-FENTON

RESUMEN

Fenol puede ser degradado a casi 100 % en pocos minutos vía los procesos Fenton y foto-Fenton. Su degradación y la relación entre las concentraciones molares iniciales de oxidante y catalizador utilizadas aumentan en sentidos inversos, y una relación de 38,4 fue óptima para soluciones acuosas contaminadas con 20 ppm de fenol. Asimismo, el uso de luz ultravioleta del tipo A aumentó la degradación comparado a menores longitudes de onda.

Palabras clave: Oxidación avanzada, Fenton, fotocatálisis, contaminantes orgánicos, aguas residuales, fenol.

INTRODUCTION

Phenols are among the most toxic organic pollutants\textsuperscript{1}. In Peru, surface waters with phenolic content above 0.003 ppm are not allowed to be made drinkable by simple disinfection\textsuperscript{2}. Lakes

\textsuperscript{a} Department of Chemical Engineering, Universidad de Ingeniería y Tecnología (UTEC), Jr. Medrano Silva 165, Barranco, Lima 04, Peru, paraujo@utec.edu.pe.
\textsuperscript{b} Department of Chemical Engineering, Polytechnic School, Universidade de São Paulo (USP), Av. Professor Luciano Gualberto, Travessa 3, 380, São Paulo/SP 05508-900, Brazil.
and rivers ought not to surpass 2.56 ppm and coastal waters must be kept below 5.8 ppm. Yet, phenols are major starting compounds in industrial chains leading to major products such as plastics, dyes, binders, adhesives, and biocides.

These non-biodegradable organics may not respond to biological treatment, and their transfer from one phase to another, as for instance in adsorption or flocculation, is not a final solution for their elimination. Fortunately, they can be degraded by advanced oxidation processes (AOPs). Nevertheless, AOPs are not broadly used in Peru despite their potential, and little seems to have been published on local attempts.

The kinetics of Fenton’s AOP is complex and extensively described in the literature. Essentially, a transition-metal (Fe$^{2+}$) in acidic aqueous medium catalyzes the decomposition of an oxidant (H$_2$O$_2$) into unselective free radicals (HO) as in the reaction Fe$^{2+}$+H$_2$O$_2$→Fe$^{3+}$+OH$^-$+HO$. In turn, these radicals oxidize organic pollutants by generating organic radicals. If reactants are present in sufficient concentrations, the organic radicals react with HO until their complete mineralization to H$_2$O and CO$_2$. Interestingly, pollutant degradation increases under electromagnetic radiation due to two new phenomena. One is the photo-reduction of Fe$^{3+}$ under near-ultraviolet and visible lights, what regenerates Fe$^{2+}$ and form new (pollutant) radicals L according to the reaction Fe$^{3+}$ L$_n$+h ν→Fe$^{2+}$ L$_{n-1}$+L (where h represents Planck’s constant and ν is the wave frequency). The other is the photolysis of H$_2$O$_2$ under ultraviolet irradiation to give more HO radicals as represented by the reaction H$_2$O$_2$+h ν→2 HO. This process is therefore termed photo-Fenton.

The multistep kinetics of the Fe$^{2+}$/H$_2$O$_2$ chemistry is affected by numerous experimental factors. For this reason, the reaction time, the pH, the relative concentrations of pollutant, oxidant and catalyst, the temperature, the wavelength and other conditions are optimized experimentally. A consensus seems to have been reached for pH only. Indeed, more Fe$^{2+}$ and less of unreactive, non-dissolvable precipitates of ferric (oxy)hydroxides are formed below pH 3, but scavenging of HO by H$^+$ combined with unfavorable iron speciation and auto-decomposition of H$_2$O$_2$ all reduce pollutant peroxidation below pH 2. As for the values recommended for the ratio of initial concentrations of Fe$^{2+}$ and H$_2$O$_2$, deviations from stoichiometric proportions by one or even two orders of magnitude are reported.

Finally, photo-Fenton efficiency is wavelength-dependent.

In the Fenton scheme, phenol is hydroxylated to hydroquinone and then oxidized to quinone before its further oxidation to aliphatic acids which are relatively stable towards HO unless irradiated. Under irradiation, Fe$^{3+}$ catalyzes light-induced reactions which eventually enhance mineralization. The current work presents an experimental method and optimal conditions for degrading phenol in diluted aqueous solutions and contributes to consolidating the application of AOPs in Peru.
EXPERIMENTAL

$H_2O_2$ (30 % in mass, J. T. Baker) at 0.3 mol L$^{-1}$ and $FeSO_4\cdot7H_2O$ (99 % purity, Scharlau) at 0.1 mol L$^{-1}$ previously dissolved in $H_2SO_4$ (98 %, J. T. Baker) at 0.1 mol L$^{-1}$ were used. Phenol (99.6 % purity, J. T. Baker) at 20 ppm was the target solution. NaOH (99 % purity, Macron) in aqueous solution at 1 mol L$^{-1}$ was added to analytical samples for inhibiting phenol degradation and so allowing for analyses to be performed. Degradation experiments were carried out in a magnetically stirred photochemical batch reactor (RFS-500, Alphatec, Brazil) of volume of 1 L equipped with a jacket for temperature control and a pH meter. For photo-Fenton tests, the reactor’s tubular ultraviolet-A or ultraviolet-C lamp (9 W, OSRAM, South Korea) or ultraviolet-B (9W, Philips, Poland) was turned on. Phenol was quantified in all samples via the 4-aminoantipyrine colorimetric method with help of an ultraviolet-visible spectrophotometer (UV-2600, Shimadzu, Japan).

For each test, 1 L of phenol solution was added to the reactor. Small volumes of $H_2SO_4$ at 50 % helped keep pH at 2.91 ± 0.02. Then, the desired amounts of catalyst and oxidant solutions were added all at once and the mixture let react at ambient temperature under vigorous stirring and isolated from ambient light. Experiments were repeated at least 3 times. Four samples of 10 mL were analyzed per test; they corresponded to reaction times of 0, 2, 5 and 10 minutes. A total of 100 μL of the inhibitor solution was systematically added to each sample immediately after its removal from the reactor in addition to the solutions necessary for the colorimetric analyses. Analytes would then rest for 15 minutes before being analyzed spectrophotometrically at 500 nm (wavelength determined during previous calibration).

RESULTS AND DISCUSSIONS

Results focus on the percentage of phenol degradation (X), defined as $X=100 \times \frac{([C]_0-[C])}{[C]_0}$ where $[C]_0$ is the initial pollutant concentration and $[C]$ is its concentration at any reaction time t. Table 1 synthesizes mean results after 10 minutes of reaction and reveals that all processes under all experimental conditions are very effective in destroying phenol. Furthermore, the table shows that photo-Fenton was able to oxidize the target pollutant up to 9 percentage points more than Fenton at similar operating conditions. Generically, average degradations ranged from 85.3 % to 96.4 % for Fenton and from 91.3 % to 99.7 % for photo-Fenton samples.
Higher degradations were obtained with lower ratios \([\text{H}_2\text{O}_2]_0/[\text{Fe}^{2+}]_0\). Indeed, scavenging of \(\text{HO}^\cdot\) radicals occur with high concentrations of \(\text{H}_2\text{O}_2\). It is also possible to note that UV-A lights gave better results than the other lamps, but more experiments are necessary for elucidating the behavior of all irradiated compounds4.

Degradation was always lower for Fenton experiments compared to photo-Fenton. Anyway, \(X\) increased always fast whenever an experiment was launched. As seen in Fig. 1, up to half of phenol could be destroyed during the first 2 minutes in some cases. The rate of degradation diminished from this instant on but remained elevated, such that photo-Fenton and optimum Fenton experiments (F3) exceeded 70% or even 80% degradation within 5 minutes. In order to evaluate the extent of mineralization, it would have been insightful to measure the total organic carbon contents of the treated samples and to compare them to those of the untreated samples. However, these analyses were not carried out in this study.

CONCLUSIONS

The effectiveness of Fenton and photo-Fenton AOPs for degrading phenol above 90 % and even close to 100 % in aqueous solutions of concentration 20 ppm is verified. Ultraviolet-A light is able to enhance degradation, but nonirradiated Fenton treatments with a ratio of initial molar concentrations of 38.4 yield equivalent degradations. Unless extremely high degradations are necessary, either treatment may be selected; in such cases, economic analyses should help decide which process is preferable. This study is a bedrock for exploring the application of the techniques to challenging phenol-containing wastewaters as is the case in niche Peruvian industries. Such studies are in course.

Table 1. Average phenol degradations after 10 minutes. UV-A wavelengths lie within 400–315 nm, UV-B within 315–280 nm and UV-C within 280–100 nm.

<table>
<thead>
<tr>
<th>Label</th>
<th>Process</th>
<th>([\text{Fe}^{2+}]_0) (10^{-3} \text{ mol L}^{-1})</th>
<th>([\text{H}_2\text{O}_2]_0) (10^{-3} \text{ mol L}^{-1})</th>
<th>([\text{H}_2\text{O}_2]_0/\text{[Fe}^{2+}]_0)</th>
<th>Light</th>
<th>(X) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>Fenton</td>
<td>5.5</td>
<td>3.0</td>
<td>54.5</td>
<td>-</td>
<td>85.3</td>
</tr>
<tr>
<td>PF1</td>
<td>Photo-Fenton</td>
<td>5.5</td>
<td>3.0</td>
<td>54.5</td>
<td>UV-A</td>
<td>94.3</td>
</tr>
<tr>
<td>F2</td>
<td>Fenton</td>
<td>6.0</td>
<td>3.0</td>
<td>50.0</td>
<td>-</td>
<td>89.3</td>
</tr>
<tr>
<td>PF2</td>
<td>Photo-Fenton</td>
<td>6.0</td>
<td>3.0</td>
<td>50.0</td>
<td>UV-A</td>
<td>95.8</td>
</tr>
<tr>
<td>F3</td>
<td>Fenton</td>
<td>7.8</td>
<td>3.0</td>
<td>38.4</td>
<td>-</td>
<td>96.4</td>
</tr>
<tr>
<td>PF3</td>
<td>Photo-Fenton</td>
<td>7.8</td>
<td>3.0</td>
<td>38.4</td>
<td>UV-A</td>
<td>99.7</td>
</tr>
<tr>
<td>PF4A</td>
<td>Photo-Fenton</td>
<td>6.0</td>
<td>2.4</td>
<td>40.0</td>
<td>UV-A</td>
<td>97.3</td>
</tr>
<tr>
<td>PF4B</td>
<td>Photo-Fenton</td>
<td>6.0</td>
<td>2.4</td>
<td>40.0</td>
<td>UV-B</td>
<td>91.3</td>
</tr>
<tr>
<td>PF4C</td>
<td>Photo-Fenton</td>
<td>6.0</td>
<td>2.4</td>
<td>40.0</td>
<td>UV-C</td>
<td>93.3</td>
</tr>
</tbody>
</table>

Figure 1. Evolution of the average phenol degradation as the reaction time increases.
ACKNOWLEDGMENTS

The authors thank INNÓVATE PERÚ for funding this work (contract 375-PNICP-PIAP-2014) and O. D. Matallana, M. E. Quintana Cáceda and O. K. Terreros Delgadillo for their support.

REFERENCES