Experimental design applied to photo-Fenton treatment of highly methomyl-concentrated water

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ABSTRACT

This work is focused on the study of the suitability of the photo-Fenton process as a pretreatment for water highly contaminated with a methomyl commercial formulation in Advanced Greenhouses devices. Initial concentrations of reagents and pesticide were evaluated according to a central composite experimental design, with methomyl depletion and biocompatibility of the final effluent as response functions. A triad of optimal operation conditions could be determined, \([\text{Met.}]_0 = 50 \text{ mg L}^{-1}, [\text{H}_2\text{O}_2]_0 = 254 \text{ mg L}^{-1}\) and \([\text{Fe}^{2+}]_0 = 77 \text{ mg L}^{-1}\) for the best elimination yield and an acceptable BOD5/COD value, and initial concentration of methomyl can be established as the most important parameter for the performance of the treatment due to the limitations that impose on the hydrogen peroxide doses in the presence of the excipients of the commercial formulation.

Key words | advanced oxidation processes, biodegradability, central composite, pesticide, photocatalytic process, photo-Fenton, water treatment

INTRODUCTION

The aim of sustainability, more important each day in every aspect of human development, is one of the impelling factors of the new concept of Advanced Greenhouses. These facilities, based on the original idea of protected agriculture, introduce structural, mechanical and functional improvements that make them more environmentally respectful than their predecessors, and even more competitive in terms of cropping yields. Among other improvements, Advanced Greenhouses are specially designed for the efficient use of water resources. The approach on which this work is based lies in the possibility of recovering lixiviates from the culturing substrate and returning the current to the greenhouse to be reused as many times as possible. Nevertheless, after several recirculation cycles, the surplus water concentration in salts and pesticides can be so high as to cause phytotoxicity problems. This is why a membrane separation stage could be used in order to condition the stream to take part again in the irrigation process, generating a permeate suitable for being resent to the cycle, and a brine highly concentrated in those named harmful substances.

In the last few decades, AOP’s have been proven to be highly effective for the removal of most pollutants in wastewaters (Pera-Titus et al. 2004). This kind of treatment is based on the generation of hydroxyl radicals, whose strong oxidizing potential has been proven as a good alternative to traditional treatments such as photo-oxidation, chemical coagulation or absorption, among others, for the elimination of pesticides (Lafi & Al-Qodah 2006; Badawy et al. 2006). In these days, photo-Fenton is considered a suitable treatment for those pollutants with numerous references in literature (Abdessalem et al. 2010; Ballesteros-Martín et al. 2009), even with practical applications (Kenfack et al. 2009).

In photo-Fenton reaction, hydroxyl radicals are produced by the decomposition of hydrogen peroxide when reacting with ferrous ions in the presence of UV light, which contributes with an additional pathway to the generation of
free radicals in comparison to the dark Fenton reaction (González et al. 2007). One of the main advantages of photo-Fenton reaction compared to other AOP’s is the fact that solar light could also be a suitable source of radiation for the process, which makes it optimum for an outdoor installation, reducing costs and risks (Mendoza-Marín et al. 2010; Zapata et al. 2009b).

In this preliminary study, Fenton reaction photoactivated by artificial light has been tested applying experimental design procedures as a proposal to decontaminate the brine coming from the separation stage, too concentrated in harmful substances to be sent directly to a public sewage system. The main objective was to establish the suitability of the photo-Fenton reaction as an effective treatment to degrade certain pesticide loads in the influent and increase its intermediates biocompatibility. In addition, thanks to the statistical information derived from the analysis of the experimental design, the most influential parameters of the process were determined for both evaluated aspects.

Biocompatibility is considered an important factor to be taken into account for the design of a real treatment, since it has been already proven that photochemical pre-treatment can be shortened when combined with biological oxidation (Ballesteros-Martín et al. 2008). Biocompatibility was tested in order to evaluate the possibility of introducing a biological treatment after photo-Fenton reaction. According to this, the final optimization derived from the experimental design results will be performed taking into account not just contaminant removal capacity, but also the biodegradability of the resulting effluents.

The experiments were carried out with methomyl as target pollutant (S-methyl-N((methylcaboamoxyl)oxy)thioacetimidate). Literature about photo-Fenton applied to different pesticides through experimental design can be found (Segura et al. 2008); however, this research introduces the use of a commercial concentrate, instead of the pure substance: Tomilo-20 L, from Aragonesas Agro S.A. (200 g/l of the active product, and ethanol as main solvent). Its non-active ingredients could cause interference with the process, which could not be observed, nor taken into account, while working with the pure substance (Zapata, et al. 2009b). Therefore the use of a commercial product places this study in a more real scenario than working with a pure compound.

**METHODS**

**Experimental conditions and analyses**

Photo-Fenton reaction was carried out in a 2 L jacketed stirred vessel with three 8W black light lamps (λmax = 365 nm), at controlled temperature between 22 and 25°C. More detailed description of the device and the procedure can be found elsewhere (González et al. 2007). pH was kept at 2.7 (optimum for the equilibrium [Fe2⁺]/[Fe³⁺] to achieve its highest ratio) at the beginning of the reaction and was monitored during the process, oscillating from 2.7 to 2.5. All the experiments were carried out until the total consumption of hydrogen peroxide from every sample, after withdrawn, was quenched with NaHSO3 (except the one corresponding to the end of the reaction, when no quenching is needed). All the testing was performed according to an experimental design described in the next section. The extreme values for the involved parameters were the following: [50, 200] mg L⁻¹ of pesticide, [50, 100] mg L⁻¹ of ferric ion and [100, 300] mg L⁻¹ of hydrogen peroxide. While the choice of pesticide concentrations is based on membrane separation capability of regulate brine dilution, the range of the concentrations of hydrogen peroxide and ferric ion needed preliminary assessments, not shown in this paper, that justify their tested levels. On the one hand, those experiments revealed that peroxide concentrations higher than 300 mg L⁻¹ (near to the stoichiometric concentrations related to 200 mg L⁻¹ of methomyl as a pure substance) showed worse reaction yields, probably caused by a radical scavenging effect of the peroxide itself, (Evgenidou et al. 2007), or by the interference of the commercial excipients known as organic substances susceptible of consuming radicals. On the other hand, catalytic inactivity of Fe²⁺ at lower concentrations than 50 mg L⁻¹ was observed, most likely due to the formation of complexes with any excipient of the commercial product, or pesticide metabolites as it happens with different organic compounds and ferrous iron (Perdue et al. 1976).

Pesticide depletion at the end of each experiment was evaluated as a first answer function to be taken into account for the optimization. For this purpose, the concentration of pesticide during the reaction and the possible formation of intermediates (not identified in this work) were monitored by high performance liquid chromatography with
Experimental design

Several works have been published already in the field of experimental design precisely in the frame of pesticide decontamination (Segura et al. 2008; Zapata et al. 2009a). Their positive results are based on the reduction of the number of experiments performed without renouncing the quality information that can be achieved using these statistical methods.

In this study, photo-Fenton reaction was evaluated using these analytical tools and according to those ideas stated by Leardi (Leardi 2009). The effect on the pesticide removal yield and biocompatibility of the mixture after the process, of initial concentrations of Fe(II), H₂O₂ and methomyl, was assessed.

Specifically, the method identifies the first and second response variables, pesticide removal yield, Y (Equation (1)), and biodegradability as BOD₅/COD; with two empiric equations that define hypersurfaces of 4 dimensions, in which independent variables are the named reagents and methomyl initial concentrations, the products between them, and their second potencies.

\[ Y = \frac{[\text{Met.}]_0 - [\text{Met.}]}{[\text{Met.}]_0} \times 100 \]  

Only these three parameters were taken into account being aware that there are many other factors that can interfere in photo-Fenton reaction, such as pH or temperature. Nevertheless they were fixed around the values expected in an implementation of the process in the field.

The experiments were performed according to a central composite design consisting on a factorial design and 6 star points, in order to obtain the information needed for defining the response surfaces (3 factors: [Met]₀, [H₂O₂]₀ and [Fe²⁺]₀; and 2 levels: [50, 200], [100, 300] and [50, 100] mg L⁻¹ respectively). A summary of the experimental design and results is presented in Table 1. Variables were coded on two normalised levels: +1 as the highest and −1 the lowest value. According to this, the central point of the design was coded as (0, 0, 0). Three replicated experiments were carried out at that central point, in order to check the statistical consistency of the data. Star points were distributed at \( \sqrt{5} \) times the distance from the central point 0 to +1; except in the case in which that distance implies negative values of one factor. In that case, identified with a star (*), the negative value was replaced with the corresponding −1 value. Statistical validation was determined by ANOVA test at 95% confidence level.

RESULTS AND DISCUSSION

Pesticide depletion

It can be observed in Table 1 how the removal percentage, Y, oscillates between low values of elimination, 29% at (200, 100, 100), in \( ([\text{Met}]_0, [\text{H}_2\text{O}_2]_0, [\text{Fe}^{2+}]_0) \) (mg L⁻¹), to the virtually complete depletion at (50, 300, 50). A multivariate regression was performed on this data to obtain a mathematical expression that represents the response hypersurface, describing Y as a function of initial concentrations of pesticide, hydrogen peroxide and ferrous ion. Equation (2) shows a corresponding model with significant coefficients.

\[ Y = 45.2 - 0.6[\text{Met}]_0 + 0.24[H_2O_2]_0 + 1.42[Fe^{2+}]_0 + 0.0009[\text{Met}]_0[H_2O_2]_0 - 0.0017[\text{Met}]_0[Fe^{2+}]_0 - 0.0010[H_2O_2]_0[Fe^{2+}]_0 + 9.1 \times 10^{-4}[\text{Met}]_0^2 - 4.1 \times 10^{-4}[\text{H}_2\text{O}_2]_0^2 - 0.0070[\text{Fe}^{2+}]_0^2 \]
The regression coefficient $R^2$ indicates that the model explains 98.95% of $Y$ variability. Figure 1 presents examples of the response surface derived from Equation (2) for a fixed value of methomyl concentration.

An ANOVA test was carried out in order to compare the model variance with the variance of the residuals (error). If the variances are different enough, the parameters taken into account are significant and have influence on the model. To measure this difference, the $F$-test is performed, and from it the $P$-Value is obtained. The parameters would have influence on the model if their $P$-Values are lower than 0.05, those with the lowest ones would have the highest influence. Table 2 shows the results of the ANOVA test.

$P$-Value for lack of fit test is higher than 0.05, showing that the model appears to be adequate for the observed data at the 95.0% confidence level.

Since the value of its $P$-Value is the lowest, initial methomyl concentration can be considered the most influential factor in this design. Furthermore, the negative value of its coefficient in Equation (2) physically implies that a higher concentration of pesticide entails lower depletion yields.

In practical terms, it is not just that the concentration of the pesticide determines the performance of the reaction, but also the lack of enough oxidant reagent to cope with the pollutant load. This fact, together with the previous experiments that bear witness to the worse depletion yields achieved with higher doses of hydrogen peroxide, indicates the presence of an important scavenging effect that consumes radicals without degrading the target compound. This scavenging could be due to the hydrogen peroxide itself however, the highest concentration used in these essays was close to the stoichiometric quantity related exclusively to the highest pesticide concentration (not taking into account the inert ingredients), weakening this first explanation. There is another possible source of radical competition, the excipients of the commercial formulation, in this case ethanol and short esters. These substances could consume radicals and make the reagent not sufficient, even for the higher doses, simulating peroxide scavenging. The presence of this excipient is obviously related to the initial concentration of the pesticide used in the experiments, which in the real proposed application would be related to the performance of the membrane. This is why the initial concentration of

<table>
<thead>
<tr>
<th>Experiments</th>
<th>$[\text{Met}]_0$ (mg L$^{-1}$)</th>
<th>$[\text{H}_2\text{O}_2]_0$ (mg L$^{-1}$)</th>
<th>$[\text{Fe}^{2+}]_0$ (mg L$^{-1}$)</th>
<th>$Y$ (%)</th>
<th>BOD$_5$/COD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50 (-1)</td>
<td>100 (-1)</td>
<td>50 (-1)</td>
<td>86.0</td>
<td>0.151</td>
</tr>
<tr>
<td>2</td>
<td>200 (1)</td>
<td>100 (-1)</td>
<td>50 (-1)</td>
<td>34.0</td>
<td>0.010</td>
</tr>
<tr>
<td>3</td>
<td>50 (-1)</td>
<td>300 (1)</td>
<td>50 (-1)</td>
<td>99.9</td>
<td>0.327</td>
</tr>
<tr>
<td>4</td>
<td>200 (1)</td>
<td>300 (1)</td>
<td>50 (-1)</td>
<td>68.0</td>
<td>0.007</td>
</tr>
<tr>
<td>5</td>
<td>50 (-1)</td>
<td>100 (-1)</td>
<td>100 (1)</td>
<td>99.9</td>
<td>0.110</td>
</tr>
<tr>
<td>6</td>
<td>200 (1)</td>
<td>100 (-1)</td>
<td>100 (1)</td>
<td>29.0</td>
<td>0.005</td>
</tr>
<tr>
<td>7</td>
<td>50 (-1)</td>
<td>300 (1)</td>
<td>100 (1)</td>
<td>97.0</td>
<td>0.242</td>
</tr>
<tr>
<td>8</td>
<td>200 (1)</td>
<td>300 (1)</td>
<td>100 (1)</td>
<td>58.8</td>
<td>0.013</td>
</tr>
<tr>
<td>9</td>
<td>125 (0)</td>
<td>26.79 (-$\sqrt{3}$)</td>
<td>75 (0)</td>
<td>42.0</td>
<td>0.000</td>
</tr>
<tr>
<td>10</td>
<td>125 (0)</td>
<td>373.71 ($\sqrt{3}$)</td>
<td>75 (0)</td>
<td>83.7</td>
<td>0.010</td>
</tr>
<tr>
<td>11</td>
<td>125 (0)</td>
<td>200 (0)</td>
<td>31.7 (-$\sqrt{3}$)</td>
<td>66.0</td>
<td>0.006</td>
</tr>
<tr>
<td>12</td>
<td>125 (0)</td>
<td>200 (0)</td>
<td>118.5 ($\sqrt{3}$)</td>
<td>58.0</td>
<td>0.006</td>
</tr>
<tr>
<td>13</td>
<td>50 (-1)*</td>
<td>200 (0)</td>
<td>75 (0)</td>
<td>99.4</td>
<td>0.205</td>
</tr>
<tr>
<td>14</td>
<td>254.9 ($\sqrt{3}$)</td>
<td>200 (0)</td>
<td>75 (0)</td>
<td>51.8</td>
<td>0.000</td>
</tr>
<tr>
<td>15</td>
<td>125 (0)</td>
<td>200 (0)</td>
<td>75 (0)</td>
<td>74.8</td>
<td>0.140</td>
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<td>16</td>
<td>125 (0)</td>
<td>200 (0)</td>
<td>75 (0)</td>
<td>76.1</td>
<td>0.120</td>
</tr>
<tr>
<td>17</td>
<td>125 (0)</td>
<td>200 (0)</td>
<td>75 (0)</td>
<td>77.0</td>
<td>0.110</td>
</tr>
</tbody>
</table>

*Point (-$\sqrt{3}$, 0, 0) had to be replaced by (-1, 0, 0) because the real variable value for (-$\sqrt{3}$) was lower than 0.
the pesticide becomes an important parameter to take into account for the design of the separation stage, due to the tight relationship between that extra organic load and the quantity of peroxide that can be added for a successful treatment. Reinforcing this hypothesis mathematically, the initial concentration of $\text{H}_2\text{O}_2$ seems to have also a remarkably influence, it has the second lowest $P$-Value.

Synergies are represented by the coefficients preceding the products of factors two by two. $[\text{Met.}]_0[\text{Fe}^{2+}]_0$ and $[\text{H}_2\text{O}_2]_0[\text{Fe}^{2+}]_0$ cross-effects have the lowest influence.

![Graph](https://iwaponline.com/wst/article-pdf/62/9/2066/446966/2066.pdf)

**Figure 1** | Biodegradability values of final effluents of photo-Fenton experiments as function of the ratio $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ in mg L$^{-1}$. Above the columns BOD$_5$ and COD numerical values can be seen as mg O$_2$ L$^{-1}$. Ratio 0: Raw solution (50, 0, 0); Ratio 2: (50, 100, 50); Ratio 3: (50, 300, 100); Ratio 6: (50, 300, 50), in (\text{[Met.]}_0, [\text{H}_2\text{O}_2]_0, [\text{Fe}^{2+}]_0)\text{ (mg L}^{-1}).

**Table 2** | ANOVA test for coefficients from Equation (2)

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>D.F.</th>
<th>Mean square</th>
<th>$F$-Ratio</th>
<th>$P$-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Met.}]_0$</td>
<td>5,703.31</td>
<td>1</td>
<td>5,703.31</td>
<td>4662.11</td>
<td>0.0002</td>
</tr>
<tr>
<td>$[\text{H}_2\text{O}_2]_0$</td>
<td>1,547.79</td>
<td>1</td>
<td>1,547.79</td>
<td>1265.22</td>
<td>0.0008</td>
</tr>
<tr>
<td>$[\text{Fe}^{2+}]_0$</td>
<td>20.397</td>
<td>1</td>
<td>20.397</td>
<td>16.67</td>
<td>0.0551</td>
</tr>
<tr>
<td>$[\text{Met.}]_0^2$</td>
<td>206.141</td>
<td>1</td>
<td>206.141</td>
<td>168.51</td>
<td>0.0059</td>
</tr>
<tr>
<td>$[\text{Met.}]_0[\text{H}_2\text{O}_2]_0$</td>
<td>347.952</td>
<td>1</td>
<td>347.952</td>
<td>284.43</td>
<td>0.0035</td>
</tr>
<tr>
<td>$[\text{Met.}]_0[\text{Fe}^{2+}]_0$</td>
<td>79.1282</td>
<td>1</td>
<td>79.1282</td>
<td>64.68</td>
<td>0.0151</td>
</tr>
<tr>
<td>$[\text{H}_2\text{O}_2]_0^2$</td>
<td>221.596</td>
<td>1</td>
<td>221.596</td>
<td>181.14</td>
<td>0.0055</td>
</tr>
<tr>
<td>$[\text{H}_2\text{O}_2]_0[\text{Fe}^{2+}]_0$</td>
<td>54.9152</td>
<td>1</td>
<td>54.9152</td>
<td>44.89</td>
<td>0.0216</td>
</tr>
<tr>
<td>$[\text{Fe}^{2+}]_0^2$</td>
<td>252.363</td>
<td>1</td>
<td>252.363</td>
<td>206.29</td>
<td>0.0048</td>
</tr>
<tr>
<td>Lack of fit</td>
<td>84.1079</td>
<td>5</td>
<td>16.8216</td>
<td>13.75</td>
<td>0.0692</td>
</tr>
<tr>
<td>Pure error</td>
<td>2.44677</td>
<td>2</td>
<td>1.22333</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total correlation</td>
<td>8,306.02</td>
<td>16</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
while $[\text{Met.}]_0[H_2O_2]_0$ is the most noticeable cross-term, confirming again the dependence of the quantity of peroxide that promotes the depletion of methomyl with the initial quantity of the pesticide itself and its related inert ingredients.

Although its contribution is also positive, ferrous ion concentration presents no influence ($P$-Value > 0.05). Nevertheless, since its cross-effects and quadratic expression are significant, the factor $[\text{Fe}^{2+}]_0$ itself cannot be removed from the model in practical terms this is caused mathematically by the quadratic term of Fe(II) concentration, and it could be chemically justified by the existence of a radical scavenging effect by ferrous iron, already referenced in the literature (Ay et al. 2009).

The curvature of the response surfaces reveals the weight of the quadratic terms. The most influential one is $[\text{Fe}^{2+}]_0^2$, followed by peroxide and methomyl concentration quadratic terms, with higher $P$-Values than some synergetic effects.

As can be seen in Figure 1(b, c), for upper values of initial concentration of methomyl, the behaviour of the surface reveals an increase of depletion rate for the higher concentration of reagents, achieving the top depletion, around 80%, for the maximum concentrations of $H_2O_2$ and ferrous ion. Nevertheless, for the lowest concentration of pesticide, 50 mg L$^{-1}$, an optimum ratio $H_2O_2/Fe^{2+}$ can be seen for the initial concentration intervals of 180 to 260 mg L$^{-1}$ of hydrogen peroxide and from 70 to 80 mg L$^{-1}$ of ferrous ion; conditions in which the depletion reached is complete. Mathematically, the optimum values are identified as $[\text{Met.}]_0 = 50$ mg L$^{-1}$, $[H_2O_2]_0 = 245$ mg L$^{-1}$, $[\text{Fe}^{2+}]_0 = 77$ mg L$^{-1}$. The presence of this optimum gives an idea of the best operation conditions, from those studied, for the oxidative process with the lowest tested pesticide concentration pesticide.

**Biocompatibility**

The biodegradability measurements were carried out in order to study biocompatibility of final effluents of the oxidative process with a subsequent biologic reactor which could finish the degradation of the organic matter not mineralized by the chemical process. The low BOD$_5$ values obtained for the highest concentrations of pesticide and its high carbonic load (due to the inert ingredients) caused low biodegradability values, practically near to 0, in all the pretreatment conditions tested. In opposition to this, 50 mg L$^{-1}$ experiments show remarkably high BOD$_5$/COD values. Figure 2 depicts the changes in biodegradability depending on the ratio of reagents used for the lowest initial concentration of pesticide, supposing they and their interaction as an important factor on biodegradability values.

Apparently, the experiments show an enhancement of biodegradability with the increase of the reagents ratio which seems to identify these parameters as capitals for obtaining maximum values of BOD$_5$/COD ratio, close to 0.4, which characterizes easily biodegradable effluents (Sarrià et al. 2002). Regarding Figure 2, an increase of BOD$_5$ is also detected in every case in comparison to the raw dilution of methomyl; while COD suffers a perceptible diminishment for ratios 3 and 6, more than 60%, slightly more intense for the lowest concentration of iron II, possibly due to a scavenging effect by the cationic metal. Both the increase of BOD$_5$, and the diminishment of COD identify a noticeable oxidation of the organic load. Nevertheless, probably, due to the presence of inert ingredients, that interferes with radical action, TOC results do not coincide with this tendency. The total organic carbon measures show negligible mineralization even in the highest $H_2O_2/Fe^{2+}$ ratio case, indicating the generation of oxidised by-products from methomyl, and even its excipiens (presumably partially oxidized), which cannot be further degraded by the chemical treatment. This fact, together with the positive evolution of biocompatibility

![Figure 2](https://iwaponline.com/wst/article-pdf/62/9/2066/446966/2066.pdf)
achieved could justify the suitability of an integrated chemical-biological treatment, introducing a subsequent bioreactor as proposed before.

Despite this, the mathematical study of the results of the experimental design should give more information about the real influence of each, and will show that indeed, it is not always what seems to be an important factor at first sight.

To start with, an ANOVA test was carried out over BOD$_5$/COD results that is reflected in Table 3. As can be seen, $F$-test and the following $P$-Value showed that there is more than one parameter that can be considered non significant for the model.

It can be observed that the highest $P$-Value, far from 0.05, corresponds to the interaction between the two reagents, hydrogen peroxide and iron (II), followed by the individual effect of the metal itself and the interaction between Fe$^{2+}$ and the pesticide. The low influence in the model of the cross effect [H$_2$O$_2$][Fe$^{2+}$]$_0$ invalidates the first consideration explained about biodegradability, showing the non real significance of the ratio [H$_2$O$_2$]$_0$/[Fe$^{2+}$]$_0$.

This means that although apparently positive results have been obtained relating to different reagents ratios, they cannot be considered significant, and in order to obtain optimal conditions for maximizing biodegradability, more parameters have to be taken into account.

Non significance of those terms, namely, [H$_2$O$_2$][Fe$^{2+}$]$_0$ and [Met.$]_0$[Fe$^{2+}$]$_0$, are reflected on the final mathematical model where both interactions in which iron takes part have been neglected. The individual effect cannot be ignored so easily again, due to the significance of the quadratic factor related to it. According to this, the equation that defines the BOD$_5$/COD versus parameters in Table 3 is presented as Equation (3).

\[
\text{BOD}_5/\text{COD} = -0.14 - 0.0018[\text{Met.}]_0 \\
+ 0.0020[\text{H}_2\text{O}_2]_0 + 0.006[\text{Fe}^{2+}]_0 \\
+ 5.73 \times 10^{-6}[\text{Met.}]_0^2 - 5.0 \\
\times 10^{-6}[\text{Met.}]_0[\text{H}_2\text{O}_2]_0 - 2.8 \\
\times 10^{-6}[\text{H}_2\text{O}_2]_0^2 - 4.43 \times 10^{-5}[\text{Fe}^{2+}]_0^2
\]

In this case, $R^2$ is only 0.898 but, as can be seen on Table 3. $P$-Value of lack of fit test is higher than 0.05, so the model appears to be adequate for the observed data at the 95.0% confidence level.

Regarding the $P$-Values of the coefficients, it can be observed that the parameter that has the most important influence on BOD$_5$/COD value is methomyl initial concentration, being also significant at its quadratic term. Their negative coefficients in Equation (3) imply that higher quantities of pesticide derive from worse biocompatibility results after the treatment. On one hand there is the possible increase of initial COD inherent to a higher concentration of organic matter at the beginning of the process, which cannot be effectively degraded by photo-Fenton reaction,
giving higher values of final COD. On the other hand, an inhibitory effect to biodegradation by methomyl itself or its metabolites, either by inert compounds of the formulation, could be suggested, even because of their own nature or because of the lack of hydrogen peroxide to perform the adequate oxidation, leading to a limited biodegradability.

After the methomyl individual effect, the most significant influence is the interaction between the pesticide and H$_2$O$_2$. Its negative coefficient indicates that higher concentrations of both substances end up with lower biodegradability results, which is a positive fact with respect to reagent consumption. It has been previously stated how the maximum quantity of efficient hydrogen peroxide depends on the quantity of initial pesticide due to the inert ingredients content that provokes radicals consumption, limiting the biodegradability that can be achieved. The statement that concentration of hydrogen peroxide could imply higher biodegradability is also supported by the coefficient of H$_2$O$_2$ quadratic term although it is contradicted by the individual effect (Figure 3).

Finally, by optimizing the mathematical expression, a trio of best initial conditions can be found corresponding to a maximum biocompatibility of the final effluent. Those initial concentrations are $[\text{Met.}]_0 = 50$ mg L$^{-1}$, $[\text{H}_2\text{O}_2]_0 = 309.1$ mg L$^{-1}$ and $[\text{Fe}^{2+}]_0 = 71$ mg L$^{-1}$, quite close to ones from the optimum set obtained for the modelization of pesticide depletion, (50, 254, 77) mg L$^{-1}$. This coincidence establishes a relationship between the level of degradation of methomyl achieved and the biocompatibility of the treatment final effluent, and states the importance of limiting the concentration of pesticide treated. This fact should be taken into account in the design of the separation stage. Its performance should provide the system with an enriched effluent, although its concentration should not exceed a certain value.

Regarding the possibility of implementing a subsequent biological reactor to oxidize the organic matter non degraded by the process, even with the set of conditions for the maximal degradation, biodegradability achieved is 0.45 (obtained by the model), more than acceptable for considering the effluent as biodegradable (Sarrià et al. 2002).

As a result, those three conditions $[\text{Met.}]_0 = 50$ mg L$^{-1}$, $[\text{H}_2\text{O}_2]_0 = 254$ mg L$^{-1}$ and $[\text{Fe}^{2+}]_0 = 77$ mg L$^{-1}$, can be considered the optimal for this study.

**CONCLUSIONS**

Photo-Fenton has been revealed as an effective process to treat waters highly polluted with methomyl in the conditions essayed, since high pesticide depletion yields have been achieved ($Y > 95\%$), together with acceptable values of biocompatibility of the final effluent ($\text{BOD}_5/\text{COD} > 0.4$).

Experimental design procedures determined the most important variables influencing those two parameters, revealing as a useful tool to obtain quality information minimizing the number of experiments in this kind of research with more than one variable to check. On the one hand, initial pesticide concentration has been shown as the factor with the highest influence in the studied responses, due to the inert ingredients it entails. These substances seem to consume radicals preventing further degradation of methomyl and higher biodegradability values. According to this, the existence of the excipients seems to be capital for hydroxyl radical oxidation processes, which suggests that the organic matter accompanying the active principles have to be taken into account for implementing designs. In this case, this fact implied the need for setting 50 mg L$^{-1}$ as the optimal pesticide concentration to work with. On the other hand, optimal values for the other two factors could be inferred also from the result of the statistical study of pesticide depletion: $[\text{H}_2\text{O}_2]_0 = 254$ mg L$^{-1}$ and $[\text{Fe}^{2+}]_0 = 77$ mg L$^{-1}$.

These optimal values were in agreement with the conclusions extracted from the evaluation of BOD$_5$/COD. This parameter improvement achieved by the photo-Fenton treatment, together with the low TOC depletion obtained,
suggested the suitability and necessity of a chemical-biological integrated system, where a subsequent bioreactor could assimilate the organic load not totally oxidized by the Advanced Oxidation Process.

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REFERENCES


