Technical Note

Evaluation of Fenton method and ozone-based processes for colour and organic matter removal from biologically pre-treated swine manure

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HIGHLIGHTS

- Advanced oxidation processes are used to treat biologically pre-treated swine manure.
- The highest efficiencies (78% for TCOD and 96% for colour) are obtained with Fenton.
- Coagulation are elucidated as an important removal mechanism in Fenton method.
- Direct reactions with ozone are the main responsible of removals in ozonation.
- Fenton is the most cost-effective technology for the post-treatment.

ABSTRACT

This work evaluates the efficiency of different advanced oxidation processes (Fenton method, O₃, H₂O₂ and O₃/H₂O₂) for removing total COD (TCOD) and colour from biologically pre-treated swine manure. The Fenton process with a dosage of 100 mg L⁻¹ of Fe²⁺ and 800 mg L⁻¹ of H₂O₂ resulted in about 78% TCOD and 96% colour reductions at an initial pH = 3 after a reaction time of 30 min. Coagulation, rather than oxidation process, was identified as a crucial mechanism for removing pollutants. Otherwise, single ozonation achieved only 27–30% TCOD and 53–88% colour removals for ozone dosages ranging between 0.7 and 4.3 g O₃ h⁻¹ at the original wastewater pH (pH = 8.1) after 30 min reaction time. The combined treatment with O₃/H₂O₂ at pH = 8.1 did not produce any significant TCOD or colour reduction improvement. Therefore, direct reactions with ozone rather than radical reactions were elucidated as the main removal mechanisms in the ozone-based processes. Finally, a rough estimation of the operational costs involved in each process was also performed to compare their economic feasibility. The findings suggested that the Fenton process was more suitable than ozonation for reducing TCOD and colour from the biologically pre-treated swine manure.

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1. Introduction

Among the alternatives to improve manure management, biological processes are often seen as a solution due to their implications in nitrogen, carbon and phosphorous cycles (Bernet and Béline, 2009). After a multistage biological treatment, most of the organic and nutrient load is removed (Vanotti et al., 2009; Riaño and García-González, 2014). However, livestock wastewater presents a dark brown colour that remains after complete secondary treatment, which can be attributed to the presence of humin-type substances and carbon-rich stable residues (Tanaka, 2002; Hong et al., 2005). Therefore, further challenges should be faced up to meet the requirements of discharge imposed by the legislation and to develop innovative technologies for reusing and/or recycling livestock wastewater to minimize its environmental impact. In particular, new treatment strategies should aim to remove non-biodegradable organic compounds and colour after biological processes.

Advanced oxidation processes (AOP) involving Fenton’s reagent, ozone and hydrogen peroxide in single or combined action, have been reported to be appropriate for the treatment of relatively low strength industrial wastewater containing non-biodegradable organic pollutants and dark colour after a biological treatment (Coca et al., 2005; Lee and Shoda, 2008; Yetilmeszsoy and Sakar, 2008). Indeed, the application of AOPs to industrial effluents might be only economically attractive in combination with other
wastewater treatment technologies, particularly considering they usually imply a high energetic demand, or an excessive reagent consumption (Merayo et al., 2013).

Fenton process can have the dual functions of oxidation and coagulation and, therefore, this technology is capable to remove almost all parts of the organics which consists of both soluble and particulate fractions of COD formed during the biological treatment (Aydin and Sarikaya, 2012). In recent years, various studies have been addressed for the application of Fenton method on the removal of organic matter and colour from different industrial wastewater such as anaerobically treated leachate (Lau et al., 2005), anaerobically pre-treated poultry manure wastewater (Yetilmезsoy and Sakar, 2008) and livestock wastewater pre-treated by means of a biological activated sludge process (Hong et al., 2005).

Chemical oxidation with ozone has also been reported to show an efficient reduction of colour and organic matter of different types of wastewaters. However, wastewater composition shows a great influence on AOP efficiency (Coca et al., 2005; Merayo et al., 2013). To the best of our knowledge, studies on biologically pre-treated livestock wastewaters using AOPs are rather limited to few investigations. The study of the mechanisms involved in organic matter and colour removal using real wastewater will improve the application of combined biological systems/AOPs. Moreover, information regarding costs is also required to successfully introduce new treatment alternatives (Oller et al., 2011; Nolan et al., 2012).

The aim of the present work was to evaluate the effectiveness of Fenton method and ozone-based processes as post-treatments for biologically pre-treated swine manure. The performance of each method was evaluated in terms of organic matter and colour removal. The molecular weight distribution of colorants in wastewater before and after each treatment was also studied. Finally, a basic economic assessment of these technologies was carried out.

2. Materials and methods

2.1. Biologically pre-treated swine manure

Wastewater came from an on-farm swine manure treatment plant located in Segovia (Spain) that consists of a solid–liquid separation phase using screw pressing followed by a coagulation-floculation process, and biological nitrification–denitrification of the liquid fraction (Riaño and García-González, 2014). Wastewater was collected after the biological treatment, homogenized by mechanical agitation and stored at 4 °C for further use. Characteristics of the wastewater used in the present work are summarized in Table 1.

2.2. Fenton method

A stock solution of 10 g L$^{-1}$ of Fe$^{2+}$ was prepared by dissolving FeSO$_4$$\cdot$7H$_2$O (Panreac) in 0.2 N H$_2$SO$_4$. In addition to iron sulphate reagent, 30% H$_2$O$_2$ solution (Panreac) was also used. Experimental runs were performed in 1 L glass beakers with 0.5 L of sample. Firstly, the pH of the sample was adjusted to 3.0 (Yetilmезsoy and Sakar, 2008) by the addition of 1 N H$_2$SO$_4$. The FeSO$_4$$\cdot$7H$_2$O and H$_2$O$_2$ solutions were then added to the wastewater that was rapidly stirred for 5 min at 90 rpm using a Jar Test Equipment (Fisher Bioblock Scientific, Flocculator 11197). The wastewater was then stirred at 10 rpm for 25 min. After that, the stirring was ceased and the flocs formed were allowed to settle for 1 h. About 50 mL of the supernatant sample was then collected for total COD (TCOD) and colour determination. To evaluate Fenton process, different experimental runs were carried out. First, the initial pH, the H$_2$O$_2$ dose and the reaction time were kept constant while the Fe$^{2+}$ dose was varied between 100 and 400 mg L$^{-1}$. Then, the initial pH, the Fe$^{2+}$ dose and the reaction time were kept constant while the H$_2$O$_2$ dose was varied between 200 and 1200 mg L$^{-1}$. All experimental runs were carried out in duplicate and results are expressed as means.

2.3. Oxidation processes with ozone and hydrogen peroxide

Ozonation experiments were conducted in a 0.75 L glass reactor connected to an ozone generator (Model Sander 301) that produced ozone from oxygen (60 L h$^{-1}$) by electrical discharge. The reactor was filled with 0.4 L of wastewater and then agitated with a magnetic stirrer at 250 rpm. The ozone-containing gas was continuously supplied for 30 min through a gas diffuser at the bottom of the reactor at different rates (0.7–4.3 g O$_3$ h$^{-1}$). Two ozone traps containing 2% potassium iodide solution were connected in series with the reactor to determine ozone concentration in the outlet gas stream. Samples aliquots (15 mL) were taken from the reactor at regular intervals for TCOD and colour determination. Single hydrogen peroxide oxidation experiments were carried out in batch mode by adding different concentrations (200–1200 mg L$^{-1}$) of 30% H$_2$O$_2$ (Panreac) to 0.5 L of wastewater. After H$_2$O$_2$ addition, samples were agitated for 5 min at 90 rpm and then stirred at 10 rpm for 25 min using a Jar Test Equipment (Fisher Bioblock Scientific, Flocculator 11197). After the oxidation process, about 50 mL of sample was collected for TCOD and colour determination.

In the experimental runs combining ozone with hydrogen peroxide, the H$_2$O$_2$ was initially added to the wastewater to set initial concentrations ranging from 200 to 800 mg L$^{-1}$ and, immediately after, ozone at a flow rate of 0.7 g O$_3$ h$^{-1}$ was continuously fed up for 30 min.

All these experimental runs were performed in duplicate, at the original pH of the wastewater (pH = 8.1) and at room temperature. Results are expressed as means.

2.4. Analytical methods

TCOD and alkalinity were performed in accordance with APHA Standard Methods (2005). pH was measured in a Crison Basic 20 pH-meter (Crisson Instruments, SA, Barcelona, Spain). Total Fe was analysed using an atomic absorption spectrometer (AA 240 FS, Varian). Colour content of samples was obtained with a Spectronic Helios Gamma UV–Visible Spectrophotometer (Thermo Fisher Scientific, USA). The visible light absorption at 475 nm that characterizes brown colour was measured with 1 cm pathlength cells (Peña et al., 2003). TOC was measured with a Shimadzu TOC-V CSH Total Organic Carbon Analyser. The ozone concentration in the feed gas stream and outlet gas stream was determined by the iodometric method (APHA, 2005).

### Table 1

<table>
<thead>
<tr>
<th>pH</th>
<th>Colour$^a$ (AU)</th>
<th>TCOD (mg L$^{-1}$)</th>
<th>TOC (mg L$^{-1}$)</th>
<th>Alkalinity (mg L$^{-1}$)</th>
<th>Fe (mg L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1 ± 0.1</td>
<td>0.8 ± 0.2</td>
<td>769 ± 127</td>
<td>235 ± 55</td>
<td>3197 ± 37</td>
<td>&lt;2.0</td>
</tr>
</tbody>
</table>

$^a$ AU: absorbance units measured at 475 nm.
The molecular weight distribution of colorants in the wastewater was determined using an Ultrahydrogel 250 column (exclusion limit 1–80 kDa). Deionized water was used as mobile phase at a flow rate of 0.7 mL min⁻¹ at 35 °C. A Waters 996 Photodiode Array Detector and a Waters 2414 Refractive index were used as detectors. Dextran was used as standards for the estimation of molecular weights.

2.5. Statistical analysis

Data were compared using ANOVA with 95% confidence level (p < 0.05) to determine whether there were significant differences in removal efficiencies obtained from the different experimental runs. Statistical analysis was carried out using Statgraphics Centurion XVI.

3. Results and discussion

3.1. Fenton process

3.1.1. Effect of Fe²⁺ dosage

The addition of Fe²⁺ concentrations higher than 100 mg L⁻¹ for a fixed dosage of 200 mg H₂O₂ L⁻¹ at initial pH of 3.0 reduced the colour removal efficiencies (Fig. 1a). The same effect was observed with the TCOD removal, obtaining the highest removal efficiency at Fe²⁺ dosage of 100 mg L⁻¹ (75%). Likewise, TOC removal efficiencies at Fe²⁺ dosages of 100 and 400 mg L⁻¹ ranged between 60% and 57%, respectively (data not shown). This result can be explained by the capture of hydroxyl radicals by the reaction with Fe (II) in excess. In addition, the Fe (III) formed can react with H₂O₂ to generate Fe (II) and hydroperoxyl radicals (HO₂⁻) in solution, consuming H₂O₂ (Benítez et al., 2001; Meric et al., 2004; Lee and Shoda, 2008). It is worth mentioning that experimental runs adding separately 100 mg Fe²⁺ L⁻¹ and 200 mg H₂O₂ L⁻¹ to the wastewater at pH = 3.0 were also performed (data not shown), but neither colour or TCOD removals were detected under these conditions. In fact, it was observed that the coagulation of particles in the pre-treated swine manure began after the addition of H₂O₂ if Fe (II) was previously added, whereas formation of flocs was not observed only with the addition of Fe (II). Therefore, TCOD and colour reductions can be attributed to the dual mechanisms of coagulation and chemical oxidation caused by the combined action of Fe (II) and H₂O₂.

3.1.2. Effect of H₂O₂ dosage

It is important to optimize the amount of H₂O₂ in the Fenton method because excessive doses of H₂O₂ cause side effects (Dutta et al., 2001; Lee and Shoda, 2008). Colour removal efficiency slightly increased from 83% to 96% when H₂O₂ dosage increased from 200 to 800 mg L⁻¹ for a fixed dosage of 100 mg Fe²⁺ L⁻¹ (Fig. 1b). Dosages higher than 800 mg L⁻¹ did not result in a significant (p = 0.79) increase of removal efficiencies. Moreover, no significant (p = 0.10) differences were found for TCOD removal for H₂O₂ concentrations higher than 800 mg L⁻¹. Indeed, a slight decrease in TCOD removals was detected when increasing H₂O₂ concentrations. This slight decrease might be explained by the fact that residual H₂O₂ could affect Fenton reduction, as H₂O₂ acts as a scavenger of the highly potent hydroxyl radical to produce the hydroperoxyl radical, which has much lower oxidation potential than the hydroxyl radical (Lee and Shoda, 2008). TOC removal efficiencies varied between 58% and 83% regardless the H₂O₂ dosage (data not shown).

The highest removals corresponded to a H₂O₂/Fe²⁺ molar ratio of 4. Fenton process removed 736 mg L⁻¹ of TCOD from the biologically pre-treated swine manure with the dosages of 100 mg Fe²⁺ L⁻¹ and 800 mg H₂O₂ L⁻¹ at initial pH of 3.0 for a reaction time of 30 min. Therefore, to remove 1 g of TCOD in the wastewater, 0.14 g of Fe²⁺ and 0.33 g of H₂O₂ (pure) were consumed. Under these conditions, the H₂O₂ dose (mg L⁻¹)/TCOD concentration (mg L⁻¹) ratio was 0.90. This calculated ratio was similar to that (1.05) reported by Lee and Shoda (2008) and may be used as a criterion to determine the optimum H₂O₂ dose needed according to the initial TCOD concentration in the wastewater. Besides, it should be stressed that optimum dosages determined in the present study were considerably lower than those reported in previous works. Thus, Hong et al. (2005) found that the optimum dosages of Fe²⁺ and H₂O₂ in Fenton oxidation of livestock wastewater were 4000 and 1000 mg L⁻¹, respectively. With these dosages, COD values decreased from 895 mg L⁻¹ to 76 mg L⁻¹. Lee and Shoda (2008) applied Fenton method for high-strength livestock wastewater treatment and obtained colour removal reductions lower than 60% with dosages of 6554 mg Fe²⁺ L⁻¹ and 4000 mg H₂O₂ L⁻¹. Yetimsez and Sakar (2008) investigated the treatment of anaerobic poultry manure wastewater with Fenton process and found the highest values of COD and colour removals (95% and 96%, respectively) at Fe²⁺ and H₂O₂ dosages of 100 and 1200 mg L⁻¹, respectively. The reduction in the use of reagents in Fenton method would result in lowering operational costs. Nevertheless, differences in performances could be due to the characteristics of wastewaters, initial pH values and, also, reaction times (Yetimsez and Sakar, 2008).

3.2. Oxidation processes with ozone and hydrogen peroxide

3.2.1. Effect of ozone dosage on colour and organic matter removal efficiencies

Single ozonation results show that colour removal efficiencies increased from 59% to 89% after a reaction time of 30 min when
ozone flow rate increased from 0.7 to 4.3 g O₃ h⁻¹ (Fig. 2a). Ozone flow rate also exerted a positive effect in colour removal rates, wastewater decolourization occurring mainly at the initial stage of the reaction (20 min). Colour in pre-treated livestock wastewater is mainly due to the presence of humic-type substances (Tanaka, 2002; Hong et al., 2005). These compounds have an aromatic structure. As ozone is able to react with compounds with high electron density groups, direct reactions may be responsible for colour removal reactions. Likewise, the initial pH of the biologically pre-treated swine manure was about 8.1 (Table 1). This value slightly increased to 8.2–8.5 throughout ozonation. Under basic pH, hydroxide ions catalyse the decomposition of ozone to form highly oxidising and non-selective hydroxyl radicals which have an oxidation potential higher than that for ozone (2.80 V). How ever, the biologically pre-treated swine manure contained a high concentration of bicarbonate ions (3200 mg L⁻¹ as CaCO₃) which are strong inhibitors of indirect reactions between hydroxyl radicals and organic matter (Glaze and Kang, 1987). If the inorganic carbon acts as a scavenger for hydroxyl radicals, the reaction rate of organic compounds with hydroxyl radicals is often negligible and the direct oxidation reactions with the organic substrates become predominant.

Chemical oxidation with ozone provided as much as 27–30% TCOD removal after 30 min reaction time regardless the dosage applied, considerably lower than colour removal percentages (Fig. 2b). TOC variations were also independent of the applied ozone flow rate (7–10%; data not shown). Accordingly, colour reduction may be due to direct reactions between ozone and chromophore functional groups responsible for pre-treated swine manure colour. Ozone transformed the structure of coloured compounds rather than completely oxidize them (Rehman et al., 2012).

Ozone uptake, defined as the percentage of ozone fed into the reactor that is consumed after 30 min, decreased from 30% to 15% when ozone flow rate increased from 0.7 to 4.3 g O₃ h⁻¹ (Table 2) that corresponded to a ratio of 0.25 and 0.77 g O₃ consumed L⁻¹ of wastewater, respectively. The ratio ozone consumed g⁻¹ TCOD removed was also calculated (Table 2). An increase in the applied ozone dosage from 0.7 to 4.3 g h⁻¹ yielded a sharply increase in the ratio from 1.5 to 12.8 g O₃ g⁻¹ TCOD. For that reason, low ozone dosages (0.7 g h⁻¹) are enough to reduce TCOD from the biologically pre-treated swine manure. Although higher ozone dosages increased colour removal efficiencies, TCOD removal remained constant and most ozone left the reactor without being consumed by organic compounds.

### 3.2.2. Effect of the combination of ozone and hydrogen peroxide

Hydrogen peroxide has an oxidant potential (1.77 V) lower than ozone (2.07 V). In aqueous solutions, hydrogen peroxide dissociates to give perhydroxyl ion and hydroxyl radicals. The perhydroxyl ion has a strong nucleophilic activity and can react with chromophore groups reducing colour (Coca et al., 2005). However, in the experimental runs carried out with hydrogen peroxide alone, neither changes in colour nor TCOD values were observed regardless of the concentration added (data not shown). Therefore, oxidation with hydrogen peroxide alone was not effective in degrading colourants in the biologically pre-treated swine manure. This could be due to the high alkalinity of wastewater that acts as scavenger of the hydroxyl radicals formed. Moreover, it has also been pointed out that, under alkaline conditions, hydrogen peroxide can be decomposed to form molecular oxygen. Therefore, low concentrations of perhydroxyl ions and hydroxyl radicals may be available in the reaction mixture under these experimental conditions.

The combination of ozone with H₂O₂ at the original wastewater pH did not result in a considerably (p > 0.05) increase in the removal efficiency of colour and organic matter in comparison to those obtained with ozone (Fig. 3). Even, it was observed a slight TCOD decrease from 28% to 24% when increasing H₂O₂ dosage. This could indicate that TCOD reduction was mainly due to direct reactions with ozone rather than radicals reactions. The addition of hydrogen promoted ozone decomposition into hydroxyl radicals, so lower ozone molecules were available for direct oxidation reactions. As it was previously indicated, radical scavengers in wastewater (bicarbonate ions) compete with coloured organics for hydroxyl radicals formed from the decomposition of molecular ozone. The ratio ozone consumed/TCOD removed slightly increased from 1.5 to 2.2 g O₃ g⁻¹ TCOD when increasing the H₂O₂ dosage, which can be explained by the decomposition of ozone catalysed by the hydrogen peroxide (Table 2). It was also noticed that TOC values remained virtually constant (4–5% TOC removed; data not shown).

<p>| Table 2 |</p>
<table>
<thead>
<tr>
<th>Average ozone uptake and ozone consumed per TCOD removed ratios in the different ozone-based processes after 30 min reaction time.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
</tr>
<tr>
<td>Single ozonation</td>
</tr>
<tr>
<td>original pH (pH = 8.1)</td>
</tr>
<tr>
<td>1.4</td>
</tr>
<tr>
<td>2.6</td>
</tr>
<tr>
<td>4.3</td>
</tr>
<tr>
<td>Ozonation with H₂O₂</td>
</tr>
<tr>
<td>addition original pH (pH = 8.1)</td>
</tr>
<tr>
<td>0.7</td>
</tr>
<tr>
<td>0.7</td>
</tr>
</tbody>
</table>
3.3. Comparison of performance of AOPs

3.3.1. Oxygen-equivalent chemical-oxidation capacity

The parameter oxygen-equivalent chemical-oxidation capacity has been used to quantify in arbitrary units the oxidants added to the wastewater, in order to compare the performance of the different AOPs evaluated (Cañizares et al., 2009). This parameter was obtained from stoichiometric calculations, taking into account the number of electrons exchanged in the reduction of hydrogen peroxide and ozone, resulting that 1 kg O₃ m⁻³ is equivalent to 1 kg O₂ m⁻³ and 0.471 kg H₂O₂ m⁻³ is equivalent to 1 kg O₂ m⁻³. According to this parameter, Fenton method seems to be the most efficient process for removing colour and TCOD under the optimum conditions determined in the present study (Table 3). It must be mentioned that the maximum value of this ratio should be 1. The higher value obtained in Fenton process can be explained in terms of non-oxidative side reactions, mainly coagulation processes caused by the action of iron ions added to the solution and/or sedimentation processes (Cañizares et al., 2009). Therefore, these high efficiencies can be attributed to these mentioned mechanisms rather than oxidation processes.

3.3.2. Molecular weight distributions of colorants

The effectiveness of the oxidation processes was also analyzed from the molecular weight distribution chromatograms corresponding to the colorants in wastewater. Colorants in raw wastewater were divided into three groups with different molecular weights corresponding to their peak apices: > 80, 9.6 and 4.9 kDa (Fig. 4a). As a result of the oxidation processes, a considerable reduction in absorbance at 475 nm was observed, that is related with a decrease in the chromophore group concentrations.

Table 3

Effectiveness of the different AOPs in removing colour and organic matter.

<table>
<thead>
<tr>
<th>Fenton method</th>
<th>Ozonation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagent dosages</td>
<td></td>
</tr>
<tr>
<td>10 mg Fe²⁺ L⁻¹</td>
<td>0.7 g O₃ h⁻¹</td>
</tr>
<tr>
<td>800 mg H₂O₂ L⁻¹</td>
<td></td>
</tr>
<tr>
<td>Initial pH</td>
<td>3.0</td>
</tr>
<tr>
<td>Reaction time (min)</td>
<td>30 (1 h settling)</td>
</tr>
<tr>
<td>Oxygen-equivalent chemical-oxidation capacity (OCC)</td>
<td>0.51</td>
</tr>
<tr>
<td>Colour removed (AU g⁻¹ OCC added)</td>
<td>1.78</td>
</tr>
<tr>
<td>TCOD removed (g TCOD g⁻¹ OCC)</td>
<td>1.44</td>
</tr>
</tbody>
</table>

Fig. 4. Molecular weight distributions of (a) the biologically pre-treated swine manure and the effluents after single ozonation (0.7 g h⁻¹) and combined O₃/H₂O₂ processes at pH 8.1 (200 and 800 mg H₂O₂ L⁻¹) and (b) the biologically pre-treated swine manure at pH 3.0 and the effluents after Fenton process (100 mg Fe²⁺ L⁻¹, 30 min reaction time) at different H₂O₂ dosages (1) 200 mg H₂O₂ L⁻¹ and (2) 800 mg H₂O₂ L⁻¹. Chromatograms run at 475 nm.
The chromatograms do not show breaking treatment for the biologically pre-treated swine manure. Limited considerably the application of this technology as post-

Sakar, 2008; Anfruns et al., 2013). Although ozonation does not always requires significantly higher initial investment than the Cortez et al., 2011). Also, it must be emphasized that ozonation attractive compared with other advanced oxidation processes simplicity of operation and design of Fenton treatment are very

advantages of Fenton method is that the sludge produced after the sedimentation is high in iron, and, therefore, this leads to the problem of disposing the sludge (Hsueh et al., 2005; Yetilmezsoy and Sakar, 2008; Anfruns et al., 2013). Although ozonation does not produce sludge, the low TCOD removal achieved using this process limited considerably the application of this technology as post-

4. Conclusions

Fenton process performed successfully in removing colour and organic matter from the biologically pre-treated swine manure, with colour and TCOD removal efficiencies up to 96% and 78%, respectively. Coagulation was elucidated as an important removal mechanism in Fenton method. For the ozone-based processes, maximum colour removal efficiency of 89% for a dosage of 4.3 g O3 h\(^{-1}\) after 30 min reaction time was obtained, whereas TCOD removals were lower than 30% regardless the dosage applied. The addition of hydrogen peroxide to promote the formation of hydroxyl radicals did improve neither colour nor TCOD removals due to the presence of bicarbonate ions that compete with organic coloured compounds for hydroxyl radicals. As a result, direct reactions between ozone and organic compound were the main mechanism for colour and TCOD reduction in this type of wastewater. To conclude, the application of Fenton method to biologically pre-treated swine manure would enhance the reusing and/or recycling of swine manure, allowing the reduction of the environmental impact of intensive pig farming. Hence, further researches should be addressed to reduce operational costs that allow presenting the combined biological process/Fenton method as a cost-competitive technology.

Acknowledgements

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References


Table 4 Operational costs associated to the two studied technologies.

<table>
<thead>
<tr>
<th>Method</th>
<th>Consumption</th>
<th>Unitary cost</th>
<th>Operating cost</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fenton method</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H\textsubscript{2}SO\textsubscript{4} (1 N)\textsuperscript{a}</td>
<td>0.07 m\textsuperscript{3} m\textsuperscript{-3}</td>
<td>8.77 € m\textsuperscript{-3}</td>
<td>0.61 € m\textsuperscript{-3}</td>
</tr>
<tr>
<td>Fe\textsuperscript{b}</td>
<td>0.1 kg m\textsuperscript{-3}</td>
<td>0.33 € kg\textsuperscript{-1}</td>
<td>0.03 € m\textsuperscript{-3}</td>
</tr>
<tr>
<td>H\textsubscript{2}O\textsubscript{2}</td>
<td>0.8 kg m\textsuperscript{-3}</td>
<td>0.23 € kg\textsuperscript{-1}</td>
<td>0.18 € m\textsuperscript{-3}</td>
</tr>
<tr>
<td>Sludge treatment and disposal</td>
<td>1 kg m\textsuperscript{-3}</td>
<td>0.50 € kg\textsuperscript{-1}</td>
<td>0.50 € m\textsuperscript{-3}</td>
</tr>
<tr>
<td>Total treatment cost</td>
<td></td>
<td></td>
<td>1.32 € m\textsuperscript{-3}</td>
</tr>
<tr>
<td><strong>Ozonation</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O\textsubscript{3} production\textsuperscript{c}</td>
<td>0.88 kg m\textsuperscript{-3}</td>
<td>2.56 € kg\textsuperscript{-1}</td>
<td>2.25 € m\textsuperscript{-3}</td>
</tr>
<tr>
<td>Total treatment cost</td>
<td></td>
<td></td>
<td>2.25 € m\textsuperscript{-3}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The amount of 1 N H\textsubscript{2}SO\textsubscript{4} needed to change the pH to the desired value (3.0 in the present study) was experimentally determined. A H\textsubscript{2}SO\textsubscript{4} price of 0.179 € kg\textsuperscript{-1} for H\textsubscript{2}SO\textsubscript{4} 95–97% (w/w) was considered (Cortez et al., 2011).

\textsuperscript{b} Power (W) was measured directly on the lab-scale set up (16 kWh m\textsuperscript{-3}). Estimation was carried out considering an electricity price in Spain of 0.14 € kWh\textsuperscript{-1}.

\textsuperscript{c} From Cañizares et al. (2009).

\textsuperscript{d} From Anfruns et al. (2013).


