Textile, paint, paper and plastic industries release huge quantities of dyes into the environment. These dyes, are highly toxic and relatively stable in the environment, which makes the treatment of dye wastewater a difficult task. Several physical and chemical processes have been developed for dye effluent treatment and among them, the electro-Fenton process (EF) has been demonstrated to be an effective and attractive method for the decolorization of dye waste water. This promising process involves the in-situ production of H2O2 by two-electron reduction of O2 at a carbonaceous cathode material such as graphite, carbon felt, reticulated vitreous carbon or, more recently, activated carbon (AC) electrodes. The H2O2 generated in the presence of ferrous ions results in the production of *OH radicals according to Fenton’s reaction (Eq. 1), which are a strong oxidant species capable of mineralizing a wide variety of organic compounds.

Fe2+ + H2O2 → Fe3+ + "OH + OH−" [1]  

Furthermore, it has been shown that the application of UV light to this system, i.e., in the photoelectro-Fenton processes (PEF), accelerates the mineralization rate of the dye by the quicker Fe2+ regeneration, the higher generation of homogeneous *OH from photo-reduction of Fe(OH)2+, the pre-eminent Fe3+ species at pH near 3, by photo-Fenton reaction or the photolysis of Fe(III) complexes with generated carboxylic acids and the hemolytic breakdown of the peroxide molecule according to reaction 2:11-15

H2O2 + hν → 2•OH [2]

Due to its homogeneous nature, however, a Fenton based process produces a high concentration of iron ions in the final effluent. The required elimination of iron from the resulting aqueous solutions produces waste sludge which is expensive and difficult to dispose of. This disadvantage can be eliminated by utilizing solid materials to support the iron species. Using this approach, different materials have been studied such as Nafion membranes, iron-exchange resins and zeolitic materials. Supported zero valent iron can be prepared by chemical synthesis, but the use of sodium borohydride as a reducing agent has the disadvantage of being a corrosive and flammable reagent.

Electrochemical synthesis on the other hand is evolving as a green method that can produce well-dispersed iron material on different support materials. Recently, Santiago et al. reported a novel electrochemical technique for platinum electrodeposition at carbon Vulcan material using a rotating disk-slurry electrode (RoDSE). The results showed that the use of the RoDSE technique is an effective method for preparing bulk quantities of carbon-supported iron for heterogeneous EF and PEF applications via an electrochemical route.

The purpose of this paper is, first, to apply the novel method for iron electrodeposition of Santiago et al. on AC support and, second, to evaluate the prepared material as a cathode electrode for the degradation of a dye using EF and PEF processes. A study of the color and total organic carbon (TOC) removal percentage of methyl orange (MO) dye has been carried out to compare the degradation activity of the prepared materials using the RoDSE technique with that of homogenous EF and PEF processes. The RoDSE technique represents a step forward in the effort to produce supported iron (Fe/AC) via a cleaner electrochemical technique in bulk quantities, thereby reducing the cost and time involved in the preparation of cathode electrodes for water treatment applications.

**Experimental**

**Materials.**— Commercial granular AC was provided by Clarimex with an 8 × 30 mesh. The textural properties of this AC are: (i) a Brunauer–Emmett–Teller (BET) (N2) specific surface area of 405 m²/g, (ii) a pore volume of 0.767 cm³/g, and (iii) an average particle size of 1 mm.

Before the electrochemical synthesis, the AC was washed several times with distilled water to eliminate all impurities, and dried in an oven at 110°C for 1 day.

The supporting electrolyte employed in the electrochemical synthesis was 0.1 M of H2SO4. The iron precursor added to the slurry solution was FeCl3 at 1, 3 and 5 mM. For the EF and PEF process, the supporting electrolyte employed was 0.05 M of Na2SO4 adjusted to pH 3 with sulfuric acid. A cationic resin (Amberite IR-120) was used as an iron source for comparison purposes. The iron-exchange resin is characterized by a total exchange capacity of ≥ 1.80 eq/L (H⁺ form), a matrix of styrene divinylbenzene copolymer and a functional sulfonic acid group. Dye solutions were prepared using
analytical grade MO (J.T. Baker). In all cases, deionized water at 25°C (Millipore, Simplicity UV) was used.

**Synthesis of Fe/AC material.**— First, a suspension was made in a beaker with 1 g of AC and 20 mL of 0.1 M H₂SO₄ (Optima, Aldrich) and then sonicated for 2 h. This step was done to increase the surface oxygen functionalities on carbon.²¹ The formed suspension was placed in the center of the three-electrode cell assembly for the iron electrodeposition. The electrochemical cell had three compartments that were separated by Luggin capillary. Finally, 2.00 mL of the 1, 3 or 5 mM FeCl₃ (Aldrich) was added to the suspension. The electrochemical cell was sealed and purged with nitrogen for 1 h, whereas the RDE (BASi Instrument Co.) rotated at 900 rpm in the slurry. The disk electrode used, which was also used to apply the necessary potential, was a glassy carbon electrode with a geometric area of 0.071 cm². A titanium wire and Ag/AgCl (+0.209 V vs. normal hydrogen electrode) were used as a counter and a reference electrode, respectively. The electrodeposition to prepare the Fe/AC was accomplished by applying a constant potential of −1.0 V (BASI potentiostat-galvanostat, software epsilon EC V 2.1.3) for 2 h. The electrodeposition was repeated 3 times. The iron precursor (2.00 mL of FeCl₃) was added at each repetition 1 hour after beginning the electrodeposition step. Afterwards, the slurry was filtrated.

**Surface analysis.**— The surface morphology of the Fe/AC material was studied via scanning electron microscope (SEM, JEOL-5400LV). All Fe/AC samples were gold plated, and an electron acceleration voltage of 20 kV was applied for SEM measurements and X-ray dispersion spectroscopy (EDS) scanning and mapping. The content of iron in the AC cathode after the electrochemical synthesis was analyzed using a Perkin Elmer Induced Coupled Plasma (ICP) model optima 3000 XL. The X-ray diffraction (XRD) analysis was conducted using a X´Bucker-AXS D8 Advanced X-ray diffractromter System and Cu Kα (λ = 1.5406 Å) radiation. Scans were recorded in the 2θ angle range between 10 and 70° with a step size of 0.040° and a power of 40 kV and 30 mA.

**Electrochemical degradation experiments.**— The experiments were performed in a 25 mL undivided cylindrical glass cell equipped with three electrodos. The working electrode was the Fe/AC material prepared and constructed as described in the Results section. The counter electrode was a platinum spiral wire, and Ag/AgCl (+0.209 V vs. normal hydrogen electrode) was used as a reference electrode. Prior to the electrolysis, oxygen (99.99% purity, Infra Co.) was bubbled through the stirred (400 rpm) aqueous solution. In the case of the PEF process, the illumination was provided by a low pressure UV mercury lamp (UVP Inc., P = 75 mW/cm², λ = 365 nm). For homogenous (EF) experiments, a 0.5 mM solution of ferrous iron was introduced into the cell, and the working electrode was an AC cathode without electrodeposited iron.

Some preliminary electrolysis experiments were conducted to test the capacity of the cathode electrode to produce H₂O₂ by cathodic reduction of dissolved oxygen, applying a constant potential difference of −900 mV between the cathode and the reference electrode as reported by Bañuelos et al.⁶ The concentration of H₂O₂ accumulated at each repetition 1 hour after beginning the electrodeposition step. The statistical results are shown in Table I. The percent error does not exceed 20% for any synthesis, which is acceptable. However, while the 1 mM synthesis had the smallest concentration of the solution used for electrodeposition, the percent error and the amount electrodeposited were the lowest. It is clearly observed that there is no overlap in the amount of electrodeposited iron between the different concentrations of synthesis. Nevertheless, because it was not known how homogeneous and/or distributed the iron on the carbon particles is, we conducted additional tests to characterize the distribution of iron on the carbon particles. Therefore, the prepared Fe/AC material by the RoDSE technique was characterized by different physicochemical techniques in order to see if the iron was deposited onto the carbon support and how it was deposited.

**Table I. Data of electrochemical synthesis experiments.**

| Solution concentration (mM) | Mean (mg Kg⁻¹) | Standard deviation | Percent error |
|----------------------------|----------------|--------------------|---------------|
| 5                          | 1973           | 28.16              | 16.25         |
| 3                          | 1188           | 25.71              | 14.84         |
| 1                          | 407            | 22.37              | 12.91         |

Figure 1a shows a micrograph of AC, before the iron electrodeposition, showing the typical irregular morphology of the AC surface with a porous texture. The second micrograph (Fig. 1b) shows the electrodeposited iron particulates on the surface of the AC support. It can be noted that the synthesis conditions utilized seem to lead to the formation of composites because changes in the texture have been observed. In this way, the iron particles are observed at 10,000× magnification to be attached to the AC. To confirm this, the corresponding spectra by EDS and a mapping of the Fe/AC material were carried out and are shown in Figure 2. Consistent with the observation of Figure 1b, Figure 2a shows a strong and clear signal corresponding to iron, thus confirming the presence of the metal on the carbon support.

**Characterization of the Fe/AC cathode electrode.**— The Fe/AC material preparations were completed using the RoDSE technique as described in Synthesis of Fe/AC material section.²¹ To ensure reproducibility of the synthesis method, the content of iron in the AC was measured by ICP. Synthesis was performed three times for each iron concentration employed in the electrochemical synthetic solution. Concentrations of iron in the carbon were 1980, 1997 and 1942 mg Kg⁻¹ for 5 mM; 1164, 1208 and 1193 mg Kg⁻¹ for 3 mM, and 436, 396 and 388 mg Kg⁻¹ for 1 mM FeCl₃. Note that, at the time of the electrochemical synthesis, particles of carbon that already had iron deposited on their surfaces (determined by weight difference) were observed to be accumulating at the bottom of the cell, while the lighter particles (i.e., without electrodeposited iron) quickly and easily came to the glassy carbon electrode functioning as an electrical contact. The statistical results are shown in Table I. The percent error does not exceed 20% for any synthesis, which is acceptable. However, while the 1 mM synthesis had the smallest concentration of the solution used for electrodeposition, the percent error and the amount electrodeposited were the lowest. It is clearly observed that there is no overlap in the amount of electrodeposited iron between the different concentrations of synthesis. Nevertheless, because it was not known how homogeneous and/or distributed the iron on the carbon particles is, we conducted additional tests to characterize the distribution of iron on the carbon particles. Therefore, the prepared Fe/AC material by the RoDSE technique was characterized by different physicochemical techniques in order to see if the iron was deposited onto the carbon support and how it was deposited.

XRD analysis was performed for the AC without iron electrodeposition and for the RoDSE Fe/AC material in order to verify the iron patterns. The Fe/AC spectra in Figure 3 show a typical diffraction peak as a result of the introduction of oxygenated functional groups on the carbon due to the acid solution used in the electrochemical synthesis. The XRD pattern corresponding to the Fe/AC material also shows a broad peak at 2θ = 26.5°, corresponding to an ordered graphitic crystal structure.²² The diffraction peaks (2θ) of the Fe/AC material at 35.2° (311), 42.9° (400), 56.9° (511) and 62.5° (440) have been reported by other research groups as characteristic patterns of iron oxides and zero valent iron.²⁰,²³,²⁶ Therefore, comparison between the

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Figure 1. SEM images obtained for activated carbon (a) before and (b) after Fe electrodeposition.

Figure 2. (a) EDS pattern and (b) mapping of the Fe/AC material.

Figure 3. Comparison of X-ray diffraction patterns of AC with and without electrodeposited iron. M: magnetite Fe$_3$O$_4$, G: geothite FeOOH.

Spectra of carbon with and without iron, allow us to conclude that both iron oxides, as well as zero valent iron, have been electrodeposited onto the activated carbon support.

**Fe/AC synthesized material as electrode in EF and PEF processes.**—To test the performance of the synthesized material as an electrode in a wastewater treatment process, the electro-generation of hydrogen peroxide and the decolorization and degradation of MO were further assessed by both EF and PEF processes using the Fe/AC synthesized material as the cathode in a conventional electrochemical cell.

For the construction of the cathode electrodes, 100 mg of Fe/AC were mixed with 2 mL of silicon oil (Aldrich) in a mortar and homogenized. The resulting mixture was placed in an insulin syringe and compacted using the plunger. Finally a titanium wire was introduced on the wide side of the tube of the syringe, and the needle was removed from the opposite end as reported by Bañuelos et al.6 The cathode electrodes were polished on sandpaper to maintain a constant and reproducible projected area of 0.071 cm$^2$.

**Electro-generation of hydrogen peroxide.**—The cathodic generation of H$_2$O$_2$ was performed in a conventional cell equipped with an Fe/AC cathode in the presence of bubbled O$_2$ and with Na$_2$SO$_4$ as a supporting electrolyte. Additionally, a blank test (without Fe) was carried out to determine if the introduction of the iron on the AC could decrease the activation sites of the surface to reduce O$_2$ molecules. As
can be seen in Figure 4, the concentration of $\text{H}_2\text{O}_2$ increased within the first 15 min for all adopted iron concentrations (1973, 1188 and 407 mg kg$^{-1}$), which was the same behavior observed for the AC cathode (without Fe). After 30 min, the greatest concentration of $\text{H}_2\text{O}_2$ was reached with the 1973 mg kg$^{-1}$ Fe/AC electrode (Figure 4a) which, according to Table I, is the electrode that contains more electrodeposited iron (1973 mg Kg$^{-1}$). If we compare this electrode with the AC blank, 48% more $\text{H}_2\text{O}_2$ was reached with the synthesized material, which is highly favorable for EF and PEF processes (see Figure 4b). The observed increase in the in-situ generation of peroxide may be due to two main reasons. First, as has been previously reported, the presence of oxygenated functional groups in the AC promotes the reduction reaction of oxygen via two electrons, which was verified by an additional test (data not shown) where hydrogen peroxide was electrogenerated under the same conditions without the activation step with sulfuric acid, reaching 40% less $\text{H}_2\text{O}_2$ than the AC previously treated with $\text{H}_2\text{SO}_4$. On the other hand, the second explanation is shown in Equation 3, which has already been reported by some authors.\textsuperscript{20,27} Zero valent iron can degrade and oxidize a range of organic compounds in the presence of dissolved oxygen, transferring two electrons to $\text{O}_2$ to produce $\text{H}_2\text{O}_2$.

$$\text{Fe}^{0} + \text{O}_2 + 2\text{H}^{+} \rightarrow \text{Fe}^{2+} + \text{H}_2\text{O}_2 \quad [3]$$

Although it is clear that the use of Fe/AC material results in an increased in-situ electrogeneration of hydrogen peroxide, the reasons are not clear and this issue is still under investigation.

**Electro-Fenton process.**— The influence of electrodeposited iron concentrations on the oxidation ability of the EF process was then comparatively examined from the color and TOC abatement measured for dye solutions. The color and TOC percentage removal with electrolysis time are depicted in Figures 5a and 5b, respectively, for 10 ppm MO in a 0.05 M $\text{Na}_2\text{SO}_4$ solution with 1973, 1188 and
407 mg Kg$^{-1}$ electrodeposited iron concentrations at pH 3.0 and 25°C under a -900 mV applied cathode potential during EF treatment. It can be observed that a higher percentage removal occurs with a higher electrodeposited iron concentration on activated carbon, indicating the formation of more oxidizing reagents corresponding to an increased production of hydrogen peroxide (Figure 4). The results shown in Figure 5 indicate that increasing the H$_2$O$_2$ electro-generation always caused a gradual rise in color and TOC removal owing to the larger production of oxidants (•OH), as stated above. After 30 min of EF treatment for a synthesis concentration of 5mM, an almost total decolorization (96%) and mineralization (88%) were obtained. At the lower electrodeposited iron concentration of 1 mM, the process was slightly less efficient; color and TOC were only reduced by 84% and 63%, respectively. Furthermore, as confirmation that the observed decrease of color and TOC of the model compound was due to the in situ electrochemically generated Fenton reagent and not due to electrochemical reactions promoted by the applied potential, to electro-generated hydrogen peroxide or by a process of adsorption on the electrode, a three-control experiment was carried out. The absorbance and TOC of MO were monitored in an Fe-free cell (AC without electrodeposition) and in the absence of oxygen (saturated with N$_2$) but subject to -900 mV of applied potential. The results of these tests are included in Figure 5. As can be clearly seen in Figure 5a, there was a decrease color of approximately 65% corresponding to the in situ generated H$_2$O$_2$ plus the applied potential, and 58% of the color removal due to the electrochemical system only (without H$_2$O$_2$ and/or Fenton reagent). However, in Figure 5b, no noticeable decrease was observed in the TOC of MO resulting from in situ generated H$_2$O$_2$ or the electrochemical system alone, and there is no adsorption process (Figure 5a), thus supporting the conclusion that the improved performance of the EF process is actually the result of the coupled generation of oxidant species at the electrode surface.

**Photoelectro-Fenton process.**—To evaluate a PEF process, the same experiments were conducted in the presence of UV radiation to perform Fenton’s reagent generation. The results of the dye discoloration and oxidation experiments after 30 min of electrolysis time are shown in Figure 6. Inspection of this figure reveals that the system with 1973 mg Kg$^{-1}$ Fe/AC shows the best performance, reaching a removal of color and TOC of 100 and 98%, respectively. If we compare these values with those obtained in the EF process, we can see that not only a complete discoloration but a greater decrease of TOC is obtained for the three different amounts of iron electrodeposited on the carbon support. The improved efficiencies of the three electrodes were probably due to two factors: (i) the increase in the Fe$^{2+}$ regeneration and production of •OH radicals by photolysis of Fe(OH)$_2$$^{2+}$ according to reaction 4, and (ii) the photodecarboxylation of complexes of Fe$^{3+}$ with generated carboxylic acids (reaction 5), which are hardly attacked by •OH radicals. The results indicate that there are iron species present in the solution from the Fe/AC electrode. This possibility will be studied in a future work by the analysis of iron in solution. In any case, considering the results obtained, it was decided to carry out all of the subsequent experiments using electrodes prepared with 1973 mg Kg$^{-1}$ of electrodeposited iron.

\[
\text{Fe(OH)}^{2+} + \text{UV} \rightarrow \text{Fe}^{2+} + \text{HO} \quad [4]
\]

\[
\text{Fe(OOCR)}^{2+} + \text{UV} \rightarrow \text{Fe}^{2+} + \text{CO}_2 + \text{R} \quad [5]
\]

**Comparative study of MO discoloration and degradation.**—To provide supporting evidence on the efficiency of the proposed electro-Fenton method using Fe electrodeposited on AC compared to other systems, MO degradation and discoloration experiments were conducted using three systems. In the first system (system 1; Fe/AC) the Fenton reagent is generated from carbon with electrodeposited iron. The second system (system 2; Fe/solution) used the same electrode of activated carbon to produce H$_2$O$_2$, but instead of having electrodeposited iron, the source of iron was Fe$^{2+}$ added in solution. The third system (system 3; Fe/resin) used the activated carbon electrode to generate the H$_2$O$_2$, but the provided iron was supported on the cation exchange resin Amberlite (R), prepared according to Ramirez et al. using enough resin to have an equivalent amount of iron to system 1. In Figure 7, the discoloration and degradation of MO over time is shown. The system in which the iron was electrodeposited on the AC (system 1) had the best performance, obtaining a color removal of 96% and a TOC reduction of 88% in the first 30 min. The system with iron in solution (system 2) had a color and TOC removal of 72 and 70%, respectively, and the least efficient was the system with iron in the resin (system 3) with 52% of color removal and a 55% TOC decrease. Because similar amounts of Fe and H$_2$O$_2$ were used in the three systems, it is possible that one of the reasons for the best performance of the first system was due to the zero valent metallic iron electrodeposited on the AC. This improvement has been referred to as an Advanced Fenton Process (AFP), which utilizes the corrosion of metallic iron surfaces to generate Fe$^{2+}$ and gives rise to potent Fenton type reactions. Additionally, a faster recycling of ferric iron is expected through reaction 6, which contributes to an increased concentration of ferrous iron in the solution, thus leading to
accelerated generation of hydroxyl radicals via Fenton oxidation.

$$2\text{Fe}^{3+} + \text{Fe}^{0} \rightarrow 3\text{Fe}^{2+}$$  [6]

Furthermore, the three systems were tested for 30 min in the presence of UV radiation to perform Fenton’s reagent generation. As shown in Figure 8, system 1 again had the best performance, reaching a removal of color and TOC of 98%. This was followed by the second system where the color and TOC removal reached 90 and 82%, respectively. The least efficient system was 3, with TOC removal and discoloration values approximately 71%. Increased removal efficiencies of color and TOC are attributed for the same reasons explained in Electro-generation of hydrogen peroxide section.

Conclusions

The novel RoDSE technique can be considered to be a promising approach to mass producing iron–carbon-supported material through an electrodeposition process. The presence and amount of iron on an AC surface are ascertained by using ICP, SEM, EDS and XRD techniques. For all syntheses, high reproducibility was obtained with an electrodeposition process. The presence and amount of iron on the electrode that had the greatest amount of iron electrodeposited than iron-supported exchange resins and a homogeneous process.

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References

1. C. Flox, S. Ammar, C. Arias, E. Brillais, A. Vargas-Zavala, and R. Abdelhedi, *Applied Catalysis B: Environmental*, 67, 93 (2006).
2. S. García-Segura, A. El-Ghenemy, F. Centellas, R. M. Rodríguez, C. Arias, J. A. Garrido, P. L. Cabot, and E. Brillais, *Journal of Electroanalytical Chemistry*, 681, 36 (2012).
3. S. García-Segura, F. Centellas, C. Arias, J. A. Garrido, R. M. Rodríguez, P. L. Cabot, and E. Brillais, *Electrochimica Acta*, 58, 303 (2011).
4. E. J. Ruiz, C. Arias, E. Brillais, A. Hernández-Ramírez, and J. M. Peralta-Hernández, *Chemosphere*, 82, 495 (2011).
5. F. J. R. J. Bañuelos, J. Manrrique, E. Bustos, A. Rodríguez, and A. Luis Godínez, in Evaluation of Electrochemical Reactors as a New Way to Environmental Protection, M. A. R. M. Juan Peralta-Hernández and Carlos A. Martínez-Huitle Editor, p. 95, Research Signpost, kerala, India (2014).
6. J. A. Bañuelos, F. J. Rodríguez, J. Manrrique Rocha, E. Bustos, A. Rodríguez, J. C. Cruz, L. G. Arriaga, and L. A. Godínez, *Environmental Science & Technology*, 47, 7927 (2013).
7. Z. Qiang, J.-H. Chang, and C.-P. Huang, *Water Research*, 36, 85 (2002).
8. E. Brillais, I. Sirés, and M. A. Oturan, *Chemical Reviews (Washington, DC)*, 109, 6570 (2009).
9. J. A. Bañuelos, A. El-Ghenemy, F. J. Rodríguez, J. Manríquez, E. Bustos, A. Rodríguez, E. Brillais, and L. A. Godínez, *Electrochimica Acta*, 140, 412 (2014).
10. J. M. Peralta-Hernández, Y. Meas-Vong, F. J. Rodríguez, T. W. Chapman, M. I. Maldonado, and L. A. Godínez, *Dyes and Pigments*, 76, 656 (2008).
11. J. M. Peralta-Hernández, Y. Meas-Vong, F. J. Rodríguez, T. W. Chapman, M. I. Maldonado, and L. A. Godínez, *Water Research*, 40, 1754 (2006).
12. E. Brillais and C. A. Martínez-Huitle, *Applied Catalysis B: Environmental*, 166–167, 603 (2015).
13. I. Sirés, E. Brillais, M. Oturan, M. Rodrigo, and M. Panizza, *Environ Sci Pollut Res, 21*, 8336 (2014).
14. L. A. G. Jonathan Ramírez, Marcela Méndez, Yummy Meas, and Francisco J. Rodríguez, *Journal of Applied Electrochemistry*, 40, 1729 (2010).
15. D. Gumy, P. Fernández-Ibáñez, S. Malato, C. Pulgarín, O. Enea, and J. Kiwi, *Catalysis Today*, 101, 375 (2005).
16. J. Feng, X. Hu, and P. L. Yue, *Chemical Engineering Journal (Lusanne)*, 100, 159 (2004).
17. M. B. Kasiri, H. A. Maleheheh, and A. Maleheheh, *Applied Catalysis B: Environmental*, 84, 9 (2008).
18. T. D. Nguyen, N. H. Phan, M. H. Do, and K. T. Ngo, *Journal of Hazardous Materials*, 185, 653 (2011).
19. H. Zhu, Y. Jia, X. Wu, and H. Wang, *Journal of Hazardous Materials*, 172, 1591 (2009).
20. T. Shahwan, S. Abu Siriah, M. Nairat, E. Boyasu, A. E. Ergülot, T. B. Scott, and K. R. Hallam, *Chemical Engineering Journal (Lusanne)*, 172, 258 (2011).
21. D. Santiago, G. G. Rodríguez-Calero, H. Rivera, D. A. Tryk, M. A. Schiboh, and C. R. Cabrera, *Journal of the Electrochemical Society*, 157, F189 (2010).
22. K. Esquivel, L. G. Arriaga, F. J. Rodríguez, L. Martínez, and L. A. Godínez, *Water Research*, 43, 3593 (2009).
23. W. Fan, W. Gao, C. Zhang, W. W. Tju, J. Pan, and T. Liu, *Journal of Materials Chemistry*, 22, 25108 (2012).
24. Y. Xi, M. Megharaj, and R. Naidu, *Applied Clay Science*, 53, 716 (2011).
25. A. Babuponnusami and M. Kuthukumar, *Separation and Purification Technology*, 98, 130 (2012).
26. J. Fan, Y. Guo, J. Wang, and M. Fan, *Journal of Hazardous Materials*, 166, 904 (2009).
27. F. Fu, D. D. Dionysiou, and H. Liu, *Journal of Hazardous Materials*, 267, 194 (2014).
28. S. García-Segura and E. Brillais, *Electrochimica Acta*, 140, 384 (2014).
29. L. Gomathi Devi, S. Girish Kumar, K. Mohan Reddy, and C. Muniyakshnappa, *Journal of Hazardous Materials*, 164, 459 (2009).
30. D. H. Bremner, A. E. Burgess, D. Houlellam, and K.-C. Namkung, *Applied Catalysis B: Environmental*, 63, 15 (2006).