Magnetic Nanoparticles for Photocatalytic Ozonation of Organic Pollutants

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Abstract: Magnetic nanoparticles (MNP) composed of iron oxide (or other metal–FeO cores) coated with carbon produced by chemical vapour decomposition (CVD) were used in the photocatalytic ozonation of oxamic acid (OMA) which we selected as a model pollutant. The incorporation of Ag and Cu on FeO enhanced the efficiency of the process. The carbon phase significantly increased the photocatalytic activity towards the conversion of OMA. As for the synthesis process, raising the temperature of CVD improved the performance of the produced photocatalysts. The obtained results suggested that the carbon phase is directly related to high catalytic activity. The most active photocatalyst (C@FeO_CVD850) was used in the removal of other compounds (dyes, industrial pollutants and herbicides) from water and high mineralization levels were attained. This material was also revealed to be stable during reutilisation.

Keywords: magnetic materials; chemical vapour deposition; photocatalytic ozonation; organic pollutants

1. Introduction

Photocatalytic ozonation (PCO) results from the combination of two different techniques, and consequently, the potential of pollutant abatement increases since the generation of hydroxyl radicals is promoted [1]. According to the literature, besides direct ozonation in the presence of suitable catalysts under illumination, O₃ can generate hydroxyl radicals (HO•) through the formation of ozonide radical (O₃•−) in the adsorption layer of the optical semiconductor (SC) where surface holes (h⁺[SC]) and electrons (e−[SC]) are generated, as described in Equations (1), (2) and (3). The generated O₃•− species rapidly reacts with H⁺ to produce the radical HO₃•, which evolves to O₂ and HO•. The generated O₃•− species quickly reacts with H⁺ in the solution to give the HO₃• radical (Equation (4)), which results in O₂ and HO• (Equation (5)).

\[
[\text{SC}] + h\nu \rightarrow h^+_{[\text{SC}]} + e^-_{[\text{SC}]}
\]

(1)

\[
\text{O}_3 + e^-_{[\text{SC}]} \rightarrow \text{O}_3^{•−}
\]

(2)

\[
h^+_{[\text{SC}]} + \text{H}_2\text{O} \rightarrow \text{HO}^• + \text{H}^+
\]

(3)

\[
\text{O}_3^{•−} + \text{H}^+ \leftrightarrow \text{HO}_3^•
\]

(4)

\[
\text{HO}_3^• \rightarrow \text{HO}^• + \text{O}_2
\]

(5)

The reaction between O₃ and electrons on the catalyst surface interferes with the recombination of electrons and positive holes. Consequently, a more significant number of radicals are produced,
themselves accelerating the photocatalytic reaction. Several studies have confirmed the synergistic effects of PCO on the degradation and removal of different substances [1,2].

Examining the papers published in recent years, most of the studies reported the use of AEROXIDE© TiO2 P25 (Evonik), the “gold standard” in photocatalysis [3], during photocatalytic ozonation. On the other hand, magnetic nanoparticles (MNP) gained increasing importance in different areas such as biomedicine/biotechnology [4–6], catalysis [7–9] and water treatment [10–16]. In spite of being widely used as catalyst supports, carbon materials as a catalyst are attracting a great deal of attention [17]. Coating MNP with a layer of different materials improves their stability and introduces new surface properties and functionalities. The use of MNP coated with carbon will enable catalyst recovery by magnetic separation and also take advantage of the catalytic properties of the carbon materials. Magnetic separation to remove the catalyst from liquid solutions eliminates the necessity of centrifugation, filtration or other impractical techniques for recycling the catalysts, avoiding their agglomeration and consequently increasing their durability [9].

Although the use of MNP has been extensively reported, the development of new catalysts with magnetic properties for application in a wide range of expertise fields is still a challenge. In the case of advanced oxidation processes (AOPs), the use of MNP has also been a subject of intense research, but few works reported the presence of MNP during PCO. Mahmoodi used CuFe2O4 MNP to study the degradation of a dye in aqueous solution, and his results showed that these nanoparticles are very efficient in the degradation of the selected pollutant [14]. Mahmoodi et al. also investigated PCO for the removal of dyes using nickel–zinc ferrite (NZFMN) nanoparticles and 100% effective removal was verified [15]. Magnetic ZnFe2O4–C3N4 hybrids prepared by a simple reflux treatment were applied in photo-Fenton discoloration of Orange II [18]. Yin et al. [16] used BiFeO3 magnetic nanoparticles as a visible light photocatalyst in the coupling of PCO for the degradation of oxalic acid and norfloxacin. A notable improvement allied to excellent stability during reuse reactions was confirmed. Recently, Hussan et al. [19] verified a high catalytic activity, stability and reuse of BiFeO3 magnetic nanoparticles during aniline degradation. CoFe2O4 particles with a predominantly mesoporous structure containing a large surface area showed a higher decolourization and mineralization of melanoidin (aminocarbonyl complex polymers containing a dark brown colour present in several distillery wastewaters) during catalytic ozonation [20]. The improvement when compared to O3 alone was attributed to the generation of HO• radicals in the reaction medium. Magnetic Fe2O3 supported on ordered mesoporous silica material (SBA-15) was synthesized by a facile impregnation and calcination method and the photocatalytic activities were also evaluated on the degradation of rhodamine B [21]. The structure and amount of catalyst and the concentration of H2O2 and the pollutant were the main influencing factors on the degradation of rhodamine B. The prepared magnetic Fe2O3/SBA-15 had excellent reusability and stability, showing only a slightly decrease after five consecutive runs. Catalytic ozonation of di-n-butyl phthalate (DBP) was carried out in the presence of Ag-doped MnFe2O4 catalysts [22]. The Ag-doped MnFe2O4 enhanced the apparent rate constants compared to O3 alone and undoped MnFe2O4 systems, and the catalyst surface hydroxyl groups were identified as a critical factor. The Bi2WO6–FeOx photocatalysts presented with stable photocatalytic activity during repetitive norfloxacin degradation experiments [22]. Ortiz-Quinonez et al. showed that MNP containing Ni prepared by a low-temperature solution combustion method were very active catalysts for the degradation of 4-nitrophenol in aqueous media [23]. Magnetic Fe3O4/SnO2 nanocomposites with different molar ratios were tested in the photodegradation of crystal violet [24]. The photoconductivity studies revealed the ohmic nature of the samples was responsible for the good photocatalytic activity due to the extended photosensitive range and increase in charge separation rate. A novel rattle-type magnetic Fe3O4@Ag@H–BiOCl nanocomposite was successfully prepared by a solvothermal method and evaluated by the photocatalytic degradation of rhodamine B and the antibiotic ciprofloxacin [25]. The characterization results showed that the composites exhibit an obvious cavity that promotes excellent adsorption, showing better performance than pure BiOCl.
The aim of this work is to evaluate the PCO performance of MNP composed of iron oxide and coated with carbon by chemical vapour decomposition (CVD). Oxamic acid (OMA) was selected as a model compound since it is a simple molecule and one of the common final products that result from the degradation of a wide range of pollutants with high refractory character to oxidation [26]. Non-catalytic combined treatment (photo-ozonation), non-catalytic individual processes (single ozonation and photolysis), and the corresponding catalytic individual processes (catalytic ozonation and photocatalysis) were also carried out to understand the reaction mechanisms and evaluate the presence of synergetic effects during OMA removal by PCO. The catalytic activity of the prepared materials was confirmed in the degradation of other pollutants (Colour Index Reactive Blue Dye 5—DYE; aniline—ANL; metolachlor—MTLC) using the most active photocatalysts.

2. Results

2.1. Catalyst Characterisation

Table 1 displays the Brunauer–Emmet–Teller (BET) surface area and the amount of carbon (C) of the prepared samples. The textural characterisation of MNP revealed that the incorporation of Cu or Co in Fe₃O₄ (sample FeO) during the synthesis of these samples increased the BET surface area in contrast with the introduction of Ag that slightly decreased this value. This decrease may rely on the use of the incipient wetness impregnation method to deposit Ag on the FeO surface. In the case of MNP coated with carbon by CVD, we calculated the surface area per gram of carbon previously determined by thermogravimetric (TG) analysis. A drastic decrease to values lower than 10 m² g⁻¹ was observed in the surface area of MNP coated by CVD. This decrease is due to the heat treatments used during synthesis, namely the heating up to 400 °C to carry out the reduction of the metal under hydrogen and, after that, a temperature increase up to 750 °C or 850 °C to coat the MNP with carbon [13].

| Sample                        | S_BET (m² g⁻¹) ±10 m² g⁻¹ | % C †  |
|-------------------------------|-----------------------------|-------|
| FeO                           | 154                         | 0     |
| CoFeO                         | 184                         | 0     |
| Cu FeO                        | 235                         | 0     |
| AgFeO                         | 134                         | 0     |
| C@FeO_CVD750                  | 63 *                        | 16    |
| C@FeO_CVD850                  | 29 *                        | 35    |
| C@CoFeO_CVD750                | 29 *                        | 34    |
| C@CoFeO_CVD850                | 33 *                        | 43    |
| C@CuFeO_CVD750                | 27 *                        | 67    |
| C@CuFeO_CVD850                | 16 *                        | 63    |
| C@TiFeO_met1_CVD850           | 25 *                        | 20    |
| C@TiFeO_met2_CVD850           | 26 *                        | 33    |

* per gram of carbon. † determined by thermogravimetric (TG) analysis.

In general, materials prepared by CVD at 850 °C had a higher amount of carbon than those at 750 °C.

In the transmission electron microscopy (TEM) of selected samples (Figure 1), it is possible to see that MNP are composed of small spheres that are not well defined and have no clear distinction of the different metals, which is indicative of a good dispersion of both metals. TEM images confirm the covering of the MNP with carbon during the CVD process. In the samples C@FeO_CVD750 and C@FeO_CVD850, we can confirm that iron oxide particles are encapsulated (coated with carbon nanotubes and nanofibers). The results suggest that the increase in temperature increased the formation of carbon, as confirmed by the TG analysis. In the case of C@CoFeO_CVD750, MNP are covered by few
carbon layers and also by carbon nanotubes and nanofibers, while C@CoFeO_CVD850 appeared to be encapsulated by carbon nanotubes and nanofibers. Most of the MNP were encapsulated by carbon, but some metal oxide is exposed on the surface.

![Image](image-url)

**Figure 1.** Transmission electron microscopy (TEM) micrographs of selected samples: (a) FeO; (b) AgFeO; (c) C@FeO_CVD750; (d) C@FeO_CVD850; (e) C@CoFeO_CVD750; (f) C@CoFeO_CVD850; (g) C@TiFeO_met2_CVD850.

The crystal structure of the prepared MNP was studied by X-ray diffraction (XRD) and the spectra of some of the tested catalysts are depicted in Figure 2. In Table 2, we show the identification of the phases identified in the MNP materials, along with the crystallite sizes. XRD analyses show that the only phase present in the FeO sample is magnetite. The main crystalline phase of AgFeO is also magnetite (92.6%). As expected, the coated MNP have a large amount of carbon in their composition, appearing as graphite with a percentage between 84% and 96%.
a.u.: arbitrary units; $2^\theta$: angle between transmitted beam and reflected beam.

Figure 2. X-ray diffraction (XRD) spectra of selected samples: (a) FeO; (b) AgFeO; (c) C@FeO_CVD750; (d) C@CoFeO_CVD850; (e) C@TiFeO_met2_CVD850. a.u.: arbitrary units; $2^\theta$: angle between transmitted beam and reflected beam.

Table 2. Properties of selected materials obtained by XRD analysis.

| Sample               | Phase (%vol/vol)          | Crystallite Size (nm) ±6% |
|----------------------|---------------------------|---------------------------|
| FeO                  | 100% magnetite (Fe$_3$O$_4$) | 20.5                      |
| AgFe$_3$O$_4$        | 7.3% chlorargyrite (AgCl) | 92.6% magnetite (Fe$_3$O$_4$) | 8.2 |
| C@FeO_CVD750        | 3% cementite (Fe$_3$C)    | 1.6% Fe $\alpha$         | 95.4% graphite | 84 |
|                      |                           | 72                        | 16                     |
| C@FeO_CVD850        | 3% cementite (Fe$_3$C)    | 1.5% Fe $\alpha$         | 95.5% graphite | 52 |
|                      |                           | 73                        | 27                     |
| C@TiFeO_met2_CVD850 | 14.1% cementite (Fe$_3$C) | 2.3% Fe $\alpha$         | 83.6% graphite | 72 |
|                      |                           | 10                        | -                      |

2.2. OMA Removal by MNP

The conversion of OMA by PCO in the presence of different MNP is displayed in Figure 3 (ratio of pollutant concentration/initial pollutant concentration, $C/C_0$, in function of the time, $t$). The non-catalytic run was also performed, as well as the individual methods in the absence of catalyst, single ozonation and photolysis as control experiments.

All tested catalysts performed better than the non-catalytic run. The incorporation of Ag and Cu in FeO particles increased the catalytic activity, while the introduction of Co slightly decreased the performance. Although the introduction of Ag in FeO particles reduced the BET surface area,
this sample had the highest OMA removal rate, suggesting that the addition of Ag leads to an increase in activity. Sampaio et al. [27] also observed increased efficiency in phenol degradation in the presence of ZnO loaded with Ag. The authors suggested that there is an optimal amount of Ag to generate an adequate quantity of holes and electrons, and an increase in the Ag load may lead to a surplus charge separation, which is not efficiently contributing to the reaction.

2.3. OMA Removal by Carbon Coated MNP by Using 750 °C CVD

FeO, CuFeO and CoFeO particles were coated with carbon by CVD at 750 °C and tested in the removal of OMA by PCO. The conversions of OMA in the presence of several MNP observed up to 120 min of reaction are shown in Figure 4.
All MNP coated with carbon by CVD at 750 °C showed better performance than the corresponding uncoated MNP. This result suggests that the carbon phase plays a vital role during PCO, increasing the catalytic activity. However, there are no significant differences among the samples prepared by CVD at 750 °C (Figure 4). The introduction of Co or Cu in FeO particles followed by a CVD treatment at this temperature did not improve the OMA removal rate. The slight increase verified in the C/C₀ value at 60 min during the PCO with C@CuFeO_CVD750 is within the experimental error (<±2%). As observed in the TEM micrographs, MNP were encapsulated by carbon after the CVD treatment, suggesting that the carbon phase is mainly responsible for the improvement in activity. This result is in line with the fact that the presence of the carbon phase reduces the electron/hole recombination due to the formation of solid–solid interfaces that facilitate charge transfer and spatial separation, and improves interfacial defect sites that act as “hot spots” [28]. It is expected that the carbon phase, due to its electric conductivity, acts as photosensitizer to promote electric charge transfer, since it can enhance electron diffusion and reduce electron/hole recombination, and consequently the catalytic activity is improved.

2.4. OMA Removal by Carbon Coated MNP by Using 850 °C CVD

FeO, CoFeO and CuFeO coated with carbon by CVD at a higher temperature, 850 °C, were tested in the same degradation of OMA by PCO (Figure 5a). Because the catalysts are more active, the running time of the experiments was cut down to only 60 min, half of the time of the runs in the presence of the 750 °C CVD coated materials. The increase of the CVD temperature produced a positive effect on the catalytic performance during OMA removal. All MNP coated at 850 °C achieved complete OMA removal after 60 min of reaction. In general terms, the result correlates with the amount of deposited carbon to attain a specific coverage of the MNP. The limit value should lie around the 67% obtained for the Cu modified catalysts. Therefore, besides a thermal effect, the coating requires a certain amount of carbon to become more efficient. Temperatures above 850 °C were outside our experimental range, but there is no significant expected increase in carbon mass production above these temperatures, judging from experience in growing carbon nanotubes by CVD [29].

Taking advantage of the pronounced photoactivity of the Ti-modified materials, we used the TiFeO particles coated with carbon by CVD at 850 °C to test the efficiency of two different preparation methods of the bimetallic photocatalysts. In the first method, TiFeO particles were prepared by co-precipitation, as in the case of CuFeO and CoFeO, while in the second method, the particles were prepared by impregnation. The performances of these photocatalysts were compared to that of pure TiO₂ (synthesised by the sol-gel procedure according to [30]), and commercial TiO₂ (P25) (Figure 5b).

Independently of the preparation method, the prepared MNP containing Ti coated with carbon had a better efficiency than TiO₂ synthesised by the sol-gel procedure and more unsatisfactory performance than P25. The photocatalyst prepared by the second method revealed a slightly higher OMA removal rate than the one obtained by the first method. Again, the observation correlates with a higher amount of carbon.

It is worth noting that all the modified samples underperformed sample C@FeO_CVD850, suggesting that it is not worth introducing a new metal in FeO before coating by CVD. Similarly to samples treated by CVD at 750 °C, we encapsulated MNP with carbon nanotubes and nanofibers after the CVD process at 850 °C, suggesting that the carbon phase is mainly responsible for the efficiency rather than MNP composition.
2.5. Testing the Removal Efficiency under Different Conditions

To better understand the processes evolving during OMA removal by PCO, additional experiments in the presence of the best catalyst, C@FeO_CVD850, were carried out. PCO resulting from the combination of two AOPs (ozonation and photocatalysis), potentiating the occurrence of synergistic effects. Thus, we compared the resulting levels of OMA removal in adsorption, catalytic ozonation and photocatalysis experiments performed under the same experimental conditions (Figure 6).

Adsorption on C@FeO_CVD850 was negligible. C@FeO_CVD850 was not a suitable catalyst for ozonation, removing only 10% of OMA after 60 min of reaction. The low catalytic activity verified during ozonation can be related to the small surface area of the C@FeO_CVD850 sample. On the other hand, the tested catalyst was photoactive, achieving a pollutant degradation of approximately 70% after 60 min of reaction. The verified catalytic activity probably resulted from the available electrons on the catalyst surface caused by the presence of metal oxide. However, the verified efficiency during PCO is higher than the sum of the performances obtained during photocatalysis and catalytic ozonation, suggesting the presence of a synergy when O$_3$, light and C@FeO_CVD850 were acting simultaneously. The high catalytic activity verified with the best sample resulted mainly due to the presence of the carbon phase. However, the presence of a metal oxide on the catalyst surface slightly contributed to
the removal achieved by PCO. A more significant number of radicals is expected to generate when O$_3$, UV radiation and an appropriate catalyst are together, accounting for the high activity observed [30,31].

![Figure 6. OMA removal by adsorption (Ads), catalytic ozonation, photocatalysis and PCO in the presence of C@FeO$_x$CVD850.](image)

The reutilisation of C@FeO$_x$CVD850 was carried out to study the eventual deactivation during photocatalytic ozonation. For these experiments, a new solution was admitted to the reactor at the beginning of every reaction cycle (Figure 7).

![Figure 7. Runs of photocatalytic ozonation in the presence of C@FeO$_x$CVD850.](image)

Although there is a systematic decrease in the conversion of OMA after 60 min of reaction with C@FeO$_x$CVD850, the photocatalyst remained active even after three cycles. A 7% loss in performance was observed from the first use to the third cycle of experiments (respectively 100%, 97% and 93% conversion measured in the consecutive runs). Since adsorption of OMA was demonstrated to be negligible, this is probably due to overoxidation of the surface by the accumulation of reactive oxygen species that will hinder the semiconductive optical properties of the material as well the active sites for ozone adsorption.
2.6. Removal of Other Pollutants by PCO

To assess the efficiency of PCO in the presence of C@FeO_CVD850 for the degradation of more complex compounds, we selected three representatives of different classes of pollutants namely: C.I. Reactive Blue 5 (DYE) as model of a textile effluent, aniline (ANL) as an example of an industrial pollutant and metolachlor (MTLC) as an emergent compound provided from the most widely used class of herbicides. Since direct ozonation is efficient to degrade compounds containing either an activated aromatic ring or double bonds, O₃ can remove these pollutants, but it presents limitations to achieve high mineralisation degrees [32,33]. The conversion of the selected contaminants over 30 min of PCO in the presence of C@FeO_CVD850 is represented in Figure 8a–c. As expected, the presence of O₃ was enough to remove the selected parent pollutants in a short reaction time. In the case of the DYE removal, the three processes had similar efficiencies. However, for ANL and MTLC, PCO was revealed to be more effective than single ozonation.

![Figure 8](image)

**Figure 8.** Evolution of dimensionless concentration of C.I. Reactive Blue 5 (DYE) (a), aniline (ANL) (b) and metolachlor (MTLC) (c) over 30 min, and the respective total organic carbon (TOC) removal after 180 min of reaction (d) by single ozonation and photocatalytic ozonation in the presence of C@FeO_CVD850 and P25.

We compared the degree of mineralisation measured in terms of total organic carbon (TOC) removal after 180 min for three standard processes: single ozonation, PCO in the presence of P25, and PCO in the presence of C@FeO_CVD850 (Figure 8d). In terms of mineralization level, the combination of O₃ with radiation and a catalyst was necessary to improve the organic matter removal. The prepared MNP coated with carbon by CVD at 850 °C showed a TOC removal between 78% and 88% after 180 min of reaction, suggesting a high rate of degradation and conversion into CO₂ and H₂O.

The photocatalyst C@FeO_CVD850 showed no lesser performance than the commercial benchmark P25 (TiO₂) in the PCO but had the additional advantage of possessing magnetic properties to facilitate separation from the aqueous solution.
3. Materials and Methods

3.1. Catalyst Preparation and Characterisation

The co-precipitation method was used to prepare FeO, CoFeO and CuFeO. Further details about FeO and CoFeO preparation can be found elsewhere [13]. For the synthesis of CuFeO, the method followed the CoFeO procedure, but replaced the cobalt precursor with Cu(NO$_3$)$_2$·3H$_2$O.

AgFeO was prepared by incipient wetness by dropping AgNO$_3$ into the FeO support. The silver content was 5% wt. After that, the sample was dried at 100 °C for 24 h and then thermal treated under nitrogen flow at 200 °C for 2 h.

As Ti-based materials are highly active for PCO, two FeTiO samples were prepared. Sample FeTiO$_m$1 was obtained as CoFeO and CuFeO samples using Ti[OCH(CH$_3$)$_2$]$_4$ as a Ti precursor instead of Co and Cu precursors. Sample FeTiO$_m$2 was synthesised by dispersing FeO in alcohol for 1 h under ultrasonication [34], followed by the addition of a mixture containing ammonia (55%) and deionised water (45%), and ultrasonication for 1 h. The resulting particles were added into the alcohol solution of Ti[OCH(CH$_3$)$_2$]$_4$, and the mixture was stirred for 30 min. After that, 0.4 mL HNO$_3$ was added and the mixture was vigorously stirred for 4 h and then ultrasonicated for 1 h. The solid was obtained by magnetic separation and thermal treated under nitrogen flow at 450 °C for 1 h.

After the synthesis, the obtained MNP were coated with carbon by CVD using the approach reported elsewhere [13]. Briefly, the MNP were thermal treated under nitrogen flow up to 400 °C and then the reduction step was carried out in a hydrogen atmosphere for 2 h. After that, the temperature was increased up to 750 °C for sample C@MNP$_{CVD750}$, or 850 °C for sample C@MNP$_{CVD850}$ (where MNP can be FeO, CoFeO, CuFeO or TiFeO) to coat the magnetic nanoparticles with carbon using ethane as a carbon precursor.

The samples were characterised by different techniques. The BET surface areas of the prepared samples were calculated from N$_2$ equilibrium adsorption/desorption isotherms, determined to be −196 °C with a Quantachrome Instruments NOVA 4200e apparatus. TG analysis was carried out to determine the relative amount of metals in the samples, and for that purpose, an STA 409 PC/4/H Luxx Netzsch thermal analyser was used. TEM micrographs were obtained using an LEO 906E microscope operating with an accelerating voltage of 120 kV. The phase purity of the samples was inferred by XRD analyses, over a range of 2θ = 20°–80° with a Philips X’Pert MPD diffractometer (Cu-Ka = 0.15406 nm). The Rietveld refinement was used to evaluate the results.

3.2. Photocatalytic Ozonation Reactions

Experiments of PCO were carried out in a glass immersion photochemical reactor loaded with 0.5 g L$^{-1}$ of catalyst concentration, as described elsewhere [30]. The reactions were performed with the following initial concentrations: C$_0$, OMA = 89.05 mg L$^{-1}$, C$_0$, ANL = 93.13 mg L$^{-1}$, C$_0$, MTLC = 283.80 g L$^{-1}$ and C$_0$, DYE = 100 mg L$^{-1}$. The gas was bubbled into the reactor at a constant flow rate (150 cm$^3$ min$^{-1}$) and inlet O$_3$ concentration (60 g m$^{-3}$). O$_3$ was produced from pure O$_2$ in a BMT 802X ozone generator. The concentration of O$_3$ in the gas phase was monitored with a BMT 964 O$_3$ analyser. Due to the magnetic behaviour of the prepared samples, the catalysts were easily recovered from the solution through the application of a magnetic field after each reaction.

The performance of the different catalysts during OMA removal by PCO was evaluated in terms of pollutant concentration as determined by high performance liquid chromatography (HPLC) analysis with an Hitachi Elite Lachrom system equipped with an ultraviolet detector. The stationary phase was an Altech AO-100 column working at room temperature under isocratic elution with H$_2$SO$_4$ (5 mM) at a flow rate of 0.5 cm$^3$ min$^{-1}$. The injection volume was 15 µL, and the detector
wavelength was 200 nm [30]. The concentration of DYE was determined by a PG Instruments T60 UV-Vis spectrophotometer at the maximum absorption wavelength (630 nm). ANL and MTLC concentrations were determined using an HPLC Hitachi Elite Lachrom system equipped with a diode array detector (DAD). For ANL concentration, the stationary phase was a Lichrocart Purospher Star column working at room temperature under isocratic elution with 40% water and 60% methanol at a flow rate of 1 mL min$^{-1}$, an injection volume of 40 µL and the wavelength used was 200 nm. In the case of MTLC, the separation of the pollutant was attained by using the same column as used for ANL but with an isocratic mobile phase containing 60% acetonitrile and 40% water.

In the case of DYE, ANL and MTLC, the catalytic activity was also evaluated in terms of mineralization degree by the determination of TOC removal by a Shimadzu TOC-L total organic carbon analyser coupled with an ASI-L autosampler using the non-purgeable organic carbon (NPOC) method.

4. Conclusions

The use of magnetic nanoparticles (MNP) of FeO and their Ag and Cu bimetallic derivatives was successfully demonstrated for the photocatalytic ozonation (PCO) of oxamic acid (OMA), a model compound, for the first time. MNP also presented high catalytic activity during degradation of other representative pollutants.

The CVD coating procedure proves to be a simple and accessible technique to efficiently carbon-coat FeO MNP, as well as their bimetallic derivatives. This procedure allowed us to take advantage of the catalytic properties of the carbon materials, in addition to the efficient recovery attained due to their magnetic character.

The increase in performance associated with the temperature of CVD demonstrated the importance of the carbon coating in the photocatalytic process. Notably, it showed that more critical than the magnetic core was the quality (amount) of the carbon coating. The best results correlate with the increasing carbon content of the surface associated with higher CVD temperatures.

The modification of the FeO core with other metals did not represent an advantage for the carbon-coated MNP. The pristine C@FeO_CVD850 displayed an obvious synergy in PCO owing to the thermal and coating effects. C@FeO_CVD850 was quickly removed from the media and successfully applied in consecutive runs, presenting a rapid recycling operation mode due to its magnetic character. The successive PCO experimental runs with OMA showed that the C@FeO_CVD850 photocatalyst is very stable, remaining highly active after three initial cyclic tests.

The PCO of other pollutants (model compound of a textile effluent, an industrial pollutant and an emergent contaminant) revealed that the synergic effect evidenced by C@FeO_CVD850 enhanced the organic matter removal of the aqueous solutions compared to single ozonation, with almost complete mineralization being achieved.

Compared to the photocatalytic performance of commercial P25 (TiO2), no significant differences were observed, suggesting that C@FeO_CVD850 emerged as a remarkable alternative to remove a wide range of pollutants by PCO, due to its additional capacity of being efficiently recovered from the solution (by means of its magnetic properties), which is very appealing in terms of practical applications. Therefore, this work successfully answered to the constant challenge of developing a catalyst with similar performance to P25.

In conclusion, C@FeO_CVD850 emerges as a promising catalyst in the PCO process of an extensive class of pollutants with the advantage of being easily recovered from the media.

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