Photocatalytic activity of electric-arc furnace flue dusts

Lorena Alcaraz a, Ana Urbíeta b, María Eugenia Rabanal c, Paloma Fernández b, Félix A. López a,∗

a Centro Nacional de Investigaciones Metalúrgicas (CENIM-CSIC). Avda. Gregorio del Amo 8. 28040 Madrid, Spain
b Universidad Complutense de Madrid (UCM). Dpto. de Física de Materiales. Facultad de Ciencias Físicas. Ciudad Universitaria s/n 28040 Madrid, Spain
c Universidad Carlos III de Madrid & IAAB, Dpto. de Ciencia e Ingeniería de Materiales e Ingeniería Química, Avda. de la Universidad 30, 28911-Leganés, Madrid, Spain

A B S T R A C T

Two electric-arc furnace flue dusts, a waste generated during the steel production process, were characterized and their photocatalytic activity was assessed. Chemical composition by X-ray fluorescence (XRF) analysis identified that both dusts were principally formed by iron, zinc and chromium oxides. Structural characterization carried out by X-ray diffraction patterns (XRD), and micro-Raman measurements demonstrated that ZnFe₂O₄ (zinc ferrite), FeCr₂O₄ (chromite) and ZnO (zincite) are present in both waste dusts as majority phases. Scanning electron microscopy (SEM) images showed that both dusts are formed by nanoparticles with a globular and octahedral morphology characteristic of the type of flue dusts formation and the obtained phases. Cathodoluminescence (CL) spectra show the characteristics bands of spinel structure ([ZnFe₂O₄] and Fe³⁺ emission. X-ray photoelectron spectroscopy (XPS) measurements indicate that Fe ions could be present in 2+ and 3+ oxidation state in the spinel structure, while zinc and chromium ions are in 2+ and 3+, respectively. In addition, the photocatalytic experiments demonstrated that the analyzed samples could be useful as photocatalyzed showing a degradation percentage above 75 %.

© 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Electric-arc steelmaking flue dusts are a type of solid waste that is produced in the purification of gases given off in furnaces used in steelmaking from smelting scrap metal [1,2]. The EC legislation classifies electric arc furnace dusts (EAFD) a hazardous waste. The EAFD is composed of different components being the principal solid iron oxides as well as zinc. Iron is found as magnetite (Fe₃O₄) and in franklinite (ZnFe₂O₄), and zinc is forming zincite (ZnO) and franklinite [3]. Due to the significant amount generated (2–14 kg of dusts per ton of steel; 3.7 million tonnes of EAFD per year) [2], is required different steel recycling alternatives are required [4]. There are different options for treating the obtained EAFD as waste among them (a) the return to the steel production process [5–7], (b) disposal in industrial waste landfills [8] and/or (c) the recycling/incorporation into other processes/products [2,9].
latter is increasingly attracting the interest of the scientific community. Therefore, the possibility of reusing the compounds of which the EAFD is formed for other processes is a way forward.

ZnO has been used as a photocatalytic material due to its high activity as well as chemical stability [10]. However, it has a wide band gap of 3.2 eV, which is unfavorable for absorption and utilization of visible light. Different investigations have been carried out using materials with lower Egap proving the effectiveness for the degradation of organic contaminants in water under solar irradiation [11–13]. In this sense, some spinel materials with narrow band gap such as ZnFe$_2$O$_4$ (about 1.9 eV) exhibit good visible light response and photochemical stability as well as favorable magnetism [14,15]. The narrow band gap enables it to absorb sunlight up to 653 nm or even larger [16]. However, this material is seldom used as photocatalysts as a single phase due to the lower valence band potential and its poor property in photoelectric conversion yield. For these reasons, the scientific community has been paid more attention to the enhanced photocatalytic activity of ZnFe$_2$O$_4$/ZnO composite [17,18]. In addition, because of the magnetic behaviour of the ZnFe$_2$O$_4$ phase, it is possible to easily recover the solid photocatalyst after the photocatalytic process [17].

In this sense, advance oxidation processes (AOP’s) have been useful as a novel and variety of green process for different pollutants present in wastewater [19–21]. In general, AOP’s are able to generate hydroxyl radicals (OH) in oxidation processes and degrade aqueous contaminants into innocuous products [20]. In this sense, organic synthetic dyes are commonly utilizing by textile industries. Due to its high stability, the exposure to these contaminants leads to harmful effect on humans and animals. In fact, methylene blue (MB) is a basic cationic dye commonly used for dying wool, cotton, silk, etc, which can cause serious diseases like hard breathing, vomiting, and mental disorders [21].

So, the use of the electric-arc furnace flue dust, a commonly generated waste, as photocatalytic material is a promising alternative to re-use and re-cycling this type of the solid wastes. In the present work, the structural and morphological characterization of two different electric-arc furnace flue dusts, an EAFD from common steel manufacturing (named as C-EAFD) and an EAFD from the manufacturing of special steel (named as S-EAFD) were carried out. In addition, the photocatalytic activity of both samples was also investigated.

2. Materials and methods

In order to investigate the physico-chemical properties of EAFD, two samples were taken at the outlet of the suppression system from Siderurgia Sevillana (Alcalá de Guadaira, Sevilla, Spain) and Fundiciones de Aceros Especiales (Santander, Spain).

The samples were homogenized, and successive quartering provided 1000 g of each sample.

The chemical composition of the samples was determined by X-ray fluorescence (XRF) using the above-mentioned analytical Axios wavelength dispersive spectrometer.

The structural characterization was carried out through X-ray diffraction (XRD) using a Siemens D5000 diffractometer equipped with a Cu anode (Cu Kα radiation) and a LiF monochromator. Rietveld method was applied for the calculation of structural parameters from XRD patterns. We have used the version 4.2 of the Rietveld analysis program TOPAS (Bruker ASX) and crystallographic information of the different phases obtained from Pearson’s crystal structure database for inorganic compounds release.

The morphological characterization was performed by scanning electron microscopy (SEM) using a JEOL-6400 electron microscope operating at 20 kV.

Micro-Raman measurements were carried out at room temperature (RT) in a Horiba Jovin-Yvon LabRAM HR800 system. The samples were excited by a 632.8 nm He-Ne laser on an Olympus BX 41 confocal microscope with a 40x objective. A charge coupled device detector was used to collect the scattered light dispersed by a 1200 lines mm$^{-1}$ grating.

The surface of both EAFD samples was analyzed by X-ray photoelectron spectroscopy (XPS). Spectra were recorded using a Fisons MTS00 spectrometer equipped with a hemispherical electron analyzer (CLAM2) and a non-monochromatic Mg Kα. X-ray source operated at 300 W. Spectra were collected at a pass energy of 20 eV (typical for high-resolution conditions). The area under each peak was calculated after subtraction of the S-shaped background and fitting the experimental curve to a combination of Lorentzian and Gaussian lines of variable proportions. Binding energies were calibrated to the C 1s peak at 285.0 eV. The atomic ratios were computed from the peak intensity ratios and reported atomic sensitivity factors.

The temperature dependence of the magnetic susceptibility was measured in the 2–300 K range in a magnetic field of 1000 Oe using a Quantum Design XL-SQUID magnetometer. Hysteresis measurements were taken at 298 K with a maximum field of 5T.

Cathodoluminescence investigations have been performed at room temperature in a HITACHI S2500 SEM operated at 15 kV. Spectra have been recorded with a CCD camera HAMA-MATSU PMA-11.

The samples were characterized by UV-visible diffuse reflectance spectra (DRS) measured in the range of 350–500 nm at RT using a UV-visible Spectrophotometer (Varian Cary 100 with DRA-CA-30I Diffuse Reflectance Accessory).

The photocatalysis experiments were carried out in a Pyrex glass reactor at RT. 5 mg of solid catalyst was dispersed in 600 mL of a solution of methylene blue (MB) of concentration 2.5 mg/L. The photocatalytic degradation was carried out for 120 min, in continuous stirring under UV-light irradiation (365 nm), in a dark room with 125 W high-pressure mercury vapor lamp (jinfie Company, Shanghai). Aliquots (3 mL) of the solution are extracted every 10 min (every 15 min for times larger than 75 min) are measured by UV-Vis absorption in a Lambda 14 P UV-visible Spectrophotometer to monitor the degradation of methylene blue (MB) solution.
Table 1 – Elemental composition (wt %) for both samples obtained.

<table>
<thead>
<tr>
<th>Compound</th>
<th>C-EAFD</th>
<th>S-EAFD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>37.68</td>
<td>38.02</td>
</tr>
<tr>
<td>ZnO</td>
<td>30.35</td>
<td>20.14</td>
</tr>
<tr>
<td>CaO</td>
<td>8.42</td>
<td>4.44</td>
</tr>
<tr>
<td>PbO</td>
<td>5.66</td>
<td>0.67</td>
</tr>
<tr>
<td>CdO</td>
<td>3.82</td>
<td>2.80</td>
</tr>
<tr>
<td>Cl</td>
<td>3.10</td>
<td>0.93</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2.30</td>
<td>7.13</td>
</tr>
<tr>
<td>MnO</td>
<td>1.92</td>
<td>2.87</td>
</tr>
<tr>
<td>SO₂</td>
<td>1.85</td>
<td>0.48</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.81</td>
<td>0.66</td>
</tr>
<tr>
<td>MgO</td>
<td>0.97</td>
<td>2.36</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.58</td>
<td>16.97</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.57</td>
<td>0.50</td>
</tr>
<tr>
<td>CuO</td>
<td>0.45</td>
<td>0.18</td>
</tr>
<tr>
<td>SnO₂</td>
<td>0.10</td>
<td>—</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.08</td>
<td>0.19</td>
</tr>
<tr>
<td>Br</td>
<td>0.08</td>
<td>0.01</td>
</tr>
<tr>
<td>NiO</td>
<td>0.06</td>
<td>1.30</td>
</tr>
<tr>
<td>Co₃O₄</td>
<td>0.06</td>
<td>0.08</td>
</tr>
<tr>
<td>BaO</td>
<td>0.05</td>
<td>—</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>0.03</td>
<td>0.09</td>
</tr>
<tr>
<td>Ta₂O₅</td>
<td>—</td>
<td>0.04</td>
</tr>
<tr>
<td>Bi₂O₅</td>
<td>—</td>
<td>0.03</td>
</tr>
<tr>
<td>Ga₂O₃</td>
<td>—</td>
<td>0.02</td>
</tr>
<tr>
<td>MoO₃</td>
<td>0.01</td>
<td>0.11</td>
</tr>
<tr>
<td>SrO</td>
<td>0.01</td>
<td>—</td>
</tr>
<tr>
<td>Nb₂O₅</td>
<td>—</td>
<td>0.01</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>—</td>
<td>0.01</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Physico-chemical characterization of EAFD flue dusts

Table 1 shows the elemental composition of the EAFD samples determined by XRF. Although the composition of EAFD can significantly vary depending on the furnace operating conditions and the scrap quality [4,22,23], the elements that are usually present mostly are Fe, Zn, Pb, Cd, and Cl. Chloride content is due to the impurities of the scrap (paints, rubbers and other by-products that are existing in packaging). A part of these impurities is transferred to the EAFD forming alkali metal chlorides (volatile organic compounds, VOCs) [24]. In most cases, the zinc content is present around 4–35 wt %, while iron varies from 25 to 50 wt % [25]. In the present case, the elemental analyses show that the compositions of both samples are very similar being Fe and Zn the more significant elements. However, even though Fe and Zn are mostly present in the sample’s composition, in the case of the S-EAFD sample around 17 wt % of Cr was found, as expected according to the dust source.

XRD patterns of C-EAFD and S-EAFD dusts are shown in Fig. 1. In both samples, the majority of the diffraction maxima, marked in Fig. 1 with an asterisk, can be attributed to ZnFe₂O₄ with the cubic spinel structure (with space group Fd-3m). Moreover, the peaks marked with a triangle can be indexed to ZnO with the hexagonal wurtzite structure (space group P63/mc). Low-intensity diffraction maxima were also detected.

In order to carry out a better structural characterization, Rietveld refinements of both samples were performed. Quantitative analyses are also shown in Table 2.

As can be seen, the obtained results show that the ZnFe₂O₄ and ZnO are present in both cases as majority phases. In the case of C-EAFD sample, the corresponding analysis exhibits approximately 5 % impurities as chlorides in different forms (KCl (sylvite) and PbCl(OH) (laurionite)). The result is in good agreement with the obtained from XRF analyses where the amount of Cl is higher in the C-EAFD sample. On the other hand, for the S-EAFD sample around 27 % of chromite was found. This result agrees again with the one obtained from XRF, where an amount of chromium was found in the corresponding analysis.

The intensity of the diffraction maxima is higher in the C-EAFD sample as compared with the S-EAFD sample showing a higher crystallinity. In addition, the average crystallite size

Table 2 – Quantitative analyses from Rietveld analyses.

<table>
<thead>
<tr>
<th>Crystalite phases (%)</th>
<th>C-EAFD</th>
<th>S-EAFD</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnFe₂O₄ (zinc ferrite)</td>
<td>75</td>
<td>66</td>
</tr>
<tr>
<td>ZnO (zincite)</td>
<td>20</td>
<td>7</td>
</tr>
<tr>
<td>Others impurities (KCl; PbCl(OH))</td>
<td>5</td>
<td>----</td>
</tr>
<tr>
<td>FeCr₂O₄ (chromite)</td>
<td>----</td>
<td>27</td>
</tr>
</tbody>
</table>
Table 3 – Raman bands positions observed and proposed assignments.

<table>
<thead>
<tr>
<th>Peak position (cm⁻¹) [24,25]</th>
<th>C-EAFD</th>
<th>S-EAFD</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>160</td>
<td>—</td>
<td>—</td>
<td>F₂g(1)</td>
</tr>
<tr>
<td>250</td>
<td>—</td>
<td>—</td>
<td>E₈</td>
</tr>
<tr>
<td>355</td>
<td>323</td>
<td>332</td>
<td>T₂g(2)</td>
</tr>
<tr>
<td>450</td>
<td>489</td>
<td>490</td>
<td>T₂g(3)</td>
</tr>
<tr>
<td>650</td>
<td>635</td>
<td>640</td>
<td>A₁g</td>
</tr>
</tbody>
</table>

(D_{hkl}) of both specks of dusts was calculated from Scherrer [26] equation (Eq. 1) using the most intense reflections observed in the XRD patterns:

\[
D_{hkl} = \frac{0.89 \cdot \lambda}{\beta \cdot \cos \theta}
\]

where 0.89 is the shape factor (assuming spherical particles), \( \lambda \) is the X-ray wavelength, \( \beta \) is the full-width at half-maximum (FWHM) of the experimental peaks, \( \theta \) is the Bragg angle.

The average crystallite sizes of both samples are within a range from 70 nm (C-EAFD) to 50 nm (S-EAFD). Larger crystallite size is found in C-EAFD sample, which confirms the observed trend of larger particle size in the sample with a higher degree of crystallinity.

Fig. 2 shows scanning electron microscopy micrographs for C-EAFD and S-EAFD samples obtained. In both samples, the particle shape is very similar. Two different particle morphologies can be appreciated. Mainly, agglomerates of globular morphology particles can be observed. As previously reported [4,27], the observed morphology is characteristic of the electric arc furnace flue dusts. This shape suggested that the mechanism of particle formation could be the ejection from the liquid metal and slag [27]. Also, octahedral crystals, typical of spinel structure phases [28,29] were also found in both samples due to the presence of ZnFe₂O₄ phases [30]. Finally, regarding the size of the constituent particles, and despite the fact that the particle size distribution is larger, particles were observed in the C-EAFD sample images compared with the other dusts. This result is in agreement with the XRD results where the C-EAFD sample exhibit higher diffraction maxima, i.e., greater crystallinity and particle size.

Fig. 3 shows the normalized Raman spectra of C-EAFD and S-EAFD samples. Table 3 summarized the observed Raman bands. Their corresponding assignments are also shown.

![Raman spectra](image)

Fig. 3 – Normalized Raman spectra of the C-EAFD and S-EAFD samples.

In bulk, ZnFe₂O₄ is a normal spinel structure with cubic symmetry and Fd3m (O’h₃) space group. Zn²⁺ divalent ions preferentially occupy the tetrahedral (A) sites, whereas, all the Fe³⁺ ions occupy octahedral (B) sites. Group theory predict five Raman-active modes (A₁g + E₈ + 3T₂g) at RT [30,31]. These Raman-active modes are related to the motion of oxygen ions and both the A-site and B-site ions in the spinel structure.

High-frequency modes appear peaked at 650 cm⁻¹, 450 cm⁻¹ and 355 cm⁻¹ and can be attributed to A₁g, T₂g(3) and T₂g(2) modes, respectively [30,31]. Raman bands in the low energy region are due to the E₈ mode at about 250 cm⁻¹ and to the F₂g(1) translational movement of the whole tetrahedron at 160 cm⁻¹. The A₁g mode represents the symmetric stretch of oxygen atoms along Fe-O tetrahedral bonds, whereas the E₈ and T₂g(3) modes are due to symmetric and asymmetric bending of oxygen with respect to Fe, respectively. The T₂g(2) represents the asymmetric stretch of Fe-O bond and T₂g(1) represents the translational movement of the tetrahedron (Fe₂O₄) [30,31]. However as observed in the spectra from Fig. 3 and in the data presented in Table 3, the position of the Raman peaks is shifted with respect to those observed in bulk material. ZnFe₂O₄ spinel ferrite with a nanoparticle size, the distribution of Zn²⁺ ions and Fe³⁺

![SEM images](image)

Fig. 2 – SEM images of the (a) C-EAFD and (b) S-EAFD investigated dust samples.
Fig. 4 – XPS spectra of Zn 2p, Fe 2p, O 1s and Cr 2p for (a) C-EAFD and (b) S-EAFD samples.
Deconvoluted in three component (at 709.6 eV, 711.0 eV, and 712.8 eV), and can be attributed to FeO or divalent Fe, Fe₂O₃ or trivalent Fe and a FeOOH, respectively [33]. In the case of XPS analysis of Zn 2p, two prominent peaks at 1021.5 eV and 1045.0 eV were also observed which corresponds to 2p⁴/² and 2p¹/² [34]. XPS analyses of the Fe and Zn show that the peak of 2p¹/² is more intense than that of 2p⁴/². This behavior is due to that the transitional metallic elements, the 2p¹/² state has four degeneracy states, while 2p⁴/² state only has two [32]. In addition, for the S-EAFD sample, the 2p Cr XPS spectrum reveals only chromium in the 3+ oxidation state [35]. Finally, the O 1s spectrum exhibits two components at around 532 eV and 530 eV. The major peak (centered at 532 eV) was assigned to absorbed water molecules (O—H) [36], while the peak at 530 eV was in good agreement with the oxygen bonded to metal ion in ZnFe₂O₄ [34, 37].

Magnetic susceptibility (χ) as a function of temperature (T) for both, C-EAFD and S-EAFD investigated samples, is shown in Fig. 5. A maximum centered on 25 K and 50 K for C-EAFD and S-EAFD, respectively, can be appreciated. This maximum temperature can be identified as the blocking temperature (Tₘ), and it is characteristic for either superparamagnetic (SP) or spin glass (SG) states [38, 39]. Ferrimagnetic behavior below a Tₘ was observed.

Magnetic field dependence of magnetization (M vs. H) at RT for both samples is displayed in Fig. 6. As can be appreciated (Fig. 6 inset), the samples exhibit practically no hysteresis at 300 K, with a coercive field of 45 Oe.

3.2. Cathodoluminescence (CL)

In ZnFe₂O₄ phases, iron ions are usually incorporated into the ZnO matrix as Fe²⁺ and Fe³⁺. Fe²⁺ ion has d⁶ electronic configuration with the free ion ground state ⁵D. In the case of the Fe³⁺, the free ion has d⁵ electronic configuration [40]. The ground state is ⁴S, and the first excited state is ⁴G. Into the ZnO matrix, the levels associated to Fe²⁺ and Fe³⁺ free ions could
be degenerated by crystal field perturbation, spin-orbit interaction and Jahn-Teller effect into the $^5\text{E}$ ground state term and the $^5\text{T}_2$ excited state term (for the Fe$^{2+}$ ions) and transforms the $^6\text{S}$ ground state into a $^6\text{A}_2$(S) state, where the first excited state is fourfold degenerated with the $^4\text{T}_1$(G) term as the lowest state (to the Fe$^{3+}$ ions) [40].

In addition, ZnO CL emission spectra are characterized by two typical features: the near-band-edge (NBE) emission at 3.25 eV, due to band-to-band transitions including bound excitons and shallow levels, and the intra-gap states related green luminescence (GL) band centered at 2.5 eV [41,42].

CL emission spectra of both samples at RT are shown in Fig. 7. A sharp band at 2.37 eV and a broad one at 1.71 eV are observed in both spectra. These bands could be related to a higher contribution of a spinel phase to luminescence emission [43] and to the phonon-assisted sideband of the intragap transition $^4\text{T}_1$(G)–$^6\text{A}_2$(S) of the Fe$^{3+}$ ion [44], respectively. In the case of the Fe$^{2+}$ emission, the transition from the ground state to the excited state term was observed in the far infrared region. Due to the fact that this region is outside of our luminescence sensitivity range, the optical properties of the Fe$^{2+}$ ion emission could not be detected [40].

3.3. Optical band gap measurements

The optical band gap has been obtained from UV-Vis absorption experiments in DRS mode. In order to obtain the energy of the band gap for each of the samples, the Kubelka-Munk and Tauc approaches were used [45,46].

The Kubelka-Munk equation (Eq. 2) is first used to obtain absorption data from the diffuse reflectance spectrum:

$$ F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} \quad (2) $$

where $R_\infty$ is the reflectance of an infinite film, and the function $F(R_\infty)$ is equivalent to the absorption coefficient, $\alpha$.

So, the optical band gap ($E_{\text{opt}}$) can be calculated by extrapolation of the linear part of the curve $(\alpha h\nu)^2$ versus $h\nu$, as shown in Fig. 8.

The calculated band gap values were 1.74 eV and 1.76 eV for C-EAFD and S-EAFD samples, respectively. As compared with the optical band gap for bulk ZnFe$_2$O$_4$ (1.9 eV) the estimated values are slightly lower and very similar to those for ZnFe$_2$O$_4$ nanoparticles ($\approx$1.77 eV) [47]. The decrease in the band gap
might be ascribed to additional sub-band-gap energy levels induced by the abundant surface and interface defects in the agglomerated nanoparticles [48]. In addition, these results could be beneficial to enhance photocatalytic activity [49].

3.4. Photocatalytic activity

The photocatalytic activity of C-EAFD and S-EAFD samples was investigated by MB degradation. When a photocatalyst absorbs light, a photocatalytic reaction takes place in several steps. The photocatalytic degradation process mechanisms are based on: i) formation of the charge carriers over the valence band (VB) and conduction band (CB) when the incident of light is at same or higher energy than the energy bandgap ($E_g$); ii) a possible recombination process of the $e^-/h^+$ pairs previously photogenerated, since these charge carriers are not stable, some of them some of them can recombine producing heat in the process; iii) capture of photogenerated charge carriers transferred to the active sites on the surface of the photocatalyst producing redox reactions which leads to the formation of some active species (e.g. $O_2^-$, $OH$) capable of initiating following redox reactions and lastly; iv) the principal photocatalytic reactions which produce the degradation of pollutants, contaminants or organic molecules, breaking them down into innocuous and simple compounds [50,51]. Normally, as previously reported by others authors [52,53], these strong radicals decompose the dye to H$_2$O, CO$_2$ and mineral acids. Fig. 9 schematically describes the described process.

Fig. 10a and Fig. 10b show comparative MB spectra without light (a) and only light irradiation without photocatalysts (b) for 0 min and 120 min of exposure time. As can be appreciated, the intensity of the MB maxima bands does not decrease, indicating that the MB degradation does not occurs without the solid photocatalyst.

Fig. 10(c,d) exhibits the degradation curves of MB for both samples under UV irradiation for 120 min. In these cases, two maxima centered at around 610 and 660 nm, characteristic of the MB absorption spectra, were registered [54]. As the UV irradiation exposure time increases, the intensity of the absorption maxima is decreased.

The kinetic of the degradation was adjusted to a pseudo-zero (Eq. 3), pseudo-first-order (Eq. 4) and pseudo-second-order (Eq. 5) [55] and the obtained results are summarized in Table 4.

\[ \text{pseudo-zero-order } \frac{[C]}{[C]_0} = 1 - k_{\text{obs},0} \cdot t \quad (3) \]

\[ \text{pseudo-first-order } \ln \frac{[C]}{[C]_0} = k_{\text{obs},1} \cdot t \quad (4) \]

\[ \text{pseudo-second-order } \frac{1}{[C]} = \frac{1}{[C]_0} + k_{\text{obs},2} \cdot t \quad (5) \]

where $[C]_0$ is initial MB concentration; $[C]_k$ is the MB concentration at different time t and $k_0$, $k_1$ and $k_2$ are the kinetics constants to the pseudo-zero, pseudo-first and pseudo-second-order, respectively.

The correlation coefficients $R^2$ show that reaction kinetics fit better to the pseudo-first-order model.

The degradation percentage rates are shown in Fig. 11. The maximum degradation is obtained after 120 min of UV irradiation, time that the percentage remains practically constant. Also, the maximum degradation of the obtained samples was 80 % and 75 % for C-EAFD and S-EAFD samples, respectively. It is known that ZnO is an excellent photocatalytic material [56,57]. XRD results found that C-EAFD sample exhibits a more considerable ZnO amount compared with S-EAFD sample.
Table 4 – Kinetics constants and R-factors calculated for both samples with MB solutions.

<table>
<thead>
<tr>
<th></th>
<th>Pseudo-zero order</th>
<th></th>
<th>Pseudo-first order</th>
<th></th>
<th>Pseudo-second order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_0$</td>
<td>$R^2$</td>
<td>$k_1$</td>
<td>$R^2$</td>
<td>$k_2$</td>
</tr>
<tr>
<td>C-EAFD</td>
<td>0,003</td>
<td>0,879</td>
<td>0,015</td>
<td>0,984</td>
<td>0,107</td>
</tr>
<tr>
<td>S-EAFD</td>
<td>0,019</td>
<td>0,894</td>
<td>0,011</td>
<td>0,957</td>
<td>0,080</td>
</tr>
</tbody>
</table>

So, the obtained degradation percentages agreed with these results.

Photocatalytic activity of the electric-arc furnace flue dusts have scarcely been assessed, previous investigations have been performed in order to degrade different dyes using these type of samples as photocatalyst. In this sense, Sapiña et al. [58] have been evaluated the potential of EAFD as photocatalytic material in the degradation of rhodamine B (RhB) in the aqueous solution under UV/visible light irradiation. Similarly, the use of activated electric arc furnace slag for the photodegradation of methylene blue (MB) and acid blue 29 (AB29) was studied by Nasuha et al. [59]. These results previously reported exhibit that these type of the materials from steel production wastes could successfully be used as photocatalyst.

4. Conclusions

Two different electric-arc furnace flue dusts (EAFD), one of them from common steel manufacturing and another one from the manufacturing of special steel (C-EAFD and S-EAFD, respectively) have been characterized by several techniques. XRF analysis show that Fe and Zn are in major concentration in the composition of the samples. Structural characterization by Rietveld refinements reveals that ZnFe$_2$O$_4$ and ZnO phases are present in both cases as majority phases. Particles agglomerates with a globular and octahedral shape were found in SEM micrographs, in good agreement with the origin of the samples. Raman spectra showed several bands which can be attributed to spinel structure. In addition, CL emission due to
spinel phase was also detected, as well as Fe\textsuperscript{3+} emission into ZnO structure characteristic of the ZnFe\textsubscript{2}O\textsubscript{4} stoichiometry. T\textsubscript{B} values around 25 K for C-EAFD sample and 50 K for S-EAFD sample were found in the magnetic measurements. Moreover, practically no coercive field has been detected from the hysteresis loops registered for the investigated samples. The calculated band gap values from Kubelka-Munk and Tauc's approaches were 1.74 eV and 1.76 eV for the C-EAFD and S-EAFD samples, respectively. These results are in good agreement with the corresponding to the ZnFe\textsubscript{2}O\textsubscript{4} phase. Finally, the photocatalytic activity was also assessed. A decrease of the UV-Vis absorption maximum spectra of MB was found with the irradiation time increase, which indicates that MB degradation occurs. Kinetic study reveals that the reactions were better fitted to the pseudo-second-order model. In addition, a degradation degree at around 75 % and 80 % for 120 min was found for C-EAFD and S-EAFD samples, respectively.

Conflicts of interest

The authors declare no conflicts of interest

Acknowledgment

This work has been partially supported by Spanish Ministry of Economy (MINECO) and Business and European Regional Development Fund (FEDER) (Grant ID MAT 2015-65274-R) and by the Comunidad de Madrid Program MULTIMAT CHALLENGE (Grant ID S2013/MIT-2862).

REFERENCES


Fig. 11 – Degradation percentages for both samples investigated under UV irradiation to MB solutions.


