

Efficient reduction of nitrobenzene into aniline using Fe-rich waste from electric furnace dust

Leandro Neves de Paula¹ · Luana Aparecida dos Reis Giusto¹ · José Domingos Ardisson² · Fabiano Magalhães³

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Abstract Nitroaromatic compounds are widely used in the industry. They are most often resistant to microbial degradation, mutagenic and carcinogenic. As a consequence, reduction of nitroaromatic compounds into less toxic and biodegradable products has been studied using Fe⁰. Here, we tested iron-rich waste from electric furnace dust to convert nitrobenzene into aniline. Thermal reduction of electric furnace dust under hydrogen at 500 °C gave a material with about 56 % Fe⁰ and 21 % FeO. This material allowed to decrease 86 % of nitrobenzene during the conversion of nitrobenzene into aniline. In conclusion, electric arc furnace dust can be transformed into an efficient reducing reagent.

Keywords Electric arc furnace dust · Nitrobenzene · Nitroaromatic compound · Reduction · Iron oxide · Organic contaminant

Introduction

Consumerism in the current society, tied to demographic growth, has demanded a greater commitment of industries to intensify their activities, which consequently increases

the generation of waste and environmental contamination (Gillham and O'Hannesin 1994). According to the report of the United Nations Environment Programme, the contamination of inland waters will be one of the greatest problems of the twenty-first century (UNEP 2012). A recently published review (Schwarzbauer and Dsikowitzky 2014) shows the great diversity in the chemical composition of industrial effluents, even among those generated by industries operating in the same segment. They also presented data showing that many water systems have a complex heterogeneous mixture of organic compounds of industrial origin. Organic contaminants such as polycyclic aromatic hydrocarbons, polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins, benzene, toluene, xylene, nitroaromatic compounds and dyes are persistent, bioaccumulative or toxic to aquatic organisms, and they are found in effluents of various types of industries (Schwarzbauer and Dsikowitzky 2014). Among the class of nitroaromatic compounds is nitrobenzene, which has a high resistance to microbial degradation, is toxic, carcinogenic and is used in various industries for the production of aniline, explosives, paints, plastic, pesticides and pharmaceutical products (Agrawal and Tratnyek 1996).

Reductive reactions of nitroaromatic compounds using metallic iron have been reported in the literature as a feasible alternative for the formation of less toxic and more biodegradable products (Zamora et al. 2009; Luan et al. 2012). An example is the study where (Zhang et al. 2007) the nitrobenzene is biodegraded more quickly when metallic iron or even the species Fe²⁺/Fe³⁺ are added to the biological treatment, which results in the conversion of nitrobenzene to aniline. Metallic iron may also be used in dye reduction, according to the study by Zamora and Souza (2005), where three dyes were first reduced by Fe⁰ and

✉ Fabiano Magalhães
fabianomagalhaes@dqf.ufla.br

¹ Instituto de Química, Universidade Federal de Alfenas, Alfenas, MG 37130-000, Brazil

² Laboratório de Física Aplicada, Centro de Desenvolvimento e Tecnologia Nuclear (CDTN), Belo Horizonte, MG 31270-901, Brazil

³ Departamento de Química, Universidade Federal de Lavras, Caixa Postal 3037, Lavras, MG 37200-000, Brazil

subsequently degraded by the species $\text{Fe}^{2+}/\text{Fe}^{3+}$ via Fenton reaction. The degradation of other classes of organic compounds using Fe^0 was also studied (Raja et al. 2005), such as the study by Gillham and O'Hannesin (1994), who estimated that approximately 1 kg of metallic iron is sufficient to dechlorinate about 500 m^3 of effluent contaminated with tetrachloromethane at 1 mg L^{-1} .

Steel mills fitted with electric arc furnaces produce a solid waste rich in iron, called electric arc furnace dust (Machado et al. 2006). This waste is disposed in landfills, about 70 % of the waste generated, due to the lack of alternative low-cost technologies for recycling, resulting in a high cost for the steel industry (Maslehuddin et al. 2011). In the literature, it is possible to find papers about recovery, treatment or transformation of electric arc furnace dust for applications in the production of ceramic materials (Sikalidis and Mitrakas 2006), civil construction (Maslehuddin et al. 2011), and heterogeneous Fenton reactions (Mecozzi et al. 2006). Due to the high content of iron present in this waste, around 45 % (Machado et al. 2006), it becomes an interesting material for use in reactions for the treatment of effluents contaminated with organic compounds. Therefore, in this study, the steel waste electric arc furnace dust was heat-treated at $500 \text{ }^\circ\text{C}$ in the presence of H_2 and characterized by powder X-ray diffraction and Mössbauer spectroscopy. The fresh electric arc furnace dust and the heat-treated electric arc furnace dust were used in reactions for the reduction of nitrobenzene to aniline in aqueous solution.

Experimental

The heat treatment of electric arc furnace dust was performed using approximately 2 g of sample, which was inserted in a quartz tube and heated at $500 \text{ }^\circ\text{C}$ using a tubular furnace and H_2 —White Martins 5.0 analytical, under a flow of 100 mL min^{-1} for 60 min. As a security measure, the reaction was performed in a fume hood, the flow of gas was carefully controlled and the quartz tube connections were properly sealed to prevent leaks. The product of this reaction was called EAFD500.

Chemical analysis

The chemical characterization of electric arc furnace dust was performed by atomic absorption flame, Shimadzu® AA-7000. The opening of the sample was performed according to the methodology proposed by Brehmet et al. (2002). The analytical curves used for metal determination in the samples were obtained from solutions prepared with $1 \times 10^3 \text{ mg L}^{-1}$ standards Specscol®.

Characterization

The materials were characterized by the following techniques: powder X-ray diffraction—XRD, Ultima IV Rigaku diffractometer, with $\text{CuK}\alpha = 1.54051 \text{ \AA}$ between the range (2θ) $15\text{--}80^\circ$, and the Mössbauer spectra were collected at room temperature, in the transmission geometry and electron back-scattering Mössbauer with a conventional spectrometer, operating with constant acceleration mode, using a $^{57}\text{Co/Rh}$ source. The standard is natural α -iron, for which all quoted isomer shifts are reduced to their centroid, δ -Fe.

Reduction of nitrobenzene in aqueous solution

For the study of the reduction of nitrobenzene, 3.5 mL of a $0.510 \text{ mmol L}^{-1}$ solution was used (Zamora et al. 2009), and it kept contact with 30 mg of EAFD500 for 60 min at $25 \text{ }^\circ\text{C}$ and $\text{pH} \sim 5$. The monitoring of the reduction kinetics of nitrobenzene was performed using an ultraviolet–visible spectrophotometer, Thermo Scientific-Evolution 60 Ultraviolet–Visible, through scanning. The concentrations were obtained from calibration curves constructed using the absorbance of nitrobenzene and aniline at 275 and 229 nm, respectively.

Results and discussion

Characterization

The electric arc furnace dust used in this study has a high iron content, around 21 %, which makes this waste a material with great potential to be used as a reducing agent in reactions with environmental applications. It is noteworthy that the levels (in wt%) of zinc—12, calcium—4.6, manganese—3.2, lead—3.1, nickel—0.01 and cadmium—0.03 are consistent with the values found by other authors (Machado et al. 2006).

The diffraction lines observed in Fig. 1 indicate the presence of magnetite (Fe_3O_4), which can be isomorphically substituted with different ions, forming ferrites such as $\text{Fe}_{3-x}\text{M}_x\text{O}_4$, where $\text{M} = \text{Zn}^{2+}$, Cr^{2+} , Mn^{2+} , Ni^{2+} and Ca^{2+} , as reported in the literature (Machado et al. 2006; Maslehuddin et al. 2011). Using the most intense peak and the Miller index 311, the lattice parameter, a , was calculated for the spinel phase present in electric arc furnace dust, and a value of 0.8429 nm was obtained. Comparing this value with pure magnetite, 0.8395 nm, and that replaced with other metals, such as ZnFe_2O_4 and MnFe_2O_4 , which have values equal to 0.8434 and 0.8431 nm, respectively (Köseoğlu et al. 2008; Hui Li et al. 2012), it is possible to observe that these phases are present in electric

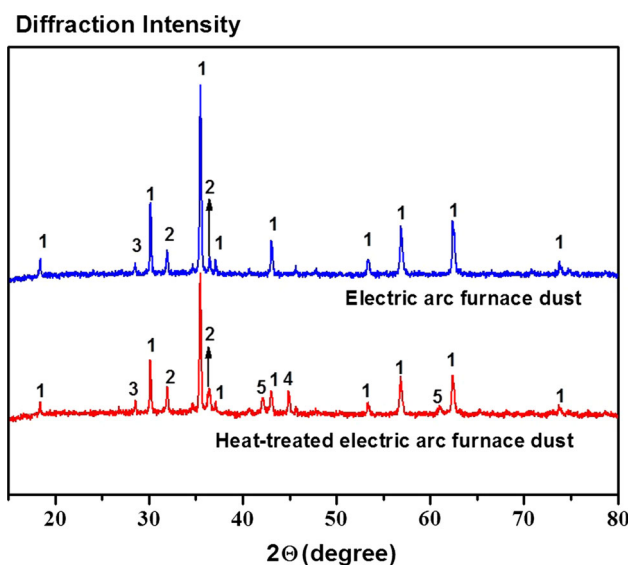
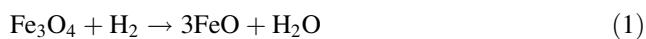


Fig. 1 X-ray diffraction (XRD) patterns obtained for electric arc furnace dust and EAFD500. The diffraction lines indicate the presence of Fe_3O_4 , $\text{Fe}_{3-x}\text{M}_x\text{O}_4$, ZnO and KCl in both samples and the phases FeO and Fe^0 in EAFD500, showing the efficiency of the heat treatment to reduce iron phases. 1 = Fe_3O_4 ; $\gamma\text{-Fe}_2\text{O}_3$; $\text{Fe}_{3-x}\text{M}_x\text{O}_4$, where $\text{M} = \text{Zn}^{2+}$, Ca^{2+} and Mn^{2+} , 2 = ZnO , 3 = KCl , 4 = Fe^0 and 5 = FeO . EAFD500 = heat-treated electric arc furnace dust

arc furnace dust. According to the chemical analysis, Ca^{2+} is also present in significant amounts in the waste. Therefore, it is likely that ferrites substituted with this ion are present in electric arc furnace dust. The diffraction lines centered at 28.4° and 31.8° confirm the presence of KCl and ZnO , respectively. In the XRD pattern for EAFD500, two other signals can be observed at 42.0° and 44.2° , confirming the formation of FeO and Fe^0 during the heat treatment, Eqs. 1 and 2.



Similar results were obtained by Mössbauer spectroscopy (Fig. 2). The hyperfine parameters obtained for the Mössbauer spectra are given in Table 1. The Mössbauer spectrum for electric arc furnace dust confirms the presence of the phases Fe_3O_4 , $\text{Fe}_{3-x}\text{M}_x\text{O}_4$, where $\text{M} = \text{Zn}^{2+}$, Ca^{2+} and Mn^{2+} , and $\alpha\text{-Fe}_2\text{O}_3$ (Adhikari et al. 2012). The hematite, $\alpha\text{-Fe}_2\text{O}_3$, identified in electric arc furnace dust by the Mössbauer spectroscopy was not observed in the powder X-ray diffraction pattern, indicating that this phase has low crystallinity. After electric arc furnace dust was reduced at 500°C , the Mössbauer spectrum showed two new signals related to the formation of FeO and Fe^0 with 21 and 56 % of relative area, respectively. These results are in agreement with those obtained by powder X-ray diffraction and confirm the reduction of oxidized iron phases. The presence of the superparamagnetic

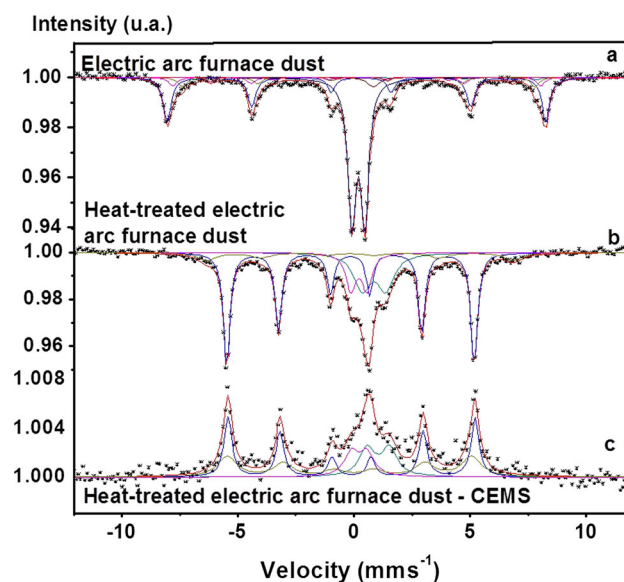


Fig. 2 Mössbauer spectra at room temperature for *a* electric arc furnace dust and *b* EAFD500. The spectra confirm that the phases $\alpha\text{-Fe}_2\text{O}_3$, Fe_3O_4 , $\text{Fe}_{3-x}\text{Ca}_x\text{O}_4$, $\text{Fe}_{3-x}\text{Zn}_x\text{O}_4$ and $\text{Fe}_{3-x}\text{Mn}_x\text{O}_4$, present in electric arc furnace dust, were reduced to FeO and Fe^0 after the heat treatment. *c* Conversion electron Mössbauer spectroscopy (CEMS) confirms the presence of 70 and 30 % Fe^0 , and reduced phases on the surface of EAFD500—heat-treated electric arc furnace dust

sextet and doublet with relative areas equal to 10 and 13 % may be related to the mixture of isomorphically substituted spinel phases, which may be dispersed in EAFD500.

The conversion electron Mössbauer spectroscopy (Fig. 2c) shows that EAFD500 has a higher content of metallic iron present in its surface than in the bulk (Table 1). This can be explained, since the reduction of electric arc furnace dust by hydrogen gas occurs from the surface to the interior of the sample. It is also possible to observe the presence of small phases of superparamagnetic Fe^{2+} at 17 and 13 % of relative area, indicating the presence of highly dispersed particles on the surface of the material.

These results show that the heat treatment of electric arc furnace dust with hydrogen at 500°C was effective, since it resulted in the reduction of the species Fe^{3+} to Fe^{2+} and Fe^0 , making it possible to obtain a material with a high content of surface metallic iron, which makes it very interesting for use in reactions in the reductive degradation of organic compounds, such as nitrobenzene.

Reduction of nitrobenzene to aniline

The reaction of nitrobenzene with EAFD500 results in its conversion into aniline, according to Eq. 3:



Table 1 Mössbauer hyperfine parameters for electric arc furnace dust and EAFD500—heat-treated electric arc furnace dust

| Sample | Phase | $\delta/\text{mm s}^{-1}$ | $\varepsilon\Delta/\text{mm s}^{-1}$ | B_{hf}/T | $AR/\%$ |
|---------------------------|--|---------------------------|--------------------------------------|--------------------------|---------|
| Electric arc furnace dust | $\alpha\text{-Fe}_2\text{O}_3$ | 0.32 | -0.13 | 51.2 | 31 |
| | Fe_3O_4 | 0.28 | -0.04 | 49.1 | 6 |
| | Fe_3O_4 | 0.66 | -0.03 | 45.7 | 2 |
| | $\text{Fe}_{3-x}\text{Ca}_x\text{O}_4$ | 0.38 | -0.05 | 47.2 | 7 |
| | $\text{Fe}_{3-x}\text{Ca}_x\text{O}_4$ | 0.48 | -0.04 | 40.1 | 3 |
| | $\text{Fe}_{3-x}\text{Zn}_x\text{O}_4$ | 0.36 | 0.50 | – | 49 |
| | $\text{Fe}_{3-x}\text{Mn}_x\text{O}_4$ | 0.98 | 0.20 | – | 2 |
| EAFD500 | Fe^0 | 0.00 | 0.00 | 33.0 | 56 |
| | FeO | 1.01 | 0.98 | – | 21 |
| | Fe^{3+} | 0.36 | 0.66 | – | 13 |
| | Fe^{3+} | 0.37 | -0.20 | 36.6 | 10 |
| EAFD500 (CEMS) | $\alpha\text{-Fe}^0$ | 0.00 | 0.00 | 33.0 | 39 |
| | Fe^{2+} | 1.15 | 0.96 | – | 17 |
| | Fe^{2+} | 0.33 | 0.66 | – | 13 |
| | Fe^0 | 0.0 | 0.02 | 32.5 | 31 |

δ = isomer shift relative to $\alpha\text{-Fe}$; ε = quadrupole shift, Δ = quadrupole splitting; B_{hf} magnetic hyperfine field, RA relative spectral area, *CEMS* Conversion electron Mössbauer spectroscopy

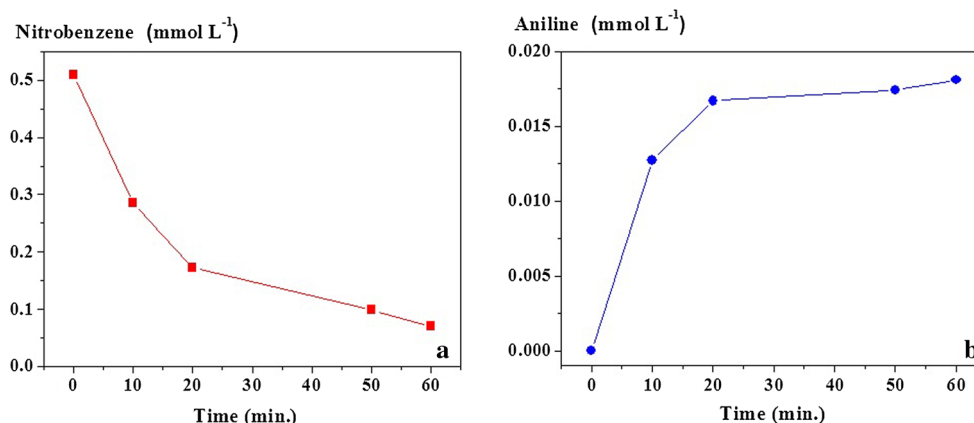


Fig. 3 Variation in the concentration of **a** nitrobenzene and **b** aniline, as a function of reaction time with EAFD500. Initial [nitrobenzene] = 0.510 mmol L⁻¹, EAFD500: 8.6 g L⁻¹, pH 5, temperature 25 °C. The concentration of nitrobenzene decreased by 86 %, while

that of aniline increased to 0.018 mmol L⁻¹ with 60 min reaction. This proves the conversion of nitrobenzene into aniline, when in contact with EAFD500—heat-treated electric arc furnace dust

This behavior can be easily observed by the spectrum in the ultraviolet–visible region, obtained during the reaction (Zamora et al. 2009). The molar concentration values obtained from calibration curves of nitrobenzene and aniline were used to construct the graphs of Fig. 3, where it is possible to observe the change in the concentration of these compounds during the reaction.

It is noted that, after 60 min of reaction, the concentration of nitrobenzene was reduced to 0.071 mmol L⁻¹, which corresponds to 86 % less than the initial concentration 0.510 mmol L⁻¹. On the other hand, the concentration of aniline in the solution reached 0.018 mmol L⁻¹ after 60 min. Similar results were found by (Zamora et al. 2009),

who used metallic iron in reductive reactions of nitrobenzene and nitrotoluene. Luan et al. (2012) used arc furnace slag in combination with Fe^{2+} to reduce nitrobenzene and demonstrated that the reaction can also occur from the species Fe^{2+} , adsorbed on the slag, rich in hematite. Thus, it can be said that EAFD500 showed an excellent activity for the reduction of nitrobenzene to aniline, due to the presence of the species Fe^{2+} and Fe^0 on the surface.

Reactions performed using electric arc furnace dust showed no significant reduction of nitrobenzene to aniline after 4 h. This is related to the presence of oxidized iron phases (Fe^{3+}) in this material, which are inactive for these reactions.

Conclusion

The obtained results show that the heat treatment of electric arc furnace dust with hydrogen at 500 °C resulted in the formation of reduced iron phases, such as Fe⁰ and Fe²⁺. The presence of these reduced species on the surface of heat-treated electric arc furnace dust showed a high activity in the reduction of nitrobenzene to aniline. This type of reaction is important; the reduction of nitroaromatic compounds typically forms less toxic and more biodegradable substances, which facilitates the biological treatment of these compounds. Therefore, it can be concluded that a new material with added value and high activity in redox reactions was obtained in this study from a simple heat treatment of electric arc furnace dust in a reducing atmosphere.

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