

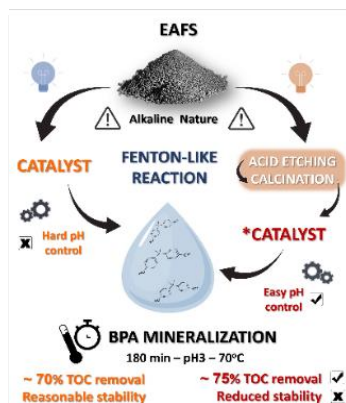
Effect of Physico-Chemical Treatments on EAFS Performance as Catalyst for Fenton-like Oxidation of Bisphenol A

POSTER

Ph.D. Student: N

Journal: JECE

T. Freije¹, N. Inchaurredo¹, C. Ramos^{2,3}, L. Fasce¹. (1) INTEMA-UNMdP, Av. Colón 10850, Mar del Plata, Argentina., inata@fi.mdp.edu.ar. (2) Dto. Física de la Materia Condensada, GlyA-CAC-CNEA, Av. Gral. Paz 1499 San Martín, Bs. As. Argentina. (3) INN, CNEA-CONICET, Av. Gral. Paz 1499, San Martín, Bs. As. Argentina.



Electric arc furnace slag (EAFS), a steel industry by-product rich in iron oxides, underwent acid etching (H_2SO_4 0.5-1 mol/L) and calcination (air, 400°C, 2 hours) to be tested as a catalyst in the Fenton-like oxidation of bisphenol A (BPA). The samples were characterized by XRD, SEM-EDS, and N_2 physisorption. The combined treatment (1 mol/L H_2SO_4 and calcined 400°C 2h) increased surface area, reduced particle size, and eliminated alkalinity, crucial for Fenton catalysis. While initially more active at 70°C (75% mineralization) compared to the raw slag (70%), the treated sample showed faster deactivation, likely due to less stable iron phases. Nonetheless, after 4 cycles of 3-hour reuse, it maintained mineralization above 40%, with easy pH control, facilitating reactor operation and reducing acid consumption and handling.

Introduction

The high production costs of heterogeneous catalysts for Fenton-like processes can limit their widespread use in water treatment plants. An effective solution is to replace synthesized catalysts with iron-containing wastes. This study proposes utilizing electric arc furnace slag (EAFS), a by-product of the steel industry, for the Fenton-like oxidation of bisphenol A (BPA). The authors have successfully tested the raw EAFS sample in catalytic ozonation of BPA, focusing on the pollutant's mineralization [1]. However, the sample's alkalinity hinders its application in the Fenton reaction, which requires acidic conditions. Previous studies have shown that modifying iron slags through thermal, acid, or alkaline treatment improves catalytic performance [2,3]. This study proposes modifying the raw EAFS sample through acid etching and thermal treatment in order to reduce alkalinity, remove impurities, increase surface area and enhance catalyst stability by transforming the wüstite phase in the raw sample into magnetite and maghemite. According to Nasuha et al. [2], the synergistic effect of maghemite and magnetite phases could accelerate redox cycles, preventing the formation of a passivated iron oxide layer and consequent deactivation.

Material and Methods

The raw sample (EAFS_R) was provided by an Argentinian metallurgical company and it was treated with 0.5, 1 and 2 mol/L H_2SO_4 solutions for 4 hours, with 125 g/L of slag. The samples were

washed with distilled water until a constant pH value. Since alkalinity was not removed with 0.5 mol/L and the Fe loss was excessive in the case of 2 mol/L, the sample treated with 1 mol/L (EAFS_1M) was selected for further investigation. A portion of the EAFS_1M sample was calcined at 400°C for 4 hours under air atmosphere (sample EAFS_1M_C). Additionally, to assess the sole effect of calcination, the raw sample was subjected to the thermal treatment (sample EAFS_C). The obtained samples were characterized by SEM-EDS, XRD, and N_2 adsorption/desorption (BET surface area) [1]. Oxidation experiments were conducted using 20 mg/L BPA and a 0.5 g/L EAFS load at temperatures of 25°C and 70°C, for 180 minutes. The pH was maintained at 3 ± 0.2 with 4 mol/L HNO_3 . H_2O_2 was added at stoichiometric doses (molar ratio $\text{H}_2\text{O}_2/\text{BPA}$ 36/1) when its concentration fell below 10 ppm for EAFS_R and the procedure was replicated in all experiments (additions at 0 and 70 min for 25°C and at 0, 15, 45, 90 and 150 min for 70°C). Concentrations of BPA, H_2O_2 , leached Fe, and total organic carbon (TOC) were monitored [1]. EAFS reusability tests were conducted with the most promising sample, in four successive reaction cycles at 70°C. The homogeneous contribution of leached Fe was evaluated using FeSO_4 solutions since EAFS leached ferrous ions under acidic conditions.

Results and Discussion

Characterization results

EAFS_R exhibits very low BET surface area (0.9

m²/g) and is rich in Fe (16.2%), C (18.9%), and Ca (13.2%) (SEM/EDS) [1]. XRD analysis identified crystalline phases of magnesiowüstite and larnite, with minor contributions of akermanite, hematite, magnetite, maghemite, as well as some quartz and metallic iron [1].

Sample EAFS_1M_C displayed a BET surface area of 16 m²/g, with reduced particle size. SEM-EDS analysis revealed a much lower Ca content (4 %). XRD showed an increase in the proportion of magnetite and hematite relative to magnesiowüstite. Larnite disappeared, and meriadinite and anhydrite were formed.

Oxidation results

BPA rapidly decomposed after the first minutes of reaction for all the samples, at both temperatures. Mineralization evolution at 25°C and 70°C for raw and modified samples is depicted in Fig. 1 while leached iron is illustrated in Fig.2.

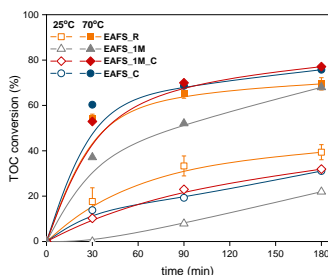


Figure 1. TOC evolution for raw and modified samples.

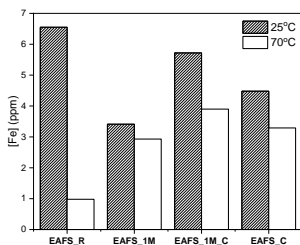


Figure 2. Fe leached at 180 min for raw and modified samples.

Conclusions

The modified EAFS_1M_C showed higher surface area, smaller particle size, reduced alkalinity, and higher magnetite proportion than the raw slag sample. Despite exhibiting higher activity in the mineralization of BPA at 70°C (75% conversion) compared to EAFS_R (70%), it deactivated more rapidly, suggesting that the treatment promoted a less stable combination of iron phases for Fenton-like reactions. Future studies will focus on selectively remove calcium oxides, thus minimizing iron loss; and on assessing the effect of thermal conditions on iron crystalline phases in EAFS, searching for an optimum combination for catalyst stability.

References

- [1] L.A. Fasce, F. Bocero, C.P. Ramos, N.S. Inchaurredo, *Chem. Eng. J. Adv.* (2023) 100576.
- [2] N. Nasuha, B.H. Hameed, P.U. Okoye, *J. Environ. Chem. Eng.* 9 (2021) 104831.
- [3] N. Nasuha, S. Ismail, B.H. Hameed, *J. Taiwan Inst. Chem. Eng.* 67 (2016) 235.

As expected, higher mineralization levels were achieved at 70°C. At 25°C, EAFS_R exhibited the highest activity, likely due to the highest Fe leaching. Conversely, at 70°C, calcined samples showed the highest activity, but EAFS_C retained its alkalinity. Calcination appeared to activate the acid-treated EAFS, as evidenced by EAFS_1M displaying a lower mineralization rate than EAFS_1M_C. Based on these findings, EAFS_1M_C was chosen for further studies due to its low alkalinity and good activity at both temperatures.

Subsequent stability tests with EAFS_1M_C were conducted at 70°C (Fig. 3), revealing a faster deactivation compared to EAFS_R.

The homogeneous contribution tests showed a linear relationship between the final TOC conversion and Fe(II) concentration in the range of 1-4 ppm: $X_{TOC-180min} = 9.87 \cdot [Fe(II)] + 21.72$. According to these results iron leaching may account for the activity in the later cycles.

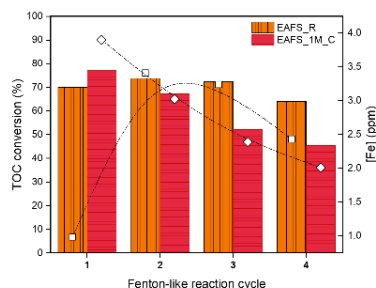


Figure 3. Catalyst stability at 70°C: TOC evolution and Fe concentration after 180 min for selected EAFS samples.

However, during the initial cycles, solid activity appears to dominate over the contribution of leached species. The decline in activity towards the end of the cycles could be attributed to changes in the iron solid phases of EAFS. Previous studies suggest that loss of activity may be linked to catalyst surface passivation (reduction in Fe(II)/Fe(III) ratio) resulting from exposure to acidic and oxidizing reaction conditions [2].