

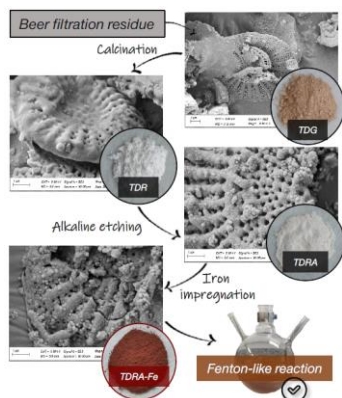
Development of Catalytic Material for Heterogeneous Fenton degradation of Bisphenol A Using a Brewing Industry Residue

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Spent diatomaceous earth used for the filtering of consumable beverages from a local brewery was regenerated through thermal treatment (calcination 4 h 550°C) and alkaline etching (2.5 M NaOH), obtaining a purified material with higher surface area (20 m²/g). The treated material was doped with iron by the incipient wetness impregnation method (TDRA-Fe sample with 11.9 % wt. Fe) and tested as a catalyst in the heterogeneous Fenton oxidation of Bisphenol A (BPA, 20 mg/L). TDRA-Fe showed effective BPA degradation and mineralization, achieving TOC removal levels about 80% at 70°C, with Fe leaching below discharge limits (<1 mg/L). The regeneration of spent diatomaceous earth addresses the disposal and handling challenges associated with this industrial waste, and furthermore, it presents a promising low-cost catalyst for water treatment oxidation processes.

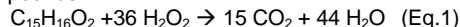
Introduction

Advanced oxidation processes (AOPs) appear as efficient and environmentally friendly proposals for the removal of emerging pollutants. Among the AOPs, the heterogeneous Fenton oxidation process requires basic equipment and mild working conditions. Nevertheless, the catalyst production costs can represent a significant drawback for their widespread application in water treatment plants. For this purpose, the use of Fe(III) modified diatomite as a low-cost catalyst for heterogeneous Fenton and Fenton-like reactions has gained significant importance [1]. However, natural diatomaceous earth (TD) is a non-renewable resource and its availability is limited. The worldwide exploitation of TD is mainly intended for the filtering of consumable beverages. The commercial TD used in these applications are generally natural TD chemically and thermally treated [2]. Once used, the TD are discarded, often resorting to practices that are not environmentally friendly [3]. The use of spent diatomaceous earth to prepare low-cost catalyst is an interesting alternative since it is an abundant industrial waste that can be regenerated.

The purpose of this work is to condition residual diatomaceous earth (TDG) from a local brewing industry to use as a heterogeneous Fenton-like catalyst for the treatment of bisphenol A (BPA), a recognized emerging pollutant present in wastewater from epoxy and polycarbonate production plants.

Previous studies reported the formation of aromatic compounds during the heterogeneous Fenton oxidation of BPA, including phenol, 4-isopropenylphenol, p-hydroquinone, 4-hydroxyacetophenone, and catechol, as primary oxidative byproducts. Additionally, ring-opened

compounds such as oxalic acid, lactic acid, fumaric acid and formic acid were detected as final reaction products [4]. Given that the toxicity of such byproducts can exceed that of the BPA, this work is focused on BPA mineralization evaluation. Mineralization is a high-performance requirement for a catalyst and shows its capability to degrade even the most refractory compounds. Theoretical mineralization implies BPA conversion to innocuous compounds:



Material and Methods

TDG supplied by a local brewery were dried at 100°C for 24 h and regenerated by a 4-hour thermal treatment at 550°C (TDR). Then, TDR were chemically activated by alkaline etching (TDRA) using 5 g of sample in 100 mL of 2.5 M NaOH solution for 4 h at 95°C to increase the surface area [5]. Afterwards, TDRA was impregnated with iron (TDRA-Fe) using Fe(NO₃)₃·9H₂O solution in ethanol, by the incipient wetness impregnation method. Salt concentration was adjusted to obtain an additional 10% wt loading of Fe. The sample was dried at room temperature overnight, then 24 h at 70°C and finally calcined at 400°C for 4 h.

Samples were characterized by scanning electron microscope (SEM) with energy dispersive spectrometry (EDS) and N₂ adsorption/desorption (BET surface area).

Batch oxidation experiments were conducted at pH 3 using 20 mg/L BPA and 1 g/L of catalyst at temperatures of 25, 50 and 70°C, for 180 minutes. The theoretical stoichiometric oxidant requirement for the complete mineralization of BPA was initially added (Eq.1).

Total organic carbon (TOC) removal was taken as a

measure of BPA mineralization degree and determined in a TOC analyser (Shimadzu, TOC-VCPN). BPA, H₂O₂ and leached Fe concentrations were respectively determined by the colorimetric assay proposed for phenolic compounds, the glycemia enzymatic test (Wiener Lab) and the 1,10-phenanthroline colorimetric method [6].

The Fenton homogeneous contribution of leached Fe was evaluated using Fe(NO₃)₃·9H₂O as catalyst.

Results and Discussion

The TDR sample did not show activity as catalyst in the Fenton-like oxidation of BPA. This can be due to the low surface area (less than 1.6 m²/g) and the low Fe content (<2 %wt, according to EDS). After the alkaline etching, BET surface area increased up to 20 m²/g, which can be attributed to the superficial roughness enhancement shown in the graphical abstract illustration. Subsequent to impregnation, Fe content achieved 11.9 %wt (EDS) and the surface area increased up to 36 m²/g.

The results of the Fenton-like oxidation of BPA using the TDRA-Fe sample as catalyst, after 180 min of reaction, are summarized in Table 1, while mineralization evolution is shown in Figure 1. A high BPA conversion was observed at 25°C while complete degradation occurred at 50 and 70°C. However, BPA mineralization was negligible at 25°C and reached approximately 40% at 50°C and an outstanding 80% at 70°C. Both oxidant conversion (X_{H₂O₂}) and oxidant efficiency (ε) increased with increasing temperature.

In all cases, leached iron concentration was lower than 1 mg/L, which is below the maximum admitted

for sewage discharge in the Argentinian region. The leaching diminished as the temperature increased. This can be related to a lower accumulation of carboxylic acids due to the higher mineralization levels. It is known that carboxylic acids can promote iron leaching by forming stable complexes with it [7]. The homogeneous contribution of 0.5 mg/L of Fe(III) was evaluated at 70°C and a mineralization level of 30% was achieved after 180 min, which is important but lower than that obtained in the heterogeneous Fenton process. Therefore, the heterogeneous Fenton reaction may include interfacial H₂O₂ decomposition into reactive oxygen species, active metal dissolution and a contribution from homogeneous Fenton chain reactions [8].

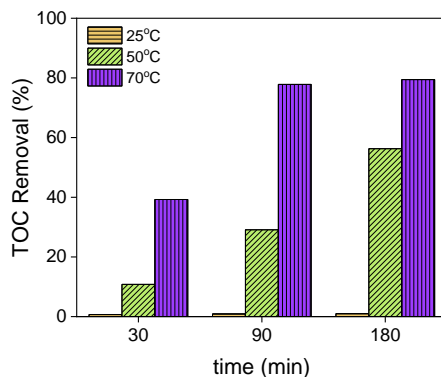


Figure 1. Effect of temperature on BPA mineralization evolution in heterogeneous Fenton experiments (1g/L TDRA-Fe).

Table 1. Summary of main results for BPA Fenton-like oxidation process using TDRA-Fe as catalyst.

Temperature (°C)	X _{BPA} (%)	X _{TOC} (%)	X _{H₂O₂} (%)	ε (mgTOC removed / gH ₂ O ₂ fed)	Fe leached (ppm)
25	72	0	7	0	0.79
50	100	56	43	98	0.68
70	100	76	69	131	0.51

Conclusions

Spent diatomaceous earth from a local brewery was regenerated through calcination and alkaline etching, which removed organic impurities and increased its surface area. The obtained material was doped with iron oxides and tested as a catalyst for the Fenton oxidation of BPA, showing remarkably high mineralization levels (80%), low Fe leaching and high oxidant efficiency. These results are significantly promising for the utilization of this industrial waste as a viable technological alternative for heterogeneous Fenton oxidation with potential benefits for the brewery industry and wastewater treatment plants. Further studies are being performed to evaluate the effect of different Fe loads in TDR and TDRA materials on BPA degradation.

Acknowledgments

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