

Degradation of Gaseous Toluene by Heterogeneous Fenton Using Macrostructured Catalysts

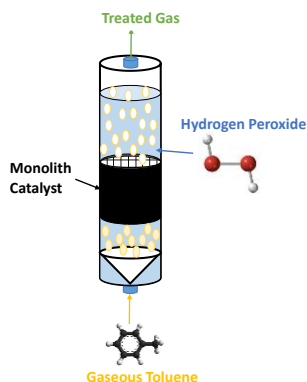
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The degradation of gaseous toluene by the heterogeneous Fenton process was evaluated in this study. The process was catalyzed by monoliths coated with carbon with and without iron incorporation. First, a processes screening was conducted, and maximum toluene transfer was achieved when the Fenton process was applied (C-Fe catalyst). The parametric study allowed to conclude that the highest ratio between toluene transfer and catalyst mass (η/W), total oxidant consumption and lower amount of intermediates formed was achieved when using monoliths with 230 cpsi, with pH = 3.0, [catalyst] = 0.8 g/L and [H₂O₂] = 20 mmol/L. During the runs, a negligible amount of iron was leached from the catalyst to the liquid phase (≤ 1.0 wt.%), proving the catalyst stability for such application; in fact, it was found that the homogenous process contribution due to iron leaching is *ca.* 10%.

Introduction

Volatile organic compounds (VOCs) are among the main pollutants emitted by the chemical and petrochemical industries, of which toluene stands out for being toxic to both humans and the environment [1]. Therefore, it is mandatory to control the respective emissions. So, it is crucial to eliminate them or reduce their concentration in gas effluents to acceptable levels to minimize environmental damage and preserve public health.

In the literature, several approaches are used for treating gaseous streams containing these compounds: absorption, adsorption, thermal destruction, and biological degradation. These processes have however some limitations, such as (for the cases of absorption and adsorption) the simple transfer of the pollutant from one phase to another (rather than its complete elimination) or the low treatment efficiency due to the toxicity of VOCs (for the case of biological processes); others present high treatment costs (like thermal destruction or wet air oxidation). To overcome these limitations, the toluene removal from gas streams by heterogeneous Fenton process is an excellent alternative. This technology is based on generating hydroxyl radicals by the catalytic hydrogen peroxide decomposition in the presence of a metal catalyst supported on a solid matrix. This study used a structured catalyst, such as monoliths coated with carbon (with and without iron incorporation), to achieve good contact among all phases (gas/liquid/catalyst).

To degrade gaseous toluene through a process that occurs in the liquid phase, firstly it is necessary to transfer the pollutant, by absorption, from the gas to the liquid phase (wherein the catalyst and hydrogen peroxide are present and form the hydroxyl radical that oxidizes the toluene). To promote such mass transfer, it is necessary to use a bubble column reactor (BCR). The use of this reactor configuration has several advantages, including the fact

that the BCR does not require mechanical agitation as it occurs, for example, in a continuous stirred tank reactor (CSTR) because efficient mixing, inside the column, is achieved by bubbling the gas [2].

A proof of concept was therefore carried out for the treatment of a gas stream containing toluene by heterogeneous Fenton using iron supported on carbon-coated monoliths as catalyst. Still, upon realizing a detailed parametric study, the selection of the operating conditions that maximize the transfer of toluene and its oxidation was also performed.

Material and Methods

Cordierite monolith (M) was coated with carbon using the chemical vapor deposition method, being obtained the material herein called CM. In this material, iron was supported by adsorption, providing the catalyst designated by CM-Fe. The materials were characterized by different techniques: N₂ adsorption isotherm at -196 °C, transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). To determine the iron load, its concentration was measured by inductively coupled plasma optical emission spectrometry (ICP-OES).

A simulated gas stream containing 0.16 g/L of toluene was fed (at flow rate of 0.15 L/min at 1 atm and 25 °C) to the BCR from the bottom through a diffuser plate. The monolithic catalyst is placed inside the BCR, and the hydrogen peroxide solution (300 mL) fed with the pH previously adjusted. Reaction runs were carried out at room temperature and atmospheric pressure. In pre-established periods, samples were collected from the outlet gas stream of the BCR to measure the concentration of toluene by gas chromatography with FID detection, and liquid samples to evaluate the dissolved organic carbon (DOC) [3] and the residual hydrogen peroxide

concentration [4]. At the end of the reaction, the iron concentration in the liquid phase was also determined by ICP-OES to evaluate the amount of iron leached from the catalyst.

Results and Discussion

First, a process screening was carried out, evaluating the toluene removal by absorption in water, by hydrogen peroxide alone, through adsorption in M, CM and CM-Fe, and finally using hydrogen peroxide and M, CM or CM-Fe (Fenton reaction) – see Figure 1. The maximum toluene transfer (10×10^{-3} mol) was achieved when the Fenton process was applied (CM-Fe + H_2O_2).

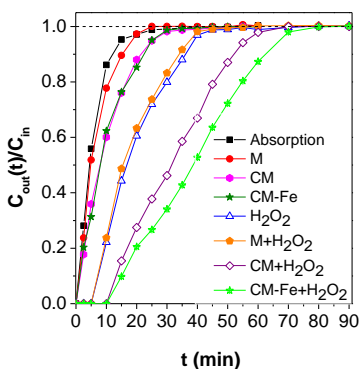


Figure 1. Ratio between toluene concentration in the outlet and inlet streams of the BCR ($V_{\text{liquid}} = 300$ mL, $pH_{\text{initial}} = 3.0$, $T = 25$ °C, $[H_2O_2]_{\text{when used}} = 5.0$ mM, $[M]_{\text{when used}} = 2.0$ g/L, $[CM]_{\text{when used}} = 2.2$ g/L, $[CM-Fe]_{\text{when used}} = 2.3$ g/L).

Regarding the effect of the monolith cell density, the worst performance was achieved over the monoliths with 64 and 300 cps (cells per square inch), which is associated with the fact that they present lower specific surface areas - S_{BET} - (235 and 238 m^2/g , respectively) and pore volume (0.42 and 0.51 cm^3/g , respectively); the maximum amount of toluene transfer was reached for the monolith with 230

Conclusions

The proof of concept of toluene gas treatment by heterogeneous Fenton process catalyzed with iron incorporated in a carbon-coated monolith was performed. Furthermore, the best operating conditions, which maximize the transfer of toluene from the gaseous to the liquid phase and reduce the organic load accumulated in the liquid phase, have been established. After reutilization cycles, catalyst stability was observed, maintaining its textural properties and catalytic performance, which is advantageous for industrial application.

Acknowledgments

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cpsi, which presents the highest S_{BET} (341 m^2/g) and pore volume (0.63 cm^3/g). A linear relationship between the S_{BET} of each monolith and the overall amount of transferred toluene was reached.

A parametric study was then performed to evaluate the effect of some operating conditions, namely the dose of hydrogen peroxide (in the range 5 to 40 mmol/L), pH (between 2.0 and 6.5), and dose of catalyst (in the range 0.8 to 3.9 mg/L) – not shown here for brevity. Maximum toluene transfer per mass of catalyst (6.8×10^{-2} mol_{toluene}/g_{cat}), total oxidant consumption and lower intermediate compounds accumulation in liquid phase (DOC = 33 mgC/L) was obtained when the process was carried out under the following conditions: $[H_2O_2] = 20$ mmol/L, pH = 3.0 and $[CM-Fe] = 0.8$ g/L.

Finally, the stability of CM-Fe was evaluated. Up to ten consecutive runs were performed, being only observed a slight decrease in toluene transfer, in the DOC that remained in the liquid phase and in the hydrogen peroxide consumption when comparing results from the first to the second cycle; this occurred because there was a slight leaching of iron from the catalyst (<1.0 wt.%) – afterwards performance remained nearly constant, without further leaching. This is corroborated by the fact that the XPS analysis shows a reduction in surface iron content in the first two cycles. An increase in the oxygen content was also observed, which indicates that oxidation of the carbon surface occurred during the Fenton process, and in the intensity of the Fe^{3+} peak (despite Fe^{2+} and Fe^{3+} species being present in both samples). It should also be noted that the EDS images allowed to conclude that iron remained well dispersed on the surface of the used catalyst. The average particle diameter, determined by TEM, reduced from 12.8 ± 3.0 for fresh to 4.5 ± 2.5 nm for the used material, leading to conclude that the larger iron particles are the ones that leach from the monolith. It should be noted that the contribution of the homogeneous Fenton process due to iron leaching is very low, both in terms of transferred toluene and accumulated DOC.