

Fenton like Method for Contaminated Groundwater

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Abstract - Advanced oxidation processes (AOPs) have been widely proposed to treat wastes, particularly less concentrated effluents. Fenton-like is a useful technique to remove different organic compounds. A supported catalyst prevents iron release during all the process. In earlier works we explored the porous structure of a modified natural clinoptilolite loaded with iron as a supported catalyst (NZ -A-Fe). This paper presents novel results for BTX (Benzene, Toluene and Xylene) removal from aqueous solution considering that adsorption and oxidation processes are taking place simultaneously. The experiment was achieved by fluxing an aqueous solution of BTX 10 mM and hydrogen peroxide using the same reservoir. After 870 min, C/C° reaches near 10% for each pollutant corresponding to 122 bed volumes. The system removed 225 mg BTX in the present conditions (45 mg/gNZ-A-Fe). Hydrophobic Fe-zeolites can therefore be regarded as promising materials for the removal of BTX from water, since they allow the combination of efficient adsorption and oxidative degradation of BTX by H₂O₂ at neutral pH.

Keywords: Heterogeneous Fenton catalyst, Zeolites, Advanced oxidation processes, organic pollutants

1. Introduction

The past century of industrial, military, and commercial activity in the World has resulted in hundreds of thousands of hazardous waste sites where organic compounds and metals contaminate surface and subsurface soils and sediments. In order to reduce risks to human and ecological receptors, considerable time and money have been spent remediating these sites since passage of major environmental legislation [1, 2]. To overcome these problems, the use of advanced oxidation processes (AOPs) has been widely proposed to treat wastes, particularly less concentrated effluents. AOPs are a group of processes that are based on the generation of highly reactive radicals, especially hydroxyl radicals, which are extremely active and nonselective oxidants, being able to oxidize a wide range of compounds that are otherwise difficult to degrade [3, 4]. Actually, the hydroxyl radical (HO·) is one of the most reactive chemical species known, second only to fluorine in its reactivity [5]. AOPs are useful techniques for the treatment of toxic or non-biodegradable compounds such as pesticides, pharmaceuticals and other organic compounds in wastewater. In these types of processes the contaminants are converted to inorganic compounds such as water, CO₂ and salts, i.e. they undergo mineralization, or they are converted into oxygen- functionalized, short-chain molecules which are more easily biodegradable [6, 7].

Among the hydrogen peroxide-based AOPs, treatment with Fenton's reagent (dissolved Fe²⁺ + H₂O₂) is a well-known, effective, and inexpensive way to degrade organic compounds in wastewater [8]. With respect to simplicity of catalyst removal and recovery, heterogeneous catalysts are more desirable than homogeneous ones. Beside the use of solid iron-oxide minerals or zero-valent iron, several solid supports such as zeolites [9, 10], activated carbon, clays resins or mesoporous materials have been studied for immobilization of iron species in heterogeneous Fenton-like catalysts [11]. Natural zeolites have been the subject of investigation by many researchers who took advantage of zeolites physical and chemical properties and used them in heavy metals adsorption, water purification and softening, soil remediation, etc. During these studies many experimental variables were investigated, such as temperature, solution ionic strength, concentration of adsorbates, contact time and present cationic/anionic species.

In previous works, the porous structure of this modified natural clinoptilolite as a supported catalyst (NZ-A-Fe) has been reported [12, 13] where the behaviour of this material (NZ-A-Fe) in two steps: adsorption and oxidation processes

were explored. This paper presents novel results for BTX removal considering that simultaneous processes are taking place. The experiment was achieved by fluxing an aqueous solution of BTX 10 mM and hydrogen peroxide using the reservoir.

2. Experimental

2.1. Materials

Powdered natural zeolite (NZ) with an average particle in the range 0.3-0.5mm was supplied by the DIATEC S.R.L., extracted from La Rioja, Argentina. Iron sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) purchased from Cicarelli p.a. was used as an iron precursor for ion exchange.

A stock BTX-contaminated groundwater, was prepared by adding the required volumes (μl) of Benzene (Bz), Toluene (Tol) and Xylene (Xyl) into a buffered solution to maintain $\text{pH}=7$ during all the experiences. Hydrogen peroxide was added to the feed solution. The final concentration of pollutants was 5, 4 and 1 mM in Bz, Tol and Xyl respectively.

2.2. Preparation of Fe-loaded Zeolite (NZ-A-Fe)

As it was earlier described, samples of this natural zeolite (NZ) were sieved and treated in NH_4Cl 3M at 353 K during 8 h (sample NZ-A). Later these samples were batch-loaded with iron salts (Fe(II)) and chemically reduced with sodium borohydride in order to prepare NZ-A-Fe [14]

2.3. Characterization Analysis

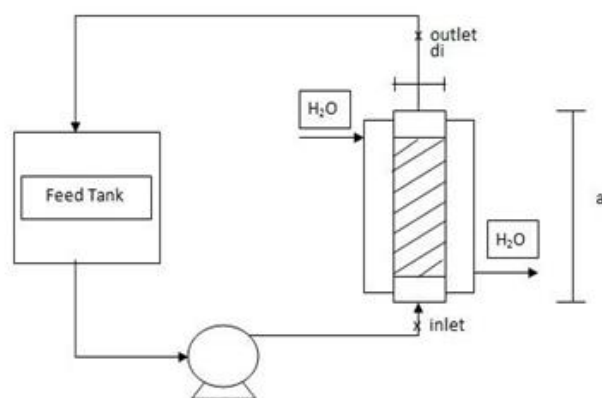
The concentration of freely dissolved BTX was determined by GC analysis.

2.4. Heterogeneous Fenton Reaction

Iron content in NZ-A-Fe catalyst was near 1.38 % w/w. Column adsorption/oxidation experiments were conducted in a glass column (10 mm inner diameter and 90 mm bed height), filled with 5.0 g of NZ-A-Fe catalyst. Temperature was fixed at 20°C and it was continuously controlled by water recirculation, while neutral pH was controlled with the buffered solution for all the experiences. Before starting the adsorption-oxidation step, the column was rinsed with deionized water for several hours in order to adjust the flow rate. A volume of 250 cm^3 of the feed solution with BTX (section 2.1) was pumped through the column in the upward direction at a flow rate of $0.88\text{ cm}^3/\text{min}$ using a rotary piston pump as show Fig. 1a) and Fig. 1b) shows a scheme of the system involved in heterogeneous Fenton-like reactions catalyzed by NZ-A-Fe.



a)



b)

Fig. 1: a) Image of experimental Set up and b) Schematic diagram of the experimental setup for column experiments.

3. Results and Discussion

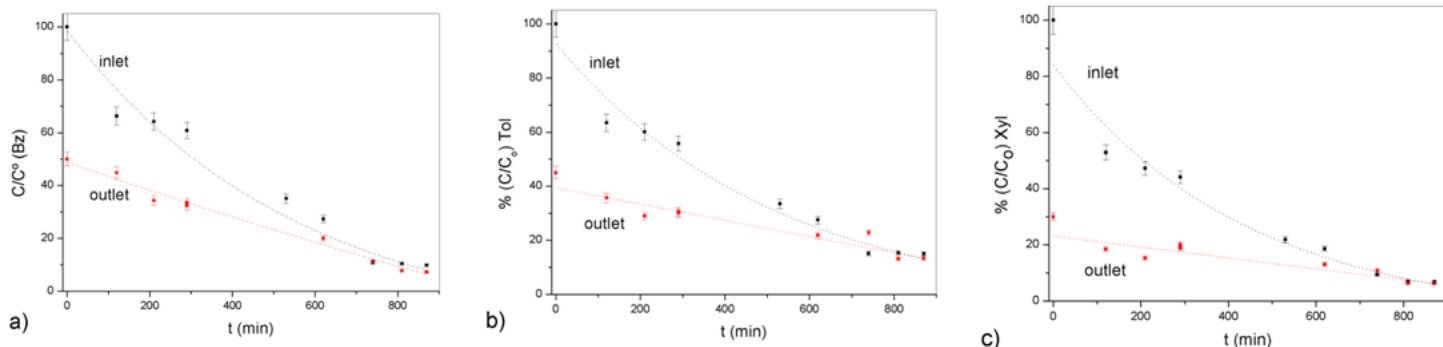


Fig. 2: Profiles of a) Bz, b) Tol and c) Xyl in a BTX solution with $\text{CoBz} = 5.0 \text{ mM}$, $\text{CoTol} = 4.0 \text{ mM}$, $\text{CoXil} = 1.0 \text{ mM}$, with NZ-A-Fe, $\text{CH}_2\text{O}_2 = 0.44 \text{ M}$ (15 g/l), $\text{pH} = 7$ and 20°C .

Figure 2 (a, b and c) shows BTX adsorption-oxidation profiles, by closed-circuit flushing with the feed solution, through the glass column using 5 g of NZ-A-Fe to treat 250 cm³ aqueous solution for the three different pollutants (Bz, Tol and Xyl respectively). Samples were tested at regular time in order to characterize inlet and outlet concentration (see Fig. 1b) of each pollutant.

Previous results showed that absorption processes take place at the preliminary steps (200 min, see Fig 2) while oxidation processes mainly happens, during all the experimental time, inside the zeolite where the catalyst is placed [13]. This analysis explains the great difference between inlet and outlet results at the very initial time. All profiles show similar characteristics. After 870 min, C/C° reaches near 10% for each pollutant corresponding to 122 bed volumes.

The system removed 225 mg BTX in the present conditions (45 mg/gNZ-A-Fe). The absorption zeolite capacity is near 10mgBTX/g NZ-A-Fe) with negligibly iron release as it was earlier reported [13].

These results confirm that both processes (adsorption and oxidation) were presented. Hydrogen peroxide analysis (not shown) supports these results.

4. Conclusion

Heterogeneous catalysis using Fe species immobilized on the zeolite by liquid ion exchange showed to be a satisfactory method to remove organic pollutants. Although these hydrophobic zeolites have a low ion exchange capacity ($\text{SiO}_2/\text{Al}_2\text{O}_3$ near 4.3), after iron loading (near 1.38 % w/w) it was possible to obtain sufficiently active catalysts. Hydrophobic Fe-zeolites can therefore be regarded as promising materials for the removal of BTX from water, since they allow the combination of efficient adsorption and oxidative degradation of BTX by H_2O_2 . The system removed 225 mg BTX in the present conditions (45 mg/g NZe-A-Fe), it works at near-neutral pH and can be easily reused. Fe-zeolites as adsorbents/catalysts showed a good stability in column experiments with negligibly iron release.

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