Adsorption with catalytic oxidation in a recirculating bed reactor for contaminated groundwater

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ABSTRACT

Keywords:
Zeolites
Adsorption
Water remediation
Fenton like
Catalyst
BTX

A novel nanoremediation concept, which is based on in situ trapping of organic contaminants by adsorption and catalytic oxidation in combination with oxidants such as hydrogen peroxide is presented. In earlier works we explored the porous structure of a modified natural clinoptilolite loaded with iron as a supported catalyst (NZ -A-Fe). The supported catalyst prevents iron release during all the process. 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 3.3 mM and hydrogen peroxide, at neutral pH, using the same reservoir. After 870 min, $C/C0$ reaches near 10% for each pollutant. The system removed 65 mg BTX in the present conditions (13 mg/g NZ-A-Fe). The results indicate that the recirculation bed reactor is an excellent system to remove by adsorption and oxidation processes BTX from water due to high mass transfer coefficients and other advantages when compare to batch reactor experiments.

1. Introduction

Water is one of the most valuable resources on planet earth. During the last few decades, the rise of world population as well as industrial revolution has caused serious environmental pollution. 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]. Benzene, toluene and xylene (BTX) isomers are monocyclic aromatic hydrocarbons, which have a moderate solubility in water at 20 °C (benzene: 22 mM; toluene: 5.1 mM and xylenes: 1.5 mM). These compounds are the major water-soluble constituents of petroleum derivatives (gasoline) [3].

Several processes have been examined for removal of BTX compounds from aqueous environment including oxidation, bioremediation and adsorption [4]. Adsorption processes involving porous solids are the most popular, and are widely utilized in engineering practice since they permit the recovery of these compounds. Shehdeh Jodeh et al. [5] reported that the use of activated carbon produced from date stones to remove the BTX from water is a good and efficient method and its effect of activating agent on the adsorption efficiency of BTX was also studied. They worked with low BTX solutions concentration (50 mg/L). Bandura et al. [6] examined the adsorption of BTX from aqueous solution by synthetic on zeolite Na-P1 obtained from fly ash and reported that the

sorption capacity, expressed as the sum of BTX adsorbed per 1 g of zeolite Na-P$_1$ was about 0.34 mg/g

To overcome adsorption restriction, the use of advanced oxidation processes (AOPs) has been widely proposed to treat wastes, particularly less concentrated effluents. AOPs are a group of processes 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 [7,8]. Currently, the hydroxyl radical $OH°$ is one of the most reactive chemical species known, second only to fluorine in its reactivity [9].

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 [1]. Regarding the 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 [10,11], activated carbon, clays resins or mesoporous materials have been studied for immobilization of iron species in heterogeneous Fenton-like catalysts [12].

Natural zeolites have been the subject of investigation by many researchers who took advantage of the 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 [13–15].

In previous works, the porous structure of this modified natural clinoptilolite as a supported catalyst (NZ-A-Fe) has been reported [16–18], where the behavior of this material (NZ-A-Fe) in both 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 3.3 mM and hydrogen peroxide using the same reservoir.

2. Experimental

2.1. Materials and methods

Benzene (Bz) was purchased from Merck Química, toluene (Tol) was obtained from Biopack Chemical and p-xylene (Xyl) was obtained from Carboclor SA.

Powdered natural zeolite (NZ) with an average particle in the range 0.3-0.5 mm was supplied by the DIATEC S.R.L., extracted from La Rioja, Argentina. Iron sulphate (FeSO4·7H2O) 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 pH = 7 during all the experiences. Hydrogen peroxide was added to the feed solution. The final concentration of pollutants was 1.8, 1.1 and 0.4 mM in Bz, Tol and Xyl respectively. The buffer solution was prepared adding the adequate amounts of Na_2HPO_4 and NaH_2PO_4 in deionized water. The flasḱs neck containing the stock solution was sealed with Teflon tape and it was stirred for 24 h until complete dissolution of the organic compounds.

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 3 M at 353 K during 8 h (sample NZ-A). Later these samples were batch-loaded with iron salts (NZ-A-Fe(II)) and chemically reduced with sodium borohydride in order to prepare the catalyst NZ-A-Fe [18]. The used catalyst remained inside the column, at the end of the experiences, was named as NZ-A-Fe(u).

2.3. Characterization analysis

The crystallinity of the zeolite samples was studied using X-ray diffraction (XRD). The spectra were obtained on a Siemens XRD instrument, using filtered Cu Kα radiation with accelerating voltage of 40 kV, current of 30 mA and scanned at 2Θ from 5° to 55°. The samples profiles were analyzed with the software X'Pert for phase's identification and with PowderCell for refining the structural parameters. Elemental analysis was estimated with Energy Dispersive Spectroscopy (EDS) in a Sigma Zeiss microscope with an Oxford EDS detector.The concentration of freely dissolved BTX was determined by Gas Chromatography (GC) analysis. Iron leaching was analyzed using an atomic absorption spectrometer (AAS) instrument while zeolités iron content was quantitatively determined by redox titration with the phosphoric technique [19]. UV–vis/diffuse reflectance spectra (DRS) of solids were recorded using UV–vis spectrophotometer with an additional integrating sphere Diffuse Reflectance Accessory and $BaSO_4$ as standard. The software used in this analysis is PeakFit by SYSTAT Software Inc.

2.4. Heterogeneous fenton reaction

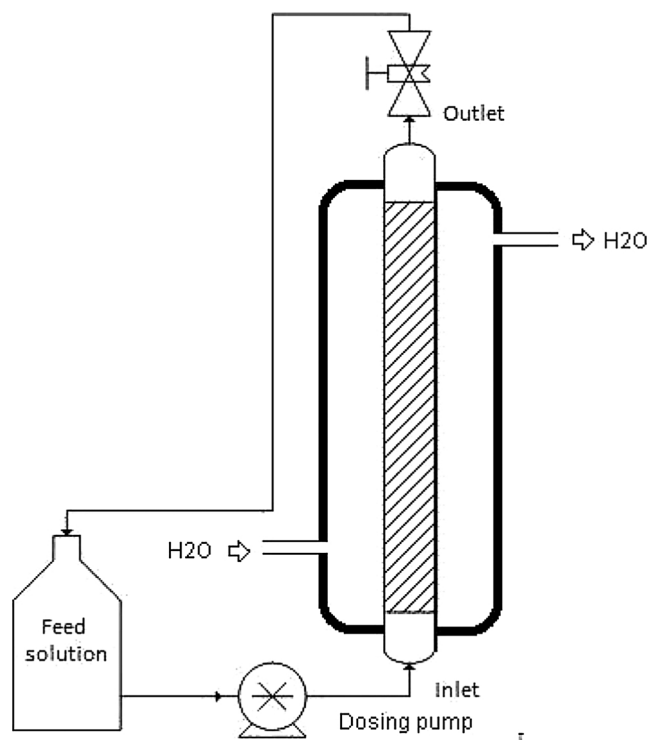The reactor consisted of a column 9.0 cm length and 1.0 cm in

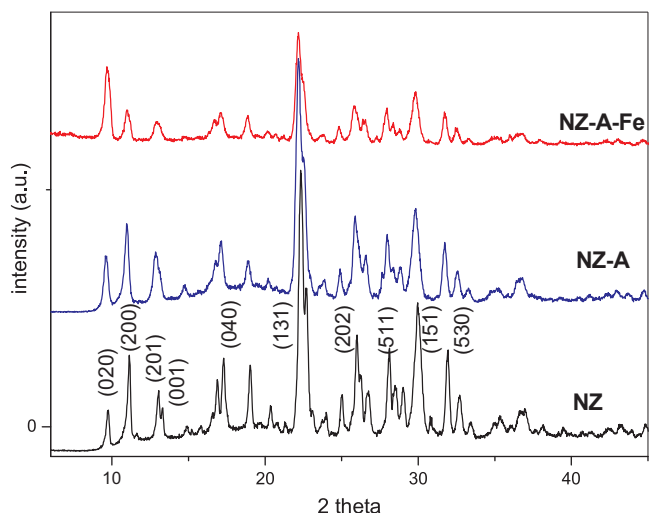**Fig. 1.** Schematic diagram of the experimental setup for column experiments.

Fig. 2. DRX of zeolite samples: natural zeolite (NZ), natural zeolite treated with amonnium chloride (NZ-A) and this sample loaded with iron and chemically reduced with sodium borohydride in order to prepare the catalyst (NZ-A-Fe).

Table 1
Chemical atomic composition (at%) of the natural clinoptilolite NZ and its modified form loaded with iron.

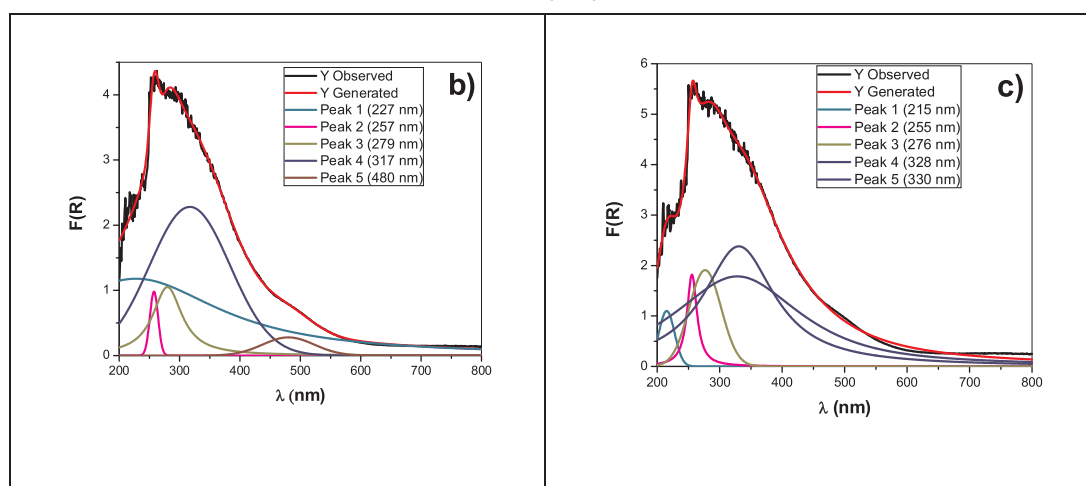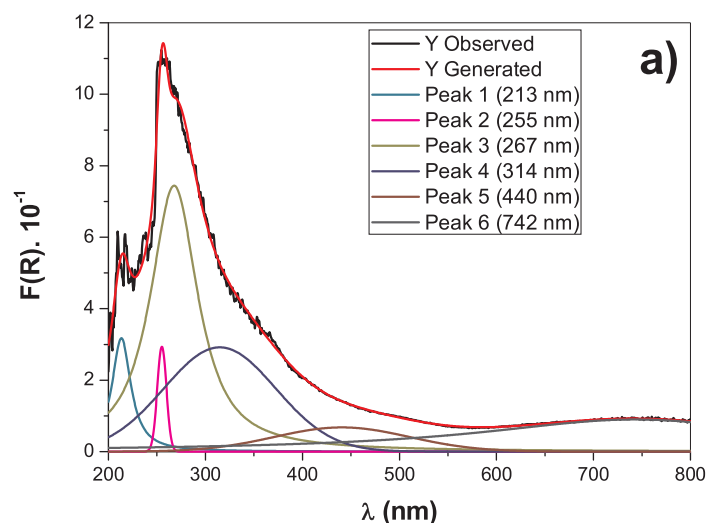|	NZ	NZ-A-Fe
O	42.37	47.27
Na	3.20	2.80
Mg	1.03	0.71
Al	8.60	7.68
Si	38.3	34.2
S	0.62	1.18
K	1.36	1.10
Ca	2.79	2.91
Fe	**0.70**	**1.50**
Si/Al	4.5	4.5

Fig. 3. Experimental UV–vis/DRS spectrum and deconvoluted sub-bands of different zeolites a): NZ (0.67 w/w% Fe), b) NZ-A-Fe (1.3 w/w% Fe), c) NZ-A-Fe u (1.3 w/w% Fe).

Table 2
Iron distribution in different sub-bands from Fig. 3. Confidential coefficients (R^2) are presented.

Sample	% w/w Fe*	% I1	% w/w Fe	% I2	% w/w Fe	% I3	% w/w Fe	R^2 (coefficient)
NZ	0.67	79	0.53	17	0.11	4	0.03	0.9944
NZ-A-Fe	1.3	56	0.73	40	0.52	4	0.05	0.9968
NZ-A-Fe u	1.3	54	0.70	46	0.60	0	–	0.9967

I_1: 200 nm < λ < 300 nm, I_2: 300 nm < λ < 400 nm, I_3: λ > 400 nnm.
  * Fe was determined by titration [19].

diameter made of Pyrex glass packed with the catalyst particles filled with 5.0 g of NZ-A-Fe catalyst (Fig. 1). Iron content in NZ-A-Fe catalyst was near 1.3% w/w.

Temperature control (20 °C) for column was performed by water recirculation with a cooling jacket, 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 cm³ of the feed solution with BTX (Section 2.1) was pumped at a flow rate of 0.88 cm3/min through the column, in the upward direction using a rotary piston pump. Fig. 1 shows a scheme of the system involved in heterogeneous Fenton-like reactions catalyzed by NZ-A-Fe. Specified amount of reaction mixture were withdrawn at regular time intervals.

Degradation experiments in batch were performed with a batch reactor system in similar experimental conditions taking in account the
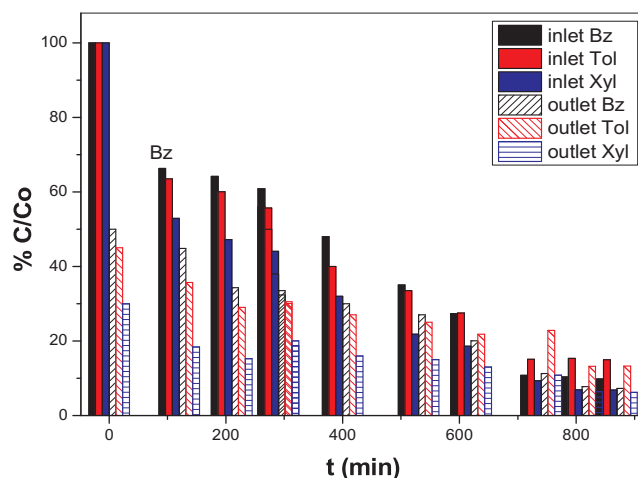

Fig. 4. Column profiles of Bz, Tol and Xyl in a BTX solution with C0Bz = 1.8 mM, C0Tol = 1.1 mM, C0Xil = 0.4 mM, CH2O2 = 0.24 M, pH = 7 and T = 20 °C.

following mass ratio for pollutants, catalyst and hydrogen peroxide: (BTX/NZ-A-Fe) = 0.016 and (H₂O₂/NZ-A-Fe) = 0.23; the experience time was 870 min; pH = 7 and T = 20 °C as it was described in Russo et al. [17]. The catalyst powder was suspended in the BTX aqueous solution. Samples were mixed in a horizontal shaker while aliquot of 1 ml were extracted at different intervals.
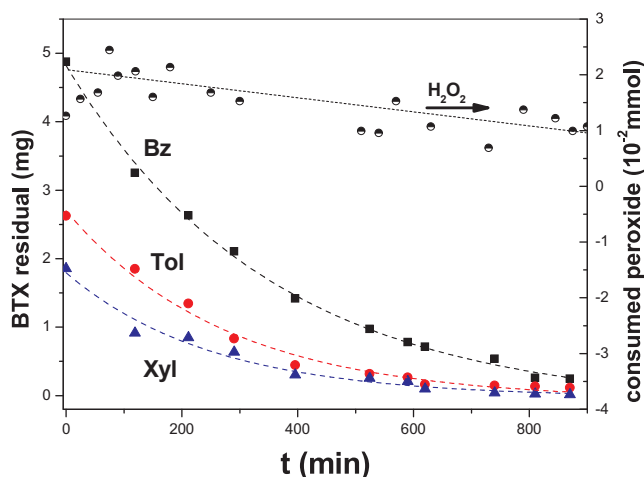
Fig. 5. Profiles of a) Bz, b) Tol and c) Xyl in a BTX solution with CoBz = 1.8 mM, CoTol = 1.1 mM, CoXil = 0.4 mM, with NZ-A-Fe, CH_2O_2 = 0.24 M, pH = 7 and T = 20°.

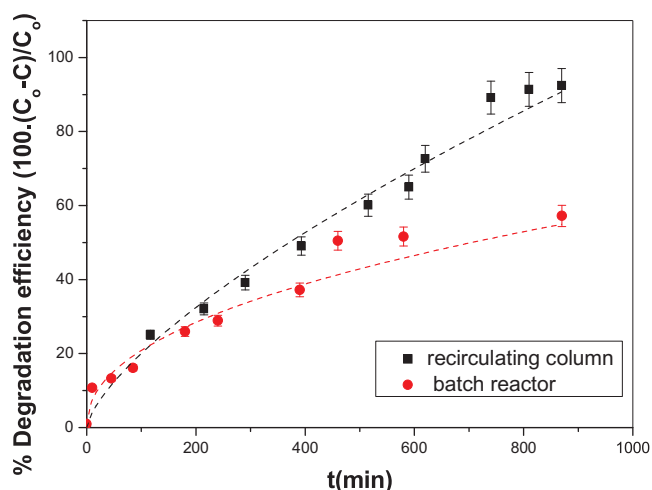**Fig. 6.** Comparison of recirculating column and batch reactor performances, mass ratio (BTX)/(NZ-A-Fe) = 0.016; mass ratio (H_2O_2)/(NZ-A-Fe) = 0.23; pH = 7; T = 20 °C.

3. Results and discussion

3.1. Catalyst characterization

The natural clinoptilolite (NZ) and the treated and iron loaded zeolites (NZ-A and NZ- A-Fe) were characterized using XRD (Fig. 2). The results indicate that the main mineral in the samples is clinoptilolite (9% quartz and feldespate) and can be fitted with the clinoptilolite reference (Ref. code 01-013-0304) corresponding to the monoclinic system, space group C2/m.

No significant change has been observed either in the position of the most intense peaks of the clinoptilolite [20] nor in its crystallinity. We can observe that the main differences between the peaks are in their intensity. The peak corresponding to the (020) and (200) planes of clinoptilolite (see Fig. 2), are the ones having the highest intensity variation. These changes in peaks intensity are mainly associated with differences in the nature, amount and position of the extra-framework species in clinoptilolite channels [21]. Fe inclusion only slightly modifies patterns intensities. Such shift must be attributed to the ion exchange of Fe^{2+} into the sites occupied by Ca^{2+} and/or Na^+ in the crystalline structure of the clinoptilolite.

During EDX analysis we normally get elemental composition in Normalized atomic% concentration (Table 1). This tecnique is a semi-quantitative method because not all elements are considered.

Although individual cationic values of both samples (NZ and NZ-A-Fe) show some variations as a consequence of the chemical treatment, Si/Al ratio remains in 4.5, ratifying preserved crystallinity in both zeolites. Iron loading increases iron content in NZ-A-Fe compared to NZ.

The state of iron in natural zeolite is an important feature for the practical applications of these materials. It has been determined that iron is located as low-spin Fe (III) in the tetrahedral sites of the framework, in extra framework octahedral sites as free $[Fe(H_2O)]_6^{3+}$, and as high-spin Fe(II) in octahedral coordination in extra framework sites or in another aluminosilicate associated with the zeolite [22].

UV–vis spectra obtained in diffuse reflectance (DRS) mode provide information on the iron speciation in Fe-zeolites. The preparation method, framework composition of the support and pretreatment conditions determine the nature and distribution of Fe species in the final catalyst [23].

The respective UV-vis/DRS spectra for samples NZ, NZ-A-Fe and NZ-A-Fe-u (Section 2.2) are presented in Fig. 3

Iron in zeolite structure can be considered in three different species. According to literature the peaks at ~200 nm and ~285 nm correspond to the presence of isolated Fe(III) ions in tetrahedral and octahedral coordination respectively. Octahedral Fe(III) ions in small oligonuclear iron-oxo clusters give bands between 300 and 400 nm and bands above 400 nm are characteristic for large iron oxide particles [24]. These large iron oxide particles are not desired but not completely avoidable. Due to the limited space inside the channel system of the zeolites, oxide clusters can only be formed at the outer surface, where they can play a significant role for the surface charge distribution. These Isolated Fe (III) species (absorbance at < 300 nm) and small oligonuclear clusters (Fe_xO_y) are considered as the most active catalytic species for the heterogeneous Fenton reaction.

Table 2 shows for NZ sample that the dominant fraction consists of iron species of low nuclearity (isolated or binuclear) (I_1 = 79%) with relative low intensity values (4%) as large iron oxide nanoparticles (I_3). Peak 6 (742.57 nm) contribution was not considered as it seems without physical meaning; probably it may be a background scan.

Iron loading in NZ-A-Fe increases iron as oligonuclear clusters Fe (III)$_x$O$_y$ (I_1 + I_2). It is interesting to remark that, after fluxing an aqueous solution of BTX 3.3 mM for 900 min, the catalyst (NZ-A-Fe u) maintains a similar Fe composition within the zeolite structure (Table 2). No contribution of large iron oxide particles was detected in this sample.

Studies of the time dependence of reduction and reoxidation at 673 K by UV/VIS-DRS reported by Kumar [24] for Nitrogen oxide catalysis with NZ-Fe show that iron in free samples, extra framework isolated $[Fe]^{3+}$ ions in tetrahedral and octahedral coordination (I_1) and iron in clusters (I_2), possess different redox properties. The former species are relatively fastly reduced but only slowly reoxidized. In contrast, iron oxide clusters are hardly reduced and very fastly reoxidized in cluster containing samples. This suggests that the properties of iron species within clusters located in the channels may be more uniform than those of isolated sites.

3.2. Catalytic oxidation

The heterogeneous Fenton reaction was performed as it was previously described in 2.4. 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 solutions for the three different pollutants (Bz, Tol and Xyl respectively), are presented in Fig. 4. Samples were tested at regular intervals in order to characterize both inlet and outlet concentration (see Fig. 1) of each pollutant
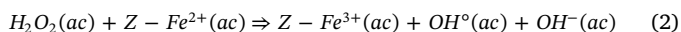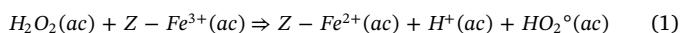
Previous results showed that absorption processes take place at the preliminary steps (100 min, see Fig. 4) while oxidation processes mainly happen, during all the experimental time, inside the zeolite where the catalyst is placed [12]. This analysis explains the great

difference between inlet and outlet results at the very initial time. All profiles show similar characteristics. After 870 min, C/C0 reaches near 10% for each pollutant. Pollutants removal amounts (C/C0) are in the sequence Xyl > Bz > Tol.

Fig. 5 shows the residual mass of each pollutant, calculated as: BTX residual (mg) = mass BTX inlet-mass BTX outlet at each time interval. Consumed peroxide is also shown. It is possible to observe that hydrogen peroxide concentration decreases continually although peroxide is not completely expended after the complete experience.

The system removed 65 mg BTX after 870 min. Russo et al. [14] preliminary results showed that adsorption capacity, at equilibrium process, of a BTX solution on NZ-A-Fe a pH = 7 was 2.7; 2.8 and 0.5 mg/L for Bz, Tol and Xyl These results confirm that both processes (adsorption and oxidation) are present.

Hydrogen peroxide analysis supports these results. BTX kinetic removal is related to adsorption processes onto zeolite surface and peroxide diffusion to zeolite surface where the catalyst (Fe) is placed in order to go through the following reactions:

$$H_2O_2(ac) + Z - Fe^{3+}(ac) \Rightarrow Z - Fe^{2+}(ac) + H^+(ac) + HO_2°(ac) \qquad (1)$$

$$H_2O_2(ac) + Z - Fe^{2+}(ac) \Rightarrow Z - Fe^{3+}(ac) + OH°(ac) + OH^-(ac) \qquad (2)$$

The catalyst and the hydrogen peroxide generate $OH°$ and HO_2^0 radicals that can degrade pollutants structures and improve the oxidation efficiency The hydroperoxyl radicals (HO_2^0) generated in Eq. (1) are less reactive than the OH° species. Reactions presented in Eqs. (1) and (2) show that the formed oxidative radicals (OH° and HO_2^0) react with the activated organic molecules to produce mineralization products ($H_2O + CO_2$).

The comparisson of this heterogeneous Fenton process in the recirculating column for a BTX aqueous solution was implemented with a batch reactor system in similar experimental conditions taking in account the following mass ratio (BTX/NZ-A-Fe) and (H_2O_2/NZ-A-Fe); time (min); pH = 7 and T = 20 °C (Fig. 6).

A higher degradation efficiency (DE) was obtained in the recirculating column in 870 min (90% compared to 50%).

These results can be related to an enhancement of the contact between the catalyst and the pollutants and high mass transfer coefficients in the recirculating column.

Specified amount of reaction mixture were withdrawn at regular time interval were leached iron species were analyzed by atomic absorption spectroscopy. Solubilized iron remains below 0.15 ± 0.05 ppm.

These results contribute to enhance the stability of the catalyst NZ-Fe prepared in this work. Such a low extent of release may be regarded as the iron resistance to the leaching process.

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 relative low ion exchange capacity (SiO_2/Al_2O_3 near 4.5), it was possible to obtain good active catalyst properties after iron loading (near 1.3% w/w).

The results indicate that the recirculation bed reactor is an excellent system to remove by adsorption and oxidation processes BTX from water due to high mass transfer coefficients and other advantages when compared to batch reactor experiments. The system removed near 90% BTX in the present conditions (13 mg/g NZ-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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