



Highly efficient (MFe)zeolite catalysts for nimesulide degradation via Fenton-type oxidation

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ABSTRACT

Highly efficient (MFe)zeolite catalysts were employed to degrade and mineralize the non-steroidal anti-inflammatory drug nimesulide (NIM) via a Fenton-type reaction. NIM was successfully extracted from generic tablets with an 80% yield, and its purity was confirmed through FTIR, ¹H NMR, and UV–Vis spectroscopy. The (MFe)zeolite catalysts—where M represents Co, Ni, Cu, or Zn—were prepared via ion exchange starting from NaY zeolite and thoroughly characterized by different techniques. In the absence of metal species, both NIM and total organic carbon (TOC) removals were low (<17%). Conversely, a significant enhancement was observed with the (CoFe)NaY catalyst, which achieved 47% NIM degradation and 25% TOC removal at natural pH and 25 °C. The optimal reaction conditions obtained by the central composite design (CCD), pH 3.0, 48 °C, 100 mg/L H₂O₂, 0.5 g/L (CoFe)NaY catalyst, and 180 min of reaction time, allowed achieving complete NIM removal (100%) and TOC reduction (88%). The catalyst demonstrated high stability, maintaining activity over five consecutive reuse cycles in a batch reactor and for ~200 h of time-on-stream in a continuous flow reactor. The oxidation mechanism was confirmed to be hydroxyl radical-based, as demonstrated by the inhibition in the presence of dimethyl sulfoxide (DMSO) as scavenger. Temperature influenced the nature of intermediate by-products: at the optimal temperature (48 °C), only oxalic acid was detected, while at 25 °C, both oxalic and oxamic acids were quantified. In the experiment conducted under optimal operating conditions, in addition to oxalic acid, other intermediate compounds were identified, however their concentrations were negligible.

1. Introduction

The 4-nitro-2-phenoxyethanesulfonamide (C₁₃H₁₂N₂O₅S), commonly known as nimesulide (NIM), is an active pharmaceutical ingredient (API) that belongs to the nonsteroidal anti-inflammatory drugs (NSAIDs), renowned for its analgesic, antipyretic, and anti-inflammatory properties [1]. NIM was initially authorized for use in Europe in 1985, primarily intended for treating conditions like painful osteoarthritis, acute pain, and primary dysmenorrhea. This drug is not fully absorbed by organisms, so it is expelled in the secretions of living beings; therefore, it is among the numerous drugs already identified in wastewater and considering that it is

not completely eliminated in wastewater treatment plants (WWTPs), it is present in water sources. Hence, the accumulation of NIM in the environment causes adverse effects, including acute and chronic toxicity for aquatic and terrestrial organisms [2,3]; still, it is harmful to public health, as it generates liver damage, gastrointestinal toxicity, cardiovascular issues, renal complications, dermal reactions, and even disorders affecting the immune and nervous systems [4,5].

To minimize harmful effects on the environment and public health, it is crucial to eliminate/reduce NIM concentrations in wastewater before its discharge. For this purpose, it is necessary to implement an effective and efficient treatment aligned with the United Nations Sustainable

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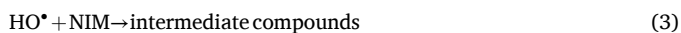
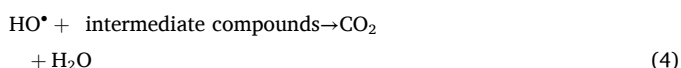
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Development Goals. Goal 6 (SDG 6) ensures universal access to sustainable water and sanitation management. Clean water and adequate sanitation are fundamental for human health and welfare, playing a pivotal role in fostering sustainable development [6,7].

The literature reports some treatment technologies for eliminating NIM, such as adsorption [8–10], advanced oxidation processes like photo-Fenton [11–13], persulfate oxidation activated by catalysts and/or radiation [14], photolysis and photocatalysis [15,16], chlorination combined with solar radiation [17], hydrogen peroxide or persulfate combined with membrane technology [18,19] or the use of hydrogen peroxide combined with UV radiation [3,13]. Some of these processes have also been employed for the removal of other substances [20,21]. Therefore, this study proposes the application of the Fenton-type process, as it is cost-effective, environmentally friendly, requires simple equipment, has low operating costs, and has proven efficient in removing toxic and refractory compounds such as NIM [22,23].

The Fenton process, carried out in acidic medium and in the presence of a transition metal (M), is based on the catalytic decomposition of hydrogen peroxide (H_2O_2), forming the hydroxyl radical through Eq. (1) and continuously regenerating the catalyst according to Eq. (2). The hydroxyl radicals formed have a high oxidation potential (2.8 eV [24]) and are responsible for oxidizing NIM into intermediate compounds, which can be further oxidized into carbon dioxide and water (Eqs. (3)–(4)).



In the literature, Fe, Cu, Ni, Zn, and Co, among others, are reported as transition metals to promote the Fenton reaction [25–27], but the homogeneous process presents significant limitations, such as the need to remove the metals from the aqueous phase at the end of the process through a subsequent treatment stage. Even so, this generates metal-containing sludges that must be appropriately disposed off, increasing implementation and operating costs [28].

To overcome the drawbacks of a homogeneous process, a Fenton-type reaction can occur in a heterogeneous phase, loading the metals on a solid matrix. In this study, NaY zeolite was selected as the support due to its microporosity and uniform porous structure with open channels and cavities, which enhance the stability of the metal active sites [29–31], making them more efficient in the Fenton-type heterogeneous process. The utilization of bimetallic catalysts, due to the combined synergistic redox effects, offering higher activity, stability, and efficiency over a broader pH range, is particularly promising [32–34]. In this study bimetallic catalysts were prepared by adding Fe (metal commonly used for catalyzing the Fenton reaction) and other metals (namely Cu, Ni, Zn or Co) on NaY through the ion-exchange method. These bimetallic catalysts were selected to exploit the synergistic effect of the two transition metals in improving the efficiency of the Fenton-type process for the degradation and mineralization of NIM, which is reported for the first time. The bimetallic catalyst with the best performance in degrading and mineralizing NIM was used to evaluate the influence of the key operational parameters, to optimize the treatment process using a central composite design (CCD) approach, and to elucidate the degradation mechanism by quantifying the intermediate compounds formed during the reaction.

This study aimed therefore to develop stable and efficient catalysts for advanced water treatment processes, targeting the elimination of NIM and its mineralization in order to minimize its impact on environmental and public health.

2. Experimental

2.1. Materials and chemicals

Iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Aldrich), copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, Aldrich), nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Aldrich), cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Merck), zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Aldrich), hydrogen peroxide (H_2O_2 , 30% w/v, VWR Chemicals), hydrochloric acid (HCl, Aldrich), sulfuric acid (H_2SO_4 , VWR Chemicals), sodium hydroxide (NaOH, Erka), disodium phosphate (Na_2HPO_4 , VWR Chemicals), orthophosphoric acid (H_3PO_4 , VWR Chemicals), methanol (HiPerSolv CHROMANORM from VWR Chemicals), and sodium bisulphite (Na_2SO_3 , Aldrich) were used as received. NaY *faujasite* zeolite was provided in powder form by Zeolyst International (CBV100). The generic *Nimuselida* from *Pharmakern* brand (20 pills of 100 mg each) was purchased commercially over-the-counter in Portugal.

2.2. Extraction and characterization of the nimuselide from the commercial drug

The principal pharmaceutical active ingredient, NIM, was obtained from the generic formulation *Nimuselida* (Pharmakern, 100 mg/tablet), using a modified extraction process adapted from a previously published method [35]. Five tablets of 100 mg each were ground to a powder and transferred into 50 mL of 0.1 M NaOH solution. The solution was stirred during 10 min, and filtered twice, in order to remove the insoluble particles from the tablet's excipients. The resulting filtrate was slowly added to 50 mL of 0.2 M HCl, stirred and left to stand in an ice bath for 15 min. The precipitated solid was filtered and dried through a Buchner funnel under vacuum at 50 °C for 30 min, and yellow crystals were obtained (m.p. = 179 °C).

The Fourier Transform Infrared (FTIR) analysis was carried out using a *PerkinElmer Spectrum Two* spectrometer equipped with the attenuated total reflectance (ATR-FTIR) accessory. The spectrum was obtained at room temperature, with a resolution of 4 cm^{-1} , in the 4000–500 cm^{-1} wavelength region, through an average of 16 scans.

The ^1H NMR spectrum was obtained at room temperature using a *Bruker Avance III* spectrometer at 400 MHz, using a 5 mm diameter glass tube and the DMSO- D_6 solvent.

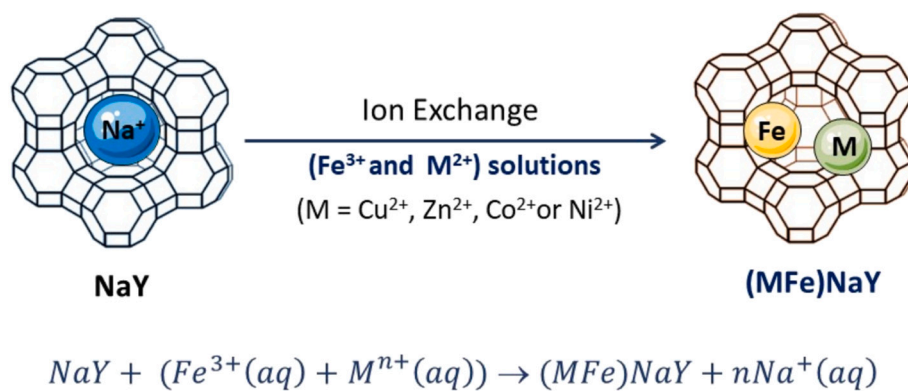
The UV/Vis absorption spectrum was obtained at room temperature on a Shimadzu UV/2501PC spectrophotometer over a wavelength range of 300–500 nm. The presence of the principal pharmaceutical active ingredient NIM was confirmed at the characteristic wavelength of the drug: $\lambda_{\text{max}} = 392$ nm.

2.3. (MFe)NaY catalysts preparation and characterization

The ion exchange method was employed to prepare four distinct (MFe)-zeolite catalysts following the procedure described by El Mrabet *et al.* [36]. These catalysts were obtained by simultaneously adding two aqueous solutions, each containing the desired amount (1.0 mmol) of the metal ion (Fe^{3+} and Cu^{2+} , Zn^{2+} , Co^{2+} or Ni^{2+}), to 1 g of the NaY zeolite, according to Scheme 1.

After stirring at room temperature for 24 h, the suspension was filtered under vacuum and the resulting solid was washed with deionized water and dried in an oven at 60 °C for 8 h. Finally, it was calcined at 350 °C for 4 h, under a dry air stream, with a heating rate of 5 °C/min. The obtained catalysts were named as (MFe)NaY, where M is Cu^{2+} , Zn^{2+} , Co^{2+} or Ni^{2+} .

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses were performed with a 5110 spectrometer (Agilent



Scheme 1. Schematic representation of the ion exchange method used for preparing the (MFe)NaY catalysts.

Technologies) to determine the metals (Na, Al, Si, Fe, Ni, Zn, Co and Cu) content. The detailed procedure was previously described elsewhere [35].

Surface area and pore volume were determined from the nitrogen adsorption/desorption isotherms at -196°C , using a Sorptomatic 1990 (CE Instruments) gas adsorption device. Before analysis, all samples were outgassed at 250°C under vacuum (7.5×10^{-6} Torr) for 12 h in order to clean the surface of any adsorbed species. The isotherms were elaborated according to the BET method. The external surface area (S_{ext}) and micropore volume (V_{micro}) were calculated by the t -method [29].

The powder samples were characterized using a desktop scanning electron microscope (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX) analysis (Phenom ProX) with an EDX detector (Phenom-World BV). All results were acquired using the ProSuite software integrated with Phenom Element Identification software; this allowed the quantification of the constituent elements, expressed both in weight and atomic concentration. The samples were added to aluminium pin stubs with electrically conductive carbon adhesive tape (PELCO Tabs™). Samples were imaged without coating. The aluminium pin stub was then placed inside a Phenom Charge Reduction Sample Holder (CHR), and different points were analysed for elemental composition. EDX analysis was conducted at 15 kV; an intensity map and SEM analysis were conducted at 5 kV.

X-ray photoelectron spectroscopy (XPS) analyses were performed with a Kratos Axis-Supra instrument (ThermoFinnigan), using Al-K α radiation as the monochromatic X-ray source ($h\nu = 1486.6$ eV). Photoelectrons were collected from a take-off angle of 90° (defined as the angle between the sample surface and the axis of the XPS analyzer lens). The measurement was carried out in a Constant Analyzer Energy mode (CAE) with an emission current of 15 mA, and 160 and 40 eV pass energy for survey spectra and high-resolution spectra, respectively. Data analysis was performed using the ESCAPE software supplied by Kratos Analytical.

2.4. Fenton-type reaction procedure

Fenton-type reactions were carried out in a glass-jacketed batch reactor, with a capacity of 250 mL, connected to a thermostatic bath (Huber, Polystat CC1) to maintain a constant reaction temperature inside the reactor. In all Fenton experiments, the reactor was charged with 100 mL of NIM solution with a concentration of 40 mg/L. After reaching the desired temperature, the pH was adjusted with 1 M H_2SO_4 or 1 M NaOH. Then the appropriate quantities of (MFe)NaY catalyst and hydrogen peroxide were added sequentially, starting the process. Adsorption tests were also carried out in the presence of the catalyst alone, without the addition of the oxidizing reagent, H_2O_2 .

Aliquots of the reaction mixture were periodically withdrawn from the reactor and immediately treated with 10 M NaOH to raise the pH to 11 and instantly decompose the H_2O_2 and stop the reaction. After

neutralization (to pH ~ 7.0) with concentrated H_2SO_4 was carried out (i. e. before analysis) to avoid damaging the analytical equipment. The collected samples were filtered to remove the catalyst, and the NIM concentration and TOC were then determined. At the end of the reaction, the remaining H_2O_2 concentration in the solution was immediately measured (without stopping the reaction) [30]. To quantify the amount of metals eventually leached, the reaction mixture was filtered through $0.45 \mu\text{m}$ nylon membrane filters, acidified to pH ~ 2.0 with concentrated HNO_3 to keep the metals dissolved, and measured by ICP-AES.

The long-term reaction run was carried out in a continuously stirred tank reactor (CSTR) with a capacity of 920 mL, coupled to a thermostatic bath (Huber Polystat CC1) to keep the temperature constant – Fig. S1. The operating conditions were fixed at pH = 3.0, $T = 48^{\circ}\text{C}$, $[\text{H}_2\text{O}_2]_{\text{feed}} = 100 \text{ mg/L}$, $\tau = 180 \text{ min}$, $W/Q = 20 \text{ mg}\cdot\text{min/mL}$ and $[\text{NIM}]_{\text{feed}} = 40 \text{ mg/L}$. The oxidant and the NIM solutions were continuously fed to the reactor by a peristaltic pump (Gilson Miniplus 2); the resulting dilution factor (2) due to mixing of both streams at the inlet was considered in the calculations for solutions preparation. The catalyst was placed within the reactor in a porous retainer support (pore opening less than 0.8 mm), to prevent its loss. Continuous agitation was ensured by a magnetic stir bar operating at 200 rpm. Further details of the experimental procedure can be found elsewhere [37].

2.5. Experimental design

The CCD statistical model with four factors – pH, temperature, catalyst dosage, and H_2O_2 concentration – was applied to optimize the removal and mineralization of NIM. This model is the most commonly used fractional factorial design in the Response Surface Methodology [38]. It was applied to evaluate the significance of each above-mentioned factor in the degradation of NIM via the Fenton-type reaction, employing (CoFe)NaY as catalyst (the one with better performance).

Table 1 shows the independent four factors studied – (i) temperature (X_1 : 10°C to 90°C), (ii) pH (X_2 : 1 to 5), (iii) concentration of hydrogen peroxide (X_3 : 0 to 200 mM) and (iv) amount of catalyst (X_4 : 0 to 1 g) – used to determine the coefficients in the quadratic terms of the model.

The response surface methodology (RSM) with a second order model

Table 1
Independent codified factors and levels used in the CCD model for NIM degradation.

Coded factor	Factor	Coded level				
		−2	−1	0	1	2
X_1	$T (^{\circ}\text{C})$	10	30	50	70	90
X_2	pH	1	2	3	4	5
X_3	$[\text{H}_2\text{O}_2] \text{ (mg/L)}$	0	50	100	150	200
X_4	$[\text{Catalyst}] \text{ (g/L)}$	0	0.25	0.5	0.75	1

was used to determine the importance of the factors and the best conditions for NIM and TOC removal, where the predicted response, Y_m , represents the NIM conversion (Y_1) and TOC removal (Y_2) calculated by Eq. (5):

$$Y_m = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^{k-1} \sum_{j=2}^k \beta_{ij} X_i X_j + \sum_{i=1}^k \beta_{ii} X_i^2 + \varepsilon \quad (5)$$

In Eq. (5), β_0 is the intercept term, while β_i , β_{ii} , and β_{ij} are the first-order

terms, the quadratic terms and the binary-interaction terms, respectively. X_i and X_j are the coded independent variables shown in Table 1, k is the number of optimized variables and ε denotes the random error of the estimated response [38,39]. CCD includes 2^k factorial runs, 2^k star runs and k_0 runs (center-point replications, usually $3 \leq k_0 \leq 5$) [39]. The adequacy and significance of the model were evaluated by analysis of variance (ANOVA).

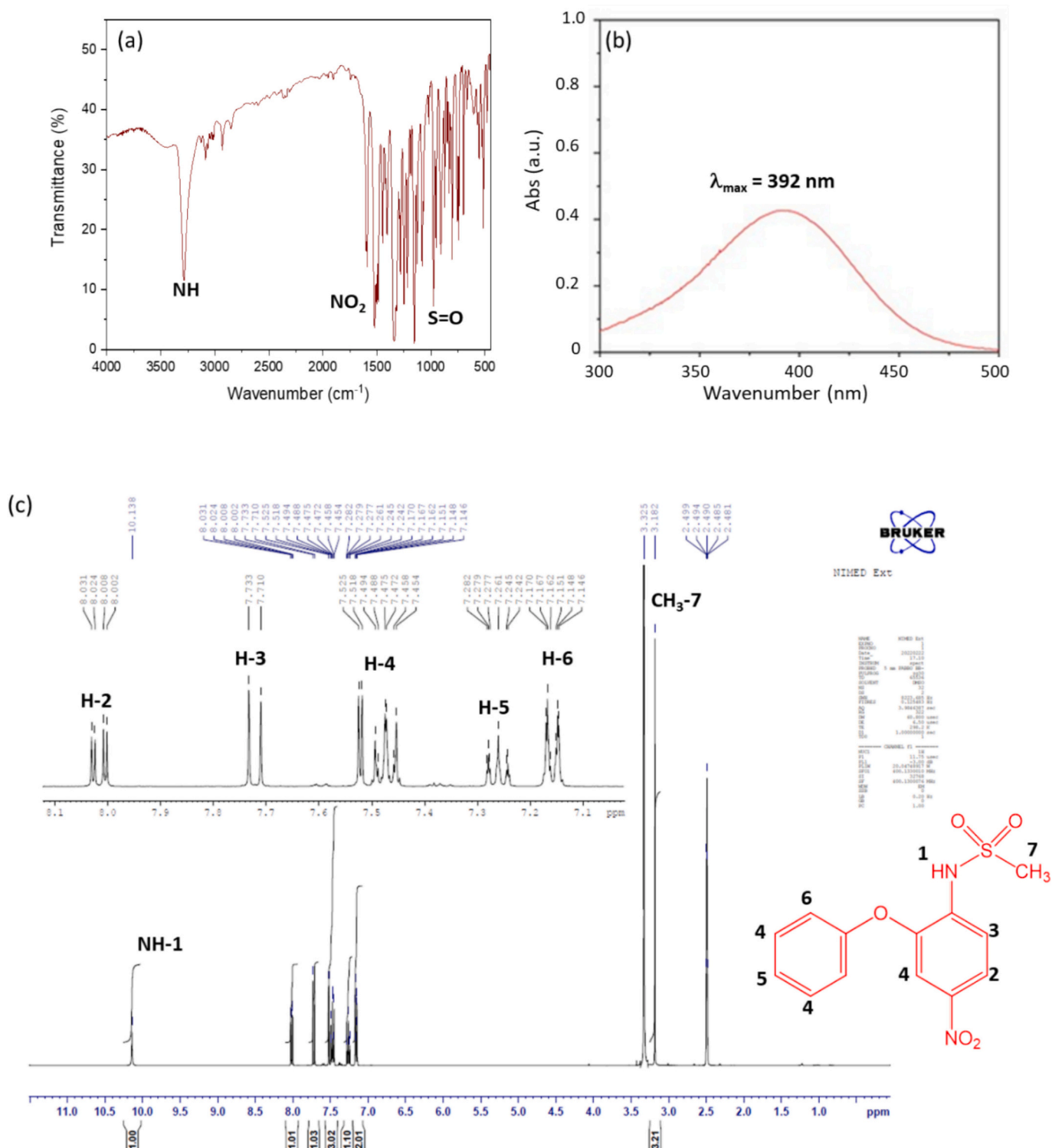


Fig. 1. FTIR (a), UV/vis (b), and ^1H NMR spectra (c) of NIM extracted from generic tablets.

2.6. Analytical methods

The NIM concentration was determined using a high-performance liquid chromatograph equipped with a diode array detector (HPLC-DAD, Hitachi Elite LaChrom). An isocratic method was employed, using a mix of 30% disodium phosphate solution (with pH adjusted to 2.8 with orthophosphoric acid) and 70% methanol as the eluent, at a flow rate of 1.0 mL/min. The separation of the compound was carried out on a Purospher STAR RP-18 column (5 mm, 250×4.0 mm) at 25°C , and the detection was conducted by UV absorbance measurement at a wavelength of 220 nm. The concentrations of carboxylic acids (intermediate compounds formed during the reaction) were quantified by chromatography using the same HPLC-DAD apparatus. The separation occurred in a Rezex ROA-Organic Acid H^+ (8%) column (250×4.6 mm) operating at 25°C , with a flow rate of 0.17 mL/min of 2.5 mM H_2SO_4 . In this case, the determinations were performed with a wavelength of 210 nm.

The TOC was determined according to Method 5310 D [40]; in this determination, the carbon dioxide formed during the catalytic oxidation of the organic carbon at 720°C is quantified by an infrared detector. For this purpose, a Shimadzu's Total Organic Carbon Analyzer TOC-L, coupled with the ASI-L autosampler, was used.

The hydrogen peroxide concentration remaining in the solution was determined according to the method developed by Sellers [41]. In this method, the hydrogen peroxide reacts with potassium titanium (IV) oxalate to form a yellow complex, and the colour intensity is measured by absorbance at 400 nm using a spectrophotometer (Thermo Electron Corporation, model Helios γ).

Electrospray ionization mass spectrometry (ESI-MS) analysis was carried out in a Thermo LxQ equipment to identify the degradation products of NIM.

All analytical determinations were carried out in duplicate, and the standard variation was below 2% for all parameters analysed.

3. Results and discussion

3.1. Nimuselide identification

The active pharmaceutical ingredient, NIM, was isolated from the generic formulation *Nimesulida* (Pharmakern, 100 mg/tablet). The extraction was carried out using five tablets, yielding NIM with an extraction yield of 80%. The purity of the NIM obtained from the commercial generic was confirmed by FTIR, NMR, and UV/vis spectroscopies (Fig. 1).

The FTIR spectrum of NIM extracted from generic tablets exhibits the typical features of a pure NIM molecule, proving its very high purity [42,43]. Notably, a distinctive band at 3284 cm^{-1} , indicative of the secondary amine (N—H stretch) group is clearly visible. Additionally, the presence of the S=O bond is evident from the bands observed at 1153 cm^{-1} and 1339 cm^{-1} , ascribable to the symmetric and asymmetric stretching vibrations of the SO_2 group, respectively. Furthermore, bands at 1311 (symmetric stretching) and 1523 (asymmetric stretching) cm^{-1} are also observed and can be assigned to the vibrational modes of the aryl NO_2 group.

The appearance of the typical band of the NIM molecule at 392 nm in the UV/vis spectrum supports the FTIR results [8].

A singlet with a chemical shift at 10.1 ppm was identified in the ^1H NMR spectrum of the NIM extracted, which is attributed to the N—H proton of the sulphonamide group [44]. The protons of the methyl group (CH_3) are responsible for a singlet signal at 3.8 ppm. In the 7.1 to 8.0 ppm region, it is possible to observe the chemical shifts associated with the protons present in the aromatic rings. No peaks corresponding to possible impurities are detected, confirming that the drug is pure.

3.2. Catalysts' characterization

The nitrogen adsorption isotherms were utilized to obtain the

textural characteristics of the (MFe)NaY catalysts, while the SEM images of all bimetallic catalysts confirm that the ion exchange method preserved the original morphology of the pristine NaY (Fig. 2).

In spite of the presence of the metals, the average particle sizes remain quite similar to those of the NaY zeolite, ranging approximately between 700 and 800 nm for all the catalysts. This observation shows that the combined addition of the metals to the zeolite is suitable.

As expected, all nitrogen adsorption isotherms of the (MFe)NaY catalysts follow the same pattern as those of NaY and, according to the IUPAC classification, the isotherms are type I and are characteristic of microporous solids [35,45,46]. Table 2 shows the results of the N_2 physisorption analysis for NaY and the (MFe)NaY catalysts.

Compared to NaY, a decrease in both S_{BET} and the external surface area, S_{ext} , is observed for all the catalysts, the latter being one order of magnitude lower for the (MFe)NaY zeolites ($14\text{--}31\text{ m}^2/\text{g}$) than for the pristine zeolite ($102\text{ m}^2/\text{g}$); this suggests that the metals may be primarily localized on the external surface. In addition, a diminution of the total volume (V_{total}) can be noted for all the (MFe)NaY catalysts, mainly due to the reduction in the micropore volume (V_{micro}), suggesting that the exchanged metals are also located inside the microporous channels.

In order to study the location of the metals within the zeolite structure, the catalysts were analysed by XPS. In the survey XPS spectra of the (MFe)NaY catalysts, the predominant surface elements commonly found in these types of catalysts (oxygen, silicon, aluminium, and sodium) were determined through the detection of photoelectron peaks corresponding to oxygen (O 1s), silicon (Si 2p), aluminium (Al 2p), and sodium (Na 1s) [36]. Likewise, Fe, Cu, Ni, Co, and Zn are identified on the surface of the zeolite according to the binding energies (BE) of the elements in the Fe 2p, Cu 2p, Ni 2p, Co 2p and Zn 2p regions. The high-resolution XPS spectra of Co 2p and Zn 2p have been previously reported in the literature [36]. Fig. 3 shows the high-resolution XPS spectra of the (CuFe)NaY and (CoFe)NaY catalysts in the copper and iron regions, respectively, as an example.

The high-resolution Fe 2p spectra of the various (MFe)NaY catalysts show two distinct peaks in both $2\text{p}_{1/2}$ and regions, ranging from 723 to 730 eV and 710–718 eV, respectively. These BE values are associated with the ferric ions (Fe^{3+}) [36,47–49]. All bimetallic catalysts exhibit the same spectral features, confirming that the oxidation state of iron remains constant regardless of its surface and the different surface iron content.

In the case of (CuFe)NaY, the Cu 2p region displays a thin peak at 952 eV for Cu $2\text{p}_{1/2}$ and two peaks in the range of 932–936 eV for Cu $2\text{p}_{3/2}$, which correspond to the Cu^{2+} oxidation state, consistent with the NIST XPS database and literature [48–50].

In the Ni 2p region, the very low Ni signal prevented the acquisition of a high-resolution spectrum [36]. Therefore, the observed binding energy of 857.75 eV in the survey spectrum is attributed to the overall 2p region of the Ni^{2+} oxidation state [36,49,51]. For (CoFe)NaY, the BE values identified in the high-resolution spectra of Co 2p region are attributed to the presence of Co^{2+} [36,49,52]. In the case of (ZnFe)NaY, the BE values identified in the high-resolution spectra of Zn 2p region are attributed to the oxidation state of zinc in the form of Zn^{2+} [36,48,49,52].

Although the same concentration (1 mmol) of metal ions was used in each starting solution for ion exchange (see Section 2.3), the NaY zeolite exhibited a higher affinity for iron compared to the other metals. Table 3 shows the surface composition determined by XPS together with the bulk composition determined by ICP-AES.

The small decrease in the Si/Al molar ratio determined by ICP-AES for the (MFe)NaY catalysts in comparison with the starting NaY (Si/Al = 2.40) suggests a slight degree of dealumination of the FAU structure following the simultaneous introduction of metals into the zeolite. Noteworthy, the Si/Al molar ratio values obtained by XPS for the bimetallic catalysts are higher than those of NaY and all are significantly higher than those obtained by chemical analysis for the bulk phase, suggesting that the surface of the zeolite and (MFe)NaY catalysts is

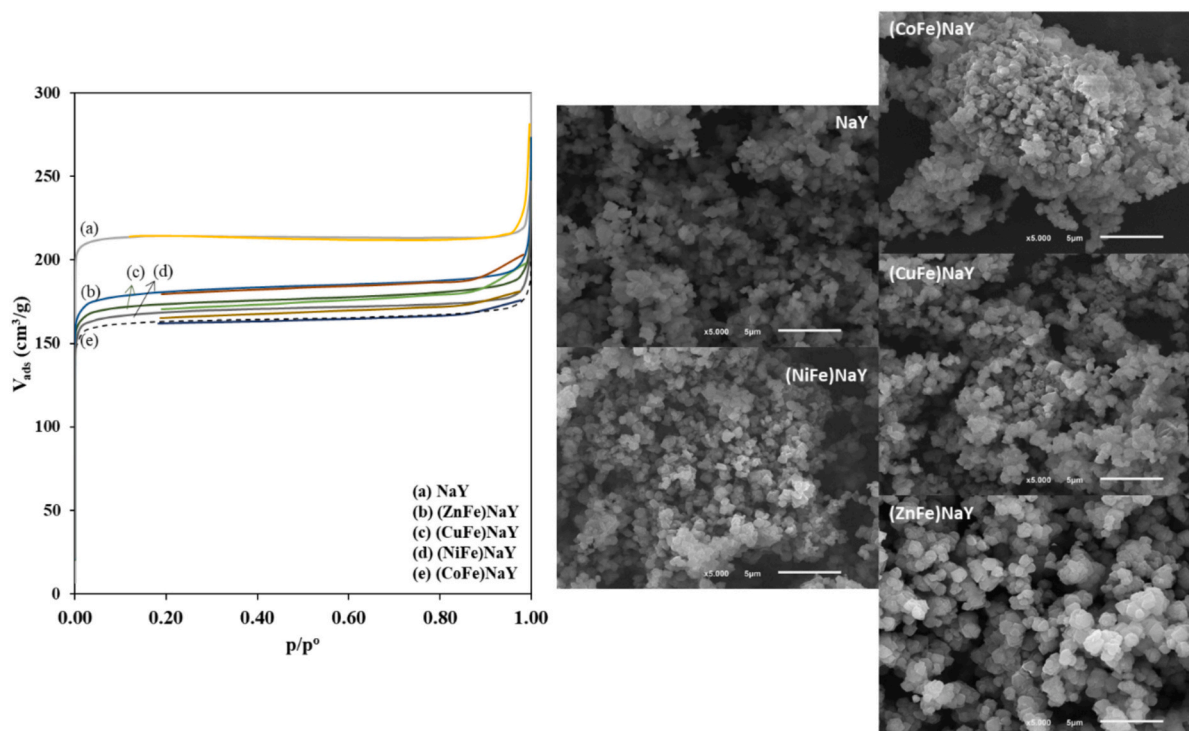


Fig. 2. N_2 adsorption isotherms and SEM images of NaY and (MFe)NaY catalysts.

Table 2

Textural values obtained for (MFe)NaY catalysts and NaY from N_2 adsorption analysis.

Samples	S_{BET} (m^2/g) ^a	V_{total} (cm^3/g) ^b	S_{ext} (m^2/g) ^c	V_{micro} (cm^3/g) ^c	V_{meso} (cm^3/g) ^d	S_{DR} (m^2/g) ^e	$V_{DR,mic}$ (cm^3/g) ^e	$V_{HK,total}$ (cm^3/g) ^f	$V_{HK,mic}$ (cm^3/g) ^f
NaY	907	0.35	102	0.29	0.06	938	0.33	0.33	0.33
(ZnFe)NaY	716	0.31	31	0.24	0.07	794	0.28	0.30	0.28
(CuFe)NaY	710	0.29	27	0.23	0.06	769	0.27	0.29	0.27
(NiFe)NaY	687	0.28	25	0.22	0.06	736	0.26	0.27	0.26
(CoFe)NaY	671	0.27	14	0.22	0.05	715	0.25	0.26	0.25

^a Specific surface area calculated from the BET equation.

^b Total pore volume determined from the amount adsorbed at $P/P_0 = 0.99$.

^c External surface area and micropore volume calculated using the *t*-method.

^d Mesoporous volume calculated from the difference $V_{total} - V_{micro}$.

^e Surface area and microporous volume calculated using the Dubinin-Radushkevich equation.

^f Total and micropore volumes calculated using the Horvath-Kawazoe equation.

enriched in silicon.

Indeed, the Fe content determined by ICP-AES remains almost constant at around 5.00 wt% for all the (MFe)NaY catalysts. On the contrary, the amount of the second metal ion, ranging between 0.98 and 1.99 wt%, seems to depend on its nature, varying in the order $Cu(II) > Zn(II) > Ni(II) > Co(II)$. The Fe/M molar ratio is the highest for (CoFe)NaY (5.48), followed by (ZnFe)NaY (4.52), (NiFe)NaY (4.24), and (CuFe)NaY (2.86). The results of XPS analysis show that the surface content of both Fe and M is significantly lower than that in the bulk, suggesting a non-homogeneous distribution of metal ions, which are preferentially localized within the structure of the (MFe)NaY catalysts (Table 3). Interestingly, the surface Fe/M ratio values vary in a much wider range (from 0.66 to 12.46) than those of the bulk (from 2.86 to 5.48) and with an almost reversed order, i.e. (NiFe)NaY (12.47) > (CuFe)NaY (3.13) > (ZnFe)NaY (0.85) > (CoFe)NaY (0.66). The lower Fe/M ratio determined in the last catalysts show that 58% of Zn and 36% of Co are in the external surface. In the case of (NiFe)NaY, the much higher Fe/M value indicates a preferential location of iron ions in the outer cavities or on the surface of the zeolite.

In addition, X-ray diffraction (XRD) analysis [36] indicates that the characteristic crystalline structure of the NaY zeolite was preserved

following metal incorporation. This observation is confirmed by Fourier-transform infrared (FTIR) spectroscopy, which reveals only minor structural modifications upon metal introduction [36]. These findings are in good agreement with the results obtained from both N_2 adsorption isotherms and scanning electron microscopy (SEM) analyses (see Fig. 2 and Table 2). Interestingly, XRD analysis using the Debye-Scherrer equation revealed that (ZnFe)NaY exhibits the largest crystallite size (87.2 nm), while (CoFe)NaY shows the smallest (35.5 nm) [36]. These crystallite sizes, along with the distribution of metals within the framework, are expected to significantly influence the catalytic performance.

3.3. Fenton-type reaction

Fig. 4 shows the results of the blank tests carried out without H_2O_2 in the presence of the catalysts to evaluate the contribution of adsorption to NIM removal. Regarding adsorption, its contribution to NIM elimination and TOC reduction is relatively low, reaching a maximum of 17% after 120 min for NaY (see Fig. 4a and b), with the maximum adsorbed amount being 34.6 mg/g, which is higher than that achieved by other authors when they used silica aerogel (15.4 mg/g) [53] or

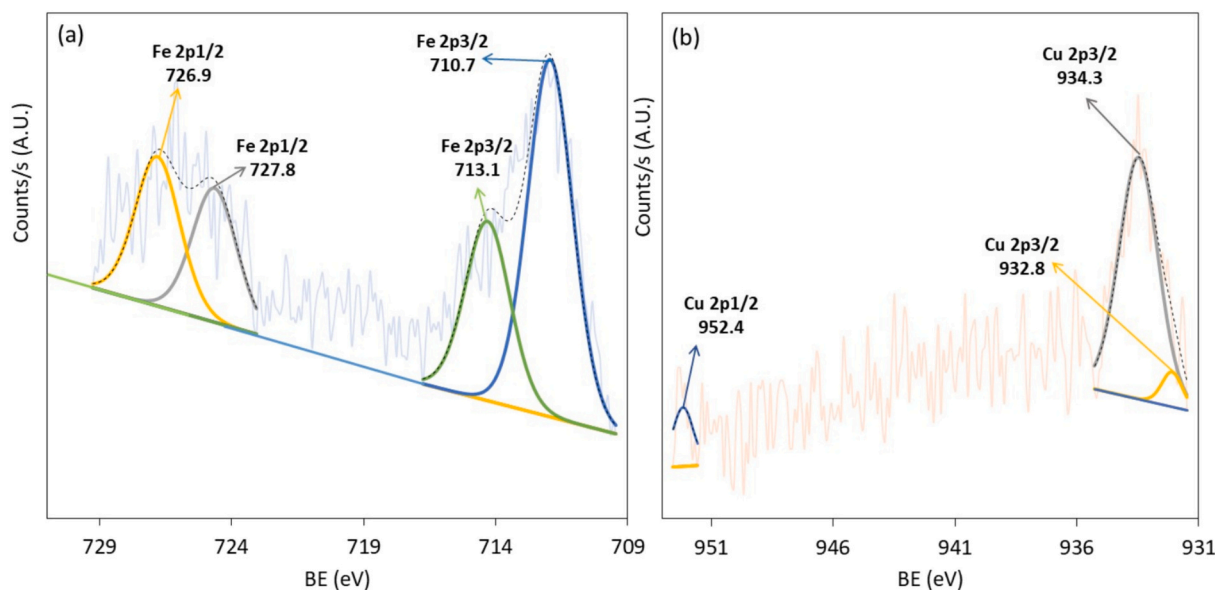


Fig. 3. High-resolution XPS spectra of Fe 2p and Cu 2p photoelectron regions from (CoFe)NaY (a) and (CuFe)NaY (b).

Table 3

Chemical results obtained for (MFe)NaY catalysts from ICP-AES and XPS analyses.

Samples	Fe (wt%)		M ^a (wt%)		Si/Al ^b	
	ICP-AES	XPS	ICP-AES	XPS	ICP-AES	XPS
NaY	–	–	–	–	2.40	3.59
(CuFe)NaY	5.00	0.33	1.99	0.12	2.23	5.09
(CoFe)NaY	5.09	0.22	0.98	0.35	2.29	7.55
(NiFe)NaY	5.20	0.83	1.29	0.07	2.30	4.50
(ZnFe)NaY	5.29	0.57	1.37	0.79	2.25	5.27

^a M = Cu, Co, Ni or Zn.

^b Si/Al molar ratio.

β -cyclodextrin-grafted fuffa biomass (5.37 mg/g) [54] as adsorbents, but lower than that obtained with activated carbon (64.7 mg/g) [55] and activated carbon prepared from cocoa shell (74.8 mg/g) [8]. The maximum NIM and TOC removals by adsorption were achieved with NaY, to the detriment of (MFe)NaY; in general, adsorption performance follows the trend: NaY > (ZnFe)NaY > (CuFe)NaY > (NiFe)NaY >

(CoFe)NaY. These results can be explained by the fact that the pristine zeolite has a higher S_{BET} , V_{total} and S_{ext} compared to the (MFe)NaY catalysts (see Table 2, which data follow exactly the same trend).

The results of the blank tests performed in the presence of hydrogen peroxide (H_2O_2) with or without the catalysts are reported in Fig. 5a and b for NIM and TOC removal, respectively, whereas Fig. 5c shows the percentage of H_2O_2 consumption. It was found that H_2O_2 alone showed the worst performance in the reaction, achieving only 7.1, 1.7, and 50.0% for NIM and TOC removal and H_2O_2 consumption, respectively, most probably due to its low oxidation potential (1.78 eV [56]). By converse, the presence of the bimetallic catalysts significantly increases the efficiency of the process, reaching a percentage of NIM degradation in the range 32–47% (Fig. 5a) and of mineralization degrees between 19 and 26% (Fig. 5b). These results can be ascribed to the formation of hydroxyl radicals, which have a high oxidation potential (2.8 eV [56]).

The best performance, 46.9% of NIM oxidation and 25.1% of mineralization, together with the highest H_2O_2 consumption (70.0%), were shown by (CoFe)NaY, for which the Fe/M molar ratio is the highest in the bulk (5.48) but the lowest at the surface (0.66) (see Table 3), indicating different amounts of Fe and Co at the surface of the zeolite,

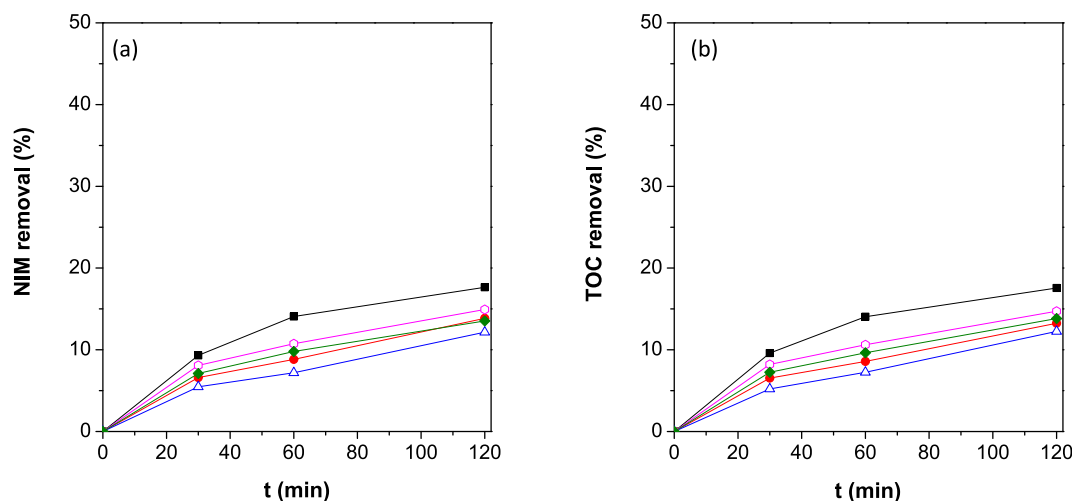


Fig. 4. Contribution of adsorption to the NIM (a) and TOC (b) removal as a function of time for NaY (■), (CoFe)NaY (Δ), (CuFe)NaY (◆), (NiFe)NaY (●) and (ZnFe)NaY (◊). Experimental conditions: pH = 5.70 (natural), $T = 25^\circ\text{C}$, [(MFe)NaY] = 0.2 g/L and [NIM] = 40 mg/L.

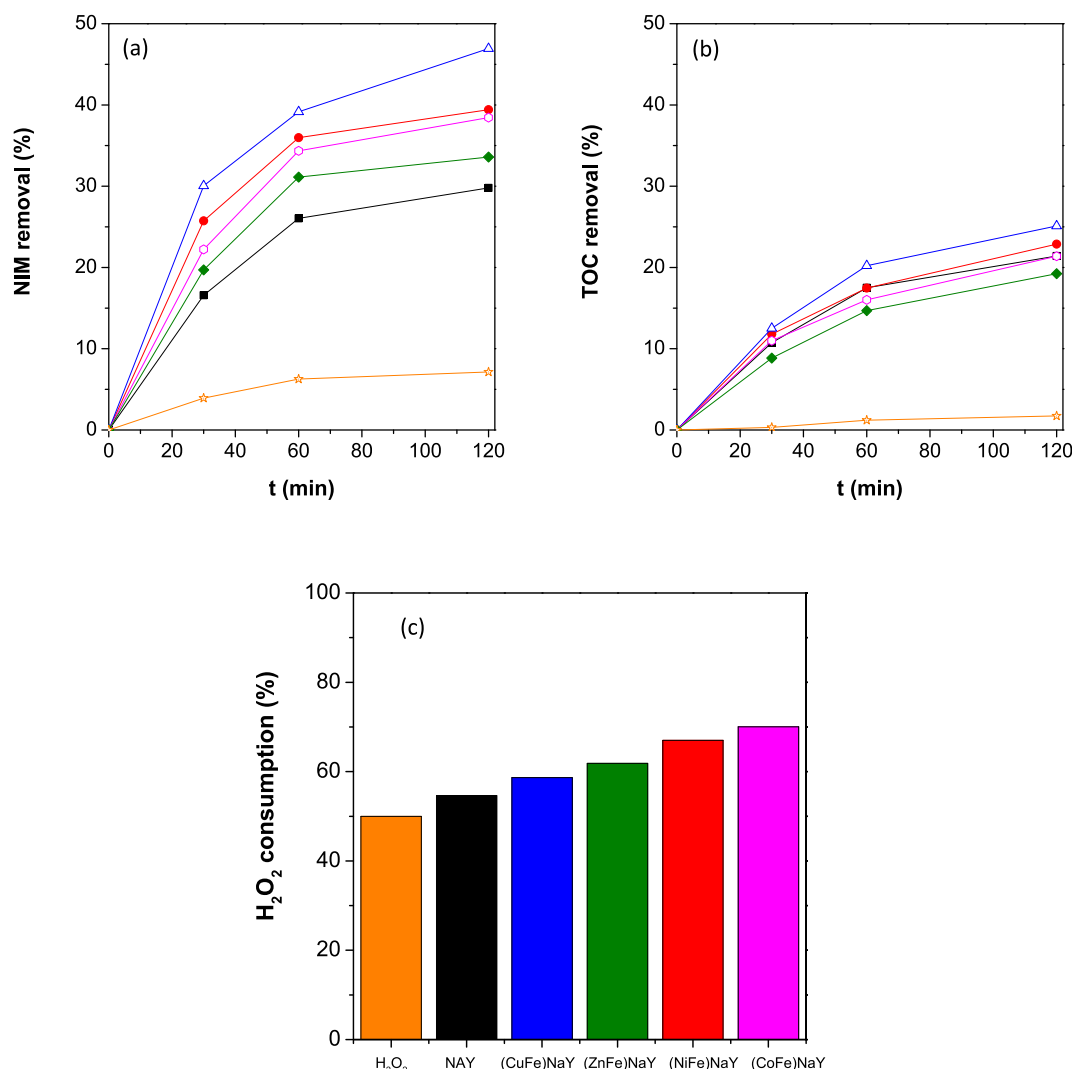


Fig. 5. Percentage of NIM (a) and TOC (b) removal as a function of time; hydrogen peroxide consumption after 2 h (c) in presence of H₂O₂ (Δ), NaY + H₂O₂ (■), (CoFe)NaY + H₂O₂ (◆), (CuFe)NaY + H₂O₂ (✱), (NiFe)NaY + H₂O₂ (●) and (ZnFe)NaY + H₂O₂ (◇). Experimental conditions: pH = 5.70 (natural), T = 25 °C, [H₂O₂] = 100 mg/L, [(MFe)NaY] = 0.2 g/L and [NIM] = 40 mg/L.

which can support the formation of more hydroxyl radicals.

(CoFe)NaY has demonstrated high performance in Fenton-type reactions compared to other catalysts, primarily due to its enhanced redox activity and synergistic electron transfer mechanisms. The Co(II)/Co(III) redox couple plays a crucial role in accelerating the Fe(III)/Fe(II) reduction cycle, facilitating faster electron transport and maintaining the availability of Fe(II) for the decomposition of H₂O₂ into hydroxyl radicals [57]. In contrast, Zn²⁺ is redox-inactive, while Ni²⁺ and Cu²⁺ exhibit relatively slower redox kinetics [27].

It should be highlighted that leaching of the metals occurred to some extent during the reaction (Table 4), being more pronounced for the (ZnFe)NaY catalyst (11.6% and 17.7% for Fe and Zn, respectively). By converse, a very low amount of metals was released into solution in the

case of (CoFe)NaY (0.5% and 1.2% for Fe and Co, respectively), indicating that they are better stabilized in the zeolite framework.

With the best performing catalyst ((CoFe)NaY) additional tests were carried out in the presence of dimethyl sulfoxide (DMSO), sodium azide and ascorbic acid (scavenger:H₂O₂ molar ratio = 10) as scavenger of hydroxyl radicals [58], singlet oxygen [59] and superoxide radicals [60], respectively, to evaluate the reaction mechanism via the formation of hydroxyl radicals.

In the presence of the DMSO, both NIM oxidation and its mineralization decreased significantly (see Fig. 6), most likely due to the decrease in the number of hydroxyl radicals available to oxidize NIM and the intermediate compounds, since they primarily react with DMSO. On the other hand, in the presence of sodium azide and ascorbic acid, the efficiency remains practically equal to that achieved when the Fenton process is performed without quenchers. This finding confirm that the NIM oxidation mechanism is radical-based, but mostly through hydroxyl radicals generated from the reaction of hydrogen peroxide and (CoFe)NaY.

It is worth stressing that the presence of scavengers did not affect the metal leaching, the extent of which was found to be the same observed in the absence of quenchers for both Fe and Co, (1.2% for Co and 0.5% for Fe, Table 4).

An additional run was performed with (CoFe)NaY to assess the

Table 4
Metals leaching during Fenton's reaction with different catalysts.

Catalyst	Metals leaching (%)				
	Ni	Zn	Cu	Co	Fe
(NiFe)NaY	6.8	–	–	–	0.5
(ZnFe)NaY	–	17.7	–	–	11.6
(CuFe)NaY	–	–	9.6	–	3.5
(CoFe)NaY	–	–	–	1.2	0.5

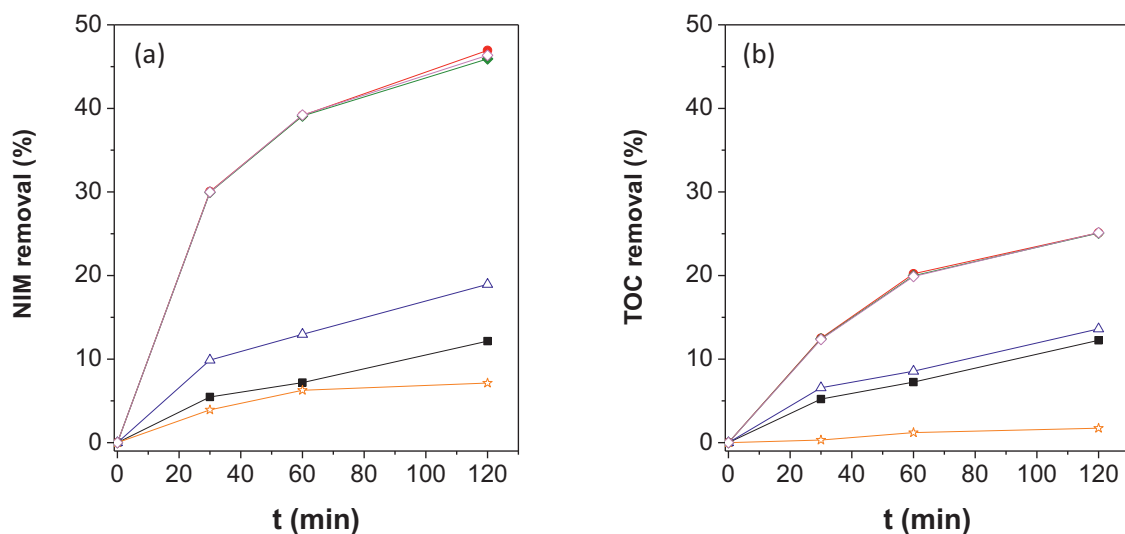


Fig. 6. Temporal evolution of NIM (a) and TOC (b) removals with (CoFe)NaY (■), in presence of H₂O₂ (★), with (CoFe)NaY + H₂O₂ (●), and with (CoFe)NaY + H₂O₂ + DMSO (△) or (CoFe)NaY + H₂O₂ + sodium azide (◆) or (CoFe)NaY + H₂O₂ + ascorbic acid (◇). Experimental conditions: pH = 5.70 (natural), $T = 25\text{ }^{\circ}\text{C}$, $[\text{H}_2\text{O}_2] = 100\text{ mg/L}$, $[(\text{CoFe})\text{NaY}] = 0.2\text{ g/L}$, Scavenger:H₂O₂ molar ratio = 1:10 and $[\text{NIM}] = 40\text{ mg/L}$.

efficiency of the Fenton-type reaction over time, as the results above indicate that the process performance continues to improve beyond 120 min. For this purpose, samples were taken up to 240 min after the reaction started (Fig. 7). The percentages of NIM and TOC removal over time shows a rapid growth during the first 30 min of reaction, followed by a slower increase, reaching a nearly constant value after 180 min of

reaction. This trend may be explained by the very fast consumption of hydrogen peroxide in the same time range (around 50%), which generates a high concentration of hydroxyl radicals available to oxidize NIM and intermediates formed. Between 60 min and 180 min of reaction, the process efficiency continues to increase, but more slowly, as the rate of radical formation decreases and the oxidant consumption rate slows. For

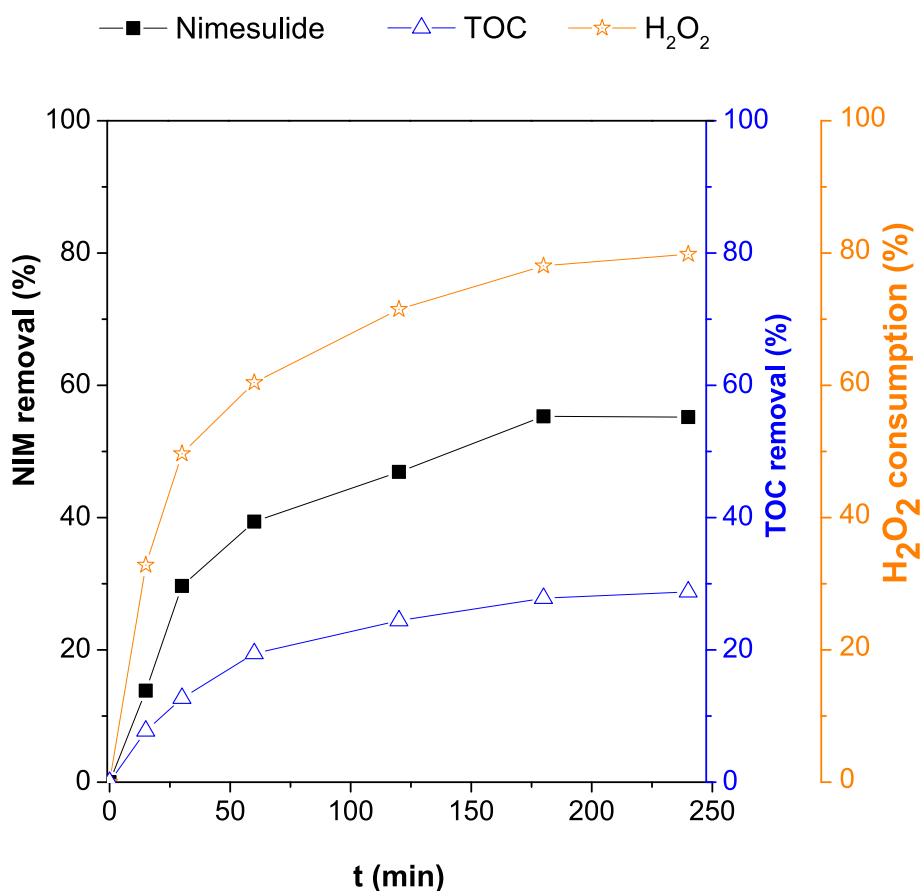


Fig. 7. Temporal evolution of NIM (■) and TOC (△) removals and hydrogen peroxide consumption (★) by Fenton-type reaction. Experimental conditions: pH = 5.70 (natural), $T = 25\text{ }^{\circ}\text{C}$, $[\text{H}_2\text{O}_2] = 100\text{ mg/L}$, $[(\text{CoFe})\text{NaY}] = 0.2\text{ g/L}$ and $[\text{NIM}] = 40\text{ mg/L}$.

reaction times longer than 180 min, NIM and TOC removals and H_2O_2 consumption nearly stabilize, indicating that the Fenton-type reaction has ceased (or considerably slowed down).

The content of Co and Fe released in solution due to leaching phenomena was found to increase from 1.2 to 2.2 and from 0.5 to 0.8 wt%, respectively, between 120 and 240 min. A reaction time of 180 min, after which the amount of leached Co and Fe was 1.5 and 0.6 wt%, respectively, was selected to carry out the parametric study, as well as the experimental design.

3.3.1. Central composite design (CCD) model

The CCD model was employed to determine the significance of key factors (pH, temperature, catalyst dosage, and H_2O_2 concentration) on the removal and mineralization of NIM, as well as on the oxidant consumption. A preliminary study was conducted to assess the individual effects of each parameter, with the primary objective of defining appropriate factor levels for the experimental design.

As shown in Fig. 8a, process efficiency increases as the pH rises from 2.0 to 3.0, but decreases at higher pH values. This behaviour is due to the decomposition of H_2O_2 into water and oxygen for pH values greater than 4.0–5.0 [61], which reduces the amount of hydroxyl radicals. This is further supported by the fact that the increased oxidant consumption observed at the highest pH values did not result in any improvement in NIM and TOC removal. Metal leaching still occurred, being more pronounced at lower pH values and decreasing with increasing pH (Fig. 8a). The best pH found (3.0) is equal with that reported by Lu *et al.* [62], who evaluated the degradation of Rhodamine B using this process catalysed with BiFeO_3 magnetic nanoparticles, by Wang *et al.* [63], who studied the removal of phenol using Fe_3O_4 MCNs as the catalyst, and by El Mrabet *et al.* [36], who assessed the azorubine dye removal applying bimetallic-zeolite as catalyst of the process. Regarding the influence of H_2O_2 concentration, the removal of NIM and TOC increases with the oxidant dose up to 100 mg/L, after which a decrease in the efficiency of the Fenton-type reaction is observed (see Fig. 8b); a similar tendency

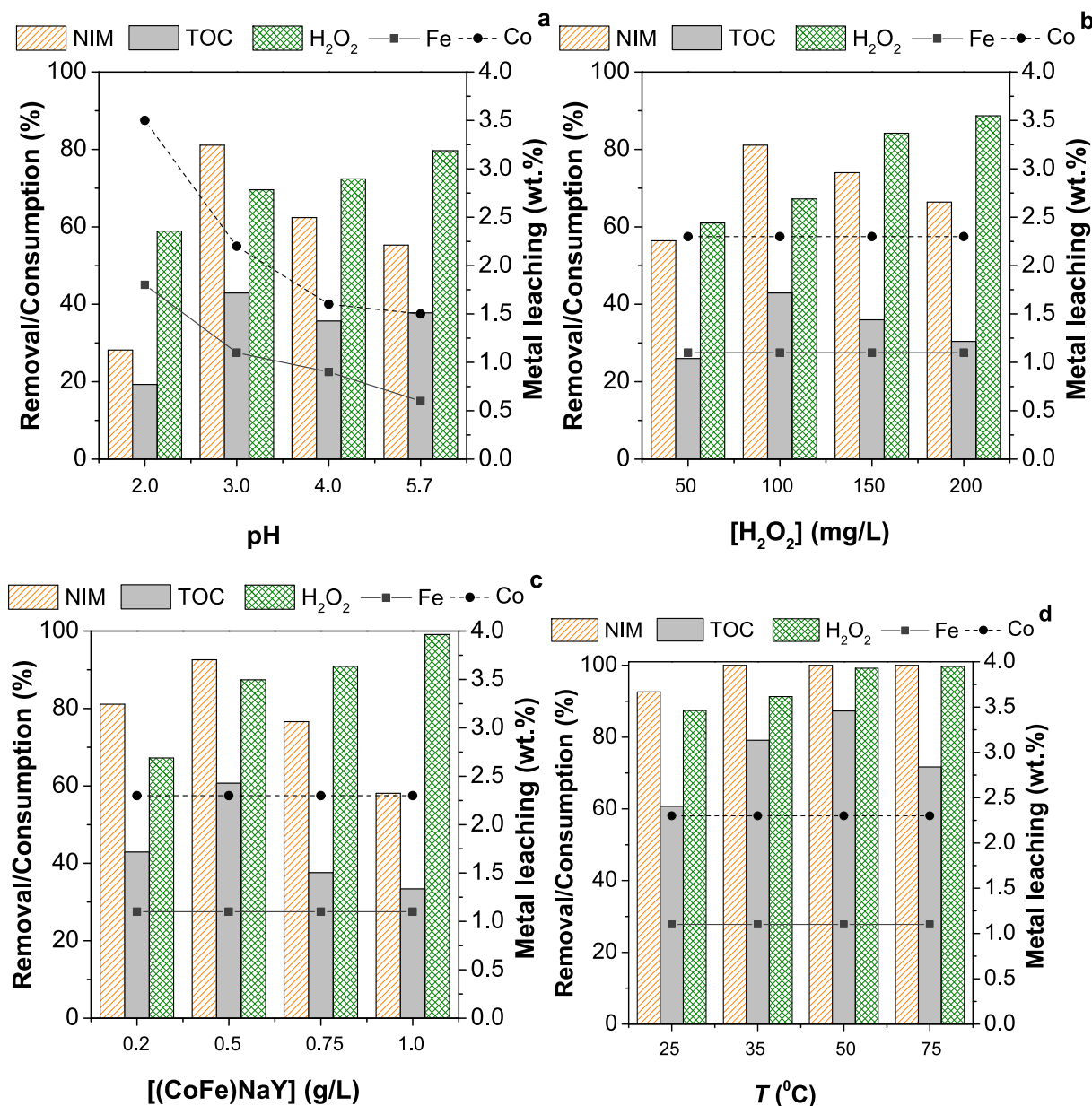


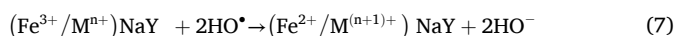
Fig. 8. NIM and TOC removals, hydrogen peroxide consumption and Fe and Co leaching after 180 min of reaction for different pHs (a), H_2O_2 (b) and catalyst (c) concentrations and temperatures (d). Experimental Conditions for $[\text{NIM}] = 40 \text{ mg/L}$: a) $T = 25^\circ\text{C}$, $[\text{H}_2\text{O}_2] = 100 \text{ mg/L}$ and $[(\text{CoFe})\text{NaY}] = 0.2 \text{ g/L}$; b) $T = 25^\circ\text{C}$, $\text{pH} = 3.0$ and $[(\text{CoFe})\text{NaY}] = 0.2 \text{ g/L}$; c) $T = 25^\circ\text{C}$, $\text{pH} = 3.0$ and $[\text{H}_2\text{O}_2] = 100 \text{ mg/L}$; d) $\text{pH} = 3.0$, $[\text{H}_2\text{O}_2] = 100 \text{ mg/L}$ and $[(\text{CoFe})\text{NaY}] = 0.5 \text{ g/L}$.

was reported by other authors when applying the heterogeneous Fenton process to degrade a variety of pollutants [39,64,65]. This result may be explained by the occurrence of the undesired scavenging reaction (Eq. 6) between hydrogen peroxide and the hydroxyl radicals that leads to the formation of $\text{HO}_2\cdot$ species [66,67] with a lower oxidation potential (1.70 eV) than the hydroxyl radicals (2.80 eV) [56]. This assumption is supported by the observed increase in the oxidant consumption as its concentration in the reacting mixture is increased.



Fig. 8c shows the results obtained with different catalyst concentrations. The highest NIM and TOC removal efficiencies, 92.6% and 60.7%, respectively, were achieved at a (CoFe)NaY dose of 0.5 g/L. However, further increases in catalyst concentration to 0.75 and 1.0 g/L led to a decline in removal performance, as also reported in the study developed by Jiménez *et al.* [68], who evaluated the treatment of distillery wastewater, and by Wang *et al.* [63], who assessed the oxidation of phenol. Additionally, H_2O_2 consumption increased with catalyst concentration, being completely consumed at a (CoFe)NaY dose of 1.0 g/L. These results may be explained by the occurrence of the scavenging reaction (Eq. (7)) between the catalyst and hydroxyl radicals [67], which leads to a reduction in the amount of $\text{HO}^\bullet$ species available to oxidize NIM and the intermediate compounds formed.

$$Y_1 = 100 - 4.84 X_1 - 2.56 X_2 + 1.68 X_3 + 3.18 X_4 - 18.39 X_1^2 - 9.37 X_2^2 - 16.33 X_3^2 - 14.03 X_4^2 - 14.49 X_1 X_2 - 5.64 X_1 X_3 - 6.15 X_1 X_4 - 0.84 X_2 X_3 + 0.20 X_2 X_4 - 0.58 X_3 X_4 \quad (10)$$



Temperature positively affected the reaction up to 50 °C, with NIM removal increasing from 92.6 to 100.0%, TOC removal from 60.7 to 88.0%, and oxidant consumption from 87.4 to 99.3% as temperature increased from 25 to 50 °C (Fig. 8d). This enhancement is ascribable to faster reaction kinetics, in agreement with Arrhenius' law. However, at 75 °C, both NIM degradation and hydrogen peroxide consumption remained constant, while mineralization decreased to 71.7%, likely due to thermal decomposition of H_2O_2 into water and oxygen above 50 °C [51], which reduces hydroxyl radicals availability for oxidizing intermediate compounds. It should be noted that neither the oxidant nor the catalyst concentration, not even the temperature, influenced the leaching of metals from the (CoFe)NaY, which was found to be 2.2–2.3 and 1.1% for Co and Fe, respectively. The best temperature found is consistent with that reported in other studies when applying the heterogeneous Fenton process [34,61].

The first-order kinetic model was applied to describe the degradation of NIM in the Fenton process catalyzed by (CoFe)NaY. In this model, the reaction rate is directly proportional to the pollutant concentration (see Eq. (8)), so the degradation slows as NIM is consumed. Linearization of the model (Eq. (9)) allowed fitting the experimental data at different temperatures (see Fig. S2 in Supporting Information), showing that the apparent rate constant (k_{app}) increased with temperature (0.024, 0.069, and 0.158 L/(g_{cat}·min) at 25, 35, and 50 °C, respectively) indicating faster reaction kinetics at higher temperatures. This trend reflects a more efficient generation of reactive $\text{HO}^\bullet$ radicals on the catalyst surface, enhancing the overall degradation process. Analysis using the Arrhenius equation (see its linearization in Fig. S3 of Supporting Information) provided a pre-exponential factor $k_0 = 6.2 \times 10^6$ L/(g_{cat}·min) and an activation energy $E_a = 59.1$ kJ/mol, confirming that NIM degradation is an activation-controlled process.

$$\frac{dC}{dt} = -k C \frac{W}{V} = -k_{\text{app}} C \quad (8)$$

$$\ln\left(\frac{C}{C_0}\right) = -k_{\text{app}} t \quad (9)$$

In these equations, C_0 and C (in mg/L) correspond to the concentration of NIM in time (t) equal to 0 min and instant t , respectively, k_{app} is the apparent reaction rate constant in min^{-1} .

The parametric study allowed the selection of the optimal operating conditions (pH = 3.0, $[\text{H}_2\text{O}_2] = 100$ mg/L, $[(\text{CoFe})\text{NaY}] = 0.5$ g/L and $T = 50$ °C) to be applied in the (CoFe)NaY-catalyzed Fenton-type process. These conditions were considered the zero level to carry out in the described CCD (Table 1). Several experiments are performed according with the CCD matrix (see Table S1 in supporting information), with the center point performed in quintuplicate (runs 17–21).

A quadratic model was developed to describe the relationship between NIM removal (Y_1) and the independent variables selected through the CCD. The model is expressed in terms of coded variables using a second-order polynomial equation, as shown in Eq. 10. This equation includes both the linear and interaction terms of the factors, representing their combined effects on NIM degradation.

The model was evaluated using the determination coefficient (R^2) and the F-test for regression [69]. The model with a determination coefficient (R^2) and F value for regression (F_{reg}) corresponding to 0.760 and 3.190 (probability (p) = 0.0189), respectively, was considered adequate for the response surface methodology (RSM). Fig. 9 presents a Pareto chart indicating the significance of the model parameters in NIM degradation. Based on the results, the quadratic (second-order) term of temperature (X_1) emerged as the most significant parameter influencing NIM removal. In contrast, the interaction terms between H_2O_2

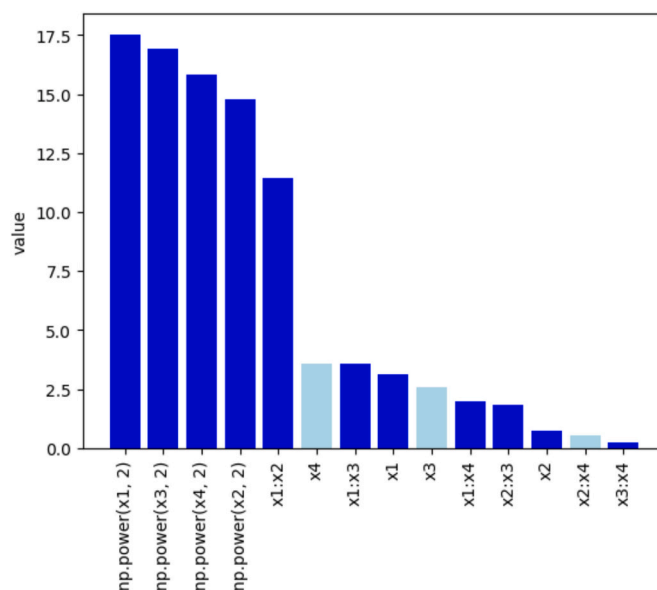


Fig. 9. Pareto chart with negative (blue) and positive (light blue) coefficients corresponding to NIM degradation.

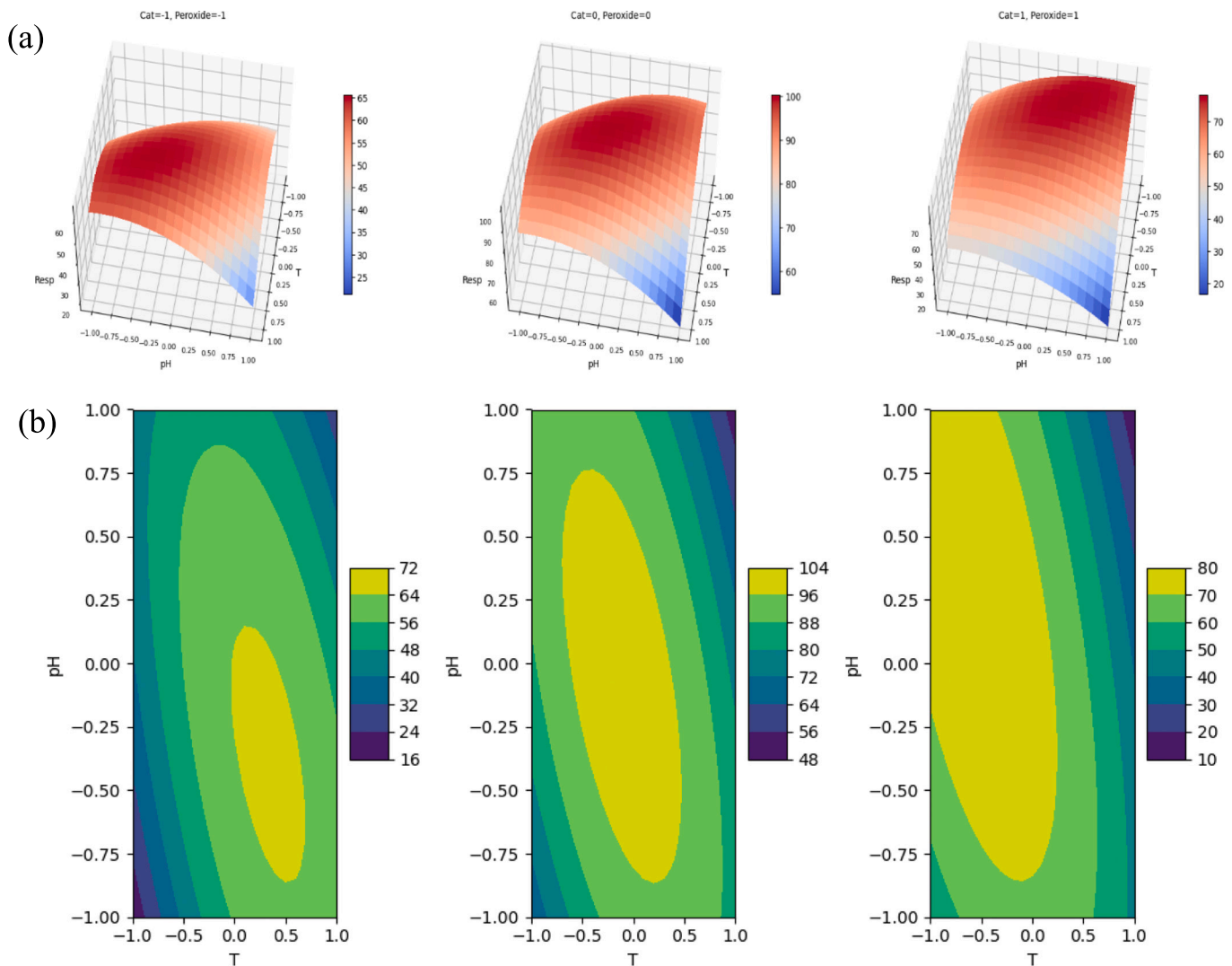


Fig. 10. (a) Surface plots and (b) Contour plots for NIM removal vs. pH and T at constant levels of H_2O_2 and catalyst amounts.

concentration and catalyst amount (X_3X_4), as well as between pH and catalyst amount (X_2X_4), were found to have minimal impact – please refer also to Eq. (10).

Fig. 10 shows the surface and contour plots for NIM removal at constant catalyst amount and H_2O_2 concentration. The best results indicate that 100% NIM degradation were found for levels near to the medium points, which correspond to: $T = 48^\circ C$, $pH = 3.0$, H_2O_2 concentration = 100 mg/L and catalyst amount = 0.5 g/L.

The design of experiments was also carried out for TOC removal (Y_2) and Eq. (11) gives the coefficients found considering a polynomial regression, involving the interaction terms.

$$Y_2 = 84.6 - 3.15 X_1 + 0.75 X_2 - 2.60 X_3 + 3.57 X_4 - 17.51 X_1^2 - 14.76 X_2^2 - 16.92 X_3^2 - 15.80 X_4^2 - 11.45 X_1 X_2 - 3.57 X_1 X_3 - 2.00 X_1 X_4 + 1.85 X_2 X_3 - 0.55 X_2 X_4 + 0.22 X_3 X_4 \quad (11)$$

For TOC removal, the model shows a satisfactory determination coefficient (0.87) and a significant F_{reg} ($F_{stat} = 6.596$) with $p = 5.67 \times 10^{-4}$.

Based on the coefficient values and the resulting Pareto chart (Fig. 11), the quadratic terms of temperature (X_1) and the concentration of H_2O_2 (X_3) are the most important factors, followed by the catalyst concentration (X_4). In contrast, the quadratic term of pH (X_2) appears to have a lower impact than the other variables. The results also indicate a

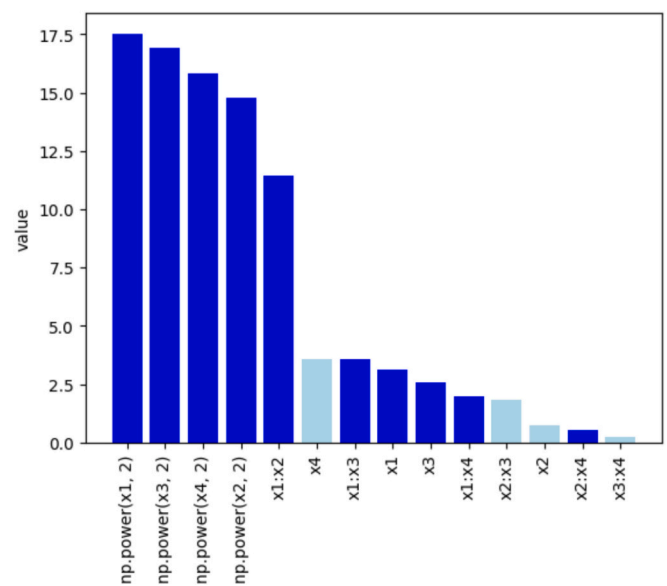


Fig. 11. Pareto chart with negative (blue) and positive (light blue) coefficients corresponding to TOC removal.

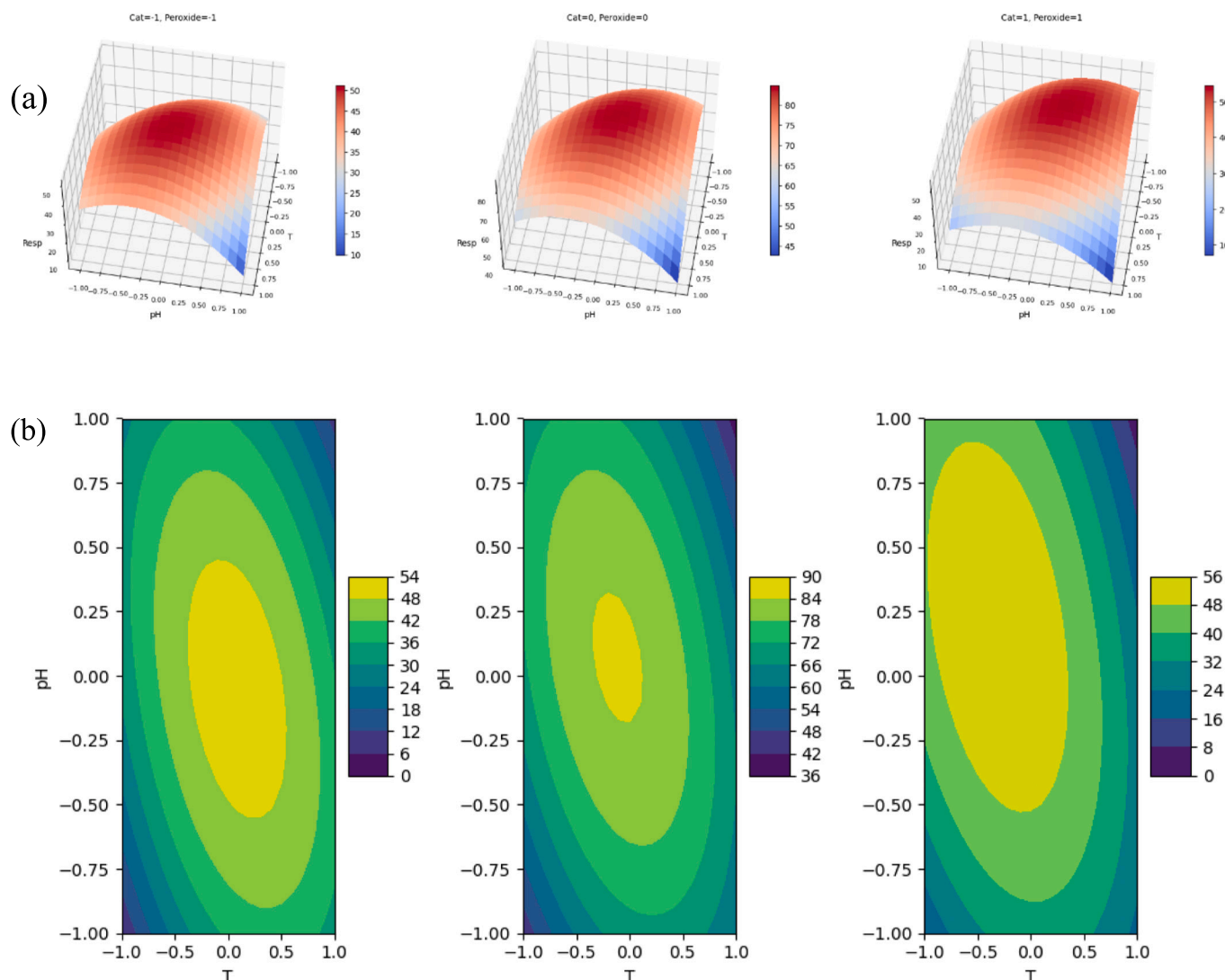


Fig. 12. (a) Surface plots and (b) Contour plots for TOC removal vs. pH and T at constant levels of H_2O_2 and catalyst amounts.

significant interaction between temperature and pH (X_1X_2), whereas no notable interaction was observed between catalyst amount and H_2O_2 concentration (X_4X_3).

Consistent with the findings for NIM removal, the experimental results for TOC removal are close to the values predicted by the model, suggesting that the model's predictions are reasonably consistent with the experimental data.

The surface and contour plots for TOC removal are presented in Fig. 12 at constant catalyst amount and peroxide concentration levels. The best results (87% of TOC removal) were found for the levels near to the central points, at the same values of T , pH, H_2O_2 concentration, and catalyst amount obtained for NIM degradation.

Under the optimized conditions identified using the CCD model, a complete NIM degradation and a very high percentage of TOC removal (87%) can be achieved through the Fenton-type process in the presence of the (CoFe)NaY catalyst.

For a NIM concentration of 40 mg/L, significantly lower values of NIM and TOC removal (47% and 25%, respectively) were obtained under less favorable conditions (pH 5.70, $T = 25^\circ\text{C}$, $[\text{H}_2\text{O}_2] = 100\text{ mg/L}$, catalyst = 0.2 g/L), highlighting the crucial role of experimental design in optimizing process efficiency.

3.3.2. (CoFe)NaY Stability

For the effective removal of organic pollutants using heterogeneous

processes, it is essential to employ catalytically stable and reusable catalysts. To evaluate the stability of (CoFe)NaY, five reuse cycles were performed under the optimized operating conditions, where the catalyst was recovered at the end of each reaction by filtration and utilized in the next cycle after drying at 40°C overnight. Still, a long-term experiment in a continuous flow reactor was also carried out (Fig. S1 shows the lab set-up).

Fig. 13a shows the removal of NIM and TOC, as well as the oxidant consumption, after 180 min in the batch reactor. It can be verified that the percentage of NIM degradation does not change during the five cycles, whereas both the TOC removal and the hydrogen peroxide consumption decrease between the 1st and 2nd cycle and then remain constant. This decrease in the catalytic activity may be ascribed to the slight loss of Co and Fe after the 1st cycle (2.3% for Co and 1.1% for Fe), due to leaching phenomena, which were no longer observed after the 2nd cycle. However, the worsened behaviour after the 1st cycle may also be related to the adsorption of pollutant or intermediate compounds on the surface of (CoFe)NaY, as suggested by the decrease in S_{BET} from 671 to $429\text{ m}^2/\text{g}$ for the used sample.

Fig. 13b shows the temporal evolution of NIM and TOC removals and hydrogen peroxide consumption for the long-term experiment with a duration of $\sim 200\text{ h}$. The performance of the process changes was only observed in the first minutes of reaction, during the reactor start-up phase. Once steady state was achieved, high efficiencies were

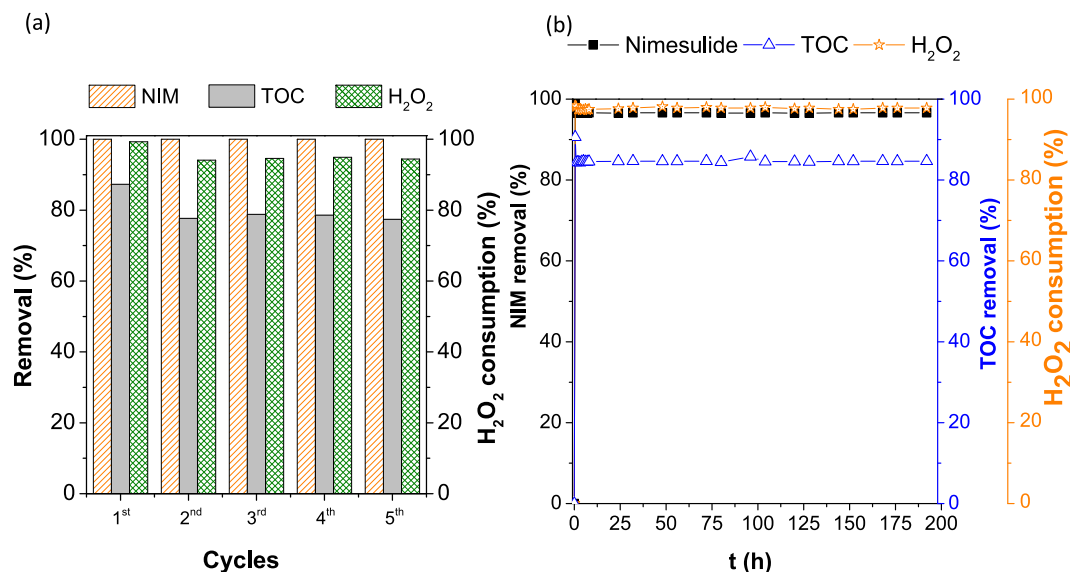


Fig. 13. Percentages of NIM and TOC removal, and hydrogen peroxide consumption after 180 min of reaction for several reutilization cycles in the batch reactor (a) and long-term run in a continuous flow reactor (b). Experimental condition: a) pH = 3.0, $T = 48\text{ }^{\circ}\text{C}$, $[\text{H}_2\text{O}_2] = 100\text{ mg/L}$, $[(\text{CoFe})\text{NaY}] = 0.5\text{ g/L}$ and $[\text{NIM}] = 40\text{ mg/L}$ and b) pH = 3.0, $T = 48\text{ }^{\circ}\text{C}$, $[\text{H}_2\text{O}_2] = 100\text{ mg/L}$, t_{res} (residence time) = 180 min, $W/Q = 20\text{ mg min/mL}$ and $[\text{NIM}] = 40\text{ mg/L}$.

obtained, with removals of 96.6% for NIM and 84.6% for TOC, and an oxidant consumption of 97.8%. Moreover, such performance was kept constant throughout the 200 h of time-on-stream.

The results obtained from the reuse cycles and long-term run allow concluding that (CoFe)NaY is highly stable and no progressive catalyst deactivation occurs, which is crucial for the future industrial-scale application of the Fenton-type process catalyzed with this material in the removal of drugs from pharmaceutical and/or hospital wastewater.

SEM/EDX analysis was performed with the catalyst (CoFe)NaY after the reuse cycles (Fig. S4). It is noticed from the SEM image of (CoFe)NaY that it shows similar morphology to the pristine NaY zeolite (Fig. 2), indicating structural preservation after the reuse cycles, which confirms the stability of the catalyst. Moreover, EDX analysis confirms the presence of both metal ions with negligible leaching.

The cost analysis was carried out for the long-term run, performed in a continuous flow reactor, using current market prices for raw materials. The overall preliminary economic assessment considered oxidant consumption and catalyst preparation costs. The cost of hydrogen peroxide (50% w/v, density at $25\text{ }^{\circ}\text{C} = 1.2\text{ g/cm}^3$) was 0.92 €/kg. The costs of iron nitrate and cobalt nitrate salts used in catalyst preparation were 92.00 €/kg and 522.00 €/kg, respectively (Sigma-Aldrich), and the cost of NaY zeolite was 200.00 €/kg (Zeolyst International). Considering all

synthesis steps, the overall catalyst preparation cost was estimated at 300.00 €/kg. The costs associated with acid and base consumption for pH adjustment were excluded, as their contribution was considered negligible. For operation in continuous mode, the treatment costs were relatively low, remaining below 0.3 €/m³.

3.3.3. Assessment of intermediate compounds forming during NIM degradation

In this work, the intermediate compounds formed during the oxidation of NIM through the Fenton-type process were quantified under the optimal conditions selected from the parametric study. As shown in Table 5, only oxalic acid was quantified, whereas other carboxylic acids and higher molecular weight compounds, which are firstly formed from NIM oxidation [3,14,15], were not observed. This result can be explained by the fact that oxalic acid is the last compound to be formed, exhibits high resistance to oxidation, and is frequently detected in wastewater after advanced oxidation processes have been applied [37,70–72]. Its concentration was found to increase up to 60 min of reaction, which corresponds to NIM's total degradation. For longer reaction times, the amount of such intermediate compound decreased, indicating that it degrades potentially generating H₂O and CO₂. It should also be emphasized that oxalic acid concentration accounted for the

Table 5

NIM and carboxylic acids concentration in terms of carbon along reaction time, total carbon based on such identified compounds, experimental TOC and carbon balance.

t (min)	NIM (mgC/L)	Oxamic acid (mgC/L)	Oxalic acid (mgC/L)	Total carbon ^a (mgC/L)	TOC (mgC/L)	Contribution ^b (%)
Optimum operating conditions						
0	16.53	nd	0.00	16.53	15.55	106.3
60	0.00	nd	4.16	4.16	4.14	100.4
120	0.00	nd	3.37	3.37	3.36	100.3
180	0.00	nd	2.57	2.57	2.56	100.3
Operating conditions which slow down the kinetic						
0	16.10	0.00	0.00	16.10	15.68	102.7
60	4.79	0.53	3.91	9.22	9.20	100.2
120	1.59	0.45	5.41	7.46	7.42	100.8
180	1.19	0.37	4.62	6.17	6.16	100.2

^a Total carbon assessed from the sum of the identified compounds.

^b Total carbon/TOC $\times 100$; nd = not detected.

entire TOC content (Table 5).

A new experiment was then performed to slow down the reaction kinetics and quantify other possible intermediate compounds. For this purpose, the temperature was reduced to 25 °C, while the other operating conditions were fixed as previously selected (pH = 3.0, [H₂O₂] = 100 m/L and [(CoFe)NaY] = 0.5 g/L). Under these conditions, in addition to oxalic acid, oxamic acid was also detected (Table 5). The concentration of both these compounds increased in the first 60 min of reaction, along with the percentage of NIM degradation. However, while the concentration of oxalic acid continued to increase until 120 min, both NIM and oxamic acid were oxidized, as shown by their decreasing amounts throughout the time range investigated, which indicates that oxalic acid can be formed by both the oxidation of NIM and oxamic acid. After 120 min, the oxalic acid concentration also decreased slightly, suggesting that its oxidation to CO₂ and H₂O is occurring, as mentioned above. Again, the sum of the quantified compounds (i.e. NIM, oxamic and oxalic acids) accounted for 100% of TOC at all reaction times.

Electrospray ionization mass spectrometry (ESI-MS) analysis was conducted in both positive and negative ionization modes to identify the degradation products of NIM during the Fenton-type reaction catalyzed by (CoFe)NaY under optimized experimental conditions. This analysis enabled the identification of several intermediate (in trace concentrations) and final degradation products, suggesting a pathway leading to complete mineralization after 180 min of Fenton reaction. The degradation process is primarily driven by hydroxyl radicals (HO•), which are responsible for the formation of the various identified products. Based on the mass-to-charge (*m/z*) peaks observed in the ESI-MS/MS spectra, numerous fragments were detected in both ionization modes. As an example, Fig. 14 presents the ESI-MS/MS spectrum of NIM degradation obtained in negative ion mode and Fig. S5 present the positive mode.

Table 6 presents the molecular structures assigned to the fragments identified in the ESI-MS/MS spectra obtained in both positive and negative ionization modes.

The ion peak at *m/z* 307 corresponds to the NIM molecule in negative ion mode. Peaks at *m/z* 230 and 255 are attributed to hydroxyl radical attacks on the NIM structure, corresponding to the loss of the

–SO₂CH₃ group and the opening of one aromatic ring, respectively. Some of these fragments have also been reported in the literature [3,10,73]. Continued HO• attacks lead to further degradation, producing fragments observed at *m/z* 138, 122, 120, and 93. Oxalic acid was also detected in the analysis, supporting the results presented in Table 5. The degradation of NIM in the presence of (CoFe)NaY resulted in a high degree of mineralization by the end of the reaction (Fig. 13a), indicating the formation of final products such as CO₂, H₂O, N₂, and sulphates.

The enhanced performance of (CoFe)NaY in Fenton-type reaction arises from its superior redox behaviour and intrinsic catalytic properties. Co²⁺, being more redox-active than Zn²⁺, Ni²⁺, and Cu²⁺, promotes rapid electron transfer and, in synergy with iron, accelerates the Fe(III)/Fe(II) redox cycling, thereby increasing H₂O₂ decomposition into reactive HO• species. The smaller crystallite size (~35 nm) further improves active-site accessibility, while the surface enrichment of cobalt (36%) and iron (5%) maximizes interfacial redox interactions. Together, these factors enhance hydroxyl radical generation, intensify the oxidizing environment, and result in higher drug and TOC removal.

4. Conclusions

The active pharmaceutical ingredient NIM was successfully extracted from generic pills, and its degradation was investigated using a Fenton-type process. Among the tested catalysts, (CoFe)NaY – with the highest Fe/M ratio – demonstrated the best catalytic performance, though the worst performance in terms of adsorption. To optimize NIM oxidation and its mineralization, a CCD was employed, achieving 100% NIM degradation and 87% TOC removal under optimal conditions in a batch reactor. The (CoFe)NaY catalyst exhibited minimal loss of activity between the first and second reuse cycles due to Fe (1.1%) and Co (2.3%) leaching. Nevertheless, it maintained catalytic stability up to the fifth cycle without additional leaching, as well as over ~200 h of operation in a CSTR, highlighting its potential for industrial-scale applications. Mechanistic studies revealed that the degradation of NIM and its intermediates is predominantly radical-based. This was confirmed by the use of several radical scavengers, particularly DMSO, which significantly

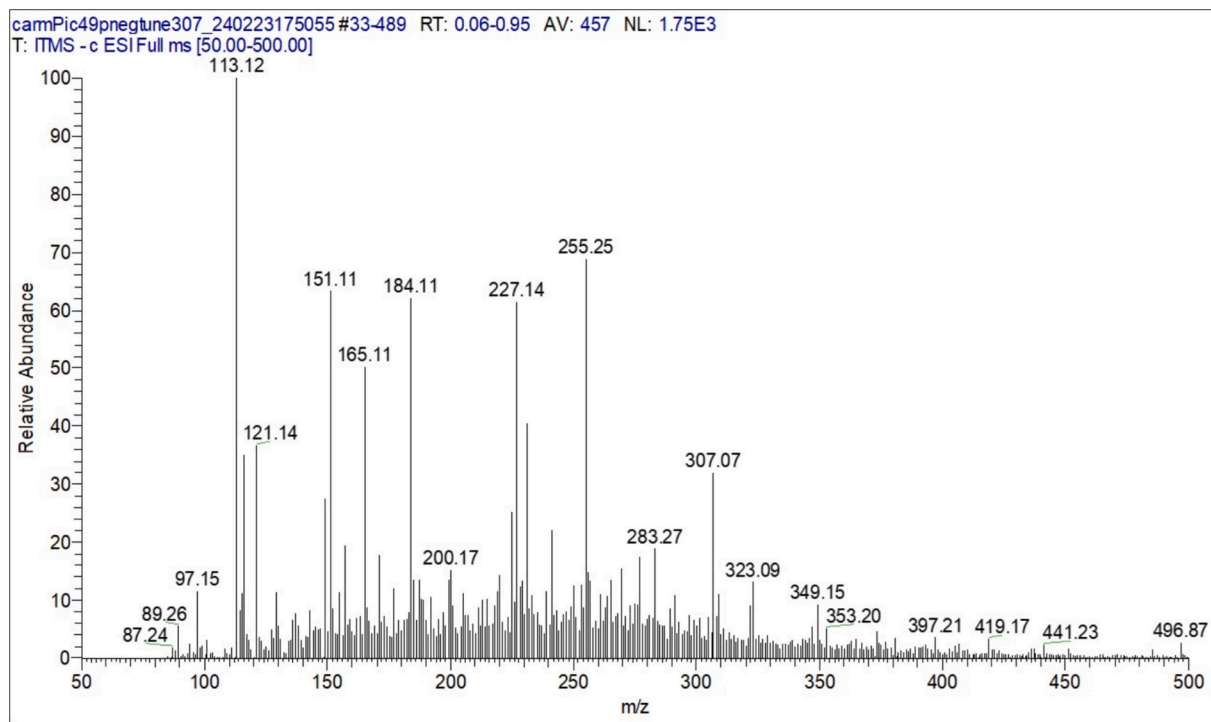
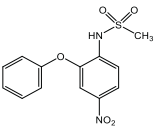
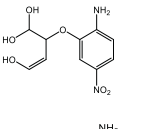
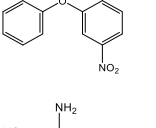
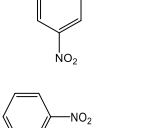
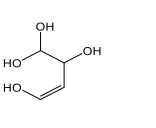
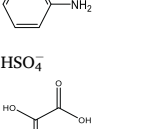
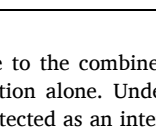
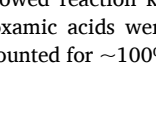
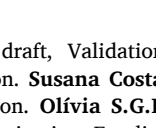


Fig. 14. Negative mode ESI-MS spectrum of NIM degradation in the presence of (CoFe)NaY catalyst (pH = 3.0, *T* = 48 °C, [H₂O₂] = 100 mg/L, [(CoFe)NaY] = 0.5 g/L and [NIM] = 40 mg/L).

Table 6

Summary of the fragments identified by ESI-MS after the NIM degradation.

Product	m/z (a.m.u)	Structural formula
C1	307	
C2	255	
C3	230	
C4	138	
C5	122	
C6	120	
C7	93	
C8	97	
Oxalic acid	90	

reduced the process efficiency to levels comparable to the combined effects of adsorption and hydrogen peroxide oxidation alone. Under optimal reaction conditions, only oxalic acid was detected as an intermediate. However, under milder conditions that slowed reaction kinetics (e.g., lower temperature), both oxalic and oxamic acids were identified. In both scenarios, these intermediates accounted for ~100% of the residual TOC.

CRediT authorship contribution statement

Carmen S.D. Rodrigues: Writing – original draft, Validation, Investigation, Funding acquisition, Conceptualization. **Susana Costa:** Writing – review & editing, Validation, Investigation. **Olivia S.G.P. Soares:** Writing – review & editing, Validation, Investigation, Funding acquisition. **António M. Fonseca:** Writing – review & editing, Validation, Funding acquisition. **Pier Parpot:** Writing – review & editing, Validation, Software. **Manuel F.R. Pereira:** Writing – review & editing, Resources, Funding acquisition. **Luis M. Madeira:** Writing – review & editing, Resources, Funding acquisition. **Elisabetta Rombi:** Writing – review & editing, Validation, Resources, Investigation. **Isabel C. Neves:** Writing – review & editing, Validation, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2026.176667>.

Data availability

No data was used for the research described in the article.

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