

Degradation of pesticides by heterogeneous Fenton using iron-exchanged clays

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ABSTRACT

The aim of this research is to study the feasibility of using low-cost and natural bentonite and kaolinite clays, compared with commercial bentonite, as raw materials to prepare catalysts for the removal of two emerging pollutants, the neonicotinoid pesticides nitenpyram and acetamiprid, by heterogeneous Fenton process. The raw materials were subjected to a simple ion exchange method to improve their textural properties using a solution containing ferric cations followed by calcination at 500 °C. Results show high activity for all the catalysts in the removal of these pesticides, Stability tests were carried out confirming the high stability of these materials.

1. Introduction

In the last decade, water pollution has become a serious and severe problem. This is mainly attributed to the significant increase in the world population, which leads to a significant rise in industrial activities and an important growth in agricultural areas [1]. Some 1500 km³ of wastewater is produced each year, which is six times more than the water in the world's rivers [2]. In addition, the lack of adequate sanitation leads to the contamination of water resources worldwide, which makes it one of the most significant causes of water pollution [3].

In recent years, special attention has been paid to the so-called "emerging pollutants" (EPs), which are defined as chemical compounds that were not previously considered pollutants and, consequently, are not covered by current water quality regulations, even though they may pose a potential threat to environmental ecosystems and human health [4,5]. For keeping a record of such contaminants, the NORMAN network was created in 2005. This is a permanent network of reference laboratories, research centers, and related organizations, for monitoring and bio-monitoring emerging environmental substances [6]. More than 1000 emerging substances have been identified, most of them widespread in everyday life, which are used in different fields, including pharmaceuticals (for both human and animal uses), hormones, household chemicals, personal care products, and endocrine disruptors, among others [7]. Some of them may persist in the environment since conventional treatments do not easily eliminate them, being toxic and bioaccumulative [8]. Thus, there is a consensus to achieve legislative

regulations to control this type of water pollutants.

Pesticides belong to one of the most persistent types of pollutants in water and soil, which create problems for biological wastewater treatment plants [9]. Among them, neonicotinoid insecticides have been widely used, since their introduction almost 30 years ago [10], due to their low toxicity to mammals, birds and fish [11,12]. They present a specific action on the postsynaptic nicotinic acetylcholine receptors of the central nervous system of insects blocking them and leading to paralysis and finally to death, being recommended as substitutes for some organophosphate and carbamate pesticides [13,14]. For this reason, they are the insecticides whose commercialization has experienced the fastest growing in the last decades. Their active species and by-products show high solubility and polarity in water, high photostability and persistence in water and soil, enabling their transference in both surface and groundwater [15]. They are used in more than 120 countries worldwide [16]. However, some of them have a negative impact, especially on pollinators such as bees [17], and have been banned in the EU [18] and Canada [19]. Inappropriate use of these insecticides and their tendency to accumulate in the environment (e.g., in soils, ground and surface water, and treated and untreated vegetation) can lead to environmental contamination and exposure of non-target organisms [20]. Residues of some pesticides can be ubiquitously found in the natural environment at the level of ng/L to mg/L [21]. Despite these drawbacks, the use of these pesticides cannot be completely forbidden because of the benefits they bring in terms of social and economic development. Two of these pesticides used worldwide are nitenpyram

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(NTP) and acetamiprid (ACP).

NTP has both agricultural [22] and veterinary uses [23] for flea control. It is applied to a variety of crops including cotton, corn, rice and other vegetables either by spraying, coating the seeds or applying to the soil [24]. The application methods, as well as the rainout/washout processes, result in the presence of NTP in agricultural products, soil, windblown dust particles, aqueous environmental systems and even in human urine [25]. ACP is a third-generation neonicotinoid insecticide used to control sucking insects in cotton, leafy vegetables, fruit trees, tobacco, cotton, and ornamental plants and flowers [26]. It is soluble in most organic solvents and shows high solubility in water (25 g/L) [11,27]. Moreover, it is stable to hydrolysis at atmospheric temperatures and photodegrades relatively slowly in water thus having a high potential to pollute both ground and surface water.

Due to the persistence of pesticides in the environment and their unpredictable influences on human health, their control and removal from possible sources have been recognized as particularly important [28]. Different technologies are under investigation for the removal of pesticide pollutants, such as adsorption, mediation by microorganisms or plants, advanced oxidation processes (AOPs), enzymatic transformation and combined methods [29,30]. AOPs are widely used for the degradation of non-biodegradable or slowly biodegradable compounds using the oxidizing power of oxidation radicals. Among these methods are ozonation, Fenton and photo-Fenton [31–33], TiO_2 -mediated photocatalysis [34], electrochemical oxidation, sonolysis [35]. Fenton technology is an interesting approach for pesticide removal, based on the use of a transition-metal catalyst (usually ferrous iron) assisted by the addition of hydrogen peroxide. In this regard, the so-called heterogeneous Fenton seems to be a promising technique in comparison with the homogenous process, reducing the sludge generation, the continuous loss of catalyst and allowing it to operate under a wider pH range [36–41]. Different materials have been used as catalysts in the heterogeneous Fenton processes for the degradation of pesticides as modified magnetite [42], magnetite composite with graphene oxide ($\text{Fe}_3\text{O}_4\text{-GO}$) [43], zero-valent iron (ZVI or Fe^0) [44,45] or bimetallic Fe/Ni nanoparticles [46].

Bentonite, a natural clay mainly composed of montmorillonite, is an attractive commercial clay due to its high surface area, eco-friendly nature, non-toxicity, low cost, high thermal stability and availability [47,48]. Also, kaolin has been studied and used in environmental engineering, cosmetics and medicine [49]. Unlike the rest of the clays, kaolin needs a previous treatment to obtain efficient catalytic support in most environmental engineering applications like heterogeneous Fenton. Such modification must be tailored towards ensuring a proper anchorage for the Fe during the catalyst precursor incorporation stage [50]. Different methods have been reported to modify the properties of kaolin such as mechanochemical activation [51], intercalation of metal ions [52], thermochemical treatment [53] or chemical activation [54]. Activation of the material under acid and alkaline conditions of kaolin has been also studied [55]. Acid treatment, a form of chemical activation, has been used to cause disaggregation of the clay structures and the increment in the surface area, eliminating volatile matters and mineral impurities and diluting the external layers which resulted in variation of its clay chemical composition and structure [54]. These modifications enhance the clay catalytic properties, increase the number of acid centers concerning the parent clay and help the catalyst minimize the leaching of the active metal after its incorporation into the clay structure [56,57].

These catalytic supports must be subjected to appropriate treatments to improve their textural, structural properties and iron content to become effective oxidation catalysts. The literature reported the application of some simple techniques for the incorporation of iron oxides into clay minerals being one of the most common methods to meet this goal the pillaring process with Al–Fe polyoxocations [58–60] or impregnation of Fe in previously Al-pillared clays [61,62]. In this way, the use of derived-clay materials including iron in its structure for

Fenton and photo-Fenton processes for the removal of emerging pollutants has been extensively reported in the literature, from modified clays in different ways (pillared clays with Al–Fe, Al–Fe–Cu or Al–Fe–La for the removal of parathion [63], $\text{Fe}_2\text{O}_3\text{-TiO}_2$ -clay heterostructures for the removal of acetaminophen [64], the depletion of atrazine by a Fe (III)-attapulgite-polyaniline composite [65], pillared montmorillonite supported ferric oxalate [66] to materials where the clays act only as catalytic support for iron (Fe(III)-saturated montmorillonite for the removal of atrazine [67], kaolinite supported ferrioxalate catalyst for the removal of amoxicillin [50] or kaolin-supported materials [68–71].

Another possible method, inexpensive and simple, is the introduction of iron in the clay by ion exchange, yielding effective catalysts in heterogeneous Fenton reactions like the degradation of dyes or different phenolic compounds [72–75]. Ion exchange is a simple method, able to improve the textural properties of different materials, incorporating a significant amount of iron within the interlayer space with good stability after calcination at 500 °C [76].

To the best of our knowledge, no studies about the removal of pesticides by heterogeneous Fenton using ion-exchanged clays have been carried out. Thus, the purpose of this study is the preparation of Fe-catalysts by a simple ion exchange process from low-cost and available bentonite and kaolinite clays. Their catalytic performance was tested for the removal of two neonicotinoid pesticides, nitenpyram and acetamiprid, by Fenton technology. The effect of operating parameters, such as reaction temperature and initial H_2O_2 concentration, was also investigated, establishing the relationship between the performance and the derived-clays properties.

2. Experimental

2.1. Catalysts preparation

Two natural bentonite clays (Maghnia (Ma) and Mostaganem (Ms)) were supplied by the Algerian society BENTAL (Société des bentonites d'Algérie) and they were used as received without further purification. Moreover, commercial purified-grade bentonite supplied by Fisher Scientific Company (F) was used as received. Another kind of clay, Tamazert kaolin (KT), was supplied by the National Society of Sanitary Ceramics, located in the El-Milia region, Jijel Province, east Algeria. Unlike bentonites, the KT was treated before its use to improve its textural properties by successive chemical treatments (Fig. 1) [77]. First, KT was subjected to calcination at 500 °C for 5 h in order to obtain metakaolin, more favorable to acid attack. Then, the obtained material was treated with 2.5 M HCl solution at 80 °C for 7 h, washed with deionized water and dried in an oven at 110 °C. Finally, the activated metakaolin was subjected to a basic treatment using 0.5 M NaOH solution. The modified kaolin in this way obtained was named KTM and further used as catalytic support.

The catalysts were prepared using an ion exchange process, adding 4 g of each clay (F, Ma, Ms. or KTM) to 200 mL of an aqueous solution containing 1 g of $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (Sigma Aldrich), maintaining the mixture under vigorous stirring for 24 h at room temperature. The resulting solids were washed several times with deionized water by centrifugation until the supernatants were free of chlorides (conductivity less than 10 $\mu\text{S cm}^{-1}$). After drying at 110 °C, the products were calcined at 500 °C for 2 h [74]. These catalysts are referred to hereafter as Fe–F, Fe–Ma, Fe–Ms and Fe–KTM, depending on the clay used.

2.2. Catalysts characterization

The structural characterization of raw clays and all synthesized materials was performed by X-ray diffraction (XRD), using a Siemens D5000 diffractometer employing $\text{Cu-K}\alpha$ radiation. The patterns were recorded at a scanning speed of $0.05^\circ/2\theta$ ranging from 5 to 80° . The chemical composition, before and after ion exchange, was determined by total reflection X-ray fluorescence (TXRF) using the EXTRA-II XRF

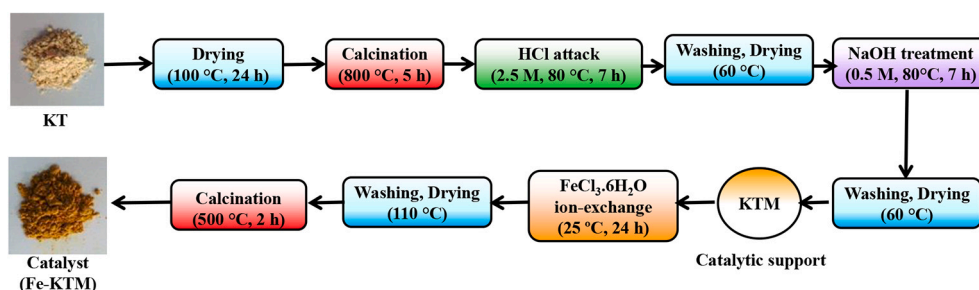


Fig. 1. Preparation method of the catalyst Fe-KTM.

spectrometer. All measurements were made on disoriented powder. The textural properties were determined from the N_2 adsorption-desorption isotherms at -196°C obtained using a Micrometrics Tristar 3020 instrument. Before the analysis, all samples were outgassed for 12 h at 160°C under vacuum pressure ($6.6 \cdot 10^{-6}$ atm). The specific surface area was calculated by the Brunauer–Emmett–Teller method from the linear part of the adsorption isotherms in the relative pressure between 0.05 and 0.35. The external surface area was determined by applying the t-method [78]. The point of zero charge of the adsorbents was determined using the pH-drift method [79].

2.3. Catalytic tests

The Fenton performance of the catalysts was tested for the conversion of two pesticides, NTP and ACP (Sigma Aldrich) in batch mode. For each test, 0.2 g of the catalyst was added to 0.2 L of 5 mg/L of the aqueous pollutant solution (deionized water). A jacketed stoppered glass reactor was used, maintaining a continuous stirring at atmospheric pressure. The initial pH of the target solution was adjusted at 3 by adding HCl solution (0.1 M, Sigma Aldrich). After the equilibrium time of adsorption was reached (different times depending on which material was used in each experiment), the stoichiometric amount of H_2O_2 (Sigma Aldrich, 33 wt%) was added to the mixture (23.2 and 26.7 mg/L of H_2O_2 for 5 mg/L of NTP and ACP, respectively). The reactions were carried out at three different temperatures (25, 40 and 55°C). Samples were collected from the reaction medium at different interval times and filtered with PTFE filters (Whatman $0.45\ \mu\text{m}$). The concentration of each target compound was determined by high-performance liquid chromatography (HPLC, Varian ProStar 410) equipped with a UV–Vis detector and a reversed-phase column (Agilent Technologies). A mixture of acetonitrile and acetic acid 0.1 vol% (1 mL/min) was used as the mobile phase. Total organic carbon (TOC) was determined using a TOC analyzer (TOC-L Shimadzu analyzer). The H_2O_2 [80] and Fe (III) concentrations were quantified in the reaction medium by colorimetric methods using the titanium oxysulfate and ortho-phenanthroline methods, at 410 and 510 nm wavelengths, respectively. For this purpose, a Cary60 UV–Vis spectrophotometer was used equipped with a liquid cell. Blank tests were performed, under the same conditions, in the presence and absence of both H_2O_2 and the catalyst. No pollutant removal was observed in any of the cases. The stability of a selected catalyst was studied during a 12-day long-term experiment in a continuous fixed-bed reactor (Pyrex glass, 30 cm length, 9 mm internal diameter). The catalyst (0.1 g) with particle size lower than $100\ \mu\text{m}$ (after sieving in metallic sieves) was mixed with glass beads of 2 mm external diameter to avoid channeling. A 5 mg/L of pollutant solution was fed at $0.42\ \text{mL/min}$ flow rate so that the space-time was $225.6\ \text{kg}_{\text{cat}}\cdot\text{h/mol}$. Liquid samples were periodically taken from the reactor exit upon the time on stream and analyzed by the same analytical techniques described above.

3. Results and discussion

3.1. Catalysts characterization

The diffractograms of the raw clays and the synthesized materials by iron incorporation are shown in Fig. 2. The different peaks observed were identified using the JCPDS database. The original bentonites are composed of montmorillonite with some reservoir impurities, mainly illite, quartz, cristobalite, calcite and orthoclase. The KTM describes an amorphous structure due to the calcination and further chemical activations of the kaolin. The peaks observed in the pattern are assigned to the impurities from the reservoir that remain after the treatments, as has been reported in previous works [74,77]. The Fe-exchange in all cases

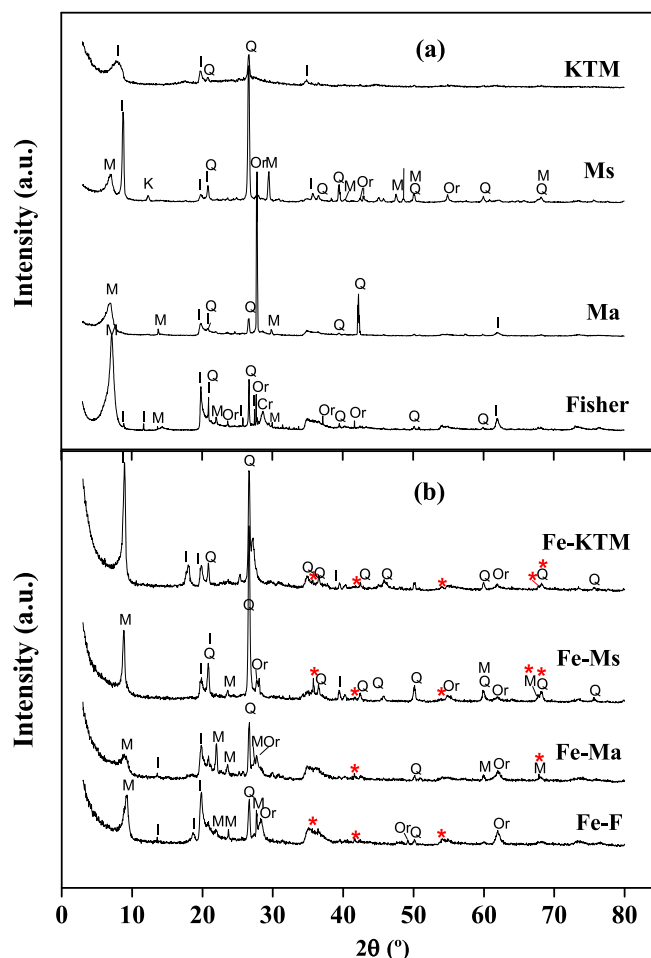


Fig. 2. XRD patterns of (a) original and (b) modified clays. M = montmorillonite; I = illite; K = kaolinite; Q = quartz; Cr = cristobalite; Or = orthoclase; * = $\alpha\text{-Fe}_2\text{O}_3$.

led to an increase in the value of the 2θ angle corresponding to the (001) basal peaks probably due to the partial collapse of the clay structure due to the calcination process and the presence of iron ions. The presence of some weak peaks indicates the presence of iron oxide in the samples [74,81,82] but they are very difficult to observe by XRD due to the small iron percentage and its high dispersion [83,84].

Regarding the N_2 adsorption-desorption isotherms, all samples showed type IV isotherms with <H3 hysteresis loops due to the capillary condensation of N_2 in mesopores (Fig. 3). This type of isotherm is typically obtained for aggregates of plate-like particles, giving rise to the slit-shaped pores typical of clay minerals [85,86]. In the case of the initial clays, the bentonites show well-developed hysteresis loops indicating the presence of mesopores but KTM did not show this loop indicating its surface area is due mainly to microporosity (Fig. 3). In all cases, surface area values increased after the incorporation of iron in the clay structure probably due to the disorder caused in the clay structure after the ion exchange process (Table 1), increasing their mesoporosity. These results were also obtained in a previous work with Ma and Ms. bentonites after an ion exchange process with iron [76]. Dealing with the total pore volume (Table 1), an increase in these values was also obtained after iron introduction in the clays structures confirming the increase in their external surface area. On the other hand, the chemical composition of these materials (Table 1) showed that the iron content of the sample increased substantially as expected after the Fe-exchange process, with different amounts of iron incorporated due to the different cationic exchange capacity of each material [76]: 97 meq/100 g for Fisher bentonite, 94 meq/100 g for Ma, 111 meq/100 g for Ms. and 23 meq/100 g for KTM.

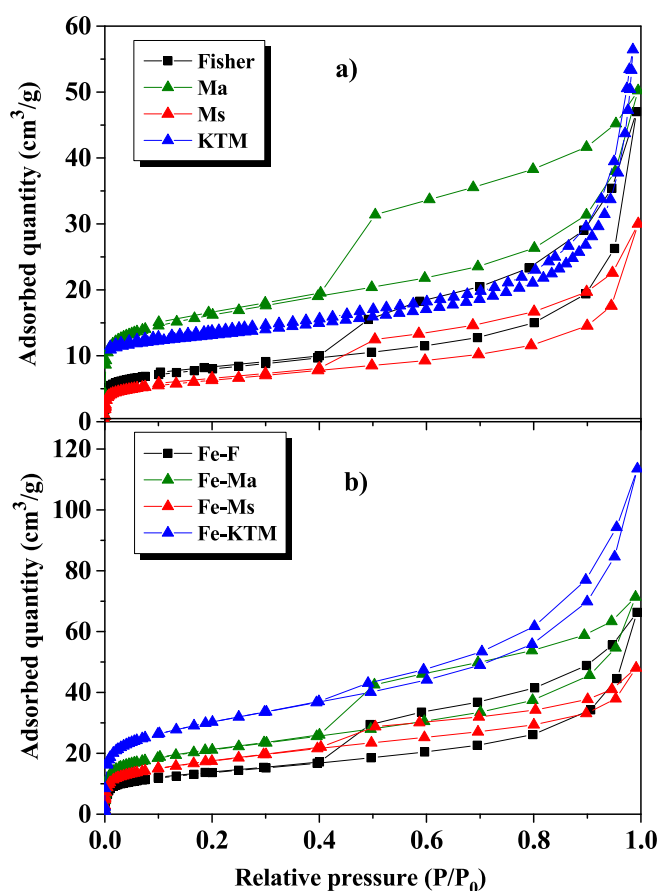


Fig. 3. Adsorption-desorption nitrogen isotherms of a) original and b) modified clays.

Table 1

Textural properties and chemical compositions of the starting materials and the modified clays.

	S_{BET}^a (m^2/g)	External surface ^b (m^2/g)	V_{total}^c (cm^3/g)	Fe load (wt%)
F	35	24	0.0727	2.9
Fe-F	48	33	0.1026	4.2
Ma	56	37	0.0777	1.6
Fe-Ma	74	57	0.1104	5.8
Ms	22	19	0.0464	2.0
Fe-Ms	62	39	0.0744	8.6
KT	14	12	0.0525	0.8
KTM	45	38	0.0712	0.7
Fe-KTM	106	90	0.1721	9.4

^a Total surface area from BET method; ^b External surface area from t-method; ^c Total pore volume at P/P_0 equal to 0.99.

3.2. Adsorption tests

The adsorption capacity and kinetic of the synthesized materials were tested for both pollutants (Fig. 4), before evaluating their catalytic performance.

According to Fig. 5, the adsorption of NTP on all synthesized materials is very fast, within the first 15 min, adsorbing around 3.0–3.5 mg of NTP/g of solid in all cases. However, ACP adsorption is slightly slower, reaching the equilibrium at 30 min, with a low adsorption capacity (1.0–2.0 mg of ACP/g of solid). In addition, the temperature has a slight effect on the adsorption extent of ACP, but this effect is higher in the case of NTP adsorption. Comparing all the synthesized materials, Fe-F achieved the highest adsorption capacity while Fe-KTM was the lowest one. To understand this difference, the pH of point zero charge (pH_{pzc}) was measured and collected in Table 2. When the solution pH is higher than the pH_{pzc} the surface of the material is charged negatively, being positively charged when the solution pH is lower [87]. Since all experiments were performed at pH 3, all the synthesized materials have a positively charged surface. However, Fe-KTM has a lower pH_{pzc} value (5.5) than the other materials, so its surface is less positively charged. Another important aspect to consider is the charge of the pollutants to be adsorbed at the pH of the solution and it can be quantified from their pK_a values (3.5 for nitenpyram and 0.7 for acetamiprid): pH values lower than the pK_a values of the pollutants yields non-dissociated forms of these compounds [88]. Adsorption of ACP is lower than for NTP: ACP is a strong acid, with a pK_a value very low (0.7) and its adsorption is not favored on positively charged surfaces since the dissociation of this strong acid releases a high amount of H^+ cations to the medium, competing with the positive adsorption centers of the adsorbent surface for the pollutants. However, NTP must be non-dissociated at the solution pH of 3 since its pK_a value is 3.5; in this case, the dispersion interactions predominate in the adsorption process and its adsorption is more favored [88].

According to these results, the equilibrium times before catalytic tests were established at 15 and 30 min for NTP and ACP, respectively. The adsorption capacity was also used to prepare the stock solutions of the target compounds so that all reaction experiments were performed with the same initial concentration after the adsorption period.

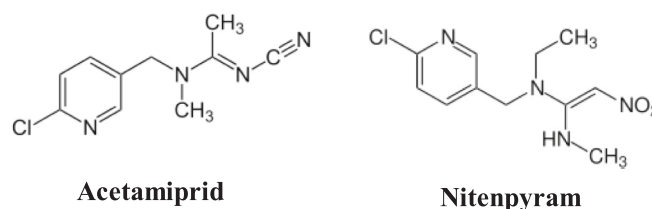


Fig. 4. Chemical structure of the target compounds used in this work.

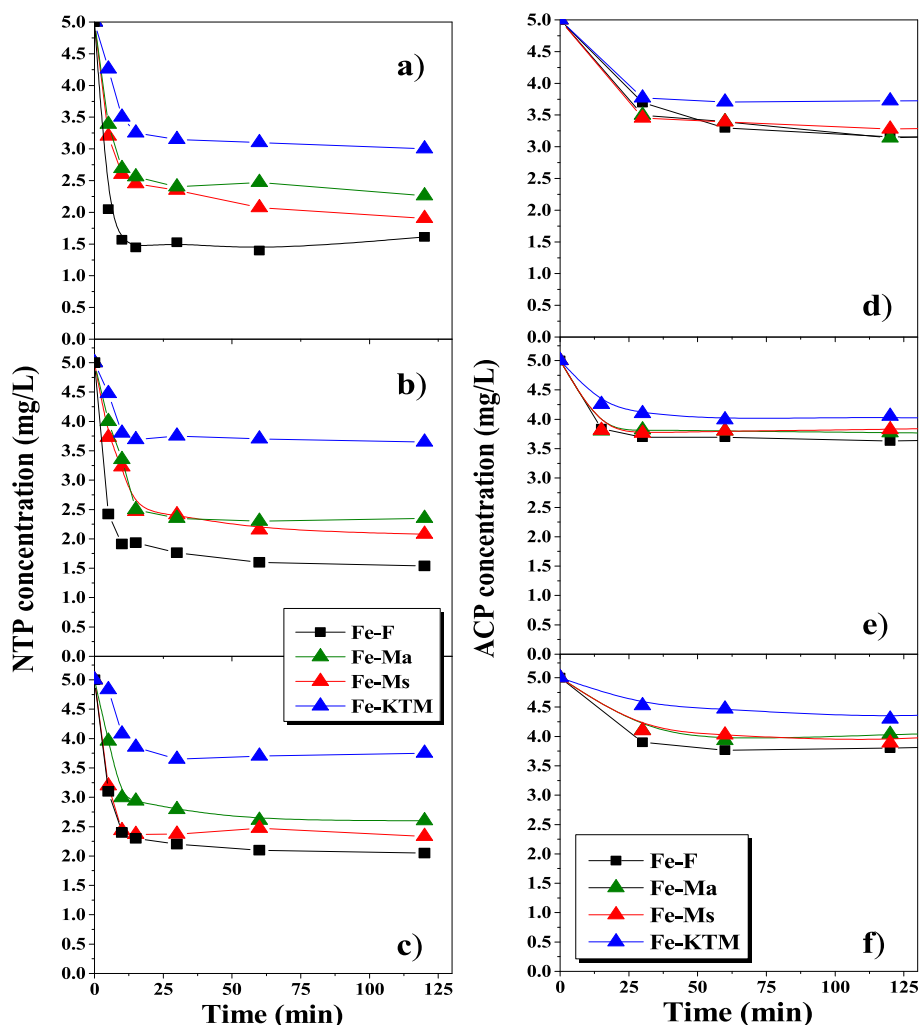


Fig. 5. Adsorption of NTP (a-c) and ACP (d-f) at pH 3 by synthesized materials at different temperatures: 25 °C (a and d), 40 °C (b and e) and 55 °C (c and f) ($pH_0 = 3$, $[pollutant]_0 = 5$ mg/L, stoichiometric H_2O_2 amount).

Table 2

pH_{pzc} values of the catalysts synthesized.

	Fe-F	Fe-Ma	Fe-Ms	Fe-KTM
pH_{pzc}	10.5	9.6	9.8	5.5

3.3. Catalytic activity

The synthesized materials were tested as catalysts for the degradation of NTP and ACP by the heterogeneous Fenton process (Fig. 6). The degradation pathways of both compounds have been previously described in the literature [42,89].

It is highlighted the difference in the catalytic performance depending on the catalyst used. Fe-F catalyst achieved the highest conversion values, being Fe-KTM the less active catalyst. This difference may be attributed to their different textural properties and not to their iron load since the Fe-KTM material, with the highest Fe load (9.4 wt%), yielded the lowest catalytic activity. Fe-F catalyst gave rise to the highest catalytic activity so, probably, active sites in this material are mainly located on the surface of the solid, finding the pollutant molecules some resistance to achieve the active sites within the pores. These results may be explained in terms of how the ion exchange takes place since this process can occur in two ways: the first one, the most common, between the clay layers in the case of the montmorillonites (Ma, Ms. and

F), but also there is another type of ion exchange which is the most important for the catalytic activity, that on the clay surface between the silanol (Si-OH) and aluminol (Al-OH) groups and the iron cations present in the exchanging solution: in this last case, and due to the acidic character of these two groups, a proton can be released and exchanged by the iron atom on the clay surface. The same occurs for the modified kaolin [90].

For both pollutants, a significant increase in conversion was observed when the temperature increased from 25 to 55 °C. This is due mainly to the generation of more oxidant radicals at higher temperatures causing rapid degradation of both NTP and ACP. While at 25 °C the complete removal of the assayed pollutants was not achieved in the 4 h of reaction time (Fig. 6a and d), the increase of temperature until 40 °C gave rise to a dramatic increase in the conversion of the pollutants reaching their total elimination except in the case of kaolin (Fig. 6b and e). It was necessary the highest reaction temperature tested, 55 °C, to reach the complete conversion of both pollutants using the catalyst based on kaolin with a time required to achieve this complete conversion of 180 min while the iron-exchanged bentonites only needed 120 min (Fig. 6c and f).

The increase in catalytic activity with temperature was also reflected in terms of TOC reduction (Table 3), increasing these values with temperature. This can be attributed to a higher H_2O_2 decomposition when increasing reaction temperature, as can be seen in Fig. 7, giving rise to higher amounts of hydroxyl radicals able to perform the degradation of

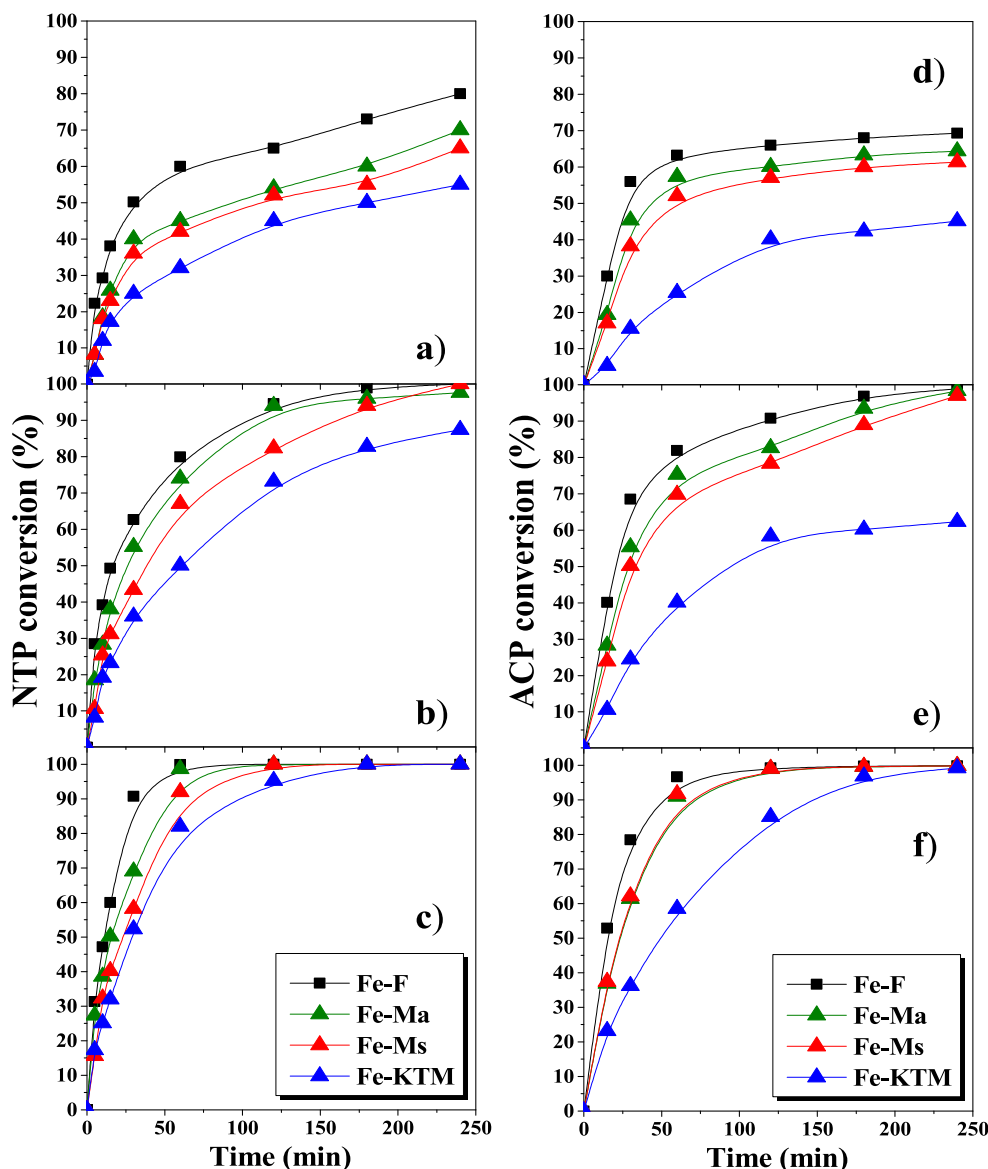


Fig. 6. Removal of NTP (a-c) and ACP (d-f) by Fenton technology with the synthesized catalysts at different temperatures: 25 °C (a and d), 40 °C (b and e) and 55 °C (c and f) ($\text{pH}_0 = 3$, $[\text{pollutant}]_0 = 5 \text{ mg/L}$, stoichiometric H_2O_2 amount).

Table 3

TOC conversion values (%) for the degradation of NTP and ACP ($\text{pH}_0 = 3$, $[\text{pollutant}]_0 = 5 \text{ mg/L}$, stoichiometric H_2O_2 amount).

		25 °C	40 °C	55 °C
NTP	Fe-F	30.9	32.3	35.8
	Fe-Ma	28.1	29.9	31.2
	Fe-Ms	25.8	27.3	28.1
	Fe-KTM	23.2	24.9	26.3
ACP	Fe-F	24.8	27.2	31.2
	Fe-Ma	19.9	23.6	28.9
	Fe-Ms	18.5	31.4	38.5
	Fe-KTM	15.6	17.5	21.4

the pollutant.

This is also clear in Fig. 7 with the Fe-F catalyst since the H_2O_2 conversion rate almost doubled when increasing the temperature from 25 °C to 55 °C. In Fig. 7 the highest H_2O_2 decomposition corresponds to this catalyst, Fe-F, the most active catalyst, being related to the highest generation of hydroxyl radicals by H_2O_2 decomposition with the highest catalytic activity and the highest TOC conversion. In all cases, the

conversion of H_2O_2 is lower than 50% being the stoichiometric H_2O_2 amount higher than the needed for the requirements of this oxidation process.

The stability of the catalysts tested has been also evaluated in terms of iron leaching, as reported in Table 4. The results showed that the catalysts can be considered stable since the iron leaching in the reaction medium remained lower than 5% with respect to the initial Fe load in all cases, even at 55 °C, proving the good fixation of Fe_2O_3 at the surface of the clay. Furthermore, this good stability confirms that the homogenous process contribution to the oxidation process is very limited.

In order to analyze the kinetics of this process, the first order model was applied to the oxidation of NTP and ACP using its linear form:

$$\ln\left(\frac{C_t}{C_0}\right) = -k_1 t$$

where C_0 and C_t (mg/L) are, respectively, the initial concentration and the concentration at any time t of the pollutants, and k_1 is the first order constant (min^{-1}). The parameters of the model are obtained by plotting $\ln\left(\frac{C_t}{C_0}\right)$ versus time. The k_1 values for each catalyst are collected in

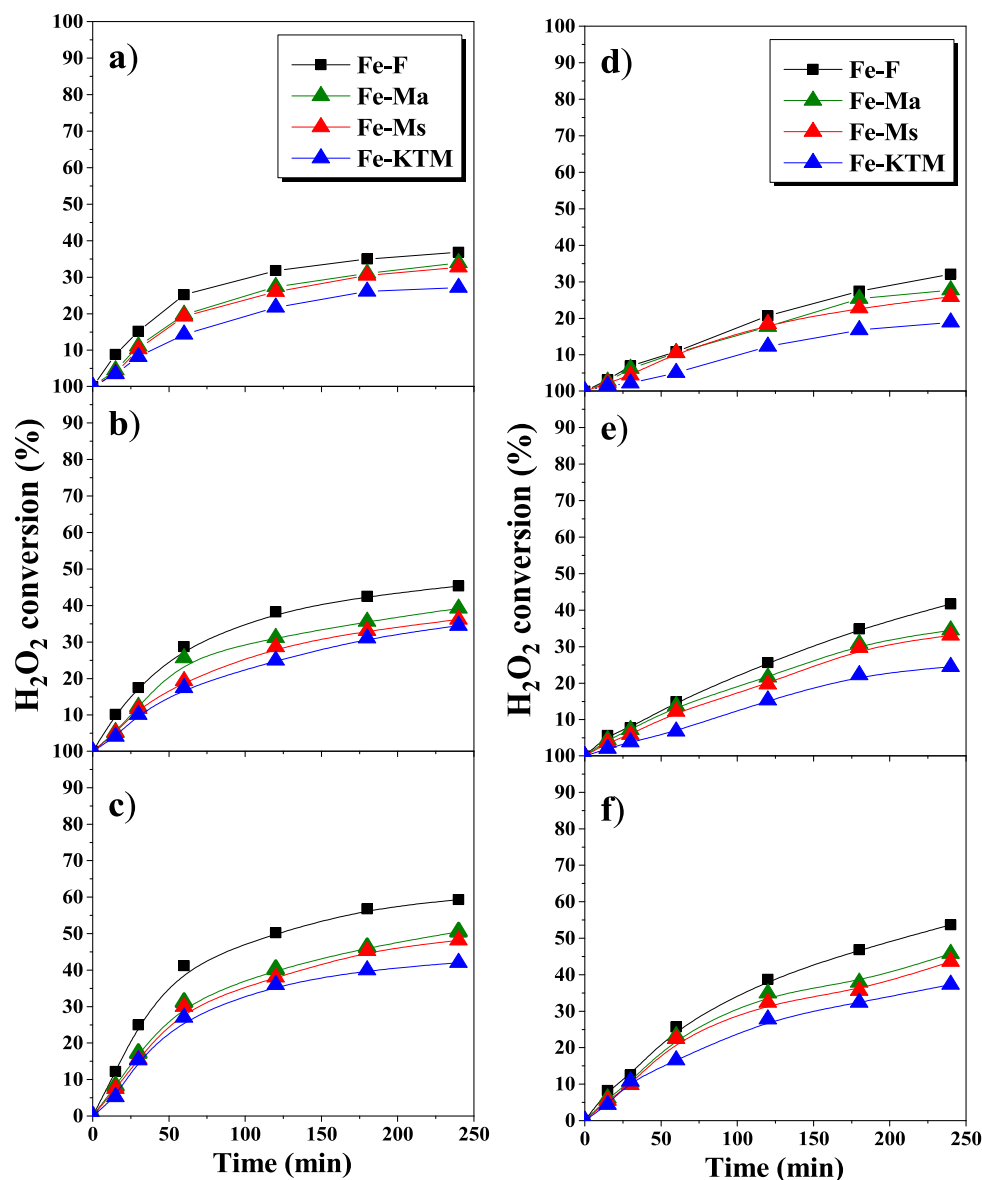


Fig. 7. H_2O_2 conversion during the Fenton degradation of NTP (a-c) and ACP (d-f) by the synthesized catalysts at different temperatures: 25 °C (a and d), 40 °C (b and e) and 55 °C (c and f) ($\text{pH}_0 = 3$, $[\text{pollutant}]_0 = 5 \text{ mg/L}$, stoichiometric H_2O_2 amount).

Table 4

Leaching of iron (% concerning the initial Fe load of each catalyst) in the heterogeneous Fenton of NTP and ACP by the synthesized catalysts at different temperatures ($\text{pH}_0 = 3$, $[\text{pollutant}]_0 = 5 \text{ mg/L}$, stoichiometric H_2O_2 amount).

		25 °C	40 °C	55 °C
NTP	Fe-F	2.1	2.7	4.1
	Fe-Ma	2.3	3.2	3.7
	Fe-Ms	2.9	3.4	3.9
	Fe-KTM	2.5	3.1	4.0
ACP	Fe-F	1.7	2.2	3.7
	Fe-Ma	1.6	2.5	3.2
	Fe-Ms	2.7	3.1	3.6
	Fe-KTM	2.2	2.9	3.3

Table 5

Pseudo-first-order degradation constants (k , min^{-1}) by heterogeneous Fenton as a function of temperature for NTP and ACP (regression coefficient R^2 higher than 0.97 in all cases).

		25 °C	40 °C	55 °C
NTP	Fe-F	0.0057	0.0234	0.0784
	Fe-Ma	0.0044	0.0161	0.0376
	Fe-Ms	0.0038	0.0148	0.0288
	Fe-KTM	0.0032	0.0087	0.0237
ACP	Fe-F	0.0039	0.0174	0.0264
	Fe-Ma	0.0037	0.0155	0.0276
	Fe-Ms	0.0035	0.0130	0.0271
	Fe-KTM	0.0025	0.0041	0.0196

Table 5. The increase in temperature led to a significant increase in the degradation rate of both pollutants regardless of the catalyst used, as also revealed in the conversion data summarized in [Tables 2 and 3](#). This effect is mainly due, as cited above, to the generation of more hydroxyl radicals from H_2O_2 at higher temperature, causing a rapid degradation

of NTP and ACP. Furthermore, the degradation rate using Fe-KTM is smaller in comparison with the other catalysts, thus confirming the lower catalytic activity of this last material probably due to the kaolin structure with the active centers located far inside the pores.

Data for the pseudo-first-order degradation constants of NTP and

ACP by heterogeneous Fenton are very scarce in the literature. In the case of the removal of NTP from wastewater, only works dealing with the use of photocatalysis or electrochemical oxidation can be found in the literature [91,92]. For ACP degradation, AOPs combining UV radiation with other systems have been reported [26,93,94] or using photocatalysis [34,95]. Only Marcelo et al. [46] have reported the use of a Fenton-like oxidation process for the removal of ACP with bimetallic Fe/Ni nanoparticles (not supported ones, with the corresponding drawbacks for their separation from the reaction media), with rate constant values in the range $0.066\text{--}0.828\text{ min}^{-1}$, an interval where some of the values obtained in the present work can be found.

Due to the low consumption of H_2O_2 observed during the degradation under stoichiometric conditions, additional tests were carried out by reducing the concentration by half (i.e. 11.62 mg/L), selecting only NTP as the target pollutant. NTP conversion was not affected by the reduction of the H_2O_2 (Fig. 8a) while a higher conversion in the H_2O_2 is observed (Fig. 8b), which means better use of the oxidant. This implies that it is possible to operate with a lower amount of oxidant, which

results in an economic saving since the main cost of the Fenton process is due to the H_2O_2 consumption. However, the use of half the stoichiometric amount of H_2O_2 gave rise to lower mineralization (Fig. 8). Thus, the low doses of H_2O_2 were enough to oxidize the NTP but not its byproducts.

3.4. Stability tests

Long-term tests in a continuous mode were essayed for 300 h to determine the catalytic stability. The Fe–F catalyst was selected for this purpose because of its superior activity. Fig. 9 shows the conversion evolution of both pollutants and H_2O_2 . The Fe–F catalyst exhibited a very stable behavior, maintaining the catalytic activity during 300 h, with no decrease in the conversion of both pollutants, suggesting that the catalyst is not deactivated at the reaction conditions. The H_2O_2 consumption also reached a constant value during the long-term experiments. In both cases, removal of pollutants and H_2O_2 conversion, these two parameters were lower than when the tests were carried out in batch mode indicating that the requirements of the process in a continuous way, with a constant inlet of pollutants solution, are higher than when the reaction is performed in batch mode. On the other hand, the concentration of leached Fe measured in the samples was very low throughout the course of the reaction, less than 0.7% in both cases, supporting the high stability of this catalyst.

4. Conclusions

Four different clays, three natural ones (two bentonites and a kaolinite clay) and a commercial bentonite, have been used as supports of homemade catalysts prepared by a simple and economic ion exchange process incorporating iron as the active phase. These materials have been used for the removal of two emerging pollutants, specifically two neonicotinoid pesticides, acetamiprid and nitenpyram, by heterogeneous Fenton oxidation, a process scarcely studied in the literature for the removal of pesticides using this kind of catalytic materials. The introduction of iron in the structure of the different clays gave rise to a considerable increase in the surface area of these materials, mainly due to the development of their mesoporosity. From adsorption tests the

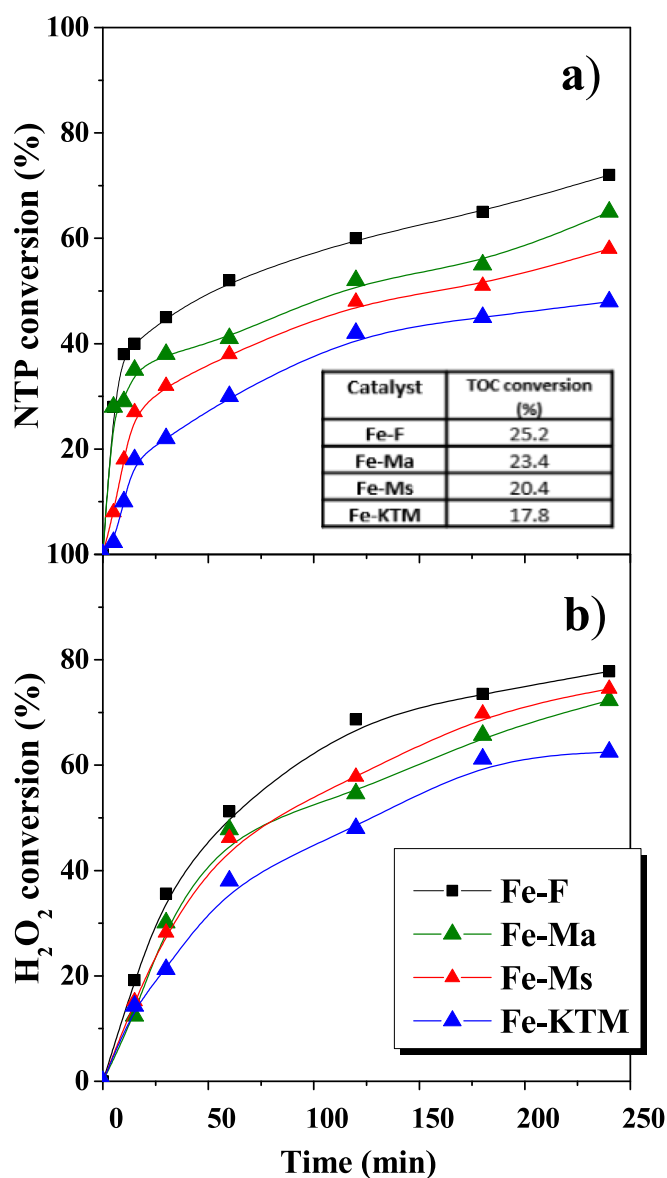


Fig. 8. Evolution of NTP (a) and H_2O_2 (b) conversions with the reaction time with all synthesized catalysts at non-stoichiometric conditions (25°C , $\text{pH}_0 = 3$, $[\text{NTP}]_0 = 5\text{ mg/L}$, $[\text{H}_2\text{O}_2]_0 = 11.62\text{ mg/L}$). Inlet: TOC conversion values (%) obtained in these tests.

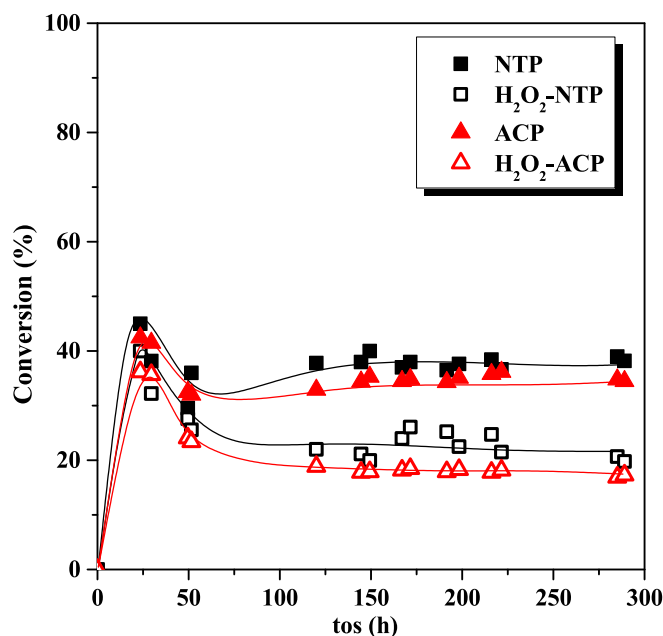


Fig. 9. Conversion evolution of NTP, ACP and H_2O_2 during long-term experiments with Fe–F catalyst (25°C , $\text{pH}_0 = 3$, space-time = $225\text{ kg}_{\text{cat}}\cdot\text{h/mol}$, $[\text{pollutant}]_0 = 5\text{ mg/L}$, stoichiometric H_2O_2 amount).

three bentonites showed a high adsorption capacity of these pollutants (mainly of NTP) while Fe-KTM showed the lowest one, probably due to its different surface properties. The catalysts obtained from the three bentonites gave rise to the complete removal of both pollutants at temperatures higher than 40 °C being the catalyst prepared from the commercial bentonite (Fe–F) the one showing slightly higher catalytic activity than the others. On the contrary, the catalyst obtained from kaolinite (Fe-KTM) was the one that provided the lowest catalytic activity for both NTP and ACP elimination. An increase in the medium temperature produced a decrease in the adsorbed amount of the studied pollutants since adsorption is generally an exothermic process and is favored at lower temperatures. The increase in the reaction temperature in the heterogeneous Fenton reactions gave rise to the increase in the conversion of both pollutants reaching similar conversion values but at a faster rate due to the increase in the kinetic constants of the reaction. This increase in temperature also carries a greater conversion of H₂O₂ due to the greater generation of hydroxyl radicals and, therefore, a greater consumption of this reagent. Moreover, the increase in the reaction temperature also achieved greater mineralization of the pollutant tested as well as a slight increase in the leached iron present in the solution but, in all cases, this amount is very low. Fe–F catalyst was selected to be submitted to long-term experiments during 300 h giving rise to a very stable behavior, maintaining the catalytic activity during all this time with negligible iron leaching. From this work, the use of natural clays, specifically bentonites, as catalytic supports, is very adequate for the removal of pollutants as pesticides by heterogeneous Fenton reactions since they are cheap and very available materials that by a simple ion exchange method with iron solutions can be converted in active catalysts with low iron leaching and high stability.

CRediT authorship contribution statement

A. Boukhemkhem: Conceptualization, Methodology, Validation, Investigation, Resources, Writing – original draft, Writing – review & editing. **J. Bedia:** Validation, Formal analysis, Writing – review & editing, Supervision, Project administration, Funding acquisition. **C. Belver:** Conceptualization, Methodology, Validation, Investigation, Resources, Writing – original draft, Writing – review & editing, Visualization, Supervision. **C.B. Molina:** Term, Conceptualization, Methodology, Validation, Investigation, Resources, Writing – original draft, Writing – review and editing, Visualization, Supervision.

Declaration of Competing Interest

The authors declare no conflict of interest.

Data availability

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

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