Fenton-like oxidation of Orange II solutions using heterogeneous catalysts based on saponite clay

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Abstract

In this work, the degradation and mineralization of Orange II solutions (0.1 mM) using catalysts based on pillared saponite impregnated with several iron salts is reported. Oxidation is carried out in a batch reactor, in presence of various hydrogen peroxide concentrations, and in a wide range of temperature and pH values. Twelve samples are prepared, with three iron loads (7.5, 13.0 and 17.0 wt.%) and four iron salts as precursors, namely Fe(II) acetate, Fe(II) oxalate, Fe(II) acetylacetonate and Fe(III) acetylacetonate. The samples are characterized using X-ray diffraction, thermal analysis, infrared spectroscopy, energy dispersive spectroscopy and adsorption of nitrogen at 77 K. The catalytic results show that these solids present good properties for the degradation and mineralization of Orange II solutions, allowing to reach, in the best conditions and after 4 h of oxidation, 99% of dye degradation with 91% of total organic carbon (TOC) reduction (at 70 °C), using only ca. 90 mg of clay catalyst per litre of solution. Nevertheless, 96% of dye removal with 82% of mineralization are also reached at 30 °C. Besides, the amount of iron released into the final solution is lower than 1 ppm, in the worst of the cases, and 0.09 ppm in the best case.

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1. Introduction

Chemical process industries, such as oil refineries, petrochemical units, dye and dye intermediate manufacturing industries, textile units, among others, are typical industries that dump toxic organic compounds to the nearer water courses, thus making the water polluted [1]. To overcome this, the use of advanced oxidation processes (AOPs) has been widely proposed, as they operate at temperature near ambient and atmospheric pressure. These processes involve the generation of highly reactive radicals (specially hydroxyl radicals) in enough quantity to effect water purification [2], and their use is justified by the low organic content of the wastewaters to be treated, besides the low reaction temperatures, thus requiring the presence of very active oxidation agents. In particular, the oxidation using Fenton’s reagent (a powerful source of oxidative HO• radicals generated from H2O2 in the presence of added Fe2+ ions [3]) has proved to be a promising and attractive treatment method for the effective destruction of a large number of hazardous and organic pollutants [4–8]. The generated HO• radicals are highly oxidative, non-selective, and able to decompose many organic compounds, including dyes [9]. However, it should be pointed out that the homogeneous Fenton process has a significant disadvantage. Homogeneously catalyzed reactions need up to 50–80 ppm of Fe ions in solution, which is well above the European Union directives that allow only 2 ppm of Fe ions in treated water to dump directly into the environment [10]. In addition, the removal/
treatment of the sludge-containing Fe ions at the end of the wastewater treatment is expensive and needs large amount of chemicals and manpower.

To overcome the disadvantages of the homogeneous Fenton process, and also considering the possibility of recovering the catalyst, some attempts have been made to develop heterogeneous catalysts, prepared by incorporating Fe ions or Fe oxides into porous supports [11–14]. Other transition metal complexes supported on several surfaces such as metal oxides, resins and mixed (Al-Cu) pillared clays have also been used as potentially active catalysts for the decomposition of H₂O₂ and for the oxidative degradation of organics [15]. Among the porous solids used as supports for the iron phases, it is worth mentioning the use of silica, alumina, silica-alumina and cation-exchanged resins, which have been used in the degradation and mineralization of dyes [11]. More complex systems have been prepared by modifying a polycrylonitrile (PAN) fibre by treatment with a mixture of hydrazine and hydroxylamine to introduce chelating functional groups onto the fibre surface. These functional groups are used to coordinate the transition metal cations Fe³⁺, Co²⁺, Ni²⁺ and Cu²⁺ to the fibre to act as the active catalytic sites for decomposition of the hydrogen peroxide [12]. Using an alternative strategy, other catalytic systems have been prepared by co-intercalation of two natural smectites (Wyoming SWy-1 and Tunisia-Gafsa VI) with Fe-Al polycations, obtained by polymerisation of a mixture of FeCl₃ and chlorhydril [13]. Tachie et al. [14] have reported other catalysts, in which Fe(II) and Fe(III) cations are complexed by the ligands DTPA, EDTA, EGTA and NTA. The use of zeolites [16] and carbons [17] to support iron catalysts is also worth mentioning.

The mechanism of H₂O₂ decomposition on homogeneous Fenton’s oxidation is not well established, where several oxidising agents have been suggested to be involved in the oxidation reactions, in addition to the HO• radicals. For the heterogeneous systems this is still less clear, being a matter of controversy. Some authors suggest an initial step of fast adsorption of the H₂O₂ molecule on (≡Fe(III)) sites [17] and others the adsorption of the organics [18]. Nevertheless, the involvement of the following steps has been suggested in most of the works found in the literature, which correspond to Fe³⁺ reduction with generation of less oxidative HO₂• radicals, followed by Fe³⁺ regeneration with formation of the hydroxyl radicals:

\[ X - Fe^{3+} + H_2O_2 \rightarrow X - Fe^{2+} + HO_2^\bullet + H^+ \]  (1)

\[ X - Fe^{2+} + H_2O_2 \rightarrow X - Fe^{3+} + OH^- + HO^\bullet \]  (2)

where X represents the surface of the catalyst. However, it must be remarked that the radicals can also be generated in the surface of the solid so they are actually “caged” in the solid structure, subsequently reacting with the adsorbed reagent(s) without radicals generation. Obviously, besides the indicated steps many other radical reactions occur, including those involving the reaction intermediates.

Among the above-mentioned catalyst supports, pillared clays (PILCs in short) is one of the families of microporous solids developed by Molecular Engineering that have been more studied in recent years, because of their particular properties and structures (with tunable pore size), as well as the abundance and low cost of natural clay minerals. Besides, they lead to active and stable solids in aqueous media, usually being very stable against leaching [19]. The PILCs synthesis procedure can be divided into three main steps: (i) preparation of polyoxocations by careful hydrolysis of certain multivalent cations, which under appropriate conditions give rise to cationic polymeric species, (ii) ionic exchange of the original charge-compensating cations of swellable smectite clays by the polyoxocations before synthesized, this exchange giving rise to the so called “intercalated clays” and (iii) stabilisation of the intercalated clays by calcination at relatively high temperatures, which transform the metastable polyoxocations into “pillars”, stable metallic clusters, close to oxihydroxidic phases, which maintain the layers of the clays separated to a long distance [20], thus able to accommodate large molecules susceptible to undergo chemical transformations. These solids are called “pillared clays”, showing a bidimensional microporous network of molecular dimensions, with the pillars occupying the interlayer space defined by the clay layers. The number and size of the pillars in the interlayer region are responsible for the pore parameters of the pillared clay structure [21].

Recently, Feng and co-workers [18,22] synthesized clay-based Fe nanocomposites by the so-called pillaring technique and used them as heterogeneous catalysts for the photo-Fenton discoloration and mineralization of azo-dyes. Their results clearly indicate that the solids are promising photo catalysts, but the use of light increases the costs of the overall process as compared to dark Fenton oxidation. However, in their conditions the oxidation is much faster, which is also important to be taken into account in economical analysis.

In this work, we have prepared several heterogeneous catalysts based on Al-pillared saponite impregnated with iron salts. Saponite is a smectite clay characterized by a high negative charge, generated by a high degree of Si–Al substitution in the tetrahedral sheet, and by a high occupancy of the octahedral layer, mainly by Mg. The high occupancy in the octahedral sheet, together with a certain degree of substitution by trivalent cations, makes the negative charge in this sheet to be very low, sometimes close to zero, and even slowly positive. Thus, the negative charge of the clay is strongly concentrated in the tetrahedral sheet, which differentiates saponite from the most known and used smectite material, montmorillonite, in which the charge is mainly located in the octahedral sheet. The other important characteristic of the saponite has already been mentioned, the highly magensic composition of its octahedral layer [23]. The amount and location of the clay charge gives saponite a particular interest from the catalytic point of view, because of the direct relation between it and the acidity of the clay. In the preparation of pillared solids, the charge has a great importance regulating the facility for intercalation, the cross-linking between the clay layers and the pillars, and the thermal stability, remarkably higher than for pillared montmorillonites [24]. Besides, saponite is a clay mineral abundant and cheap in the Iberian Peninsula.
Thus, a saponite has been intercalated with Al polycations, and the pillared solid obtained after calcination at 500 °C has been used as support for the impregnation with iron. Four iron salts have been used as precursors and three loads of iron have been prepared. The obtained heterogeneous catalysts have been used in the Fenton-like oxidation of the non-biodegradable azo-dye Orange II (abbreviated “OII” from here) in water solution, using a batch reactor. The choice of OII as model pollutant lies in the fact that it is a typical dye which is widely used in textile, pulp and paper industries. The effectiveness of these catalysts in the oxidation of the dye, as well as the influence of the variables of the synthesis and of the reaction conditions on the catalytic activity are discussed.

2. Materials and methods

2.1. Preparation of the catalysts

Saponite from Yunclillos (Toledo, Spain) was kindly supplied by TOLSA (Madrid, Spain). The fraction with particle size smaller than 2 μm, obtained by dispersion in water and controlled decantation of the natural clay, was used for intercalation/pillaring experiment. Its chemical composition, expressed in wt.% of oxides and referred to water-free solid, is the following: SiO₂, 62.20; MgO, 29.45; Al₂O₃, 5.21; Fe₂O₃, 1.46; TiO₂, 0.30; Na₂O, 0.54; K₂O, 0.30; CaO, 0.53 (analytical method described below, Section 2.2). It is a well-ordered smectite with basal spacing of 14.4 Å, BET specific surface area of 152 m²/g and cation exchange capacity (CEC) of 0.9 meq/g.

Saponite was intercalated with [Al₁₃(OH)₂₄(H₂O)₁₂]⁺ polycations (in short, Al₁₃), by using a standard procedure [25,26]. First, the Al₁₃ solution to be intercalated was obtained by careful hydrolysis of an Al³⁺ solution, derived from AlCl₃/C₁/C₀ of 2.2, stirring vigorously for 24 h, and then washed by centrifugation and dialysis until absence of chloride (evaluated by a J.H. Ramirez et al. / Applied Catalysis B: Environmental 71 (2007) 44–56 signal-to-noise ratio.

FT-Infrared spectra were recorded in the 4000–350 cm⁻¹ range of 2–65° by a Siemens D-500 diffractometer at 40 kV and 30 mA using filtered Cu Kα radiation (λ = 1.5418 Å).

Powder X-ray diffraction patterns (XRD) of the solids were recorded in the 2θ range of 2–65°, using a Siemens D-500 diffractometer at 40 kV and 30 mA using filtered Cu Kα radiation (λ = 1.5418 Å).

BET specific surface areas were determined by adsorption of nitrogen at 77 K, by using a Micromeritics Gemini apparatus and measuring five adsorption points between 0.01 and 0.2 of relative pressure. The samples were previously outgassed by treatment at 110 °C for 2 h, under flow of nitrogen.

Simultaneous thermal gravimetric (TG) and differential scanning calorimetric (DSC) analyses of samples were carried out using a TA-SDT Q600 Instrument. Samples of about 40 mg were heated in air (flow-rate = 100 mL/min) from room temperature up to 900 °C, with a heating rate of 10 °C/min.

2.3. Catalytic activity

Chemical oxidation of Orange II (Fluka p.a.) was carried out using 1 L of a 0.1 mM solution, in a jacketed glass batch reactor under continuous stirring (by means of a FALC F30ST magnetic stirrer—230 rpm), and with a permanent control of the temperature by a Huber (Polystat CCI unit) thermostatic bath. After stabilisation of both temperature and pH, the powder catalyst was added and the beginning of the reaction (t = 0) was considered when H₂O₂ (30%, w/w, from Merck) was added. Absorbance, temperature and pH were permanently measured by means of a Philips PU8625 UV–vis spectrophotometer, a thermocouple and a pH/EDT Instruments RE 357 TX electrode, respectively. Prior to the absorbance measurements, a calibration curve was obtained that showed a good linear relationship between the absorbance at 486 nm (characteristic wavelength of the Orange II molecule) and the concentration up to 0.1 mM. For the on-line determination of the absorbance at λ = 486 nm a flow-through cell was used, recirculation being obtained by a
peristaltic Watson–Marlow S055 pump, using a flow-rate of 100 mL/min. It is worth of mentioning that due to the low mass of catalyst used, 91.5 mg, with an average volumetric diameter of 3.342 μm – determined in a Coulter Counter particle size analyser, ref.: LS230 – no interference in the absorbance data was noticed. In the runs where a significant concentration of clay was used (1 g/L), samples taken along time were filtered before measurement of absorbance. Acquisition of data was carried out by means of a home-built interface using Labview 5.0 software, from National Instruments, with a frequency of 1/3 Hz (although in the OII concentration figures much less data are displayed, for a better visualization). Each run lasted for 4 h. All the experiments were repeated at least twice (the average relative error along the runs was of 11%, while at the end of the oxidation, t = 4 h, conversion values differed only, on average, 2%).

Complete discoloration of OII does not mean that it has been completely oxidized into CO₂ and H₂O, as reaction intermediates can be formed during oxidation. Therefore, it is important to evaluate the mineralization of organic dyes. So, in all cases, total organic carbon (TOC) was measured using a Shimadzu 5000A spectrophotometer, model TOC-5000 CE, equipped with an automatic sample injector. TOC values represent the average of at least two measurements. After taking the sample and before measuring TOC, reaction was stopped by adding excess Na₂SO₃ (which quickly consumes remaining H₂O₂), followed by centrifugation and filtration for separation of the catalyst from the liquid phase.

The total Fe in the solution was determined using a UNICAM 939/959 atomic absorption spectrophotometer.

3. Results and discussion

3.1. Characterization of the catalysts

Intercalation/pillaring experiment, as indicated above, was carried out under standard conditions and proceeded successfully. The solid intercalated with Al₁₃ polycations and then calcined at 500 °C, used as support for further experiments, shows the typical features of Al-PILCs. It has a layered structure with a basal spacing of 18.2 Å (Fig. 1) and a BET specific surface area of 240 m²/g. Its thermal analysis curves (not shown) and FT-IR spectrum (vide infra) also show the typical behaviour of Al-PILCs.

The impregnated solids also maintain the layered structure, but with a remarkable loss of ordering if compared to the support. These catalysts, once calcined at 500 °C, show a weak diffraction peak, between 16.8 and 17.3 Å (2θ = 5–7°), due to 0 0 1 reflection (Fig. 1). However, as can be observed in these diffractograms, although the long-range ordering in the c-axis is low, it is not negligible, and all solids show a certain degree of layered-structure ordering. At the same time, the impregnation-drying process, mainly in the solids treated with acetylacetonate solutions, for which various impregnation cycles are needed, and the further calcination at 500 °C, produce a certain collapse and delamination of the structure. Reflections independent of c-axis ordering do not show any variation with respect to the support, indicating that the impregnation does not affect the individual layers, but only their stacking.

On the other hand, it may be underlined that no peaks due to iron phases are observed in the diffractograms, even for samples with 17.0 wt.% of iron (not shown in the figure). Considering the preparation method used and the results obtained from other techniques, it may be reasonably expected that phases of composition close to Fe₂O₃ be formed after calcination of the impregnated solids at 500 °C, by the removal of the organic moieties of the precursors and oxidation, if needed, of iron. However, no peaks of oxides or oxi-hydroxides are found in the diffractograms, although the amounts of iron used in the impregnations are relatively high. So, it may be proposed that iron is in form of a very disperse phase on the surface of the support (very small crystallite size, thus not detected by XRD). The presence of such well dispersed phase on the catalyst surface, particularly Fe(III) oxide, was confirmed by XPS (data not shown).

FT-IR spectra of the support and of various impregnated solids, both dried and calcined, are shown in Fig. 2. The FT-IR spectrum of the support shows, as indicated before, the characteristic bands of Al-PILCs. Thus, in the high wave number region, the spectrum is dominated by the stretching vibrations of the hydroxyl groups bonded to metallic cations and to water molecules. Bending of water molecules also produces an important effect close to 1630 cm⁻¹, while the bands characteristic of the tetrahedral layer of the clay dominate the region of low wave numbers, the band at 1007 cm⁻¹, assigned to Si–O–Si bonds, being the most intense of the spectrum, and the bands due to M–O bonds in the octahedral layer (mainly Mg–O and Fe–O, because of the chemical nature of saponite) appearing at lower wave numbers.

Spectra of solids impregnated and dried show, in all cases, the bands due to the support and bands assigned to the precursors. The first bands do not display important variations with respect to those of the support (they only show small differences in the intensity). This is an expectable observation,
because of the low influence of the impregnation on the structural bonds of the clay, where only surface hydroxyl groups may be affected, giving rise to interfacial coordination bonds with Fe$^{2+}$ and Fe$^{3+}$ cations of the precursors. On the other hand, the bands due to the precursors are strongly intense, as can be expected because precursors containing organic moieties have been employed. The characteristic bands of each precursor are observed in each case, with vibrations of C–H bonds, carboxylate or carbonyl groups, etc. All these bands disappear completely when the impregnated solids are calcined at 500 °C, meaning that organic moieties are completely removed at this temperature, by transformation of the precursor molecules into iron oxide-like phases. However, no peak due to Fe oxides neither oxy-hydroxides are observed in the spectra.

The contents of Fe (determined by elemental analyses) present in the final catalysts are shown in Table 1, together with the BET specific surface areas. Slight variations (<8.3%) are noticed between the expected and the determined iron content of the samples, which is due to the high hydration degree of the solids at the stages of the preparation procedure, thus making difficult to obtain the targeted iron contents. The values of specific surface areas are comprised between 128 and 192 m²/g, which represents a percentage of 53–80% of the value of the support. These values are relatively high considering the subsequent steps of the preparation of the catalysts, including impregnation, drying and calcination at 500 °C. It has been reported that the impregnation of clay supports with precursors containing organic moieties causes a strong decrease in surface area, by blocking of the interlayer porosity by such organic groups; sometimes the impregnated solids only showing the external surface area of the support. However, the further calcination of the impregnated solids produces, if the temperature is high enough to remove all the organic moieties, the recuperation of the access to the internal porosity of the support [20]. Sometimes, these successive processes cause a strong deleterious effect in the surface properties of the solids, although this is not the case for the solids prepared in this work. It may be noticed that part of this surface area may be due to the particles of iron incorporated, considering that they form phases of composition close to iron oxide phase and that they are very dispersed on the support surface.

The thermogravimetric analyses curves of the impregnated samples are displayed in Fig. 3. Several weight losses can be observed. The removal of adsorbed water and physisorbed
solvent occurs until ca. 150 °C. This is associated with a weight loss of around 7–8 wt.% for samples containing acetate and lower (3 wt.%) for those prepared with oxalate and acetylacetonate. The decomposition of the organic precursors occurs in the 150–325 °C range for Fe(II) acetate and Fe(II) acetylacetonate samples and in a wider range (150–425 °C) for the rest of samples. In addition, when using oxalate and acetylacetonate as precursors, the complexity of the salts, which are decomposed in several successive steps, determines the presence of more steps of weight loss in the corresponding TG curves of these samples than in those of the acetate samples. The values of total weight loss of the samples prepared in this work are comprised between 19.5 wt.% for Fe 7.5 acetate and 47 wt.% for Fe 17.0 oxalate, the values depending on the nature of the precursor used and the load of the same. The final weight loss observed in all cases in the 415–825 °C range is due to the dehydroxilation of the clay. For all samples, it is clear that the temperature of calcination guarantees the removal of the organic fragments and the obtaining of iron-like phases.

The DSC curves for the samples containing 13 wt.% of Fe are shown in Fig. 4. An endothermic peak is observed in the 30–150 °C for the sample containing acetate (Fig. 4A), as consequence of the highest weight loss of adsorbed water and solvent detected in the TG curve of this sample, with respect to those prepared with other precursors. The DSC peak corresponding to the decomposition of the most part of the organic material is centred at around 315 °C for acetate, 275 °C for Fe(II) acetylacetonate and 350 °C for oxalate and Fe(III) acetylacetonate. For these last three samples, other exothermic peaks of lower intensity can be observed in the 150–275 °C with associated weight losses in their corresponding TG curves. The removal of the last hydroxyl groups in the clay is observed as a clear weight loss close to 800 °C, associated to an endothermic effect, and once this dehydroxilation is completed, it is followed by an exothermic effect corresponding to the phase transformation from saponite to enstatite, not associated with any weight loss in the TG curves. No peaks that could be associated to transformation of iron phases are observed.

3.2. Catalytic behaviour

3.2.1. Effect of the precursor nature and iron load on the degradation of OII solution

As above-mentioned, catalytic experiments were performed using a 0.1 mM solution of OII, which is in the range of azo dyes concentrations usually found in industrial waste streams [27]. Although the natural clay has already some iron (ca. 1 wt.%), no degradation of the OII solution was noticed when using it as catalyst under the typical conditions adopted in this work (\( [\text{C}_{10} \text{H}_3 \text{O}_7]_0 = 6 \text{ mM}, \ T = 30 ^\circ \text{C}, \ \text{pH} \ 3, \ w_{\text{clay}} = 91.5 \text{ mg/L}, \ t = 4 \text{ h}) , which may be related to the inaccessibility of such iron, located in the octahedral positions of the clay structure. Besides, dye removal by adsorption (blank run in the same conditions but without hydrogen peroxide) was not detectable, what is due to the remarkably low concentrations of clay used in our work. The use of \( w_{\text{clay}} = 1 \text{ g/L} \), an amount commonly found in the literature, provided about 36% removal by adsorption after 4 h (but no equilibration was yet reached).
Fig. 5 shows the UV–vis spectrum obtained for the dye solution (0.1 mM) and also for samples taken along time in a typical experiment. Regarding the dye spectrum, it is characterized by two bands in the ultraviolet region located at ca. 235 and 315 nm and by one band in the visible region, with a maximum located at 486 nm. The absorbance peaks in the UV region are due to the benzene and naphthalene rings of OII, respectively [28], while the band in the visible region is due to the chromophore-containing azo linkage [29]. If one compares the original spectrum with that achieved after 240 min of oxidation, it is evident that the treated dye sample was almost colorless and did not show significant absorbance in the visible region, indicating that color removal was practically complete. The disappearance of the absorbance peak at 486 nm reflects, unequivocally, the breakdown in the chromophoric group. However, the spectrum in the UV region shows that the dye was not completely mineralized, even though the absorption intensity was reduced within the UV range. The slower decrease of the intensities of the bands at 235 and 315 nm, with respect to that of the azo bond, can be attributed to the formation of intermediates, resulting from the degradation of the azo dye, which still contain benzoic- and naphthalene-type rings. Another issue of interest is that the spectrum of the 60 min sample is, in the visible region, quite similar to that of the OII solution. Actually, both spectra almost overlap (by multiplying the original one by a factor smaller than 1), and no additional bands appear, indicating that intermediates formed do not absorb in the visible wavelengths, although they do it in the UV. This is also corroborated by other authors. For instance, Bandara and Kiwi [30] mention that in later stages discoloration of the OII leads to long-lived intermediates which absorb the smaller UV component, while Fernández et al. [31] refer that no colored intermediate species were generated in solution.

Mechanistic studies reported in the literature, either in homogeneous or heterogeneous processes, point for numerous intermediates formed from OII degradation, which include, among others, HSO₄⁻, NH₄⁺, NO₃⁻, 4-hydroxybenzenesulfonic acid, nitrogen and sulfo-containing products, benzenesulfonate, carboxylic and dicarboxylic acids and their anions, and also iron complexes [32–37]. However, none of these compounds absorb in the visible region, indicating that the absorbance decrease at 486 nm is only due to the dye degradation.

The results obtained for the oxidation of OII solution with the twelve catalysts prepared are displayed in Fig. 6. The effect of the nature of the precursor as well as the amount of active phase used on the catalytic activity can be observed. In each case, the referred concentration of OII is normalized with respect to the initial one (0.1 mM), and plotted as a function of the reaction time. The degradation reached after 4 h was, in most cases, quite significant. For the catalyst with lowest (7.5 wt.%) and highest (17.0 wt.%) iron contents, the best samples seem to be that prepared with the acetate precursor (Fig. 6A and C, respectively), while for the catalysts containing the intermediate concentration (13.0 wt.%), the best sample seems to be that prepared with the acetate precursor (Fig. 6B). Using the clay impregnated with 13.0% of Fe(II) acetate and 17.0% of Fe(II) oxalate, degradations of 95.2 and 95.9% were obtained.
obtained after 4 h, respectively. In contrast, the precursor that gave rise to the less active catalyst was the Fe(II) acetylacetonate with 13.0% of Fe, which produced an efficiency of only 66.4%.

It is noteworthy that for samples with ca. 7.5, 13.0 or 17.0 wt.% of Fe, Fig. 6A–C, respectively, there is no apparent relationship between the reaction rate for each set of catalysts and the effective amount of iron in the samples. This means that the slight differences in the amount of iron between different samples, which ranges between 7.54 and 8.12, between 13.81 and 14.02 and between 16.50 and 17.56 wt.% of Fe, respectively, for each one of the iron contents targeted (see Table 1), are not responsible for the differences recorded. On the other hand, the sample that exhibits higher reaction rate in Fig. 6B (Fe(II) acetate) is the one that loses more iron (Table 1), suggesting that the homogeneous process contribution could be of importance. However, for the samples with 7.5 or 17.0% of Fe (Fig. 6A and C, respectively) such relationship is not observed. Therefore, not only the homogeneous, but also the heterogeneous catalytic process, seems to have an important role in the degradation reaction.

It can also be observed in Fig. 6 that the influence of the iron concentration on the degradation of Orange II is not equal for all the precursors, but, in general, the final performances are not too different (with a few exceptions). The reason behind this fact is not yet clear, and a deeper insight regarding the mechanisms occurring in the system is required. Nevertheless, Table 1 shows clearly that TOC elimination, at the end of the runs, increases, for each precursor, with the iron load. This increment in the mineralization with the iron concentration occurs because when the amount of active phase increases, more radicals are produced for the oxidation reaction (Eqs. (1) and (2)).

To use a heterogeneous catalytic system in industrial practice, it is important to evaluate the loss of catalyst from the support. This was done by measuring the iron concentration in the solution along time (samples were taken every hour, although in Table 1 only data after 4 h of reaction time are shown). Some important results must be stressed. First, in almost all cases the iron leaching is considerably low (<1 mg/L, thus being below the EU directives (<2 mg/L)). Secondly, catalysts that exhibit higher iron leaching values are those prepared with the acetate precursor, independently of the iron load. Finally, the 17.0 wt.% samples are those that lose a smaller percentage of iron (except Fe(III) acetylacetonate). This is particularly interesting from the practical point of view due to the possibility of using these last catalysts for a longer operation time (slower deactivation). In this concern, it is especially remarkable the Fe(II) oxalate 17.0 catalyst, which shows a very good behaviour in terms of mineralization (81.6% of TOC reduction) and discoloration (95.9% of OII removal), and its performance seems to be mainly due to the heterogeneous Fenton-like process.

The importance of the heterogeneously catalyzed reaction is also put in evidence when one compares the performance of the catalysts prepared with precursors of Fe(II) versus Fe(III). While OII degradation is much more significant for the Fe(III)
acetylacetonate 17.0 sample as compared with the Fe(II) one (Fig. 6), in agreement with the iron leaching (Table 1), thus supporting the importance of the homogeneously catalyzed process, any relationship exists between these parameters for the 13 wt.% catalysts. In this case, the Fe(III) sample shows again better catalytic performance, without significant difference in iron leaching, which mean an involvement of the solid surface on the catalytic process.

The catalytic differences observed when several precursors are used are not clear, and will be the aim of further work (anion nature and iron oxidation state effect). Nevertheless, several factors might be indicated, which are known to affect the catalytic performance: (i) the iron dispersion [38], (ii) the Fe₂O₃ crystalline form (hematite or maghemite-Q) [22], (iii) the location of the iron species (bonded to the aluminium pillars or engaged in small oxide clusters dispersed in the solid, inside or outside the porosity) [39] or (iv) the oxidation states, nature and coordination of the iron species [19].

Based on the results described above, two catalysts were chosen to study into more detail the effect of the temperature, pH and initial H₂O₂ concentration. They were those prepared with oxalate with Fe content of 7.5 and 17.0 wt.%. As shown in Table 1, the best performances for mineralization are achieved for the catalysts prepared with oxalate, for all the iron contents. The same applies for the color removal, except for the 13.0 wt.% samples, where Fe(II) acetate 13.0 provides the best results (Fig. 6B). However, this sample looses much more iron than the rest (Table 1). Among the 13.0 wt.% catalysts, the Fe(II) oxalate sample also shows good decolorisation results, but differences between performances achieved by this catalyst and the Fe(II) oxalate 7.5 are minimal, thus being preferable, from an economical point of view, to use the catalyst with less iron content.

3.2.2. Temperature effect

The results obtained for the OII degradation at four different temperatures (10, 30, 50 and 70 °C), using catalysts prepared with Fe(II) oxalate with 7.5 and 17.0 wt.%, are shown in Fig. 7. The results show clearly that the reaction rate increases when increasing the temperature, which was expected due to the exponential dependency of the kinetic constants with the reaction temperature (Arrhenius law). Nevertheless, the final OII concentrations, after 4 h of oxidation, are very similar at 50 and 70 °C. In fact, the eliminations obtained at these temperatures are already quite similar after 2 h of reaction, with values around 98% whereas at 10 °C the elimination is practically negligible (ca. 8% after 4 h of reaction for both samples). Other authors have also found similar results during catalytic wet peroxide oxidation of phenol over Fe-exchanged clays [40,41], the similar performances achieved at higher temperatures being due to the accelerated decomposition of H₂O₂ into oxygen and water.

Table 2 shows the overall TOC removal for both catalysts at several temperatures (Runs 1–4). Once again, and as expected, the mineralization increases with the temperature, the performances reached being better for Fe oxalate 17.0, in agreement with previous results (Table 1). For this sample, it is remarkable that the TOC removal is near 91% at T = 70 °C and around 82% at 30 °C. Although lower than those obtained at higher temperatures, the values of OII and TOC removal achieved at 30 °C might be considered satisfactory. Taking into account that a lower temperature might reduce the process costs, 30 °C was the temperature chosen to carry out the following runs, where other parameters are changed. In addition, the iron leaching is smaller at 30 °C than at 70 °C.

| Run no. | Experimental conditions | Catalyst | TOC removal (%) after 4 h of oxidation 
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>pH</th>
<th>[(CH₂O₂)₆]o (mM)</th>
<th>Fe(II) oxalate 7.5</th>
<th>Fe(II) oxalate 17.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>3.0</td>
<td>6</td>
<td>8.0</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>3.0</td>
<td>6</td>
<td>70.3</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>3.0</td>
<td>6</td>
<td>80.5</td>
</tr>
<tr>
<td>4</td>
<td>70</td>
<td>3.0</td>
<td>6</td>
<td>84.7</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>2.0</td>
<td>6</td>
<td>61.6</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>3.5</td>
<td>6</td>
<td>39.8</td>
</tr>
<tr>
<td>7</td>
<td>30</td>
<td>3.0</td>
<td>3</td>
<td>67.3</td>
</tr>
<tr>
<td>8</td>
<td>30</td>
<td>3.0</td>
<td>12</td>
<td>64.6</td>
</tr>
<tr>
<td>9</td>
<td>30</td>
<td>3.0</td>
<td>24</td>
<td>66.2</td>
</tr>
</tbody>
</table>
and is not very significant after 4 h (<0.25 mg/L, thus being below the value of the EU directives), although we have not experimentally observed any clear relationship between the loss of catalyst from the support and the reaction temperature.

3.2.3. pH effect

The results obtained for the OII degradation using the Fe(II) oxalate catalysts at three pH values are displayed in Fig. 8. The best results of the OII degradation were obtained at pH 3.0, for both iron loads. At the lowest value of pH tested, pH 2.0, the reaction is very slow and an important increase of decolorisation activity was only noticed after ca. 2.5 h of reaction. However, at pH 3.5 performances achieved are even worst, with color removals after 4 h of only 43 and 51% for 7.5 or 17.0 wt.% of Fe, respectively (Fig. 8A and B). It must be stressed that additional experiments have also been performed at pH 4.0 (not shown for brevity) but practically no dye degradation was produced, even for much longer reaction times. Regarding TOC removal, conclusions are similar, with better performances for both samples at pH 3.0 (Table 2). Curiously, this was exactly the best pH value found by Feng et al. [42] during OII degradation using clay-based Fe nanocomposites with photo-Fenton process, with a reaction rate decrease similar to that reported by us when one deviates from such pH value. Other authors also found, using pillared clays, that the reaction rate was much higher for the pH value corresponding to the optimum pH determined when homogeneous Fe species were used as catalysts [43].

A dependence of the reaction performance with the pH similar to that obtained by us is normally observed in homogeneous reaction, and the decreased performance at lower pHs is usually attributed to the inhibition of the reaction between Fe$^{3+}$ and hydrogen peroxide, because the formation of the iron(III) peroxocomplexes (as intermediates) decreases when pH decreases [44]. Besides, the stability of H$_2$O$_2$, which is independent of having a homogeneous or heterogeneous process, is affected by the pH, with the lower degree of decomposition observed at pH values between 3 and 4 [41]. Above pH 4, the rapid H$_2$O$_2$ decomposition produces molecular oxygen without formation of appreciable amounts of hydroxyl radicals.

Fig. 9 shows the effect of the reaction pH on the iron leaching. It is clear that iron lost is more significant at pH 2.0, especially for the 7.5 wt.% catalyst. Therefore, for long-term stability, it would be preferable to work at higher pH values. Feng et al. [42] also found that iron leaching was much more significant at pH around 2. The Fe leaching at this low initial
solution pH can be attributed to the dissolution of iron oxide at very acidic conditions. At pH 2.0, the amount of iron leached into solution is much higher for the Fe oxalate 7.5 than for the Fe oxalate 17.0 (Fig. 9A versus B), although the catalytic performance of the first catalyst is not better (Fig. 8A versus B and Table 2), thus supporting the importance of the heterogeneous catalytic process. Finally, it is noteworthy that in the pH range studied (2.0–3.5) the sample with more iron (17.0 wt.%) shows almost always lower percentages of iron lost (Figs. 9A and B), and thus can be in practice used for more operation cycles.

### 3.2.4. Initial H$_2$O$_2$ concentration effect

The initial hydrogen peroxide concentration was varied between 3 and 24 mM, using the same catalysts as in previous sections. The results obtained (Fig. 10) show, for both samples, a similar behaviour in terms of dye degradation for the intermediate H$_2$O$_2$ concentrations (6 and 12 mM), whereas the reaction goes by more slowly when the concentration is lower (3 mM) or higher (24 mM). The increase of the oxidant concentration from 3 to 12 mM leads to an increase in the reaction rate, as expected, because more radicals will be formed (Eqs. (1) and (2)). Nevertheless, for a very high hydrogen peroxide concentration (24 mM) the performance decreases. The existence of an optimum hydrogen peroxide concentration is typical and well-known in Fenton’s oxidation. This optimum value was previously found by us to be 10 mM for OII degradation in homogeneous Fenton reaction, using a solution of Fe(II) sulfate as catalyst [45]. At higher H$_2$O$_2$ concentrations the scavenging of HO$^*$ radicals will occur, which can be expressed by the following reaction:

$$H_2O_2 + HO^* \rightarrow H_2O + HO_2^* \tag{3}$$

Although other radicals (HO$_2^*$) are produced, their oxidation potential is much smaller than that of the HO$^*$ species [46].

It is important to remark that all decolorisation curves in Fig. 10 show a sigmoidal profile, which is typical for autocatalytic or radical reactions, and that it was also observed in other studies concerning organics degradation with pillared clay catalysts [41]. Basically two regions can be identified, the initial one representing the induction period, and the second one after the inflection point representing the steady state.

The influence of the H$_2$O$_2$ concentration on the mineralization (see Table 2) is similar as for decolorisation, with an optimum oxidant concentration of 6 mM for both catalysts. In spite of the final performances attained seem to be only slightly affected by the peroxide dose, it is clear that for H$_2$O$_2$ concentrations above that value the final TOC removal decreases a little bit, this effect being similar to those reported by other researchers [1,47].

Regarding iron leaching, it is noteworthy that, once again, the concentrations reached are always small (below 0.4 mg/L for both samples), but we have not found any relationship between the loss of catalyst from the support and the hydrogen peroxide concentration (data not shown for brevity).

### 3.2.5. Stability and recycling of the catalyst

For a practical implementation of a heterogeneous catalytic system, it is crucial to evaluate the stability of the catalysts. For that purpose, a sample that shows a low iron leaching, but presenting simultaneously good catalytic performance, should be selected. The Fe(II) oxalate 17.0 sample meets all these criteria, as shown before (see Section 3.2.1).

Fig. 11 shows the performance reached in terms of OII degradation in four consecutive runs. To recover the catalyst, the final effluent was filtered. After the first cycle, and in order to check if the leached iron was responsible for the catalytic activity, both OII and H$_2$O$_2$ were added to the solution in the same concentrations as at the beginning of the experiment. Fig. 11 shows that in these conditions OII conversion is only a very small fraction of that recorded in the presence of the pillared clay, thus demonstrating that the Fe leached is not capable to destroy the dye, i.e., the process is essentially heterogeneous. For subsequent cycles, the filtered clay was dried overnight between consecutive runs. Even though a slight activity decay is observed, which might be due to the iron loss (ca. 1.5% per cycle that represents a final concentration smaller than 0.3 mg/L, data not shown), OII conversion decreases only from 95.8 to 90.3% in 4 cycles, i.e., 16 h of operation.

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**Fig. 10.** Effect of the hydrogen peroxide concentration on the degradation of OII solution using different catalysts: (A) Fe(II) oxalate 7.5 and (B) Fe(II) oxalate 17.0. pH 3, $T = 30^\circ$ C.
4. Conclusions

- Twelve supported Fe-saponite catalysts have been prepared, by means of the incipient wet impregnation method, using a pillared clay support and four salts of Fe precursors at different Fe loads. The characterization of the catalysts shows that the decomposition of the precursors gives rise to solids that present laminar structure, with active phases of Fe highly dispersed on the support, and high specific surfaces (in most of the cases with values comprised between 130 and 170 m$^2$/g), characteristics that make them potentially good catalysts for oxidation in the Fenton-like process.

- All the catalysts revealed to be quite active in the Fenton-like oxidation of Orange II, because clay concentrations used are much below than those usually found in the literature (typically around 1 g/L).

- The effects of the nature of the catalyst’s precursor, hydrogen peroxide concentration, temperature and pH of the reaction medium were analysed in the present work. The obtained results show a high degradation of OII and of the intermediary oxidised compounds. At optimal conditions, 99% discoloration and 91% of mineralization were reached (after 4 h of reaction), using the catalyst prepared from Fe(II) oxalate with 17.0 wt.% of Fe and in the following reaction conditions: $T = 70{^\circ}C$, pH 3.0 and $(C_{H_2O_2})_o = 6$ mM. However, good performances with high selectivities to $CO_2$ and $H_2O$ were also reached at significantly lower temperatures (30 °C).

- All the catalysts exhibit not only good catalytic activity but also a reasonable small iron leaching (below the EU directives values), indicating that the active phases are strongly fixed to the support (possibly iron strongly bonded to the aluminium pillars or engaged in small oxide clusters dispersed in the solid, inside or outside the porosity). This characteristic makes possible the Fe-saponite catalysts to have long-term stability, without generating iron hydroxide sludges.

- It was shown that the nature of the salt and the content of iron used to prepare the catalyst have a significant effect on the process performance, the Fe(II) oxalate 17.0 being the most promising one. Consecutive reaction cycles carried out with this sample showed a minor deactivation, which is possibly due to some iron leaching, thus evidencing the possibility of being used in continuous processes.

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