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Pillared Clays as Catalysts for Methyl parathion removal by Advanced Oxidation Processes

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Abstract:

A natural Bentonite from Mostaganem in Algeria was modified by intercalation with polyoxocationic solutions (Al.Fe, Al.Co, Al.Cu, Al.Fe.Cu or Al.Fe.La), the modification of the Bentonite occured via pillaring by ionic exchange with the prvious solutions. The addition of these solutions led to the formation of pillared clays with important catalytic properties in environmental impact reactions.

The structural and textural properties of materials that had been calcined at 500°C were determined by several techniques: X-ray fluorescence (XRF), X-ray diffraction (XRD), the Fourier transform infrared (FTIR spectra) and N2-adsorption/desorption analysis.

The pillared clays have been used as a Fenton-type heterogeneous catalyst then for heterogeneous Sono-Fenton process for the oxidation of Methyl parathion in water.

The catalytic tests revealed the activity of the introduced iron species and the promoter effect of the Lanthanide or Copper on the catalytic activity of these species.

The Sono-Fenton method showed promising results for the degradation of Methyl parathion when compared with Fenton. Therefore, Sono-Fenton can be a viable alternative technology to the existing methods for treating Methyl parathion in wastewater.

Keywords: Pillared Montmorillonite clays; Heterogeneous catalysts; Aluminum-iron- copper - polyoxocation; ; Fenton and Sono-Fenton processes; Methyl parathion; Pesticides wastewater;

1. Introduction:

Organophosphorus pesticides (OPs) are widely applied for plant and crop protection and frequently detected in surface water and ground water with concentrations at ng/L to µg/L levels [1, 2]. The toxicity of OPs is due to the non-specific inhibition of enzyme acetyl cholinesterase (AChE) in the nervous system [3, 4].

Methyl parathion (MP) (O,O-dimethyl-O-(4-nitrophenyl)phosphorothioate; 1) (see Fig 1) is an organophosphorous pesticide (OPs) introduced into the agricultural market in the early 1950s. This insecticide is widely used to control chewing and sucking insects in a wide range of crops including cereals, fruits, vines, vegetables, ornamentals, cotton and field crops [5].

In addition to that, MP is classified as ‘‘extremely hazardous’’ by the World Health Organization [6], and it is frequently used on crops as an agricultural insecticide in Algeria.

MP is generally applied as a spray and can contaminate soils, water and ground water, and then can constitute a potential hazard for animals and human being. It can lead to the degradation of some products such as methyl paraoxon which is more toxic than the initial product [7]. The accepted concentration of MP in ground water is 0.1 µg L^{-1} for European Union [8].

Because MP are highly toxic and hardly biodegradable, different methods have been tested to remove them from water. Among the processes used for the removal of these pollutants, it can be found the advanced oxidation processes (AOP’s) that have been defined as those aqueous phase oxidation processes based on the use of hydroxyl radical as oxidant [9]. The group of these methods has attracted an increasing interest due to the fact that it avoids the use of costly reactors (as other methods, like wet air oxidation). One of the most promising AOP’s is based on the use of Fenton’s reagent [10]. The Fenton process uses Fe^{+2} as catalyst to generate hydroxyl radicals from hydrogen peroxide. The Fenton reaction can be written in its general form:

$$M^{n+} + H_2O_2 \longrightarrow M^{(n-1)+} + OH^- + HO^\cdot \qquad (M = Fe, Cu, Mn)\ [11].$$

The main disadvantage of this process is the continuous loss of the catalyst in the effluent which furthermore has to be removed from it before discharge. Besides, this process requires acidification of the initial solution since the optimum operating pH is around 3, corresponding to the maximum concentration of the active Fe^{+2} species and to the lowest rate of H_2O_2 parasitic decomposition[12].

The use of solid Fenton-type catalysts, using different Fe-bearing catalysts, offers a promising solution due to its easier recovery after the oxidation treatment. The low contamination of the effluents with metals could negatively influence a possible subsequent biological treatment step and a wider operative pH range. Heterogeneous catalysts for catalytic wet peroxide oxidation (CWPO) consist most commonly of transition-metal oxides and noble metals as active phases supported on zeolites [13] or activated carbon [14]. Deactivation has been often observed together with leaching of the catalytically active elements.

Clay-based catalysts pillared by Fe^{+3} hydroxo complexes or mixed Al-Cu or Al-Fe pillared clays have shown encouraging results for oxidizing organic compounds in aqueous media using hydrogen peroxide [15-16].

Pillared clays are a class of microporous materials with high surface area and acidic property. The intercalation of the inorganic cationic clusters as pillars imparts thermal stability generating new micropores and acidic sites in the clay materials [17–18]. Recently, these materials have been increasingly used as catalysts for several important catalytic reactions [19, 20].

Among the AOPs, strong efforts are being done to develop solid catalysts able to generate the reactive radicals under ambient conditions of temperature and pressure, often being referred to catalytic wet peroxide oxidation (CWPO). The Al/Fe-pillared clays constitute one of the most promising groups of structured materials that have successfully accomplished such a task [21,22]. Pillaring of natural or synthetic clays consists in the intercalation of voluminous inorganic polycations driven by cationic exchange, wherein by far the system more studied has been the Keggin polycation $(Al_{13})^{7+}$ [23,24].

Among the materials suitable for catalytic applications, laminar clays, such as Montmorillonite which shows good physical–chemical properties that are useful for a great number of applications principally because of their sorption capacity and their acidic properties [25].

Montmorillonite can be pillared by different polyhydroxymetal cations. Upon calcination, the resulting materials contain metal oxide pillars that sustain the clay sheets, thereby exposing the internal surfaces of the clay layers.

Na-Montmorillonite (Na-Mt) is one kind of cationic clay [26] and can be modified to obtain materials for specific applications [27]. The cations of Na-Mt can be easily replaced by large polynuclear cations, which form stable metal oxide pillars during thermal treatment that link permanently the silicate layers [28].

The intercalation and pillaring processes produce a porous structure with particular surface sites, which determine the potential use of these solids in catalytic applications.

One of the most studied subjects related to pillared clays is their use as supports for catalytically active phases, and the application of the resulting solids in several reactions; particularly in environmentally friendly ones as a Fenton-type heterogeneous catalyst [29]. Combination of Fenton with sonolysis, Sono-Fenton process, can be applied to increase the mineralization efficiency of the organic compounds [30].

Interestingly, ultra-sound irradiation favors the removal of reactive intermediates or by products from the catalyst surface, thereby providing clean and reactive surfaces for subsequent reactions over heterogeneous catalytic systems [31].

The advantage of using a heterogeneous system is the easy removal of catalysts by filtration. Moreover, ultrasonic irradiation generates benefits in heterogeneous systems by decreasing mass transfer limitations and fragmentation of the solid into small particles that provide a higher surface area [32], also account for the main advantages of ultra sound system over other AOPs [33,34].

2. 2. Experimental

2.1. Materials

The clay used in this work is Bentonite extracted from Mostaganem, Algeria. It is a natural Bentonite derived from the Montmorillonites family [35].

In the frame of this work, the obtained samples of Bentonite have the following total composition after drying conditioning: SiO_2: 65.83 wt.%; Al_2O_3: 13.96 wt.%; Fe_2O_3: 10.17 wt.%; MgO: 0.39 wt.%; CaO: 5.28 wt.%; K_2O : 2.89 wt.% Na_2O: 0.25 wt.%; TiO_2: 1.09 wt.%. The Bentonite was purified by washing it several times with distilled water to eliminate the surface impurities. The Montmorillonite fraction was obtained by the sedimentation of 100g of our Bentonite, in 10 L of water.

In order to separate the pure Mt particles (particle size-fractions required: < 2 μm) from associated minerals (quartz, calcite…), The clay was purified by conventional sedimentation collecting the <2 μm fraction, the used Bentonite were found containing montmorillonite (65%), and other impurities including (quartz, K-feldspars, plagioclases). The cation exchange capacity of the separated montmorillonite was determined by adsorption of a copper ethylenediamine complex. For the starting montmorillonite, the cation exchange capacity (CEC) is 83 meq/100 g.

The sodium containing Montmorillonite (Mt-Na) used for the preparation of the pillared samples was synthesized by the treatment of the Montmorillonite with 1 M NaCl at a ratio 1/100 (w/w) between solid and liquid phases at 80 °C for 2 h, followed by centrifugation at 3000 rpm during 15 min.

2.2. Catalysts preparation:

For pillaring the clay Montmorillonite (Mt-Na), several clay samples were exchanged with an appropriate aqueous metal ion polyhydroxycationic solution of Al.Fe(20%) ; Al.Co(20%), Al.Cu(20%) Al.Fe(10%).Cu(10%) or Al.Fe(10%).La(10%).

2.2.1. Preparation of pillaring solutions:

These solutions were prepared from a 0.2 mol/L Al^{3+} solution containing calculated quantities of Fe^{3+},Co^{2+} ,Cu^{2+},La^{3+} to obtain molar ratios of 20%:

[100×M/(Al+M)=20; M (Fe^{3+},Co^{2+}, Cu^{2+},La^{3+}), so each solution contains the following:

Al.Fe(20%) : [100×Fe/(Al+Fe) = 20;

Al.Co(20%) :100×Co/(Al+Co)= 20;

Al.Fe(10%).Cu(10%) : 100×Fe/(Al+Fe+Cu) =10 , 100×Cu/(Al+Fe+Cu)= 10;

Al.Fe(10%).La(10%) :100×Fe/(Al+Fe+La)= 10 , 100×La/(Al+Fe+La)= 10].

Synthesis of the Al.Fe polyoxocation:

The pillaring solution was prepared by adding 0.5 mol/L NaOH to $AlCl_3$ and $FeCl_3$ [0.2mol/L, Al (80%): Fe (20%)] that solution drop wise with vigorous stirring to obtain the OH/ (Al+Fe) ratio of 2,2. The hydrolysis is carried out by using an ultrasonic bath (35 KHz) during 45min. Then the pillaring solution was aged for 8 days at room temperature.

Synthesis of the Al.Co polyoxocation :

The pillaring solution was prepared by adding 0.5 mol/L NaOH to $AlCl_3$ and Co (NO3) (0.2mol/L, Al (80%): Co (20%)) that solution drop wise with vigorous stirring to obtain the OH/ (Al+Co) ratio of 2,2. The hydrolysis is carried out by using an ultrasonic bath (35 KHz) during 45 min. Then the pillaring solution was aged for 8 days at room temperature.

Synthesis of the Al.Cu polyoxocation:

The pillaring solution was prepared by adding 0.5 mol/L NaOH to $AlCl_3$ and $CuCl_3$ (0.2mol/L, Al (80%): Cu (20%)) that solution drop wise with vigorous stirring to obtain the OH/ (Al+Cu) ratio of 2,2. The hydrolysis is carried out by using an ultrasonic bath (35 KHz) during 45 min. Then the pillaring solution was aged for 8 days at room temperature.

Synthesis of the Al.Fe.Cu polyoxocation :

The pillaring solution was prepared by adding 0.5 mol/L NaOH to $AlCl_3$, $FeCl_3$ and $CuCl_3$ (0.2mol/L, Al (80%):Fe (10%):Cu (10%)) that solution drop wise with vigorous stirring to obtain the OH/ (Al+Fe+Cu) ratio of 2,2. The hydrolysis is carried out by using an ultrasonic bath (35 KHz) during 45 min.Then the pillaring solution was aged for 8 days at room temperature.

Synthesis of the Al.Fe.La polyoxocation:

The pillaring solution was prepared by adding 0.5 mol/L NaOH to $AlCl_3$, $FeCl_3$ and $LaCl_3$ (0.2mol/L, Al (80%) : Fe (10%) : La (10%)) that solution drop wise with vigorous stirring to obtain the OH/ (Al+Fe+La) ratio of 2,2. The hydrolysis is carried out by using an ultrasonic bath (35 KHz) during 45 min. Then the pillaring solution was aged for 8 days at room temperature.

2.2.2. Preparation of pillared Montmorillonite clays catalysts:

After the aging process, the final pillaring solution was used to intercalate the clay samples, 1% Mt-Na clay aqueous suspensions that had been previously hydrated for 24 h at 20°C, and then was dispersed by ultrasonic treatment for 30min, by cationic exchange of the clay Montmorillonite with the polyhydroxycations contained in the aqueous medium, to obtain a ratio of 10 milliequivalents of total metal ions per gram of clay was used.

The pillaring solution was added drop wise to the clay aqueous suspension (1% Mt-Na) under constant stirring at room temperature with the ultrasonic process for 45 min, always using (M+Al)/clay ratio of 10 mmol/g. The suspensions were kept in contact with the solution at room temperature for 24 h, then separated by centrifugation and washed with distilled water (5 times). The intercalated solids were finally dried at 60 °C and calcined at 500 °C for 02 hours, using a heating ramp of 5°C/min.

The resulting catalyst product was referred as Mt-Fe/Al, Mt-Co/Al, Mt-Cu/Al, Mt-Fe.Cu/Al, Mt-Fe.La/Al (The sub index values indicate the metal percentage in the initial pillaring solution).

2.5. Catalysts characterization:

The chemical composition of all materials is tested using PANalytical PW4025 X -ray fluorescence spectrometer (XRF) Philips equipment with Rhodium tube, a maximum power of 9 Watt and maximum Voltage of 30 kV. The current intensity used for this analysis is 20mA with a voltage of 13KV.

The structure of the host (starting) clay and the pillared intercalated clays, was studied by X-ray diffraction using a PANalytical XPERT-PRO diffractometer using Cu K (λ=1.5418A°) radiation at 45 kV and 20 mA. XRD patterns were recorded with 0,0170 (2θ) steps over the 5–90° angular range with 91,7599 s counting time per step. These recordings allowed to calculate the d(001)-spacing characteristic of the interlamellar spacing for a pillared clays.

The Fourier transform infrared (FTIR) spectra of each sample was recorded between 400cm^{-1} and 4000cm^{-1} by the KBr drift technique on a Jasco FT/IR-4200 Fourier transform infrared spectrometer.

N_2 adsorption–desorption isotherms were measured at liquid nitrogen temperature with a gas sorption analyzer (Quantachrome NovaWin2 - Data Acquisition and Reduction for NOVA instruments). Before measurement, samples were out gassed at 300°C a pressure less than 10^{-3} Torr for at least 2h. The specific surface area was calculated by the BET equation and the total pore volume was evaluated from nitrogen uptake at a relative pressure of 0.985. The *t*-plot according to De Boer’s method was used to calculate the micropore volume, The Barrett Joyner–Halenda (BJH) method was used to evaluate the average pore diameter (APD) and the pore size.

2.6. Catalytic activity:

2.6.1. Heterogeneous Fenton Process

The catalytic activity experiments for catalytic wet peroxide oxidation of Methyl parathion (MP) with the different pillared clays were performed in a 200mL thermostated Pyrex reactor. The pesticide methyl parathion (MP) was analytical grade ([98% purity) from Riedel-de Haën (Germany), and it was used as received. Solutions of 50 mg/L were prepared with ultra-pure water. The reaction temperature was regulated with circulation of thermal fluid at 298K using Julabo MC 4 heating circulator.

The reactor containes 0.1L of aqueous (MP) solution (50 mg/L). The pH was adjusted to 3.0 by concentrated H_2SO_4. Then an amount of 0,2 mL hydrogen peroxide (30 wt.%) was added to initiate the reaction.

The pH was continuously controlled within the range of 3–3.2, which has been reported as the optimal for Fenton oxidation as well as for catalytic wet peroxide oxidation with pillared clays catalysts (Mt-Fe/Al, Mt-Co/Al, Mt-Cu/Al, Mt-Fe.Cu/Al, Mt-Fe.La/Al) [16,28].

The catalyst in these samples was removed using a nylon filter of 0.2 µm pore size. The Samples were periodically collected at specified intervals and the reaction was stopped immediately by adding 0.1M sodium hydroxide. Analytical samples were stored in plastic bottles at 4^{o}C.

2.6.2. Heterogeneous Sono-Fenton Process

Experimental condition was identical to that of the Fenton process. The reactor was immersed into the ultrasonic bath (Elma, Trans Sonic TH-I-10, Germany) where the ultrasonic wave frequency was 35kHz.

The degradation studies on MP were investigated by Sono-Fenton method. The efficiency of this method was compared with the degradation efficiency of Fenton.

2.7. Chemical analysis

The samples that collected at different times of reaction were filtered through 0.2 µm Millipore disks (Nylon) to remove catalyst particles before analysis. The progress in the degradation of Methyl parathion was captured by a High pressure liquid chromatography-diode array detector (HPLC-DAD), analyses were performed with a Shimadzu HPLC system. The analytical column used was an HDO-C18 (150 mm×3 mm, 3µm). The flow rate was 0.5 ml min^{-1} and the injection volume was 20µl. The isocratic elution conditions were acetonitrile (15%)/water (85%). The wavelength for detection was 275 nm.

Absorption spectra (200–800 nm spectral range) of aqueous solutions of MP ($1mgL^{-1}$) were recorded on Shimadzu UV-2101 spectrophotometer (Fig. 2).

The formation of inorganic ions was detected using a Metrohm 850 Professional IC Ion Chromatograph equipped with a 850 Professional IC conductivity detector.

An Metrosep-A-Supp 16-250/4 column (250 mm × 4 mm) and a mobile phase Na_2CO_3/NaOH at a flow rate of 0.8 ml min^{-1}were used for the analysis of the anions.

The intermediate products degradation of Methyl parathion were extracted with dichloromethane (3mL × 3). The combined organic fraction was dried by Na_2SO_4, and concentrated under rotary evaporator. A GC/MS (VARIAN SATURN 2200) was used for the separation and the detection of the intermediate products. The GC was equipped with a HP-5 capillary column (30 m×0.25 mm i.d.) in helium carrier gas (1.5 mL min^{-1}) and with splitless injection system. The GC oven temperature was set to hold 50°C for initial 3 min, to increase from 50 to170 °C at a rate of 25°C min^{-1} and to increase from 170 to 250°C at a rate of 4°C min^{-1} and to hold at 250°C for 4 min. The injector and interface temperatures were kept at 250°C. Mass spectra were obtained by the electron-impact (EI) mode at 70 eV using the full scan mode.

3. Results and Discussion

3.1. Catalysts Characterization

The chemical composition of the Bentonite , Montmorillonite (Mt-Na) used and the pillared Montmorillonite (Mt-Fe/Al, Mt-Co/Al, Mt-Cu/Al, Mt-Fe.Cu/Al, Mt-Fe.La/Al) by XRF is shown in (Table.1),The elemental chemical analysis show the effective Chemical modification of all the solids and clearly the effective incorporation of Na, Fe, Co, Cu, La and Al into the modified Montmorillonite.

A decrease in the SiO_2/Al_2O_3 ratio compared to that of the natural clay confirms incorporation of the aluminum species. For synthetic samples, the lower contents of K, Ca and Na demonstrate that polyoxocations pillars have entered into the interlaminar zone of Mt-Na via ion-exchange, which is further confirmed by the presence of iron, copper, cobalt and Lanthanide in these pillared Montmorillonite in all cases.

XRD is used to investigate the phase structures of the samples and the XRD patterns of catalysts are shown in Fig. 3.

According to X-ray diffraction patterns Fig. 3 the following phases were identified in the investigated samples: Montmorillonite, quartz, feldspar and calcite. As shown in the Fig. 3.a, the diffraction peaks at 5.8° ,8.8°, 12.8°, 19.8°, 20.9°, 26.8°, 31.9°, 36.6°, 45.5° corresponding to Montmorillonite [35] and the diffraction peaks at 21.88°, 29.18°, 35.58° corresponding to cristobalite as a small impurities [36].

We have to notify the shifting of reflection d 001 corresponding to a basal spacing of 12.55 Ǻ for 2θ=5.8° for the initial Bentonite, to a basal spacing of 14.77 Ǻ for 2θ=5.8° corresponding to the Mt-Na. This result confirms the effective introduction of the Na to the interlamellar spacing.

Fig. 3.c shows the X-ray diffraction results for the catalysts synthesized with different pillaring solutions (Al.Fe, Al.Co, Al.Cu, Al.Fe.Cu or Al.Fe.La), Mt-Na shows a basal spacing (d001) of 14.77 Å, where the corresponding signals for the other catalysts (d001 of 16.1, 16.4, 16.1, 16.2 and 17.0 Å) show a shift of basal spacing to higher values (lower angles °2θ), confirming the successful pillaring [37].

The polyoxocations structural peaks were not observed in any of the catalysts during XRD analysis, which clearly indicated that polyoxocations oxides were well dispersed throughout the support structure and on the other hand, the amount of its crystalline was too small to be detected [33].

The FTIR spectrum shown in the Fig. 4 reveals the presence of two absorption bands located at 3200-3800 cm^{-1} and 1600-1700 cm^{-1}. The band situated in the range 1600-1700 cm^{-1} is attributing to the deformation of OH of the water adsorbed between lamellar sheets. The strongly intense peaks at 3500 cm^{-1} correspond to the stretching modes of the hydroxyl bands Al-OH [38]. The Si–O stretching band 900-1200 cm^{-1} centered at 1036 cm^{-1} is related to crystalline silica [39]. In the case of Mt-Na, it is situated at the band 1115-1020 cm^{-1} and exactly at 1041 cm^{-1}[40]. The bands situated at 519, 471 and 424 cm^{-1} are assigned respectively to the deformation of Si-O-Al, Si-O-Mg and Si-O-Fe. The sharing of the hydroxyl bands OH between the Fe and Al which are in octahedral positions can shift the vibration of the band Al-OH to low frequencies (approximately between 840 and 915 cm^{-1}). As shown in the Table 2, the shift observed for the two peaks situated at 1041 cm^{-1} and 1093cm^{-1} is related to the changes occurred as soon as the polyoxocations were inset.

Nitrogen adsorption–desorption isotherms recorded for the modified clay samples are presented in Fig. 5 and shows the adsorption isotherms of the natural Bentonite and of the solids (Mt-Na. Mt-Fe/Al, Mt-Co/Al, Mt-Cu/Al, Mt-Fe.Cu/Al and Mt-Fe.La/Al) which are representatives to all pillared clays obtained .

The pillared clays show an increase in the adsorption compared with natural clay, this behaviour is general for all the series of synthesized solids. The modified solids, including natural clay, show type I isotherms according to the IUPAC classification, which is a characteristic of microporous solids and of a predominant adsorption in a monolayer. In all cases, a type H3 hysteresis is observed, which is a characteristic of pores with a laminar shape.

The textural properties of the solids, summarized in Table 3, show the increase in the micropore areas and volumes of pillared clays compared to those of the natural clay as a result of micropore formation in all the synthesized solids.

The S_{BET} values between 78 and 152 m^2g^{-1} are much higher than that of the original clay (24 m^2g^{-1}); thus, confirming that the pillaring process took place successfully in both size fractions. In fact, the inclusion of oxidic species (pillars) in the interlamellar space of the clay generates a micropore volume between the clay layers, which is responsible for the observed increase of the specific surface area.

3.2. Catalytic performance

In order to determine the best catalyst for the process, we have investigated the oxidation of 50 mg/L of Methyl parathion (MP) by 0,2 mL (600 mg/L) of hydrogen peroxide (30 wt.%), 0.5 g/L of catalyst at pH of 3, and a temperature of 25°C. All the results are presented by plotting the conversion of MP, X_{MP}, versus time.

Fig.6 shows the main results of the catalytic activity for solids in the MP oxidation reaction. The starting natural clay presents a very low activity (MP conversion) due to the absence of active sites. The solid Mt-Co/Al, Mt-Cu/Al, in which no iron species are introduced, also shows catalytic activity which can be referred to the effect of cobalt or copper in Fenton process, as it can be related with the existence of iron species coming from the natural clay (as detected by XRF), which after the pillaring process becomes accessible to reactant molecules.

Synthesized solids (Mt-Fe/Al, Mt-Fe.Cu/Al and Mt-Fe.La/Al) are excellent catalysts with an almost total transformation of Methyl parathion in less than two hours. It is clear that the introduction of iron species leads to obtain more active solids, being Mt-Fe.La/Al sample the most active one.

On the other hand, the clay modified with Al.Fe.La polyoxocation is a very active (100% of Methyl parathion conversion in the first 2 h of reaction) catalyst in the total oxidation of Methyl parathion, at 25°C in atmospheric pressure.

In order to confirm the mineralization degree of MP in the heterogeneous Fenton Process with the catalyst Mt-Fe-La/Al, the determination of ion chromatogram is also carried out within 120 min at 30 min interval. In the ion chromatogram as shown in Fig. 7, there are three kinds of peaks, which belong to N, S and P anions, respectively, resulting from the N, S and P atoms in MP molecule. It illuminates that the N, S and P heteroatoms are mineralized into N, S and P anions (NO_3^-, SO_4^{2-} and PO_4^{3-}), respectively, in heterogeneous Fenton reaction. In addition, it can be found that the peaks of N, S and P anions become higher and higher along with the increase of oxidation reaction time, which indicates that more and more MP is degraded.

After 3 hours from the reaction of the degradation, by examining the presence of MP using the GC/MS shown in Fig. 8, no signal of Methyl parathion and of other organic compounds was observed. The main products issued in Methyl parathion (MP) oxidation by H_2O_2, were CO_2 and H_2O. The aromatic groups were almost decomposed which indicated the total decomposition of Methyl parathion. The final products are CO_2, H_2O and inorganic ions (PO_4^{3-}, SO_4^{2-}, NO_2^-, and NO_3^-) as found in the previous study [42].

The comparison of Sono-Fenton and Fenton on the degradation of MP shows the influence of an ultrasonic wave on Fenton's process (Sono-Fenton) for the degradation of MP and which was compared with the degradation efficiency of the Fenton method with respect to the decrease of the MP concentration. Both of the experiments were carried out simultaneously as described earlier.

Fig.9also includes results of experiments performed using ultrasound in presence of hydrogen peroxide, but without catalyst (curve1),

In the selected conditions, the degradation of MP in the Sono-Fenton reaction (Fig.9, curve3) is much higher than that in the Fenton's process (Fig.9, curve2)

Comparison between the ultrasonic runs carried out in presence (Fig.9, curve3) and in absence (Fig.9, curve1) of the heterogeneous catalyst reveals the benefits of the catalyst in the mineralization of MP.

The heterogeneous Sono-Fenton process demonstrates a much higher efficiency (with 60%). Such increasing efficiency can be related by providing promotion of mixing, mass transfer, and a better homogenization, also it induced a great amount of cavitation bubbles and the continuous cleaning of the catalyst surface using ultrasound, leading to a global increase in activity of the heterogeneous catalyst. Evidently, ultrasound is also known for its ability to disperse agglomerated particles and generate hydroxyl radicals during sonication of the aqueous phase. These effects can also be considered as reasons of the high efficiency of the process.

Finally, the content of iron in the filtered solution after heterogeneous Fenton oxidation and sono-Fenton oxidation of MP in all the cases was measured by ICP-AES analysis collected in a Varian Vista AX spectrometer in order to determinate the leaching degree from the catalyst in the effluent.

The amount of iron dissolved in the solution was determined after all heterogeneous Fenton oxidation and sono-Fenton oxidation processes. Table 4 summarizes the leaching level of iron species (mg/L) in the reaction medium at the end of each catalytic test.

Leaching of Fe was negligible within the reaction time required for a practically complete MP conversion. As it can be seen in Table 4, concentration of iron species was not higher than 5 mg/L for any of the used catalysts after treatment. It has been demonstrated that Fenton oxidation and sono-Fenton oxidation of MP is mainly due to the heterogeneous role of the catalysts instead of homogeneous Fe dissolved species, and this is due to The thermal treatment which gives longterm stability to the catalyst because it minimizes iron leaching from the catalysts.

4.Conclusion

New heterogeneous Fenton catalysts have been prepared by using the Algerian natural Bentonite. Montmorillonite clay was intercalated and pillared with Al.Fe , Al.Co, Al.Cu , Al.Fe.Cu or Al.Fe.La. polyoxocationic solutions. The samples were prepared with ultrasound process and calcined at 500°C. All samples were characterized by: X -ray fluorescence (XRF), X-ray diffraction (XRD), the Fourier transform infrared (FTIR) spectra, and N_2-adsorption/desorption analysis.

The XRF, XRD patterns confirmed the effectiveness of the chemical modification of all samples and clearly the effective incorporation of polyhydroxymetal cations into the modified Montmorillonite clays confirming successful pillaring.

The FTIR spectra showed that these metal pillars are linked with Al–O in the alumina octahedral sheet and Si–O in the silica tetrahedron plates.

Nitrogen adsorption–desorption analysis confirmed that the pillaring process with polyoxocations changed the textural properties of the solids and shows the increase in the micropore areas, specific surface area and micropore volume compared to those of the natural clay, confirming that the pillaring process took place successfully in both size fractions. In fact, the inclusion of oxidic species (pillars) in the interlamellar space of the clay generates a micropore volume between the clay layers, which is responsible for the observed increase of the specific surface area.

The catalytic tests revealed that pillaring clay modified by Al.Fe , Al.Fe.Cu or Al.Fe.La polyoxocations shows high activity in the oxidation of Methyl parathion, it has also been shown that the total degradation of Methyl parathion takes place during the first 3 hours. The complete mineralization of Methyl parathion is achieved by using heterogeneous Fenton reaction, leading to the formation of CO_2, H_2O and inorganic ions (PO_4^{3-}, SO_4^{2-}, NO_2^{-}, and NO_3^{-}) as final products.

These results prove the high activity of the Sono-Fenton system in the degradation of MP solutions, in comparison to a Fenton process or an US/hydrogen peroxide combination under similar reaction conditions. Likewise, it must be pointed out to a clear synergetic effect of Sono-Fenton (US/catalyst/H_2O_2) system when it is compared to the Fenton reaction (catalyst/H_2O_2), while ultrasound (US) interims of the MP degradation rate.

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Tables:

Table 1: Chemical analysis of Bentonite and the pillared Montmorillonite clays

Table 2: Positions and assignments of observed IR vibration bands for all samples

Table 3: The textural characterization of Bentonite and pillared Montmorillonite clays

Table 4: The leaching level of iron species (mg /L) in the reaction medium at the end of each catalytic tests

Figures captions:

Fig. 1: The chemical structure of Methyl Parathion

Fig. 2: UV–vis spectra of Methyl Parathion in aqueous solutions

Fig. 3: The X-ray diffraction pattern of **(a):** Bentonite; **(b)**: Bentonite and Mt-Na **(c)**: Mt-Na and catalysts (Mt-Fe/Al, Mt-Co/Al, Mt-Cu/Al, Mt-Fe.Cu/Al, Mt-Fe.La/Al)

Fig. 4: FTIR spectra of Mt-Na and catalysts (Mt-Fe/Al, Mt-Co/Al, Mt-Cu/Al, Mt-Fe.Cu/Al, Mt-Fe.La/Al)

Fig. 5: Isotherms of N_2 adsorption–desorption of Bentonite and the pillared Montmorillonite clay

Fig. 6: Catalytic activity of the pillared Montmorillonite clays in the MP heterogeneous Fenton reaction

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Fig.9: Comparison of degradation efficiencies of MP by Sono-Fenton and heterogeneous Fenton **(a):** Mt- Fe/Al, **(b):** Mt-Co/Al , **(c):** Mt-Cu/Al , **(d):** Mt-Fe.Cu/Al , **(e):** Mt-Fe.La/Al.

Tables:

Table 1 : Chemical analysis of Bentonite and the pillared Montmorillonite clays

Composition (%)	**Bt**	**Mt-Na**	**Mt-Fe/Al** 10 mmol/g	**Mt-Cu/Al** 10 mmol/g	**Mt-Co/Al** 10 mmol/g	**Mt-Fe.Cu/Al** 10 mmol/g	**Mt-Fe.La/Al** 10 mmol/g
Na_2O	0.25	5	0.23	0.24	0.26	0.20	0.25
MgO	0.39	0.65	0.01	0.05	0.08	0.01	0.01
Al_2O_3	13.96	15.2	22	14.15	30	27	31
SiO_2	65.83	70.10	25.77	31.26	28.74	25.8	25.75
K2O	2.89	1.71	1.1	18.77	0.68	1.1	1
CaO	5.28	0.51	0.91	0.68	0.33	0.99	1.6
TiO_2	1.09	0.84	0.51	0.48	0.2	0.56	0.55
Fe_2O_3	10.17	6.36	50.2	6.56	6.92	24.2	32.3
CuO	0	0	0	30.4	0	19.7	0
Co3O4	0	0	0	0	33.1	0	0
La	0	0	0	0	0	0	7.7
SiO_2/ Al_2O_3	4.71	4.61	1.73	1.03	0.9	0.9	0.9

Table 2: Positions and assignments of observed IR vibration bands for all samples

sample	Stretching and deformation of **Al-OH**		Stretching and deformation of **OH**		Stretching of **Si-OH**		Stretching and deformation of **Al-Mg-OH**	Stretching of cristobalite **Si-O**	Deformation of **FOOH**	Coupled **Al-O**and **Si-O**	Deformation of **M-O-Si** M(Al, ,Mg, Fe)
Bent	3619	915	3393	1637	1092	1036	840	799	694	625	519 - 471- 424
Mt-Na	3619	917	3445	1637	1093	1041	842	798	694	624	526 - 469-424
Mt-Fe	3619	920	3444	1635	1091	1050	838	798	695	623	522 - 473-430
Mt-Fe/Al	3619	916	3446	1635	1090	1050	839	798	693	627	525 - 471-424
Mt-Fe/Al	3619	916	3440	1640	1090	1041	840	798	695	625	522 - 466-418
Mt-Co/Al	3619	916	3442	1644	1090	1042	843	798	693	625	521 - 465-420
Mt-Cu/Al	3619	917	3442	1644	1091	1042	843	798	693	625	521 - 465-420
Mt-Fe-Cu/Al	3619	916	3444	1640	1090	1042	839	798	693	625	522 - 468-422
Mt-Fe-La/Al	3619	916	3444	1645	1091	1042	843	798	695	625	522 - 468-422

Table 3: The textural characterization of Bentonite and pillared Montmorillonite clays

catalysts	S_{BET} $(m^2 g^{-1})$	$V_p(cm^3 g^{-1})$	d_p(A°)
Bentonite	24	0.02	20.67
Mt-Na	58	0.07	24.21
Mt- Fe/Al	117	0.1149	19.58
Mt-Co/Al	78	0.07979	18.08
Mt-Cu/Al	79	0.06578	16.12
Mt-Fe.Cu/Al	116	0.1345	15.96
Mt-Fe.La/Al	152	0.1859	15.95

S_{BET}: surface area, **V_p:** Volume of pore, **d_p:** Average diameter of the pore (A°),

Table 4: The leaching level of iron species (mg /L) in the reaction medium at the end of each catalytic tests

catalysts	Heterogeneous Sono-Fenton	heterogeneous Fenton
Mt- Fe/Al	4.6	3.3
Mt-Co/Al	0.15	0.1
Mt-Cu/Al	0.2	0.1
Mt-Fe.Cu/Al	4.95	3.5
Mt-Fe.La/Al	4.5	4.1

Figures captions:

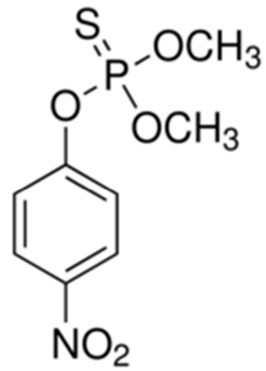


Fig. 1: The chemical structure of **Methyl Parathion**

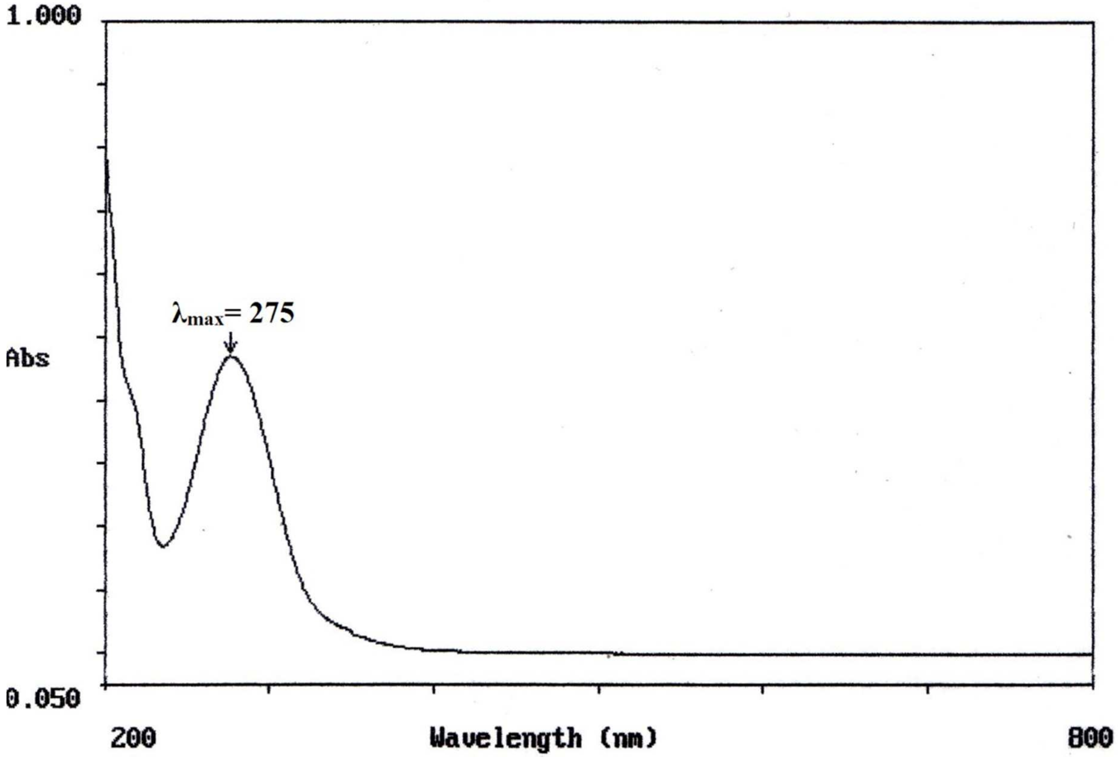
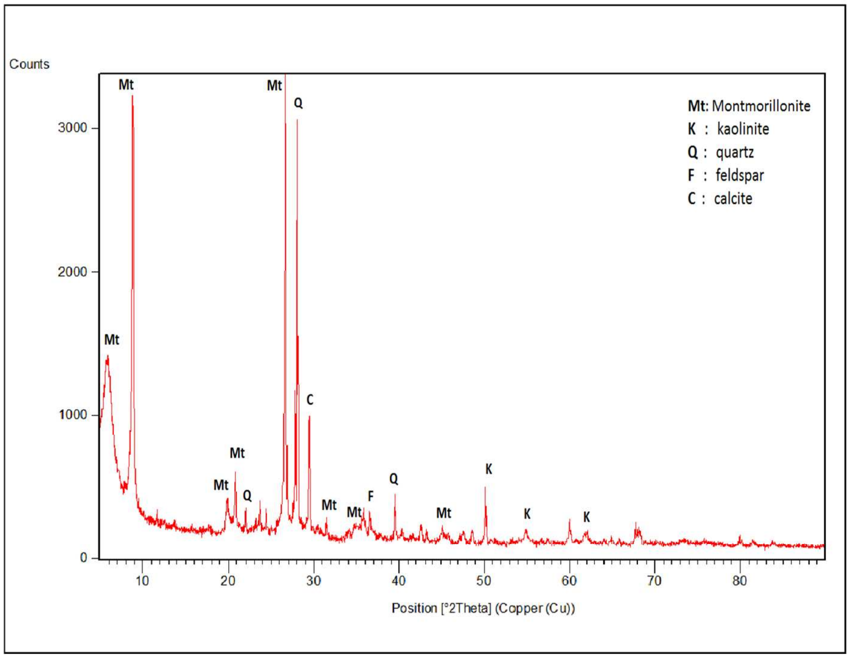


Fig. 2 : UV–vis spectra of Methyl Parathion in acetonitrile aqueous solutions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Mt
Q
Mt
C
Mt
Mt
Q
Mt
Mt
F
Q
K
Mt
K
K
Mt: Montmorillonite
K : kaolinite
Q : quartz
F : feldspar
C : calcite
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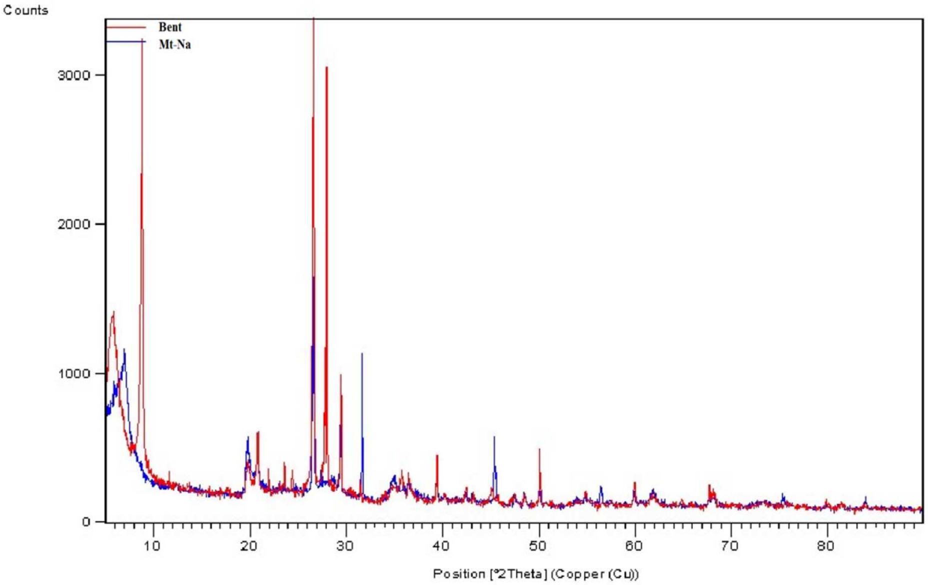
20
30
40
50
60
70
80
Position [°2Theta] (Copper (Cu))

(a)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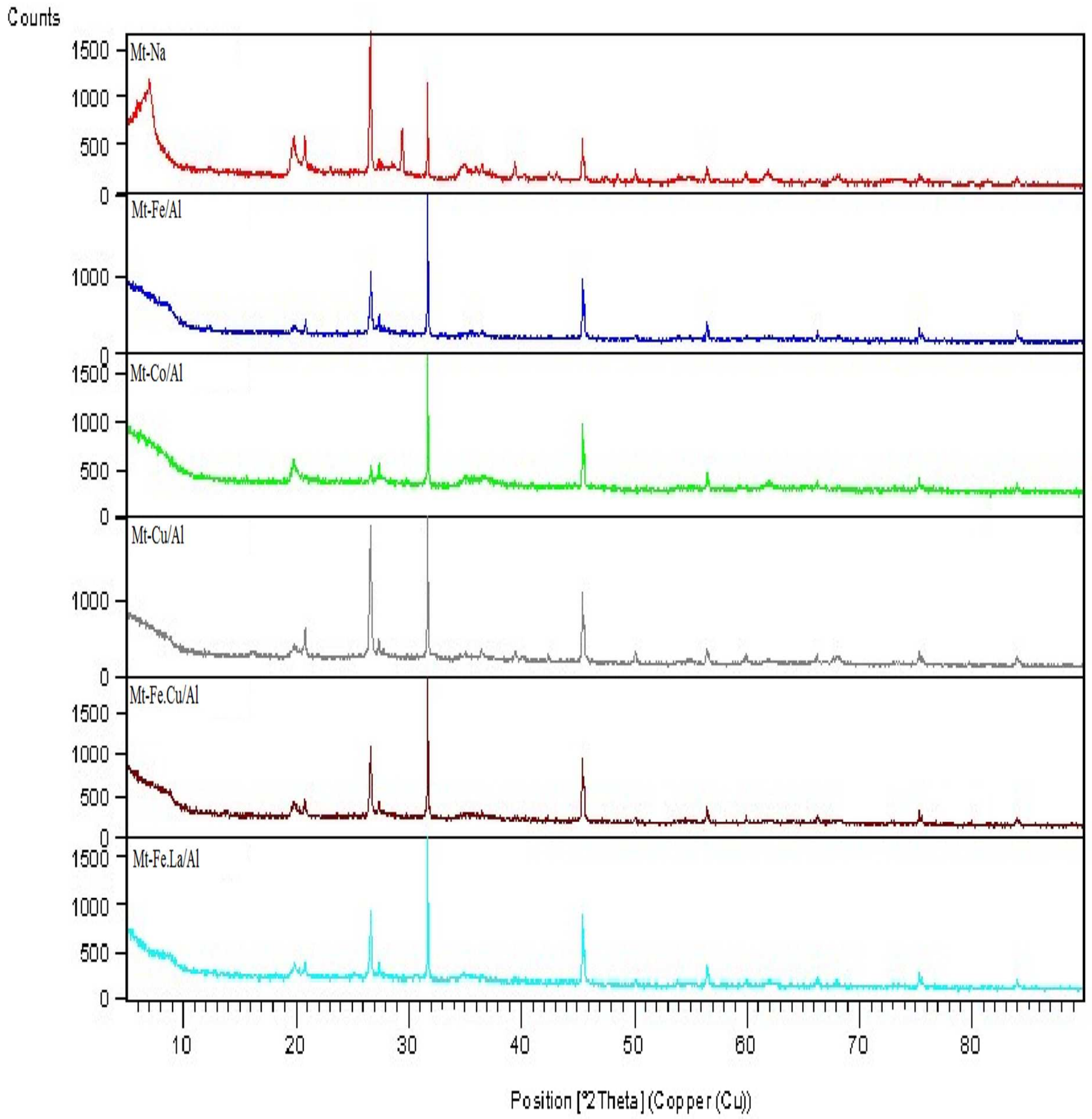
Position [°2Theta] (Copper (Cu))

(b)



(c)

Fig. 3: The X-ray diffraction pattern of (a): Bentonite ; (b): Bentonite and Mt-Na; (c): Mt-Na and catalysts (Mt-Fe/Al, Mt-Co/Al, Mt-Cu/Al, Mt-Fe.Cu/Al, Mt-Fe.La/Al)

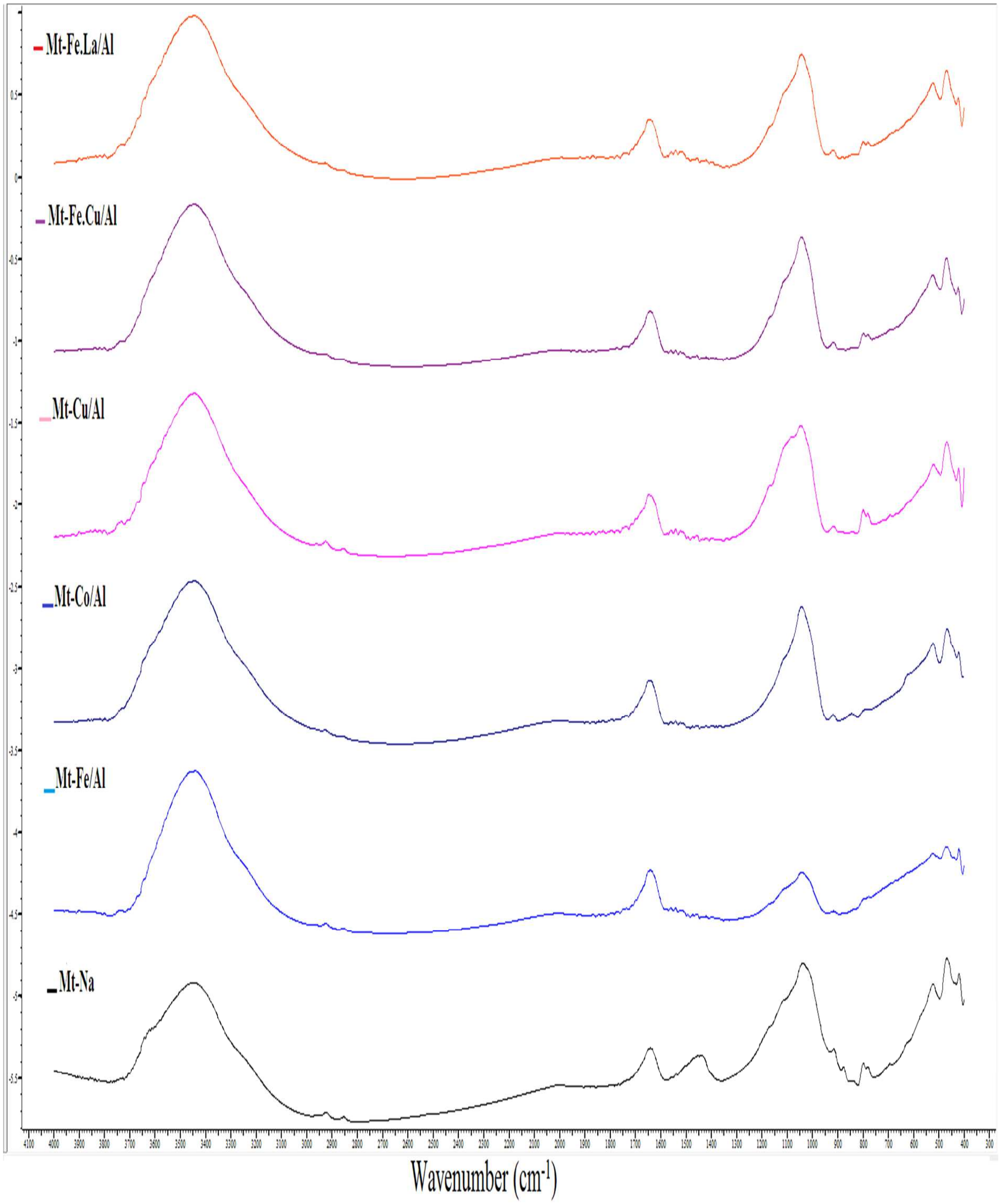


Fig. 4: FTIR spectra of Mt-Na and catalysts (Mt-Fe/Al, Mt-Co/Al, Mt-Cu/Al, Mt-Fe.Cu/Al, Mt-Fe.La/Al)

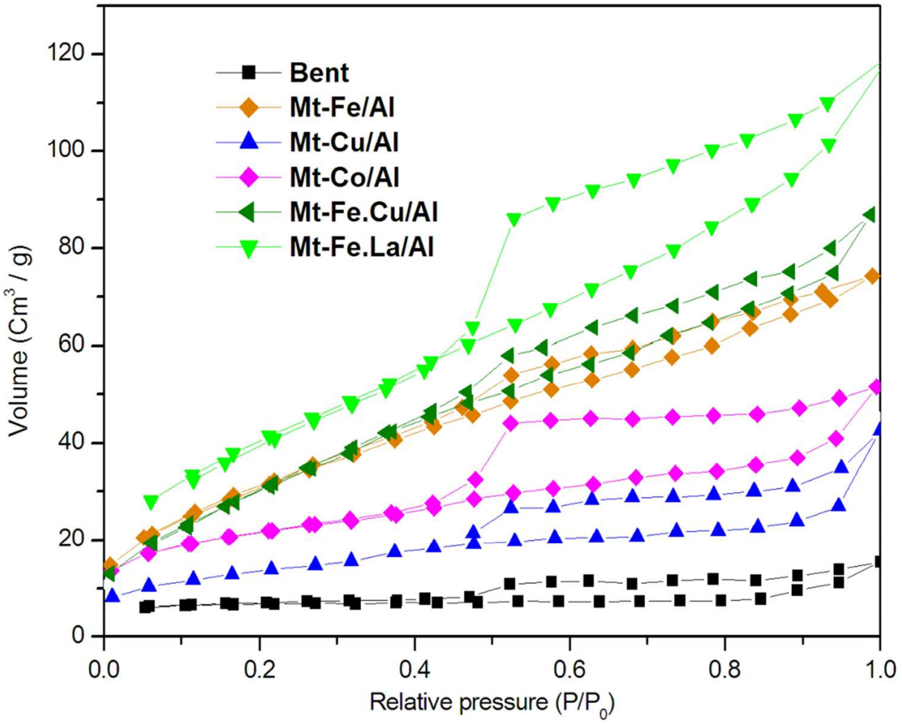


Fig. 5: Isotherms of adsorption–desorption of Bentonite and the pillared Montmorillonite clay

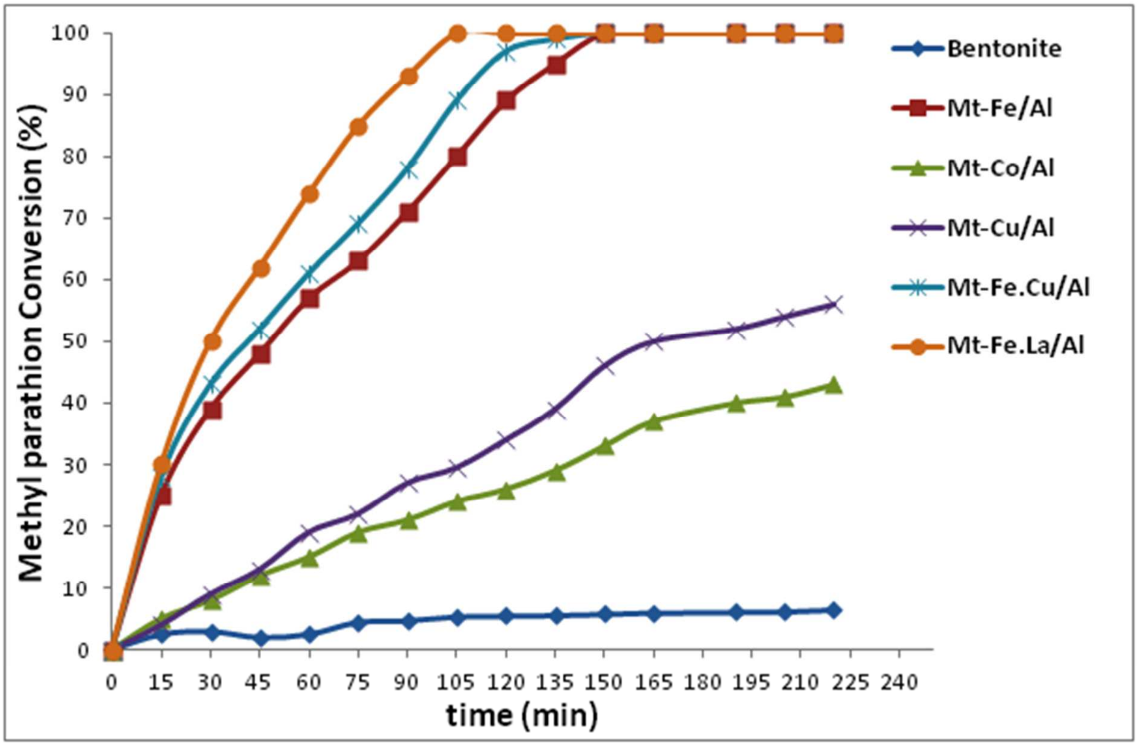


Fig. 6: Catalytic activity of the pillared Montmorillonite clays in the heterogeneous Fenton MP oxidation reaction

(MP =50 mg/L ; H_2O_2=600mg/L ; catalyst = 0.5g/L ; pH = 3 ; T = 25°C)

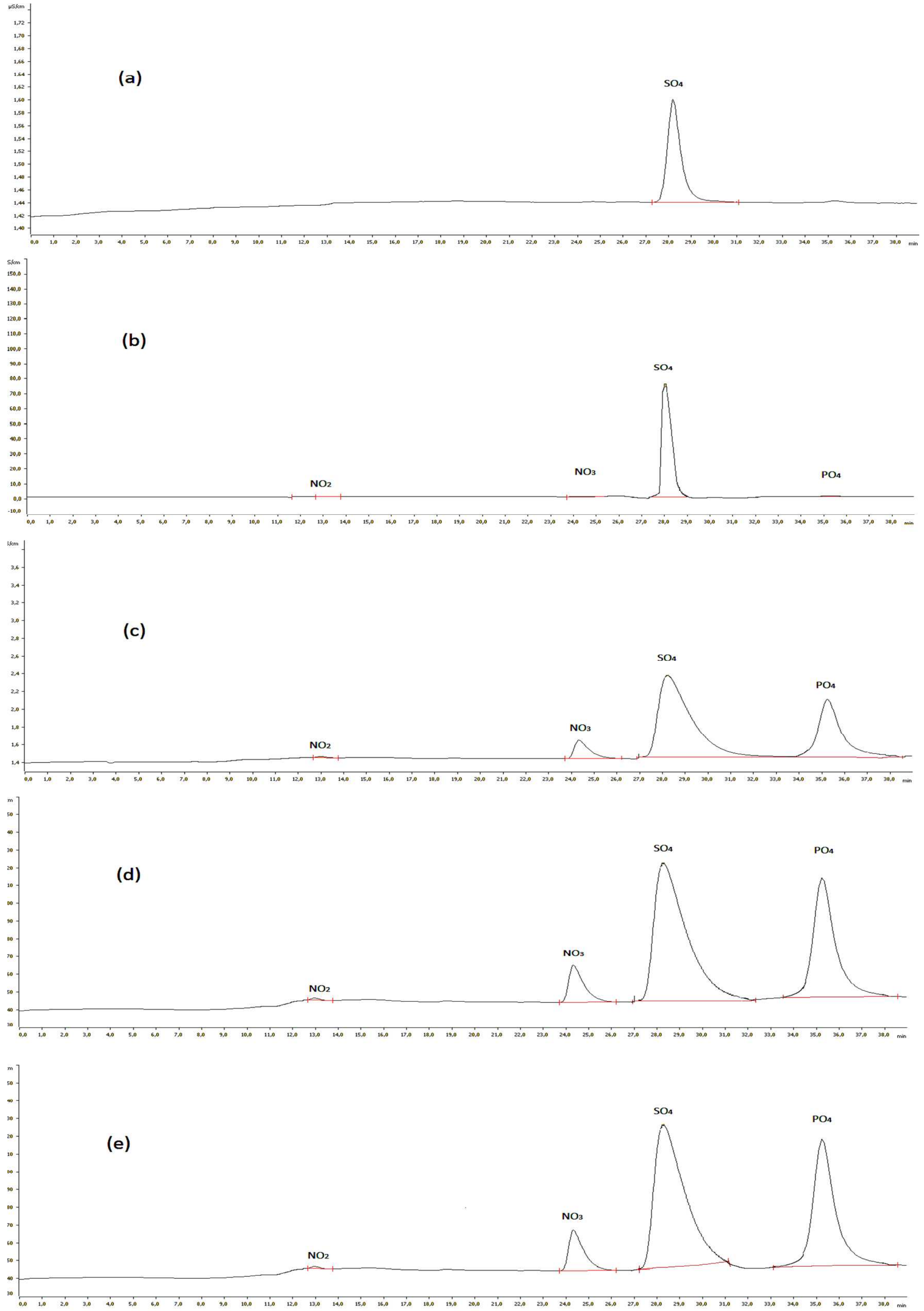


Fig. 7: Ion chromatography of MP solution under different heterogeneous Fenton time: 0 (a), 30 (b), 60 (c), 90 (d), (e) 120 min with the catalyst Mt-Fe.La/Al

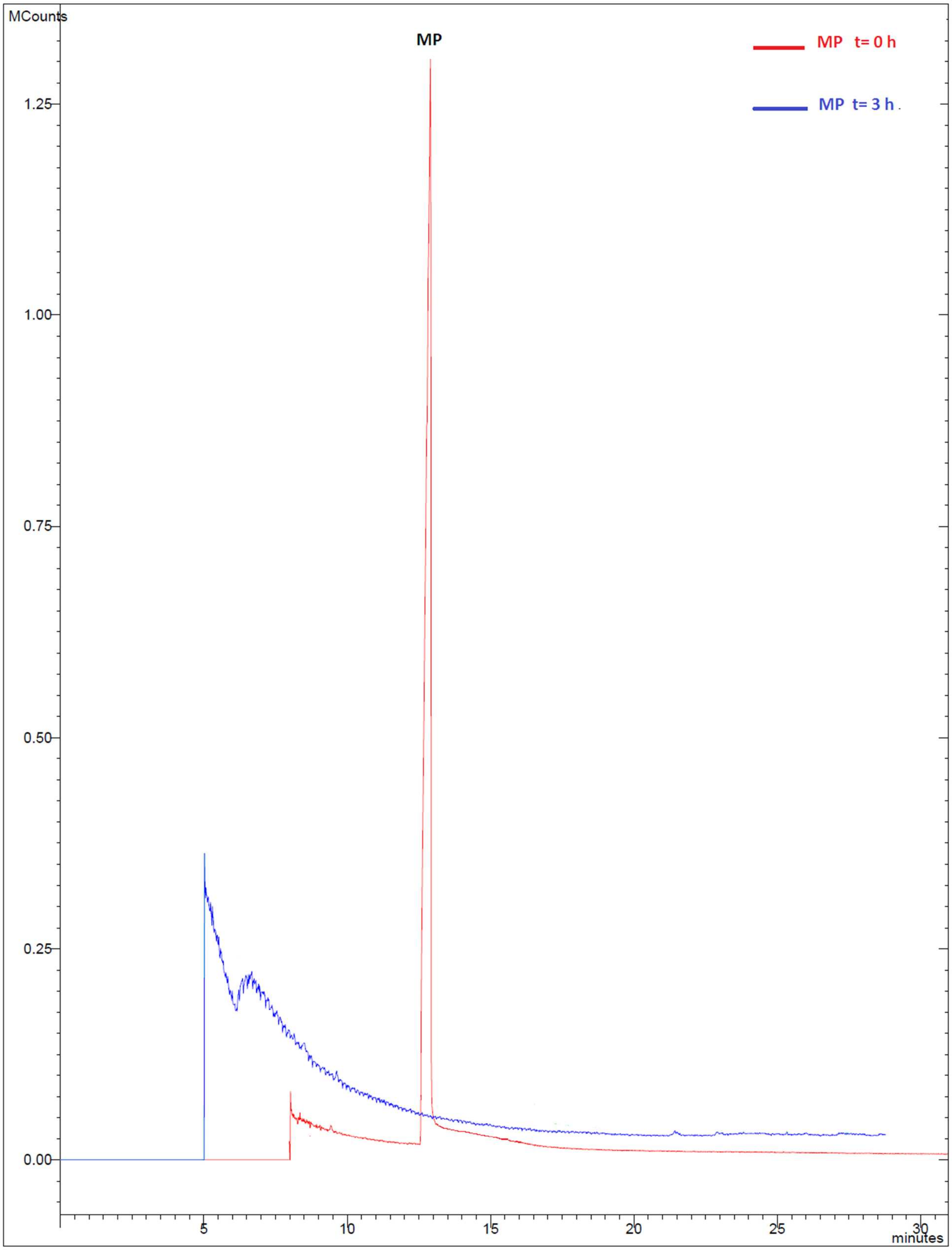
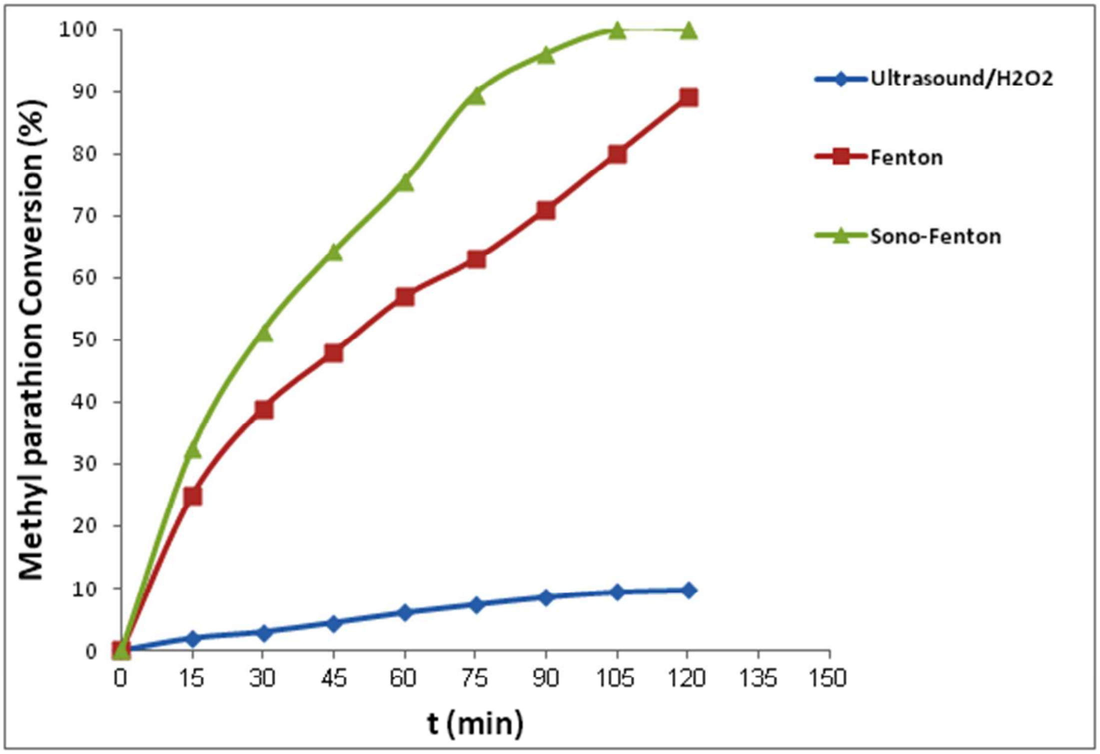


Fig. 8 : GC-MS spectra for initial MP and MP treated by heterogeneous Fenton oxidation after 3h with the catalyst Mt-Fe.La/Al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30
20
10
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0
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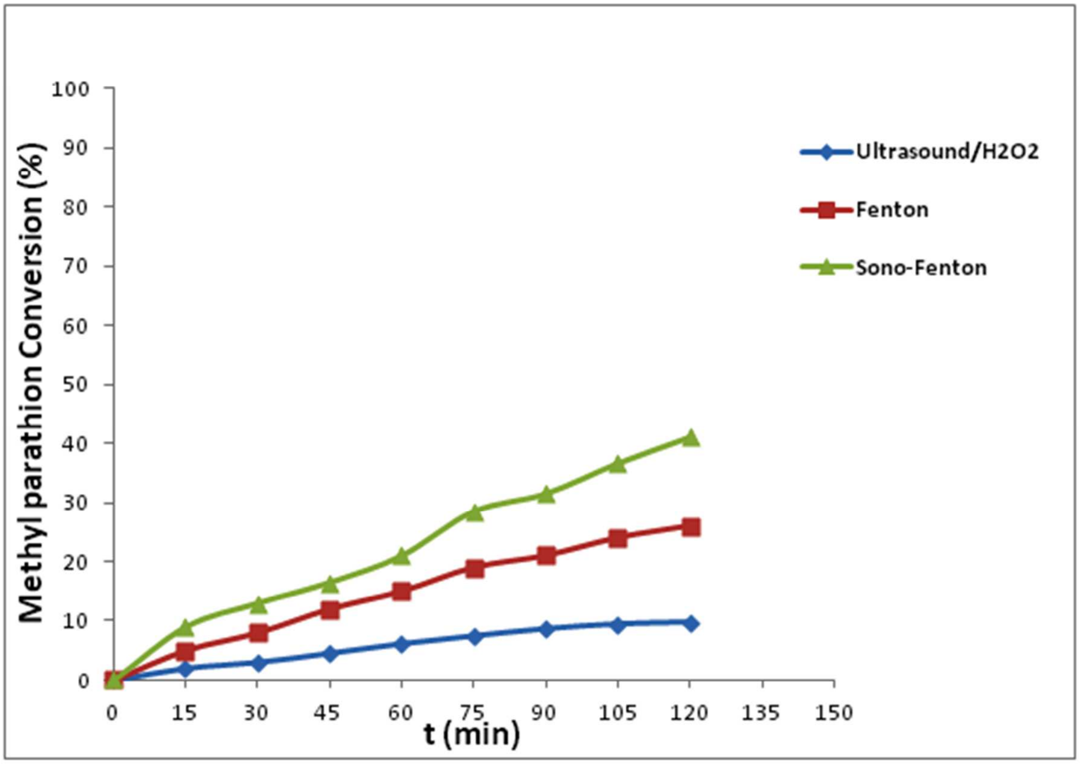
75
90
105
120
135
150
t (min)
Ultrasound/H2O2
Fenton
Sono-Fenton

(a)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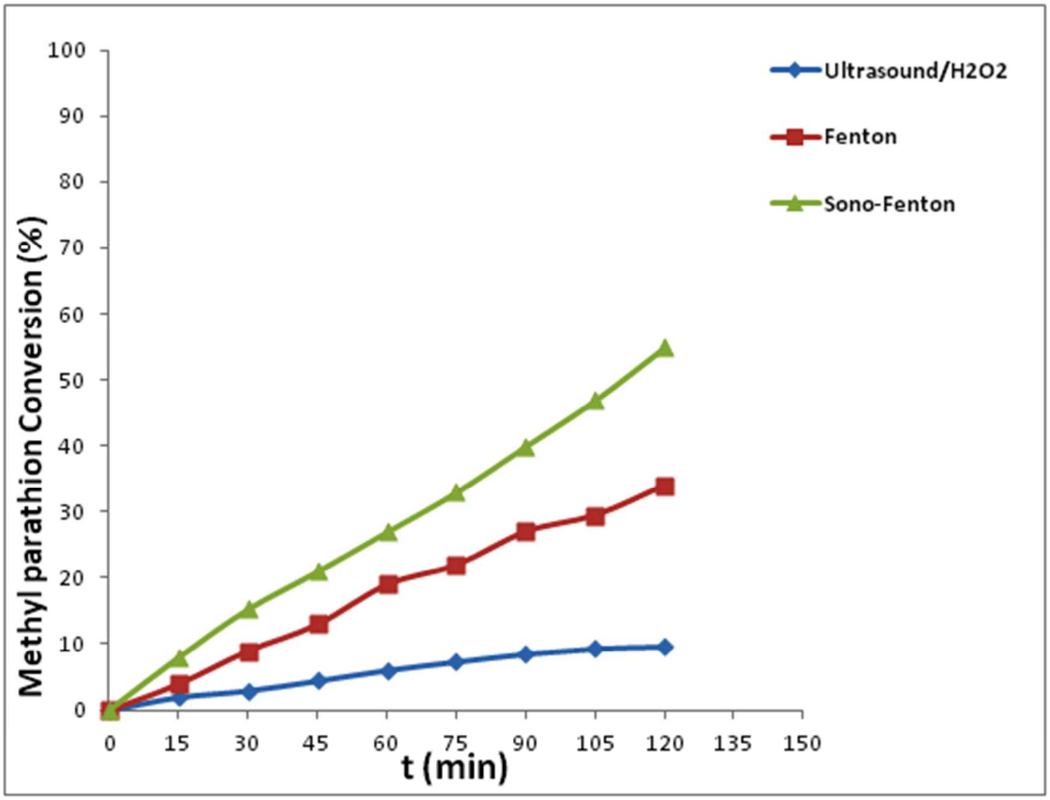
t (min)
Ultrasound/H2O2
Fenton
Sono-Fenton

(b)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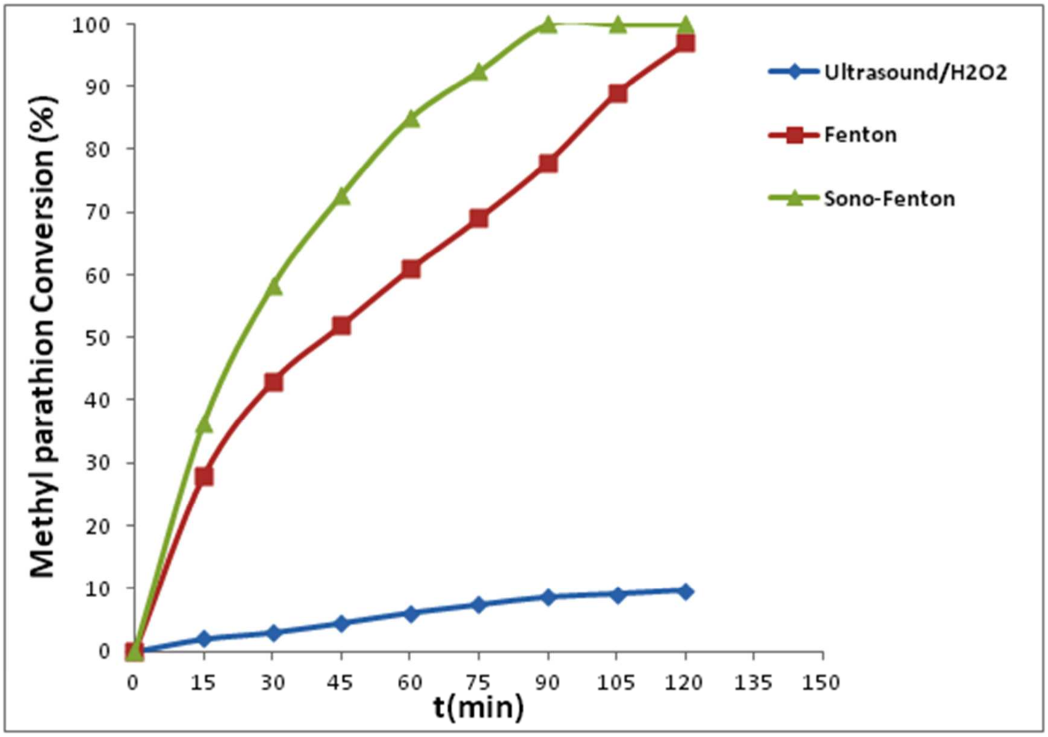
t (min)
Ultrasound/H2O2
Fenton
Sono-Fenton

(c)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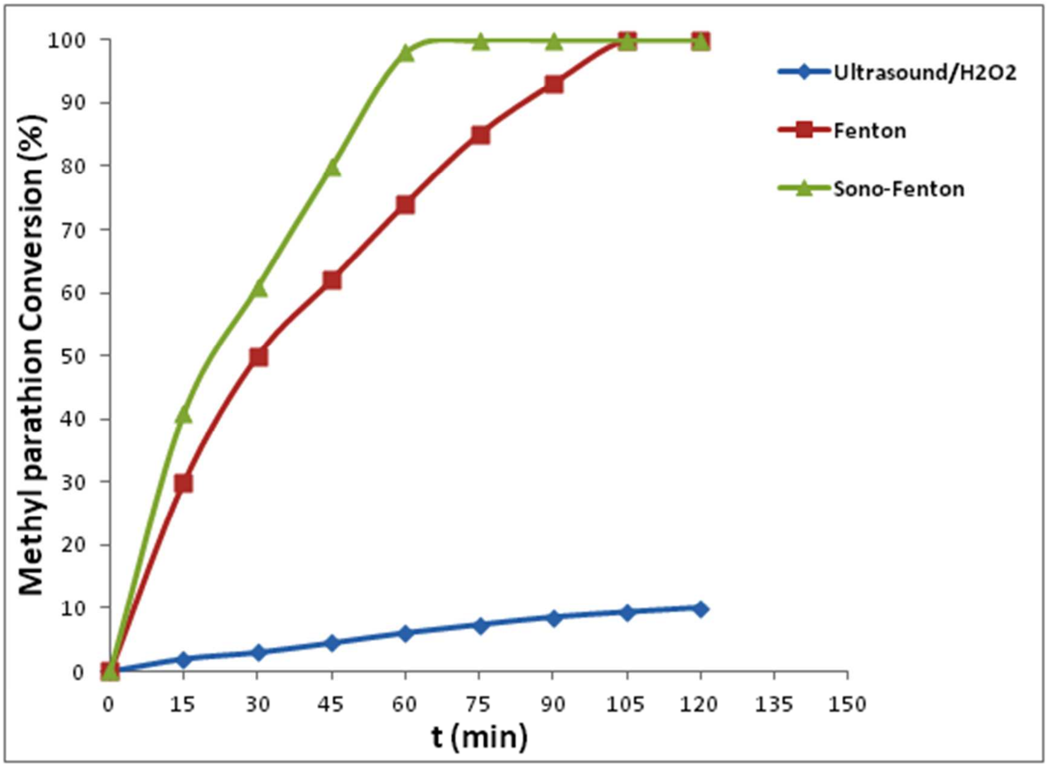
t(min)
Ultrasound/H2O2
Fenton
Sono-Fenton

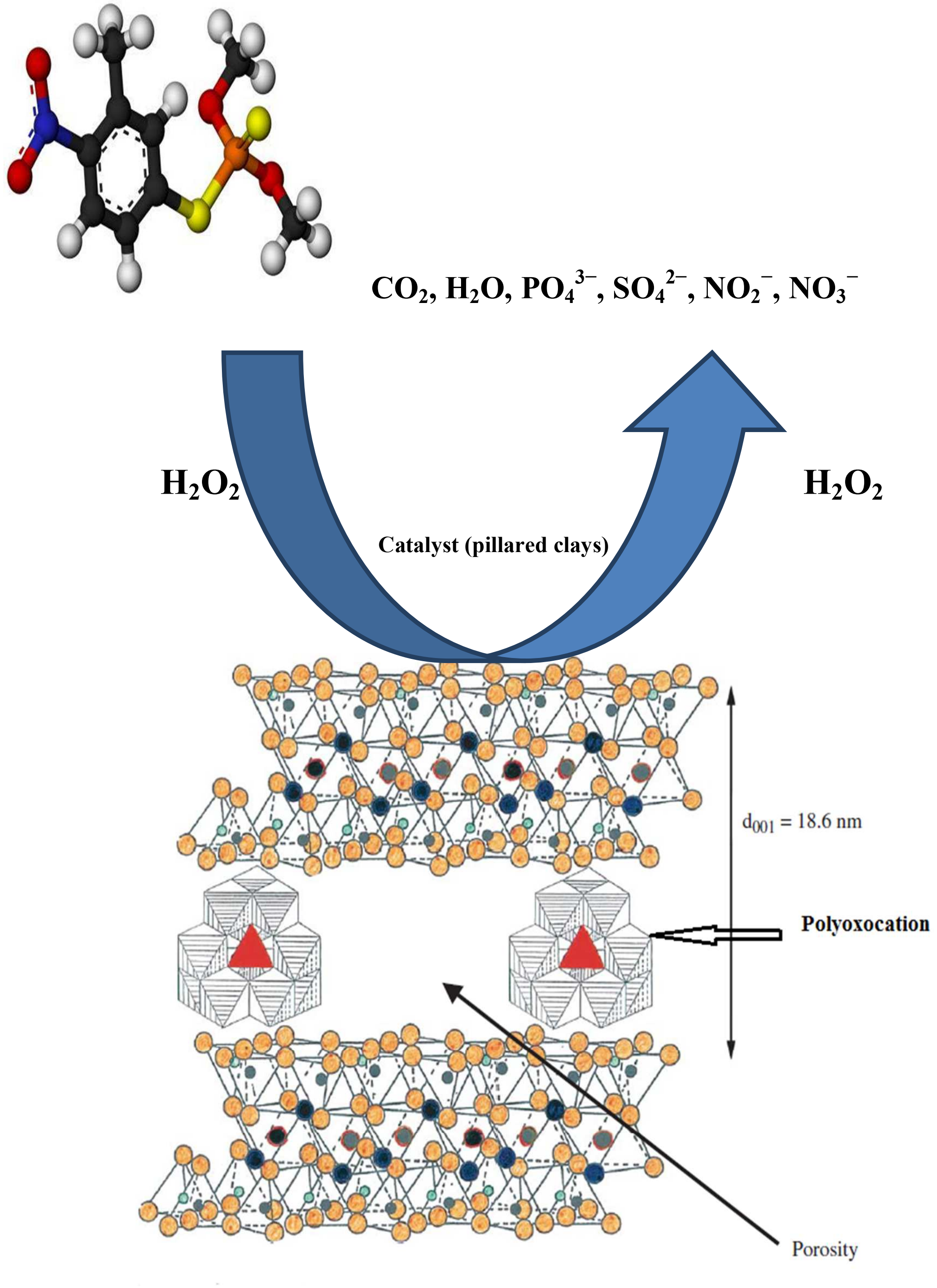
(d)



(e)

Fig. 9. Comparison of degradation efficiencies of MP by Sono-Fenton and Fenton **(a): Mt- Fe/Al, (b): Mt-Co/Al , (c): Mt-Cu/Al , (d): Mt-Fe.Cu/Al , (e): Mt-Fe.La/Al.**

(Condition: MP=50 mg/L, H2O2=600 mg/L, catalyst =0.5 g/L, pH=3 m, T = 25°C).



Mineralisation of Methyl parathion with the advanced Fenton process