Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.23528

143 (2019) 217–228
March

Comparative study on degradation of p-nitrophenol from aqueous solution by catalytic wet peroxide oxidation using pillared bentonite clay catalysts

Fidâ Baragh[a,b], Oussama El Bouadi[b], Khalid Draoui[c,*], Brahim El Bali[b], Mahfoud Agunaou[a], Abdelhak Kherbeche[b]

[a]*Laboratory of Coordination and Analytical Chemistry (LCCA), Faculty of Sciences, Chouaib Doukkali University, UCD, Route Ben Maachou, 24000, El Jadida, Morocco, emails: m.agunaou@gmail.com (M. Agunaou), f.baragh@gmail.com (F. Baragh)*
[b]*Laboratory of Catalysis, Materials and Environment (LCME), Higher School of Technology, Sidi Mohamed Ben Abdellah University, USMBA, EST, 30000 Fez, Morocco, emails: kherbecheabdelhak@gmail.com (A. Kherbeche), b_elbali@yahoo.com (B. El Bali), oussama.elbouadi.ntk1@gmail.com (O. El Bouadi)*
[c]*Laboratory MSI, Faculty of Sciences, Abdel Malek Essaadi University, B.P. 2121, M'hannech II, 93002, Tetouan, Morocco, email: khdraoui@gmail.com*

Received 12 March 2018; Accepted 26 November 2018

ABSTRACT

In order to enhance depuration of organic persistent pollutants from wastewater, the effect of metal loading in pillared clays on the catalytic degradation performance was studied. A local bentonite clay was treated with Al and Cu solutions with different metal loading percentage and the resulting pillared clays were used in the catalytic wet peroxide oxidation of 4-nitrophenol (4-NP). The catalysts were characterized with X-ray diffraction (XRD) analysis, Fourier-transform infrared spectroscopy and inductively coupled plasma atomic emission spectroscopy. Tests were carried out in a batch reactor, following along time the 4-NP degradation. A detailed parametric study was conducted, changing only one experimental variable at a time, while keeping the others constant. The experimental parameters investigated in this work were temperature, catalyst dose, and initial concentration of H_2O_2 or 4-NP. The optimum conditions were found to be 3 g L^{-1} catalyst, 10 mM H_2O_2, 50°C T and 50 mg L^{-1} 4-NP, under which more than 90% of 4-NP, 70% COD and 50% TOC were experimentally removed after 4 h of reaction.

Keywords: Clays; Bentonite; Pillared clay catalysts; Catalytic wet peroxide oxidation; 4-Nitrophenol

1. Introduction

The water contamination by organic non-biodegradable and inorganic pollutants has increasingly become a serious environmental concern and a real challenge for both industrialists and researchers. Thus the elimination, or reduction to an acceptable level, of their concentration in wastewater, has become a necessity. Among these pollutants, phenols and their derivatives have received much attention [1–5].

The p-nitrophenol, also known as 4-nitrophenol (referred to as 4-NP), is one of the most ubiquitous challenging phenol's derivative requiring removal from wastewater streams. It is widely used to manufacture drugs, fungicides, insecticides, and dyes and is recognized as hazardous, bioaccumulative, carcinogenic and highly toxic. It has been classified as one of the 129 priority pollutants by the United States Environmental Protection Agency (USEPA) with limit of discharge less than 0.5 mg L^{-1} [6–8]; hence there is an urgent request to remove it or at least reduce its concentration in wastewater before discharge into the nature.

Typical technologies used in wastewater treatments by physical [9–11], chemical [12,13] and biological [14,15]

---

* Corresponding author.

processes, may show good removal efficiency. However, this remains impotent to reach a real degradation of such recalcitrant pollutants instead of only transferring them from one phase to another. Nevertheless, advanced oxidation processes (AOPs) have attracted tremendous attention in the past years thanks to the generation of highly reactive and non-selective hydroxyl radicals (·OH) by processes such as photolytic, catalytic, photocatalytic, etc., which can oxidize and mineralize a wide range of organic compounds under moderate conditions [16–19]. Although Fenton-like process in homogenous phase can successfully fulfil the task, it encounters several drawbacks including the large amount of cations of metals, such as Fe, Cu, or Al, required to have an efficient degradation and the need to recover the metal from the liquid phase which is difficult and highly expensive. Besides, the large amount of resulting sludge makes the reaction becoming highly sensitive to pH, and hence requires its adjustment [20–23]. In order to overcome these setbacks, it is thoughtful to develop heterogeneous catalysts, by supporting transition metals on porous solids that can degrade pollutants without pH adjustments. Accordingly, several porous materials have been studied as support for heterogeneous catalysts, among them: zeolites [24], polymer supported metal complexes [25], activated carbon supported metal oxides [5], clays and pillared clays [1–4,20]. However, the performance of pillared clays in catalytic wet peroxide oxidation of phenolic compounds is remarkable.

Indeed, in the present work, the efficiency of copper-based pillared local bentonite clay (Cu-PILC) have been investigated and compared with those of aluminium-based clays (Al-PILC) in the catalytic wet hydrogen peroxide oxidation (CWPO) of model phenolic compound (4-nitrophenol) without pH adjustment.

2. Materials and methods

2.1. Materials

The clay used in the present study was a bentonite, sampled in the North-East of Morocco, with a cationic exchange capacity (CEC) of 89 meq/100 g [26,27].

For the experiments of intercalation and pillaring, NaOH (97%), HCl (37%, w/w), $Al(NO_3)_3{\cdot}9H_2O$ (99%) and $Cu(NO_3)_2{\cdot}3H_2O$ (99.99%) were all from Sigma-Aldrich Chimie S.a.r.l. (Lyon, France). For the catalytic runs, 4-nitrophenol (4-NP) was from Merck Millipore (Germany) while hydrogen peroxide (H_2O_2) solution (30%, w/w) was from Sigma-Aldrich. All the materials were used as received. Deionized water used throughout the experiment was prepared with a Millipore Milli-Q system.

2.2. Catalysts preparation

The preparation of the pillared clay catalysts was achieved in a two-step technique: (1) support preparation and (2) incorporation of transition metal precursors.

2.2.1. Starting material

The raw bentonite (denoted Raw-Ben) was purified following a modification to the method described by Belaroui et al. [28]. It was ground, sieved to ≤63 μm, dispersed into distilled water for 2 h and then allowed to settle for 16 h. The fraction corresponding to a particle size of less than 2 μm was extracted by sedimentation and dried at 100°C for 24 h. The material obtained was then treated with HCl (0.1 N) in order to eliminate carbonates, thoroughly washed with distilled water and dried at 60°C overnight [29]. The purified clay was homoionized (denoted Na-Ben) following Ben Achma et al. [30] Na-exchange procedure until the negative test with $AgNO_3$. The Na-Ben CEC was enhanced to 137 meq/100 g.

2.2.2. Catalysts synthesis

The Al-pillared bentonite sample was prepared following a modification to the method described by Khalaf et al. [31]. The Al-pillaring solution was carried out by the slow addition of NaOH solution (0.225 M) to a solution containing $Al(NO_3)_3$ (0.5 M) at a rate of 1 mL/min, up to an hydrolysis molar ratio OH/Al of 2, under vigorous stirring in a water bath at 60°C. The mixture was allowed to age for 24 h. The pillaring process was achieved by drop wise adding of the pillaring solution into the previously prepared aqueous solution of homoionized bentonite (Na-bent) suspension (2 wt%), under continuous vigorous stirring and kept at 80°C. After adding the bentonite and the dispersion completed, the mixture was continuously stirred and kept at 80°C for 3 h and then aged at room temperature for one night in the presence of the mother liquor. The solid was recovered by centrifugation and washed thoroughly with distilled water, dried at 60°C overnight and finally calcined at 400°C for 3 h. The heating rate was of 3°C/min to reach thermally and chemically resistant pillars. The catalysts prepared will be referred to as Al (2)-PILC, Al (5)-PILC and Al (7)-PILC, the number in parentheses relates to the Al-content (in wt), that is, respectively, 2%, 5%, and 7%.

The copper-pillared bentonite was prepared following a modification to the method described by Ayodele and Hameed [22]. The Cu-pillaring solution was prepared by the slow addition of 0.225 M NaOH solution to another containing metal salts $Cu(NO_3)_2$ (0.5 M) at a rate of 1 mL/min up to the hydrolysis molar ratio OH/Cu = 2, under vigorous stirring in a water bath at 30°C. The mixture was then allowed to age for 24 h. The pillaring process was the same as mentioned previously. The prepared catalysts will be referred to as Cu (2)-PILC, Cu (5)-PILC, and Cu (7)-PILC, containing respectively 2%, 5%, and 7% wt Cu.

2.3. Catalysts and bentonite clay characterizations

The XRD patterns were measured using BRUKER D2 Phaser CuK_α (λ = 1.54184 Å) with a Lynxeye detector. Chemical characterization of the samples was conducted by using X-ray fluorescence (XRF) spectroscopy analysis using an AXIOS Panalytical (Hassan IUniversity, Settat).

The Fourier transform infrared (FTIR) spectroscopy patterns were obtained using a Bruker Vertex 70 infrared spectrometer with a 4 cm^{-1} resolution and 400–4,000 cm^{-1} scanning range.

The elemental composition of Raw-Ben was determined using an energy dispersive X-ray (EDX) detector in combination with a field emission scanning electron microscope (FESEM) (Quanta 200, FEI, Sidi Mohamed Ben Abdellah University, Fez).

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used to determine the percentage of metal pillared into the catalysts as well as the leaching percentage.

The CEC was determined using the methylene blue method [32,33].

2.4. Catalytic activity test

Fenton-like reactions were carried out in a 250 mL three-neck glass flask fitted with a reflux condenser, a magnetic stirrer and a thermostated water bath. For a typical run, the reactor was filled with 100 mL of 4-NP and maintained at the desired temperature with continuous stirring. After the stabilization of temperature, the catalyst was added to the solution. The mixture was continuously stirred for 15 min to allow the adsorption of 4-NP onto the surface of the catalyst until reaching equilibrium. It was found that the adsorption of 4-NP was almost negligible onto the catalyst surface in agreement with the surface electrostatic conditions. Then subsequently, the CWPO reaction was started by the addition of the appropriate amount of hydrogen peroxide. The initial pH of the aqueous solution of 4-NP was 5.7 and it was not adjusted during the reaction, in an attempt to evaluate the activity of the PILC catalysts to degrade 4-NP without pH pre-treatment. During the reaction, the pH decreased owing to the formation of HNO_3 and CO_2.

Samples (2 mL) were withdrawn from the reaction mixture at regular intervals of 10 min in the first half hour of the reaction and 30 min intervals later on. The reaction was carried out for 4 h. The catalyst was removed from the samples by centrifugation and filtering by means of 0.22 μm pore size nylon filter and the samples were immediately analyzed by UV-Vis spectrophotometer VR-200 at λ_{max} of 401 nm.

The degradation efficiency of 4-NP was evaluated as follows:

$$\text{Degradation efficiency (\%)} = \left[\frac{C_0 - C_t}{C_0}\right] \times 100 \tag{1}$$

where C_0 is the initial concentration of 4-NP while C_t is the concentration at the time of withdrawal.

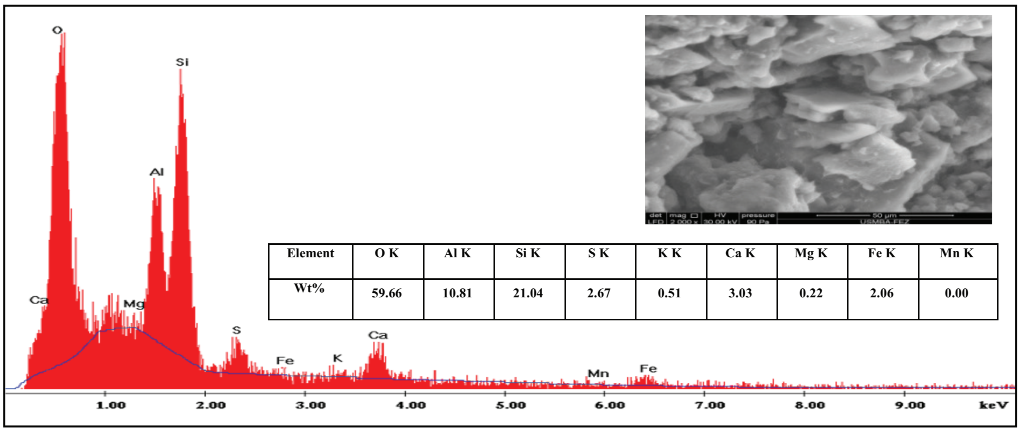
3. Results and discussion

3.1. Characterization of catalysts and bentonite clay

In order to know the elemental composition and morphology of the raw clay (Raw-Ben), EDX and SEM analysis were performed. The results presented in Fig. 1 show that the starting clay has a typical layer structure characteristic of the smectite family, mainly composed of Al and Si.

The chemical analysis of Raw-Ben sample determined by XRF analysis (Table 1) indicated the presence of large amounts of silica and alumina yielding a very high SiO_2/Al_2O_3 ratio, which is correlated with the presence of a great amount of impurities (mostly quartz) and can also be justified by the substitution of Al^{3+} cations by Fe^{3+} and Mg^{2+} in octahedral sites; this assumption is based on the high presence of MgO and Fe_2O_3 [34]. This result shows the probable presence of smectites, which is in accordance with the EDX result, as well as illite.

The mass ratio of $(Na_2O+K_2O)/(CaO+MgO)$ in the Raw-Ben is 0.23, implying that the high-silica montmorillonite are enriched with alkaline earth metal oxides (CaO and MgO).



Element	O K	Al K	Si K	S K	K K	Ca K	Mg K	Fe K	Mn K
Wt%	59.66	10.81	21.04	2.67	0.51	3.03	0.22	2.06	0.00

Fig. 1. EDX spectra and SEM image of Raw-Ben.

Table 1
Chemical composition and textural properties of Raw-Ben and Na-Ben

Sample	d_{001} (nm)	CEC (meq/100 g)	Chemical composition (%)									
			SiO_2	Al_2O_3	MgO	Fe_2O_3	Na_2O	CaO	K_2O	MnO	OO[a]	SiO_2/Al_2O_3
Raw-Ben	1.48	89[b]	68.4	12.7	2.23	4.50	0.15	3.46	1.2	0.94	3	5.38
Na-Ben	1.37	137	55.8	16.25	1.09	4.01	2.11	0.44	0.7	0.89	2	3.43

[a] Other oxides in trace.
[b] CEC of the 2 μm fraction of Raw-Ben.

The CaO content is higher than alkali metal oxides (Na_2O and K_2O), so this kind of raw ore belongs to the Ca-bentonite category [35]. This type of clay has a slightly lower swelling properties and cationic exchange capacities than the Na-bentonite. However, after the purification and Na-activation, the SiO_2/Al_2O_3 ratio decreased to 3.43 and Na_2O percentage increased to 2.11 leading to a higher CEC value (from 89 in the raw bentonite to 137 meq/100 g).

The XRD patterns of Raw-Ben, Na-Ben and the pillared clay catalysts are shown in Figs. 2 and 3, respectively. The peak at $2\theta = 6.4°$ of activated clay (Na-Ben) was attributed to the basal reflections (001), which corresponds to a d_{001} value of 1.37 nm, linked to the presence of montmorillonite (M) with smaller amount of illite (I) [36]. The reflection (060) appearing at 0.15 nm indicates that Raw-Ben is a dioctahedral smectite [37]. The purification process successfully reduced the impurities, such as quartz (Q), dolomite (D) and calcite (C), present in the raw clay but had a shifting effect on the d_{001} from 1.48 (Raw-Ben) to 1.37 nm (Na-Ben) [38,39]. Upon pillaring with Al and Cu, the d_{001} signal shifted toward values around 1.7 and 1.6 nm, respectively, while the rest of the structure remained unaffected. This shifting indicates the successful pillaring of metal contents into the activated clay. However, a new reflection appeared at around $2\theta = 10.7°$ while pillaring with copper; which can be attributed to the presence of copper hydroxide [22,40].

The ICP analysis data reported in Table 2 confirms previous results and proves the successful pillaring of Cu and Al.

The FT-IR spectra of all the samples are shown in Fig. 4. First, regardless of the raw clay, in the characteristic vibration region, the band at 3,628 cm^{-1} is attributed to the stretching vibration of structural OH group (Al-OH) which is typical for the high content of Al in the raw clay. The band at 3,434 cm^{-1} is due to stretching vibration band of adsorption water between the clay's sheets. The band at 1,635 cm^{-1} corresponds to the bending vibrations of H_2O in the bentonite at dioctahedral surface. In fingerprint region the band at 1,036 cm^{-1} represents the stretching vibration of Si–O–Si, while the band corresponding to Si–O vibration is observed at 477 cm^{-1}. Al–Al–OH bending vibration was observed at 917 cm^{-1}. The band at 792 cm^{-1} implies the presence of quartz in the raw clay, while the small band at 1,376 cm^{-1} could be attributed to calcite and the one at 528 cm^{-1} corresponds to Si–O–Mg [41–44]. After purification, the peaks attributed to impurities were reduced in the Na-Ben. Upon pillaring, the FT-IR spectrum of all PILCs showed the same pattern as the starting clay, which indicates that the intercalation process maintained the layered structure. However, a much stronger absorption at 1,638; 3,450 and 3,628 cm^{-1} reflected a remarkable increase in the amount of OH groups (H–OH and Al–OH). Furthermore, when copper was intercalated into clay, a band

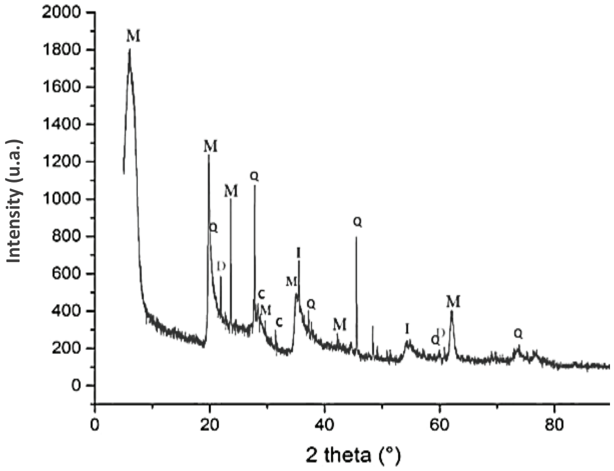


Fig. 2. XRD profile of Raw-Ben.

Table 2
Metal loading and textural properties of PILCs samples

Sample	Cu[a] (wt%)	Al[a] (wt%)	d_{001} (Å)
Cu (2) - PILC	1.89	–	16
Cu (5) - PILC	4.91	–	16.1
Cu (7) - PILC	6.69	–	16.3
Al (2) - PILC	–	1.59	17
Al (5) - PILC	–	4.81	17.4
Al (7) - PILC	–	6.78	17.6

[a]Total Cu and Al content were known from ICP.

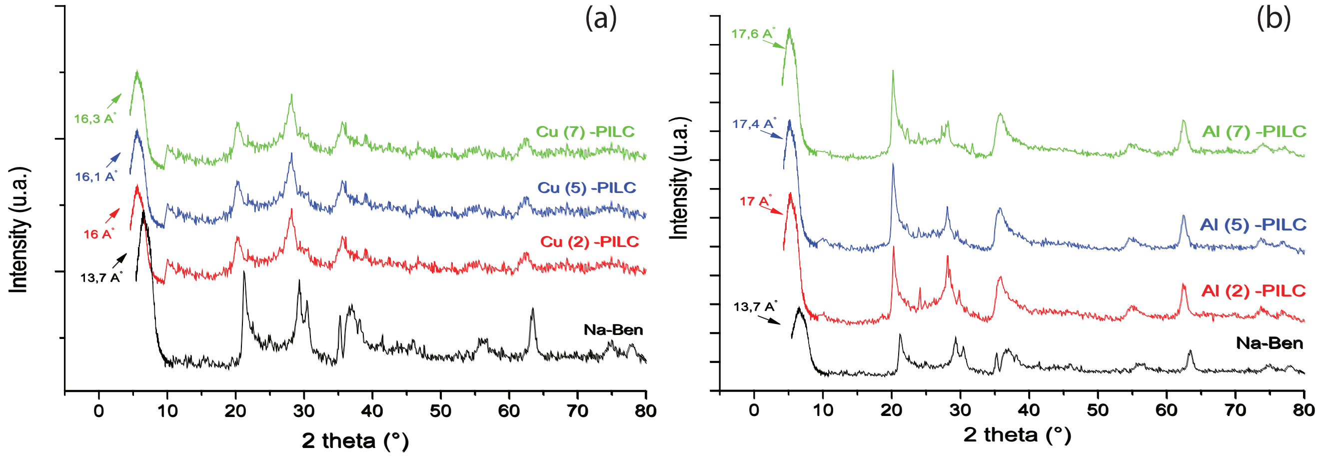
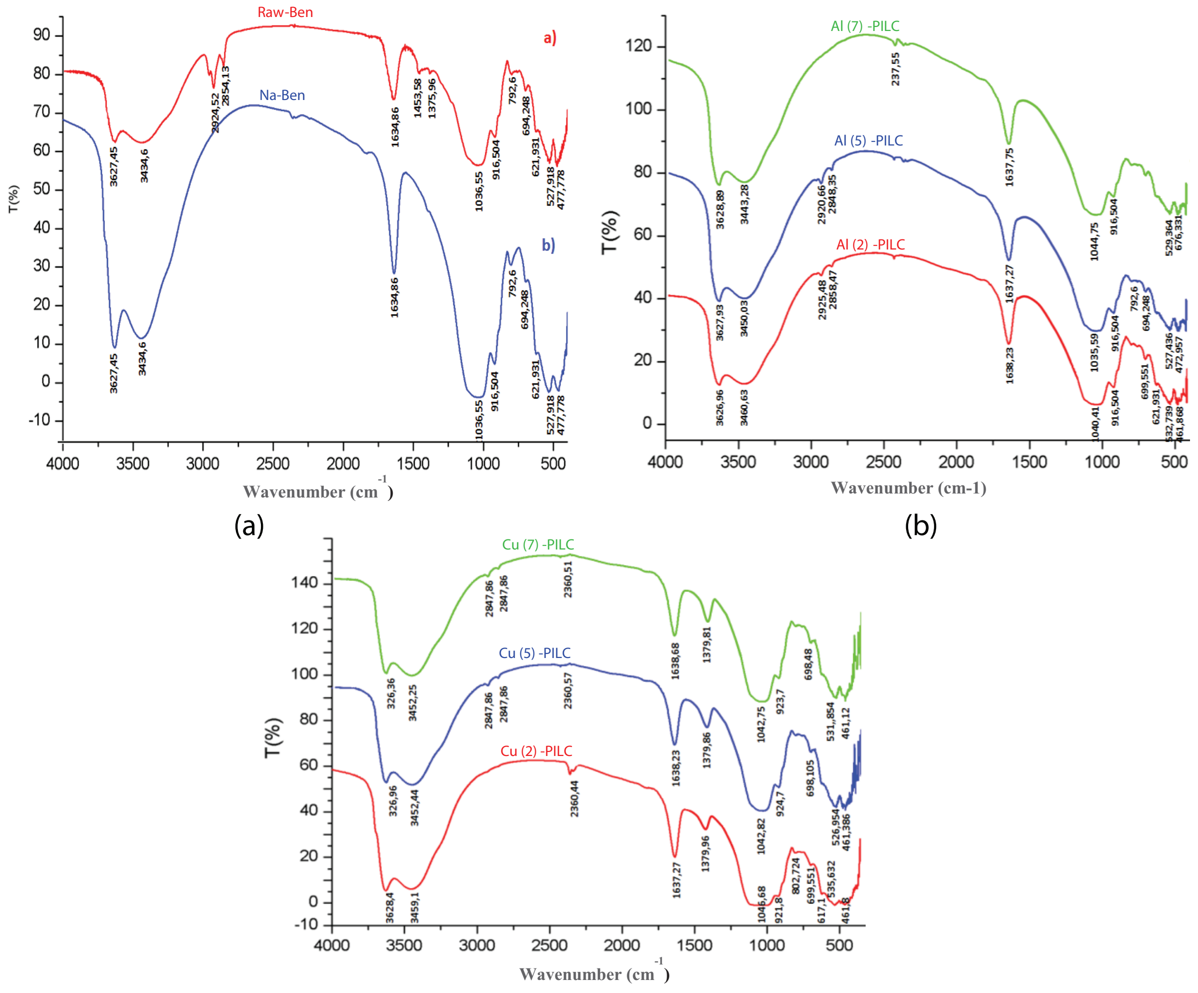


Fig. 3. X-ray diffraction patterns of (a) Cu-PILCs and (b) Al-PILCs.



(a) (b)

(c)

Fig. 4. FT-IR spectra of (A) Raw-Ben and Na-Ben, (B) Al-PILCs and (C) Cu-PILCs.

at 1,379–1,382 cm^{-1} was observed which was probably related to the insertion of copper into the inter-foliar space of the bentonite [22].

3.2. Degradation of 4-NP process

The degradation of 4-NP follows a parametric study to determine the best experimental conditions (temperature, catalyst dose, and initial concentration of H_2O_2 and 4-NP). Prior to this study, preliminary blank experiments were carried out in order to evaluate the catalytic performance of Raw bentonite (calcined at 400°C for 3 h) in the removal of 4-NP and to ascertain whether the degradation of organic pollutant is due to catalytic reaction or to adsorption. In presence of calcined raw bentonite, the degradation did not exceed 15% and was basically by adsorption; while in the presence of peroxide, no more than 17% decrease of the initial concentration of 4-NP was observed and this might be justified by the presence of activated Fe that can contribute in Fenton reaction (Fig. 5). These results show that the raw clay has a very low catalytic and adsorption capacity toward 4-NP removal.

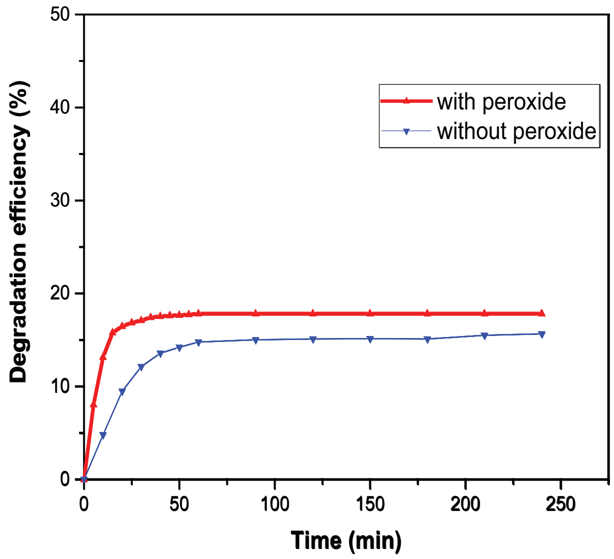


Fig. 5. Degradation of 4-NP over 1 g/L Raw-Ben (calcined) ([4-NP] = 50 mg/L, pH = 5.7, $[H_2O_2]$ = 4mM and T = 30°C).

3.2.1. Effect of H_2O_2

The results of the effect of peroxide dosage on the degradation of 4-NP are presented in Fig. 6. The degradation rate significantly increased with the increase in peroxide dosage from 4 to 10 mM (Eqs. (2) and (3)) up to a saturation point which beyond it further increase in H_2O_2 leads rather to a decrease of the removal efficiency:

$$C_6H_5NO_3 + 14H_2O_2 \rightarrow 6CO_2 + 16H_2O + HNO_3 \quad (2)$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (3)$$

This behavior is likely the result of the scavenging effect of H_2O_2 on $HO^\bullet$ radicals to form the hydroperoxy radicals ($HO_2^\bullet$) and inactive molecular oxygen (O_2), as shown in Eqs. (4) and (5). In fact, hydroperoxy radicals are less reactive and do not significantly contribute in the CWPO reaction, due to their much lower oxidation potential (1.7 eV) than hydroxyl radical (2.8 eV) [22,23,45–47].

$$H_2O_2 + HO^\bullet \rightarrow HO_2^\bullet + H_2O \quad (4)$$

$$HO_2^\bullet + HO^\bullet \rightarrow H_2O + O_2 \quad (5)$$

3.2.2. Effect of catalyst loading

Fig. 7 depicts the effect of catalyst loading on the degradation of 4-NP. The plot revealed that initial increase in the Cu-PILC loading from 1 to 3 g/L enhanced remarkably the degradation efficiency up to the optimum point which beyond it further loading retards the degradation efficiency. When the concentration of catalyst increases, the amount of active sites for the generation of $HO^\bullet$ radicals is greater. Therefore, the degradation is enhanced. However an excessive increment of the catalyst, from 3 to 5 g/L, without increasing the peroxide concentration leads to a probable scavenging effect of excess active metal on $HO^\bullet$ radicals, these radicals generated at high concentration, can dimerize to form H_2O_2 (Eq. (6)) [22,23,46,48]:

$$HO^\bullet + HO^\bullet \rightarrow H_2O_2 \quad (6)$$

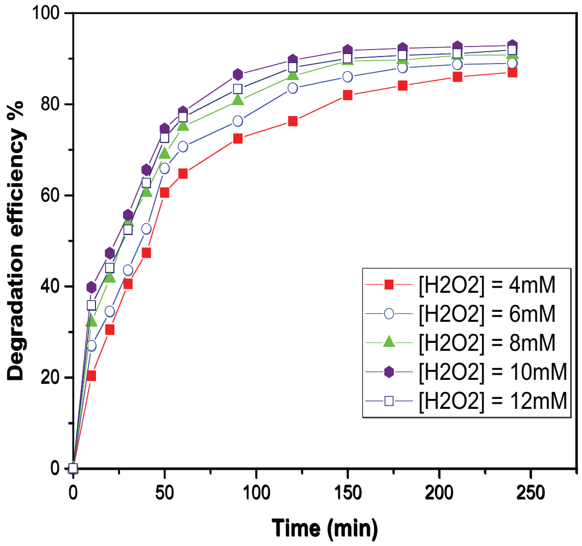


Fig. 6. Effect of H_2O_2 dosage on 4-NP degradation, [4-NP] = 50 mg/L, pH = 5.7, $m_{Cu(5)-PILC}$ = 1 g/L and T = 30°C.

3.2.3. Effect of the temperature

The effect of temperature on the CWPO degradation of 4-NP was studied and the results are shown in Fig. 8. The results revealed that temperature has a slight influence.

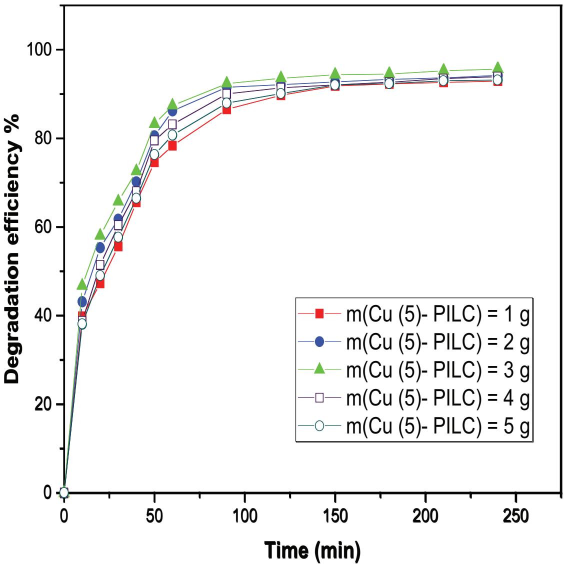


Fig. 7. Effect of catalyst loading on 4-NP degradation, [4-NP] = 50 mg/L, pH = 5.7, $[H_2O_2]$ = 10 mM and T = 30°C.

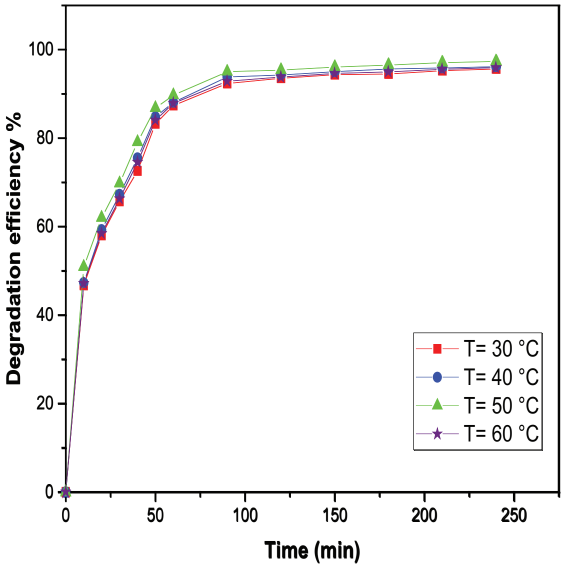


Fig. 8. Effect of temperature on 4-NP degradation, [4-NP] = 50 mg/L, pH = 5.7, $[H_2O_2]$ = 10 mM and $m_{Cu(5)-PILC}$ = 3 g/L.

The removal efficiency increased with the increment of the reaction temperature up to 50°C, due to the increased rate of hydroxylation at the catalyst active sites producing more $HO^{\bullet}$, which is in agreement with the Arrhenius theory. However, a rise of temperature from 50°C to 60°C produces a decrease in the 4-NP removal efficiency. Caudo et al. [49], Ayodele and Hameed [22], and Ayodele et al. [23] suggested that this decrease could be attributed to the start of the thermal decomposition of peroxide. In fact, peroxide has been described thermally unstable at elevated temperatures [23,28,50].

3.2.4. Effect of initial concentration of 4-NP

The effect of initial 4-NP concentration on the degradation efficiency is presented in Fig. 9. The results show that initial pollutant concentration has a very important and significant role in the CWPO degradation process. Indeed, the increase of initial concentration [4-NP] in the range of 50, 75 and 100 ppm, results in a decrease of the degradation efficiency, respectively, from 97% to 92% and down to 90%. The plot in Fig. 9 shows that 50 ppm achieved 90% removal of 4-NP within 60 min reaction time, while 75 and 100 ppm reached it after 120 min and 240 min, respectively. This tailing off is probably because of the reactive radicals $HO^{\bullet}$ are insufficient to degrade rapidly a much higher concentration of organic pollutant. Furthermore, an increase of the initial concentration of 4-NP is automatically related to an increase of intermediate compounds which can be more recalcitrant than the starting pollutant and needs much higher concentration of peroxide to be degraded completely and effectively and thus they can trap the reactive radicals and so decrease the 4-NP's removal [51].

3.2.5. Effect of pillared catalysts

The effect of the pillared clay catalyst on the degradation of 4-NP is plotted in Fig. 10. The reaction's condition for all the used catalyst Al-PILCs and Cu-PILCs are the optimum condition deduced from the previous studies of the effects of peroxide dosage, catalyst loading, temperature and the initial concentration of 4-NP. These conditions are $[H_2O_2] = 10$ mM, $m_{PILC} = 3$ g/L, $T = 50°C$, and [4-NP] = 50 mg/L.

The copper-based catalysts show higher affinity toward the degradation of 4-NP without pH adjustment, such behavior is fully expected since Cu^{2+} is a strong oxidant from the first transition metal row, which can induct homolytic O–O bond cleavage of H_2O_2 into $HO^{\bullet}$ radicals, based on Eqs. (7) and (8) [1,52,53]. The mechanism of the radical's generation for Cu-containing heterogeneous systems differs from the one known in the Fenton systems [1,52,54].

$$\equiv Cu^{2+} + H_2O_2 \rightarrow \equiv Cu^{+} + HO_2^{\bullet} / O_2^{\bullet} + H^{+} \tag{7}$$

$$\equiv Cu^{+} + H_2O_2 \rightarrow \equiv Cu^{2+} + HO^{\bullet} + OH^{-} \tag{8}$$

Li et al. [55], based on the temperature-programmed reduction analysis of copper pillared catalyst Cu-Ti-PILC-0, which means containing only copper as pillaring metal, showed the presence of two peaks: one attributed to the reduction of amorphous CuO to Cu^0, but most importantly, the second peak at higher temperature which indicates the reduction of isolated Cu^{2+} to Cu^{+} but no reduction of Cu^{+} to Cu^0 and thus indicating that the species Cu^{+} are stable. These results and mechanisms are in agreement with those reported by Caudo et al. [56].

The increase of the percentage of pillared copper in the inter-foliar space of the bentonite clay leads to the increase of the degradation efficiency up to a certain saturation point when the scavenging effect of the copper metal occurs on hydroxyl radicals, as explained in the effect of catalyst loading.

Compared with the Cu-PILCs, the Al-PILCs behave differently. In fact, the increase of the Al content leads to the increase of the removal of 4-NP and no scavenging effect was seen. This is expected since Al^{3+} does not initiate neither homolytic nor heterolytic peroxide degradation. Nevertheless, Al-PILCs catalyst showed good degradation efficiency which can be attributed to the reactive iron present in the Na-Ben. The insertion of Keggin Al_{13} structure in

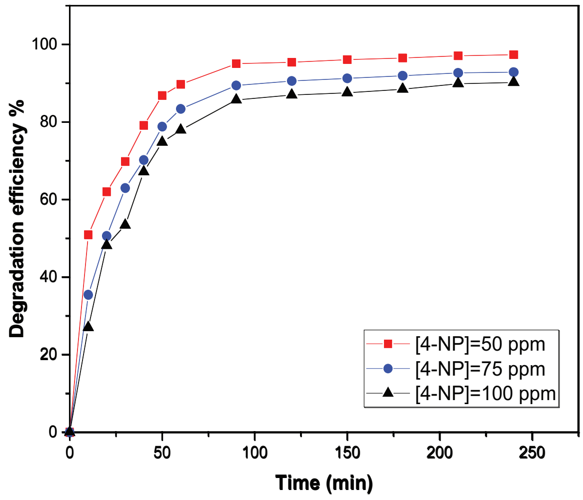


Fig. 9. Effect of initial concentration of 4-NP, pH = 5.7, $[H_2O_2] = 10$ mM, $m_{Cu (5) \text{-PILC}} = 3$ g/L and $T = 50°C$.

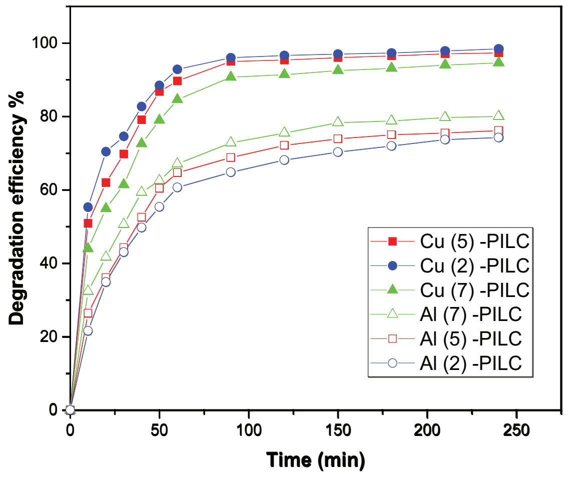


Fig. 10. Catalytic activity of the pillared clays in the 4-NP oxidation under optimum conditions, pH = 5.7, $[H_2O_2] = 10$ mM, $m_{PILC} = 3$ g/L, $T = 50°C$ and [4-NP] = 50 mg/L.

the catalyst leads to a higher basal spacing d_{001} and by that increases the thermal stability of the catalyst as well as the access to the iron already present in the raw clay and activated by means of the calcination at 400°C for 3 h.

In order to investigate the coke deposits on the prepared Al-PILCs and Cu-PILCs, pillared clay catalysts used in this study were analyzed by FT-IR spectroscopy, the catalysts after being washed with distilled water and dried at 100°C for 48 h. The FT-IR spectra (Supplementary material, Fig. S1) did not reveal the presence of carbonaceous deposits. On the other hand, no color change of the Cu-PILCs was noticed after 4 h reaction.

3.3. Mineralization of 4-NP

Total organic carbon (TOC) and chemical oxygen demand (COD) are widely used for wastewater monitoring. They were used by several researchers in the survey of the mineralization degree of catalytic wet peroxide oxidation [2,3,5,22]. However, COD analysis is vulnerable to the presence of interferents such as ferrous ion [57], nitrites [58], chlorides [59], and hydrogen peroxide [60,61]. In fact, the latter has been a challenging problem in the COD determination in Fenton reactions because residual H_2O_2 leads to overestimation of COD [61]. Although TOC and dissolved organic carbon were increasingly used recently as a measure of mineralization level, thanks to their less vulnerable aspect and their rapidness. COD is still an important parameter when evaluating the efficiency of the used catalysts for organics mineralization and adjudging whether the treated effluent could meet discharge standards. Therefore, coupling COD and TOC tests seem to be the adequate way to better monitor the mineralization level of 4-NP's CWPO using the prepared catalysts.

Several methods have been suggested to overcome this drawback such as removing the residual H_2O_2 by Na_2SO_3 [62], MnO_2 [63], Na_2CO_3 [64], and catalase [65] or by adjusting sample pH to above 10 and then neutralize it to 7 [5]. In this study, we used the later method. Indeed, before the COD and TOC analysis, samples were filtered through a 0.22-µm nylon syringe filter and their pH was first raised to 10 by adding 1 M NaOH and then neutralized to nearly 7 with 0.1 M H_2SO_4.

Despite the good catalytic 4-NP removal efficiency shown by the prepared catalysts, these PILCs cannot be assumed as good Fenton catalysts unless they can achieve a high abatement of not only the starting refractory pollutant but also its oxidation by-products. Thus, the study of the degree of mineralization turned a key parameter in the judgement of the reliability of our PILC catalyst.

The mineralization of the 4-NP removal was monitored in terms of those of COD and TOC as follows:

$$\text{COD removal (\%)} = \left[\frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0}\right] \times 100 \tag{9}$$

$$\text{TOC removal (\%)} = \left[\frac{\text{TOC}_0 - \text{TOC}_t}{\text{TOC}_0}\right] \times 100 \tag{10}$$

where COD_o and TOC_o are, respectively, the initial COD and TOC concentration (mg/L) and COD_t and TOC_t the respective values at time *t*.

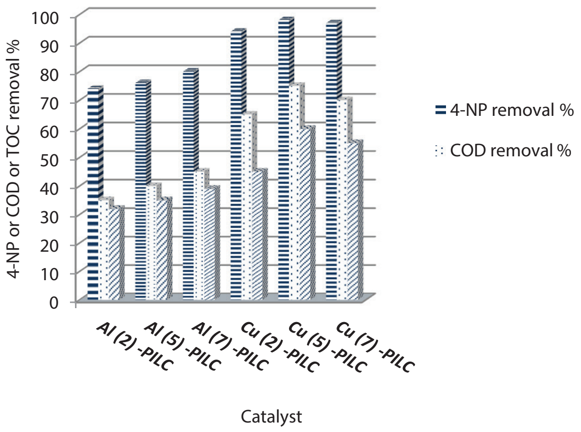


Fig. 11. Profile of 4-NP mineralization, experimental conditions: pH = 5.7, $[H_2O_2]$ = 10 mM, m_{PILC} = 3 g/L, T = 50°C, [4-NP] = 50 mg/L and 4 h.

COD was determined by the closed reflux titrimetric method 5220 C [66], while TOC was measured in a MDA Photometer Dr. Lange ISIS 9000 using TOC cuvette test LCK380 (difference method) 2–65 mg/L. For the COD analysis three replicates were measured.

The results of the COD and TOC measurements, illustrated in Fig. 11, showed that the mineralization rate has been improved with the use of Cu-PILCs. In fact, COD and TOC removal reached, respectively, 75% and 60% using Cu (5)-PILC. These findings are synonymous to what was seen in the study of the effect of pillared clay activated catalyst.

Although higher 4-NP removal can be achieved in the CWPO, a higher accumulation of oxidation by-products takes place, as proves the higher differences between the TOC, COD and 4-NP removal results especially seen in the case of AL-PILCs (only 40% COD and 30% TOC removals were reached). These intermediates are mostly refractory low molecular weight carboxylic acids (maleic, malonic, oxalic, acetic and formic), that compete with 4-NP molecules over hydroxyl radicals and thus parasitic reactions occur. The process, therefore, has to not only mineralize the starting pollutant but also the intermediate compounds. The higher value of COD, compared with TOC observed for all the PILCs, might be due to the fact that the COD value is related to the oxidation state of both organic and inorganic constituents [67], unlike TOC that strictly measures organic carbon converted to CO_2 independently of the oxidation state of the organic matter.

However, the COD and TOC removal percentage of the Cu-PILCs and AL-PILCs are in a good agreement with the known findings [2,22,30,50].

4. Conclusions

In this study, the successful pillaring of the local bentonite clay by Cu and Al leads to an increase in the basal spacing d_{001} from 1.37 nm (Na-Ben) to 1.6 nm (Cu-PILCs) and 1.7 nm (Al-PILCs).

The Cu-PILCs and Al-PILCs have demonstrated excellent degradation efficiency of 4-nitrophenol (4-NP) without pH adjustment. The removal efficiency of 4-NP using the heterogeneous catalyst prepared was tested addressing the effect of hydrogen peroxide dosage, catalyst loading, temperature and initial concentration of the recalcitrant pollutant. The optimal experimental conditions allowing to achieve 98% of 50 ppm of 4-NP, 75% COD and 60% TOC removals, were 3.0 g/L of PILCs catalysts loading, 10 mM of hydrogen peroxide dosage at 50°C.

Acknowledgements

The authors gratefully acknowledge the financial support of CNRST-Maroc (Projets dans les domaines Prioritaires de la Recherche scientifique et du développement technologique PPR2). F. Baragh would like to thank the XIVth International Symposium on Environment, Catalysis and Process Engineering (ECGP'14-IMT Lille Douai) committee for acknowledging this work and rewarding the first author with the price of the best presentation.

References

[1] M.N. Timofeeva, S.Ts. Khankhasaeva, E.P. Talsi, V.N. Panchenko, A.V. Golovin, E.Ts. Dashinamzhilova, S.V. Tsybulya, The effect of Fe/Cu ratio in the synthesis of mixed Fe, Cu, Al-clays used as catalysts in phenol peroxide oxidation, Appl. Catal., B, 90 (2009) 618–627.

[2] J. Carriazo, E. Guélou, J. Barrault, J.-M. Tatibouët, S. Moreno, Catalytic wet peroxide oxidation of phenol over Al–Cu or Al–Fe modified clays, Appl. Clay Sci., 22 (2003) 303–308.

[3] J. Carriazo, E. Guélou, J. Barrault, J.-M. Tatibouët, R. Molina, S. Moreno, Synthesis of pillared clays containing Al, Al-Fe or Al-Ce-Fe from a bentonite: characterization and catalytic activity, Water Res., 39 (2005) 3891–3899.

[4] A. El Gaidoumi, A. Loqman, A.C. Benadallah, B. El Bali, A. Kherbeche, Co(II)-pyrophyllite as catalyst for phenol oxidative degradation: optimization study using response surface methodology, Waste Biomass Valor., (2017) 1–9. http://dx.doi.org/10.1007/s12649-017-0117-5.

[5] S.D. Rodrigues Carmen, O.S.G.P. Soares, M.T. Pinho, M.F.R. Pereira, M. Madeira Luis, p-Nitrophenol degradation by heterogeneous Fenton's oxidation over activated carbon-based catalysts, Appl. Catal., B, 219 (2017) 109–122.

[6] U.S. EPA, National Pesticide Survey: 4-NitroPhenol, National Service Center for Environmental Publications, 2015.

[7] U.S. Department of Health and Human Services (HSS): Toxicological profile for chlorophenols, Sciences International, Inc., Research Triangle Park, Inc, 1999.

[8] Inventory TR: Toxicological Profile for Nitrophenols: 2-Nitrophenols and 4-Nitrophenols, Office of Toxic Substances, Washington, 1992.

[9] P.-T. Huong, B.-K. Lee, J. Kim, C.-H. Lee, Nitrophenols removal from aqueous medium using Fe-nano mesoporous zeolite, Mater. Des., 101 (2016) 210–217.

[10] J. Zhang, C. Wu, A. Jia, B. Hu, Kinetics, equilibrium and thermodynamics of the sorption of p-nitrophenol on two variable charge soils of Southern China, Appl. Surf. Sci., 298 (2014) 95–101.

[11] S. Hamidouche, O. Bouras, F. Zermane, B. Cheknane, M. Houari, J. Debord, M. Harel, J-C. Bollinger, M. Baudu, Simultaneous sorption of 4-nitrophenol and 2-nitrophenol on a hybrid geocomposite based on surfactant-modified pillared-clay and activated carbon, Chem. Eng. J., 279 (2015) 964–972.

[12] Y.-H. Shen, Removal of phenol from water by adsorption–flocculation using organobentonite, Water Res., 36 (2002) 1107–1114.

[13] D. Mantzavinos, E. Psillakis, Enhancement of biodegradability of industrial wastewaters by chemical oxidation pre-treatment, J. Chem. Technol. Biotechnol., 79 (2004) 431–454.

[14] J.-L. Wang, G. Zhao, L.-B. Wu, Slurry-phase biological treatment of nitrophenol using bioaugmentation technique, Biomed. Environ. Sci., 18 (2005) 77–81.

[15] Z. Jemaat, M. E. Suárez-Ojeda, J. Pérez, J. Carrera, Simultaneous nitritation and p-nitrophenol removal using aerobic granular biomass in a continuous airlift reactor, Bioresour. Technol., 150 (2013) 307–313.

[16] E.G. Garrido-Ramírez, B.K.G. Theng, M.L. Mora, Clays and oxide minerals as catalysts and nanocatalysts in Fenton-like reactions-a review, Appl. Clay Sci., 47 (2010) 182–192.

[17] L.F. Liotta, M. Gruttadauria, G. Di carlo, G. Perrini, V. Librando, Heterogeneous catalytic degradation of phenolic substrates: catalysts activity, J. Hazard. Mater., 162 (2009) 588–606.

[18] S. Perathoner, G. Centi, Wet hydrogen peroxide catalytic oxidation (WHPCO) of organic waste in agro-food and industrial steams, Top. Catal., 33 (2005) 207–224.

[19] E.V. Rokhina, J. Virkutyte, Environmental application of catalytic processes: heterogeneous liquid phase oxidation of phenol with hydrogen peroxide, Crit. Rev. Environ. Sci. Technol., 41 (2011) 125–167.

[20] J. Herney-Ramirez, M.A. Vicente, L.M. Madeira, Heterogeneous photo-Fenton oxidation with pillared clay-based catalysts for wastewater treatment: a review, Appl. Catal. B, 98 (2010) 10–26.

[21] N. Inchaurrondo, E. Contreras, P. Haure, Catalyst reutilization in phenol homogeneous cupro-Fenton oxidation, Chem. Eng. J., 251 (2014) 146–157.

[22] O.B. Ayodele, B.H. Hameed, Synthesis of copper pillared bentonite ferrioxalate catalyst for degradation of 4-nitrophenol in visible light assisted Fenton process, J. Ind. Eng. Chem., 19 (2013) 966–974.

[23] O.B. Ayodele, J.K. Lim, B.H. Hameed, Degradation of phenol in photo-Fenton process by phosphoric acid modified kaolin supported ferric-oxalate catalyst: optimization and kinetic modeling, Chem. Eng. J., 197 (2012) 181–192.

[24] A. El Gaidoumi, A.C. Benabdallah, B. El Bali, A. Kherbeche, Synthesis and characterization of zeolite HS using natural pyrophyllite as New Clay Source, Arab. J. Sci. Eng., 43 (2017) 191–197.

[25] N. Nath, A. Routaray, Y. Das, T. Maharana, A.K. Sutar, Synthesis and structural studies of polymer-supported transition metal complexes: efficient catalysts for oxidation of phenol, Kinet. Catal., 56 (2015) 718–732.

[26] M. Ddani, A. Meunier, M. Zahraoui, D. Beaufort, M. El Wartiti, C. Fontaine, B. Boukili, B. El Mahi, Clay mineralogy and chemical composition of bentonites from the Gourougou volcanic massif (north east morocco), Clays Clay Miner., 53 (2005) 250–267.

[27] M. Aalaoul, A. Azdimousa, K. El Hammouti, Bentonite's reserves Geometry of Trebia deposit in Nador region (North eastern Morocco); contributions of geophysical surveys and core drilling campaign, J. Mater. Environ. Sci., 6 (2015) 3564–3573.

[28] L.S. Belaroui, J.M.M. Millet, A. Bengueddach, Characterization of lalithe, a new bentonite-type Algerian clay, for intercalation and catalysts preparation, Catal. Today, 89 (2004) 279–286.

[29] F. Bergaya, G. Lagaly, In: F. Bergaya, G. Lagaly, Eds., Handbook of Clay Science, Purification of natural clays, Elsevier, Amsterdam, 2013, pp. 213–219.

[30] R. Ben Achma, A. Ghorbel, A. Dafinov, F. Medina, Copper-supported pillared clay catalysts for the wet hydrogen peroxide catalytic oxidation of model pollutant tyrosol, Appl. Catal., A, 349 (2008) 20–28.

[31] H. Khalaf, O. Bouras, V. Perrichon, Synthesis and characterization of Al-pillared and cationic surfactant modified Algerian bentonite, Microporous Mater., 8 (1997) 141–150.

[32] P.T. Hang, G.W. Brindley, Methylene blue adsorption by clay minerals. Determination of surface areas and cation exchange capacities (clay-organic studies XVIII), Clays Clay Miner., 18 (1970) 203–212.

[33] G. Rytwo, C. Serben, S. Nir, L. Margulies, Use of methylene blue and crystal violet for determination of exchangeable cations in montmorillonite, Clays Clay Miner., 39 (1991) 551–555.

[34] H.-J. Muñoz, C. Blanco, A. Gil, M.-Á. Vicente, L.-A. Galeano, Preparation of Al/Fe-pillared clays: effect of the starting mineral, Materials, 10 (2017) 1364.

[35] D. Zhou, Z. Zhang, J. Tang, X. Zhang, Q. Wang, L. Liao, Influence of different exchangeable cations (Li^+, Na^+ and Ca^{2+}) on the modification effects and properties of organomontmorillonites used in oil-based drilling fluids/muds, RSC Adv., 5 (2015) 90281– 90287.

[36] S.A. Hassan, F.Z. Yehia, H.A. Hassan, S. Sadek, A. Darwish, Various characteristics and catalytic performance of iron (II) phthalocyanine immobilized onto titania- and vanadia-pillared bentonite clay in in situ polymerization of methyl methacrylate: an attempt to synthesize novel polymer/iron phthalocyanine/pillared clay nanocomposites, J. Mol. Catal., A, 332 (2010) 93–105.

[37] S. Azarkan, A. Peña, K. Draoui, C.I. Sainz-Díaz, Adsorption of two fungicides on natural clays of Morocco, Appl. Clay Sci., 123 (2016) 37–46.

[38] I. Daou, O. Zegaoui, R. Chfaira, H. Ahlafi, H. Moussout, Physico-chemical characterization and kinetic study of methylene blue adsorption onto a Moroccan Bentonite, Int. J. Sci. Res. Pub., 5 (2015) 293–301.

[39] I. Daou, O. Zegaoui, A. Amachrouq, Study of the effect of an acid treatment of a natural Moroccan bentonite on its physicochemical and adsorption properties, Water Sci. Technol., 75 (2017) 1098–1117.

[40] H.Y. Liu, T. Shen, T.S. Li, P. Yuan, G. Shi, X.J. Bao, Green synthesis of zeolites from a natural aluminosilicate mineral rectorite: effects of thermal treatment temperature, Appl. Clay Sci., 90 (2014) 53–60.

[41] E. Eren, B. Afsin, An investigation of Cu(II) adsorption by raw and acid-activated bentonite: a combined potentiometric, thermodynamic, XRD, IR, DTA study, J. Hazard. Mater., 151 (2018) 682–691.

[42] S.W. Wang, Y.H. Dong, M.L. He, L. Chen, X.J. Yu, Characterization of GMZ bentonite and its application in the adsorption of Pb(II) from aqueous solutions, Appl. Clay Sci., 43 (2009) 164–171.

[43] P. Yuan, F. Annabi-Bergaya, Q. Tao, M.D. Fan, Z.W. Liu, J.X. Zhu, H.P. He, T.H. Chen, A combined study by XRD, FTIR, TG and HRTEM on the structure of delaminated Fe-intercalated/pillared clay, J. Colloid Interface Sci., 324 (2008) 142–149.

[44] M. El Miz, H. Akichoh, D. Berraaouan, S. Salhi, A. Tahani, Chemical and physical characterization of Moroccan bentonite taken from Nador (North of Morocco), Am. J. Chem., 7 (2017) 105–112.

[45] M.A. De Leoǹ, J. Castigliona, J. Bussi, M. Sergio, Catalytic activity of an iron-pillared montmorillonitic clay mineral in heterogeneous photo-Fenton process, Catal. Today, 133–135 (2008) 600–605.

[46] N. Inchaurrondo, J. Cechini, J. Font, P. Haure, Strategies for enhanced CWPO of phenol solutions, Appl. Catal., B, 111–112 (2012) 641–648.

[47] J. Pignatello, E. Oliveros, A. MacKay, Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, Crit. Rev. Environ. Sci. Technol., 36 (2006) 1– 84.

[48] N. Daneshvar, M.A. Behnajady, Y.Z. Asghar, Photooxidative degradation of 4-nitrophenol (4-NP) in UV/H_2O_2 process: influence of operational parameters and reaction mechanism, J. Hazard. Mater., 139 (2007) 275–279.

[49] S. Caudo, C. Genovese, S. Perathoner, G. Centi, Copper-pillared clays (Cu-PILC) for agro-food wastewater purification with H_2O_2, Microporous Mesoporous Mater., 107 (2008) 46–57.

[50] A.C.K. Yip, F.L. Lam, X. Hu, Chemical-vapor-deposited copper on acid-activated bentonite clay as an applicable heterogeneous catalyst for the photo-Fenton-like oxidation of textile organic pollutants, Ind. Eng. Chem. Res., 44 (2005) 7983–7990.

[51] H. Feng, L. Le-cheng, Degradation kinetics and mechanisms of phenol in photo-Fenton process, J. Zhejiang Univ. Sci., 5 (2004) 198–205.

[52] Z. Mojović, P. Banković, A. Milutinović-Nikolić, J. Dostanić, N. Jović-Jovičić, D. Jovanović, Al,Cu-pillared clays as catalysts in environmental protection, Chem. Eng. J., 154 (2009) 149–155.

[53] C.M. Lousada A.J. Johansson, T. Brinck, M. Jonsson, Reactivity of metal oxide clusters with hydrogen peroxide and water—a DFT study evaluating the performance of different exchange-correlation functionals, Phys. Chem. Chem. Phys., 15 (2013) 5539–5552.

[54] S. Caudo, G. Centi, C. Genovese, S. Perathoner, Homogeneous versus heterogeneous catalytic reactions to eliminate organics from waste water using H_2O_2, Top. Catal., 40 (2006) 207–219.

[55] X. Li, G. Lu, Z. Qu, D. Zhang, S. Liu, The role of titania pillar in copper-ion exchanged titania pillared clays for the selective catalytic reduction of NO by propylene, Appl. Catal., A, 398 (2011) 82–87.

[56] S. Caudo, G. Centi, C. Genovese, S. Perathoner, Copper- and iron-pillared clay catalysts for the WHPCO of model and real wastewater streams from olive oil milling production, Appl. Catal., B, 70 (2007) 437–446.

[57] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, Washington, D.C., 2005.

[58] J.J. Su, B.Y. Liu, Y.C. Chang, Identifying an interfering factor on chemical oxygen demand (COD) determination in piggery wastewater and eliminating the factor by an indigenous *Pseudomonas stutzeri* strain, Lett. Appl. Microbiol., 33 (2001) 440–444.

[59] R.A. Dobbs, R.T. Williams, Elimination of chloride interference in the chemical oxygen demand test, Anal. Chem., 35 (1963) 1064–1067.

[60] Y.W. Kang, M.-J. Cho, K.-Y. Hwang, Correction of hydrogen peroxide interference on standard chemical oxygen demand test, Water Res., 33 (1999) 1247–1251.

[61] I. Talinli, G.K. Anderson, Interference of hydrogen peroxide on the standard COD test, Water Res., 26 (1992) 107–110.

[62] Y. Wang, W. Li, A. Irini, A novel and quick method to avoid H_2O_2 interference on COD measurement in Fenton system by Na_2SO_3 reduction and O_2 oxidation, Water Sci. Technol., 68 (2013) 1529–1535.

[63] S. Zhou, C. Zhang, X. Hu, Y. Wang, R. Xu, C. Xia, H. Zhang, Z. Song, Catalytic wet peroxide oxidation of 4-chlorophenol over Al-Fe-, Al-Cu-, and Al-Fe-Cu-pillared clays: sensitivity, kinetics and mechanism, Appl. Clay Sci., 95 (2014) 275–283.

[64] T. Wu, J.D. Englehardt, A new method for removal of hydrogen peroxide interference in the analysis of chemical oxygen demand, Environ. Sci. Technol., 46 (2012) 2291–2298.

[65] M. Fidaleo, R. Lavecchia, Kinetic study of hydrogen peroxide decomposition by catalase in a flow-mix microcalorimetric system, Thermochim. Acta, 402 (2003) 19–26.

[66] APHA, WEF, Standard methods for the examination of water and wastewater, American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington, D.C., 1998.

[67] H. Zhang, J.C. Heung, C.P. Huang, Optimization of Fenton process for the treatment of landfill leachate, J. Hazard. Mater., 125 (2005) 166–174.

Supplementary material

Carbonaceous deposits study on the PILCs catalysts:

The carbonaceous deposits usually referred to as carbon or coke are the main cause of the deactivation of heterogeneous catalysts by covering their active sites and/or by pore blocking [1,2]. Even though carbon and coke are used to describe the same thing but an arbitrary distinction is made between them depending mostly on their origin. In fact, coke is created by condensation or decomposition of hydrocarbons on catalyst surfaces while carbon is typically a product of carbon monoxide disproportionation and thus the use of the term coke to refer to carbonaceous deposition on heterogeneous catalysts is mostly used [3]. Therefore, we will refer to the carbonaceous deposits on the PILCs as coke. The chemical structures of cokes may vary with reaction type and conditions, catalyst type, and the age of the coke formed. They may contain aromatic and/or aliphatic compounds as well as primarily carbons such as graphite [4].

Several studies have investigated the coke formation on the supported metal catalysts for the catalytic reactions involving hydrocarbons, especially in the catalytic wet oxidation of phenolic compounds [1,2,5]. In order to characterize the nature and distribution of coke deposits, various analytical techniques have been used. However, the chemical identity of the coke deposits has been mostly investigated by FT-IR [3,6].

Many authors have investigated the nature of coke deposits in the catalytic wet air oxidation (CWAO) of phenolic compounds which is oxidizing these organic pollutants using molecular oxygen as oxidant at elevated temperatures (125°C–320°C) and pressures (0.5–20 MPa) [1,2,7–9]. Among others, Kim and Ihm [1,2] studied the nature of the coke formed upon CWAO of phenol in a batch reactor using supported transition metal (Mn, Cu, Fe, Co, and Ni) on γ-Al_2O_3. The results of FT-IR spectroscopy led them to conclude that the catalyst deactivation was caused by deposition of mostly aromatic compounds and some oxygen-bearing groups such as carboxylic acids and alcohols as well as aliphatic carbon rings only in the case of copper-based catalysts. While Pintar et al. [7] reported that the strong adsorption on Ru/TiO_2 catalyst surface of partially oxidized C6-intermediates produced in the CWAO of phenol at temperatures below 190°C, leads to the deactivation of the catalysts.

Furthermore, Baloyi et al. [9] investigated the stability of Al/Zr-PILCs catalyst in the CWAO of phenol under mild conditions (100°C and 10 bars). The used PILCs showed remarkable catalytic performance with 100% phenol and 88% TOC removals and were found to show no significant loss in its catalytic activity since XRD results illustrated the retain of the structural stability of the catalyst with similar crystallinity as that of the fresh catalyst after 6 runs. Nevertheless, Jiang et al. [8] reported that Fe-ZSM-5 zeolite membrane catalyst prepared for CWPO of phenol at the optimized condition (catalyst bed height of 4.0 cm, the temperature of 80°C, and H_2O_2 concentration of 5,100 mg/L), showed no coke deposits after 8 h reaction and only after 40 h reaction two new absorption bands around 1,359 and 1,315 cm^{-1} were observed and were attributed to the carbon coked on the surface of the zeolitic catalysts. However, little information is found on the coke deposits on pillared clay catalysts surfaces in CWPO of phenolic compounds.

In order to investigate the coke deposits on the prepared Al-PILCs and Cu-PILCs, pillared clay catalysts used in this study were analyzed by FT-IR spectroscopy after being washed with distilled water and dried at 100°C for 48 h. Fig. S1 shows the FT-IR spectra of all the used PILCs. Moreover, Kim and Ihm [2] noticed that after 3 h reactions, a change of color of the copper-based catalyst occurred, from light aquamarine to dark brown. This change was attributed to a probable coke deposition on the catalyst surface, even for the Cu-PILCs no such color change was noticed after 4 h reaction.

Table S1 summarizes a comparison of our results with those reported in the literature. Different heterogeneous catalysts have been used in the CWPO of 4-NP. These catalysts have proved a good catalytic capacity and mineralization degree. Even though the reaction conditions does not allow to have a clear comparison between the Al-PILCs and

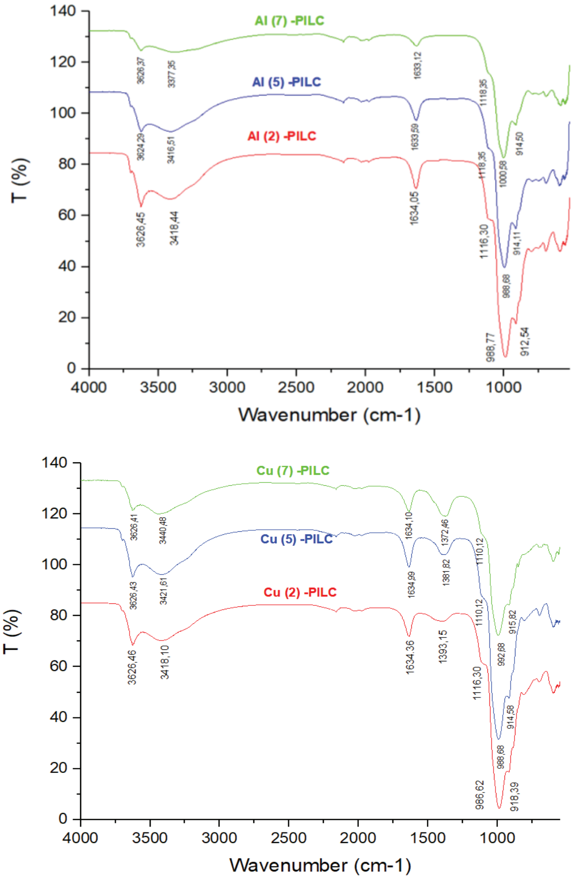


Fig. S1. FT-IR spectra of used Al-PILCs and Cu-PILCs after 4 h of 4-NP oxidation under experimental conditions: pH = 5.7, $[H_2O_2]$ = 10 mM, m_{PILC} = 3 g/L, T = 50°C, [4-NP] = 50 mg/L.

Table S1
Performance comparison of various heterogeneous catalysts for 4-nitrophenol oxidation

Catalyst	Process	Conditions	Results	References
CuO/Al_2O_3	Microwave-assisted Fenton-like process	pH = 6.0 (adjusted); [catalyst] = 4 g/L; [H_2O_2] = 25 mM; [4-NP]= 50 mg/L; microwave power = 100 W; radiation time = 6 min	4-NP removal % = 93%; TOC removal % = 68%	Pan et al. [10]
Copper-pillared bentonite catalyst	Visible light–assisted Fenton process	pH = 5.25 (not adjusted); [catalyst] = 2 g/L; T = 40°C; [H_2O_2] = 20% excess; [4-NP] = 100 mg/L; visible light, λ= 495 nm; radiation time = 6 min	4-NP removal % = 96%; COD removal % = 80%	Ayodele and Hameed [11]
Fe_3O_4	CWPO	pH =7.0 (adjusted); [catalyst] = 1.5 g/L [H_2O_2] = 620 mM; [4-NP] = 25–45 mg/L; t_{reaction} = 10 h	4-NP removal % = 90%	Sun and Lemley [12]
Al-PILCs	CWPO	pH = 5.7 (not adjusted); [catalyst] = 3 g/L; T = 50°C; [H_2O_2] = 10 mM; [4-NP] = 50 mg/L	4-NP removal % = 75%; COD removal % = 40%; TOC removal % = 30%	This study
Cu-PILCs	CWPO	pH = 5.7 (not adjusted); [catalyst] = 3 g/L; T = 50°C; [H_2O_2] = 10 mM; [4-NP] = 50 mg/L	4-NP removal % = 98%; COD removal % = 75%; TOC removal % = 60%	This study

Cu-PILCs used in our study with the known catalysts, we can assume, based on the final degradation results, that the prepared catalysts have similar performances as the other catalysts in Table S1.

Conclusively, more detailed study should be done regarding the coke deposits on the catalytic wet peroxide oxidation of 4-nitrophenol using pillared clay catalysts. Many reviews and studies have been done regarding the deactivation of Al_2O_3-based catalysts and of some PILCs in the CWAO of phenol but not much on the PILCs in the CWPO of phenolic compounds. Therefore, based on this study we cannot be sure if the carbonaceous deposits accrued or not nor specify the amount and nature of the carbonaceous deposits. The deactivation study of these heterogeneous catalysts would be of great interest and further analysis should be done such as N_2 adsorption–desorption, X-ray diffraction, field emission scanning electron microscopy, thermal gravimetric, and Raman spectra analyses.

References

[1] K.-H. Kim, S.-K. Ihm, Heterogeneous catalytic wet air oxidation of refractory organic pollutants in industrial wastewaters: a review, J. Hazard. Mater., 186 (2011) 16–34.
[2] K.-H. Kim, S.-K. Ihm, Nature of carbonaceous deposits on the alumina supported transition metal oxide catalysts in the wet air oxidation of phenol, Top. Catal., 33 (2005) 171–179.
[3] C.H. Bartholomew, Mechanisms of catalyst deactivation, Appl. Catal., A, 212 (2001) 17–60.
[4] P. Forzatti, L. Lietti, Catalyst deactivation, Catal. Today, 52 (1999) 165–181.
[5] S. Hamoudi, K. Belkacemi, F. Larachi, Catalytic oxidation of aqueous phenolic solutions catalyst deactivation and kinetics, Chem. Eng. Sci., 54 (1999) 3569–3576.
[6] S. Pasieczna, J. Ryczkowski, T. Borowiecki, K. Stołecki, Spectroscopy in carbon deposits characterization, J. Phys. IV France, 117 (2004) 41–46.
[7] A. Pintar, J. Batista, T. Tisler, Catalytic wet-air oxidation of aqueous solutions of formic acid, acetic acid and phenol in a continuous-flow trickle-bed reactor over Ru/TiO_2 catalysts, Appl. Catal., B, 84 (2008) 30–41.
[8] S. Jiang, H. Zhang, Y. Yan, X. Zhang, Stability and deactivation of Fe-ZSM-5 zeolite catalyst for catalytic wet peroxide oxidation of phenol in a membrane reactor, RSC Adv., 5 (2015) 41269–41277.
[9] J. Baloyi, T. Ntho, J. Moma, Synthesis of highly active and stable Al/Zr pillared clay as catalyst for catalytic wet oxidation of phenol, J. Porous Mater., (2018) 1–15. https://doi.org/10.1007/s10934-018-0667-3.
[10] W. Pan, G. Zhang, T. Zhenga, P. Wang, Degradation of p-nitrophenol using CuO/Al_2O_3 as a Fenton-like catalyst under microwave irradiation, RSC Adv., 5 (2015) 27043–27051.
[11] O.B. Ayodele, B.H. Hameed, Synthesis of copper pillared bentonite ferrioxalate catalyst for degradation of 4-nitrophenol in visible light assisted Fenton process, J. Ind. Eng. Chem., 19 (2013) 966–974.
[12] S.-P. Sun, A.T. Lemley, p-Nitrophenol degradation by a heterogeneous Fenton-like reaction on nano-magnetite: process optimization, kinetics, and degradation pathways, J. Mol. Catal., A, 349 (2011) 71–79.