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SCIENTIFIC PAPER

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## REMOVAL OF ISOPROPYL ALCOHOL FROM WASTEWATER USING MODIFIED BENTONITE BY Fe, Cu, AND Fe-Cu

### Highlights

- Catalysts based on pillared clays with Fe, Cu, and Fe-Cu were utilized.
- IPA is one of the most common pollutants in semiconductor manufacturing wastewater.
- Using catalytic wet peroxide oxidation processes for the removal of IPA.

### Abstract

*Catalysts based on purified bentonite (Be) pillared with Fe<sup>3+</sup> (BeFe), Cu<sup>2+</sup> (BeCu), and Fe-Cu (BeFe/Cu) were synthesized from Algerian bentonite and used to treat isopropyl alcohol (IPA) by catalytic wet peroxide oxidation (CWPO) with H<sub>2</sub>O<sub>2</sub> at 298 K. The BeFe showed higher activity than the BeFe/Cu one for IPA removal, although the second was more active for H<sub>2</sub>O<sub>2</sub> decomposition. The reaction kinetics were examined with both catalysts using the pseudo-first-order reaction model. The mechanism of H<sub>2</sub>O<sub>2</sub> decomposition was known through different values of apparent activation energy (E<sub>a</sub>) were determined from the Arrhenius equation 46 kJ/mol for BeFe with abundant formation of •OH radicals and 67 kJ/mol for BeFe/Cu with mainly production of O<sub>2</sub> which has a low oxidation capacity at 298 K.*

*Keywords: Isopropyl alcohol oxidation; Pillared clays; Cu; Fe; Fe-Cu.*

### INTRODUCTION

Isopropyl alcohol (IPA) is commonly used as an organic solvent such as a cleaning agent for silicon wafers [1] and a drying agent for removing residual organic matter on the water surface in the semiconductor industry [2]. This industry is a significant water consumer and producer of wastewater, which can be hazardous to the environment if not treated properly. The resulting wastewater is characterized as highly turbid due to its high solid content, high chemical oxygen demand (COD) (normally ranging between 3000 and 5000 mg/L), and major contamination from organic and inorganic solvent particles ranging from nano to micro-sized [3]. These organic compounds pose direct or indirect harm to the liver, kidney, central nervous system, and skin, and some of them have already been verified as carcinogens, teratogenic agents, and genetic mutagen for humans. Traditional wastewater treatment approaches involving physical-chemical decomposition or

microorganisms have shown only limited efficiencies [4]. Therefore, the wastewater is generally treated using the activated sludge method. However, this method has problems such as a long treatment time, the necessity of pre-treatment and post-treatment, and the generation of excess sludge. Therefore, a wastewater treatment technique with a short time and less environmental load is required. Currently, advanced oxidation processes (AOPs) are commonly used to oxidize complex organic contaminants that are found in wastewater and that are difficult to degrade into simpler end products through biological processes [5]. Catalytic wet peroxide oxidation (CWPO) is one of these successful AOPs, utilizing steady catalysis for the reduction of pollutants in industrial wastewater in the presence of an active catalyst [6]. AOPs are characterized by the production of •OH radicals [7], which are potent (2.8 V) and unselective oxidants that can oxidize and mineralize organic pollutants in water, yielding CO<sub>2</sub> and other inorganic compounds [8]. Hydroxyl radicals can be generated from H<sub>2</sub>O<sub>2</sub> by using activated carbon and Fenton's reagent, among other decomposition catalysts. Fenton's reagent utilizes Fe ions as a homogeneous catalyst, producing hydroxyl and perhydroxyl radicals from water [9]:

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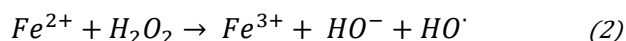
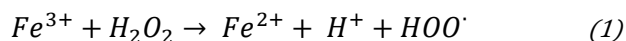
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AOPs can also be carried out under heterogeneous conditions by immobilizing the iron catalyst on a support such as zeolite [10], MnOx [11], carbon material [12], and polymers [13]. Bentonite is natural clay abundantly available with good exchanging ability and unique physical and chemical properties. Modified bentonite (Be) is of great importance in the preparation of some high-technology materials such as pillared clays (PILCs). PILCs have received increasing interest in the last 2 decades as green heterogeneous catalysts in wastewater treatment due to their textural and catalytic properties in different reactions [14]. They represent a new class of microporous materials that have potential applications as catalysts [15]. In principle, any metal oxide or salt-forming polynuclear species upon hydrolysis can be inserted as a pillar [16]. The hydroxyl polycations of polynuclear metals are commonly used as pillaring agents in bentonite to modify its structures such as Al, Fe, Cu, Zr, Cr, Ce, and Ti individually or mixed, yielding PILC materials with thermal and mechanical stability [16,17]. On the other hand, as indicated before, iron is the metallic ion used in Fenton's reagent. Thus, the intercalation of cations Cu-Fe, in the interlayer spacing of Be, should produce catalytically active materials for the oxidation of organic compounds with hydrogen peroxide. Be-(Cu, Fe, Al, and Cr) are the most studied, as they have been proposed as active catalysts for the oxidation of organic compounds [18-19]. Some advantages of BeFe in AOPs are their stability, their capacity to work with pH values in a range of 3-3.5, and where leaching of Fe ions is minimal [18]. Cu as oxide is a Lewis acid that has very advantageous photocatalytic properties. It is a non-toxic material, is very stable over long periods, is environmentally friendly, and has strong light absorption [18]. The use of BeCu as a catalyst of the AOPs has been mainly studied without the use of light [19]. BeFe/Cu was used in the mineralization of paracetamol by AOPs under neutral pH conditions, obtaining about 80% mineralization; this result was only 2% less than the degree of mineralization achieved at acidic pH after 180 min of the reaction [20]. The use of BeCu as a catalyst for AOPs has been studied mainly without the use of light [19,21], and some have reported its effectiveness in phenol mineralization. In some studies, Cu was added to the pre-prepared BeFeAl; the addition of Cu enhanced the oxidation of organic compounds, which was attributed to the synergy between Cu and Fe [20,22]. It has been concluded [23] that in addition to the typical Fenton reaction (Eq. (2)), other species might be appearing, like the reactive intermediate  $\equiv\text{Cu}^{2+}-\text{OH}^{\cdot}$  that contribute to organic compound degradation. It has also been recently demonstrated that  $\text{Cu}^{+}$  activates oxygen to produce powerful reactive oxygen species ( $\text{H}_2\text{O}_2$ ,  $\text{O}_2^{\cdot-}$  and  $\cdot\text{OH}$ ) [23]. Despite the extensive literature reported about the removal of IPA by CWPO using microwave [24], catalysts, such as  $\text{ZrO}_2$  [25],  $\text{Pt}/\text{Al}_6\text{Si}_2\text{O}_{13}$  [26],  $\text{Mo}/\text{V}$  [27],  $\text{ZnO}$  [28], and  $\text{NaX}$ -zeolite [29,30], and by adsorption on activated bentonite [31], to the best of our knowledge, there is no work where Be-(Fe, Cu, Fe/Cu) is used as catalysts for this reaction. The present investigation deals with the study of the removal of IPA from wastewater by CWPO using BeFe, BeCu, and BeFe/Cu catalysts, and the decomposition of  $\text{H}_2\text{O}_2$  was also discussed.

## MATERIALS AND METHODS

### Preparation of catalyst

All substances used in this study were highly purified (> 99%), mostly Fluka AG, Buchs SG, and ultrapure water.

The raw from Maghnia (western Algeria), supplied by Bental Company, Algeria, was purified and classified by sedimentation, and then the <2  $\mu\text{m}$  fraction was collected for the pillaring experiment. The cation exchange capacity (CEC) was 98 meq/100 g of clay determinate by copper ethylenediamine ((EDA) $_2\text{CuCl}_2$ ) complex.

A Be powder (4 g) was put with 1 g of  $\text{FeCl}_3$ ,  $\text{CuCl}_2$ , and a Fe/Cu mix (50/50% mass ratio) in a Morton press to mix the mixture well. Afterward, 1 M NaOH solution was added by 0.0625 mass ratio ( $\text{OH}/\text{M}$ ,  $\text{M} = \text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ) in a dropwise manner in this mixed powder to make a suspension. It rested for 24 h until a suitable paste was obtained. Further, very small beads were formed from the dough, which were calcined at 500  $^{\circ}\text{C}$  for 2 h. Be with Fe, Cu, and Fe/Cu were named by BeFe, BeCu, and BeFe/Cu, respectively.

### Characterization methods

The surface morphology and elemental composition of the samples were observed by a scanning electron microscope (SEM) with an energy-dispersive X-ray spectroscopy (EDS) using the JEOL5510 model. The range of accelerating voltage was from 200 V to 30 kV with a resolution of 2 mm and magnification up to 5000 $\times$ . The powder X-ray diffraction (PXRD) patterns were taken on a Philips P3710 X-ray diffractometer equipped with  $\text{CuK}\alpha$  radiation ( $\lambda = 0.154 \text{ nm}$ ) at 40 mA and a scan rate of 0.039 $^{\circ}$  (2 $\theta$ )/900 s. Brunauer-Emmett-Teller (BET) surface area values were determined from 77 K  $\text{N}_2$  adsorption using a Quantachrome Quadrasorb SI surface analyzer. The samples were previously outgassed at 363 K and  $10^{-7}$  T for 16 h.

### CWPO experiments

The maximum legal IPA concentration in wastewater effluent had not been established, so, to simulate the real situation in CWPO experiments, 10-200 ppm was used. The catalytic activity experiments for CWPO of IPA with the different catalysts were performed in a 500 mL three-necked round-bottom flask equipped with a mechanical stirrer. The pH was continuously controlled within the range of 3-3.5, which has been reported as optimal for AOP processes [18,20], as well as for CWPO with BeFe catalysts. After stabilization of the temperature at 298 K, the desired amount of Be was added to 125 mL of an aqueous IPA solution (10, 100, and 200 ppm) and it was stirred for 15 min to allow IPA adsorption onto the catalyst. The amount adsorbed was always less than 7% of the initial IPA weight. Next, add 125 mL of an aqueous  $\text{H}_2\text{O}_2$  solution (10, 20, and 30 ppm) corresponds to the stoichiometric amount for complete oxidation of IPA. Samples from the reaction medium were withdrawn at the initial time and after 15 min, 30 min, and each hour until completing 4 h of reaction. The catalyst in these samples was removed using a nylon filter of 0.2  $\mu\text{m}$  pore size. The oxidation process was followed by the evolution of total organic carbon (TOC), IPA, and  $\text{H}_2\text{O}_2$  concentrations.

IPA was analyzed by gas chromatography-mass spectrometry (single quadrupole: Thermo Scientific). The  $\text{H}_2\text{O}_2$  concentration was determined by a colorimetric titration method based on the formation of the yellow color of complex  $\text{Ti(IV)}-\text{H}_2\text{O}_2$ , using a UV-vis spectrophotometer at 410 nm. TOC was determined with a 5050-analyzer model. Since the stability of a catalyst is essential for the evaluation of its performance, a colorimetric method was used for the leaching of  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$ .

### Catalytic $\text{H}_2\text{O}_2$ decomposition experiments

Experiments were carried out to study the decomposition of  $\text{H}_2\text{O}_2$  using a catalyst. Certain amounts of the catalysts were placed in glass bottles (25 mL). The catalysts were used in powder form to avoid diffusion limitations [18]. These flasks were deposited into a thermostatic bath and were magnetically stirred during the experiment. For each flask, a 100 ppm  $\text{H}_2\text{O}_2$  solution was added quickly and the time was recorded. After a given time, an aliquot volume (2  $\mu\text{L}$ ) was taken from the flask, and the catalyst was removed employing a nylon filter of 0.2  $\mu\text{m}$  pore size. Analyses of  $\text{H}_2\text{O}_2$  were performed according to the above-described method [32].

## RESULTS AND DISCUSSION

### Characterization of the pillared clays

The variations in the chemical composition of catalysts, obtained by SEM-EDS are shown in Table 1. The results revealed an increment in the amount of Fe content in BeFe (8.76 wt%) and BeFe/Cu (9.15 wt%) as compared to Be (3.84 wt%). In Be, the Cu content was 0.13 wt% and increased to 6.53 wt% in BeFe/Cu and to 7.40 wt% in BeCu. The increase in wt% of Fe and Cu in BeFe, BeCu, and BeFe/Cu implied that Fe and Cu had been intercalated onto Be. Also, the Na content decreased after pillaring the Be with Fe and Cu ions (Table 1) due to the formation of FeO and CuO pillars between the silicate layers. Figure 1 shows the SEM images and EDX specters of Be (Figure 1 (a)), BeFe (Figure 1 (b)), BeCu (Figure 1 (c)), and BeFe/Cu (Figure 1 (d)). All samples exhibited heterogeneous surface morphology of Be surface, characterized by smooth (Figure 1(a)) and rough particles that tended to agglomerate with different sizes and irregular shapes, becoming rougher and more wrinkled ((Figure 1 (b), Figure 1 (c), and Figure 1 (d)) after the pillaring process. This difference may indicate that the oxide columns were stabilized due to the introduction of

massive cations into the spaces between the clay layers. Peaks from the major elements Si, Al, and O are clearly observed in the EDX spectra of all samples (Figure 1), which were the most common chemical elements in the composition of bentonite compounds Figure 1(a). Fe (Figure 1 (b)), Cu (Figure 1 (c)), and Fe/Cu (Figure 1 (d)) were also determined, confirming the success and stability of the oxide pillared as a result of the introduction of massive cations into the spaces between the clay layers. The oriented powder X-ray diffractograms of Be and the resultant BeFe, BeCu, and Be/FeCu samples are shown in Figure 2 and Table 2 reports the basal spacing  $d_{(001)}$  and the surface area values of the Be and pillared Be after calcination at 773 K. As observed from Figure 2 and Table 2, for the starting (Be), the (001) smectite peak occurred at  $2\theta = 7.83^\circ$  corresponding to a basal spacing of 11.3 Å. The  $d_{001}$  value of Be up to higher values in the range of 17.47 Å, 16.84 Å, and 15.73 Å for BeFe, BeFe/Cu, and BeCu, respectively, indicating that the modification carried out over the clay leads, in all the cases, to the successful pillaring of the material. It points out the stabilization of oxide pillars due to the introduction of bulky cations into the interlayer spaces of clay that prevents its silicate layers from closing on heating [18].  $\text{N}_2$ -adsorption/desorption isotherms for Be, BeFe, BeCu, and BeFe/Cu were obtained (Figure 3). All samples showed typical type-IV sorption isotherms, classified by IUPAC, and both showed an H3-type hysteresis loop at 0.45-0.99, indicating the mesoporosity of the materials. As can be seen from Table 2, the pillaring process substantially increases both the basal spacing and BET surface area. It can be seen that the surface area increased from 99  $\text{m}^2/\text{g}$  for Be to 278  $\text{m}^2/\text{g}$  for BeFe but the introduction of the Cu onto BeFe reduces the surface area that is due to the blocking of part of the catalyst pores.

### Catalytic oxidation of IPA with pillared clays

Figure 4 shows the results obtained for IPA conversion,  $\text{H}_2\text{O}_2$  decomposition, and TOC reduction in 10 ppm IPA, 1 g catalyst, and 20 ppm of  $\text{H}_2\text{O}_2$  condition. It is clear that the pillared clay by Fe greatly increases their activity for the oxidation of IPA. Figure 4(a) shows a decrease in TOC removal, which is in all cases significantly lower than IPA conversion; this means that oxidation of IPA proceeds through the formation of different intermediates and the final result is far from complete mineralization, i.e., oxidation to  $\text{CO}_2 + \text{H}_2\text{O}$ .

Table 1. Chemical composition of catalysts by EDX.

Catalysts	Elemental composition (%)											
	OK	MgK	NaK	AlK	SiK	FeK	CuK	KK	CaK	TiK	LaL	Toal
Be	56.27	1.28	2.46	8.94	24.42	3.84	0.13	1.03	0.46	0.21	0.96	100.00
BeFe	53.72	2.01	1.04	12.51	18.24	8.76	0.21	1.76	0.16	1.19	0.40	100.00
BeF/Cu	53.15	0.23	0.02	12.51	18.07	9.15	6.53	0.13	0.18	0.01	0.02	100.00
BeCu	52.47	2.65	1.88	9.01	24.21	0.11	7.40	1.44	0.28	0.38	0.17	100.00

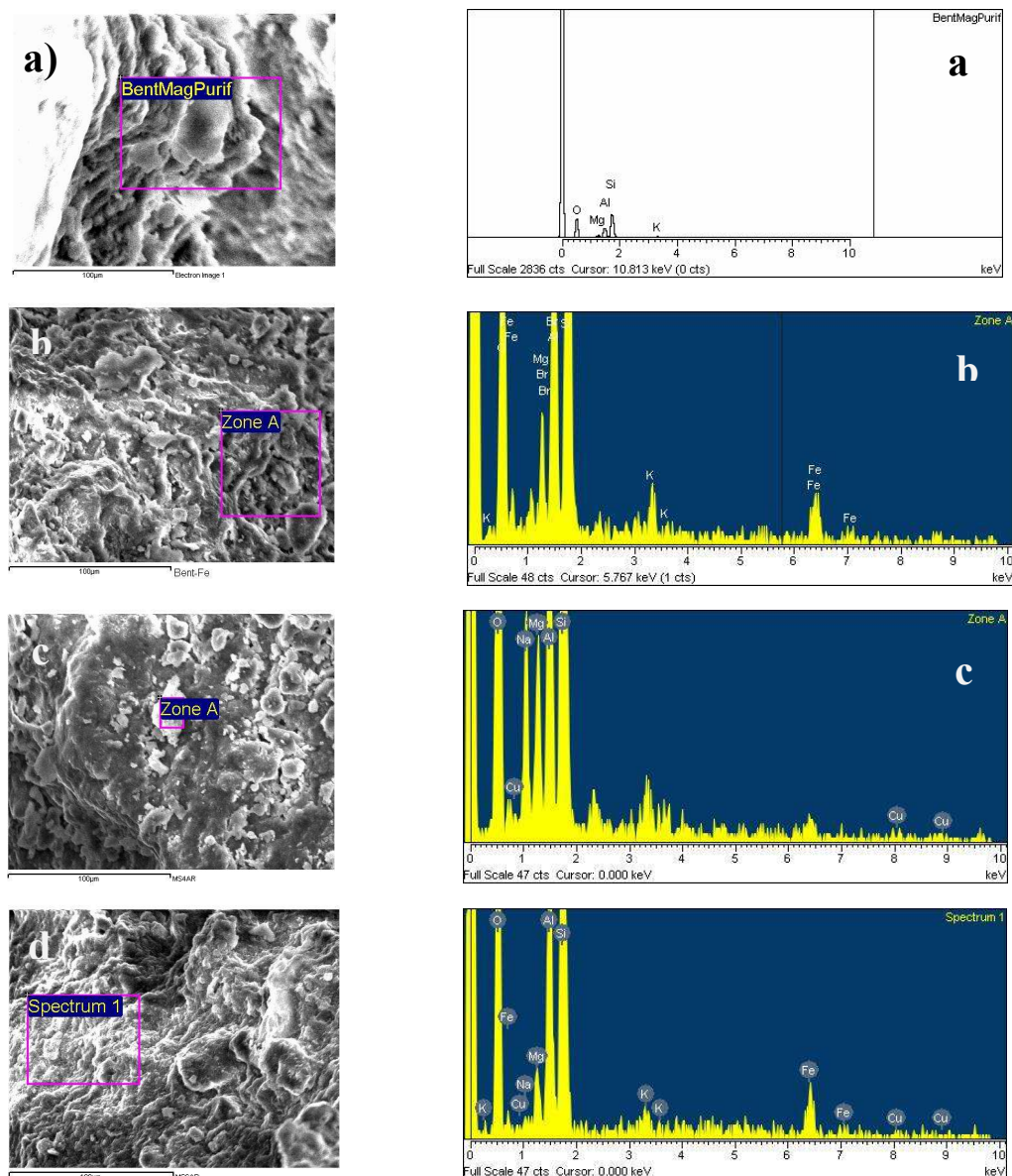


Figure 1. SEM images and EDX specters of catalysts.

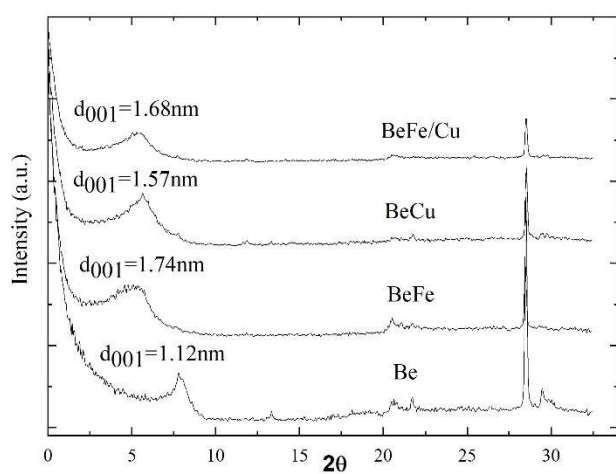


Figure 2. X-ray diffractograms of catalysts.

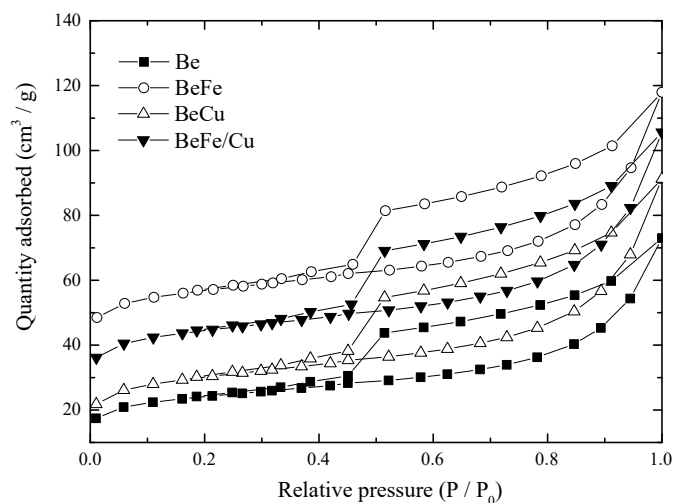
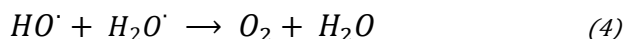
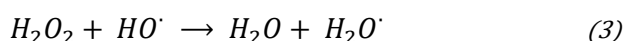
Figure 1.  $N_2$ -adsorption/desorption isotherms of catalysts

Table 1. Basal spacing (d001) and BET surface area values of catalysts.

	2θ (°)	d <sub>001</sub> (nm)	S <sub>BET</sub> (m <sup>2</sup> /g)
Be	7.83	1.13	99
BeFe	5.07	1.74	278
BeFe/Cu	5.29	1.67	204
BeCu	5.67	1.56	136

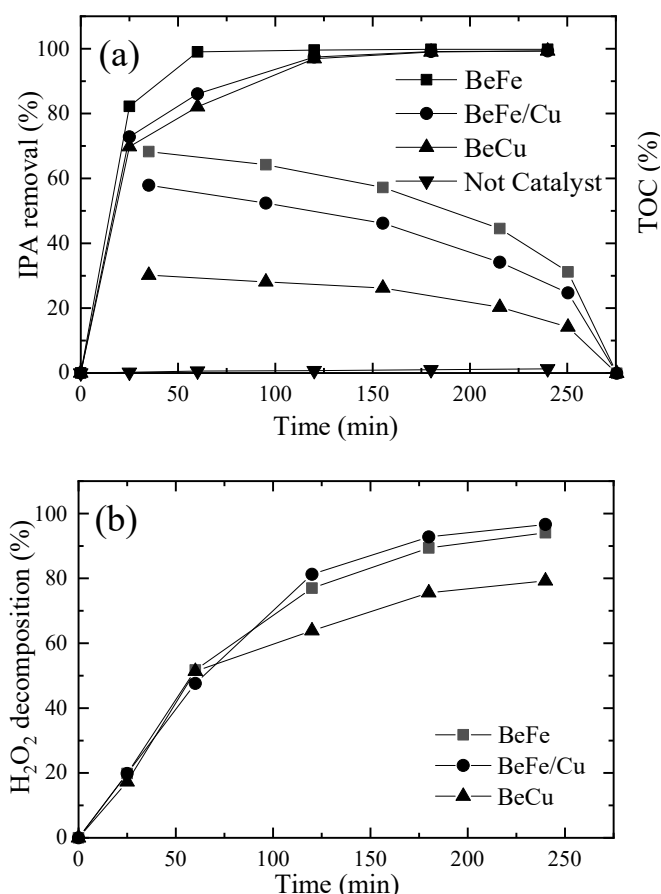
The maximum TOC decrease after 3 h reaches 68% and close to 57% for both BeFe and BeFe/Cu, respectively, which means that significant amounts of intermediates remain in solution even at high reaction times. However, as Figure 4(a) shows, the presence of catalysts significantly enhances the oxidation rate of IPA compared to their absence. With BeFe, the IPA is almost completely removed (99%) in 60 min and the BeFe/Cu to 90% whereas BeCu leads to no more than 82% in the same time and complete removal requires more than 3 h of the reaction. Previous studies [18] have shown that, under acidic conditions, copper's catalytic activity is lower than iron's. As shown in Figure 4(b), the rate of H<sub>2</sub>O<sub>2</sub> decomposition appears fairly similar for both BeFe and BeFe/Cu during the first 60 min of the reaction. This suggests that a different decomposition route is prevailing in both cases whereas BeFe promotes mainly the generation of OH radicals. Table 3 shows the effect of IPA removal of varying the H<sub>2</sub>O<sub>2</sub> concentration on oxidation using the three catalysts for 1 h of the reaction. The oxidation rate increased as the amounts of H<sub>2</sub>O<sub>2</sub> increased up to 20 ppm, indicating that the amount of •OH radicals generated by the catalyst was sufficient to degrade 10 ppm of IPA. The removal efficiency of IPA decreased with increasing concentration from (100 to 200 ppm) despite increasing H<sub>2</sub>O<sub>2</sub> concentration. Because •OH generation is reduced under high IPA concentration due to blocking of catalyst active site by IPA molecules and prevents the H<sub>2</sub>O<sub>2</sub> catalysis. When the H<sub>2</sub>O<sub>2</sub> concentration exceeded 20 ppm, the removal of IPA decreased because of the well-known scavenging effect of •OH radicals [18,23]:



Reaction (3) reduces the probability of attack by •OH radicals on organic molecules, causing the oxidation rate to fall. Although other radicals (e.g., •OH<sub>2</sub>) are also produced, that were generated in reaction (3), their oxidation potential is much lower than that of •OH species impairing the removal of organic compounds [18, 24]. But •OH<sub>2</sub> can have an additional scavenging effect on the •OH (reaction (4)) and thus the production of O<sub>2</sub>. Thus, in subsequent experiments, 20 ppm of H<sub>2</sub>O<sub>2</sub> was used in all the experiments.

#### Effects of the reaction temperature

To analyze this more in deep, the effects of the reaction temperature in the range of 298-323 K on the catalytic oxidation of IPA were investigated. Figure 5 shows the effects of reaction temperature for the catalytic oxidation of IPA with 20 ppm H<sub>2</sub>O<sub>2</sub> and 1 g of the three catalysts. Also,

Figure 2. Results obtained in CWPO of IPA (10 ppm IPA, 1g of catalyst, 20 ppm of H<sub>2</sub>O<sub>2</sub>) by pillared clays.Table 2. % Removal of IPA with catalysts before and after H<sub>2</sub>O<sub>2</sub> addition.

H <sub>2</sub> O <sub>2</sub> Conc.(ppm)	IPA Conc.(ppm)	IPA removal (%)		
		Pillared clay		
		BeFe	BeCu	BeFe/Cu
10	200	10.74	10.11	12.52
	20	30.36	29.78	44.75
	30	17.23	14.13	16.79
100	10	11.14	10.07	17.64
	20	55.01	51.19	70.37
	30	40.36	38.36	52.36
10	10	30.98	28.32	40.52
	20	90.16	83.18	99.02
	30	57.83	50.69	69.72

the TOC removal increases with the reaction temperature. After 3 h, at 323 K the TOC removal was more than 99.3% of all three samples whereas it was constant for a long time at low reaction temperatures of 298-313 K. This was because acetone and acetic acid were produced via the oxidation of IPA and C-C bond cleavage. Therefore, the low

rate of TOC oxidation decomposition is due to the formation of acetone, which contains the same amount of carbon as IPA and acetic acid is stable [24]. The kinetics of TOC decomposition with each of these three catalysts were studied to obtain the corresponding values of the apparent activation energy ( $E_a$ ). For the leaching test, five consecutive IPA oxidation tests were performed with BeFe and BeFe/Cu catalysts. As can be seen in Figure 6, the leaching amount of metal oxides  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  were lower than 0.22 mg/L for  $\text{Fe}^{3+}$  in the case of BeFe and BeFe/Cu and 0.12 mg/L for  $\text{Cu}^{2+}$  in the case of BeFe/Cu after five times catalysts reuse, which can be neglected and this indicates the successful production of a stable catalyst characterized by a strong interaction between the metal oxides and PILC catalyst surfaces, and its suitability for continuous operation. Thus, it cannot explain the differences observed in the activity of both catalysts.

### $\text{H}_2\text{O}_2$ decomposition

The kinetics of  $\text{H}_2\text{O}_2$  decomposition with BeFe and BeFe/Cu catalysts to obtain the corresponding values of the apparent activation energy was studied. An initial  $\text{H}_2\text{O}_2$  concentration of 200 ppm (5.67 mmol/L) with 1g/L of catalysts was used for  $\text{H}_2\text{O}_2$  decomposition in the absence of IPA at different temperatures within the 298-323 K temperature range. Figure 7 shows the results obtained which, the rate of decomposition is significantly higher with the BeFe/Cu catalyst. It was found that the rate of decomposition of  $\text{H}_2\text{O}_2$  increases with the increase in temperature, and significantly higher with the BeFe/Cu catalyst (Figure 7(a)). Additionally, the results reveal that the decomposition of  $\text{H}_2\text{O}_2$  follows pseudo-first-order (PFO) kinetics [33,34]:

$$-\frac{d[\text{H}_2\text{O}_2]}{dt} = k_{app}[\text{H}_2\text{O}_2] \quad (5)$$

$$\ln\left(\frac{[\text{H}_2\text{O}_2]}{[\text{H}_2\text{O}_2]_0}\right) = -k_{app}t \quad (6)$$

where  $k_{app}$  is the apparent first-order rate constant, and  $[\text{H}_2\text{O}_2]$  and  $[\text{H}_2\text{O}_2]_0$  are the concentrations of  $\text{H}_2\text{O}_2$  in the solution at any time  $t$  and time zero, respectively. The experimental values of  $\text{H}_2\text{O}_2$  concentration versus time were fitted and demonstrated to be a good fit to the first-order reaction with the lines shown in Figure 7b to the data by linear regression, resulting in correlation coefficients  $>0.990$ .

The temperature dependence of the reaction rate constants was expressed by the Arrhenius equation:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (7)$$

where  $A$  is the frequency factor ( $\text{s}^{-1}$ ),  $E_a$  is the activation energy (J/mol),  $R$  is the universal gas constant (J/(mol K)), and  $T$  is the reaction temperature (K).

The  $E_a$  is calculated by using the following equation:

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (8)$$

The Arrhenius plot of the apparent kinetic constant values is presented in Figure 8. The different prevailing mechanisms of  $\text{H}_2\text{O}_2$  decomposition mentioned above can be explained by the difference in apparent  $E_a$  values of BeFe and BeFe/Cu. The corresponding values of the  $E_a$  were 46 and 67 kJ/mol for BeFe and BeFe/Cu, respectively. As indicated in the section on the effects of reaction temperature,  $E_a$  for BeFeCu was calculated using the Arrhenius equation, which found 109 kJ/mol. It is noted that the inclusion of Fe in these catalysts in the presence of  $\text{H}_2\text{O}_2$  drastically lowers the  $E_a$  and increases their activity for IPA oxidation. The results of the  $E_a$  values for the  $\text{H}_2\text{O}_2$  decomposition were obtained in literature in the range of 80.2 kJ/mol for  $\text{ZrO}_2$  [25], 48 kJ/mol for  $\text{ZnO}$  [28], and 5.32 kJ/mol for activated bentonite [31].

To test the feasibility of the present work compared to some catalysts commonly used for IPA oxidation reported in the literature, the catalytic activity data of catalysts in the removal of IPA was summarized in Table 4. This study showed that our catalysts exhibit high efficiency, being as efficient as materials such as  $\text{Pt/Al}_6\text{Si}_2\text{O}_{13}$  for BeFe/Cu while significantly outperforming those reported in the literature for BeFe (Table 4).

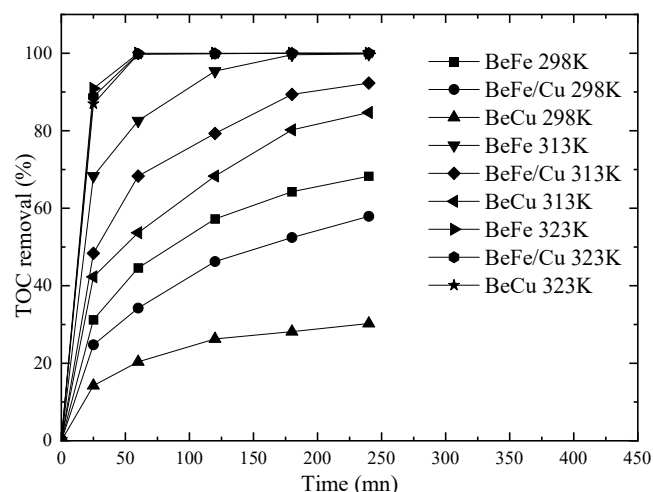


Figure 3. TOC removal by CWPO of IPA (20 ppm  $\text{H}_2\text{O}_2$  and 1 g of BeFe, BeCu, and BeFe/Cu) at different temperatures.

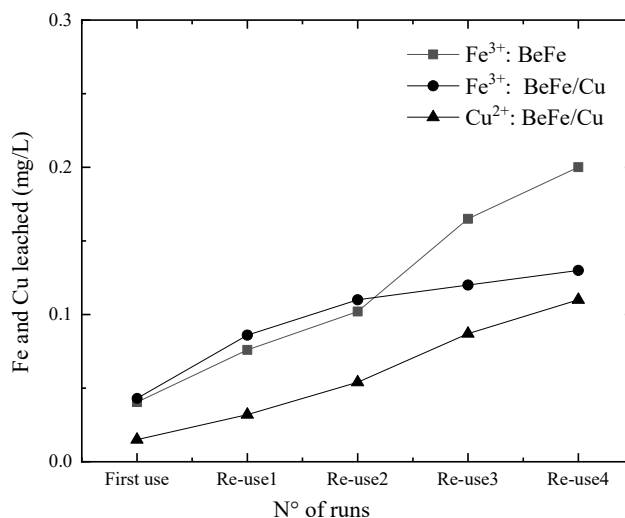


Figure 4. Evolution of Fe leached from BeFe and BeFe/Cu during the oxidation runs.



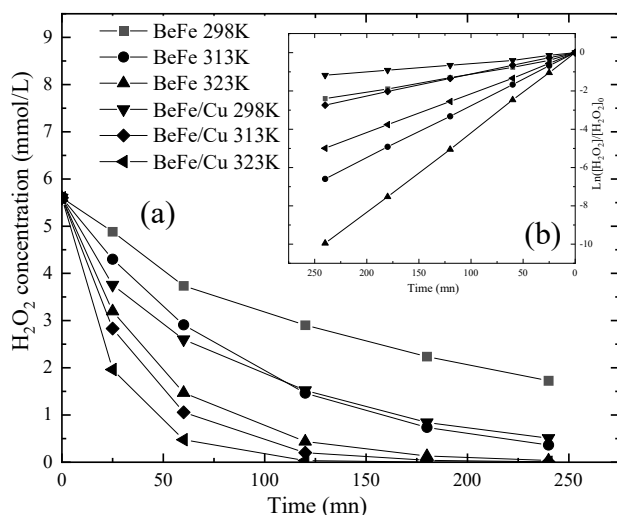


Figure 5. Decomposition kinetics of  $\text{H}_2\text{O}_2$  with BeFe and BeFe/Cu at three different temperatures.

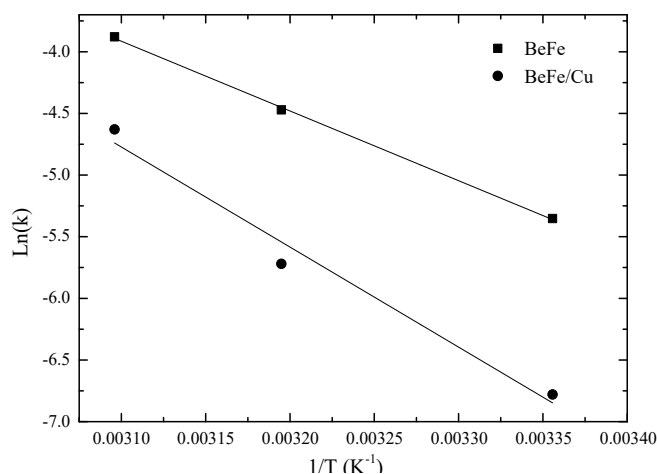


Figure 6. Arrhenius plot of the apparent kinetic constant for  $\text{H}_2\text{O}_2$  decomposition with BeFe and BeFe/Cu.

Table 3. Comparison of the catalytic activity of the present catalysts in the removal of IPA with reports published in other literature.

Catalysts	Reaction temperature (K)	Removal efficiency (%)	Refs.
$\text{ZrO}_2$	473	100	[25]
$\text{Pt/Al}_6\text{Si}_2\text{O}_{13}$	573	90	[26]
Mo/V	423	90	[27]
ZnO	333	97	[28]
NaX-zeolite	393	97	[29]
Activated bentonite	303	62	[31]
BeFe	303	99	In this study
BeCu	303	82	In this study
BeFe/Cu	303	90	In this study

## CONCLUSIONS

Wastewater containing IPA is difficult to decompose using conventional treatment processes. An AOPs has been recognized as a promising process for IPA and other hazardous organic wastewater treatment. PILCs prepared from Fe, Cu, and Fe/Cu with commercial Algerian bentonite were used for the removal of IPA using AOPs with  $\text{H}_2\text{O}_2$  at 298 K. The catalysts based on Be with Fe showed a higher activity for the IPA and TOC removal, while BeFe/Cu decomposed  $\text{H}_2\text{O}_2$  more rapidly, producing more  $\cdot\text{OH}$  radicals than BeFe. This last species is much less active for oxidation in the mild conditions used. The kinetic analysis of the  $\text{H}_2\text{O}_2$  decomposition showed that the reaction correlated well with the PFO reaction model. On the other hand, the  $E_a$  values obtained for the decomposition of  $\text{H}_2\text{O}_2$  using both BeFe and BeFe/Cu catalysts supported the conclusions about the different oxidation mechanisms of these two clays. The high activity of BeFe/Cu for the decomposition of  $\text{H}_2\text{O}_2$  gives it great importance for removing organic pollutants from wastewater.

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NAUČNI RAD

## UKLANJANJE IZOPROPIL-ALKOHOLA IZ OTPADNIH VODA KORIŠĆENJEM BENTONITA MODIFIKOVANOG POMOĆU Fe, Cu I Fe-Cu

*Katalizatori na bazi prečišćenog bentonita (Be) sa  $Fe^{3+}$  (BeFe),  $Cu^{2+}$  (BeCu) i Fe-Cu (BeFe/Cu) sintetizovani su iz alžirskog bentonita i korišćeni za tretman izopropil-alkohola (IPA) katalitičkom mokrom peroksidnom oksidacijom sa  $H_2O_2$  na 298 K. BeFe je pokazao veću aktivnost za uklanjanje IPA od BeFe/Cu, koji je bio aktivniji za razgradnju  $H_2O_2$ . Kinetika reakcije je ispitana sa oba katalizatora korišćenjem modela reakcije pseudo-prvog reda. Vrednosti prividne energije aktivacije razgradnje  $H_2O_2$ , koje su određene iz Arenijusove jednačine, iznosile su 46 kJ/mol za BeFe sa obilnim formiranjem  $OH^\bullet$  radikala i 67 kJ/mol za BeFe/Cu sa produkcijom  $O_2$ , koji ima nizak oksidacioni kapacitet na 298 K.*

*Ključne reči: Oksidacija izopropil-alkohola, pilarne gline, Cu, Fe, Fe-Cu.*

