OXIDATION OF AZO DYE CARMOISINE (E122) IN AQUEOUS SOLUTION BY HETEROGENEOUS CATALYST CuO/Al$_2$O$_3$ SYSTEM

Djedjiga Bousalah[1,2*], Ahmed Réda Yeddou[3], Messaoud Hachemi[1], Abdelmalek Chergui[3,4], Boubekeur Nadjemi[3]

[1]Research Unit: Materials, Processes and Environment (URMPE), M'Hamed Bougara University, Independence Avenue, 35000 – Boumerdes, Algeria
[2]Research Center scientific and technical in physico-chemical analyzes (CRAPC), PB 384, Industrial Zone Bou-Ismail RP 42004, Tipaza, Algeria
[3]Laboratory of Study and Development of Techniques of Water Treatment and Environmental Management - L.E.D.T.E.G.E, Department of Chemistry, E.N.S Kouba, BP 92 Kouba 16308, Algiers, Algeria.
[4]Laboratory Sciences and Techniques of Environment, Department of Environmental Engineering, National Polytechnic School, 10 Hassen Badi Avenue, BP 182, El-Harrach 16200, Algiers, Algeria.

Abstract

Heterogeneous oxidation system for the removal of azo-food dye from aqueous solution was studied in the presence of CuO/Al$_2$O$_3$ catalyst. This catalyst was prepared by impregnation method using a cupric salt solution at pH=5, followed by calcination at 450 °C. The result catalyst was characterized by X-ray Diffraction (XRD) and Scanning Electron Microscopy- Energy Dispersive X-Ray Spectroscopy (SEM-EDX), where the results confirmed a high crystallinity, good chemical stability of the catalyst used in four consecutive cycles and the presence of the elements (Cu, O, Al) composing the catalyst. Several parameters affecting dye degradation such as: solution pH, H$_2$O$_2$ concentration, catalyst dose, and reaction temperature were investigated. CuO/Al$_2$O$_3$ catalyst offers higher activation efficiencies than the homogeneous Cu^{2+} ions, as well as good operational stability and efficiently generate HO$^\bullet$ in neutral aqueous solutions. Complete decolorization (100 %) of Carmoisine (500 mg/L) was achieved in 240 min at neutral pH.

Key words: advanced oxidation processes, copper-impregnated activated alumina, food dye, heterogeneous catalysis, hydrogen peroxide, removal

1. Introduction

The coloured wastewater discharged into the water of rivers makes the water inhibitory for aquatic life and causes visible pollution, the dyes have a tendency to sequester metals, so causing micro-toxicity to fish and other aquatic organisms. It is difficult to remove the dyes from the effluent, because the dyes are stable to light and heat, and are biologically non-degradable. Hence, the conventional methods of water treatment generally used (physicochemical and biological treatments), have proved effective for well-controlled pollution. However, these water treatment technologies are generating other secondary issues, such as the additional use of chemical reagents, the generation of by-products or sludge production whose management is difficult (Nassar and Magdy, 1997).

Recent developments in the chemical water treatment have made it possible to apply novel processing methods such as Advanced Oxidation Processes (AOPs), that we can be divided into four

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* Author to whom all correspondence should be addressed: e-mail: bousalahdj2015@gmail.com; Phone: (+213) 0795 553 650; Fax: (+213) 024 819 424

groups: homogenous chemical oxidation processes (H_2O_2/Fe^{2+} and H_2O_2/O_3), homogenous/heterogeneous photocatalytic processes (H_2O_2/UV, O_3/UV and $Fe^{2+}/H_2O_2/UV$; TiO_2/UV), sonification oxidation processes (ultrasound oxidation) and electrochemical oxidation processes (Zaviska et al., 2009), which are very useful for the degradation of non-biodegradable organic molecules. These technologies are all based on the production of radical entities, in particular hydroxyl radicals ($^\bullet OH$), which are the most powerful oxidizing species that can be used in the domain of water treatment and industrial effluents (Alp et al., 2019; Benhamouda et al., 2017; Bousalah et al., 2019; Chergui et al., 2015; Li et al., 2020; Yeddou et al., 2010; Yeddou et al., 2011; Zaviska et al., 2009). These techniques aim at the complete mineralization of aqueous pollutants to carbon dioxide, water and corresponding mineral acids (Bouafia, 2010; Li et al., 2006).

Carmoisine (Disodium salt of hydroxy-4-(sulpho-4-naphthylazo-1)-3naphthalenesulfonic acid-1), also named Azorubine, Carmoisine, CI Acid Red 14, CI Food Red 3, or E122 in Europe. This synthetic dye is added to food, beverages, medicine, and cosmetics to give a red colour (Karatepe et al., 2017), this dye was also employed in textile industries (Majeed Ahmed et al., 2018). Several processes have been suggested for removal of Carmoisine from wastewater including, manganese dioxide in the absence and presence of ultrasonic irradiation (Ge and Qu, 2003), UVA/ZnO System (Majeed Ahmed et al., 2018), UV-LEDs (Light-emitting diodes) assisted peroxymonosulfate/Fe^{2+} (Ahmadi et al., 2017), Fenton and photo Fenton processes (Sohrabi et al., 2014), sono–photolysis degradation (Chakma and Moholkar, 2016), photocatalytic degradation (UV irradiation and TiO_2 particles) (Daneshvar et al., 2003), by adsorption and catalytic combustion using magnetic $CuFe_2O_4$ powder (Wu et al., 2004), electrochemical degradation (Thiam et al., 2015), by using different types of porous media (Fahim, 2016).

The heterogeneous advanced oxidation processes use heterogeneous catalysts to degrade organic pollutants, among the catalysts used for heterogeneous oxidation, we can quote: metallic oxides (oxides of Mn, Fe, Co, Ni, Cu, Zn, …), mixed metal oxides were also used to improve the catalyst by taking advantage of the best properties of each metal, the supported metal oxides (are generally dispersed on supports with a large specific surface, generally transition alumina (preferably γ-Al_2O_3), SiO_2, TiO_2 (Anatase), ZrO_2 (Tetragonal) and carbons) (Deutschmann et al., 2009). This technique offers many advantages, some of which are not displayed by their homogeneous counterparts, including recyclability, easily separated from the reaction mixture and use in continuous flow processes (Atalay and Ersöz, 2016). CuO/γ-Al_2O_3 catalysts are considered promising candidates for solving the main drawbacks of the use of ion-based systems, as well as for replacing high-cost catalysts containing Pt-based metal. Copper catalysts heterogeneous products

should offer higher activation efficiencies than homogeneous Cu^{2+} ions, as well as good operational stability. Porous γ-Al_2O_3 plays an important role in the dispersion of CuO particles, in the minimization of leaching of copper ions in the liquid phase, as well as in the generation of Cu-OH complexes at the surface (crucial step of the heterogeneous activation of H_2O_2) via a certain amount of base saces (Al_2O_3) (Covinich et al., 2016).

In this work, one of the advanced oxidation systems in heterogeneous phase has been studied. Activated alumina impregnated with copper in the form of CuO "CuO/Al_2O_3" prepared by a simple impregnation method followed by calcination at 450 °C, which makes it possible to form crystalline CuO, which promotes the formation of hydroxyl radicals in the presence of H_2O_2, which therefore has the potential catalysing activity. γ-Al_2O_3 has the advantage of a high specific surface, a low cost and a high resistance, which is therefore often used as a support. CuO/Al_2O_3 has been used in the catalytic degradation of an azo dye "Carmoisine" in the presence of hydrogen peroxide. The effect of various parameters including: the pH, the catalyst dose and its reuse, H_2O_2 concentration and the temperature on the degradation kinetics was evaluated and discussed.

2. Material and methods

2.1. Reagents and analytical procedures

All chemicals and reagents were used as received without any purification. Aluminium oxide (98.0 %, Riedel-de Haên), Copper (II) chloride dihydrate (97 %, Fluka), hydrogen peroxide (30.0 %, Biochem, chemo pharma), Hydrochloric acid (37.0 %, Analar-Normapur VWR), Sulfuric acid (Rectapur BDH Prolabo, 98.0 %) and sodium hydroxide (> 95.0 %-100.0 %, Biochem, chemo pharma).

The Carmoisine (E122) dye are supplied as food's dye from Tunisia. It is regarded as mono-azo-dye which having a formula structure $C_{20}H_{12}N_2Na_2O_7S_2$ and MWt 502.42 g/mol, with a maximum absorption in water at 516 nm.
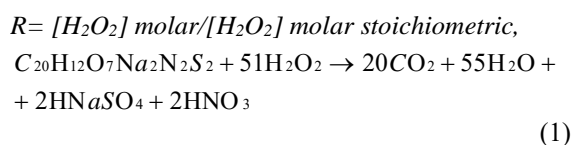
2.2. Preparation and characterization of copper impregnated activated alumina

The copper-impregnated activated alumina was prepared by impregnation method (Pillewan et al., 2011) with some modifications (Bousalah et al., 2019). 10 g of Alumina (Al_2O_3) are mixed with 100 ml of an aqueous solution of copper (II) chloride dihydrate ($CuCl_2.2H_2O$, 1 mole/L) under continuous stirring (16 h, 250 rpm) at pH 5. The suspension is dried at 105°C for 6 hours then calcined at 450 °C for 4 hours and finally, the powder obtained is finely ground (particle size 21-376 μm) and then washed with distilled water and dried at 105 °C to constant weight (Fig. 1). The prepared catalyst was characterized by X-ray diffractometer powder (XRD XPERT PRO, Phillips, $2\Theta = 5$-120°, copper anode (λ

= 1.54056 Å)) and Scanning Electron Microscope (SEM-EDX Quanta TM, Bruker, and EDS Quantax 200 for microanalysis).

2.3. Oxidation experiments

Degradation tests of Carmoisine dye was released in a Pyrex cylindrical reactor (double-walled reactor linked to a thermostatic cell) using 100 ml (500 mg/L) of initial concentration dye, the dye solution was continuously stirred at pH adjustment value (with a calibrated pH meter HANNA Instruments pH 301), then the H_2O_2 solution was injected and the catalyst was dispersed last. This last step was considered as time zero (t_0) (Fig. 1). The temperature was maintained at 293.2 K using thermostat water bath circulating around the reactor. The concentration of dye was monitored by measuring the absorbance at λmax = 516 nm, using a UV-Vis spectrophotometer (T60 V/Vis, PG. Instruments). In this study, the ratio R is defined as the ratio of the molar concentration of H_2O_2 used with respect to the molar concentration defined by the stoichiometry.

$R= [H_2O_2] molar/[H_2O_2] molar stoichiometric,$
$$C_{20}H_{12}O_7Na_2N_2S_2 + 51H_2O_2 \rightarrow 20CO_2 + 55H_2O +$$
$$+ 2HNaSO_4 + 2HNO_3$$

(1)

The oxidation of one mole of $C_{20}H_{12}O_7Na_2N_2S_2$ needs 51 moles of H_2O_2. The decolorization efficiency E was determined according to (Eq. 2).

$$E = ((C_0 - C_t) / C_0) \times 100 \qquad (2)$$

where: C_0 and C_t are the concentrations of dye at reaction time 0 and t, respectively.

The effect of different parameters on the efficiency of degradation of the dye was investigated i.e : pH in the range of 3 to 10, the concentration of hydrogen peroxide in the range of 0.05 to 1.014 mol/L,

the dose of catalyst of 0 to 30 g/L and the temperature of 20 to 35 °C.

3. Results and discussion

3.1. Catalyst characterization

The successful synthesis of CuO/Al₂O₃ and their crystallinity were evident from the XRD pattern displayed in Fig. 2. The peaks observed at 2Θ = 32.5°, 35.4°, 38.9°, 48.8°, 61.5°, 66.6°, 68.1° and 72,3° were in good agreement with the JCPDS" Joint Committee on Powder Diffraction Standards ", card No. 00-089-2529 of CuO. All the peaks were well indexed to the monoclinic phase of CuO. however, the peaks observed at 2Θ =25.6°, 35.1°, 43.4°, 52.62°, 57.58°, 66.6°, 68.29° and 77.1° were in good agreement with the JCPDS card No.01-071-1124 of Aluminum Oxide (Al₂O₃). The sharp intensity of the XRD peaks demonstrated the good crystallinity of the product. The XRD pattern of the catalyst after the fourth use confirms its good stability.

The surface morphology of the catalysts was investigated using SEM. The morphology of the catalyst and that of the raw alumina are shown in the SEM micrographs (Figs. 3-4). The SEM image of the raw alumina (Fig. 3) shows a smooth shape varying between the cylindrical and round shape. However, after impregnation (Fig. 4), the appearance of a smaller sized granular form with a heterogeneous distribution on the surface of the alumina particles was observed, this could be due to the presence of CuO.

To assess the overall chemical composition of the catalyst (Fig. 5), the use of the scanning electron microscopy combined with X-ray microanalysis (SEM-EDX) was carried out. The results revealed that the catalyst is composed essentially of alumina, oxygen and copper (dominant peaks). Fig. 5B illustrates the presence of X-ray emission peaks of Cu, O with an atomic concentration of 13.29 % and 38.2 %, respectively. This is in good agreement with the chemical composition of CuO formed.
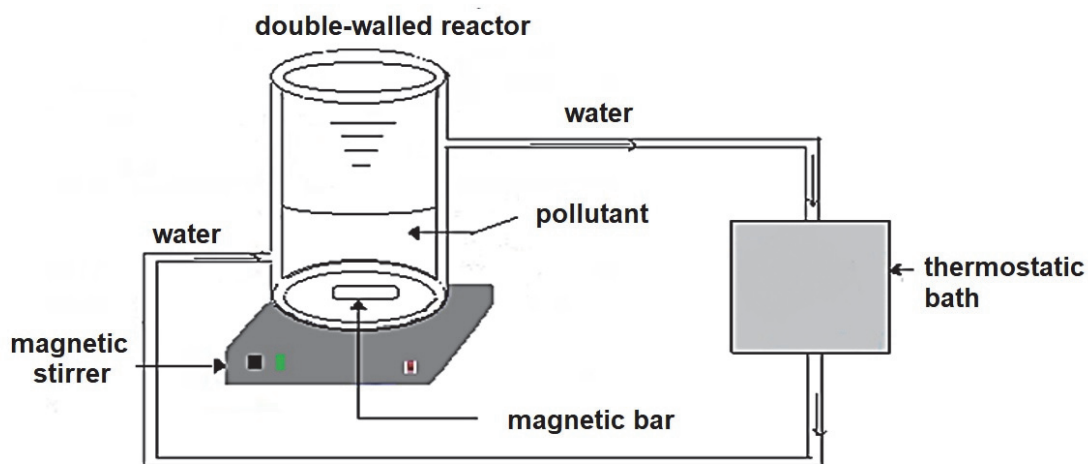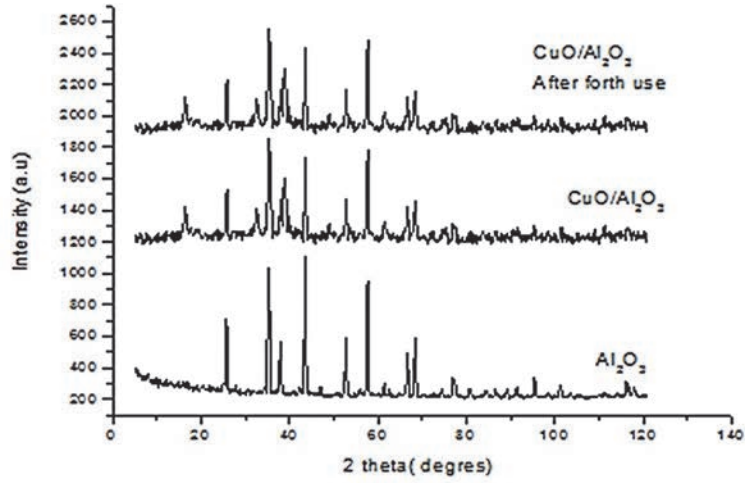

Fig. 1. Schematic of the experimental setup

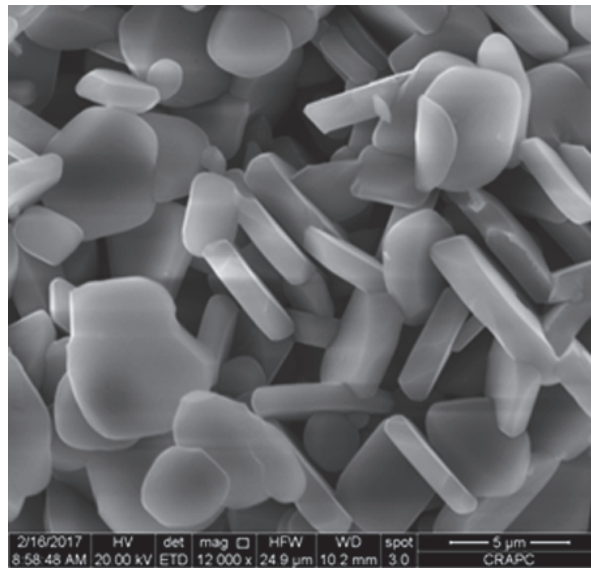**Fig. 2.** XRD patterns of raw alumina; fresh catalyst; catalyst after fourth use
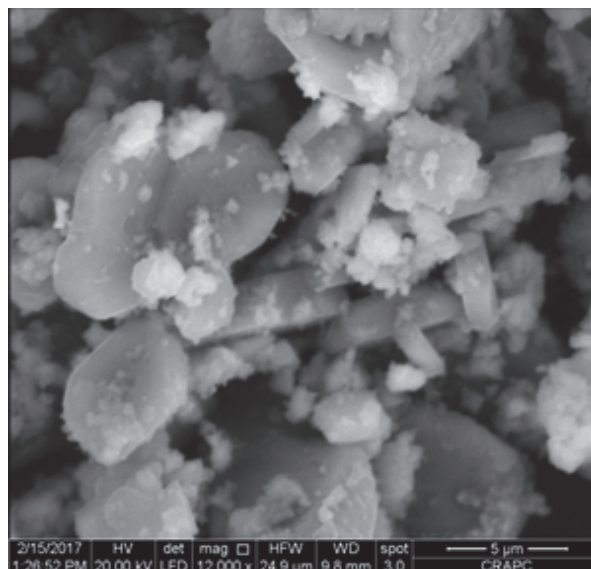

Fig. 3. SEM image of the raw alumina to 5 μm (MEB)

Fig. 4. SEM image of the copper-impregnated activated alumina to 5 μm (MEB)

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3.2. Catalytic degradation: Effect of various experimental parameters

Initial pH

It is known that pH plays an important role in oxidation process. To investigate the influence on the degradation of Carmoisine in heterogeneous reaction, the dye solution was adjust to the desired pH from 3 to 10 by adding sodium hydroxide or hydrochloric acid. Fig. 6 showed that the variations of decolorization rate of dye were 100 % for the entire pH range studied after 5.5 Hours, which confirms that CuO-Al₂O₃/H₂O₂ system can work over a broader pH range. Copper-based catalysts efficiently generate $^\bullet$OH in neutral or near-neutral aqueous solutions. The pH = 3 shows the best rate of dye removal after three hours, this may be due to the substantial production of hydroxyl radicals in the solution at this pH (Karatas et al., 2012; Khataee et al., 2011; Khataee and Pakdehi, 2014). The pHzc of our copper-impregnated activated alumina is 6.8.

This makes its charge positive for a lower pH and negative for a higher pH. The Carmoisine dye molecule is anionic (its mobile ion is Na⁺ in basic medium and H⁺ in acidic medium). For pH below 6.8, there is an attraction between the catalyst and dye thus promoting the catalytic action.

The degradation of dye is less efficient at higher pH (pH = 10) because of the instability of H_2O_2 in an alkaline solution and can be quickly decomposed into oxygen (O_2) and water (H_2O) (Eq. 3) (Wang et al., 2012; Zhou et al., 2014).

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad (3)$$
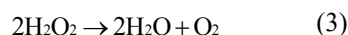
Hydrogen peroxide concentration

The concentration of oxidizing agent is an important parameter. Hence, the effect of initial concentration of H_2O_2 was studied for R = 1, 5, 10, 15 and 20 (respectively for 0.05, 0.253, 0.515, 0.761, 1.014 M) in the following conditions: 500 mg/L of dye, 10 g/L of catalyst, pH = 6.5 and T= 20 °C.
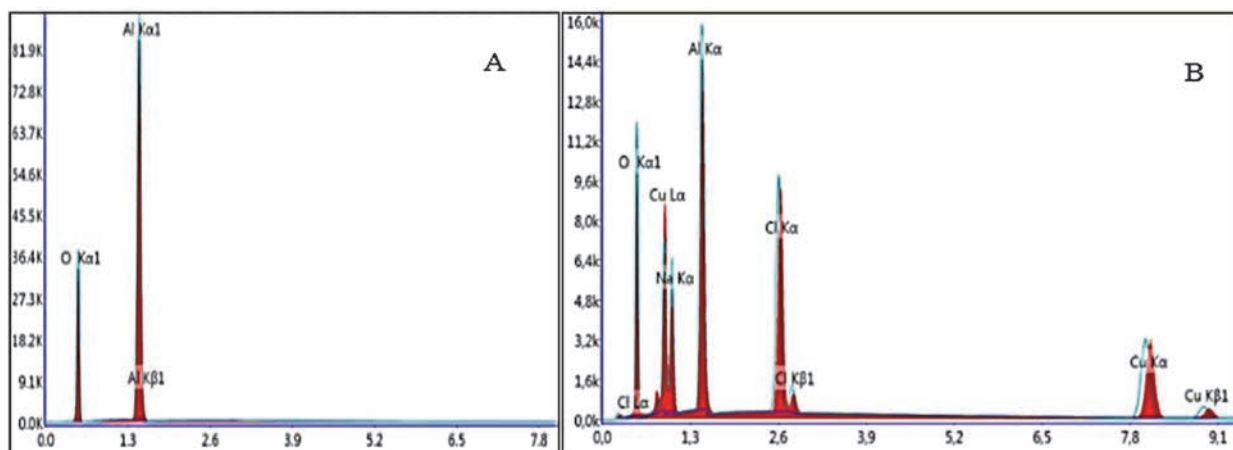

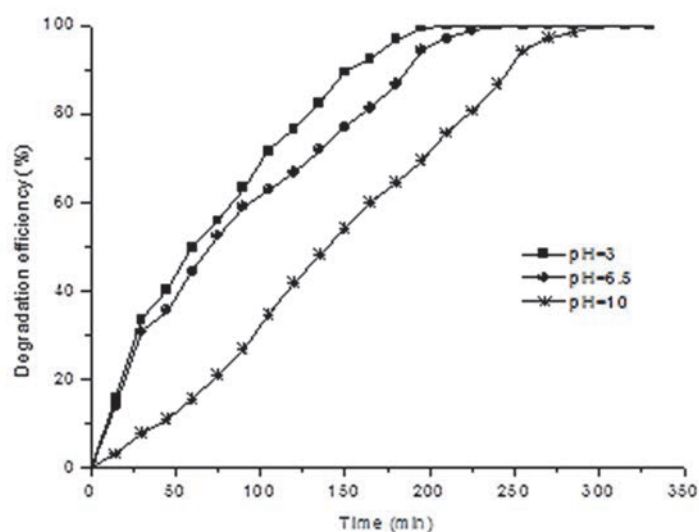**Fig. 5.** EDX spectrum of raw alumina (A) and Copper impregnated activated alumina (B)

Fig. 6. Effect of pH on the decolorization of dye (Carmoisine) by H_2O_2
(Reaction conditions: 500 mg/L of dye, R= 10, 10 g/L of copper-impregnated activated alumina, T=20 °C)

The ratio of hydrogen peroxide R ranges from 1 to 20 (respectively for 0.05, 0.253, 0.515, 0.761, 1.014 mol/L of initial H_2O_2 concentration (Reaction conditions: 500 mg/L of dye, pH= 6.5, 10 g/L of catalyst and T=20 °C).

The results obtained in Fig. 7 show that the effect of increasing in H_2O_2 concentration from R = 1 to R = 10 was positive for the dye degradtion which can be explained by the formation of more radicals.
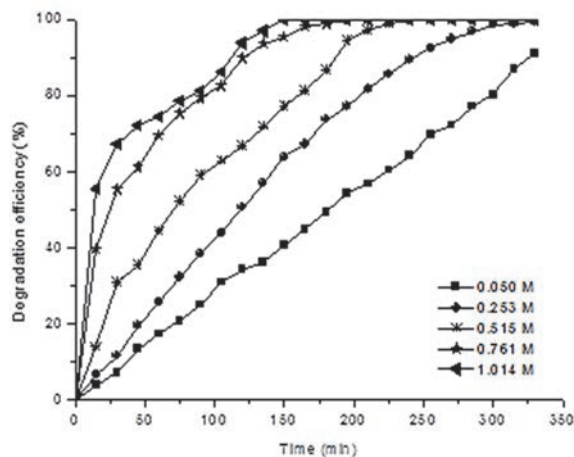

Fig. 7. Effect of concentration of H_2O_2 on the oxidation of dye

The same effect of hydrogen peroxide has been observed for other organic compounds and other catalysts, notably those studied by Idrissi et al. (2014) and Sun et al. (2007). However, with a continuous increase in H_2O_2 concentration R=15 and R=20, we noticed a reduction in the rate of degradation of the dye, (94 and 97 % after 135 minutes). An excess of oxidant can promote its reaction with hydroxyl radicals Eqs. (4-5) (Khataee and Pakdehi, 2014; Li et al., 2006; Martínez et al., 2005; Murugananthan et al., 2008; Salem et al., 2014; Tekbaş et al., 2008).

$$H_2O_2 + {}^\bullet OH \rightarrow H_2O + HO_2{}^\bullet \qquad (4)$$

$$HO_2{}^\bullet + {}^\bullet OH \rightarrow H_2O + O_2 \qquad (5)$$
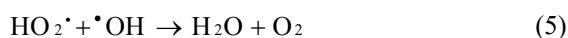
At a small H_2O_2 concentration (R=1), a few hydroxyl radicals are generated and the removal rate is limited. It is important to control the $[H_2O_2]_0$; the dye degradation requires a sufficient amount of hydrogen peroxide, but a high concentration will be unfavorable to degradation of the dye and increases the cost of the wastewater treatment (Sun et al., 2007).

Catalyst dose and reusability

To elucidate the role of initial concentration of catalyst dose on the degradation of dye by heterogeneous Fenton-like oxidation, a series of experiments catalytic oxidation were conducted with different dose of catalyst from 0 g/L to 30 g/L using the following experimental conditions: 500 mg/L of dye, pH=6.5, R= 10 and T = 20 °C). The results (Fig. 8) indicated that the degradation of dye is remarkably dependent on the catalyst dose at fixed the concentration of hydrogen peroxide and dye and temperature.
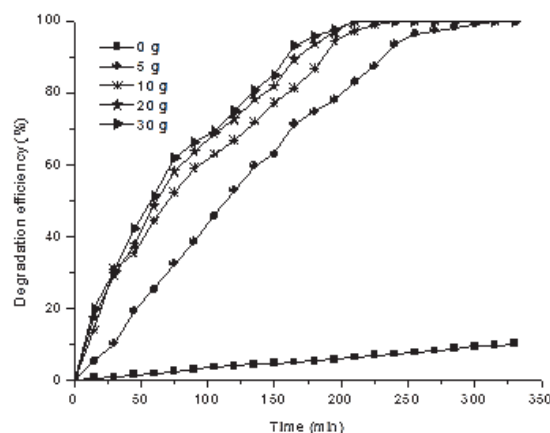

Fig. 8. Effect of catalyst dose on dye oxidation (Reaction conditions: 500 mg/L of dye, pH= 6.5, hydrogen peroxide ratio R=10 and T = 20 °C)

The degradation of the dye was very slow in the absence of the catalyst. A significant improvement in the dye oxidation was observed in the presence of H_2O_2 and the catalyst because its surface promotes the rapid formation of OH radicals (Benhamouda et al., 2017; Covinich et al., 2016; Han et al., 2016; Kasiri et al., 2008; Khorramfar et al., 2011; Pan et al., 2015; Ramirez et al., 2007; Subbulekshmi and Subramanian, 2017; Sun et al., 2007; Sun et al., 2018). It has been recorded rates of degradation of 83, 97, 100 and 100 %, respectively, for the initial catalyst doses of 5, 10, 20 and 30 g/L after 210 min.

It is clear that an increase in the catalyst dose increases the active sites, i.e. the number of oxidized dye molecules. An increase in the catalyst dose improved the efficiency in the dye degradation but, above 10 g/L, the effect is not significant. The stability of CuO/A_2O_3 was studied by the re-use of the same sample for four successive times.

Before each reuse, the catalyst is washed with deionized water and dried at 105 °C to constant weight. The results (Fig. 9) show that the rate of elimination of the dye decreases slightly between the first and the fourth use (at 270 min, a degradation rate of 100 % was recorded for the same catalyst sample used in four times under the same operating conditions). These values show a stability of catalyst activity. The same RDX patterns (Fig. 1) for fresh catalyst and the fresh catalyst used four times confirm this stability. we also found that less than about 4.0–5.0 mg/L of copper concentration in the solution of copper concentration in the solution after complete elimination of the dye for all the pHs studied with a catalyst dose of 10 g/L, dye concentration of 500 mg/L, $[H_2O_2]0 = 0$, 515 Mol/L (R = 10) and T = 20 °C.
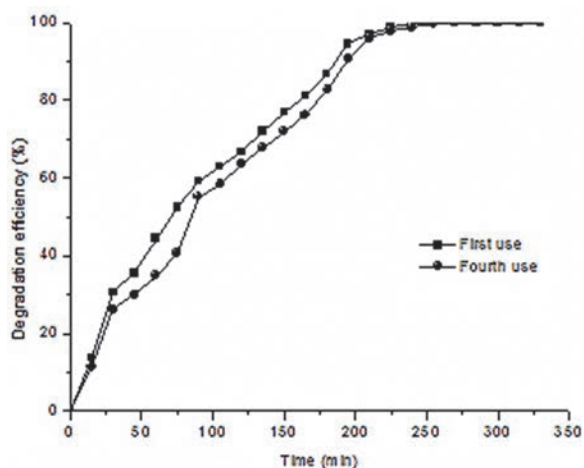
Fig. 9. Reusability test of catalyst (Reaction conditions: 500 mg/L of dye, pH= 6.5, hydrogen peroxide ratio R=10, 10 g /L of catalyst and T = 20 °C)

Temperature

The effect of the temperature in the oxidation of Carmoisine by the hydrogen peroxide catalysed by copper-impregnated activated alumina is illustrated in the Fig.10. The elevation of temperature from 20 °C to 35 °C improves the catalytic performance from 72 to 100 % of the decolorization after 135 min. The same effect of temperature was observed with other dyes and other catalysts (Ayodele et al., 2012; Benjelloun et al., 2012; Salem et al., 2014; Zhan et al., 2011).
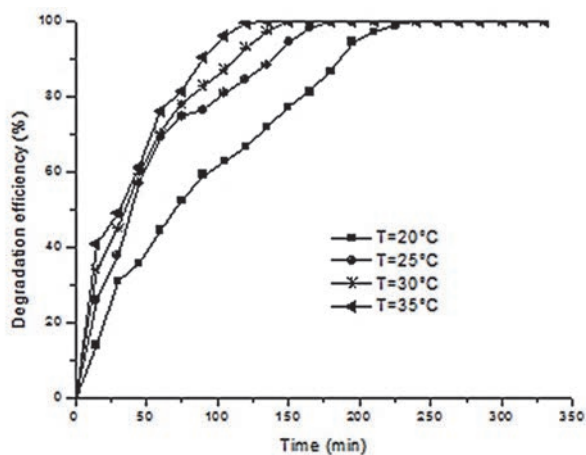

Fig. 10. Effect of temperature (Reaction conditions: 500 mg/L of dye, pH= 6.5, 10 g/L of copper-impregnated activated alumina, hydrogen peroxide ratio = 10)

Kinetics order of removal of Carmoisine during oxidation by hydrogen peroxide

The rate constants for the elimination of carmoisine by hydrogen peroxide catalyzed by activated alumina impregnated with copper for the various temperatures studied were calculated and the suitable model is the pseudo first order.The following relation can express the rate of dye removal (Eq. 6):

$$- dc / dt = Kapp\, C \tag{6}$$

where: C, t and *Kapp* are respectively Carmoisine concentration, time and apparent rate constant. The linear plots of ln C_0/C, where C_0 is the initial concentration of Carmoisine, versus time are plotted and Kapp was determined from the slopes (Fig. 11). The result shows that the dye removal by oxidation with hydrogen peroxide catalyzed by copper-impregnated activated alumina follows a pseudo – first order.
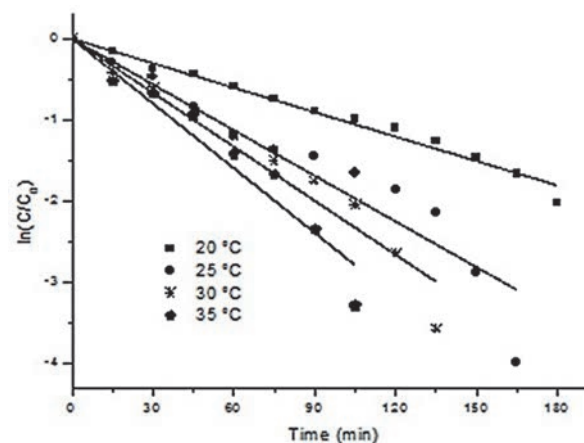

Fig. 11. ln (C/C_0) versus time (t). (Reaction conditions: 500 mg/L of dye, pH= 6.5, 10 g/L of copper-impregnated activated alumina, hydrogen peroxide ratio, R = 10

The Apparent rate constants Kapp and coefficient of determination R^2 at different temperature are presented in Table 3.

Table 3. Apparent rate constants Kapp and coefficient of determination R2 of dye removal by hydrogen peroxide at different temperature

T(°K)	Pseudo-first ordre	
	k(min⁻¹)	R^2
293	0.01005	0.99457
298	0.01879	0.96617
303	0.02221	0.98109
308	0.02662	0.97571

The apparent activation energy of the dye removal by hydrogen peroxide in presence of copper-impregnated activated alumina is calculated from the linear form of the Arrhenius equation (Eq. 7).

$$\ln Kapp = \ln K_0 - E_a / RT \tag{7}$$

where: K_0 is the pre-exponential factor and Ea the apparent activation energy (kJ/mol). After plotting ln Kapp as a function of 1/T (Fig. 12), the value of the apparent activation energy was determined from the slope of regression line. The apparent activation energy of catalytic decomposition of dye is 46.55 kJ/mol. The value of the activation energy found can confirm that the oxidation mechanism of azorubine is radical (Yeddou et al., 2010).
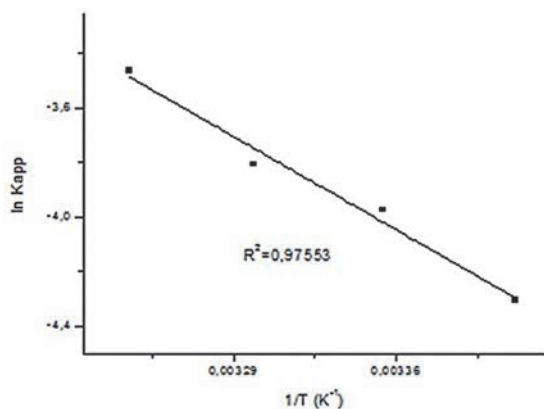
Fig. 12. Plot of ln K versus 1/T in the temperature range of 20-35 °C

4. Conclusions

The results obtained from our study showed that the catalyst prepared by the impregnation technique (copper-impregnated activated alumina) has a beneficial effect in the catalytic oxidation of Carmoisine dye by the hydrogen peroxide.

The tests carried out show that the degradation of the dye by H_2O_2 in the presence of copper-impregnated activated alumina gives good performances over the entire pH range (3-10).

The kinetic study shows that removing dye by oxidation with hydrogen peroxide catalysed by activated alumina impregnated with copper follows the pseudo-first order. The reuse of catalyst for four successive cycles shows good catalytic stability.

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