1   **Cyanide removal from aqueous solution by oxidation with hydrogen peroxide in the presence**

2   **of activated alumina-supported copper catalyst**

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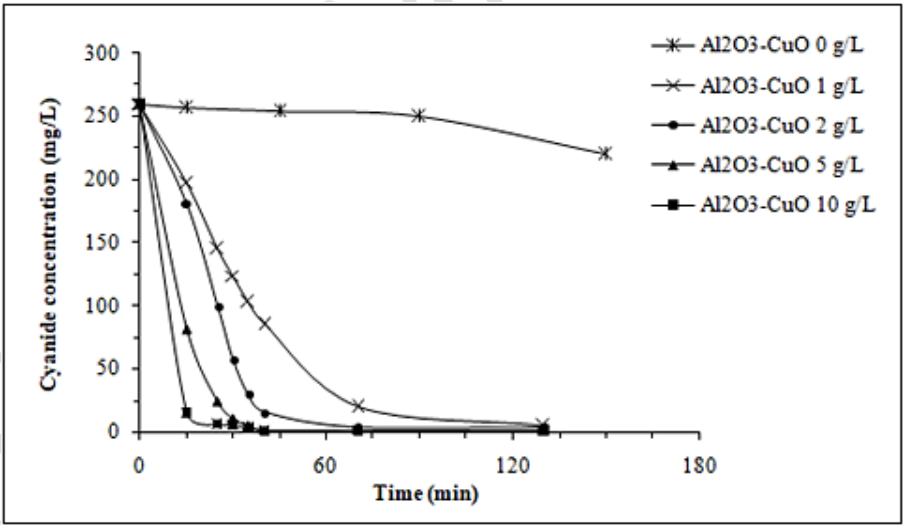19   Ismail, RP 42004 Tipaza, Algeria.

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Graphical Abstract

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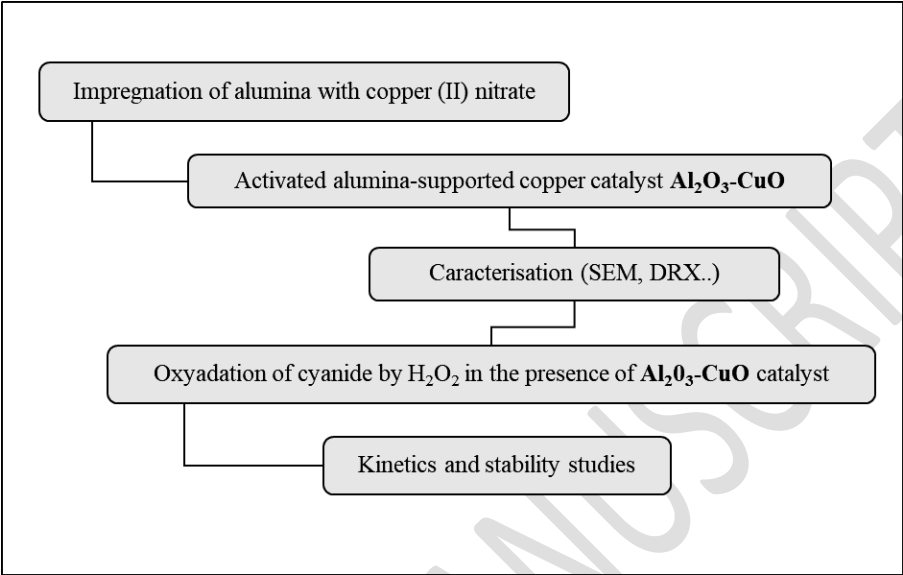
ABSTRACT

Cyanide compounds are widely used in some electroplating, chemical, and metallurgical industries. They are often found in their liquid discharges. This work highlights the performance of an activated alumina-supported copper catalyst in the removal of cyanide by oxidation with hydrogen peroxide in aqueous solution. The influence of catalyst dose, initial molar ratio of hydrogen peroxide/cyanides, temperature, and catalyst reuse was studied. The activated alumina-supported copper significantly enhanced the reaction rate showing a good catalytic activity. The efficiency of cyanide elimination was increased after 30 minutes of oxidation from 48% to 98% by increasing the catalyst dose from 1 to 10 g/L. Rising the temperature from 30°C to 40°C promoted cyanide removal. The catalyst can be recycled four times and show good stability. The kinetics of cyanide oxidation was revealed to be pseudo-first-order regarding cyanides. The rate constants as well as the activation energy were determined.

Keywords: Cyanide; Oxidation; hydrogen peroxide; Catalysis; Activated alumina-supported copper.

1. Introduction

Today, the industry is experiencing an increasing use of chemicals. Some products, although very useful in production or transformation processes, are considered very dangerous and end up in the discharges of the industries that use them. Cyanides are among these compounds. They are found in the liquid effluents of a large number of industries, namely chemical, metallurgical, and even food (Somboonchai & Nopharatana 2008; Kuyucak & Akcil 2013; Anupong *et al,* 2022; Costa *et al,* 2022). Cyanides can be in the form of stable metal complexes (Strong Acid Dissociable SADs), nonstable metal complexes (Weak Acid Dissociable WADs), or free cyanides (Akcil 2010). The latter two forms are the most dangerous because they have the ability to release very toxic cyanide ions (Kuyucak & Akcil 2013; Uppal *et al,* 2016). The removal of cyanides from industrial effluent can be done by different processes, like hydrogen peroxide oxidation (Yubo *et al,* 2018; Amaouche *et al,* 2019), Alkaline chlorination oxidation (Kuyucak & Akcil 2013; Kamrani *et al,* 2019), electro-oxidation (Berenguer *et al,* 2017; Dobrosz-Gomez *et al,* 2020; Ken & Sinha 2021), ozone oxidation (Morillo Esparza *et al,* 2019), photo-oxidation (Núñez-Salas *et al,* 2019; Chegini *et al,* 2020) biological oxidation (Singh & Balomajumder 2016), precipitation (Liu *et al,* 2021) and adsorption on activated carbon (Halet *et al,* 2015; Ravuru *et al,* 2019; Eskandari *et al,* 2021; Chergui *et al,* 2022).

The hydrogen peroxide oxidation catalyzed by dissolved copper Cu (II) is currently widely used and is very effective. It allows cyanides to be oxidized to much less toxic cyanates (Knorre & Griffiths 1984; Akcil 2010). This process has the advantage of not producing dangerous by-products. However, copper is not recoverable and is itself a heavy metal that should be removed. To circumvent this, heterogeneous catalysis could be the right alternative. Indeed, much work on the elimination of pollutants by oxidation proposes to use heterogeneous catalysts based on oxides of transition metals (Hussain *et al,* 2020; Magalhães *et al,* 2020). These oxides can be supported on materials such as activated carbon (Ruimei *et al,* 2018), activated alumina (Covinich *et al,* 2016;

Bousalah *et al,* 2021), and even on natural supports (Kitis *et al,* 2005). Following several works to improve cyanide hydrogen peroxide oxidative removal using heterogeneous catalysts (Yeddou *et al,* 2010; Chergui *et al,* 2015; Amaouche *et al,* 2019; Tu *et al,* 2019; Behnami *et al,* 2021) we propose here to prepare a catalyst having both good stability and high efficiency. We thus suggest using activated alumina-supported copper. Activated alumina is renowned for its great surface area and surface characteristics, while copper is chosen for its catalytic performance. The study addresses the influence of different parameters such as catalyst dose, the initial molar ratio of hydrogen peroxide/cyanides, and temperature on catalyst efficacy, and studies catalyst stability.

2. Materials and Methods

2.1. Reagents and Analytical Procedure

The chemicals employed in this study are of analytical reagent grade and are utilized as obtained without additional purification (sourced from Merck, Darmstadt, Germany, and Sigma-Aldrich, St. Louis, USA). Cyanide solutions were produced using potassium cyanide (99%). The pH of the solution was adjusted with NaOH solution (1 N) or HCl solution (1 N).

The cyanide concentration was assessed through two methods: a titrimetric approach utilizing silver nitrate, and a potentiometric method employing a cyanide-specific electrode (Orion 96-06, Boston, USA) (Baird *et al,* 2017). pH measurement was conducted with a pH meter (HI 221, HANNA instruments). Cyanates concentration was determined by quantifying the ammonia resulting from their acid hydrolysis (1.5-2.0) through a potentiometric method (Baird *et al,* 2017) using the ammonia-specific electrode WTW NH 500/2. Copper (Cu^{2+}) in the aqueous solution was analyzed using an atomic absorption spectrophotometer (Perkin Elmer, Model A Analyst 700).

2.2. Preparation and characterization of the activated alumina-supported copper

The catalyst support utilized in this study was neutral activated alumina obtained from Sigma-Aldrich (St. Louis, USA) with a particle size of 149-250 μm, BET surface area of 155 m²/g, and pores volume of 0.4 cm³/g. The activated alumina-supported copper, denoted as Al_2O_3-CuO, was prepared using the pore volume impregnation method (Zhao *et al,* 2004; Yeddou *et al,* 2011;

98   Shelepova *et al*, 2017). This involved impregnating the activated alumina with an aqueous solution

99   of copper (II) nitrate ($Cu(NO_3)_2$, $3H_2O$), followed by drying for 12 hours in ambient air at 50 °C,

100 then at 110 °C for 12 hours, and finally calcination in air at 450 °C for 2 hours. The resulting Al_2O_3-

101 CuO catalyst holds 5 wt.% of copper.

102 The analysis of Al_2O_3-CuO was performed by X-ray diffraction (XRD) (Inel cps 120, iron anti-

103 cathode, k=1.936 A°) allowing angular measurements in the range of $2\theta = 5–125°$. The surface

104 morphology of the activated alumina-supported copper catalysts was determined using scanning

105 electron microscopy (SEM, Philips ESEM XL 30). The mass titration method was used for the

106 determination of the zero-charge point (pHzc).

107 *2.3. Experimental*

108 The experiments were conducted in a double-walled glass batch reactor containing 1 liter of cyanide

109 solution. The solution was mixed with activated alumina-supported copper (Al_2O_3-CuO) using a

110 magnetic stirrer at a speed that allows a homogeneous suspension of the catalyst. At different times,

111 the residual cyanide concentration was measured. The concentration of cyanate was analyzed at the

112 time the experiments were completed. The studied parameters were the Al_2O_3-CuO dose, the initial

113 molar ratio of hydrogen peroxide/cyanide concentration ($[H_2O_2]_0/[CN^-]_0$), and the temperature. The

114 study of catalyst stability was evaluated by measuring its activity when reused.

115 **3. Results and discussion**

116 *3.1. Characterization of activated alumina supported-copper (Al_2O_3-CuO)*

117 Figure 1 illustrates the X-ray diffraction spectra of Al_2O_3-CuO. The presence of crystalline CuO is

118 shown in our catalysts (peaks at $2\Theta = 32.5°, 35.4°, 38.9°, 48.7°, 61.5°, 68.1°$, and $72.3°$). This

119 crystalline structure is still present after four successive oxidation tests with no visible thinning or

120 widening of the peak indicating good stability in time.

121 The scanning electron micrograph (Figure 2) of Al_2O_3-CuO shows the appearance of aggregate

122 particles (probably of CuO) on the surface of the alumina. They are distributed in a homogeneous

123 way. The pH of zero charges (pHzc) for Al_2O_3-CuO is found to be 6.2.

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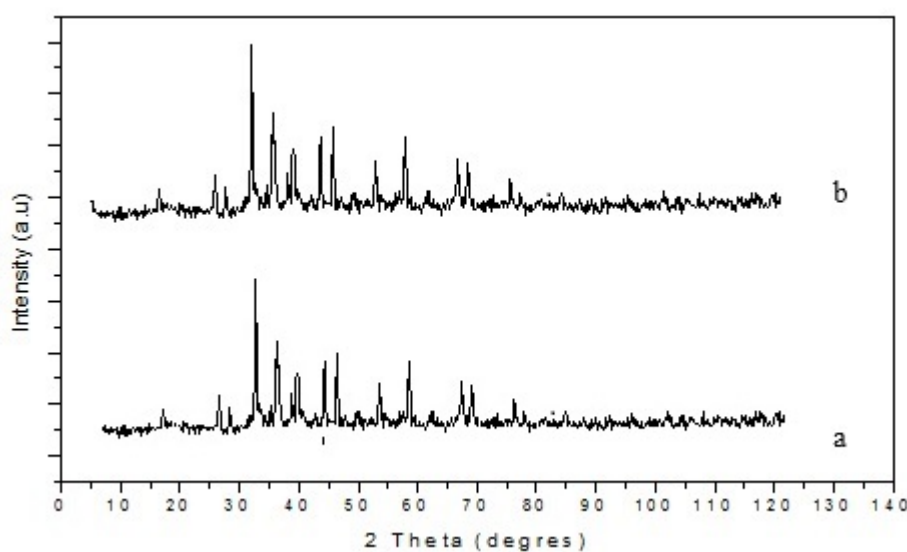
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126 **Figure 1.** XRD spectra of (a) fresh Al_2O_3-CuO, (b) Al_2O_3-CuO (fourth use)
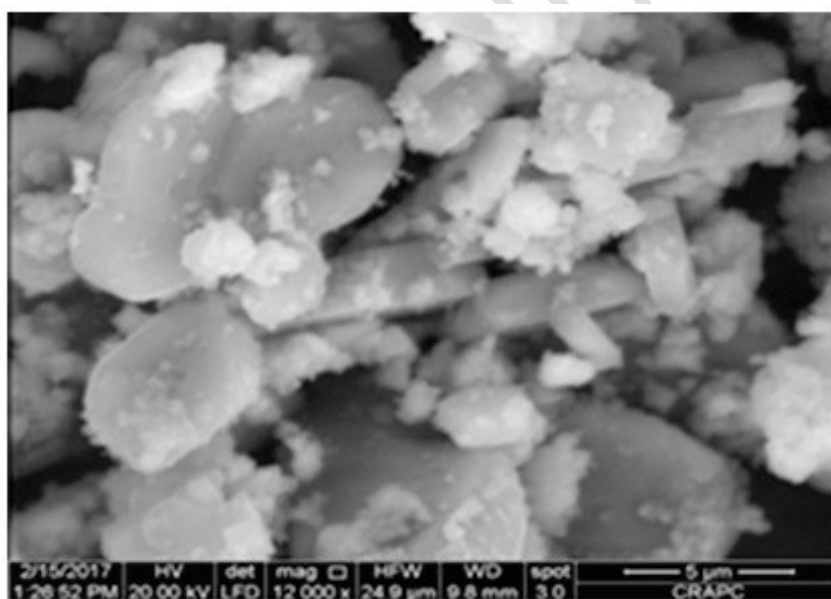
127 **Figure 2.** Scanning electron micrograph of Al_2O_3-CuO

128 *3.2. Effect of activated alumina supported-copper dose (Al_2O_3-CuO)*

129 The influence of the concentration of activated alumina-supported copper on the cyanide oxidation

130 (Figure 3) was studied for doses of 0, 1, 2, 5, and 10 g/L, for an initial cyanide concentration of 10

131 mM (260 mg/L), and for an initial molar ratio $[H_2O_2]_0/[CN^-]_0$ equal to 3. Temperature and pH were

132 maintained at 20°C and 11, respectively. In the case without an Al_2O_3-CuO catalyst (Figure 3),

133 cyanide oxidation is very slow. The presence of Al_2O_3-CuO significantly improves the kinetics and

efficiency of the oxidation, especially at high doses. Indeed, after 30 minutes, cyanide concentrations of 255, 124, 58, 11, and 5 mg/L (elimination percentages of 2, 52, 78, 96, and 98%) are reached for the respective doses of Al$_2$O$_3$-CuO of 0, 1, 2, 5 and,10 g/L. As reported in the literature (Bradu *et al,* 2010; Covinich *et al,* 2016; Bousalah *et al,* 2021 ; Meng *et al,* 2021) copper oxide CuO was able to decompose the hydrogen peroxide and to produce highly reactive hydroxyl radicals that oxidize the pollutant. Therefore, it can be hypothesized that the activated alumina-supported copper catalyst produces hydroxyl radicals according to reaction equation 1 which allows for the oxidation reaction of cyanide ions.

$$Al_2O_3 - CuO + H_2O_2 \rightarrow Al_2O_3 - CuO^+ + OH^\circ + OH^- \quad (1)$$
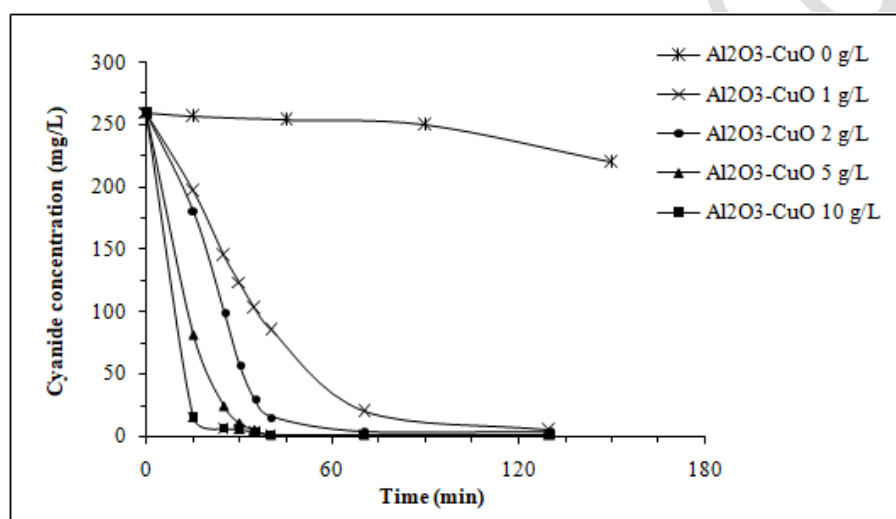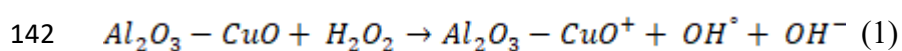
Figure 3. Effect of Al$_2$O$_3$-CuO dose on cyanide removal by peroxide hydrogen oxidation:

[H$_2$O$_2$]$_0$/[CN$^-$]$_0$= 3, CN$^-_0$ = 260 mg/L, T = 20 °C, pH = 11.0

3.3. Initial concentration effect of hydrogen peroxide

The effect of hydrogen peroxide dose was studied for initial molar ratios [H$_2$O$_2$]$_0$/[CN$^-$]$_0$ varying from 1.5 to 20. The initial cyanide concentration was 10 mM (260 mg/L), the catalyst dose was 3 g/L, and the temperature was fixed at 20° C. Figure 4 showed that after 30 minutes, the cyanide concentrations of 30, 20, 15, and 11 mg/L were reached for the molar ratios of 1.5, 5, 10 and 20, respectively. This corresponds to percentages of elimination of 88, 92, 94, and 96 %, respectively. It could be pointed out that for the range of hydrogen peroxide initial concentration studied, the cyanide elimination rate was high, thus showing the beneficial contribution of the catalyst even for

154   low molar ratios, that is to say with molar ratios close to the stoichiometry of oxidation reaction.

155   This is because, at a molar ratio of 1.5, the catalyst can produce enough $OH°$ radicals to oxidize the

156   cyanide ions. The presence of the catalyst significantly improved the rate and yield of cyanide

157   oxidation. Yeddou et al. (2010) studied the removal of cyanides by hydrogen peroxide without,

158   under the same conditions as the present work, they found the oxidation kinetics to be slow and they

159   obtained an 80% of cyanide elimination for an initial molar ratio $[H_2O_2]_0/[CN^-]_0$ of 20 after 8 hours.

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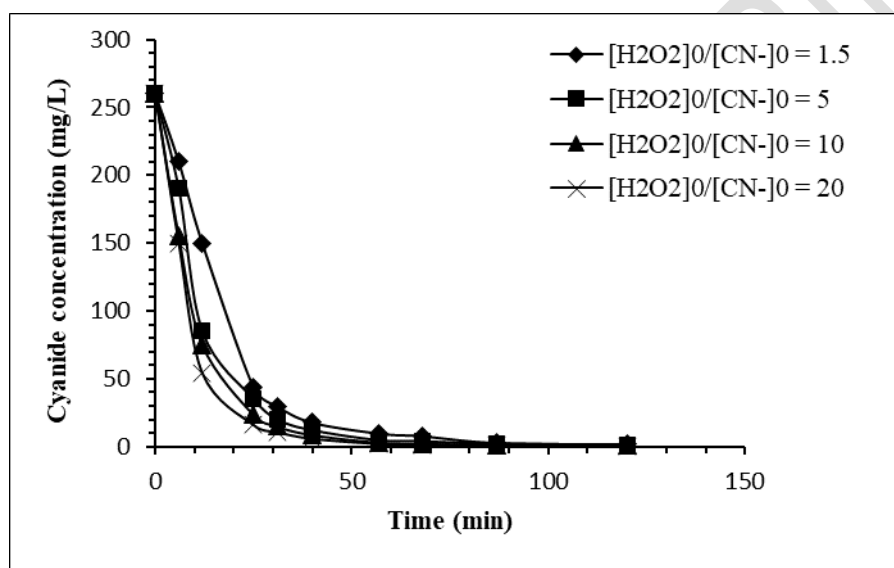
161   **Figure 4.** Effect of initial molar ratio $[H_2O_2]_0/[CN^-]_0$ on cyanide removal by peroxide hydrogen

162   oxidation: Al_2O_3-CuO (3 g/L), CN^-_0 = 260 mg/L, T = 20 °C, pH = 11.0

163   *3.4. Effect of temperature*

164   The influence of temperature on the cyanides oxidation by hydrogen peroxide catalyzed by Al_2O_3-

165   CuO was performed for 20, 30, and 40° C. The initial cyanide concentration ions were 10 mM (260

166   mg / L), the pH was maintained at 11.0, the initial molar ratio $[H_2O_2]_0/[CN^-]_0$ was equal to 3 and the

167   dose ofAl2O3-CuO was 3g/L. An improvement in yield and kinetics is observed (Figure 5) with

168   increasing temperature. Indeed, after fifteen minutes removal rates of 62, 85, and 92% are achieved

169   for temperatures of 20, 30, and 40° C, respectively.
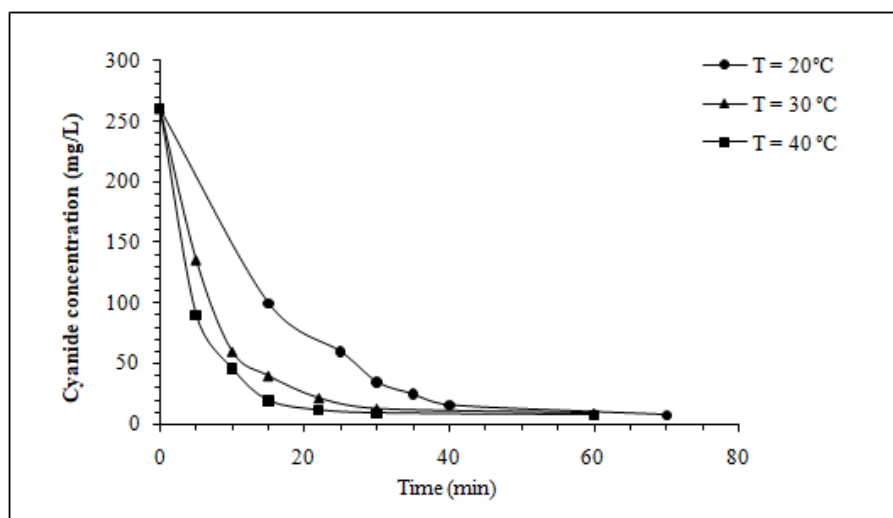
Figure 5. Effect of temperature on cyanide removal by peroxide hydrogen oxidation:

$[H_2O_2]_0/[CN^-]_0 = 3$, Al_2O_3-CuO (1 g/L), $CN^-_0 = 260$ mg/L, pH = 11.0

3.5. Reuse of catalyst

The stability of Al_2O_3-CuO was studied by the reuse of the sample for four successive times. Before each use, the sample was washed with deionized water and dried at 60 °C for a few hours. The results (Figure 6) showed no major loss of activity between the first and the fourth use, indeed, after sixty minutes, the cyanide elimination yield was 98 and 93 %, respectively. The identical XRD patterns (Figure 1) for fresh under-reused reused four successive times catalyst confirmed the catalytic stability.

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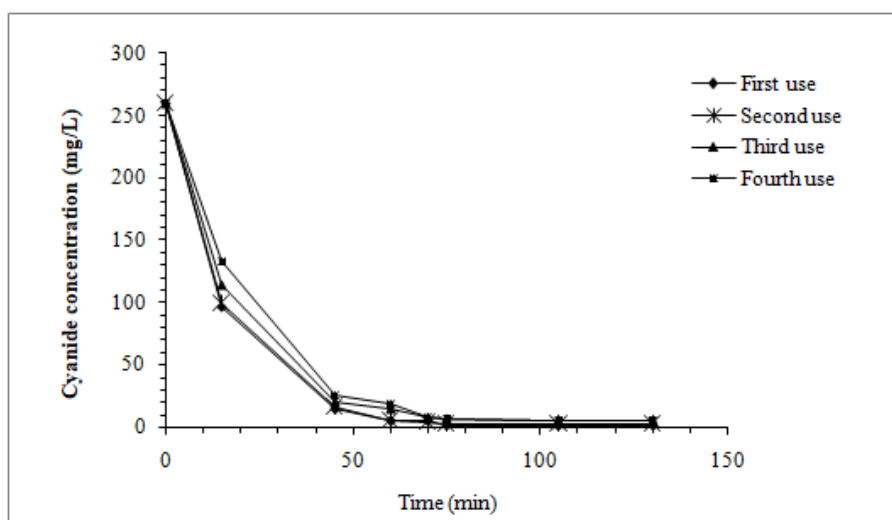
193   **Figure 6.** Cyanide removal by peroxide hydrogen oxidation: reuse of Al_2O_3-CuO (3 g/L),

194    $[H_2O_2]_0/[CN^-]_0 = 3$, $CN^-_0 = 260$ mg/L, T = 20 °C, pH = 11.0.

195   *3.6. Kinetics of cyanide oxidation and determination of the activation energy*

196   Kinetics of cyanide elimination in the presence of Al_2O_3-CuO, for different doses, were studied

197   using the pseudo-first-order (Eq.2) and the pseudo-second-order (Eq. 3) models with regard to

198   cyanide:

199   Pseudo-first order model

200    $-\dfrac{dC}{dt} = k_{app}C$ (2)

201   Pseudo-second order model

202    $-\dfrac{dC}{dt} = k_{app}C^2$ (3)

203   Where C_0, C, and K_{app} are the initial cyanide concentration, cyanide concentration at time t, and

204   apparent rate constant, respectively.

205   Plotting the curves representing $\ln\dfrac{C_0}{C}$ and $(\dfrac{1}{C} - \dfrac{1}{C_0})$ versus time (figures not shown) showed that the

206   cyanide oxidation kinetics data are fitted well by the pseudo-first-order model with highly

207   determination coefficients R^2 values. The values of the apparent kinetic constants as well as the

208   coefficients of determination R^2 for each model are given in Table 1. It is noted that the K_{app} values

209   calculated under different conditions increase significantly with the presence of activated alumina-

210   supported copper, supporting its role as a catalyst.

211 The activation energy of the cyanide elimination by hydrogen peroxide catalyzed with Al_2O_3-CuO

212 is determined from the linearized Arrhenius equation (Eq.4)

213 (4)

214 $$lnK_{app} = lnK_0 - E_a/RT$$

215

216 Where K_o is the pre-exponential factor and E_a is the apparent activation energy (kJ/mol).

217 The apparent activation energy value is determined from the plot of ln Kapp versus 1/T (Figure 7).

218 It is 32.36 kJ/mol for cyanide oxidation in the presence of 3 g/L Al_2O_3-CuO. In a previously

219 reported study, Yeddou et al. (2010) found values of 82.7 and 46.2kJ/mol in the absence of a

220 catalyst and the presence of 10 g/L of activated carbon, respectively. Chergui et al. (2015) reported

221 a value of 55.7 kJ/mol with 10 g/L of alumina (Al_2O_3). Amaouche et al. (2019), with similar

222 working conditions, found a value of 32.2 kJ/mol by using copper oxide CuO (1 g/L) as a catalyst.

223 The activated alumina-supported copper Al_2O_3-CuO, with a dose of 3 g/L, significantly reduced the

224 value of activation energy, demonstrating its role as a catalyst.
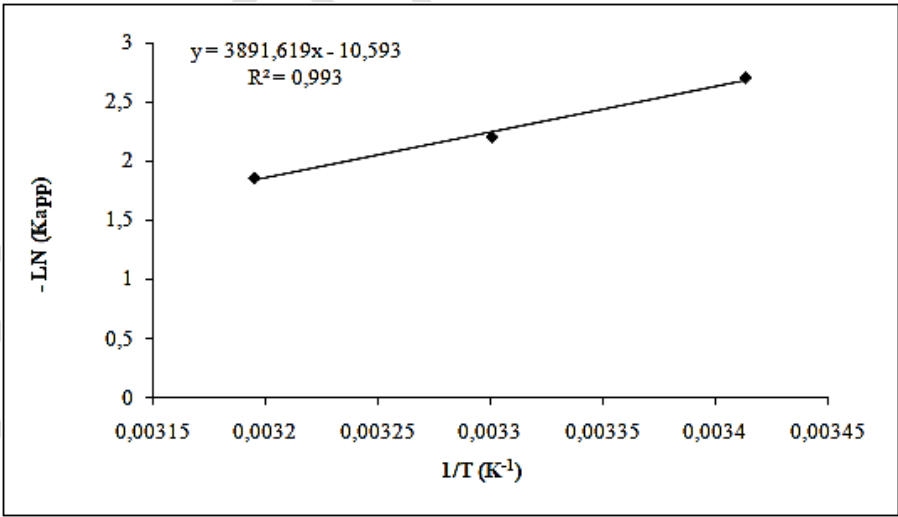
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226 **Figure 7.** Validation of the Arrhenius law for cyanide removal in the presence of Al_2O_3-CuO:

227 $[H_2O_2]_0/[CN^-]_0 = 3$, Al_2O_3-CuO (3 g/L), $CN^-_0 = 260$ mg/L, pH = 11.0.

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Al_2O_3-CuO dose (g/L)	Initial molar ratio $[H_2O_2]_0/[CN^-]_0$	Temperature (°C)	Pseudo-first-order		Pseudo-second-order	
			K_{app} (min^{-1})	R^2	K_{app} (L.mmol$^-$	R^2

				$^{1}.min^{-1}$)		
0	3	20	0.0005	0.960	0.0001	0.614
1	3	20	0.031	0.928	0.004	0.882
2	3	20	0.058	0.934	0.023	0.555
5	3	20	0.117	0.913	0.094	0.614
10	3	20	0.143	0.932	0.571	0.341
3	3	20	0.067	0.989	0.027	0.893
3	3	30	0.109	0.953	0.053	0.912
3	3	40	0.155	0.954	0.087	0.954
3	1.5	20	0.054	0.957	0.080	0.815
3	5	20	0.069	0.962	0.122	0.883
3	10	20	0.078	0.960	0.184	0.772
3	20	20	0.093	0.961	0.275	0.865

229 **Table 1.** Kinetic model parameters for cyanide removal in oxidation by hydrogen peroxide, pH =

230 11.0, $[CN^-]_0$= 10 mM (260 mg/L)

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4. Conclusion

This study consists of the oxidation of cyanides by hydrogen peroxide in the presence of the activated alumina-supported copper Al_2O_3-CuO as the catalyst, prepared by the impregnation method. The characterization of Al_2O_3-CuO shows the presence of copper oxide CuO on the surface of the catalyst. The alumina-supported copper considerably enhanced the reaction rate indicating good catalytic activity. The rate of cyanide removal is improved by increasing the catalyst dose, initial hydrogen peroxide concentration, and temperature. In almost all cases, over 90% of the cyanides are removed within 30 minutes. Good stability was observed after four consecutive reuses of the catalyst. The kinetic study showed that the oxidation of cyanides with hydrogen peroxide catalyzed by Al_2O_3-CuO is of pseudo-first order.

The benefit of the proposed process is that it avoids the use of soluble catalysts, whose disposal after treatment can be problematic. In another aspect, this process allows for rapid cyanide removal kinetics and, at the same time, only consumes hydrogen peroxide as a chemical. Good cyanide removal rates can be achieved even with lower initial molar ratios $[H_2O_2]_0/[CN^-]_0$.

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