

Removal of methylene blue in aqueous solution by oxidation with hydrogen peroxide in presence of copper-impregnated activated alumina

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ABSTRACT/RESUME

Abstract: In this work, methylene blue in aqueous solution is removed by oxidation with hydrogen peroxide in the presence of copper impregnated activated alumina. After preparation and characterization of the catalyst, the catalytic oxidation tests are performed. The effects of pH, H₂O₂ concentration, catalyst dose, and temperature have been investigated. The tests show that adding activated alumina increases significantly the degradation efficiency of methylene blue. The reuse of catalyst for four cycles shows a good catalytic stability. The elevation of the temperature affects positively the kinetics of degradation. The acidified medium increases the decolorization efficiency of dye.

I. Introduction

Many industries discharge into the environment effluents containing dyes which can cause environmental pollution. The presence of dyes in receiving waterways limits considerably the penetration of light through the water surface, and reduces as a result the photosynthetic activity [1, 2]. These organic compounds are resistant to conventional processes in industrial wastewater treatment and very resistant to natural biodegradation [3]. The implementation of an effective treatment for these effluents has been the subject of much research [4]. Currently, the advanced oxidation processes (AOPs) concept initiated by Glaze et al. 1987 appear to be one of the best techniques for the degradation of organic bio-recalcitrant pollutants [5-16]. AOPs

are based on the production of hydroxyl radicals ([•]OH), which are very active oxidizing and non-selective species [10]. These species can be produced by various methods: chemical (Fenton), photochemical, electrochemical, sonochemical, radiolytic and electrical discharge [17]. However, the high operating costs of these processes are the main disadvantage [18,19]. The Heterogeneous advanced oxidation processes use catalysts to carry out the degradation of organic pollutants. Heterogeneous catalysts also offer many advantages, some of which are not displayed by their homogeneous counterparts, including recyclability, ease of separation from the reaction mixture and use in continuous flow processes. It is highly desirable to develop new systems that blend the many

advantages of heterogeneous catalysis with the versatility of homogeneous catalysts [1,7]. In this work, copper impregnated activated alumina is used as catalyst for the oxidation of methylene blue by hydrogen peroxide. Effect of pH, catalyst dose, H_2O_2 concentration and temperature was investigated.

II. Materials and methods

II.1. Analytical Reagents and Procedures

All chemical products supplied by Merck, Fluka, Sigma Aldrich and Biochim; were of analytical grade and used without further purification. Neutral activated alumina obtained from Sigma-Aldrich (St. Louis, USA) is used as a catalytic support in this work (particle size 149-250 μm and BET surface area 155 m^2/g). The pH is adjusted adding NaOH (1N) and HCl (1N) and measured with a calibrated pH meter (HANNA Instruments pH 301). The degradation tests of the methylene blue (MB) were performed during a series of experiments in a closed glass vessel at temperature of 20 °C. In this oxidation tests, 100 ml of methylene blue (100 mg/L) was maintained under continuous stirring (200 rpm), hydrogen peroxide was injected simultaneously with the catalyst, This latter step was considered as t_0 (time zero). After a determined interval of time, the absorbance of the supernate at 664 nm was analysed by UV-visible absorption spectrophotometer (T60 UV/Vis, PG. Instruments).

II.2. Preparation and Characterization of Copper Impregnated Activated Alumina

The copper impregnated activated alumina was prepared by mixing 10 g of Alumina (Al_2O_3) with 100 ml of an aqueous solution of copper (II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$, 1 mole/L) under continuous stirring (16 h, 250 rpm) at pH 5. The suspension is then dried at 105 °C for 6 hours and calcined at 450 °C for 4 hours and finally, the preparation was washed with distilled water and dried at 105 °C till constant weight. The resulting product was characterized by X-ray powder diffraction (XRD XPERT PRO, Phillips, $2\theta = 5-120^\circ$, copper anode ($\lambda = 1.54056 \text{ \AA}$)) and Scanning Electron Microscopy (SEM-EDX Quanta TM, Bruker, and EDS Quantax 200 for microanalysis). The analysis of chemical elements was performed by X-ray fluorescence spectrometer (XRF, ZSX Primus II).

III. Results and discussion

III.1. Catalyst characterization

The crystallinity of the copper impregnated activated alumina has also been demonstrated using the XRD technique, as shown in Figure 1(a). The peaks observed at $2\theta = 32.5^\circ, 35.4^\circ, 38.9^\circ, 48.7^\circ, 61.5^\circ, 68.1^\circ$ and 72.3° compatible with the JCPDS card No. 00-048-1548 are attributed to the monoclinic crystalline phase of CuO. The CuO is present after four consecutive oxidation tests with H_2O_2 .

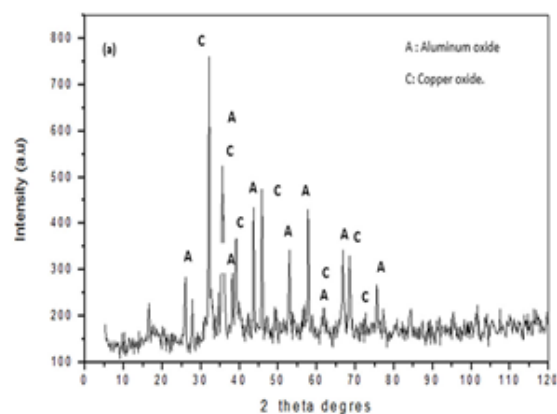


Figure 1 (a). XRD patterns of fresh catalyst

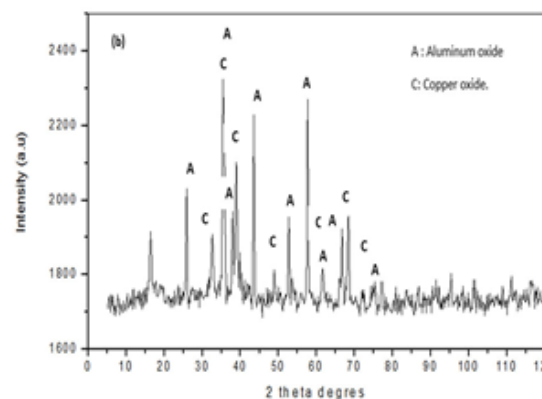


Figure 1 (b). XRD patterns of catalyst (fourth use).

The morphology of the catalyst and of the raw alumina is shown in the SEM micrographs Figure 2 and 3. Figure 3 shows the appearance of particles of homogeneous distribution on the surface of the alumina, this could be due to the presence of CuO.

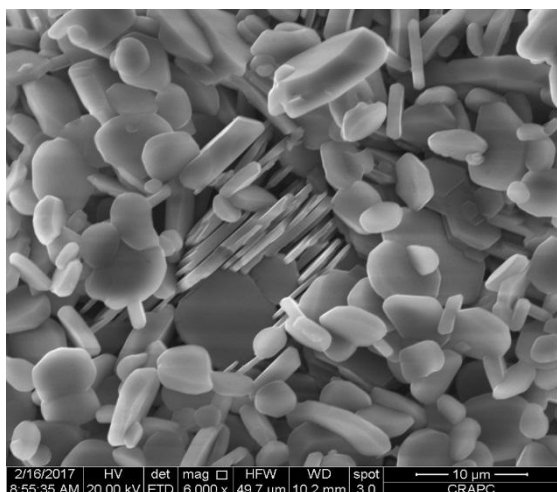


Figure 2. SEM image of the copper impregnated activated alumina.

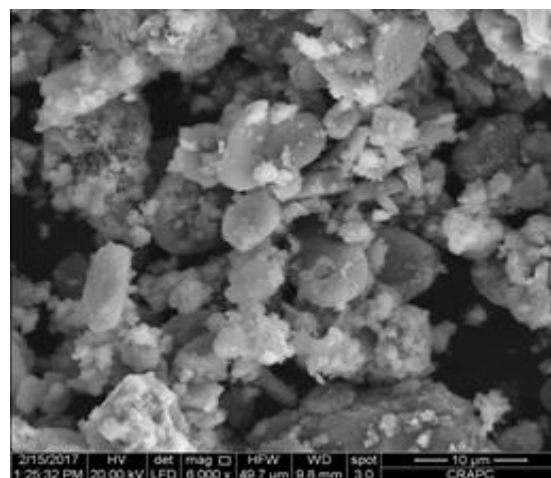


Figure 3. SEM image of the raw alumina.

The XRF analysis of copper impregnated activated alumina is presented in Table 1.

Table 1. XRF analysis of catalyst

Component	O	Al	Cu	Na	Cl
mass %	35,7	30,5	15,5	7,7	10,5

III.2. Catalytic oxidation of MB

III.2.1. The influence of pH

The catalytic activity tests of methylene blue were performed under the conditions indicated in section II.1 for three initial values of pH 3, 6.5 and 10.

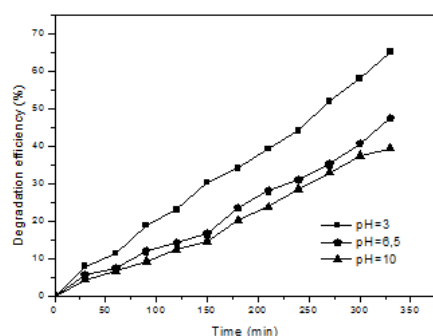


Figure 4. Influence of pH on catalytic oxidation of MB. (Reaction conditions: 100 ml of MB (100 mg/L), 0.16 M of hydrogen peroxide, 10 g/L of catalyst (copper impregnated activated alumina) at T=20 °C).

The decolorization efficiency obtained after 5.5 h are about 65 %, 48 % and 39 %, respectively for pH = 3, 6.5 and 10. It appears that the pH = 3 recorded the better removal of dye, this may be explained by the substantial production of hydroxyl radicals in the solution at this pH [20, 25]. Higher pHs (pH=10) lead to the decomposition of H₂O₂ into oxygen (O₂) and water (H₂O) [25-27] which explains the decrease in the dye removal rate. In this study, the pH selected is 6.5 for all experimental tests, which is in compliance with the Algerian standards of wastewater [28].

III.2.2 The influence of hydrogen peroxide concentration

In this part, we tried to determine the concentration of H₂O₂ to improve the process efficiency, for this reason, H₂O₂ concentration varied from 0.032 to 0.32 M; 100 ml of MB (100 mg/L); pH= 6.5; 10 g/L of catalyst at T=20 °C.

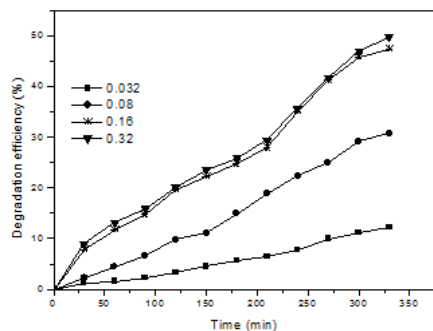
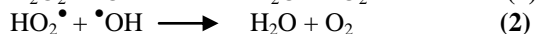
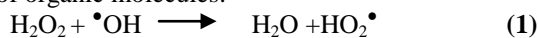


Figure 5. Effect of concentration of H₂O₂ on the oxidation of methylene blue. (Reaction conditions: 100 ml of methylene blue (100 mg/L), pH= 6.5, 10 g/L of catalyst and T = 20 °C).

The decolorization efficiency of MB (Figure 5) increases from 1.6 % to 13 %, respectively for 0.032 to 0.32 M after 30 minutes. This can be explained by production of important quantity of radical hydroxyls, [29, 30]. It was notice that, after 5.5 h, using H₂O₂ concentration of 0.16 and 0.32 M have substantially the same degradation efficiency with a respective yield of 47.5 % and 49.8 %, this can be explained by the two reactions below, which show the consumed hydroxyl radicals (•OH) and the hydroperoxyl (HO₂•) needed for the degradation of organic molecules:



It appears that a high H₂O₂ concentration (0.32 M), H₂O₂ acts as a hydroxyl radical quencher [Equations (1), (2)] consequently lowering the hydroxyl radical [25, 29, 31]. At low H₂O₂ concentration (0.032 M), a few hydroxyl radicals are generated enough and the removal rate is limited and the oxidation rate is logically slow [31, 32].

III.2.3. The influence of catalyst dose

To evaluate the efficiency of the catalyst in the MB degradation, a serie of experiments by varying the catalyst dose have been carried out. For each test the same operating conditions were used: 100 ml of methylene blue (100 mg/L), pH= 6.5, 0.16 M of hydrogen peroxide at T = 20°C). Initial preliminary tests before calcination were carried out in the same conditions as the catalyst and gave very low dye removal rates.

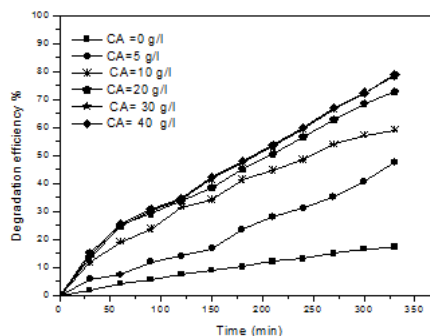


Figure 6. Effect of catalyst dose on MB oxidation. (Reaction conditions: 100 ml of MB (100 mg/L), pH= 6.5, 0,159 M of hydrogen peroxide at T = 20 °C).

The results (Figure 6) show that the MB concentration decreases over the time for all tested samples. MB degradation was very slow in absence of catalyst (a rate of 17 % after 5.5 h), because surface that promotes rapid formation of radicals •OH is absent. A significant improvement in MB oxidation is observed by combining H₂O₂ and catalyst (copper impregnated activated alumina) [33]. It is clear that increasing the catalyst dose increases the active sites, which an increase of oxidized MB molecules. Therefore, the efficiency of the degradation is improved with the increase of the catalyst. However, beyond the dose of 20 g/L of catalyst, the effect of catalyst is not significant.

III.2.4. Stability and recycling of the catalyst

The main advantage of the heterogeneous catalysis is the reusability of the catalyst, the stability of the catalyst is studied by the re-use of the same sample of copper impregnated activated alumina four successive times under the same initial conditions: 100 ml of methylene blue (C₀ = 100 mg/L), pH= 6.5, 0.16 M of hydrogen peroxide at T = 20 °C. Before each re-use, the copper impregnate activated alumina is washed with distilled water and dried at 105 °C till constant weight.

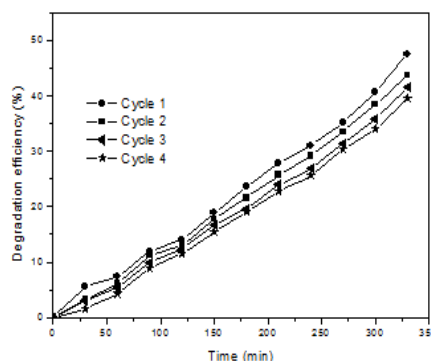


Figure 7(a). Decolorization efficiency of MB.

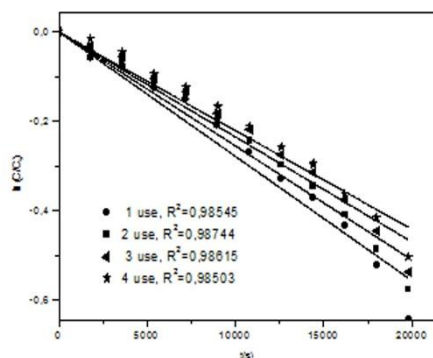


Figure 7(b). $\ln(C/C_0)$ versus time.

According to the results obtained (Figure 7(a)), it was recorded rates of 47.5 %, 43.8 %, 41.5 % and 39.5 % respectively for the first, second, third and fourth use. This results show that the activated alumina has a high chemical stability with no decomposition of the structure during the four repeated tests on the same sample. The RDX patterns [Figure 1] for the two comparative tests (fresh catalyst and catalyst used four times) confirm this stability. The good catalytic performance of composite could be attributed to a synergy between the support functions of the porous alumina and CuO nanoparticles [34].

The kinetic study shows that the methylene blue removal by oxidation with hydrogen peroxide catalyzed by copper impregnated activated alumina follows the pseud-first order (Figure 7(b)). The degradation rate constants decreased slightly from

$2.78 \times 10^{-5} \text{ s}^{-1}$ to $2.2 \times 10^{-5} \text{ s}^{-1}$, respectively for the first and the fourth use.

III.2.5. Temperature effect and determination of activation energy

The temperature effect was investigated for three values : 25, 30 and 35 °C, while the other parameters were fixed, 100 ml of of methylene blue (100 mg/L), pH= 6.5, 10 g/L of catalyst and 0.16 M of hydrogen peroxide.

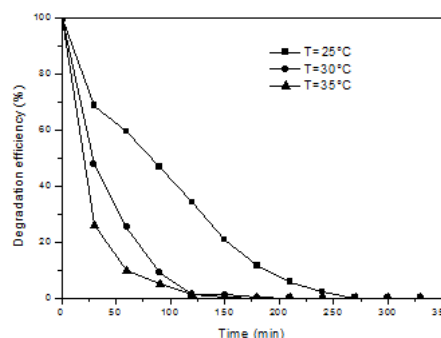


Figure 8. Temperature effect. (Reaction conditions: 100 mg/L of methylene blue, pH= 6.5, 10 g/L of copper impregnated activated alumina, 0.16M of hydrogen peroxide).

Elevating the temperature from 25 °C to 35 °C enhances the catalytic performance from 35 % to 100 % of decolorization after 270 min (Figure 8), [30, 32, 35-39]. The rate constants increased from $1.29 \times 10^{-2} \text{ min}^{-1}$ to $3.72 \times 10^{-2} \text{ min}^{-1}$ for the temperatures from 25 to 35 °C, respectively (table 2).

Table 2. Apparent rate constants K_{app} and coefficients of correlation R^2 of methylene blue removal by hydrogen peroxide at different temperature.

T (°C)	K (min ⁻¹)	R ²
25	0,01295	0,965
30	0,0311	0,982
35	0,0372	0,994

The apparent activation energy of the methylene blue removal by hydrogen peroxide is calculated from the linear form of the Arrhenius equation 3:

$$\ln K_{app} = \ln K_0 - E_a / RT \quad (3)$$

Where K_0 is the pre-exponential factor and E_a the apparent activation energy (kJ/mol), R is the universal gas constant which is 8.314 J/mol.

After plotting $\ln K_{app}$ versus $1/T$ (Figure 9), the value of the apparent activation energy is determined from the slope of regression line. The apparent activation energy for the catalytic oxidation of methylene blue is **72.23 kJ/ mol**.

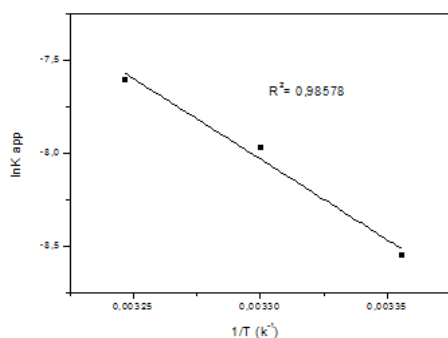


Figure 9. Plot of $\ln K$ versus $1/T$ in the temperature range of 25-35°C

IV. Conclusion

The results from our study showed that the catalyst prepared by impregnation method (copper impregnated activated alumina) has a beneficial effect in catalytic degradation of methylene blue in the presence of hydrogen peroxide. The tests carried out show that the degradation of methylene blue by H_2O_2 in the presence of copper impregnated activated alumina gave good performances on all the range of pH (3-10).

An improvement in the kinetics of degradation of dye was observed in the presence of activated alumina by increasing: the H_2O_2 concentration from 0.032 to 0.32 mol/L, the dose of catalyst up to 20 g/L and the temperature from 25 °C to 35 °C.

The kinetic study shows that the methylene blue removal by oxidation with hydrogen peroxide catalyzed by copper impregnated activated alumina follows the pseud – first order. The most important advantage of heterogeneous catalysis is the reusability of the catalyst. The reuse of catalyst for four cycles shows a good catalytic stability. The proposed process has the advantage of avoiding the use of soluble metals catalyst that can cause a problem after treatment. This heterogeneous process allows to remove methylene blue with fast kinetics and less consumption of chemical reagents (hydrogen peroxide consumption only). This work can be completed by a study including the effect of other parameters such as agitation, the copper content percentage and the presence of other pollutants.

V. References

1. Willmott, N.J.; Guthrie, J.T.; Nels, G. The biotechnology approach to color removal from textile effluent. *Journal of the society of dyers and colourists* 114 (1998) 38-41.
2. Koller, E. *Treatment of industrial pollution*, 3rd Ed, Dunod, Paris, 2013.
3. Pagga, U.; Brown, D. The degradation of dyestuffs part II: behaviour of dyestuffs in aerobic biodegradation tests. *Chemosphere* 15 (1986) 479-49.
4. Minero, C.; Pellizzari, P.; Maurino, V.; Pelizzetti, E.; Vione, D. Enhancement of dye

sonochemical degradation by some inorganic anions present in natural waters. *Applied Catalysis B: Environmental* 77 (2008) 308-316.

5. Mertz, J.; Waters, W. Some oxidation involving the free hydroxyl radical. *Journal of the Chemical Society* 15 (1949) 515-525.
6. Kuo, W.G. Decolorizing dye wastewater with Fenton's reagent. *Water Research* 26 (1992) 881-886.
7. Andreozzi, R.; Caprio, C.; Insola, A.; Marotta, R. Advanced oxidation processes (AOP) for water purification and recovery. *Catalysis today* 53 (1999) 51-59.
8. Mota, A.L.N.; Albuquerque, L.F.; Beltrame, L.T.C.; Chivone-Filho, O.; Machulek, J.R.A.; Nascimento, C.A.O. Advanced oxidation processes and their application in the petroleum industry: a review. *Brazilian Journal of Petroleum and Gas* 2 (2008) 122-142.
9. Ghodbane, H.; Hamdaoui, O. Degradation of Acid Blue 25 in aqueous media using 1700 kHz ultrasonic irradiation: Ultrasound/Fe (II) and ultrasound/ H_2O_2 combinations. *Ultrasonics Sonochemistry* 16 (2009) 593-598.
10. Zaviska, F.; Drogui, P.; Mercier, G.; Blais, J.F. Advanced oxidation processes in water treatment and industrial effluents: Application to the degradation of refractory pollutants. *Journal of Water Science* 22 (2009) 535-564.
11. Mokhbi, Y.; Korichi, M.; Sidrouhou, H. M.; Chaouche, Kh. Treatment heterogeneous photocatalysis; Factors influencing the photocatalytic degradation by TiO_2 . *Energy Procedia* 50 (2014) 559-566.
12. Yeddou, A.; R. Nadjemi, B.; Halet, F.; Ould-Driss, A.; Capart, R. Removal of cyanide in aqueous solution by oxidation with hydrogen peroxide in presence of activated carbon prepared from olive stones. *Minerals Engineering* 23 (2010) 32-39.
13. Yeddou, A. R.; Chergui, S.; Chergui, A.; Halet, F.; Amaouche, H.; Nadjemi, B.; Ould-Driss, A.; Belkouch, J. Removal of cyanide in aqueous solution by oxidation with hydrogen peroxide in presence of copper-impregnated activated carbon. *Minerals Engineering* 24 (2011) 788-793.
14. Chergui, S.; Yeddou, A. R.; Chergui, A.; Halet, F.; Amaouche, H.; Nadjemi, B.; Ould-Driss, A. Removal of cyanide in aqueous solution by oxidation with hydrogen peroxide in presence of activated alumina. *Toxicological & Environmental Chemistry* 97 (2015) 1289-1295.
15. Munter, R. Advanced oxidation processes status and prospects. *Proceedings of the Estonian Academy of Sciences, Chemistry* 50 (2001) 59-80.
16. Liu, P.; Li, C.H.; Zhao, Z.; Lu, G.; Cui, H.; Zhang, W. Induced effects of advanced oxidation processes. *Scientific Reports* 4 (2014) 4018.
17. Milan-Segovia, N.; Wang, Y.; Cannon, F. S.; Voigt, R.C.; Furness, J. C. Comparison of Hydroxyl Radical Generation for Various Advanced Oxidation Combinations as Applied to Foundries. *Ozone Science Engineering* 29 (2007) 461-471.
18. Malato, S.; Blanco, J.; Vidal, A.; Richter, C. Photocatalysis with solar energy at a pilot-plant scale: an overview. *Applied Catalysis B: Environmental* 37 (2002) 1-15.
19. Zaman, S.; Zainelabdin, A.; Amin, G.; Nur, O.; Wilander, M. Efficient catalytic effect of CuO nanostructures on the degradation of organic dyes. *Journal of Physics and Chemistry of Solids* 73 (2012) 1320-1325.
20. Sabhi, S.; Kiwi, J. Degradation of 2, 4-dichlorophenol by immobilized iron catalysts. *Water Research* 35 (2001) 1994-2002.
21. Neamtu, M.; Zaharia, C.; Catrinescu, C.; Yediler, A.; Macoveanu, M.; Ketrup, A. Fe-exchanged zeolite as catalyst for wet peroxide oxidation of reactive

- azodye procion marine H-EXL. Applied Catalysis B: Environmental 48 (2004) 287–294.
22. Tekbas, M.; Yatmaz, H.C.; Bektas, N. Heterogeneous photo-Fenton oxidation of reactive azo dye solutions using iron exchanged zeolite as a catalyst. Micro-porous Mesoporous Mater 115 (2008) 594–602.
 23. Khataee, A.R.; Zarei, M.; Khataee, A.R. Electrochemical treatment of dye solution by oxalate catalyzed photoelectro-Fenton process using a carbon nanotube-PTFE cathode: optimization by central composite design. Clean-Soil. Air. Water 39 (2011) 482–90.
 24. Karatas, M.; Argun, Y.A.; Argun, M.E. Decolorization of anthraquinonic dye, reactive blue 114 from synthetic wastewater by Fenton process: kinetics and thermo-dynamics. Journal of Industrial and Engineering Chemistry 18 (2012) 1058–1062.
 25. Khataee, A.R.; Pakdehi, S.G. Removal of sodium azide from aqueous solution by Fenton-like process using natural laterite as a heterogeneous catalyst: Kinetic modeling based on nonlinear regression analysis. Journal of the Taiwan Institute of Chemical Engineers 45 (2014) 2664–2672.
 26. Zhang, S.X.; Zhao, X.L.; Niu, H.Y. Superparamagnetic Fe₃O₄ nanoparticles as catalysts for the catalytic oxidation of phenolic and aniline compounds. Journal of Hazardous Materials 167 (2009) 560–566.
 27. Wang, P.; Bian, X. F.; Li, Y. X. Catalytic oxidation of phenol in wastewater - A new application of the amorphous Fe₇₈Si₉B₁₃ alloy. Chinese Science Bulletin 57 (2012) 33-40.
 28. Official Journal of Algerian Republic. (2006) Nos. 06–141 of April 19.
 29. Salem, I.A.; El-Ghamry, H.A.; El-Ghobashy, M.A. Catalytic decolorization of Acid blue 29 dye by H₂O₂ and a heterogeneous catalyst. Journal of basic and applied sciences 3 (2014) 186 -192.
 30. Idrissi, M.; Miyah, Y.; Lahrichi, A.; Chaouch, M.; Zerrouq, F. Preparation and characterisation a catalytic system cu-clay for catalytic oxidation of methyl orange with H₂O₂. International Journal of Innovative Research in Science. Engineering and Technology 3 (2014) 2303-2308.
 31. Murugananthan, M.; Yoshihara, S.; Rakumab, T.; Shirakashi, T. Mineralization of bisphenol A (BPA) by anodic oxidation with boron-doped diamond (BDD) electrode. Journal of Hazardous Materials 154 (2008) 213-220.
 32. Daud, N.K.; Ahmad, M.A.; Hameed, B.H. Decolorization of Acid Red 1 dye solution by Fenton-like process using Fe-Montmorillonite K10 catalyst. Chemical Engineering Journal 165 (2010) 111–116.
 33. Khorramfar, S.; Mahmoodi, N. M.; Arami, M.; Bahrami, H. Oxidation of dyes from colored wastewater using activated carbon/hydrogen peroxide. Desalination 279 (2011) 183–189.
 34. Zhou, L.C.; Shao, Y.; Liu, J.; Ye, Z.; Zhang, H.; Ma, J.; Jia, Y.; Gao, W.; Li, Y. Preparation and Characterization of Magnetic Porous Carbon Microspheres for Removal of Methylene Blue by a Heterogeneous Fenton Reaction. ACS Applied Materials & Interfaces 6 (2014) 7275–7285.
 35. [Chen, J.; Zhu, L. Heterogeneous UV-Fenton catalytic degradation of dyestuff in water with hydroxyl-Fe pillared bentonite. Catalysis Today 126 (2007) 463–470.
 36. Zhan, Y.; Zhou, X.; Fu, B.; Chen, Y. Catalytic wet peroxide oxidation of azo dye (Direct Blue 15) using solvothermally synthesized copper hydroxide nitrate as catalyst. Journal of Hazardous Materials 187 (2011) 348-354.
 37. Ayodele, O.B.; Lim, J.K.; Hameed, B.H. Degradation of phenol in photo-Fenton process by phosphoric acid modified kaolin supported ferric-oxalate catalyst: Optimization and kinetic modeling. Chemical Engineering Journal 197 (2012) 181–192.
 38. Ibrahim, A.S.; El-Ghamry, H.A.; El-Ghobashy, M.A. Catalytic decolorization of acid blue 29 dye by H₂O₂ and a heterogeneous catalyst. Journal of basic and applied sciences 3 (2014) 186-192.
 39. Benjelloun, Y.; Miyah, Y.; Idrissi, M.; Boumchita, S.; Lahrichi, A.; El Ouali Lalami, A.; Zerrouq, F. Study of catalytic performance during the oxidation of methylene blue using a MnO-Argile catalyst in the presence of H₂O₂ (Study of catalytic performance for the oxidation of methylene blue using MnO-Clay catalyst with H₂O₂. Journal of Materials and Environmental Science 7 (2016) 9-17.

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