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Synthèse d'un nano-composite environnemental (αP2W15Mo2Co) comme catalyseur pour la dégradation d'un colorant diazoïque

Nacéra Zabat[1] and Nawel Nedjah[2]

[1]*Laboratory of Organic Synthesis-Modeling and Optimization of Chemical Processes, Department of Process Engineering, Faculty of Engineering, Badji Mokhtar-Annaba University, Annaba, Algeria,*
[2]*Physical Metallurgy and Materials Properties Laboratory, National Higher School of Technology and Engineering ENSTI, Badji Mokhtar University,Annaba,Algeria, Annaba, Algeria*

Résumé

L'objectif de ce travail, consiste à la dégradation d'un colorant diazoïque susceptible de se trouver dans les eaux usées par l'application d'un procédé d'oxydation catalytique en phase homogène, en utilisant un matériau nanopolyoxométallate (nanoPOM) synthétisé, de type Dawson (aP2W15Mo2Co)8- comme catalyseur, vis à vis de la dégradation du rouge Congo en présence d'un oxydant le peroxyde d'hydrogène (H2O2). Les paramètres optimums favorisant le contrôle de cette réaction d'oxydation sont comme suit : pH initial de la solution aqueuse, masse du catalyseur, concentration de l'oxydant, concentration initiale du colorant, effet de la température et de la nature du catalyseur. Dans ces conditions l'efficacité de décoloration atteint 91,93%.

Mots clés : Oxydation catalytique, H2O2, nano-(POM)s, Pollution des eaux, Colorant Diazoïque.

Synthesis of an environmental nano-composite (αP2W15Mo2Co) as a catalyst for the degradation of a disazo dye

Abstract:

The objective of this work is the degradation of a diazo dye likely to be found in wastewater. And this by the application of a process of catalytic oxidation in homogeneous phase, by using a material with character nanopolyoxometallate (nanoPOM) synthesized of the Dawson type (aP2W15Mo2Co)8- as catalyst, with respect to the degradation of Congo red in presence of an oxidant hydrogen peroxide (H2O2). The optimum parameters favoring the control of this oxidation reaction are as follows: initial pH of the aqueous solution, mass of the catalyst, concentration of the oxidant, initial concentration of the dye, effect of the temperature and the nature of the catalyst. Under these conditions, the bleaching efficiency reaches 91.93%.

Key Words*:* Catalytic oxidation, H2O2, nano-(POM)s, water pollution, diazo dye.

[1] Corresponding author: zabatnassira@yahoo.fr

INTRODUCTION

Polyoxometallates (POMs) constitute a very extensive family of inorganic clusters with metal-oxygen bonds, the first polyoxometallate of which was synthesized in 1826 by Berzelius [1]. With the development of X-ray diffraction techniques, Keggin provided definitive evidence for the structural composition of an acid form polyoxometallate [2]. Since that time, the research intensity in the field of POM chemistry has grown rapidly, with ongoing research all over the world. It is possible to establish rational methods for the stereospecific synthesis of compounds substituted by transition metals starting from suitable vacancy compounds [3]. These substituted compounds are notable for their diversity in molecular and electronic structure and their importance in a variety of disciplines. For example, medicine [4], materials science and catalysis [5]. This last area is considerably the most developed.
In recent years, interest has focused on the synthesis of nano-composites and their applications. In this sense, POMs have attracted much attention as building blocks of functional composite materials due to their interesting nanometers structures [6]. This property is exploited in green chemistry [7] and in particular in catalytic oxidation reactions for the degradation of organic compounds such as dyes. The synthetic dyes contained in industrial effluents from textiles, cosmetics, leather, paper and pharmaceuticals... cause water pollution [8], due to their toxicity. Most synthetic dyes are carcinogenic and mutagenic, posing a serious threat to the environment and human health [9]. These pollutants are ubiquitous and persistent; they are difficult to remove by conventional techniques such as adsorption [10] and membrane filtration [11], as these methods have a high operating cost [12]. New technologies based on chemical oxidation have been developed to reduce these recalcitrant pollutants, in particular, advanced oxidation methods (AOPS) [13] that are currently one of the best technologies for the destruction of these dyes, in particularly azo dyes, which are not biodegradable by aerobic treatment processes [14]. Advanced oxidation processes (AOP) are based on the generation of highly reactive hydroxyl (•OH) radicals which have an unpaired electron and are very strong oxidants [15]. However, the catalysts used for these oxidation reactions can lead to new pollution, which leads to the discharge of a large amount of Fe2+ and Fe3+ sludge [16]. Polyoxometalates (POMs) used as catalysts in the oxidation of dyes, can provide an alternative approach to solve this problem, due to their stability, separability, their harmlessness to the environment and their oxido-redox properties [17].
They are known as good catalysts for the oxidation of organic compounds. They can also be used in the degradation of azo dyes [18]. For this reason, a cobalt-substituted $(\alpha P_2W_{15}Mo_2Co)^{8-}$ Dawson-type thungstophosphomolybdic nanocomposite catalyst was used in this study to accelerate the oxidation reaction of a disazo dye Congo red (RC) by H_2O_2 in aqueous solution. The advantage of this system used ($\alpha P_2W_{15}Mo_2Co$ / H_2O_2) is that the reaction by-products are weakly toxic [7].

2. EXPERIMENTAL METHODE

2.1. Synthesis of catalysts (POMs)

The catalyst $(\alpha P_2W_{15}Mo_2Co)^{8-}$ was prepared by adding cobalt chloride to the vacancy compound $(\alpha P_2W_{15}Mo_2Co)^{10-}$ according to the method described in the literature [19].
The vacancy heteropolyanion $(\alpha P_2W_{15}Mo_2O_{61})^{10-}$ was obtained by reaction of the addition of two molybdates MoO_{42-} to the trivalent compound $(P_2W_{15}O_{56})^{12-}$. The compounds $((\alpha P_2W_{15}Mo_2O_{61})^{10-}$, and $(P_2W_{15}O_{56})^{12-}$ were prepared respectively according to the methods described in the literature [20,21].
Les différentes structures de ces hétéropolyanions sont présentées sur la Fig.1.

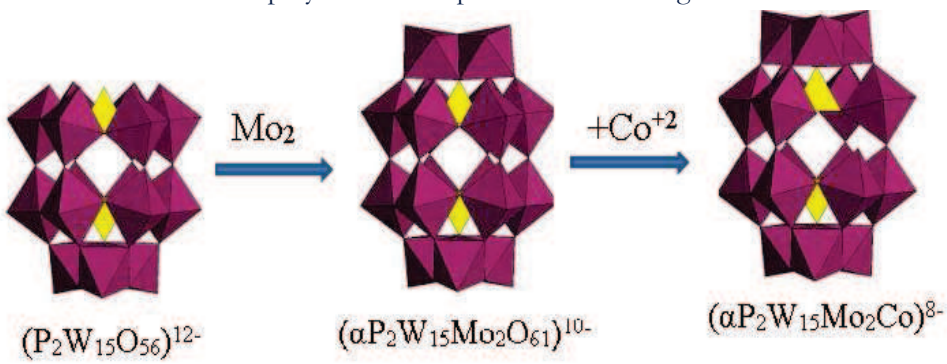

Fig1 : structures des polyoxométalates

2.1. Procedure for the oxidation of Congo red by H_2O_2 in the presence of $(aP_2W_{15}Mo_2Co)^{8-}$

In all experiments, a 100mL solution of RC containing appropriate amounts of catalyst $(\alpha P_2W_{15}Mo_2Co)^{8-}$ and oxidant H_2O_2 were magnetically stirred at room temperature. The pH of the solution was adjusted using 0.1N H_2SO_4 or NaOH in aqueous solutions.

The study of the degradation of Congo red by H_2O_2 using $(\alpha P_2W_{15}Mo_2Co)^{8-}$ as a catalyst is influenced by the following parameters: initial pH of the aqueous solution, mass of the catalyst, concentration of the oxidant, initial concentration of the dye, effect of the temperature and the nature of the catalyst.To optimize these parameters, the bleaching efficiency was monitored. All parameters were kept constant, except for the parameter to be optimized. The bleaching efficiency is given according to the following equation:

ED = (Ci–Cf / Ci)×100 (1)

Where ED, Ci, Cf are the decolorization efficiency, the initial concentration and the final concentration of Congo red.

3. RÉSULTATS ET DISCUSSION

3.1. *Effet of pH*

To study the effect of pH on the kinetics and efficiency of discoloration of congo red (RC), a series of experiments was carried out from a value of pH=3 to pH=8. The results obtained in figure.2 show that the oxidation reaction of RC by H_2O_2 in the presence of $(\alpha P_2W_{15}Mo_2Co)^{8-}$ as a catalyst is not favored in acidic and basic environments. On the other hand the natural environment (PH= 6.86) is the most favorable to the realization of this reaction. Hence its kinetics is faster comparing to that of acidic pH and basic which is very slow, therefore the pH = 6.86 represents the best efficiency of decolorization (ED= 55.56%).This result is consistent with what was observed in the study of the oxidation of azo dyes by the advanced oxidation system, where the reaction is favored at natural pH [22].

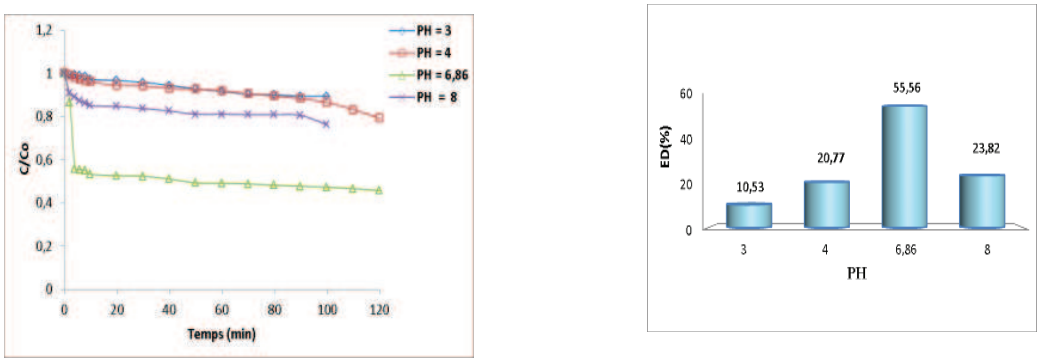

Fig.2. *Effect of pH on the oxidation of RC by the system $(aP_2W_{15}Mo_2Co/H_2O_2)$ (C_0=10ppm; C_{H2O2}=12,5mM; m_{cat}= 0.01g; T=25°C)*

3.2. *Effect of catalyst mass*

To find the optimum catalyst mass giving the best decolorization efficiency, a series of experiments were performed at different catalyst masses ranging from 0.005g to 0.08g. The results are shown in Fig.3. It can be seen that without a catalyst (m=0), the oxidation reaction is very slow, hence ED=18.66%. As soon as a quantity of catalyst is added, the bleaching efficiency increases. So, increasing the mass of the catalyst leads to an improvement in the decolorization efficiency of Congo red up to a value equal to 0.03 g where the kinetics are clearly fast at this mass. The excess of the catalyst does not seem to play a positive role in the degradation process of Congo red, using the system $(\alpha P_2W_{15}Mo_2Co/H_2O_2)$. This phenomenon can be explained by the fact that the excess catalyst causes side reactions consuming hydroxyl radicals [23]. The best bleaching efficiency is 76.22% for a mass of 0.03g.

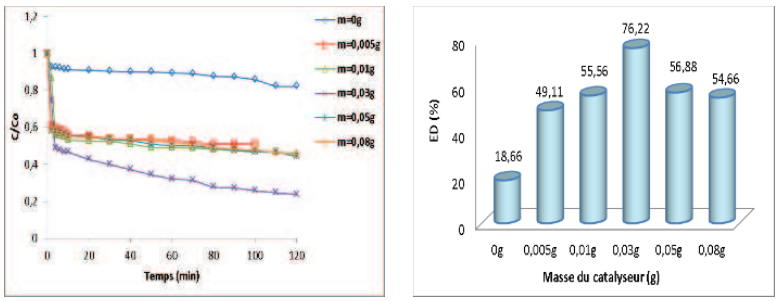

Fig.3. *Effect of Catalyst mass on RC Oxidation by System $(aP_2W_{15}Mo_2Co/H_2O_2)$ (PH=6.86; C_0=10ppm; C_{H2O2}=12,5mM; T=25°C).*

3.3. Effect of H_2O_2 concentration

To investigate the decolorization efficiency of Congo red dye as a function of H_2O_2 concentration, a series of solutions at different H_2O_2 concentrations were made. The results presented in figure.4, indicate that the oxidation reaction of Congo red depends on the concentration of H_2O_2. Indeed, the increase in the concentration of H_2O_2 causes an increase in the bleaching efficiency up to a value of H_2O_2 equal to 10 mmol. Beyond this concentration, there is a decrease in bleaching efficiency. This is due to the excess of H_2O_2, which favors the recombination between the hydroxyl radicals on one side and the reaction between the hydroxyl radicals and H_2O_2 on the other side, as it is described according to the literature [24]. The optimum concentration of H_2O_2 is 10mM giving a decolorization efficiency of 80.95%.

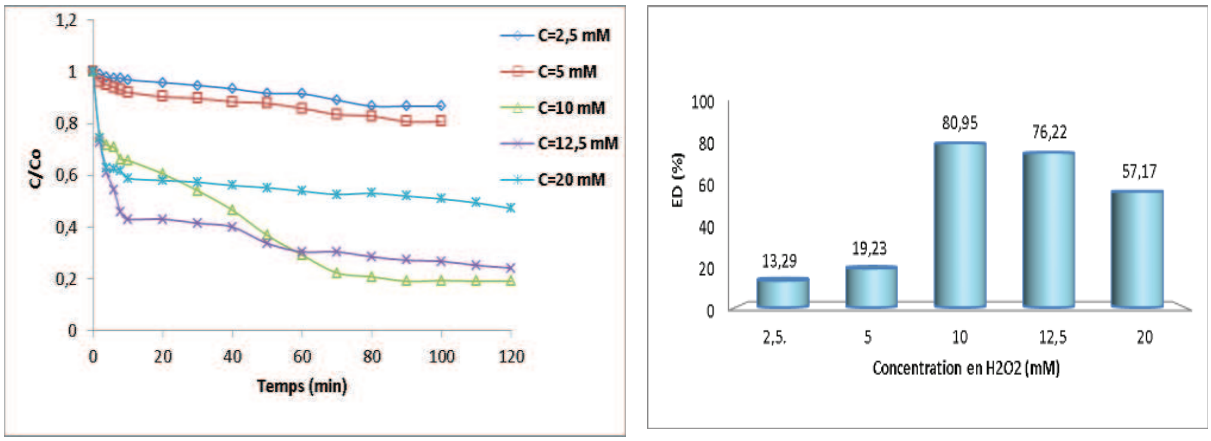

Fig.4. *Effect of H_2O_2 concentration on RC oxidation by the system ($aP_2W_{15}Mo_2Co/H_2O_2$) (PH=6.86; C_0=10ppm; m_{cat}=0.03g; T=25°C)*

3.4. Effect of the initial concentration of Congo red

To study the effect of the initial concentration of Congo red on the kinetics and the bleaching efficiency, a series of experiments were carried out at different concentrations (5ppm-25ppm). The results obtained are shown in Fig. 5, it can be seen that the kinetics of RC degradation is slow when the initial concentration of the dye is increased. This phenomenon can be explained by the fact that the increase in the initial concentration of the Congo red dye leads to an increase in the number of Congo red molecules, while the number of hydroxyl radicals remains constant (the concentration of H_2O_2 and the mass of catalyst are kept constant, thus causing a decrease in the kinetics of the degradation reaction as well as in the decolorization efficiency [25]. The best decolorization efficiency is 91.93% for a minimum concentration of 5ppm in RC.

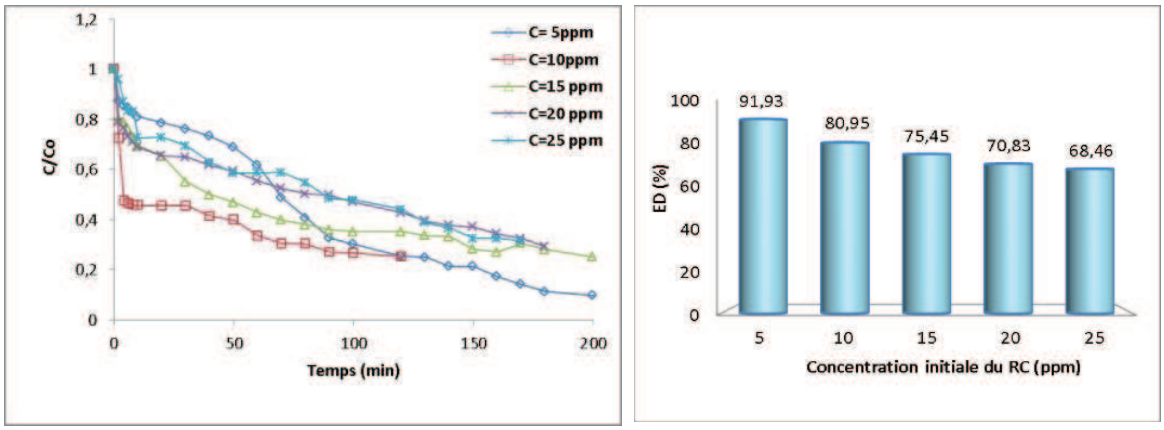

Fig.5. Effect of Initial Dye Concentration on System Oxidation ($\alpha P_2W_{15}Mo_2Co/H_2O_2$). (PH=6.86; m_{cat}=0.03g; C_{H2O2}=10mM; T=25°C)

3.5. Effect of temperature

Knowing that the temperature is an important factor to accelerate a chemical reaction, for this purpose, the temperatures chosen for the oxidation reaction of the RC are between 25 and 40 °C.

From Figure 6, it was found that increasing the temperature slightly increases the decolorization efficiency of Congo red; therefore, it does not have a apparent influence on the kinetics of this reaction. This is probably due to the bleaching efficiency value which was already sufficiently high at 5ppm (ED=91.93%). It is preferable in this case to work at ambient temperature (T=25°C), which is considered as an energy gain for the system studied ($\alpha P_2W_{15}Mo_2Co/H_2O_2/RC$) [26].

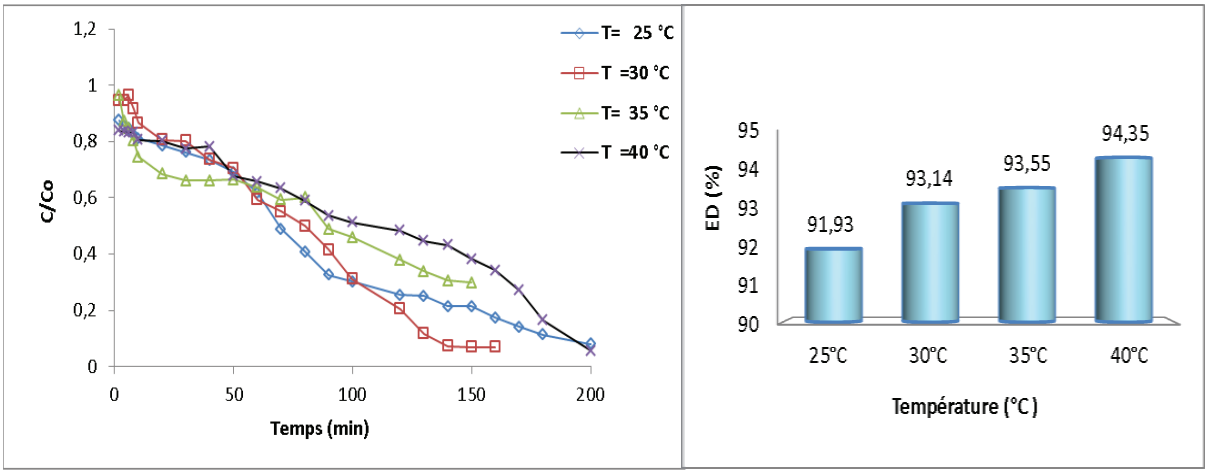

Fig.6 *Effect of temperature on system oxidation of RC ($aP_2W_{15}Mo_2Co/H_2O_2$) (PH=6.86; C_0=5ppm; C_{H2O2}=10mM; m_{cat}=0.03g).*

3.6. Effect of the nature of catalyst

To study the effect of the nature of the catalyst on the oxidation of RC, we tested the catalytic activity of a series of POMs prepared according to the procedure already described in the literature. The experiments were carried out under previously determined optimal conditions.

The POMs used are: P_2W_{18}, $P_2W_{15}MO_2$, $P_2W_{15}MO_2Ni$, $P_2W_{15}MO_2Fe$ and $P_2W_{15}MO_2Pb$ and $P_2W_{15}MO_2Co$. On Figure 7, it appears that the RC discoloration efficiency is very low (ED=18.66%), in the absence of the POM type catalyst. However, the presence of the catalyst (P_2W_{18}) which is the mother molecule saturation significantly improves the decolorization efficiency of RC (ED=53.63%), also the presence of the monovacant mixed lacunar species ($P_2W_{15}MO_2$) considerably improves ED (75.8%). On the other hand, for the addition compounds ($P_2W_{15}MO_2Ni$, $P_2W_{15}MO_2Fe$ and $P_2W_{15}MO_2Pb$) in turn improve this oxidation reaction, but in a varied way, and this according to the nature of the transition metals substituted with the vacancy compound, however the compound studied in this work $(P_2W_{15}MO_2Co)^{8-}$ represents the best bleaching efficiency (ED=91.93%) [27].

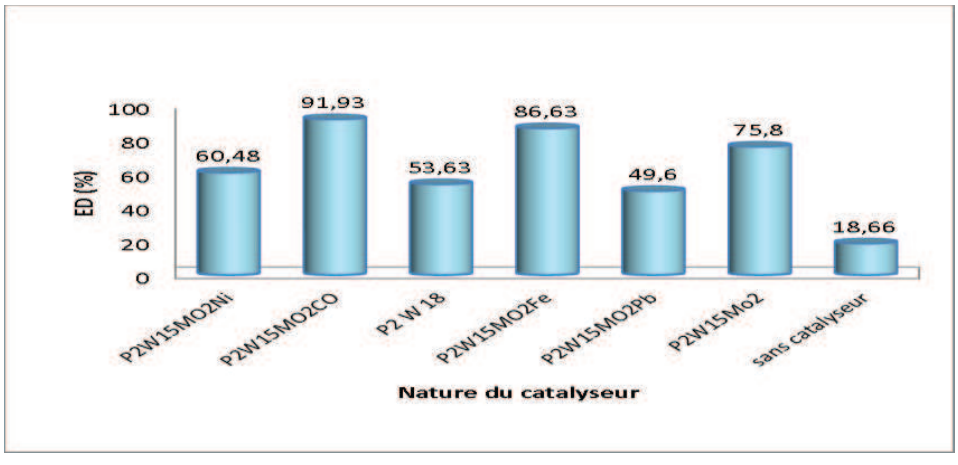

Fig.7. *Variation in decolorization efficiency depending on the nature of the catalyst. (PH=6.86; C_0= 5ppm; C_{H2O2}=10mM; m_{cat}=0.03 g; T=25°C).*

CONCLUSION

The elimination of congo red in aqueous medium by a catalytic oxidation process, using H_2O_2 as oxidant and catalyzed by a synthesized nano-material $(P_2W_{15}MO_2Co)^{8-}$ has been successfully carried out under normal conditions (ambient temperature and normal ph) .

The optimal conditions favoring this reaction led to the following results:

- Ph of the initial solution =6.86
- Mass of catalyst =0.03g
- Concentration of H_2O_2 = 12.4 Mm
- Dye concentration (RC) =5ppm

Under these conditions, the discoloration efficiency of the RC reaches (91.93%).

Tests of the catalytic activity of dawson-like nano-polyoxometallates ($\alpha_2P_2W_{18}$, $\alpha_2P_2W_{15}MO_2$; $\alpha_2P2W_{15}MO_2Ni$, $\alpha_2P_2W_{15}MO_2Fe$ AND $\alpha_2P_2W_{15}MO_2Pb$ and $\alpha_2P_2W_{15}MO_2Co$) on the rc oxidation reaction showed that the cobalt-substituted nano-polyoxometallate catalyst $(\alpha P_2W_{15}MO_2Co)^{8-}$ is the most active compared to other catalysts.

This study presents a homogeneous catalysis approach for the degradation of a diazo dye by means of oxidation. This system ($\alpha P_2W_{15}MO_2Co/H_2O_2$/RC) then constitutes a simple, effective and non-polluting method compared to those previously reported for the oxidation of diazo dyes [22].

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