

ORIGINAL RESEARCH PAPER

## Catalytic oxidation of naphthol blue black in water: Effect of Operating Parameters and the Type of Catalyst

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### ABSTRACT

The main objective of this work is to study the oxidation of naphthol blue black (NBB) in aqueous solution by hydrogen peroxide using a recyclable Dawson type heteropolyanion  $[H_{1.5}Fe_{1.5}P_2W_{12}Mo_6O_{61} \cdot 23H_2O]$  as catalyst. The effects of various experimental parameters of the oxidation reaction of the dye were investigated. The mineralization of the dye was investigated by the total organic carbon (TOC) measurement in optimum conditions.

The influence of the catalyst nature (Dawson- type iron-substituted heteropolyanion) and (Dawson- type copper-substituted heteropolyanion) on the oxidation process was investigated. The catalytic oxidation using a recyclable heteropolyanions as catalysts is an economically and environmentally friendly process to remove the toxicity of the recalcitrant compounds in water.

**Keywords:** Dye removal, Naphthol blue black (NBB), Water treatment, Catalytic oxidation.

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## INTRODUCTION

Among the water consuming industries in large quantity, the textile industry is found at the top of the list, constituting a major source of water pollution. The waters released by the textile mills usually are highly concentrated colorants, usually with little to no degradable potential, making biological treatments hardly applicable. Therefore, it is necessary to find alternative techniques of biodegradable efficiency and that are also cost-effective. The last twenty years there has been much work published that is devoted to the emergence of new treatment processes; among which is advanced oxidation processes.

The advanced oxidation process (AOP) is an alternative method for the degradation of many organic pollutants [1, 2, 3]. (AOP)s are oxidation processes which generate hydroxyl radicals

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(OH) that are very effective at degrading organic pollutants because of their strong oxidizing capabilities. One of them is the homogeneous Fenton process, which is widely studied as an alternative for the treatment of industrial waste water containing non-biodegradable organic pollutants [4, 5, 6].

But often this method needs ultra filtration for the separation of catalyst; it is an especially big problem when applying it for treating large waste streams. The use of a recyclable heteropolyanions as catalysts in oxidation of organic dyes by hydrogen peroxide may provide the best alternative approach to solve this problem.

The heteropolyanions, molecular oxides to the properties, are many and varied, in both the homogeneous phase and the heterogeneous phase. These compounds, which are fully minerals, are

generally easy to synthesize from simple and little polluting reagents [7, 8].

Heteropolyanions with Dawson structure [9] may be promising catalysts in homogeneous and heterogeneous systems because their redox and acidic properties can be controlled at both the atomic and molecular levels. Dawson-type heteropolyanions are formidable catalysts, which have proved their effectiveness in many reactions of oxidation [10, 11, 12]. Recently, there has been considerable interest in the use Dawson-type heteropolyanions as environmentally catalysts due to their unique properties such as high solubility in polar solvents and fairly high thermal stability in solid state, low cost, ease of preparation and ease of recyclability [13].

In this study, we report a detailed discussion on the oxidative degradation of Naphthol blue black (NBB) in aqueous solution containing hydrogen peroxide and a Dawson-type heteropolyanion as catalyst.

This reaction is part of the depollution of water, in particular to the treatment of discharged water by the textile industry, soiled by the organic dyes. The choice of the naphthol blue black is dictated by the fact that it is an azo dye which presents a high toxicity to the environment because of the presence of phenolic, anilino, naphthalene and sulfonated groups, (see Fig.1)

NBB is an industrially important acidic diazo dye, which has a high photo- and thermal- stability [14].

Due to its high degree of reaction to light, the commercial grades of naphthol blue black (NBB) are widely used in the textile industry for dyeing wool, nylon, silk and textile printing. Other industrial use includes coloring of soaps, anodized aluminum and casein, wood stains and writing ink preparation [14].

The degradation and removal of NBB dye was investigated by several authors in the literature

Ferkous *et al.* [15] used ultrasound for the degradation on NBB dye, in this study ( $5 \text{ mg L}^{-1}$ ) NBB

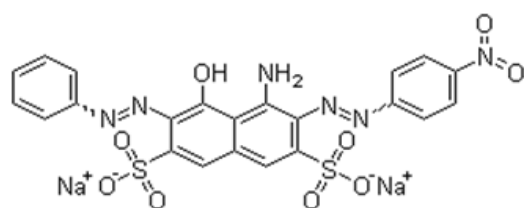


Fig. 1: Developed formula of Naphthol blue black (NBB)

was completely destroyed after 45 min of sonication. The photoelectrochemical degradation of NBB dye using different semiconductor electrodes was studied. A higher photoelectrocatalytic activity has been observed for  $\text{WO}_3$  film electrodes, prepared by electrodeposition, than for  $\text{TiO}_2$  nanoparticulate film electrodes [16]. The heterogeneous photocatalysis degradation of NBB in the presence of zirconia-supported Ti-substituted Keggin-type polyoxometalates [17] And synthesized nanocomposite polyaniline-coated oxide (PTO) [18] was also performed. Moreover, we have investigated the degradation of NBB dye by  $\text{H}_2\text{O}_2$  using Dawson-type Fe(III)-substituted heteropolyanion  $(\alpha_2\text{P}_2\text{W}_{12}\text{Mo}_5\text{O}_{61}\text{Fe})^{7-}$  as catalyst. This compound was synthesized by the addition of iron on the lacunary heteropolyanion  $(\alpha_2\text{P}_2\text{W}_{12}\text{Mo}_5\text{O}_{62})^{10-}$  [19]. The optimal values of operating parameters during the oxidation of the NBB dye by the  $\text{Fe(III)P}_2\text{W}_{12}\text{Mo}_5/\text{H}_2\text{O}_2$  system are pH: 3,  $[\text{NBB}]_0 = 10 \text{ mg/L}$ , Catalyst  $(\alpha_2\text{P}_2\text{W}_{12}\text{Mo}_5\text{Fe})^{7-}$  mass : 0.3g,  $[\text{H}_2\text{O}_2]_0 = 2 \text{ m M}$ .

In this work, we have investigated the removal of NBB dye from water by  $\text{H}_2\text{O}_2$  using  $\text{HFe}_{1.5}\text{P}_2\text{W}_{12}\text{Mo}_6\text{O}_{61} \cdot 22\text{H}_2\text{O}$  ( $\text{HPA Fe}^{3+}$ ). This catalyst was synthesized by the addition of  $\text{Fe}^{3+}$  ions to the Dawson acid form  $\text{H}_6\text{P}_2\text{W}_{12}\text{Mo}_6\text{O}_{62} \cdot 24\text{H}_2\text{O}$  [20]. The influence of different parameters such as the initial pH, the initial  $\text{H}_2\text{O}_2$  concentration, the catalyst mass, and the initial dye concentration have also been studied. The mineralization of the dye was investigated by the total organic carbon (TOC) measurement in optimum conditions.

Even the effect of using the heteropolyanion ( $\text{HPA Fe}^{3+}$ ) as a catalyst on the oxidation of NBB has been compared with a copper substituted heteropolyanion  $[\text{H}_{1.2}\text{Cu}_{2.4}\text{P}_2\text{W}_{12}\text{Mo}_6\text{O}_{61} \cdot 21\text{H}_2\text{O}]$  ( $\text{HPACu}$ ).

## EXPERIMENTAL SECTION

### Reagents

The catalyst  $\text{HFe}_{1.5}\text{P}_2\text{W}_{12}\text{Mo}_6\text{O}_{61} \cdot 22\text{H}_2\text{O}$  was prepared starting from  $\text{H}_6\text{P}_2\text{W}_{12}\text{Mo}_6\text{O}_{62} \cdot 24\text{H}_2\text{O}$  according to the following protocol [20].

5g (1.2 mmol) of  $\text{H}_6\text{P}_2\text{W}_{12}\text{Mo}_6\text{O}_{62}$  were dissolved in 20 ml of water at room temperature and 0,541g (3.56 mmol) of solid  $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$  was then added. The mixture was stirred for 10 min. Dark yellow powder of ( $\text{HPA Fe}^{3+}$ ) was obtained after five days by slow evaporation.

The heteropolyanion precursor  $\text{H}_6\text{P}_2\text{W}_{12}\text{Mo}_6\text{O}_{62} \cdot 24\text{H}_2\text{O}$  was synthesized according to published procedure [21].

Naphthol blue black (abbreviation: NBB; class: azo, C.I. number: 13025, molecular formula:  $C_{14}H_{14}N_3SO_3Na$ ) was used as a compound model. It is also known as [Noir amido 10 B, Acid Black 1, Buffalo Black NBR]. Naphthol blue black was supplied by Fluka. Its molecular structure is shown in (Fig. 2). ( $H_2O_2$  35%, W/W) was obtained from Merck. All other reagents (NaOH, HCl,  $H_2SO_4$ ,  $HNO_3$  and  $H_3PO_4$ ) that are used in this study were analytical grade.

#### Procedure - analysis

The initial concentration of NBB solution was  $30\text{ mg L}^{-1}$  for all experiments, except for those carried out to examine the effect of initial dye concentration. In all experiments 100 mL of NBB solution containing the appropriate quantity of catalyst and  $H_2O_2$  was magnetically stirred at room temperature. The pH of the reaction was adjusted by using 0.1N of acids ( $H_2SO_4$ ,  $HNO_3$ , HCl and  $H_3PO_4$ ) or NaOH aqueous solutions. The NBB concentration is measured by means of a 6705 UV visible spectrophotometer JENWAY. The wave length corresponding to the maximum absorbance is  $\lambda_{\text{max}}=620\text{ nm}$  [14]. The resolution of the wavelength and bandwidth, were 1nm and 0.5 nm. The cells used during the experiments were made of 1 cm thick quartz.

#### The effects of operational parameters on NBB oxidation

The oxidation of NBB by  $H_2O_2$  using (HPA  $Fe^{3+}$ ) as catalyst has been studied according to the following factors: initial pH of the solution, mass of the catalyst,  $H_2O_2$  concentration and the dye concentration.

The oxidation efficiency (discolouration) was determined as it is shown below:  
 $DE = (C_i - C_f) / C_i \cdot 100$  [19, 20].

DE: Discolouration efficiency;

$C_i$ : Initial dye concentration;

$C_f$ : Final dye concentration.

#### The effect of solution pH

In order to find the optimum pH for the oxidation of NBB, a series of experiments at initial pH values in the range 3-8 was conducted. For more acidic pH (<3) there is a risk of dimerization of the catalyst [7], while for pH above 10, the catalyst is likely to deteriorate [7]. Fig. 2 shows the variation of the discolouration efficiency in function of time, under the following experimental conditions: (NBB concentration is  $30\text{ mg L}^{-1}$ ,  $[H_2O_2]=0.005\text{m M}$ , catalyst mass=0.05g).

The results presented in (Fig. 2) show that the optimum pH value for NBB oxidation by  $H_2O_2$  using Wells-Dawson-type heteropolyanion iron substituted as catalyst is achieved at pH 3 (DE=82.37% after 70 min of treatment). A similar behavior was observed by several studies reported in the literature [19, 20]. This result can be explained by the stability of the catalyst at this pH. It has also been shown that the catalytic efficiency of the  $Fe^{3+}/H_2O_2$  system towards the oxidation of organic dyes is better at pH= 3 than the other pH [22, 23].

At neutral pH, the discolouration efficiency increases (51.36% is reached after 89 min of treatment). Previous studies [24, 25] showed that the addition of iron ( $Fe^{3+}$ ) to the heteropolyanionic matrix extends the working pH range of the  $Fe^{3+}/H_2O_2$  system up to neutral pH.

$H_2O_2$  molecules are unstable in alkaline solution [26-27] and therefore, the degradation of dye decreases in alkaline solution (DE=33% after 89 min of treatment).

The optimal value is chosen pH = 3.

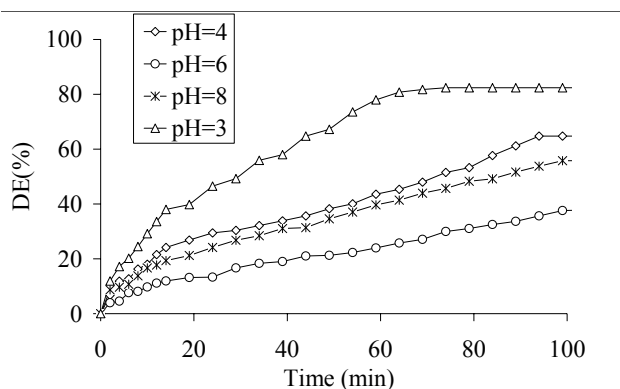


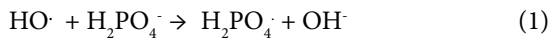
Fig. 2: Effect of solution pH on NBB oxidation ( $C_i=30\text{mg/L}$ ,  $[H_2O_2]=0.005\text{m M}$ , catalyst mass=0.05g)

*The effect of the nature of the acid used to adjust the pH*

To evaluate the influence of these anions such as  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{PO}_4^{3-}$  on the oxidation of NBB dye by a catalytic system (HPA  $\text{Fe}^{3+}$ )/ $\text{H}_2\text{O}_2$ , we adjusted the pH of an aqueous solution of NBB by different acids  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{H}_3\text{PO}_4$  at previously established optimum pH=3.

Fig. 3 shows the effect of these acid ions (chloride, sulphate, nitrate, and phosphate) on the dye oxidation. Depending on the nature of the acids, the discoloration efficiency is about 82.37%, 70%, 57.8% and 11.6 % in the presence of HCl,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and  $\text{H}_3\text{PO}_4$  acids respectively after 70 min of treatment.

It appears that the presence of phosphate ions inhibits the oxidation. These results agree with those found at the degradation of other organic pollutants [28]. The inhibitory effect of phosphate ions may be due to the catching of  $\cdot\text{OH}$  radicals according to the following equation:

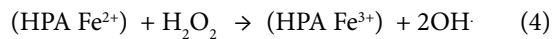
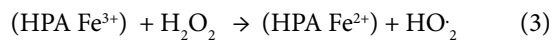


*The effect of catalyst mass*

It was shown [19] that (HPA  $\text{Fe}^{3+}$ ) can catalyze the decomposition of  $\text{H}_2\text{O}_2$ . The reaction of  $\text{H}_2\text{O}_2$  with a complex containing  $\text{Fe}^{3+}$  result in the reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  with apparition of  $\text{HO}_2\cdot$ .

The action of  $\text{H}_2\text{O}_2$  on the complex of  $\text{Fe}^{2+}$  leads to the generation of hydroxyl radicals  $\text{OH}\cdot$ . These hydroxyl radicals cause the degradation of the dye.

In agreement with the mechanism proposed below, we can propose the following mechanism:



The catalyst mass is one of the critical parameters in catalytic oxidation process. In the present study, the influence of different catalyst mass  $[m((\text{HPA } \text{Fe}^{3+})) = [0\text{g} - 0.08\text{g}]]$  on the decolorization efficiency of NBB is illustrated in (Fig.4). The concentration of hydrogen peroxide is fixed as 0.05mM, and NBB concentration is 30 mg  $\text{L}^{-1}$ .

It can be seen from the results that the decolorization efficiency of NBB oxidation increase when increasing the catalyst mass. This is due to the

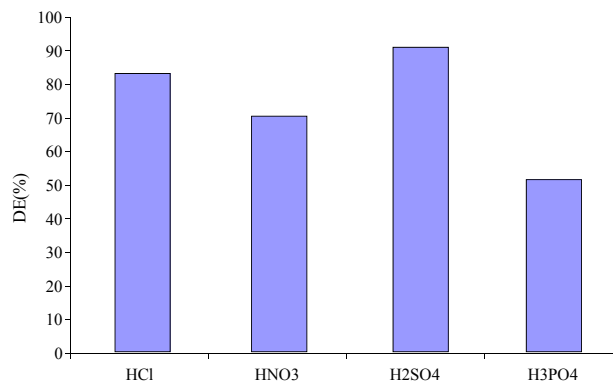


Fig. 3: Effect of the nature of the acid used to adjust the pH (pH = 3,  $C_i=30\text{mg/L}$ ,  $[\text{H}_2\text{O}_2]=0.005\text{m M}$ , catalyst mass=0.05g)

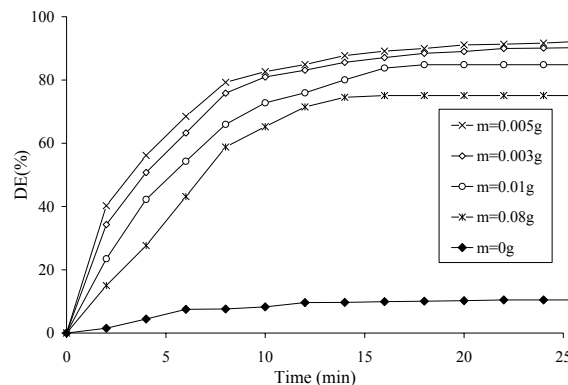


Fig. 4: Effect of catalyst mass on NBB oxidation (pH=3,  $C_i= 30\text{mg/L}$ ,  $[\text{H}_2\text{O}_2]=0.005\text{mM}$ ).

fact that (HPA Fe<sup>3+</sup>) plays a very important role in the decomposition of H<sub>2</sub>O<sub>2</sub> to generate the OH·. The lower degradation capacity of the catalyst at small mass (0g-0.005g) is probably due to the lowest of OH· radicals producing a variable for oxidation, for higher mass of catalyst(0.005g-0.08g), there is a decrease of the decolorization efficiency. The decrease of the decolorization efficiency of (NBB) oxidation by the increase the catalyst mass can be explained by the presence of the reaction (5) which enters in competition, at higher (HPA Fe<sup>3+</sup>) mass, with (NBB) oxidation reaction :



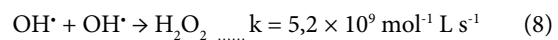
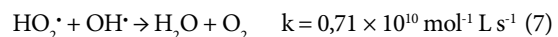
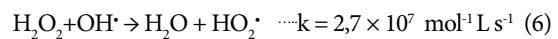
Consequently, a mass of (HPA Fe<sup>3+</sup>) of 0.005g was chosen throughout this work.

*The effect of initial H<sub>2</sub>O<sub>2</sub> concentration*

The effect of H<sub>2</sub>O<sub>2</sub> concentration is an important parameter for NBB degradation and for the decolorization efficiency. This effect was studied by varying the H<sub>2</sub>O<sub>2</sub> concentration from 0.003 mM to 0.2 mM in the following optimal conditions: pH=3, NBB concentration is 30 mg L<sup>-1</sup>, catalyst mass=0.005g).

According to the results shown above (Fig.5), the critical H<sub>2</sub>O<sub>2</sub> concentration for the degradation of 30 mg L<sup>-1</sup> NBB is about 0.08mM.

The activation of hydrogen peroxide by homogeneous catalysts was attributed to the formation of highly active hydroxyl radicals [29]. High concentrated H<sub>2</sub>O<sub>2</sub> solution undergoes self quenching of ·OH radicals, with formation of hydro peroxy radicals HO<sub>2</sub>·. Although HO<sub>2</sub>· is an effective oxidant itself, its potential oxidation is much lower than that of ·OH radicals [30].



*The effect of the NBB concentration:*

The study of the initial concentration effect of NBB dye on the oxidation kinetics was carried out from a concentration of 10 mg/L to 50 mg/L.

From Fig.6, we can note that the oxidation kinetics decreases with increasing the initial concentration of the dye. This result is in agreement with existing literature [30].

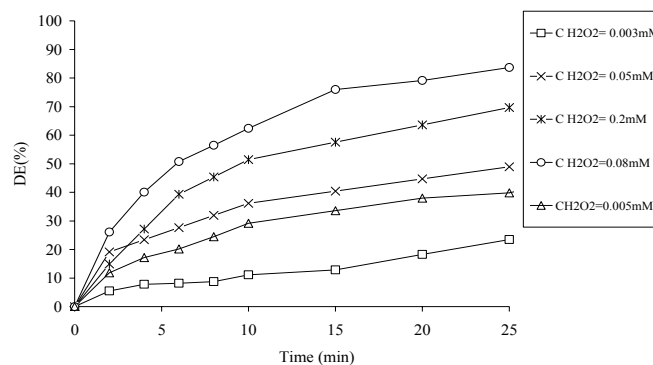


Fig. 5: Effet of initial H<sub>2</sub>O<sub>2</sub> concentration on NBB oxidation (pH=3, [C<sub>i</sub>]= 30mg/L, catalyst mass=0.005g)

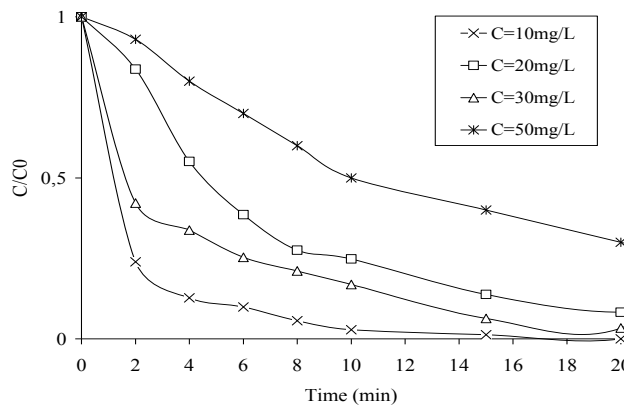


Fig. 6: Effect of initial dye concentration on NBB oxidation (pH=3, [catalyst mass]=0.005g, [H<sub>2</sub>O<sub>2</sub>]=0.01mM)

This phenomenon can be explained by the fact that increasing the initial concentration of dye leads to an increase in the number of molecules of (NBB), while the number of the radicals hydroxyls remain constant ( $H_2O_2$  concentration and catalyst kept constant), thereby causing a decrease in the discoloration efficiency [31].

*UV- Vis absorbance spectra of dye before and after oxidation*

The UV-vis absorbance spectra of the NBB before and after oxidation are shown in Fig. 7. In general, the absorbance at 400-700 nm corresponds to the n/p\* transition of the azo and hydrazone forms, which is the origin of the color of azo dyes and is used to monitor the decoloration. The absorbance at 200-400 nm was attributed to then/p\* transitions in benzene and naphthalene rings of azo dyes [32]. These four characteristic bands were markedly weakened during the degradation reaction, tending to disappears completely after 80 minutes, without the appearance of new absorption bands in the visible or ultraviolet regions due to destruction of the chromophoric and auxochromic structures by oxidation reaction.

*The mineralization study of NBB*

A complete mineralization of the dye molecules is always a major concern in catalysis because if this is not sufficiently accomplished, it may result in the formation of even more toxic intermediates.

Therefore, it is always desirable to degrade the dye molecules into smaller and less toxic species such as carbon dioxide, water and ionic species. Total organic carbon (TOC) analysis which measures the amount of carbon chemically bound.

The mineralization of aqueous NBB solution can be monitored by measuring the TOC evolution during oxidation process.

The TOC removal ratio (TOC) is defined as follows:

$$TOC (\%) = (1 - TOC_t) / TOC$$

The TOC values as a function of the time which is shown in Table 1.

As Table 1 shows, TOC decreased with the increasing reaction time. TOC removal was obtained at 250 min. This signifies a fairly high degree of complete mineralization of NBB which is essential for efficient dye pollution treatment.

*A comparative study of oxidation of NBB in the presence of  $[H_{1,2}Cu_{2,4}P_2W_{12}Mo_6O_{61}, 21H_2O]$*

In this study we compared the catalytic activity of an iron substituted Dawson-type

Table1. TOC removal ratio on the mineralization of NBB solution at different reaction time. (pH=3, [catalyst mass]=0.005g,  $[H_2O_2]=0.01$ mM, [NBB]=30mg/L).

| Time (min) | TOC removal ratio (%) |
|------------|-----------------------|
| 30         | 23.84                 |
| 60         | 67.2                  |
| 90         | 75.26                 |
| 260        | 91.35                 |

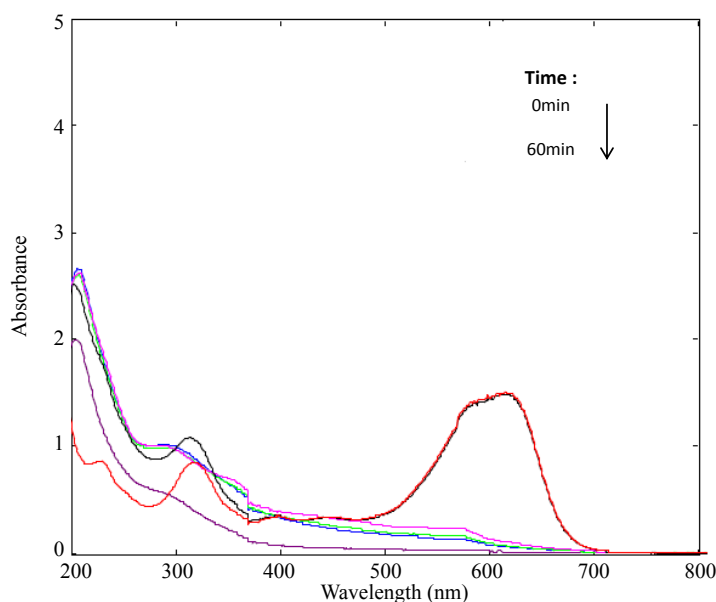


Fig. 7 : UV-Vis spectra of NBB water solutions during the treatment process with Fe(III)  $P_2W_{12}MO_6/H_2O_2$  system. (pH=3, [catalyst mass]=0.005g,  $[H_2O_2]=0.01$ mM).

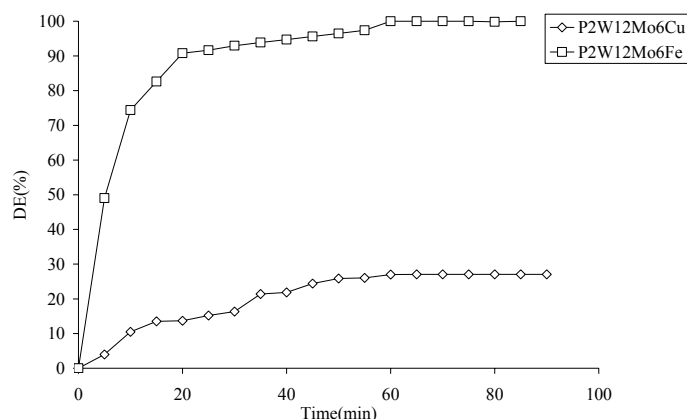


Fig. 8: Comparison of oxidation of NBB using Dawson- type iron -substituted heteropolyanion and Dawson-type copper -substituted heteropolyanion as catalysts. Experimental condition: [pH=3, [catalyst mass]=0.005g, [H<sub>2</sub>O<sub>2</sub>]=0.01mM.

heteropolyanion (HPA Fe<sup>3+</sup>) with a copper substituted heteropolyanion [H<sub>1.2</sub>Cu<sub>2.4</sub>P<sub>2</sub>W<sub>12</sub>Mo<sub>6</sub>O<sub>61</sub>·21H<sub>2</sub>O]. The compound [H<sub>1.2</sub>Cu<sub>2.4</sub>P<sub>2</sub>W<sub>12</sub>Mo<sub>6</sub>O<sub>61</sub>·21H<sub>2</sub>O] was prepared, by the addition of Cu<sup>2+</sup> ions to the Dawson acid form H<sub>6</sub>P<sub>2</sub>W<sub>12</sub>Mo<sub>6</sub>O<sub>62</sub>·24H<sub>2</sub>O according to the methods described in the literature [33]. The experiments were conducted under the same conditions as previously mentioned, by taking into consideration the optimised parameters. The results are illustrated in (Fig. 8).

Several Cu-containing systems for homogeneous catalytic decomposition of H<sub>2</sub>O<sub>2</sub> have recently been demonstrated [32, 35].

Through these results, it is clear that the iron substituted heteropolyanion (HPA Fe<sup>3+</sup>) is more effective compared to that of copper substituted heteropolyanion (HPA Cu<sup>2+</sup>).

All compounds used catalyzed the decomposition of hydrogen peroxide and the formation of hydroxyl radicals ·OH. The extent of peroxide to hydroxyl radical conversion was, however different from the particular substituted heteropolyanions.

The findings of this study are consistent with other results reported in the literature [23]

## CONCLUSIONS

The oxidation of an azo dye (NBB), in an aqueous solution, by H<sub>2</sub>O<sub>2</sub> in presence Dawson-type iron -substituted heteropolyanion (HPA Fe<sup>3+</sup>) as catalyst was studied.

The optimum conditions had been determined, and it was found that the efficiency of the degradation obtained after 15 minutes of reaction, was about 100%.

The optimal parameters were: initial pH=3; [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub>=0.08 mM; catalyst mass=0.005g; for a concentration of dye [NBB]<sub>0</sub>=30 mg L<sup>-1</sup>.

Total organic carbon (TOC) analysis revealed degree of complete mineralization of naphthol blue black (91.35 % TOC removal after 260 min) which minimizes the possible formation of toxic degradation by-products such as the aromatic amines.

(HPA Fe<sup>3+</sup>) is more effective compared to that of copper substituted heteropolyanion (HPA Cu<sup>2+</sup>).

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## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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