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Decolorization of organic dye (NBB) using Fe(III)$P_2W_{12}Mo_5/H_2O_2$ system

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ABSTRACT

This study evaluates the potential of Fe(III)$P_2W_{12}Mo_5/H_2O_2$ system in the decolorization of one common industrial azo dye, naphthol blue black (NBB). The effects of different parameter's dye decolorization were investigated. The studied parameters were: the initial pH, the initial H_2O_2 concentration, the catalyst mass, and the initial dye concentration. The optimal conditions for a maximum discoloration efficiency (100%) are: pH: 3, $[NBB]_0 = 10\,mg/L$, Catalyst mass: 0.3 g, $[H_2O_2]_0 =: 2\,mM$. The spectrophotometric analysis indicated that the decolorization of the azo dye with Fe(III)$P_2W_{12}Mo_5/H_2O_2$ was due to the reduction of the azo bonds. This study verifies the viability of the use of Fe(III)$P_2W_{12}Mo_5/H_2O_2$ in the decolorization of NBB.

Keywords: Dye decolorization; Naphthol blue black (NBB); Water treatment; Oxidation

1. Introduction

Water pollution due to discharge of colored effluents from textile dye manufacturing and textile dyeing mills is one of the major environmental concerns in today's world. Strong color azo dyes have been widely used as colorants in a variety of products such as textiles, paper, and leather. Approximately, half of all known dyes are azo dyes, making them the largest group of synthetic dyes [1–4]. Due to its high degree of fastness 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. NBB has a structure consisting of azo, phenolic, anilino, naphthalene, and sulfonated groups (see Fig. 1). It is an industrially important acidic diazo dye, which has a high photo- and thermal stability [5]. Advanced oxidation technologies (AOTs) have been considered as methods for treatment of textile pollutants [6]. AOTs are oxidationprocesses which generate hydroxyl radicals (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 wastewater containing non biodegradable organic pollutants [7–9].

However, the homogeneous Fenton process needs up to 50–80 mg/L of iron ions in solution and the reacted iron ions need to be separated from the system at the end of the reaction, which requires a

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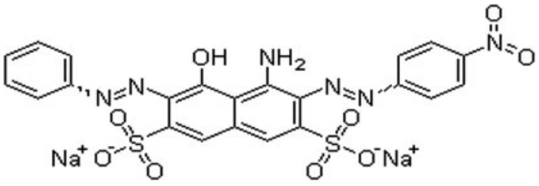

Fig. 1. Molecular structure of NBB.

complex and expensive removal process [10]. The use of a recyclable Dawson-type iron-substituted heteropolyanion [α_2 $K_7P_2W_{12}Mo_5Fe\cdot18H_2O$], as catalyst, may provide an alternative approach for solving this problem. In this work, Fe(III)$P_2W_{12}Mo_5/H_2O_2$ system was used for decolorization of NBB. The aim of the study is to examine the influence of different parameters such as the oxidation efficiency. The parameters, which are examined separately, are the solution pH, the catalyst mass, the concentration of H_2O_2, and the initial dye concentration.

2. Experimental section

2.1. Synthesis and characterization [$\alpha_2K_7P_2W_{12}Mo_5Fe\cdot18H_2O$]

2.1.1. Synthesis

[α_2 $K_7P_2W_{12}Mo_5Fe\cdot18H_2O$] was prepared starting from lacunary compound [α_2 $K_{10}P_2W_{12}Mo_5\cdot14H_2O$] according to the following protocol: a sample of 43 g (6 mmol) of $Fe(NO_3)_3\cdot9H_2O$ was dissolved in 90 ml of water and 23 g (5,27 mmol) of [$\alpha_2K_{10}P_2W_{12}Mo_5\cdot14H_2O$] was added with stirring. To the solution was added 90 ml of KCl saturated solution. The pale yellow crystals that appeared were filtered off and dried in air. [α_2 $K_{10}P_2W_{12}Mo_5\cdot14H_2O$] and [$\alpha$ $K_6P_2W_{12}Mo_6\cdot16H_2O$] were prepared according to the methods described in the literature [11].

2.1.2. Characterization of complexes by infra-red spectroscopy

IR spectra were recorded in 1% weight of HPA in a KBr pellet on a (Shimadzu Japon) spectrophotometer. Fig. 3 shows a comparison of the IR characteristics of a main heteroplyanions synthesized in this work.

In tungstophosphomolybdate compounds, the most characteristic IR band shifts correspond to P–O vibrations between 1,200 and 1,000 cm^{-1}. These shifts characterize the vacancy [12]. With an iron atom added into the vacancy, the whole symmetry is restored (the area of the bands P–O becomes similar to that observed on the spectrum of the saturated species [α $K_6P_2W_{12}Mo_6O_{62}\cdot16H_2O$].

2.2. Behavior of NBB oxidation by H_2O_2 in presence of [α_2 $K_7P_2W_{12}Mo_5Fe\cdot18H_2O$] as a catalyst

2.2.1. Reagents

NBB (class: azo, C.I. number:13025, molecular formula: $C_{14}H_{14}N_3SO_3Na$) was used as model compound. It is also known as Noir amido 10 B, Acid Black 1, Buffalo Black NBR. The NBB was supplied by Fluka. Its molecular structure is shown in (Fig. 2). H_2O_2 was purchased from Aldrich Chemical Company. All other reagents (NaOH or H_2SO_4) used in this study were analytical grade.

2.2.2. Procedures analysis

The experiments were performed in a reactor batch of 500 ml capacity. Various solutions of NBB were prepared at different concentrations. They were then homogenized by stirring them until the dye is completely dissoluted of the dye. pH was adjusted by using 0.1 N H_2SO_4 or NaOH aqueous solutions. In all experiments, 100 ml of dye (concentration to be optimized) solution containing the appropriate quantity of catalyst and H_2O_2 was magnetically stirred at room temperature. The NBB decreasing concentration of dye was monitored by a JENWAY UV–vis spectrophotometer. The Wave length corresponding to the maximum absorbance is given below: $\lambda_{max} = 620$ nm [13].

The resolution of the wave length and bandwidth are 1 and 0.5 nm. The cell used during the experiments was made of 1-cm thick quartz.

2.2.2.1. Effects of operational parameters on NBB oxidation. The oxidation of NBB by H_2O_2 using [α_2 $K_7P_2W_{12}Mo_5Fe$, $18H_2O]^{7-}$ as catalyst has been studied according to the following factors: initial pH of the solution, H_2O_2 concentration, and mass of the catalyst and dye concentration.

The oxidation efficiency (discoloration) was determined as shown below [13]:

$$DE = (C_i - C_f)/C_i \quad (1)$$

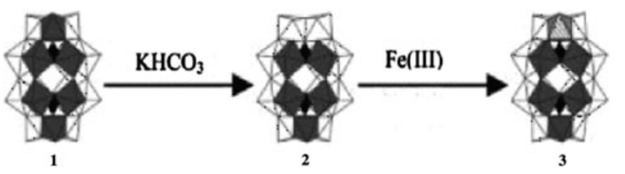

Fig. 2. Synthesis of complex **1** from **2** and **3**, respectively. **1**: [α_2 $K_7P_2W_{12}Mo_5Fe\cdot18H_2O$]; **2**: [$\alpha_2$ $K_{10}P_2W_{12}Mo_5\cdot14H_2O$]; **3**: [$\alpha$ $K_6P_2W_{12}Mo_6\cdot16H_2O$].

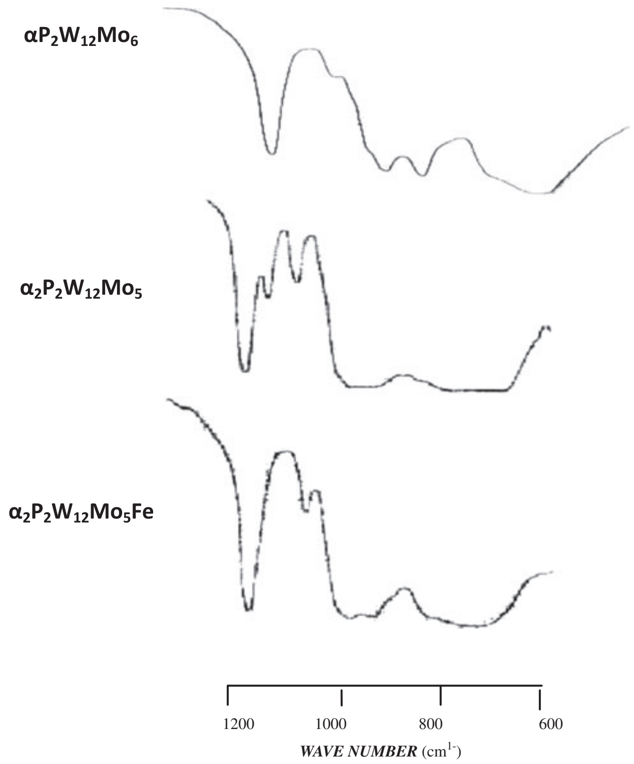

Fig. 3. Infra-red spectra of different heteropolyanions studied in this work.

DE: Discoloration efficiency.
C_i: Initial dye concentration.
C_f: Final dye concentration.

2.2.3. Effect of solution pH

Fig. 4 illustrates the effect of pH on the discoloration efficiency of NBB in water. It was found that the discoloration efficiency of NBB is strongly pH dependent. The optimal pH is about three giving a discoloration efficiency equal to 76%. This result can be explained by the stability of the catalyst at this pH. Also, it has been shown that the catalytic efficiency of the Fe^{3+}/H_2O_2 system towards the oxidation of organic dye is better at pH = 3 [14]. At pH = 10, the kinetics of oxidation is more effective compared with other pH (4, 6, 8). Knowing that in basic medium, the degradation of heteropolyanion [α_2 $K_7P_2W_{12}Mo_5Fe{\cdot}18H_2O$] gives MoO_4^{2-} molybdates and tungstates WO_4^{2-}, the iron precipitates as hydroxide $Fe(OH)_3$ [15]. Previous studies [16] showed that the iron hydroxide has no influence on the organic dyes oxidation catalysis. Other studies have shown that discoloration efficiency of organic dyes oxidation, in presence of MoO_4^{2-} and WO_4^{2-} as catalysts, is better at pH = 10 [17]. The optimal value is chosen pH = 3.

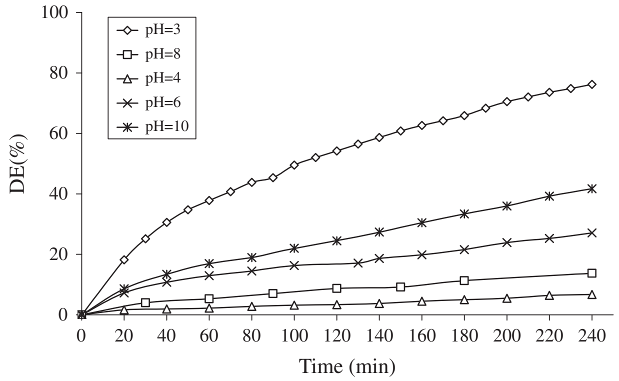

Fig. 4. Effect of pH on decolorization of NBB.
Conditions: temperature, 25°C; catalyst mass: 0.5 g; $[H_2O_2]_0$: 1 mM; dye concentration: 10 mg/L.

2.2.4. Effect of catalyst mass

The effect of the catalyst mass was investigated, keeping operational parameters identical to those of the above-mentioned experiment. The following catalyst quantities have been used: 0.05; 0.1; 0.3; 0.5; 0.8 g. The results are illustrated in Fig. 5.

These results show that the decolorization efficiecy of NBB oxidation increase when increasing the catalyst mass up to 0.3 g where the decolorization efficiecy is optimal. Beyond this value, there is a decrease of the decolorization efficiecy. The excess of the catalyst does not appear to ply a positive role in the NBB oxidation using $P_2W_{12}Mo_5Fe/H_2O_2$ system.

This result is in good agreement with literature [18]: the decrease of the discoloration efficiency of

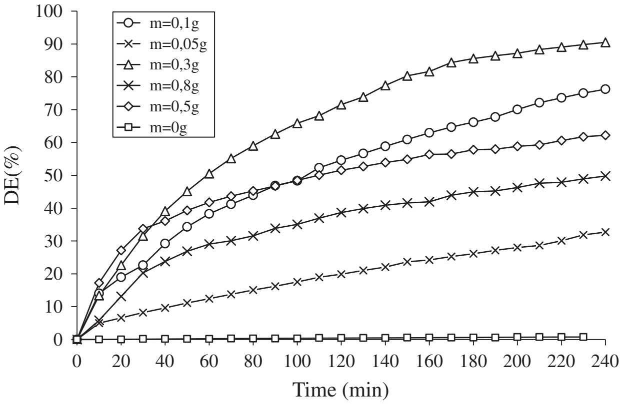

Fig. 5. Effect of catalyst mass on decolorization of NBB. *Conditions*: temperature: 25°C; H_2O_2 concentration: 1 mM; pH = 3; dye concentration: 10 mg/L.

NBB when increasing the mass of the catalyst can be explained by the presence of side reaction consuming the radical's hydroxyls. The mass of catalyst that gives the best result is 0.3 g.

2.2.5. *Effect of H_2O_2 concentration*

To determine the effect of H_2O_2 concentration on kinetics of NBB oxidation, a series of experiments at different H_2O_2 concentrations were carried out: (10^{3-}; 2. 10^{3-}, 3. 10^{3-}; 5. 10^{3-}; 9. 10^{3-}; 10^{2-}) M. The results are illustrated in Fig. 6.

The results indicate that the degradation of NBB was increased by increasing the concentration of H_2O_2 up to a value of concentration of H_2O_2 equal to 2 mM. This may be due to recombination of hydroxyl radicals and also hydroxyl radicals reaction with H_2O_2, contributing to the $^{\cdot}$OH scavenging capacity (Eqs. (2)–(4)) [19].

$$H_2O_2 + OH^{\cdot} \rightarrow H_2O + HO_2^{\cdot} \tag{2}$$

$$HO_2^{\cdot} + OH^{\cdot} \rightarrow H_2O + O_2 \tag{3}$$

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2 \tag{4}$$

It can be postulated that H_2O_2 should be added at an optimum concentration to achieve the best degradation. Hence, 2 mmol/L of H_2O_2 appears as an optimal.

2.2.6. *Effect of the NBB concentration:*

It is important from an application point of view to study the dependence of removal efficiency on the initial concentration of the colorant NBB.

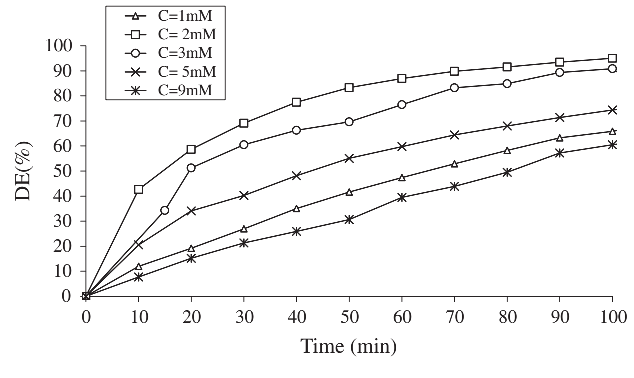

Fig. 6. Effect of H_2O_2 concentration on decolorization of NBB.
Conditions: temperature, 25°C; catalyst mass, 0.3 g; pH = 3; dye concentration: 10 mg/L.

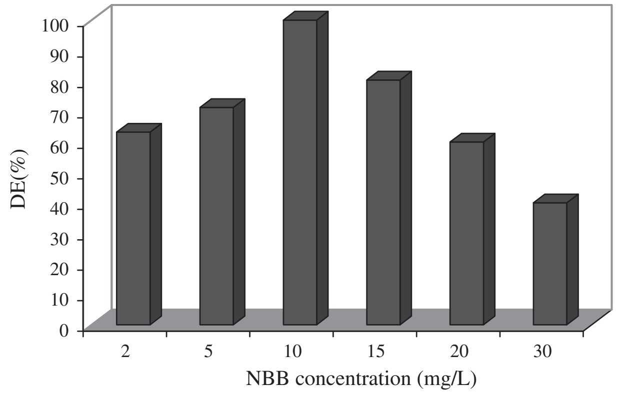

Fig. 7. Effect of dye concentration on decolorization of NBB.

To determine the effect of NBB concentration on oxidation reaction kinetics, a series of experiments was realized between 2 and 30 mg/L. The results are represented in Fig. 7.

From this figure, we can note that the discoloration efficiency decreases with increasing the initial concentration of the dye. At low concentration of substrate, the discoloration efficiency is higher compared to that at higher concentration, whereas the discoloration efficiency increases with an increase in the initial concentration of substrate. The presumed reason is that when the initial concentration of the colorant increased, the hydroxyl radical concentrations remain constant for all colorant molecules and hence, discoloration efficiency decreases [20,21].

2.2.7. *UV–vis absorbance spectra of dye before and after oxidation using Fe(III)$P_2W_{12}Mo_5$/H_2O_2*

The UV–vis absorbance spectra of the NBB before and after oxidation areshown in Fig. 8. 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 the n/p* transitions in benzene and naphthalene rings of azo dyes. The decrease in this absorbance indicates the degradation of the aromatic part of the dye. These results are in agreement with the results reported in case of photocatalytic discoloration and degradation of azo dyes [22].

2.2.8. *Possible reaction mechanism*

It was shown [23] that the action of H_2O_2 on a complex containing Fe^{3+} results in the reduction of Fe^{3+} to Fe^{2+} with apparition of $HO_2^{\cdot}$.

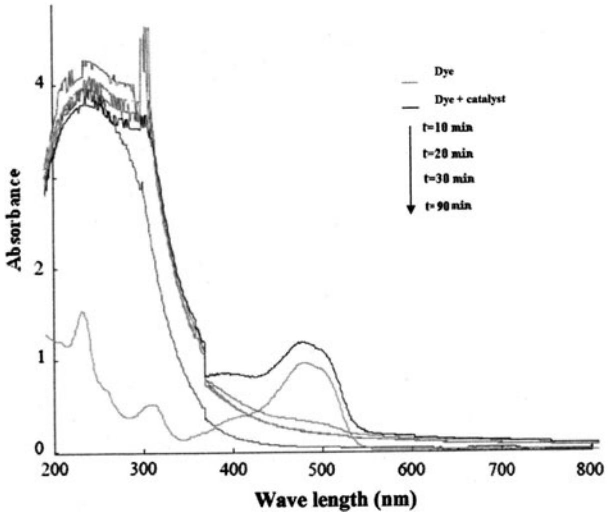

Fig. 8. UV–Vis spectra of NBB water solutions during the treatment process with Fe(III)$P_2W_{12}MO_5/H_2O_2$ system.

The action of H_2O_2 on the complex of Fe^{2+} leads to the generation of hydroxyl radicals $OH^{\cdot}$. These hydroxyl radicals cause the degradation of the dye.

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

$$P_2W_{12}Mo_5Fe^{3+} + H_2O_2 \longrightarrow P_2W_{12}Mo_5Fe^{2+} + HO_2^{\cdot} \quad (5)$$

$$P_2W_{12}Mo_5Fe^{2+} + H_2O_2 \longrightarrow P_2W_{12}Mo_5Fe^{3+} + 2OH^{\cdot} \quad (6)$$

3. Conclusion

The Fe(III)$P_2W_{12}Mo_5/H_2O_2$ system is a new homogeneous Fenton-like system that is capable of oxidizing organic dye compounds. The experimental results show that the initial pH, the initial concentration of H_2O_2, Fe(III)$P_2W_{12}Mo_5$, and NBB concentration had a great influence on the degradation of NBB dye. The optimal values of operating parameters during the oxidation of the NBB dye by the Fe(III)$P_2W_{12}MO_5/H_2O_2$ system are pH: 3, $[NBB]_0 = 10\,mg/L$, Catalyst $[\alpha_2\ K_7P_2W_{12}Mo_5Fe,\ 18H_2O]^{7-}$ mass: 0.3 g, $[H_2O_2]_0 =$: 2 mM.

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