Effect of the Operating Parameters on the Discoloration of the Black Azo Dye Blue Naphtol (NBB) by the Fenton Process

Effet des paramètres operatoires sur la décoloration d'un colorant azoique noir bleu naphtol (NBB) par le procédé fenton

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ABSTRACT

The effluents loaded with synthetic and natural dyes are difficult to remove; therefore it becomes necessary to find alternative methods to treat dyes that are recalcitrant to conventional treatments. Nowadays, Advanced Oxidation Processes (AOPs) are increasingly used and Fenton process is one of these technologies. In this work, the discoloration of Naphtol Blue Black (NBB) by Fenton process was studied. The Effects of operating parameters such as the nature of the acid and pH, the concentrations of hydrogen peroxide, iron and dye, temperature and stirring speed, the presence of salts, anions, metallic cations and the influence of real matrices, were examined. For a initial concentration of NBB equal to 30 mg/L, an efficiency of 98 % was obtained under pH = 3, SS = 250 rpm and [H_2O_2] = 55 mg/L.

Les effluents chargés de colorants synthétiques et naturels sont difficiles à éliminer. Il devient donc nécessaire de trouver d'autres méthodes pour traiter les colorants qui sont récalcitrants aux traitements conventionnels. De nos jours, les procédés d'oxydation avancés (POA) sont en plein essor et le procédé Fenton est l'une de ces technologies. Dans ce travail, on a étudié la décoloration du Naphtol Blue Black (NBB) par le procédé Fenton. Les effets des paramètres opératoires tels que la nature de l'acide et du pH, les concentrations de peroxyde d'hydrogène, de fer et de colorant, la température et la vitesse de rotation, la présence de sels, d'anions, des cations métalliques et l'influence de matrices réelles ont été examinés. Dans les meilleures conditions opératoires, pH = 3, vitesse d'agitation = 250 rpm, [H_2O_2] = 55 mg/L, une efficacité de 98% a été obtenue.

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1. INTRODUCTION

The use of dyes is increasing day after day worldwide due to the tremendous acceleration of the industrialization and the growing need for a variety of colors. As a result, huge amounts of wastewater contaminated with organic dyes and chemicals are released into the environment provoking water pollution. Azo dyes are commonly used in leather, paper and textiles industries due to their wide range of colors. They are stable, easily modifiable structurally and have a great capacity to bind to most synthetic fibers [1]. Despite of that 20 to 40 % of the initial dye may remain unbound and eventually end up in the effluent [2]. The continuous release of unused dyes into water plants, introduces these harmful toxic chemicals to the aquatic life, humans and animals as well as negative aesthetic damage of sites and eutropication phenomena [3-5]. In addition, dyes and their intermediates are also mutagenic and carcinogenic [6]. It is therefore urgent to maintain a clean environment for the survival of aquatic and terrestrial animals. This has forced many governments to establish environmental restrictions and laws regarding the quality of the wastewater discharged by industries into natural flows.

An effective treatment and elimination of the color require the rupture of the dye's chromophore. The most important chromophores in dyes are: azo (–N = N–), carbonyl (–C = O), nitro (–N=O) and quinoids [7]. One of the most promising pathways for the degradation of these pollutants is their conversion to the most stable oxidation state; namely CO_2, H_2O and inorganic anions. In this context, advanced oxidation processes (AOPs) have emerged as a promising technology for wastewater treatments [8]. AOPs oxidation processes are methods that rely on the formation of highly reactive chemical entities. This is the in situ formation of $^{\bullet}OH$ (hydroxyl radicals) which have a higher oxidizing power than traditional oxidants, such as Cl_2, ClO_2 or O_3. These radicals are capable of partially or totally mineralizing most organic compounds and the final products are simple organic compounds such as mentionned above CO_2 and H_2O [9-11].

The Fenton process was discovered by Fenton in 1894. The Fenton reagent is a mixture of hydrogen peroxide and ferrous iron for the oxidation of organic compounds [12]. In 1934, Fritz Haber and Gerber Weiss (Fritz Haber holds the Nobel Prize in Chemistry in 1918) discovered that the ferrous ion catalyzes the decomposition of peroxide, thus generating hydroxyl radicals. The latter involve a complex reaction sequence in an aqueous solution [13-14]:

$$Fe^{3+} + O_2^{\bullet -} \rightarrow Fe^{2+} + O_2 \qquad (1)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \qquad (2)$$

Reaction of Fenton and Gerber Weiss:

$$O_2^{\bullet -} + H_2O_2 \rightarrow O_2 + OH^- + {}^{\bullet}OH \qquad (3)$$

2. MATERIAL AND METHODS

2.1. Chemical products

Naphtol blue black supplied by Sigma-Aldrich (C.I. 20470) with molecular formula $C_{22}H_{14}N_6Na_2O_9S_2$ (FW 616.49) was used as molecule test for dye discoloration. The other chemicals such as iron sulfate, hydrogen peroxide, various acids, salts, metal salts used in this work were supplied either by Sigma-Aldrich or Biochem-Chemopharma, they are high purity products. The solutions of Naphtol Bleu Black were prepared at different concentrations in distilled water and were homogenized by stirring until the dye was completely dissolved. The pH of the reaction mixture was adjusted by adding nitric acid and measured by a brand pH meter (Eutech instruments).

2.2. Procedure

The oxidation of the dye was carried out using Fenton's reagent which was composed of a mixture of $FeSO_4.7H_2O$ and hydrogen peroxide. The required amounts of Fe^{2+} and H_2O_2 were added to the dye solution simultaneously, the experimental device consisted of a perfectly discontinuous reactor with a capacity of 1000 mL and into which 500 mL of the solution were introduced (Fig.1). The temperature of the reaction was controlled by a thermostated bath (Tectron Bio Selecta). The stirring was continuous and maintained using a mechanical stirrer (Janke & Kunkel RW 20), ensured with a four bladed empeler inclined at 45°.

The kinetics and the oxidation efficiency of the dye were monitored by a series of samples taken at well-defined time intervals. The residual concentration of the dye in the solution at different times was determined by UV-visible spectroscopy. The concentration was determined from a calibration curve produced at pH 3 and a wavelength which corresponds to the maximum of absorbance (λ=619 nm), using a G705 Jenway spectrophotometer (Fig. 2). The resolution of the wavelength and the bandwidth were 1 nm and 0.5 nm respectively, the cell was based on quartz and a thickness of 1 cm.

The rate of degradation or abatement of the color was calculated according to the equation:

$$Y_{col} = (1 - C_{tf}/C_{to})*100 \tag{4}$$

where C_{tf} and C_{to} correspond respectively to the concentrations at final and initial times.

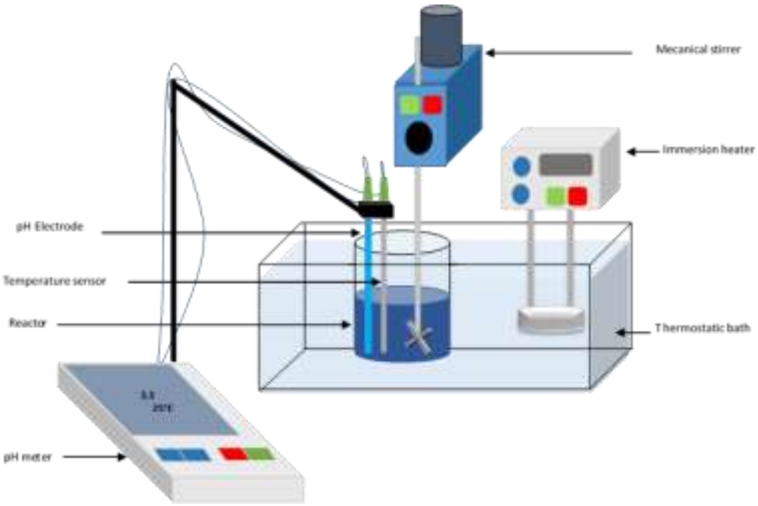

Figure 1. Experimental setup of the Fenton process

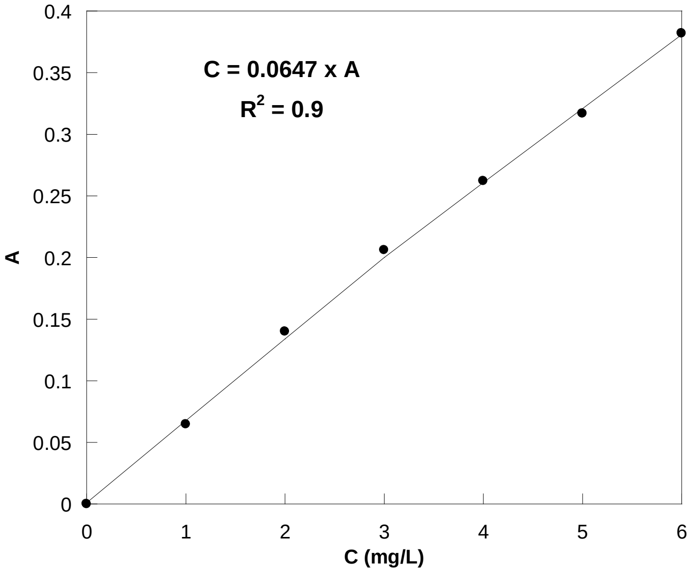

Figure 2. Calibration curve of NBB

3. RESULTS AND DISCUSSION

3.1. Influence of the nature of the acid

The results obtained show that the presence of phosphate ions leads to a remarkable decrease of the discoloration efficiency and that within 20 minutes of contact time, the efficiency was 51 % instead 90 %, the final yield was only 69 % (Fig. 3). In the case of the other ions studied, the removal efficiency of the pollutant was greater than 90 % within 20 minutes and ended with a final yield of 98 % after 60 minutes of contact time with more or less rapid kinetics relative to each other.

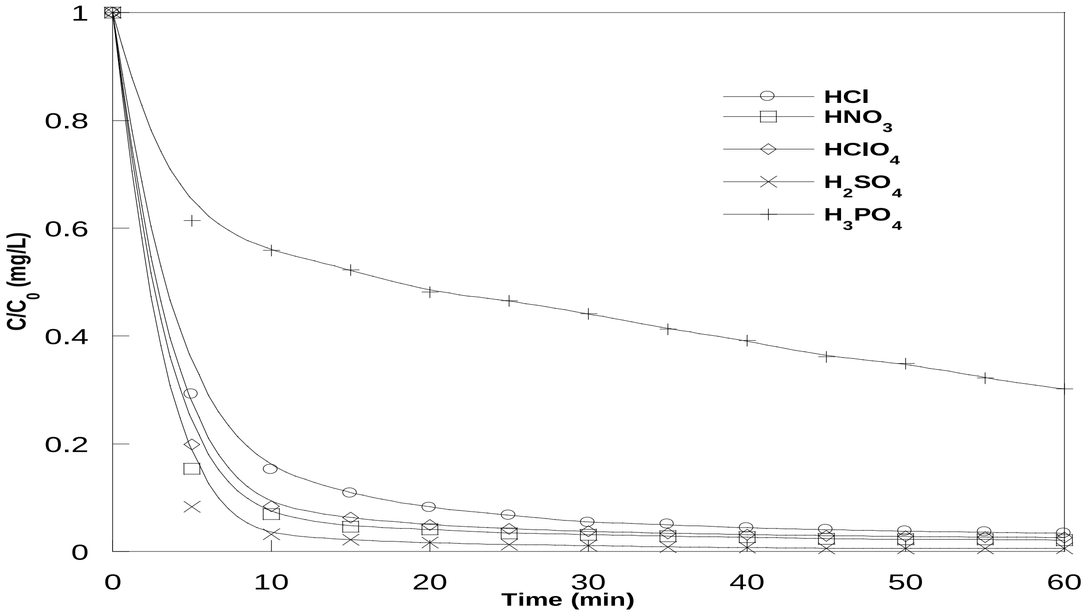

Figure 3. Effect of the used acid to adjust pH, on the kinetic degradation of NBB
([NBB] = 30 mg/L, $[Fe^{2+}]$ = 3 mg/L, $[H_2O_2]$ = 50 mg/L, pH = 3, T = 25±2°C, SS = 250 rpm)

To shed light on the effect, Bouasla and al., [15] plotted curves of discoloration efficiency as a function of time, also histograms of the rate constants for the discoloration of Methyl Violet and Acid Yellow. They found the following classification, based on the value of the apparent rate constant k_{app}

- For Methyl Violet :

$k_{app}(H_2SO_4) > k_{app}(HNO_3) > k_{app}(HCL) > k_{app}(H_3PO_4)$

- For Acid Yellow :

$k_{app}(H_2SO_4) > k_{app}(HCL) > k_{app}(HNO_3) > k_{app}(H_3PO_4)$

Similar results were found by Pignatello and al., [16] so it can be concluded that the presence of the sulfate ions SO_4^{2-} and nitrates NO_3^-, has a negligible effect on the degradation efficiency. On the other hand, the presence of phosphate ions PO_4^{3-} influences the yield and the kinetics of the reaction, this can be explained by two ways [17, 18]:

- The phosphate ions can trap hydroxyl radicals according to the reactions:

$$OH^{\bullet} + H_2PO_4^- \rightarrow H_2PO_4^{\bullet} + OH^- \quad (5)$$
$$OH^{\bullet} + H_2PO_4^{3-} \rightarrow H_2PO_4^{2-} + OH^- \quad (6)$$

- The phosphate ions can complex the ferrous and ferric ions responsible of the production of hydroxyl radicals according to the reactions:

$$Fe^{2+} + H_2PO_4^- \rightarrow FeH_2PO_4^+ \quad (7)$$
$$Fe^{3+} + H_2PO_4^- \rightarrow FeH_2PO_4^{2+} \quad (8)$$

The chloride ions Cl^- influence the yield and the kinetics of the reaction. Their influence will be discussed in the study of the influence of salts. From these results we can conclude that nitric acid HNO_3 has no effect and so it will be used in the rest of the study.

3.2. Influence of the initial pH of the solution

The maximum of discoloration was 99 %. Good efficiency (around 93%) was obtained at pH 3.5 and 4 but the reactions took longer time (50 min) when compared to the discoloration at pH 3 (Fig. 4). It was reported that pH 3 was the most effective in degrading organic matter [19-20].

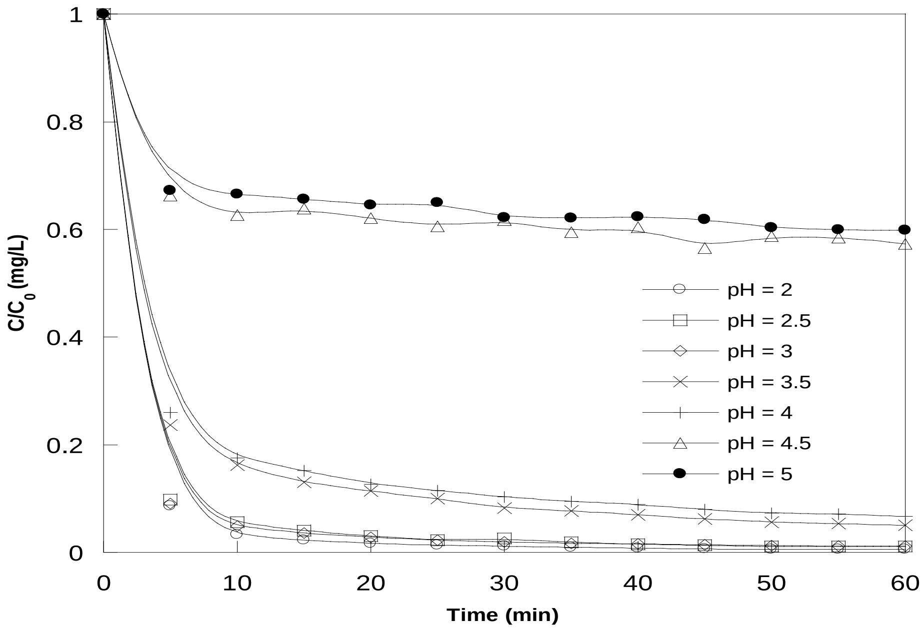

Figure 4. Effect of pH on the kinetics of the NBB degradation
([NBB]0=30 mg/L, $[Fe^{2+}]$=3 mg/L, $[H_2O_2]$=50 mg/L, pH=2-5, T=25±2°C, SS=250 rpm)

Knowing that H_2O_2 and Fe^{2+} ions are very stable at low pH, optimal degradation of other organic pollutants by the Fenton process was obtained at pH 3. These results were reported by several other studies [21, 22]. For pH values ranging from 4.5 to 5 the discoloration efficiency decreases significantly from 98% to 40% after 60 min. Similar numerous results have revealed that the degradation of organic dyes by the Fenton process is mainly regulated by pH. It is effective between pH 2 and 4, generating the optimal amount of hydroxyl radicals necessary for degradation. Low pH value (below 2) leads to the formation of complexes with iron, the formation of oxonium ions ($H_3O_2^+$) and the trapping of hydroxyl radicals by H^+ ions. The main reason for reduced efficiency in very acidic solutions is the formation of oxonium ions. This reaction reduces the concentration of H_2O_2 useful for the generation of hydroxyl radicals [20, 23]. The amount of hydroxyl radicals ($^{\bullet}OH$) produced according to the reaction (9) is significant at optimal pH due to the strong regeneration of the hydrogen peroxide molecules. Thus, the solubility balance can be controlled by ferrous ions and ferric hydroxides [24].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (9)$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {}^{\bullet}O_2H + H^+ \quad (10)$$

However, at pH above 4, the efficiency of degradation decreases significantly. This is due to the precipitation of ferric cations by hydroxyl ions forming the complex ($Fe(OH)_3$) and the equilibrium is controlled only by ferric hydroxide. The latter reduces the rate of decomposition of hydrogen peroxide [24]. At higher pH values (pH>5), the efficiency of the Fenton process decreases even more. Hydrogen peroxide becomes unstable in solution and decomposes into molecular oxygen quickly. Consequently, the formation of hydroxyl radicals is reduced.

Some attempts have been made to increase the transformation of Fe^{3+} into Fe^{2+} by using chelating or reducing agents. Hydroxylamine is an inorganic reducing agent of Fe^{3+} has reducing activity over a wide pH range. The presence of hydroxylamine facilitates the generation of Fe^{2+} in a Fenton system and thereby increases the working pH range to 5.7 [7,25].

3.3. Effect of the concentration of hydrogen peroxide

Increasing the concentration of hydrogen peroxide [H_2O_2] enhances the efficiency of the Fenton process (Fig. 5). After 10 minutes, the degradation efficiency increases from 68.7 % corresponding to a peroxide concentration equal to 5 mg/L, up to 96.2 % for a peroxide concentration equal to 50 mg/L. The concentration of hydrogen peroxide increases the elimination of the pollutant because this increase is mainly attributed to the accelerated reactions of Fenton and to the generation of later hydroxyl radicals [26].

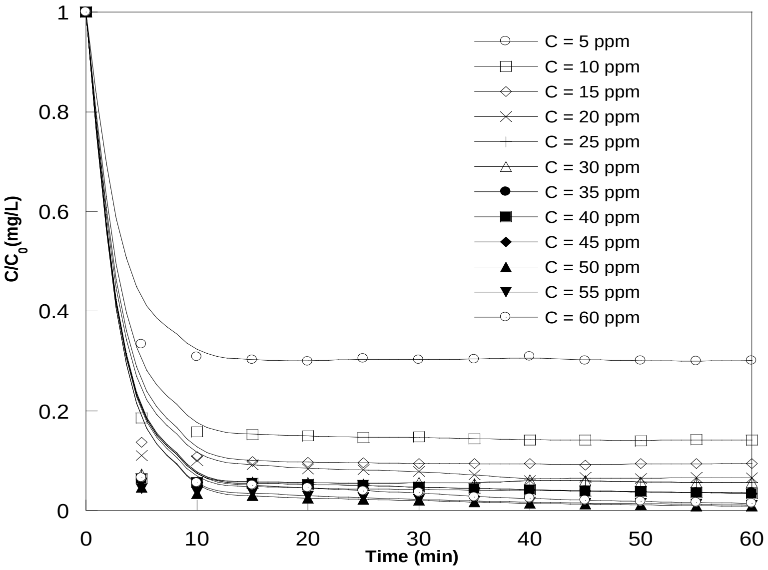

Figure 5. Effect of the concentration of H_2O_2 on the kinetics of the degradation of NBB ([NBB]=30 mg/L, [Fe^{2+}]=3 mg/L, [H_2O_2]=5-60 mg/L, pH=3, T=25±2°C, SS=250 rpm)

A decrease in the efficiency of the Fenton process has been observed with an increase in the concentration of hydrogen peroxide from 55 mg/L due to the reaction between hydrogen peroxide and hydroxyl radicals as in the reaction (11) [26]. The recombination of hydroxyl radicals at high concentration of hydrogen peroxide reaction (12) is similar to the other trapping reaction which reduces the efficiency of the Fenton process. Similar results were observed by other authors [20,27,28].

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet} \quad (11)$$
$$^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \quad (12)$$

Similar trend and results have been published [24,29] where the discoloration efficiency increased from 26.6 % to 84.3 % within 15 minutes when the concentration of H_2O_2 increased from 0.02 M to 0.4 M.

3.4. Influence of iron concentration

The results show that the addition of ferrous ions even at low concentrations leads to the degradation of NBB with an efficiency of 78 % within 60 min of contact time for a concentration of Fe^{2+} of the order of 1 mg/L. The addition of Fe^{2+} ions at a concentration of 3 mg/L achieves discoloration efficiency in the order of 98 % after 20 min of treatment. Indeed, the addition of ferrous ions promotes the generation of hydroxyl radicals in the solution according to the Fenton reaction (equation 2) [30].

The formed ferric iron can then react with hydrogen peroxide to regenerate the ferrous iron:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \quad (13)$$

On the other hand, Figure 6 shows that the kinetics of degradation of NBB varies according to the initial concentration of ferrous iron. Indeed, increasing the concentration of Fe^{2+} ions from 1 to 3 mg/L, increases the effectiveness of discoloration from 78 to 98 % after 20 min of treatment. For values ranging from 3 to 10 mg/L, the addition of Fe^{2+} has no longer influence on the kinetics or on the effectiveness of the treatment.

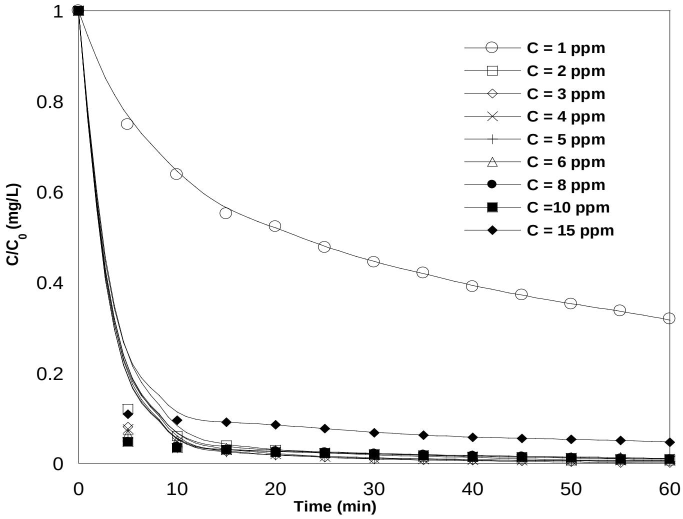

Figure 6. Effect of the concentration of ferrous ions on the kinetics of the degradation of NBB ([NBB]=30 mg / L, $[Fe^{2+}]$=1-15 mg / L, $[H_2O_2]$=50 mg / L, pH=3, T=25 ± 2°C, SS=250 rpm)

However, the excessive addition of the catalyst affects negatively the degradation efficiency of the dye. The use of 15 mg/L of Fe^{2+} ions decreases the efficiency of degradation from 98 to 90 % within 20 min of treatment. This phenomenon was observed in other research works using the Fenton method [31-34]. In fact, it was reported that excess of ferrous ions consumed hydroxyl radicals (scavenging effect) according to the reaction (14):

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \quad (14)$$

Grymonpré et al. [35] worked on the degradation of pesticides such as chlortoluron, carbofuran and bentazone in aqueous media by advanced oxidation processes. They confirmed that the use of a high concentration of iron as a catalyst results in a decrease of the efficiency due to the parasitic reaction (14) which takes place between ${}^{\bullet}OH$ and Fe^{2+}. However, after the first 5 minutes of reaction, the reaction mechanism is independent of the system chosen because Fe^{3+} predominates in both cases.

3.5. Influence of the temperatue

From Figure 7 it can be seen that the higher the temperature, the faster the degradation kinetics. In fact the increase of the temperature accelerates the reaction between hydrogen peroxide and ferrous iron in all its forms, thus it makes it possible to produce more hydroxyl radicals and therefore to obtain faster kinetics and higher efficiency [37-39].

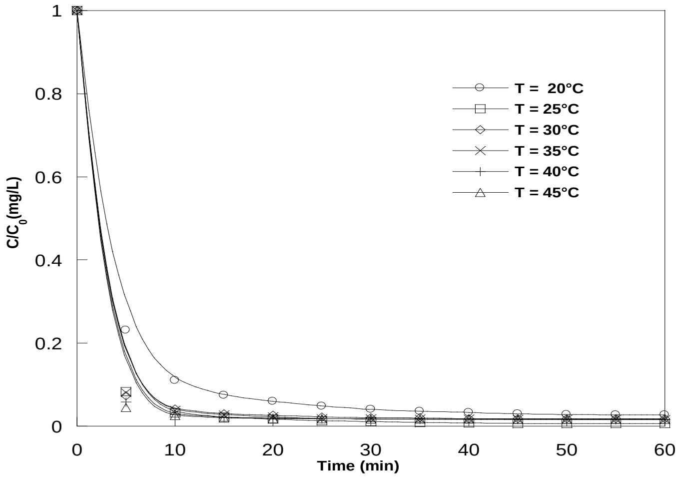

Figure 7. Effect of temperature on the kinetics of NBB degradation ($[NBB]_0$=30 mg/L, $[Fe^{2+}]$=3 mg/L, $[H_2O_2]$=50 mg/L, pH=3, T = (20-45) ± 2°C, SS=250 rpm)

Therefore, the temperature acts positively on the kinetics of degradation. Sufficient temperature is necessary for the oxidation reactions to take place. Thus, a study has shown that a temperature of +4°C inhibits the mineralization of benzo [a] pyrene [40]. Above 55°C the temperature favors the decomposition of hydrogen peroxide into oxygen and water which will influence the degradation [38]. Other work has found that Methyl Violet degrades better at an optimal temperature of 50°C [41]. On another study, the temperature range 60-70°C was found to be optimal for the degradation of acid Yellow 99 [42]. Generally, temperatures above 60°C are no longer used [43] because the process becomes energy intensive.

3.6. Influence of stirring speed

From Figure (8) it can be seen that the stirring speed plays a very important role on the kinetics of the reaction without affecting the final yield. In the absence of stirring, we notice that the kinetic is very slow compared to the stirred solutions. A final yield greater than 98 % was obtained after 55 min in the absence of stirring and after 20 min at higher values up to 250 rpm after which no influence of stirring could be observed.

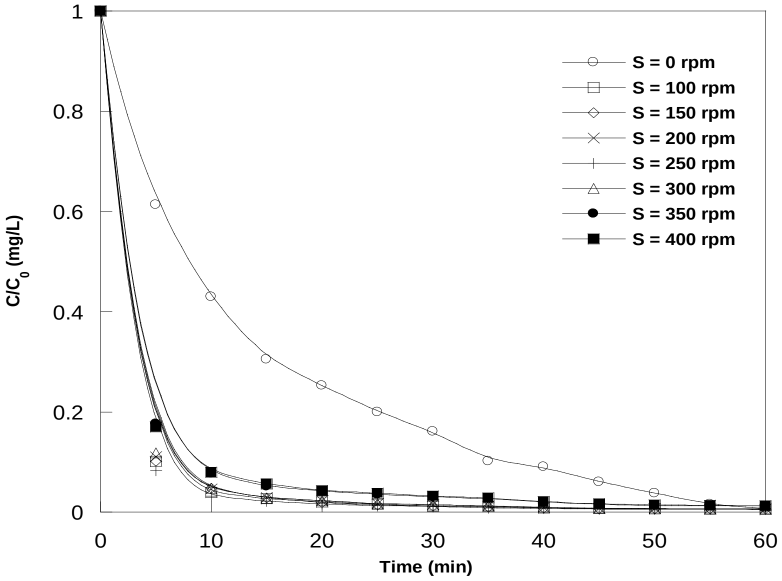

Figure 8. Effect of the stirring speed on the kinetics of NBB degradation
([NBB]=30 mg / L, [Fe^{2+}]=3 mg / L, [H_2O_2]=50 mg / L, pH=3, T=25 ± 2°C, SS=(250-400) rpm)

In general, the agitation improves the homogenization and mass transfer between the different chemical species. When stirring increases it is accompanied by the rapid increase of the discoloration. High speeds lead to the suction of gases such as CO_2 and O_2 under the influence of agitation. The dissolved CO_2 in the solution produces HCO_3^- and CO_3^{2-} ions (reactions 15 and 16). These ions are capable to complex ferrous iron (reactions 16-19) [15].

$CO_2 + H_2O \rightarrow HCO_3^- + H^+$ (15)
$HCO_3^- \rightarrow CO_3^{2-} + H^+$ (16)
$Fe^{2+} + HCO_3^- \rightarrow Fe\,HCO_3^+$ (17)
$Fe^{2+} + HCO_3^{2-} \rightarrow Fe\,HCO_3$ (18)
$Fe^{2+} + 2\,HCO_3^- \rightarrow Fe\,(HCO_3)_2$ (19)
$Fe^{2+} + CO_3^{2-} + OH^- \leftrightarrow Fe\,(CO_3)\,(OH)^-$ (20)

Likewise, they can also trap hydroxyl radicals and reduce the efficiency of the process according to equations (21) and (22) [11]:

$^{\bullet}OH + HCO_3^- \rightarrow H_2O + CO_3^{\bullet-}$ (21)
$^{\bullet}OH + HCO_3^{2-} \rightarrow OH^- + CO_3^{\bullet-}$ (22)

3.7. Influence of dye concentration

As shown in Figure 9, the color removal efficiency decreased gradually with increasing initial dye concentration. This is due to the unavailability of a sufficient amount of hydroxyl radicals. This could be due to the fact that increasing the concentration of dye means an increase in the number of molecules of the dye while the number of $^{\bullet}OH$ remained the same. It is known that the lower the dye concentration, the faster the discoloration. In our case 20 minutes were sufficient to discolor the dye with a concentration lower than 40 mg/L.

Another work has shown the dependence of the bleaching efficiency as a function of the initial concentration of the dye, in the range 2.10^{-5} - 10^{-4} M with hydrogen peroxide of 0.2 M and a catalyst amount of 0.1 g. It was observed a decrease in bleaching efficiency as the dye concentration increases [29]. Other studies have obtained an efficiency of 78.2 % after 10 min of contact time for a dye concentration equal to 2.10^{-5} M. An efficiency of 92.8 % was obtained after 60 min of contact for an initial dye concentration equal to 10^{-4} M [44].

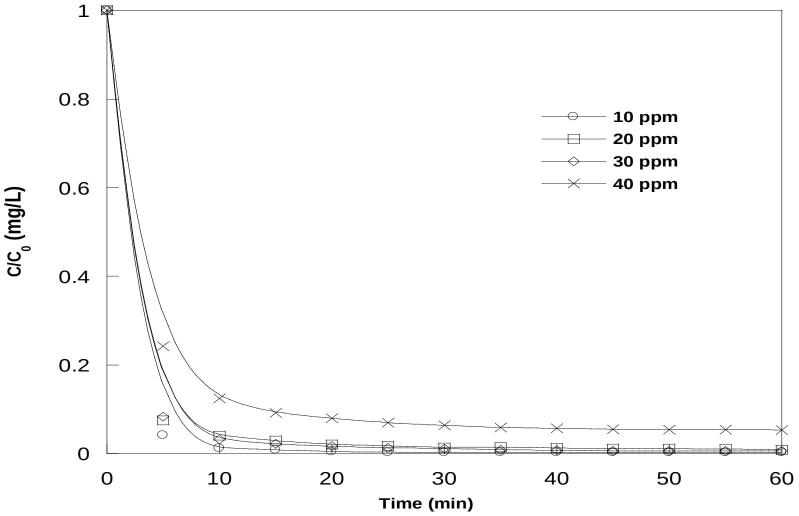

Figure 9. Effect of the initial concentration of the pollutant on the kinetics of NBB degradation ([NBB]=10-40 mg/L, [Fe^{2+}]=3 mg / L, [H_2O_2]=50 mg / L, pH=3, T=25 ± 2 ° C, SS=250 rpm)

Other results found in literature are similar to our results. Hassan H. et al. have shown that for constant concentrations of hydrogen peroxide and iron and due to a high concentration of pollutant, the degradation efficiency has decreased considerably [45]. Bouasla and al., obtained similar results during the degradation of Methyl violet 6B by the Fenton process [15]. The same result was also reported by Lounis et al. during the degradation of orange acid by the same process [46].

Wycliffe et al. investigated the degradation of textile effluents by enzymes [47]. They found that for all of the initial concentrations studied, the degree of discoloration was rapid during the initial period of contact time (40 hours), after which the rate of discoloration gradually decreased with increasing concentration of the pollutant. This can be attributed to the higher dye concentrations, the efficiency of enzymes to recognize dye molecules as substrate decreases, which in turn lowers the rate of reaction.

3.8. Influence of real matrices

According to figure (10) the degradation of the dye in spring water has no effect on the degradation and we manage to have an efficiency level greater than 90 % in the first 20 minutes, something promising for this process to be actually applied in the decontamination of spring waters.

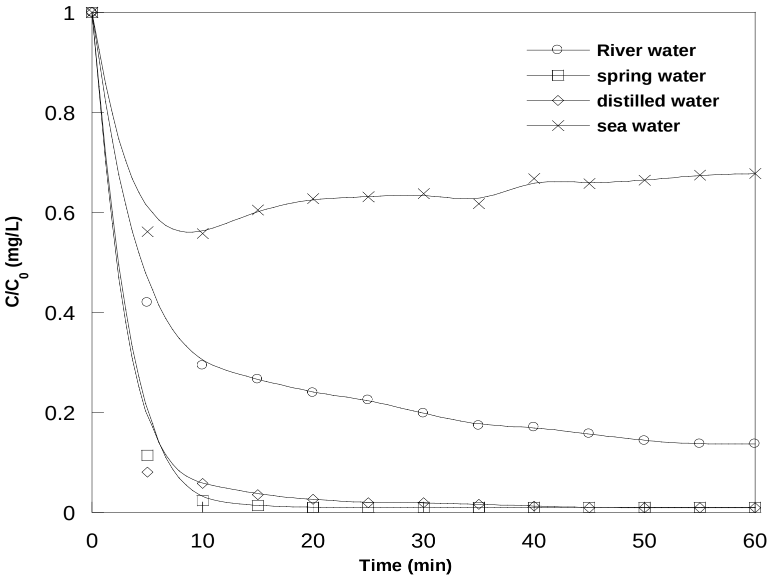

Figure 10. Effect of real matrices on the degradation of NBB
([NBB]=30 mg/L, $[Fe^{2+}]$=3 mg/L, $[H_2O_2]$=50 mg/L, pH=3, T=25±2°C, SS=250 rpm)

For the river water, we notice that the degradation has been inhibited and after 20 minutes the kinetics became slow, we reached an efficiency of only 72 %, while for spring water and distilled water, an efficiency level greater than 90 % was obtained with a final yield equal to 81.6 %. This can be explained by the presence of the phosphate ions in the river water. For the seawater, the degradation was inhibited from the first minutes, only 32 % of the dye has been removed, this inhibition of degradation can be explained by the presence of salts which can complex iron and trap hydroxyl radicals [48]. To fully explain this inhibition of the degradation of NBB in seawater and river water, the study of the influence of salts and metals is then necessary.

3.9. Influence of adding salts

Figure (11) shows that in the presence of NaCl, the degradation efficiency of the dye decreased dramatically due to the addition of 2 g/L of NaCl. This behavior can be attributed to the trapping of $^{\bullet}OH$ radicals by the Cl^- ion.

We know that Cl^- reacts with the $^{\bullet}OH$ radical thus forming the $OHCl^{\bullet}$ radical according to reaction (23) with a reported rate constant of 3.0×10^9 M^{-1} s^{-1} at pH between 2 and 3 [49, 50]. The $OHCl^{\bullet -}$ radical generated is less reactive than the $^{\bullet}OH$ radical, which results in slower degradation of the NBB dye.

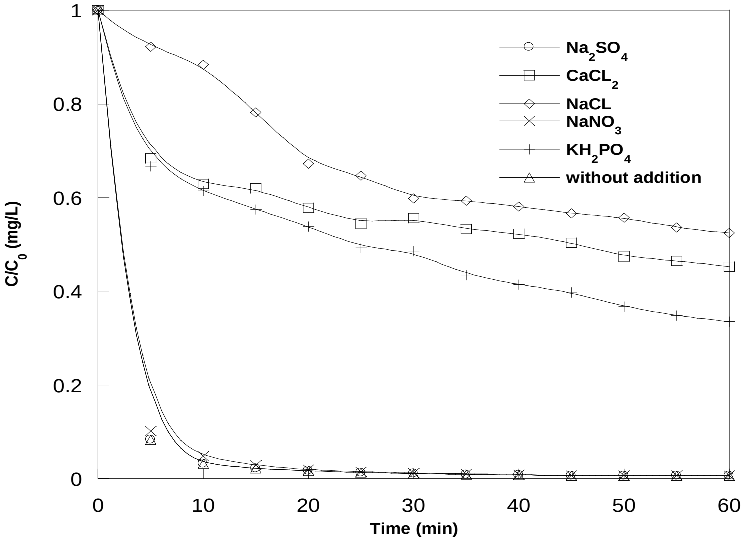

Figure 11. Effect of adding salts on the kinetics of NBB degradation
([NBB]=30 mg/L, $[Fe^{2+}]$=3 mg/L, $[H_2O_2]$=50 mg/L, pH=3, T=25 ± 2 ° C, SS=250 rpm)

$$Cl^{-} + {}^{\bullet}OH \rightarrow OHCl^{\bullet} \quad (23)$$

Cl^{-} ions can also decrease the degradation efficiency by complexing iron and forming complexes according to the following reactions:

$$Fe^{2+} + Cl^{-} \leftrightarrow FeCl^{+} \quad (24)$$
$$Fe^{3+} + Cl^{-} \leftrightarrow FeCl^{2+} \quad (25)$$
$$Fe^{3+} + 2\,Cl^{-} \leftrightarrow FeCl_2^{+} \quad (26)$$

3.10. Effect of nitrate ions

From Figure (11) we see that effects of nitrate ions on the degradation efficiency of NBB by the Fenton process are negligible. Previous reports have shown the same results [52, 41, 46]. This is due to the fact that nitrate ions do not react with ferrous iron with hydroxyl radicals to form complexes or [52].

Elmorsi et al. [53] investigated the discoloration of Mordant red 73 in water under H_2O_2/UV and photo-Fenton treatment. They found that in the presence of 0.05 g/L of NO_3^{-}, the rate constant decreased by about 50 %, from 0.081 (in the absence of NO_3^{-}) to 0.041 min^{-1}. This can be attributed to the trapping of ${}^{\bullet}OH$ radicals by NO_3^{-} ions thus reducing the availability of ${}^{\bullet}OH$ radicals for the photodegradation process. However, by increasing the NO_3^{-} concentration from 0.05 to 1 and from 1 to 2 g/L, the constant photodegradation rate increased to 0.057 and to 0.053 min^{-1} respectively. The irradiation of the NO_3^{-} ion can produce ${}^{\bullet}OH$ radicals due to the rapid protonation of $O^{\bullet-}$ produced as follows:

$$NO_3^{-} + light \rightarrow NO_3^{\bullet -} \rightarrow NO_2^{-} + O^{\bullet -} \quad (27)$$
$$O^{\bullet -} + H_2O \rightarrow {}^{\bullet}OH + OH^{-} \quad (28)$$
$$NO_2^{-} + {}^{\bullet}OH \rightarrow NO_2^{\bullet} + OH^{-} \quad (29)$$

It seems that at a low concentration of NO_3^{-} the trapping effect (equation 29) by the chemically generated NO_3^{-} photo (equation 27) is predominant while, at higher concentrations, the competitive reactions become predominant leading to the production ${}^{\bullet}OH$ radicals (equation 28) which contribute to improving the discoloration rates.

From Figure 11, we also notice that the addition of sulfate ions does not affect the degradation efficiency of NBB. This result is confirmed by several works in the literature [15, 46, 42]. In very acidic media (pH 3), SO_4^{2-} ions can be transformed into $SO_4^{\bullet -}$ and $S_2O_8^{2-}$ [51] according to the reactions below, their oxidizing power is 2.60 V [46].

$$2\,SO_4^{2-} \rightarrow S_2O_8^{2-} + 2\,\bar{e} \quad (30)$$
$$SO_4^{2-} + {}^{\bullet}OH \rightarrow SO_4^{\bullet -} + OH^{-} \quad (31)$$

Under neutral or alkaline conditions (pH 7.0 and 9.0), the sulphate radicals can convert to hydroxyl radicals according to the equation (32):

$$SO_4^{\bullet -} + H_2O \rightarrow HSO_4^{-} + {}^{\bullet}OH \quad (32)$$

In the case of hydrophosphate ions, the oxidation is clearly inhibited, and the efficiency of degradation decreases significantly. The inhibiting effect of anions on the degradation rates of organic compounds depends not only on the phenomenon of trapping of ${}^{\bullet}OH$ radicals but also on the complexation of ferrous ions, the ions which are involved in the generation of ${}^{\bullet}OH$ radicals. At $pH \leq 3$, phosphate exists mainly in the form of $H_2PO_4^{-}$ and can also give complex reactions with ferrous and ferric ions, reactions (7) and (8). These complexes delay the reaction, preventing the production of hydroxyl radicals and reducing the rate of oxidation [54].

3.11. Influence of metallic cations

From Figure 12, it is clear that the decrease of the kinetics and the degradation performance of the dye depend on the nature of the metal used. The effects of metallic cations on the degradation of dyes are negligible [15]. This inhibition is due to the chloride and sulfate ions released into the solution. Several metals are capable of initiating decomposition reactions of hydrogen peroxide [55].

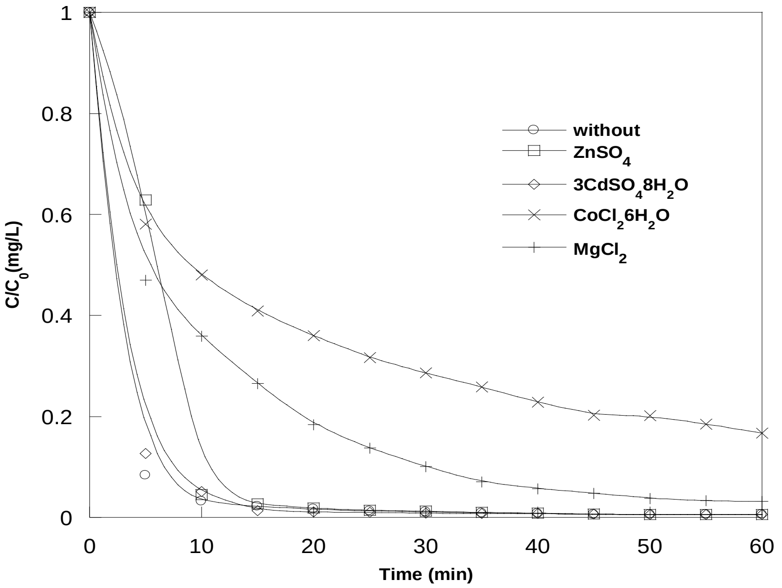

Figure 12. Effect of adding metals on the kinetics of NBB degradation
([NBB]=30 mg/L, [Fe^{2+}]=3 mg/L, [H_2O_2]=50 mg/L, pH=3, T=25 ± 2 ° C, SS=250 rpm)

$$M^{n+} + H_2O_2 \rightarrow M^{(n+1)} + OH^- + {}^\bullet OH \qquad (33)$$

In this equation, (n) represents the degree of oxidation of the metal (M). The metals capable of promoting the radical decomposition of hydrogen peroxide are the following: Fe, Cr (VI), Ti, Cu, Mn, Co (I), Al, etc. The most widely used catalysts remain copper and aluminum [56].

4. CONCLUSION

In this work, we have studied the influence of operating parameters on the kinetics and the efficiency of the oxidation of a solution contaminated by an azo dye, which is Naphtol Blue Black by Fenton process. The results found indicated that some parameters influence the discoloration significantly. For a temperature of 25±2°C and pH=3, hydrogen peroxide concentration equal to 50 mg/L and iron concentration of 3 mg/L, more than 98% of the dye has been eliminated.

The choice of the acid to adjust the pH of the solution is very important following the ions they provide in the reaction medium and which can inhibit the Fenton reaction either by the complexation of Fe^{2+} ions or by trapping hydroxyl radicals.

The pH value plays a very important role in the Fenton process, for pH values below 2 there is the formation of iron complexes or oxonium ions ($H_3O_2^+$), the latter reduces the net concentration of hydrogen peroxide and therefore the generation of hydroxyl radicals. A pH greater than 4 leads to the precipitation of ferric cations by hydroxyl ions, forming the complex ($Fe(OH)_3$). For higher pH (pH>5), the process becomes ineffective. The peroxide becomes unstable in solution and decomposes quickly into molecular oxygen.

The temperature has a positive effect on the kinetics of the reaction. The stirring speed allows a good homogenization of the solution and improves the mass transfer between the different chemical species, which results in an increase of the yield.

The concentration of peroxide plays a double role in the Fenton process; a low concentration leads to a weak degradation due to the small amount of generated hydroxyl radicals. An excess concentration of hydrogen peroxide affects negatively the degradation efficiency due to the increased reactions between hydrogen peroxide and hydroxyl radicals.

Chloride and phosphate ions inhibit greatly the degradation of the dye by Fenton process. These ions form complexes with iron and trap hydroxyl radicals. On the other hand, the effect of metallic cations is negligible and results in the associated ions.

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