KINETIC STUDY OF DEGRADATION OF RHODAMINE B IN AQUEOUS PHASE BY FENTON PROCESS

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Abstract

The main objective of this work was to study the degradation of Rhodamine B (RhB) in aqueous solution using Fenton process. Effects of various experimental parameters of the oxidation reaction of the dye were investigated. The parameters studied were the initial concentrations of $FeSO_4$, of H_2O_2, and of the Rhodamine B (RhB), the temperature and the addition of salts. The optimum conditions had been determined, and it was found that efficiency of degradation of RhB obtained after 20 min of reaction was about 83.96%. The optimal parameters were: initial pH = 3; ; $[H_2O_2]_0$ = 0,1 mM ; $[Fe^{2+}]_0$ = 0,1 mM ; for a concentration of dye $[RhB]_0$ = 10 mg/L. The experimental results showed that the Fenton's reagent was effective for the degradation of RhB dye with a low concentration of H_2O_2 and Fe^{2+}.

Keywords: *Fenton’s reagent, Rhodamine B , Oxidation Advanced, chemical oxidation , Hydrogen peroxide*

I. Introduction

Synthetic dyes are extensively used in many industries such as the textile, leather, paper production, food technology, etc., to color their products. The removal of color synthetic organic dyestuff from waste effluents becomes environmentally important. In recent years, advanced oxidation processes using ozone, titanium dioxide (TiO_2), ultra violet (UV), and Fenton’s reagent (H_2O_2 and ferrous ion) have received considerable attention as effective pretreatment processes of less biodegradable wastewater [1]. Among them, Fenton’s reagent has been widely used because it is cost effective, easy to treat, reacts well with organic compounds and does not produce toxic compounds during oxidation.

Fenton’s reaction [2] is one of the most effective methods of oxidation of organic pollutants that are degraded by hydroxyl radicals generated from H_2O_2 in the presence of Fe2+ as a catalyst [3]:

$Fe^{2+} + H_2O_2 \rightarrow OH^{\bullet} + OH^-$ (1)

When ferrous salts are used, the hydroxyl radical is produced immediately by the rapid reaction between ferrous ion and hydrogen peroxide (Eq.(1)).With ferric salts, the hydroxyl radical is produced in a two-stage process with the slow reaction between ferric ion and hydrogen peroxide (Eq. (2)) followed by the rapid reaction between the produced ferrous ion and additional hydrogen peroxide [3,4]:

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^- + H^+$ (2)

The efficiency of Fenton’s process depends on H_2O_2 and Fe^{2+} concentrations and pH of the reaction. According to a previous researcher’s report, pH value should be in the range of 3–5 [3,5–7]. Fenton’s reagent was found to be very effective in treating various industrial wastewater components, including removal of COD and color from livestock wastewater [8], treatment of textile wastewaters with high organic load [9], cosmetic wastewaters treatment [10], alkydic resin wastewaters treatment [11], oxidation of dye-Reactive Black B [12], decolorization of an azo dye Orange G in aqueous solution [13], decolorization of C.I. Acid Yellow 23 [14] and dye wastewater [15]. Therefore, the Fenton’s reagent has been applied to treat a variety of wastes such as those associated with the textile and chemical industries.

The purpose of the present work was to determine the efficiency of Fenton's reaction in the process of RhB removal from aqueous solution. In the Fenton system, the definition of the optimum operational conditions is important. Experiments were conducted to investigate the effects of various operating conditions on the performance of treatment system.

2. Materials and methods

2.1. Reagents

Rhodamine B (RhB) is belong to xanthene dye, extensively used as model compound because it shows a strong absorption band in the visible region of the electromagnetic spectrum (554 nm) and this dye is characterized by having a high stability at different pH values. The RhB is also used as a dye for wool and as analytical reagent during the determination of metals in solution, especially alkali, and alkaline earth metals. This dye is used in the textile, food and cosmetic industries but can cause pollution in the aquatic environments showing high resistance to biological and chemical degradation.

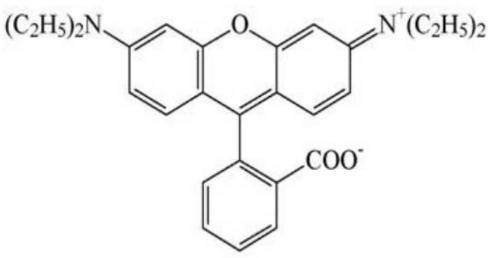

Fig.1: Structures of Rhodamine B (RhB)

2.2. Materials

The oxidation of the organic material by the Fenton process was carried out in a perfectly stirred reactor (batch reactor) with a capacity of 250 ml. The reactor is stirred using a magnetic stirrer (SELECTA AGIMATIC-N). The pH of the solution is measured using a pH electrode (HANNA INSTRUMENTS). The temperature is controlled using a temperature probe connected to the pH meter (HANNA INSTRUMENTS).

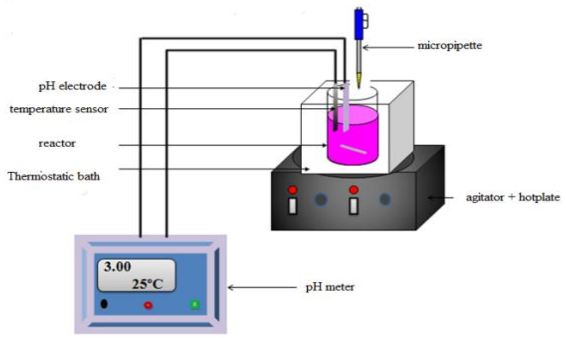

Fig.2.Experimental apparatus

2.3. Methods

The kinetics of the oxidation was followed by taking samples at regular time interval. The residual concentration of the dye in the solution at different times of sampling was determined by UV-Visible spectroscopy. Measurement of species concentration during the treatment was carried out in quartz cells of 1 cm optical path using a UV-Visible spectrophotometer (JENWAY 6705).The resolution of the wavelength and the bandwidth, were 1 nm and 0.5 nm. The cells used were in quartz 1 cm thick.

3. Results and discussion

3.1. Effect of $FeSO_4$ concentration

To see the effect of Fe^{2+} on the yield of RhB degradation by the Fenton process and to determine the most appropriate concentration of Fe^{2+}, a series of experiments were conducted at different concentrations of $[Fe^{2+}]$ from 0.1 to 2 mM. The results obtained are presented in Fig 3. This Figure clearly shows that the efficiency of the degradation of Rhb is significantly influenced by the addition of different concentrations of $[Fe^{2+}]$. The low degradation efficiency was obtained at $[Fe^{2+}] = 0.1$ mM, while the highest degradation efficiency was obtained at $[Fe^{2+}] = 0.5$ mM.

Many studies reported in literature have revealed that the use of a much higher concentration of Fe2+ could lead to the selfscavenging of $^\bullet OH$ radical by Fe^{2+} (Eq. (3)) [16, 17] and induce the decrease in degradation rate of pollutants:

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

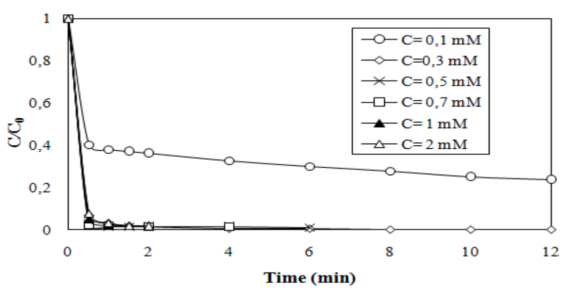

Fig. 3. Kinetics of degradation of RhB according to different concentrations of $FeSO_4$ C_0=0.1-2 mM, $[H_2O_2]$=0.1 mM, pH=3.

3.2. Effect of H_2O_2 concentration

Oxidation of dyes by the Fenton process is carried out by $HO^{\bullet}$ radicals that are directly produced from the reaction between H_2O_2 and Fe^{2+}. To determine the concentration of H_2O_2 giving the maximum RhB degradation efficiency, experiments were conducted and results obtained are represented in Fig. 4. According to these Figures, it appears that the increase in the concentration of hydrogen peroxide beyond 0.1 mM causes a reduction in the degradation of Rhodamine B. This can be explained by the fact that the increase in H_2O_2 concentration can trap HO● radicals following reactions (4-6) :

$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O$ (4)

$H_2O_2 + HO_2^{\bullet} \rightarrow HO^{\bullet} + O_2 + H_2O$ (5)

$HO_2^{\bullet} + HO^{\bullet} \rightarrow H_2O + O_2$ (6)

Thus, the addition of higher concentration of H_2O_2 did not improve the degradation. This could be due to the fact that hydroperoxyl radicals ($HO_2^{\cdot}$) was generated in the presence of excess of H_2O_2. Although $HO_2^{\cdot}$ promotes radical chain reactions and is an effective oxidant itself, its oxidation potential is much lower than that of $OH^{\cdot}$. The hydroperoxyl radicals are much less reactive and do not contribute to the oxidative degradation of organic substrates, which occur only by reaction with $OH^{\cdot}$ [18,19].

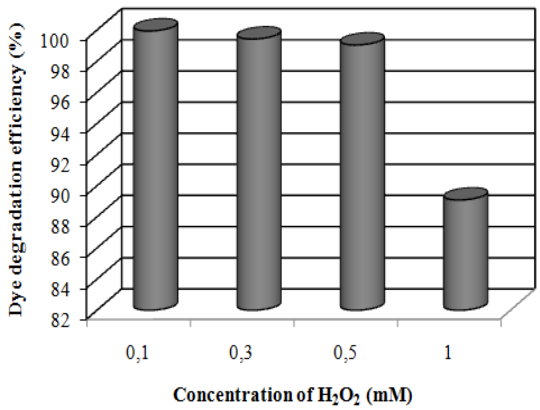

Fig. 4. Dye degradation efficiency in presence of different concentrations of H_2O_2, C_0=0.1-1 mM, $[FeSO_4]$=0.1 mM, pH=3.

3.3. Effect of the initial RhB concentration

To study the effect of the initial dye concentration on the efficacy of the Fenton process, solutions of RhB at different concentrations (0.5-15 mg / L) were treated at pH 3 in the presence of $[Fe^{2+}]$ = 0.1 mM, $[H_2O_2]$ = 0.1 mM. The results obtained are illustrated in Fig 5. From this figure, the degradation efficiency decreases as the initial concentration of RhB increases. For an initial concentration of 0.5 mg / L, complete removal of the dye is achieved after 20 minutes of treatment while removal efficiencies of 98.03, 97.03, 90.28, 83.96 and 66.71% are achieved for RhB concentrations of 1 , 3, 5, 10 and 15 mg / L , respectively. The hydroxyl radical is the main element responsible for the degradation of the dye, its concentration remains constant while that of the dye increases. The increase in the dye concentration increases the number of molecules to be degraded for the same number of hydroxyl radicals, which implies a decrease in degradation.

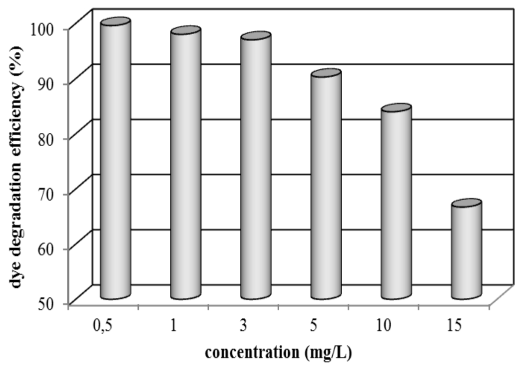

Fig .5. Effect of initial RhB concentration on dye degradation efficiency by Fenton process

3.4. Effect of temperature

Temperature affects the reaction between H_2O_2 and Fe^{2+} and therefore, it should influence the kinetics of dyes degradation. Experiments were performed by varying the temperature from 25 °C to 50 °C. Fig. 6 illustrates the effect of temperature on the reaction of RhB degradation according to time at different temperatures. It may be noted that the temperature has a great effect on the initial rate of RhB degradation. The degradation efficiency of Rhodamine B increases with increasing temperature. In general, the temperature of the solution affects viscosity, gas solubility, surface tension and vapor pressure. The increase in the temperature of the solution makes it possible to lower the viscosity and / or the surface tension and therefore increase the rate of production of the hydroxyl radicals. The increase in degradation can also be due to the fact that at high temperature, the reaction rate between hydrogen peroxide and any form of ferrous / ferric iron (chelate or non-chelate) increases, which leads to an increase in speed. of producing oxidizing species such as the hydroxyl radical or the high valence iron species.

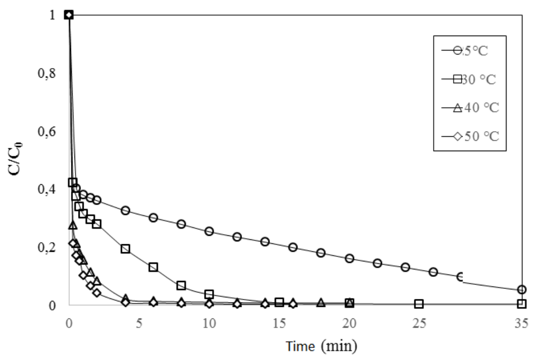

Fig .6.kinetics of degradation of Rhb as a function of temperature

3.5. Effect of addition of salts

Since industrial discharges may contain a significant amount of salts, it is important to study the impact of the presence of these salts on the effectiveness of the treatment. In this study, the influence of the addition of different salts like NaCl, Na_2SO_4 and $NaHCO_3$ (1 g / L) on the degradation of RhB by Fenton process in aqueous solution was examined for an initial dye concentration of 10 mg / L. kinetics of degradation of Rhb in the absence and in the presence of 1 g / L of NaCl, Na_2SO_4 and $NaHCO_3$ are presented in Fig.7. According to this figure, it appears that the degradation of RhB slightly decreases in the presence of Na_2SO_4, for against it decreases dramatically in the presence of NaCl and especially in the presence of $NaHCO_3$. The decrease in degradation in NaCl presence is due to an inhibitory effect of the anions Cl-. It can be explained by equations 7 and 9.

$Cl^- + HO^\bullet \rightarrow ClOH^{\bullet-}$ (7)

$ClOH^{\bullet-} + Fe^{2+} \rightarrow Cl^- + OH^- + Fe^{3+}$ (8)

$Fe^{2+} + 2Cl^- \rightarrow FeCl_2$ (9)

The slight decrease in the degradation of RhB in the presence of Na2SO4 can be explained by the fact that Na^+ ions do not form complexes with ferrous iron and do not trap free radicals and may also be due to the reaction of sulphate ions with iron leading to the formation of complexes that can inhibit dye degradation following reactions (10 to 14) :

$Fe^{2+} + SO_4^{2-} \leftrightarrow FeSO_4$ (10)

$Fe^{3+} + SO_4^{2-} \leftrightarrow FeSO_4^+$ (11)

$Fe^{3+} + 2SO_4^{2-} \leftrightarrow Fe(SO_4)_2^-$ (12)

$SO_4^{2-} + HO^\bullet \rightarrow SO_4^- + HO^-$ (13)

$HSO_4^- + HO^\bullet \rightarrow SO_4^{\bullet-} + H_2O$ (14)

The significant decrease in the degradation of RhB in the presence of $NaHCO_3$ is mainly due to the consumption of the hydroxyl radicals available by the bicarbonate ions known as being an effective scavenger of the hydroxyl radicals following the reaction:

$$HCO_3^- + HO^\bullet \rightarrow CO_3^{\bullet-} + H_2O \quad (15)$$

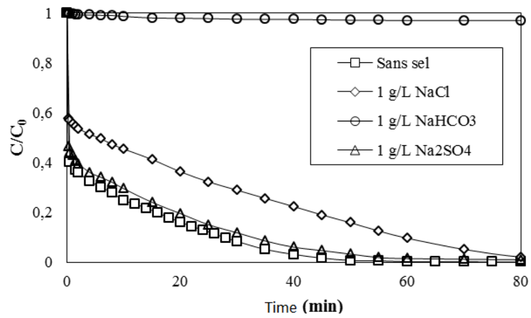

Fig.7. Influence of the addition of salts on the degradation efficiency of RhB

VI. Conclusions

The examined Fenton's reaction was found to be very efficient for removing RhB from aqueous solutions.

The results obtained allowed us to show that the rate of degradation of RhB depends on the initial concentration of the dye, the pH, the temperature of the solution and the concentration of FeSO4 and H_2O_2. The degradation efficiency decreases significantly in the presence of NaCl and $NaHCO_3$. The slight decrease in degradation in the presence of Na^2SO_4 is due to the fact that the Na^+ ions do not form complexes with ferrous iron and do not trap the hydroxyl radicals and can also be due to the reactions of the sulphate ions with the iron conducting complex formation that can inhibit dye degradation.

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