Environment Protection Engineering

Vol. 51 2025 No. 3

DOI: 10.37190/EPE/208013

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OXIDATIVE DEGRADATION OF METHYL BLUE AND BROMOPHENOL BLUE. KINETICS AND INFLUENCING PARAMETERS

The degradation of Methyl Blue (MB) and Bromophenol Blue (BPHB) by the Fenton process, kinetics, and some other influencing parameters, was the objective of this study. The degradation was performed in a beaker under stirring conditions at pH 3. The kinetics of the compounds' degradation was followed by UV-Vis spectrophotometry. Both compounds can be effectively degraded, with MB degrading more rapidly than BPHB. Increasing pH reduced the efficiency of the degradation process, but even at pH 5.2, significant amounts of both compounds could still be oxidized. This is due to the pH decrease during the process, probably caused by the formation of carboxylic acids.

1. INTRODUCTION

Chemical pollution is very common in every environmental compartment, and its detrimental effects are being observed [1–4]. Organic synthetic substances are increasingly present in water bodies, thus posing a threat to the living organisms [5, 6]. They are introduced into the waters in various ways, but one of them is the simple disposal of industrial effluents and urban wastewaters into the rivers and streams. The best way to prevent pollution is to reduce the amount of toxic effluents or treat them to reduce or remove the toxic substances. For this purpose, many water treatment methods have been developed, such as microbiological destruction of organic pollutants [7]. Also, separation methods, adsorption, and membrane filtration have been extensively studied [8, 9].

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Among methods for organic pollutants removal from water are the advanced oxidation processes, which destroy pollutants by hydroxyl radicals $^{\bullet}OH$, which have a very high redox potential ($E°(^{\bullet}OH/H_2O)$ = 2.8 V/SHE). Hydroxyl radicals can be generated in various ways, by chemical [10–12], photochemical [13–16], and electrochemical methods [17, 18]. The Fenton process is one chemical method to destroy organic pollutants in water by oxidative degradation through the use of hydroxyl radicals $^{\bullet}OH$ [19, 20]. It operates based on a reaction involving iron ions Fe^{2+} and hydrogen peroxide H_2O_2, which produces $^{\bullet}OH$ radicals, according to the reactions:

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

$$^{\bullet}OH + \text{pollutants} \rightarrow \text{molecular fragments}$$

Fe^{3+} ions are reduced by some reactions to Fe^{2+}, which enter again the Fenton reaction [21]. The oxidation of organics by the Fenton reaction takes place at pH 3, to avoid the precipitation of iron hydroxides, and the consumption of iron ions in waste reactions. Hydrogen peroxide and Fe^{2+} compounds are added in small quantities and also in intervals of proportions, because if they are added in larger excess, the process of pollutant oxidation starts to lose efficiency. This occurs because of some parasitic reactions [21].

In this work, the oxidative degradation of Methyl Blue (MB) and Bromophenol Blue (BPHB) was performed by the Fenton process. Their degradation efficiency and kinetics were studied, as well as some parameters influencing the degradation process: reactor volume, stirring conditions, pH, and initial concentration of the targeted compounds.

2. MATERIALS AND METHODS

MB and BPHB over 97% pure were used as such. The degradation trials were performed in 150 cm^3 beakers. Iron(II) ions were added in the form of $FeSO_4$, whereas H_2O_2 was prepared as a stock solution; proper volumes were taken and added to the process system. The process was performed under stirring at 300 rpm. The samples were taken for analysis of the targeted molecule at predefined intervals. The initial concentrations of MB and BPHB in the solutions were 0.01 mM. The concentration of Fenton's reagent, H_2O_2, and Fe^{2+} were 0.01 mM, but equal to each other, varied when the concentration dependences were studied. pH of the solution was adjusted to 3 with 1 M H_2SO_4. The concentration of the MB and BPHB during the process was measured using a PG Instruments T70 UV-Vis spectrophotometer.

3. RESULTS AND DISCUSSIONS

Figure 1 presents the time-dependent MB concentration during oxidative degradation. The concentration of the Fenton's reagents increased from 0.01 mM to a maximum

of 0.3 mM. First, H_2O_2 was added, then Fe^{2+}, and the time was set to be recorded. Once Fe^{2+} was added, the degradation of MB started immediately. The degradation was very fast at the beginning of the process, then it became slower because of the Fenton's reagents consumption, but also as a result of some parasitic reactions which become more significant as the reaction continues [21]. The increase in the concentration of Fenton's reagents resulted in an acceleration of the degradation process. The four curves of the plot showed a characteristic long period of very slow decrease in the concentration. Complete degradation of MB was achieved only at 0.3 mM of Fenton's reagents concentration.

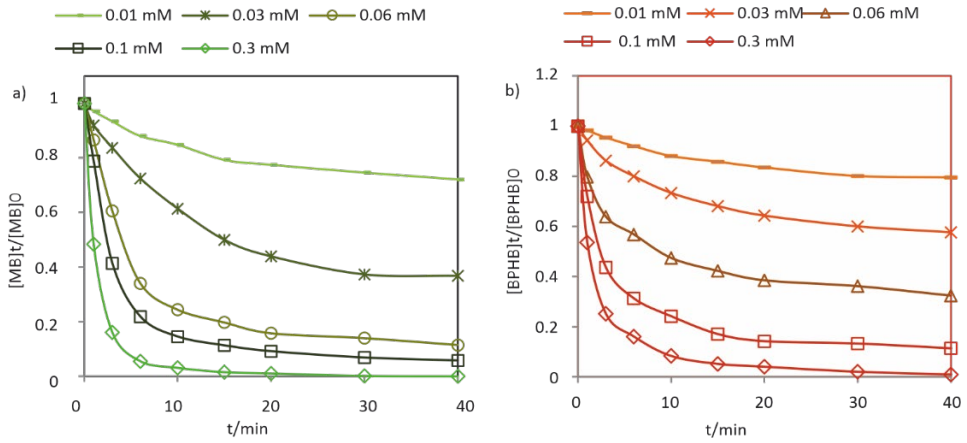

Fig. 1. Degradation trails of MB (a) and BPHB (b) at different Fenton's reagent concentrations; $[H_2O_2] = [Fe^{2+}]$, [MB] = [BPHB] = 0.01 mM, V = 150 cm^3, pH = 3

BPHB was treated using the same Fenton's reagent concentrations under similar experimental conditions. The degradation curves were similar to those obtained for MB, but here a tendency toward a slower degradation process was observed. The two distinct zones of the degradation curves – the steeper beginning part and the flatter part – are also observed for the degradation of BPHB. It could also be effectively degraded at Fenton's reagent concentration of 0.3 mM; however, some small traces could still be detected even after 40 min of treatment.

A more detailed kinetic study was performed applying the kinetic model proposed by Behnajady et al. [22]. According to this model, the normalized concentration of the targeted compound (C_t/C_0) at any time during the degradation process can be given by the equation:

$$\frac{C_0}{C_t} = 1 - \frac{t}{m + bt}$$

and after transformation

$$\frac{t}{1-\frac{C_t}{C_0}} = m + bt$$

If $t/(1 - (C_t/C_0))$ is plotted against t, a straight line is obtained with an intercept m on C_t/C_0 axis. Then, $d(C_0/C_t)/t = -1/m$ is determined [22], where $1/m$ is related to the initial rate of compound degradation. Considering this, m values were extracted from the plots given in Fig. 2, and $1/m$ was calculated.

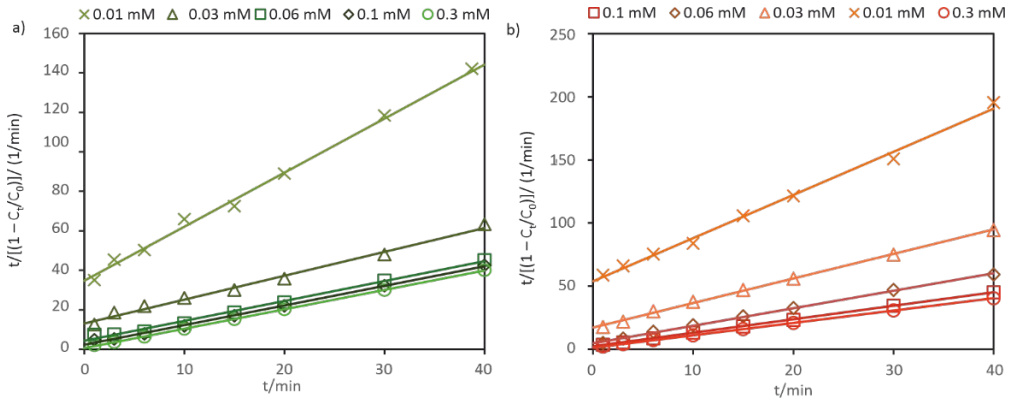

Fig. 2. Kinetic analysis of MB (a) and BPHB (b) at different Fenton's reagent concentrations; $[H_2O_2] = [Fe^{2+}] = [MB] = [BPHB] = 0.01$ mM, $V = 150$ cm^3, pH = 3

Table 1

Efficiency of Methyl Blue and Bromophenol Blue degradation by the Fenton process

Indicator	$[H_2O_2] = [Fe^{2+}]$ [mM]	$1/m$ [min^{-1}]	Removal [%]
Methyl Blue	0.01	0.03	28
	0.03	0.08	63
	0.06	0.24	88
	0.1	0.43	94
	0.3	1.58	99.99
Bromophenol Blue	0.01	0.02	21
	0.03	0.06	43
	0.06	0.21	68
	0.1	0.44	90
	0.3	0.87	99

The values of the initial rate of degradation of MB and BPHB are presented in Table 1. MB tends to be degraded faster than BPHB (except for the case of 0.1 mM concentration of Fenton's reagent, where BPHB has a slightly higher $1/m$ value), probably because

MB is a bigger molecule than the BPHB; it also has a structure richer in unsaturated bonds, which are very reactive towards hydroxyl radicals [23]. These characteristics make MB more susceptible to undergoing successful collisions with •OH, resulting in a degradation reaction.

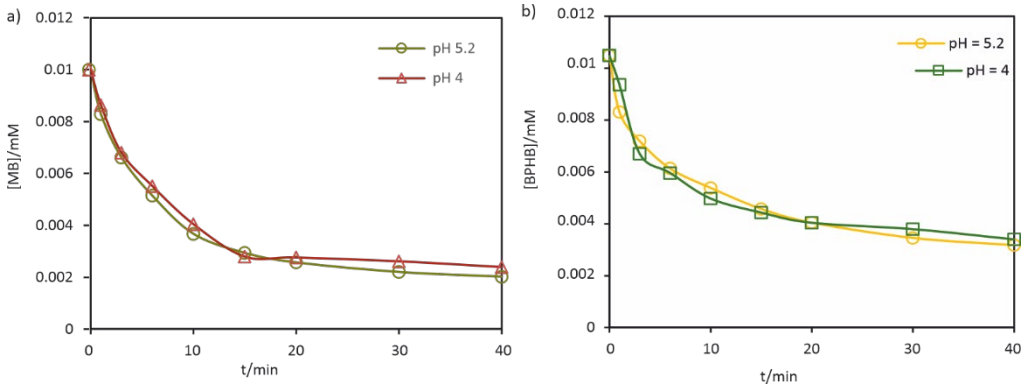

Fig. 3. Degradation trails of MB (a) and BPHB (b) at two pHs higher than 3; $[H_2O_2] = [Fe^{2+}] = [MB] = [BPHB] = 0.01$ mM, $V = 150$ cm^3

The degradation of MB and BPHB was carried out at two more pH values, in order to observe the degradation efficiency. In Figure 3 are presented the degradation curves of these processes. As expected, at pH higher than 3, the degradation efficiency deteriorated at pH 4 and 5.2. However, at pH 5.2, the degradation process was not slower than at pH 4, as one should expect, but it was just about the same as at pH 4. As a pH change during the process was suspected, an experiment of the degradation process was carried out, and the pH value was monitored. It was found that when pH was set at 5.2, after the degradation process started, the pH also started to decrease up to about 4, which revealed the reason the degradation process at pH 5.2 was just as efficient as at pH 4.

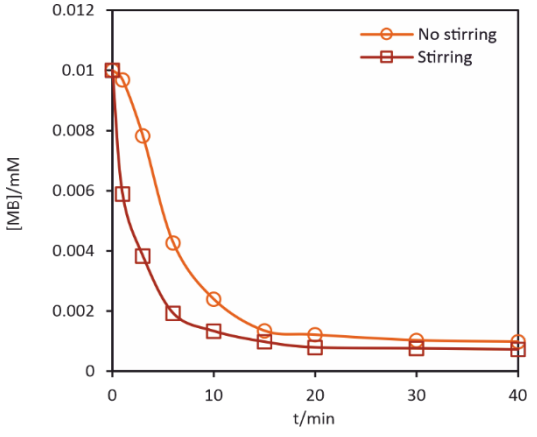

Fig. 4. Degradation trails of MB with and without stirring; $[H_2O_2] = [Fe^{2+}] = [MB] = 0.01$ mM, $V = 2000$ cm^3, pH = 3

Although stirring the solution during the treatment enhances mass transport, the process without stirring would be more economical and easier to operate. Thus, MB was treated with the Fenton process under stirring conditions and without stirring, to check the difference. When the process was carried out without stirring in the 150 cm^3 beaker, no significant difference was observed compared to the process performed with stirring. Further, another experiment was performed in a beaker of 2000 cm^3 with and without stirring, and the results are shown in Fig. 4. Clearly, when the degradation was performed at the larger volume, the degradation curve shifted upward, indicating slower kinetics of degradation because the slower mass transport conditions in the system in the absence of the mixing.

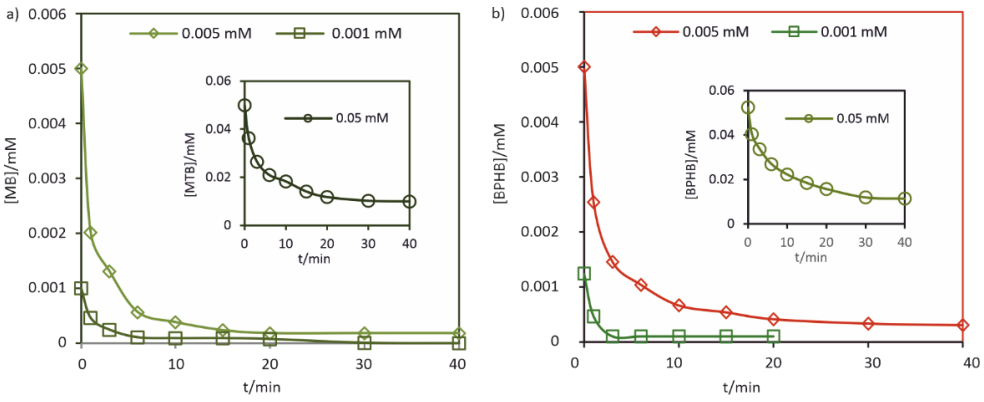

Fig. 5. Degradation trails of different concentrations of MB (a) and BPHB (b);
$[H_2O_2] = [Fe^{2+}] = 0.01$ mM, $V = 150$ cm^3, pH 3

The effect of the concentration of the MB and BPHB on the degradation efficiency is shown in Fig. 5. When the concentration of the compound was 0.001 mM, complete elimination was attained, and almost the same occurs when a 0.05 mM solution is treated. In the case of BPHB, there could still be traces of it, whereas MB at 40 min did not give even a clear signal of absorbance. No complete degradation was reached for none of the compounds when a 0.05 mM solution was treated, although 80% of MB and 78% of BPHB were oxidized. A less efficient removal is a result of the quicker and higher consumption of the oxidizing reagent, but also because of the accumulation of a lot of byproducts of degradation, which are also degraded by hydroxyl radicals [23]. Also, the oxidation byproducts can form complexes with iron ions, thus hampering Fenton's reaction.

4. CONCLUSION

The degradation of MB and BPHB can be effectively completed by the Fenton process. The degradation of MB, although similar, has a tendency to be quicker than that

of BPHB, as indicated by the initial rate of degradation. At higher pH, the oxidation rate diminishes, but not as fast as expected, since a decrease in its value is observed, probably as a result of carboxylic acids that form during the degradation of organics. The degradation rate without mixing also decreases only for large volumes of the treated solution as a result of very slow mass transport. Lower concentration solutions (which is the case for the micro pollutants in some industrial waters) are more effectively treated.

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