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Decolorization Kinetics of Organic Pollutant Dye Compounds from Wastewater

Organik Kirletici Boyar Maddelerin Atıksudan Renk Giderme Kinetiği

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ABSTRACT

The removal of colored-toxic materials from industrial wastewater has been subject to investigations since years. There are more than several methods to overcome these problems. In this article, sodium sulfite as a scavenger was used to remove the color of basic red 46 and methylene blue in solution as model pollutant materials in water. Color removal kinetics was studied by using sodium sulfite amount, pH of the solution, time and temperature as parameters. The effect of these parameters was reported according to the decay kinetics of absorbance of the dye compounds in solution by using molecular absorption spectroscopy. It observed that the color degradation of basic red 46 obeys bi-exponential decay whereas methylene blue obeys single exponential decay. The kinetic rate constants were determined from fit of the absorbance decay studies and temperature dependence of process was discussed with Arrhenius equation.

Keyword: Basic red 46, Methylene blue, Color removal, Absorbance decay, Rate constant

ÖZ

Endüstriyel atık sulardan renkli zararlı maddelerin giderilmesi yıllardan beridir incelenmektedir. Bu problemin üstesinden gelmek için birçok metot bulunmaktadır. Bu makalede, model kirletici olan bazik kırmızı 46 ve metilen mavisinin sulu çözeltisinin renk giderilmesinde sodyum sülfit kullanıldı. Renk giderim kinetiği, sodyum sülfit miktarı, çözelti pH'sı, zaman ve sıcaklık parametreleri üzerinden incelendi. Bu parametrelerin etkisi moleküler absorpsiyon spektroskopisi kullanılarak boyar maddelerin absorbans durulma kinetiği şeklinde rapor edildi. Bazik kırmızı 46'in durulma kinetiği iki üstel bir durulma gösterirken metilen mavisinin durulma kinetiği tek üstel olarak gerçekleşmiştir. Absorbans durulma çalışmalarından kinetik hız sabitleri hesaplandı ve proseslerin sıcaklığa bağımlılığı Arrhenius denklemiyle tartışıldı.

Anahtar Kelimeler: Bazik kırmızı 46, Metilen mavisi, Renk giderme, Absorbans durulması, Hız sabiti

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INTRODUCTION

There are multiple causes for water contamination with color change to occur. Industries may cause color change of the water due to different production processes.[1] For example, the textile industries, cosmetics, food processing, paper industries, leather processing and dyeing, and dye manufacturing industries are the major sources of water effluents.[2] Therefore, the color of water is a general determinant cleanliness. In general, some by products are not easily degradable and, therefore they are not easily removed from wastewater by conventional methods.[3,4] As waste industrial materials may be toxic toward living organisms[5,6], the degradation of this type of materials is a critical aspect of

wastewater treatment before discharge.[7-9] Since the environment and human health are the main concern, it would be more important to treat the water accordingly. Therefore, it is important to find an effective treatment method for wastewater in order to remove the color and degrade the organic pollutants.[10] For these reasons, different physical, chemical, biological and oxidative technologies are used for the removal of organic pollutants such as reverse osmosis[11], biodegradation[12], heterogeneous photo-catalysis[13,14], adsorption[15], electrochemical oxidation[16,17], sedimentations[18], nano-filtration[19], ozonolysis[20] and sonolysis.[21]

Nowadays, some researchers use sodium sulfite addition with semiconductor materials to the systems to overcome this problem. Sodium sulfite has a role as a food preservative and a reducing agent. It is recently reported that the photocatalytic degradation of colored materials can be promoted with sulfite addition.[22] Particularly, sulfite radicals are reactive species for the degradation of organic pollutants. However, there is still argument over the reactive species. The mechanism is still not clear to the researchers.[23] A direct measurement or evidence of the generation of sulfite radicals is thus another subject area. Sulfite radicals are usually created upon the photolysis of sulfite anions under middle UV light or via sulfite anions reacting with transition metal ions and other radicals like hydroxyl radicals. In another study, the UV-Vis absorption band of sulfite ion, 200 to 260 nm, was monitored in the BiOBr/Methyl Orange system under visible light irradiation to indicate the dependence of sulfite consumption rate upon isopropyl alcohol supplement[10]. There was no absorbance band from 200 to 260 nm in the absence of sulfite whereas a clear absorption band appeared upon the addition of sulfite and the absorbance decreased with time, indicating the consumption of sulfite upon illumination.

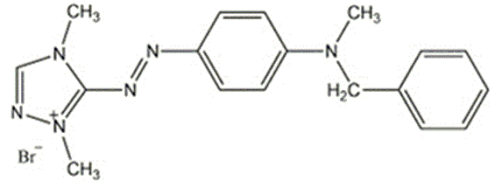
In this study, first time decolorization decay kinetics of the model system that contain either basic red 46 (BR46) or methylene blue (MB) in solution was investigated with the effect of sodium sulfite and the parameters were chosen as sodium sulfite amount, pH of the solution, time and temperature.

METHODS

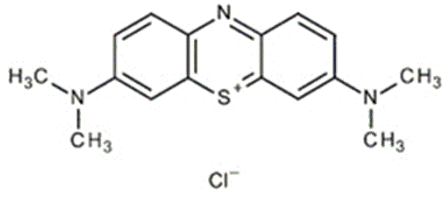
Methylene blue, basic red 46 and sodium sulfite from Sigma and ethanol from Merck were purchased. The stock solution of dye compounds was prepared as $1.0x10^{-3}$ M in ethanol. For the experimental studies, $1.0x10^{-5}$ M BR46 or MB was prepared in deionized water to overcome inner filter effect and violation of Lambert-Beer Law by using stock solutions. For this aim, know amount dye compound from stock solution transferred to the test tube and purge with the argon gas to evaporate ethanol and, then, deionized water was added to the sample for the final concentration. The experimental temperatures were 20°C, 30°C and 40°C and temperature control of the samples was obtained with Grant W14 circulating water bath. Absorption studies carried out three times by using Varian Cary 50 Bio UV-Visible Spectrophotometer and absorbance of the samples were determined by using 10x10 mm quartz cuvette.

RESULTS

The beginning of experimental studies, $1.0x10^{-5}$ M BR46 and MB dye solutions were prepared in pH 7.5 and at temperature 20°C. The molecular structures and normalized absorption spectra of the samples in deionized aqueous solution were given in Figure 1 and 2, respectively. In Figure 2, there is no effect of $NaSO_3$ effect on the dye solution.



Basic red 46



Methylene blue

Figure 1. Molecular structure of the dye compounds used for experimental model systems.

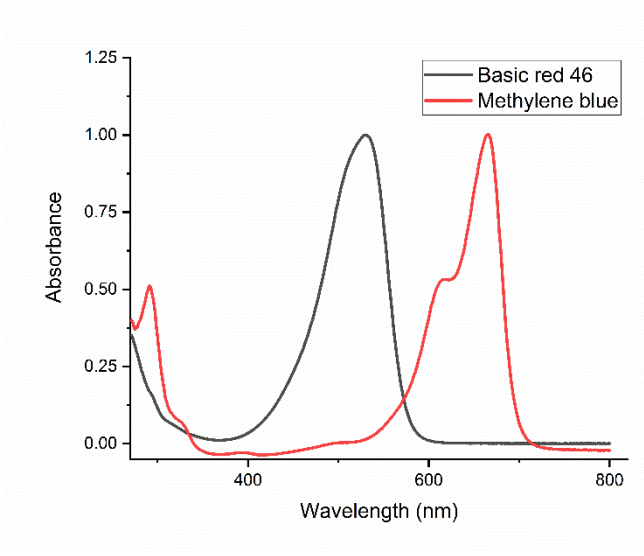


Figure 2. Normalized absorption spectra of the dye compounds in deionized aqueous solution.

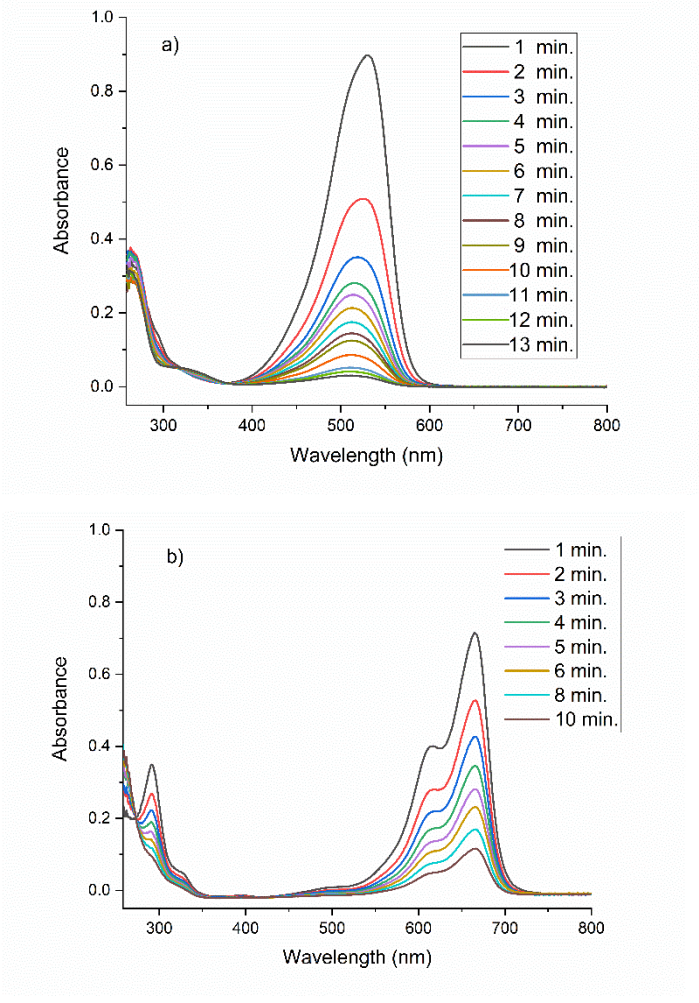


Figure 3. Absorption spectra of the dye compounds BR46 (a) and MB (b) taken with 0.25 g $NaSO_3$ and pH 7.5 at 20°C.

Three different amounts of $NaSO_3$ were chosen as 0.25, 0.50 and 0.75 g at the pH 7.5 to see the effect of salt on the decolorization. Each experiment was carried out at the temperature 20°C and time dependency of color removal followed by measuring absorbance of each sample certain time intervals. Absorbance readings were done at the absorption maxima of the dye compounds in solutions. These values are 530 nm and 665 nm for the BR46[24] and MB[25], respectively, as shown in Figure 2. Absorption spectra of the samples including salt in the solutions at conditions mentioned previously were given Figure 3a and b. As seen from the absorption spectra (Figure 3), the addition of salt causes absorbance decrease for the both compounds that means model wastewater solution becomes clear with time. Studies were carried out for the solutions to become completely clear. Moreover, there is no interestingly new additional band at the spectra during the decolorization process. Therefore, it is for sure that there is no absorbing species in the region of UV-Vis with these observations. Here, the focus of this study is on the color removal kinetics instead of structural changes or final products. For these purposes, data analysis carried out exponential decay model of the absorbance values. Experimental data for BR46 indicated biexponential decay whereas data for MB obeyed single exponential decay. The equations used to calculate rate constants for biexponential decay and single exponential decay, respectively, are given as

$$A(t) = A_1 \exp(-k_1 t) + A_2 \exp(-k_2 t) \quad (1)$$

and

$$A(t) = A_0 \exp(-kt) \quad (2)$$

Where, A_0, A_1, and A_2 are preexponential factors, $A(t)$ is the absorbance value with time, k, k_1, and k_2 are the rate constants, and t is the time. According to these approach, parameter of salt effect results were given in Figure 4a and b for the conditions of constant pH 7.5 and 20°C.

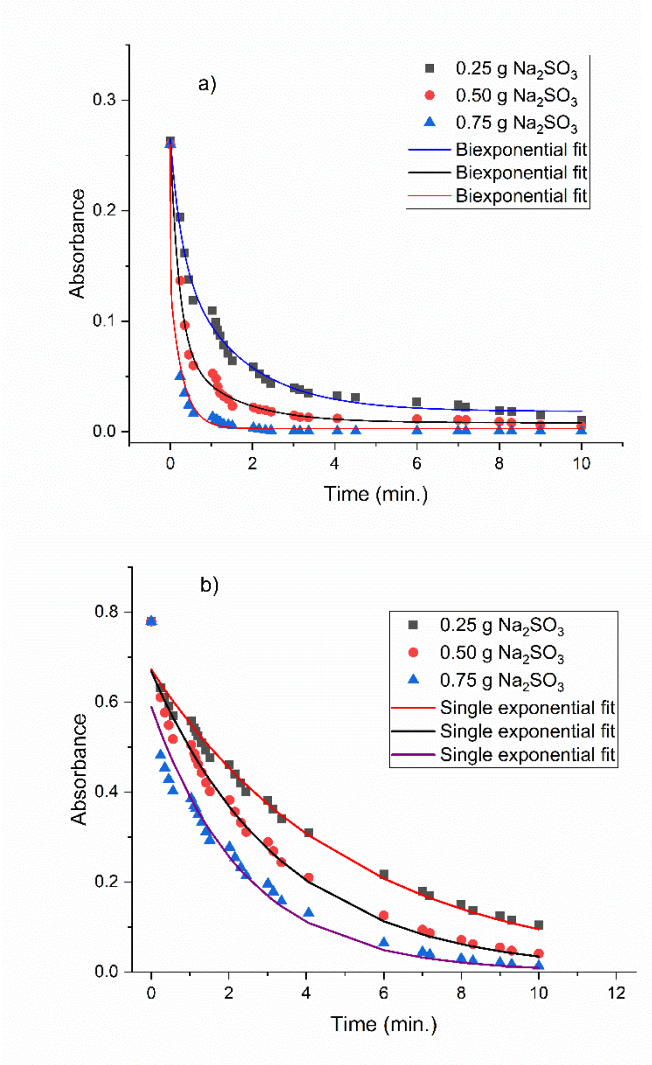


Figure 4. Sodium sulfite effect on absorbance decays for BR46 (a) and MB (b) at pH 7.5 and 20°C.

Table 1. Sodium sulfite effect on the rate constants and color removal efficiencies.

Basic red 46				
$NaSO_3$ (g)	k_1 (min.$^{-1}$)	k_2 (min.$^{-1}$)	$k_{Ave.}$ (min.$^{-1}$)	Removal Efficiency (%)
0.25	4.35	0.80	2.58	90.5±0.3
0.50	4.76	0.83	2.80	96.0±0.5
0.75	20.0	3.00	11.50	99.8±0.1
Methylene blue				
$NaSO_3$ (g)	k (min.$^{-1}$)			Removal Efficiency (%)
0.25	0.20			86.5±0.7
0.50	0.30			94.8±0.2
0.75	0.42			98.3±0.4

Rate constants for each dye samples from curve fitting studies as shown in Figure 4 were calculated. In addition, efficiency of effluents removal from wastewater was also calculated according to the equation given as follows

$$Removal\ Efficiency\ (\%) = \frac{A_0 - A_t}{A_0} x100 \qquad (3)$$

Where A_0 and A_t are the initial and at time t absorbance values. The rate constants and removal efficiency values originated from $NaSO_3$ effects were given in Table 1.

One of the other parameters was the pH of the solution. For this aim, the same procedure was applied model wastewater samples at the conditions of $1.0x10^{-5}$ M dye samples including 0.25 g $NaSO_3$ at 20°C with varying pH of the solutions from 5.0 to 10.0. The absorbance decay plots are given in Figure 5a and b.

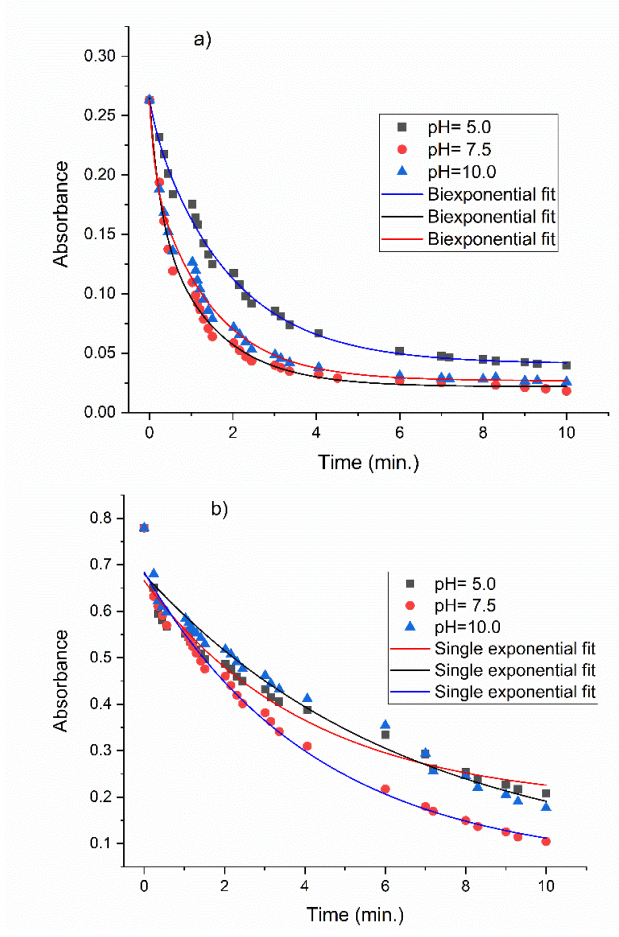


Figure 5. The effect pH on absorbance decays for BR46 (a) and MB (b).

The values of rate constants obtained from curve fitting by using plots in Figure 5 and removal efficiencies by using equation 3 were given in Table 2.

Table 2. The pH effect on the rate constants and color removal efficiencies.

Basic red 46				
pH of solution	k_1 (min.$^{-1}$)	k_2 (min.$^{-1}$)	k_{Ave} (min.$^{-1}$)	Removal Efficiency (%)
5.0	5.50	0.53	3.02	82.0±1.3
7.5	4.35	0.80	2.58	90.5±0.3
10.0	7.70	0.70	4.20	88.7±0.2
Methylene blue				
pH of solution	k (min.$^{-1}$)			Removal Efficiency (%)
5.0	0.12			68.0±1.5
7.5	0.20			86.5±0.7
10.0	0.14			76.0±1.7

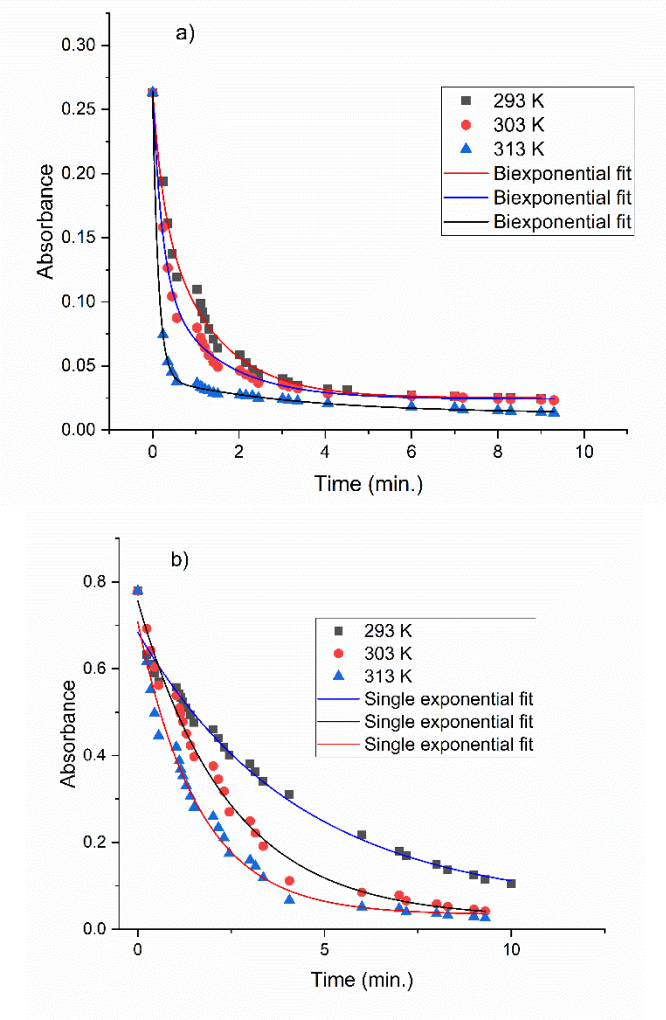


Figure 6. Temperature effect on absorbance decays of $1.0x10^{-5}$ M BR46 (a) and MB (b). (pH=7.5 and 0.25 g $NaSO_3$).

Temperature dependency of the color removal from the model solutions was also investigated and the results obtained absorbance reading are given in Figure 6a and b. The same mathematical approach was applied for these data as well. From fitting parameters, one can obtain rate constants by using equations 1 and 2.

The data of temperature studies were exploited to calculate removal efficiencies for the colored solutions and results were given in Table 3 including rate constants.

Table 3. Temperature effect on the rate constants and color removal efficiencies.

Basic red 46				
Temperature (K)	k_1 (dak.$^{-1}$)	k_2 (min.$^{-1}$)	k_{Ave} (min.$^{-1}$)	Removal Efficiency (%)
293	4.35	0.80	2.58	90.5±0.3
303	4.54	0.72	2.63	91.2±0.8
313	5.70	0.32	3.01	95.0±0.6
Methylene blue				
Temperature (K)	k (min.$^{-1}$)			Removal Efficiency (%)
293	0.20			86.5±0.7
303	0.38			95.0±1.1
313	0.58			97.0±0.9

DISCUSSIONS

In this study, the reason of sodium sulfite use for decolorization was because of its advantages of low cost, convenient source and one of the most environmentally and energy saving methods compared to the other applications. If one evaluates the data given in Table 1, it is seen that increasing salt amount increases the removal efficiencies for both model dye compounds as the kinetic rate constants are also indicated the similar trend with the removal efficiencies. This means that salt addition has proportional effect on the color removal of this type wastewater systems. In case of Table 2, the best pH for color removal seems to be 7.5. This is very clear for the methylene blue data. The reason is that both rate constant and removal efficiency values are consistent with each other. On the other hand, basic red 46 rate constant is not consistent with the removal efficiency but this does not mean that rate constant is the only limiting parameter for kinetic decay study. This is why we introduce the removal efficiencies for each parameter. Therefore, all experiments were carried out with pH 7.5 except pH trials. The last, temperature studies indicated that the increase the temperature the remove the color

of effluents from wastewater system. In addition, activation energies of the dye removal were calculated by using Arrhenius equation. For this aim, 1/T vs. $\ln k_{Ave}$ plot was drawn and activation energy (E_a) from the slope, Arrhenius constant (A) from intercept were calculated. These values were obtained as Ea =6.30±0.40 kJ/mol A=32.9 min^{-1} for BR46 and Ea =42.5±3.60 kJ/mol A=7.5x10^6 min^{-1} for MB. These data show that both dye compound observe different decay kinetics as well as different energy barrier of color removal.

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