Decoloration of Disperse blue 56 Using UV/H$_2$O$_2$/MWCNTs

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ABSTRACT

I*n this study, oxidation of dye from colored wastewater by H$_2$O$_2$/ Multiwall Carbon Nanotubes solution assisted with UV radiation was investigated. Disperse Blue 56 was used as a model dye. Adsorption behavior of Disperse Blue 56 from aqueous solution onto Multiwall Carbon Nanotubes was investigated under various conditions such as initial pH value, dye concentration, H$_2$O$_2$ and Multiwall Carbon Nanotubes content. Maximum adsorption capacity for Disperse Blue 56 at pH 7.0, 5.0 and 3.0 was found to be 0.53, 0.56 and 0.97 mmol/g, respectively. Isotherm results demonstrated that the linear correlation coefficients and standard deviations of Nernest and Freundlich isotherms were specified and that the Freundlich isotherm best fitted the experimental results. The adsorption kinetics was more precisely denoted by a pseudo second-order model revealed by regression grades. Furthermore, it was shown that the UV/H$_2$O$_2$/ Multiwall Carbon Nanotubes process could be used as eco-friendly method to degrade dyes from colored wastewater. Prog. Color Colorants Coat. 8 (2015), 123-133 © Institute for Color Science and Technology.*

1. Introduction

Due to ever-growing demands in textiles, synthetic organic dyes are broadly used for dyeing textile fibers. But, these materials create confident health hazards and environmental contamination. Dye effluents not only are aesthetic pollutants as far as their colors are concerned but may also interfere with light penetration in the receiving water bodies, thereby disturbing the biological methods. Further, dye effluents could contain chemicals that demonstrate toxic effects toward microbial populations [1, 2]. During past decades, a number of physical, chemical and biological methods for purification–decoloration were published and some of them were accepted by the textile industry. Some of the various processes were developed to treat wastewater from textile industry include filtration process [3], biological process [4], adsorption process [5], electrochemical process [6, 7], advanced-oxidation process [8-10], and etc. The advanced oxidation processes have been investigated for many years and it is one of important processes due to their high

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reactivity but low selectivity. The mechanism of chain reactions involves hydroxyl (OH$^\bullet$) and hydroperoxy radicals (HO$_2^\bullet$). The main advantages of this method are the reduction of byproduct generation, absence of kinetic limitations, production of highly reactive free radicals, removal of overdosing hazardous oxidizing agents, high efficiency and process rate [11]. Among the treatment choices, adsorption process appears to have significant potential for the removal of color from industrial effluents and it has been used with great success [12]. Also, adsorption by activated carbon (AC) is an identified method for micro pollutants removal [13]. It has many advantages over several other conventional treatment methods for wastewater treatment. These include less land area (half to quarter of what is required in a biological system), lower sensitivity to diurnal variation, unaffected by toxic chemicals, greater flexibility in the design and operation, and superior removal of organic contaminants [14]. But, the high cost of the activated carbon coupled with the problems associated with regeneration, has necessitated the search for alternate techniques [2].

Despite the diversity of dye decoloration methods, there is no single process capable of adequate treatment, due to the complex nature of colored effluents. Hence, it seems that the best solution for dye removal from textile wastewater is a combination of different techniques. In this study, the decoloration kinetics of disperse dye solution is studied by UV/H$_2$O$_2$/MWCNTs (multi-walled carbon nanotubes) technique. The main goal of this study is to evaluate the synergic effect between H$_2$O$_2$ and MWCNTs in the presence of UV light, considering changes of the initial solution pH and dye concentration. Moreover, dye oxidation rate constants and regression coefficients are also investigated.

2. Experimental

2.1. Materials and methods

The multi-wall carbon nanotube (MWCNT) with outer diameter of 10-20 nm, inner diameter of 5-10 nm, length of 10-30 μm and about 95% purity (Figure 1) was purchased from the Neutrino, Co. Ltd. (Iran). Disperse Blue 56 (DB56) dye was supplied from Alwan-Sabet Co. Ltd. (Iran). The DB56 with molecular weight of 304.69 g/mol is a low energy disperse dye. Table 1 shows the characteristics of DB56. Acetic acid, Sulfuric acid and Hydrogen peroxide from Merck were of analytical grade. For UV radiation, OSRAM HNS 15W OFR (Japan) with UVC radiated power and light cabinet with dimension of 50*50*50 cm^3 (Figure 2) was used.
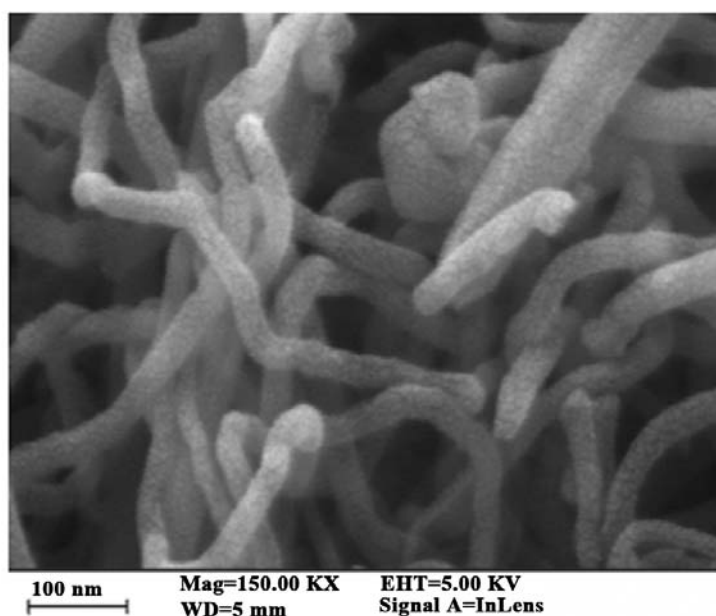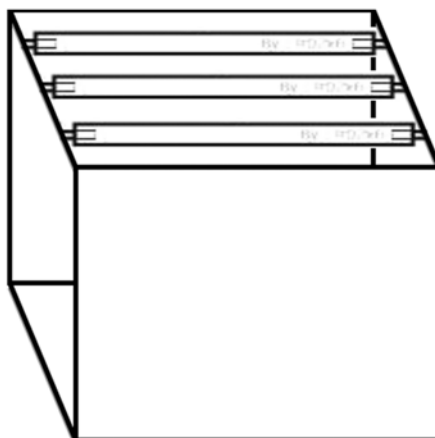
Figure 2: UV cabinet (50*50*50 cm³).

Table 1: chemical structure of DB56

C.I. Generic Name	C.I. Constitution No	Dye structure	Commercial Name
C.I. disperse blue 56	63285		Ariapres Blue EBL

2.2. Adsorption of DB 56

2.2.1 Dye removal

The experiments were carried out in a dye bath containing 0.2 g MWCNTs and 50 ml dye solution while stirring at 250 rpm. Hydrogen peroxide (H_2O_2) was used as oxidation agent. The acidity of the solution was adjusted by sulfuric acid and acetic acid. DB56 solution was treated with the suspension at pH 3, 5 and 7 for 2.5 h. The suspensions were filtered with 0.2 mm filter paper after every period. Shimadzu UV-mini1240 spectrophotometer was used at 535 nm (absorption maximum wavelength of DB56 dye) for determining the solutions optical density.

2.2.2. Kinetics of adsorption

First and second order kinetics which have been evaluated using experimental data are defined as:

$$Ln(C_\infty - C_t) = LnC_\infty - Kt \tag{1}$$

$$\frac{t}{C_t} = \frac{1}{K_2 C_\infty^2} + \frac{1}{C_\infty} \tag{2}$$

Where C_∞ and C_t are dye concentrations at equilibrium and time t, respectively. K_1 and K_2 are the rate constants of the first and second order pseudo equation (K_1: min^{-1}, K_2: $g.mg^{-1}.min^{-1}$). Since neither the pseudo first-order nor the second order model can identify the diffusion mechanism, the kinetic results were analyzed using intraparticle diffusion model (equation 3) to elucidate the diffusion mechanism:

$$C_t = K_i t^{1/2} + C \tag{3}$$

where C is the intercept and k_i is the intraparticle diffusion rate constant (mg/g $h^{1/2}$), which can be evaluated from the slope of the linear plot of C_t versus $t^{1/2}$ [15].

2.2.3. Adsorption isotherm

The Nernest and Freundlich models were employed to define the equilibrium adsorption in this study. For Nernest model

$$C_a = KC_s \qquad (4)$$

where C_a is the amount of dye adsorbed per gram of MWCNTs (mg/g), C_s is the equilibrium concentration of the dye in the solution (mg/l), K is the Nernest constant that depends on the affinity.

3. Results and discussion

3.1. Effect of oxidation agent on DB56 removal

Solutions with different concentrations of H_2O_2 (2, 3 and 1.7 M) were studied for investigating the effect of H_2O_2 concentration.

The Freundlich model is (equation 5):

$$C_a = K_F C_s^n \qquad (5)$$

where C_a is the dye concentration on MWCNTs (g/Kg), C_s is the dye concentration in solution (g/l), K_F and n are the Freundlich constants, which represent the adsorption capacity and the adsorption strength. Figure 3 shows the results of DB56 absorption for different concentrations of H_2O_2 at pH = 5 and 3 (pH=7 is not shown).

As can be seen from Figure 3 and Table 2, the decoloration increases from 28.84% to 34.61% at pH=5 and from 42.33% to 59.87% at pH=3 by increasing H_2O_2 from 0.85 to 1.7 M. At higher H_2O_2 contents, decoloration decreases due to the hydroxyl radical scavenging effect of H_2O_2 and recombination of hydroxyl radicals [16]. At higher pH values, some excess OH$^•$ radicals are produced according to equations 6 and 7.
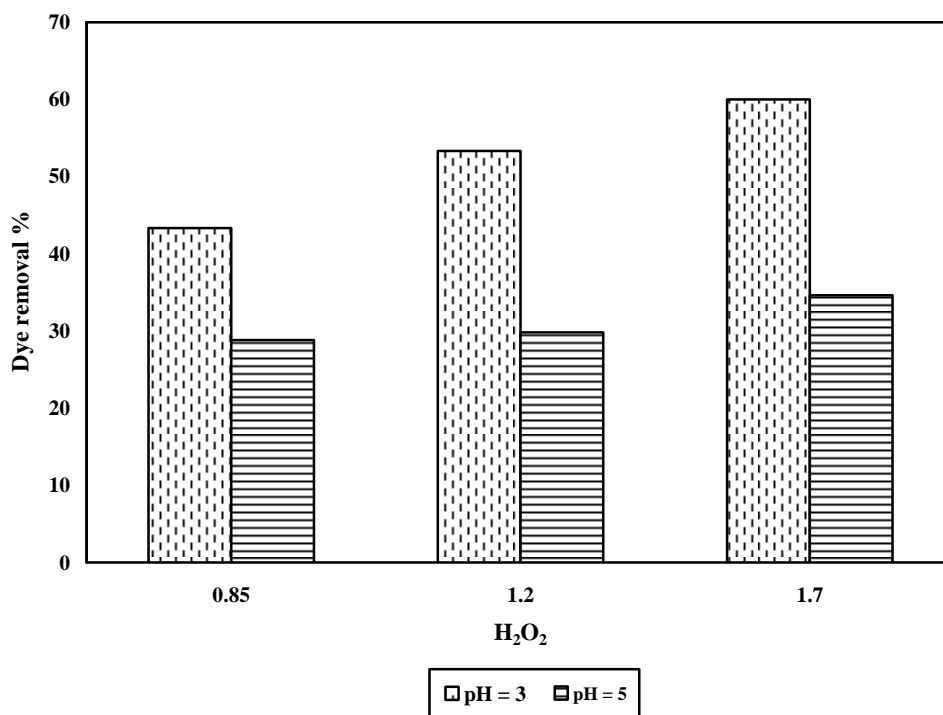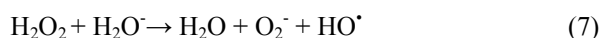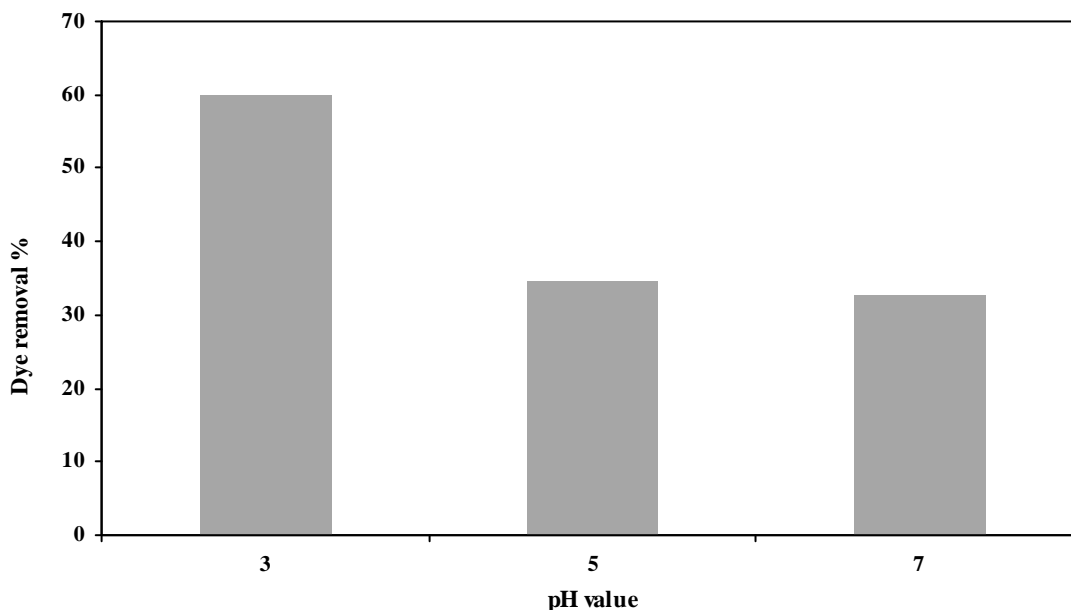
$$H_2O_2 \rightarrow H^+ + H_2O \qquad (6)$$

$$H_2O_2 + H_2O^- \rightarrow H_2O + O_2^- + HO^• \qquad (7)$$

$$H_2O_2 + UV \rightarrow 2HO \qquad (8)$$

Figure 3: Effect of hydrogen peroxide concentration at pH = 3 and pH = 5.

Table 2: dye oxidation rate constants and regression coefficients (pH=5).

H₂O₂ Conc.(g/L)	% Dye removal	K₁	R²	K₂	R²	Kᵢ	R²
0.85	28.84	0.0037	0.85	0.0086	0.94	13.40	0.88
1.2	29.8	0.0039	0.84	0.00907	0.89	13.83	0.87
1.7	34.61	0.0047	0.86	0.0113	0.95	14.74	0.90

Figure 4: Effect of initial solution pH on the amount of dye removal (H_2O_2 Concentration = 1.7 M).

From Table 2, the decolorizing reaction rate constants (k) increase with the initial H_2O_2 concentration.

Figure 4 shows that lower pH values yield better dye removal results compared with pH 5 and pH 7 at constant H_2O_2 and MWCNTs concentrations [12]. Similar adsorption behavior with variation in solution pH has been reported in the literature [17-20]. Furthermore, hydroxyl radicals are strong enough to reduce the organic structures (i.e. organic dyes to toluene, benzene, phenol and etc). It was suggested that the CNTs have good adsorption performance for wastewater due to their pore structure and the existence of a wide range of surface functional groups [20].

3.2. Effect of initial dye concentration

The effect of dye concentration in wastewater treatment is shown in Figure 5. Increasing the dye concentration reduces the oxidation rate (at constant amounts of hydrogen peroxide and MWCNTs). Figure 5 clearly reveals that the increase in dye concentration decreases the removal efficiency and decolorizing reaction rate constant. The increase in dye concentration increases the number of dye molecules in the water and not the hydroxyl radical, so the removal rate decreases.

3.3. Kinetics studies

According to kinetic data in Table 2, oxidation of dyes using MWCNTs/hydrogen peroxide solution, assisted with UV radiation (at pH=5) follows the second-order kinetics, i.e. the oxidation depends on the amount of H_2O_2 and the pH value. Table 3 shows the data at pH=3.

To determine the effect of initial dye concentration on the oxidation rate, kinetics data are presented in

Table 2. The kinetics of DB56 degradation by MWCNTs / H_2O_2 was investigated and the results are shown in Figure 6a which shows that the DB56 degradation will be in equilibrium after 120-150 min. The decoloration efficiency increases from 60% to 85% by decreasing the pH value from 5 to 3 (Figure 6b). The second-order kinetics was also investigated. Table 3 shows the dye oxidation rate constants and regression coefficients at pH 3. It was revealed that the rate of dye oxidation at different hydrogen peroxide concentrations follows the second-order kinetics. By increasing the amount of hydrogen peroxide, dye removal will increase. It is more significant at acidic pH values. Regression and rate constants data at different pH values are illustrated in Table 4 which confirms the second order rate model with excellent coloration.
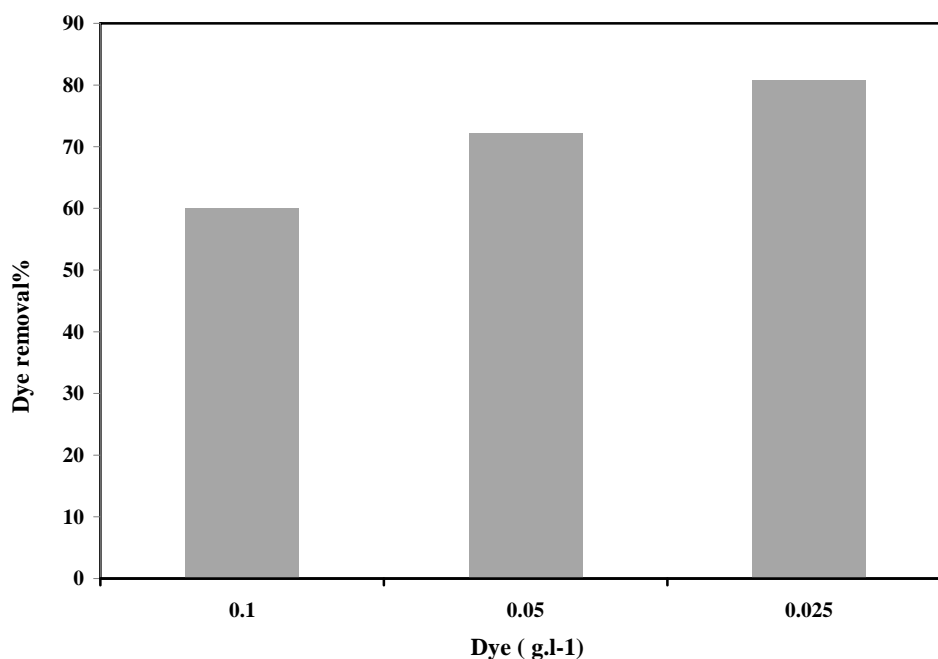

Figure 5: effect of dye initial concentration (H_2O_2 concentration = 1.7 M at pH=3).

Table 3: dye oxidation rate constants and regression coefficients (pH=3).

H_2O_2 Conc.(g/L)	% Dye removal	k_1	R^2	k_2	R^2	k_i	R^2
0.85	43.33	0.0063	0.9	0.0141	0.91	13.28	0.91
1.2	53.33	0.0084	0.85	0.0211	0.89	13.63	0.86
1.7	60	0.01018	0.86	0.0277	0.9	14.8	0.88

Table 4: dye oxidation rate constants and regression coefficients (pH value & Dye Conc.)

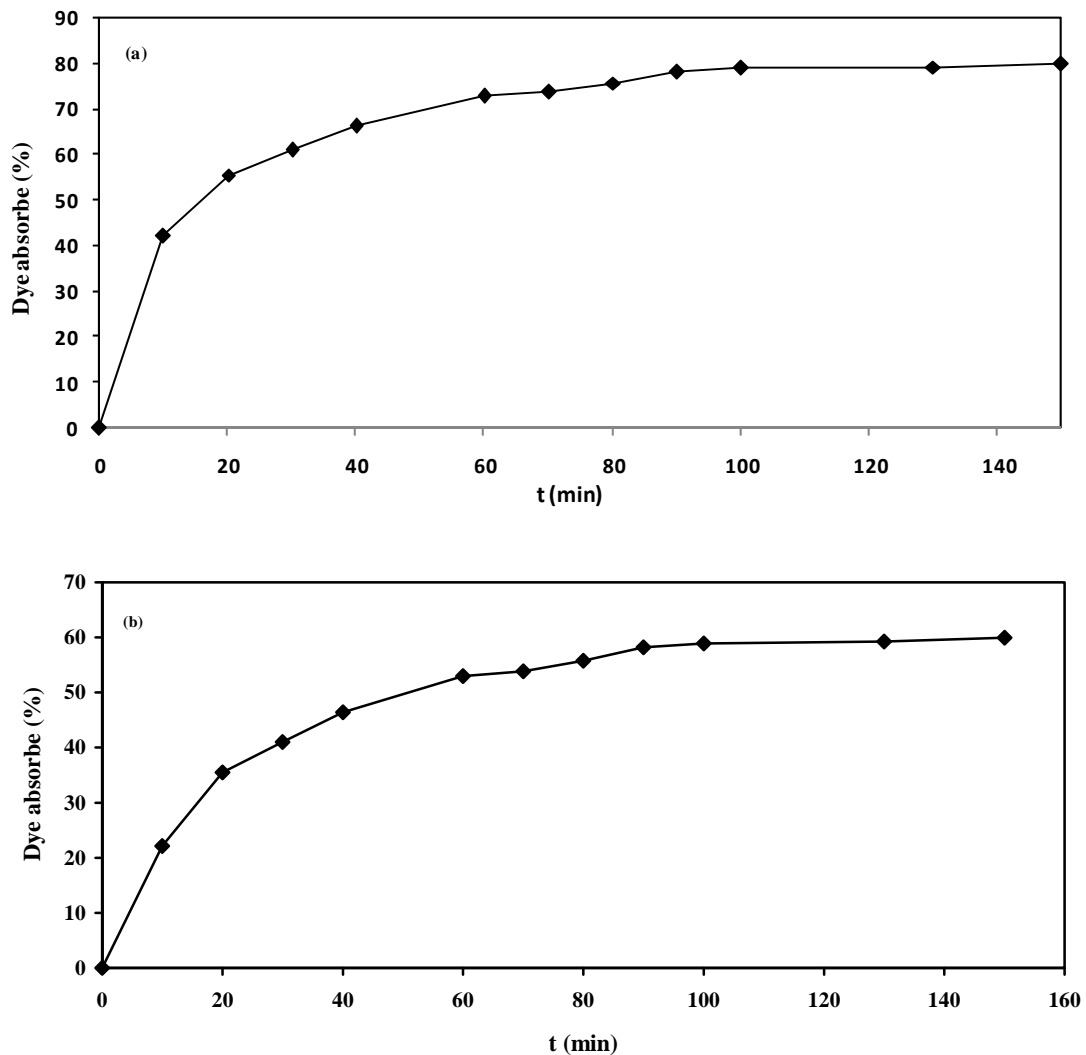| Properties		% Dye removal	R^2	k_i	R^2	k_2	R^2	k_1
Dye Conc. (g/l)	0.1	60	0.84	14.8	0.92	0.0277	0.86	0.01018
	0.05	72.24	0.79	14.93	0.94	0.0482	0.81	0.01424
	0.025	80.82	0.79	15.06	0.93	0.078	0.73	0.01834
pH	3	0.88	14.8	0.95	0.0277	0.86	0.01018	60
	5	0.89	13.69	0.95	0.0113	0.86	0.0047	34.61
	7	0.92	13.04	0.93	0.0103	0.88	0.0043	32.69

Figure 6: kinetic analysis of pH effect at 298 K (a) pH= 3 and (b) pH= 5.

3.4. Effect of MWCNTs

Figure 7 presents the effect of MWCNTs on the adsorption of DB56. As can be seen, the amount of adsorbed dye significantly increased by introducing MWCNTs to the solution. For example, the color removal increases from 22% to 64% after 3 h. However, the amount of MWCNTs for the adsorption enhancement is low enough to compensate its cost. On the other hand, the adsorption of DB56 significantly declined without MWCNTs. similar observations can be found in the literatures [20-24]. Chung-Hsin Wu suggested that the adsorption enhanced by addition of CNTs [21].

There is a significant cooperative effect when oxidation is carried out in the presence of MWCNTs. MWCNTs catalyze the decomposition of hydrogen peroxide into free radicals such as hydroxyl radicals which are very active in oxidation reactions in the aqueous phase. The electron transfer from the surface of MWCNTs seems to be involved in the corresponding mechanism, accordingly to a pathway similar to the activated carbon reaction [22] (equations 9 to 12).

$$MWCNTs + H_2O_2 \rightarrow MWCNTs^+ + HO^- + HO^\bullet \qquad (9)$$

$$HO^\bullet + RH \rightarrow H_2O + R^\bullet \qquad (10)$$

$$R^\bullet + MWCNTs^+ \rightarrow R^+ + MWCNTs \qquad (11)$$

$$R^+ + H_2O^\bullet \rightarrow ROH + H^+ \qquad (12)$$

The OH$^\bullet$ radicals formed are capable of oxidizing the organic pollutants (RH), thus causing the chemical decomposition of these compounds as expressed by reactions (equations 10 to 12) [23]. MWCNTs also can absorb organic dyes by immobilizing them via covalent bonds, as reported in literatures [24, 25] where MWCNTs and MWCNTs$^+$ represented reduced and oxidized, respectively.

3.5. Adsorption isotherms

The Freundlich and Nerest adsorption isotherm of the dye at pH=3 was illustrated in Figures 8a and 8b. By comparing the values of R^2, it can be concluded that the adsorption of DB56 in Freundlich was more favorable than Nernest. The model parameters and R^2 values are presented in Table 4, which indicates that the Nernest model showed lower correlation with the experimental adsorption data compared to the Freundlich model.
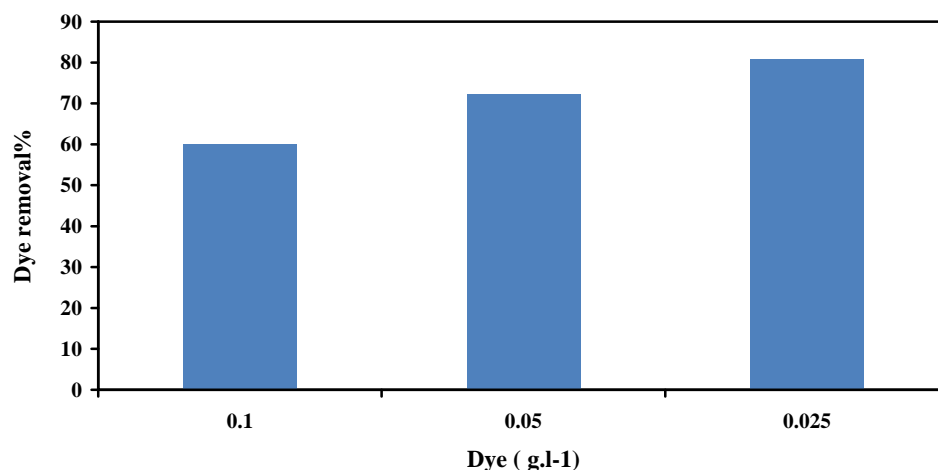

Figure 7: effect of dye initial concentration without MWCNTs (H_2O_2 concentration = 1.7 M at pH=3).
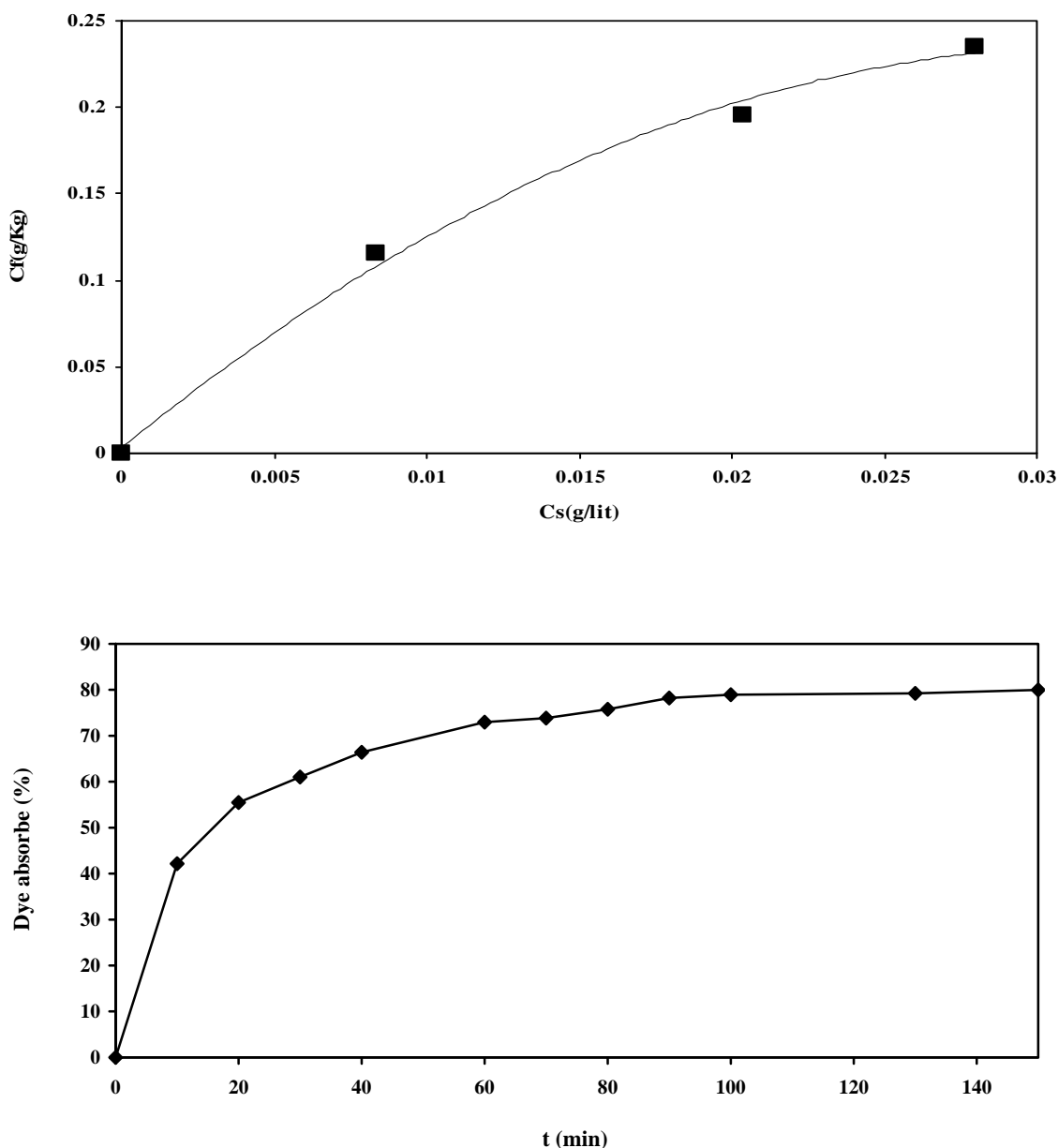
Figure 8: Adsorption isotherm of DB56 at 298 K: (a) Freundlich and (b) Nernest plots (H_2O_2 concentration = 1.7 M at pH=3).

4. Conclusions

In this paper, the effect of MWCNTs / hydrogen peroxide in the presence of ultraviolet light on the equilibrium and dynamic adsorption of DB 56 was investigated. The regression results of the adsorption recommended that the Freundlich model is more suitable than Nernest model. Effect of dye concentration, pH and H_2O_2 on the process was also investigated. MWCNTs catalyze the oxidation with hydrogen peroxide and its rate decreases by increasing of dye concentration. Also, the results showed that the performance of this method decreases with increasing the solution pH. Obtained results indicated that using of MWCNTs with H_2O_2 is 15% to 20% better than using H_2O_2 individually.

MWCNTs have good adsorption performance for wastewater and aromatic structures (i.e. benzene, phenol, etc.) by degradation of dye structure through oxidation process. MWCNTs catalyze the

decomposition of hydrogen peroxide into free radicals, such as hydroxyl radicals, which are very active in oxidation reactions in the aqueous phase. Furthermore, the absorbent can absorb organic dyes by immobilizing them via covalent bonds, as reported in literatures.

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