

PHOTOCATALYTIC DEGRADATION AZO DYE DIRECT RED 23 USING CARBON NANOTUBES PARTICLES BY UV/H₂O₂ PROCESS IN BATCH PHOTOREACTOR

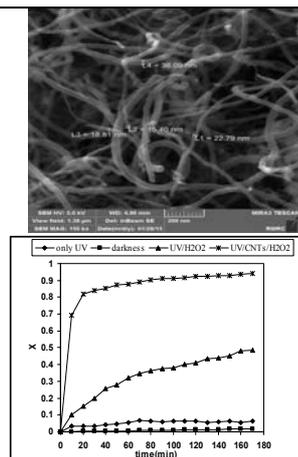
Misagh TORKAMAN,^a Reza MORADI^{b*} and Bahram KEYVANI^a

^aDepartment of Chemistry, Faculty of Engineering, Saveh Branch, Islamic Azad University, Saveh, Iran

^bDepartment of Chemistry, Toyserkan Branch, Islamic Azad University, Toyserkan, Iran

Received December 21, 2015

In this paper, photocatalytic degradation of azo dye Direct Red 23 (DR23) in aqueous solution using multi walled carbon nanotubes (MWCNTs) particles was employed to degrade rate of the dye increased. The MWCNTs particles were characterized by scanning electron microscopy (SEM), Transmission Electron Microscopy (TEM) and Fourier transform infrared (FT-IR). Regarding the specified scale in the SEM image size of the particles is nanometer. Optimum conditions were determined for the photocatalytic degradation of dye using a factor at the time the experimental design method. The most efficiency in optimum conditions (pH= 6, catalyst amount= 4mg/L, dye concentration= 60 ppm and H₂O₂ concentration= 450 ppm) was observed. The effect of UV irradiation, UV/H₂O₂ and UV/CNTs/H₂O₂ on photo-degradation of DR23 were studied. So first order reaction with $k= 0.0321 \text{ min}^{-1}$ was observed for the photocatalytic degradation reaction.



INTRODUCTION

Dyes are one of the most hazardous materials in various industries which can cause severe health problems in human beings, since they exhibit high biotoxicity and potential mutagenic and carcinogenic effects.¹⁻² Different types of dyes have been extensively used in industry for applications such as textiles, leathers, paper, foodstuffs, additives, gasoline, cosmetics, xerography, laser materials, and so on.³ The release of wastewater containing these dyes is a dramatic source of aesthetic pollution, eutrophication and perturbations to the environment and aquatic life.

Due to the complex molecule structure of azo dyes, conventional methods of waste treatment have several drawbacks which are not effective for complete degradation of azo dye.⁴⁻⁵ Most of these technologies including chemical or biological ways can only break little part of the azo bonds and remove some degree of color, while the azo linkages are just reduced to aromatic amines that are colorless but can also be toxic and potentially carcinogenic.⁶ Among Different techniques for the removal of colored compounds, the traditional ones, such as adsorption, ultra-filtration, coagulation-flocculation, ozonation, H₂O₂ oxidation, photooxidation, and combination of

* Corresponding author: reza.moradi_bi@yahoo.com, r.moradi@tuyiau.ac.ir

several techniques have been applied.⁷⁻⁹ The simultaneous use of CNTs and H₂O₂ to a certain extent yielded a significant improvement of dye photooxidation compared to that of the H₂O₂ oxidation alone. Hydrogen peroxide can be activated on the CNTs surface to generate hydroxyl free radicals. The CNTs is an electron-transfer catalyst. The catalytic decomposition of H₂O₂ by CNTs involves the exchange of a surface hydroxyl group on CNTs surface with a hydrogen peroxide anion (HO₂⁻) to on the surface, which then decomposes another generate peroxide H₂O₂ molecule producing oxygen and regenerating the CNTs active site.¹⁰⁻¹² Recently, CNTs have attracted great interest as a new type of catalyst for removing environmental pollutants (*e.g.* small molecules, heavy metal ions and colored wastewater).¹³

CNTs are nanometric cylinders consisting of a graphene sheet wrapped up to form a tube. There are different kinds of methods to produce CNTs, such as thermal chemical vapor deposition (CVD), laser ablation, catalytic chemical vapor deposition (CCVD), plasma enhanced chemical vapor deposition (PECVD) or arc discharge. The scientific contribution and the goal behind this paper are as follows: (1) the process offers great potential as an industrial technology to detoxify wastewaters, and (2) wastewater treatment sectors and textile industry will benefit from the results. In this paper, MWCNTs particles were characterized by SEM, TEM and FT-IR analysis. The reaction kinetic of dye was studied. The effects of

operational parameter such as pH, catalyst amount, dye concentration and H₂O₂ concentration on the process were studied and optimized. The results indicated that the UV/CNTs/H₂O₂ could be used as an eco-friendly process to degrade dye.

EXPERIMENTAL

1. Materials

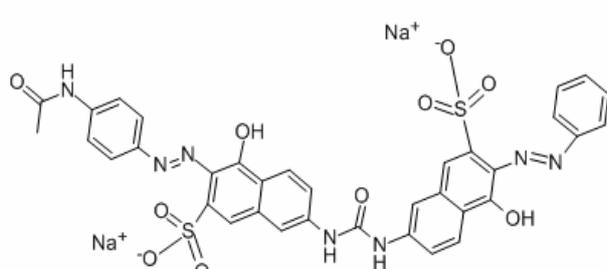
The diazo dye, DR23 was obtained from Alvan Sabet Company (Iran) and was used without further purification. The structure and characteristics of DR23 is shown in Table 1. The pH values were adjusted at desired level using dilute NaOH and H₂SO₄. MWCNTs (appearance: black powder, length: 5–15 μm, outer diameter: 15–40 nm, purity (carbon): ≥92%, density: 0.03-0.16 g/cm³, and specific surface area (BET, N₂): 127 m²/g) was received from Research Institute of Petroleum Industry (Iran). Other chemicals used in the paper were purchased from the Merck Company (Germany). Double distilled water was used for preparation of requisite solutions.

2. Apparatus

Fig. 1 shows the schematic diagram of batch photoreactor which was used for photocatalytic decomposition of DR23. In this equipment, capacity 1 L with a mercury lamp Philips 15W (UV-C) was used in photoreactor. UV/Vis Spectrophotometer, Jenway (6505) was employed to measure the absorbance using glass cells of path length 1 Cm. The morphologies of the catalyst were taken by SEM model MIRA3 TESCAN and TEM model EM10C–Zeiss. The FT-IR spectroscopy was measured on PerkinElmer Spectrometric Analyzer using KBr pellets. For COD measurement, COD meter analyzer model AL250 AQUALYTIC was used.

Table 1

The structure and characteristics of dye DR23.

Dye	Structure	λ_{\max} (nm)	MW (g/mol)
Direct Red 23 (DR23)		500	813.72

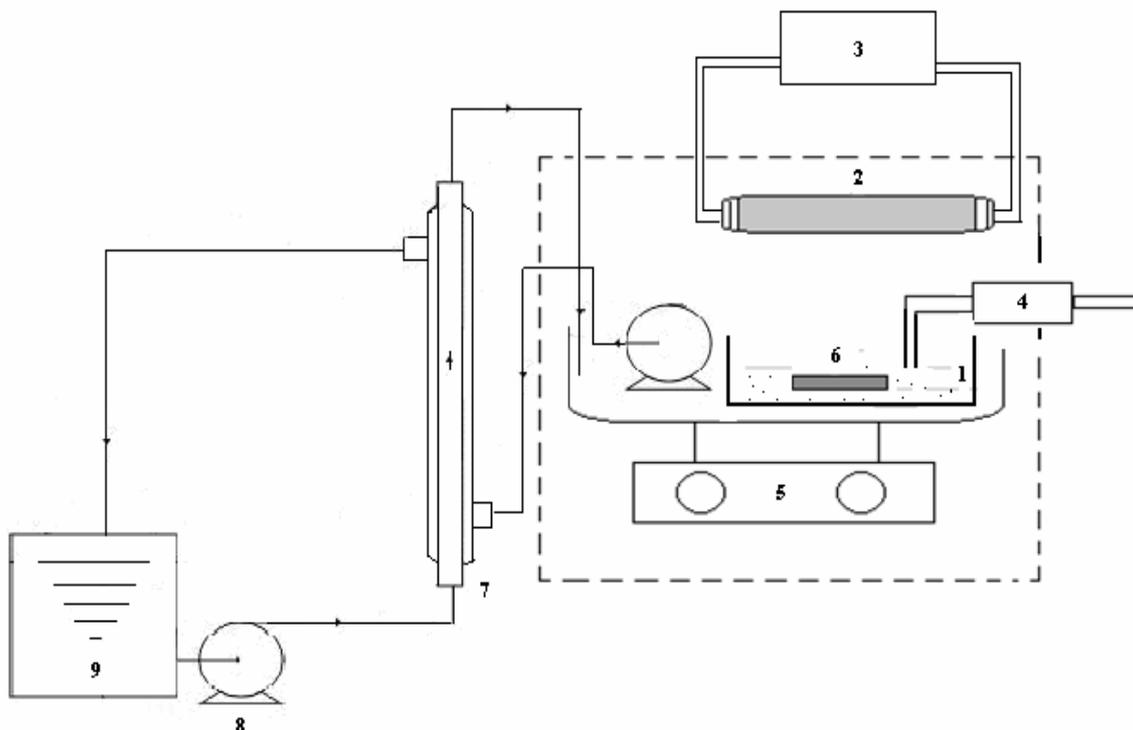


Fig. 1 – Schematic diagram of batch photoreactor: (1) reaction flask (Pyrex); (2) UV lamp; (3) power supply; (4) sampling; (5) heater stirrer; (6) magnet; (7) condenser; (8) pump; (9) tank.

3. Procedures

For the photo-degradation of DR23, a solution containing known concentration of dye and catalyst was prepared. The suspension pH values were adjusted at the desired level using dilute NaOH 0.1N and H₂SO₄ 0.1N (the pH values were measured with Metrohm pH meter) and then were allowed to equilibrate for 30 min in darkness. Then, the prepared suspension was transferred to reaction flask (Pyrex). The degradation reaction took place under the radiation of a mercury lamp while agitation was maintained to keep the suspension homogeneous. The concentration of the samples was determined (at 10 min intervals and centrifuged with centrifuge 4232 ALC) using a spectrophotometer (UV-Vis spectrophotometer, Jenway (6505) at $\lambda_{max} = 500$ nm. The degree of photo-degradation (X) as a function of time is given by:

$$X = \frac{C_0 - C}{C_0} \quad (1)$$

where C_0 and C are the concentration of dye at $t = 0$ and t , respectively.

RESULTS AND DISCUSSION

1. The Characterization of MWCNTs particles

Fig. 2 shows the SEM image of MWCNTs particles. Regarding the specified scale in the Fig. 2 size of the particles is nanometer. The size

and morphology of MWCNTs powder were characterized. Fig.3 shows the TEM image of MWCNTs powder. The TEM was used due to its ability to measure nanotubes diameter. From the TEM image it is possible to determine directly the diameter of one nanotubes and bundle diameter. Due to this information, a number of nanotubes in the bundle can be found. Fig. 4 shows the FT-IR spectrum of MWCNTs particles in the wave number range from 400 of 4000 cm⁻¹. The bands at 3462 and 1703 cm⁻¹ are due to O-H stretching and O-H bending, respectively. The bands at 2929 and 2873 cm⁻¹ correspond to asymmetric and symmetric aliphatic C-H stretching, respectively. Bands at 1300-1000 cm⁻¹ correspond to C-O and C-C stretching.¹⁴

2. UV- Vis spectra

The absorbance of DR23 solutions during the process at initial and after 170 min irradiation time versus wavelength (λ) are shown in Fig. 5. The spectrum of DR23 in the visible region exhibits a main band with a maximum at 500 nm. The decrease of absorption peaks of DR23 at $\lambda_{max} = 500$ nm in this figure indicates a rapid degradation of the azo dye. Complete discoloration of dye was observed after 200 min under optimal conditions.

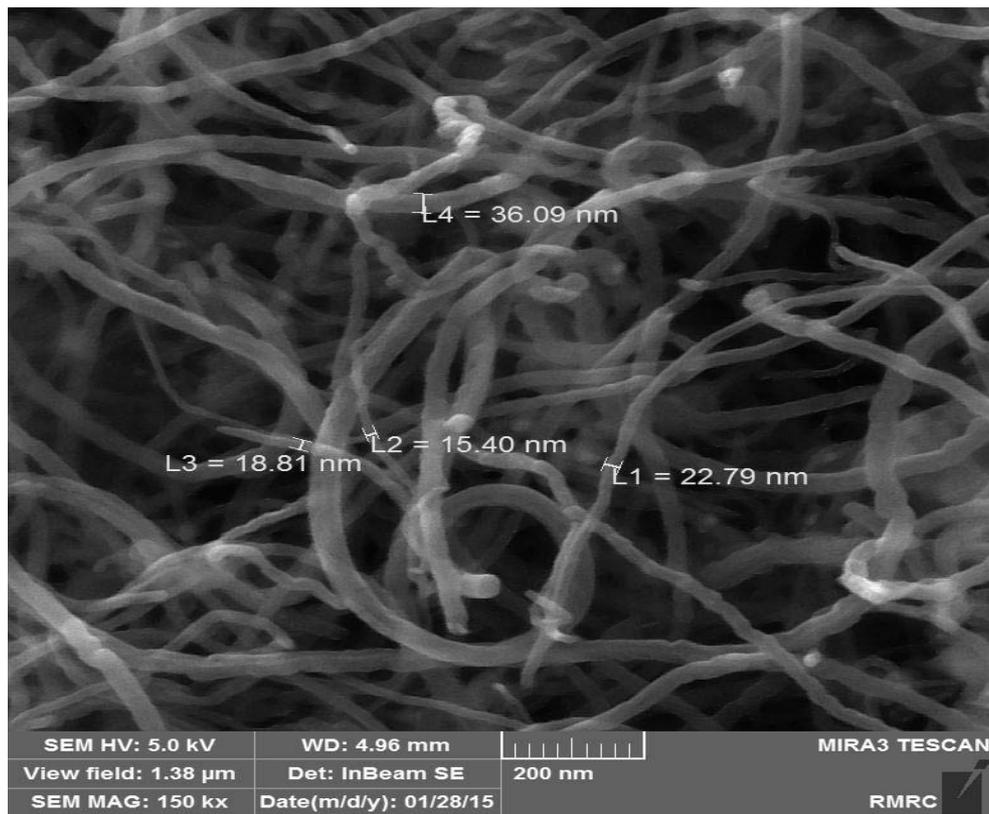


Fig. 2 – SEM image of MWCNTs.

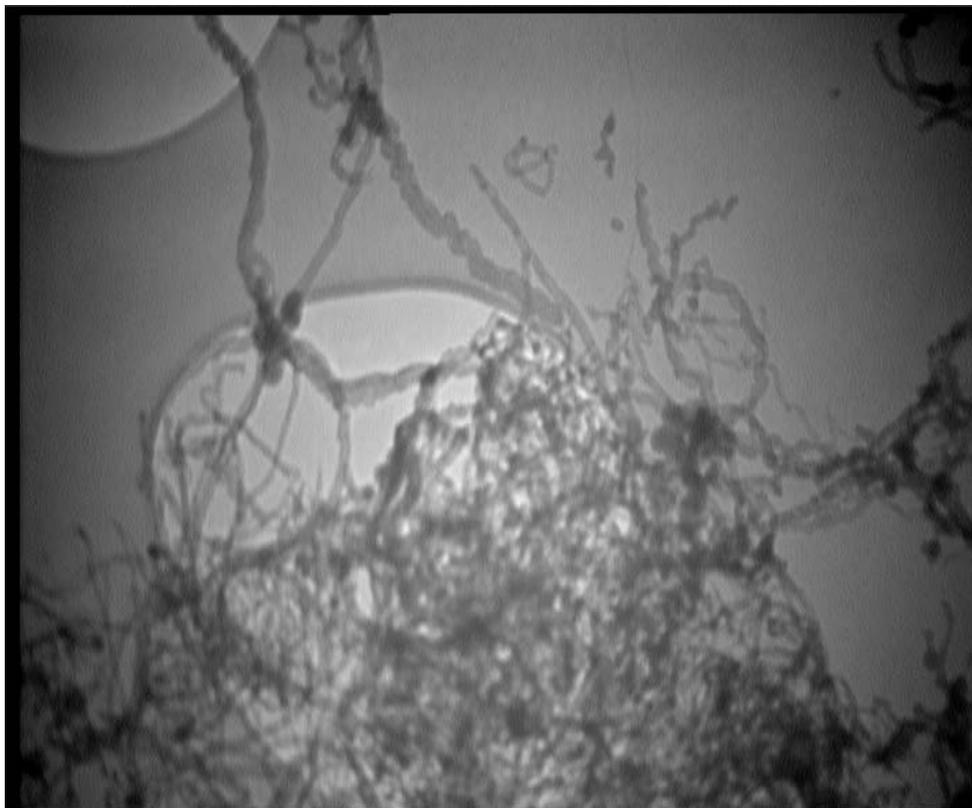


Fig. 3 – TEM image of MWCNTs.

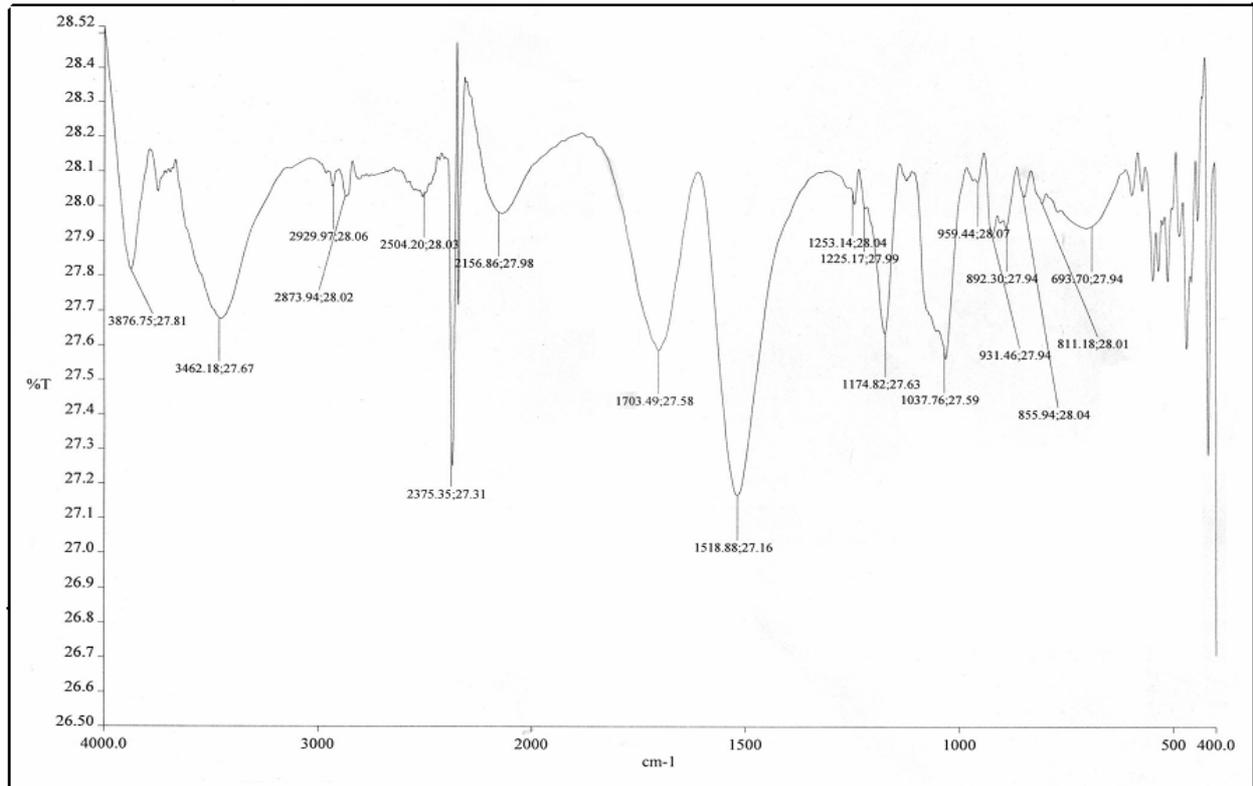


Fig. 4 – FT-IR spectrum of MWCNTs.

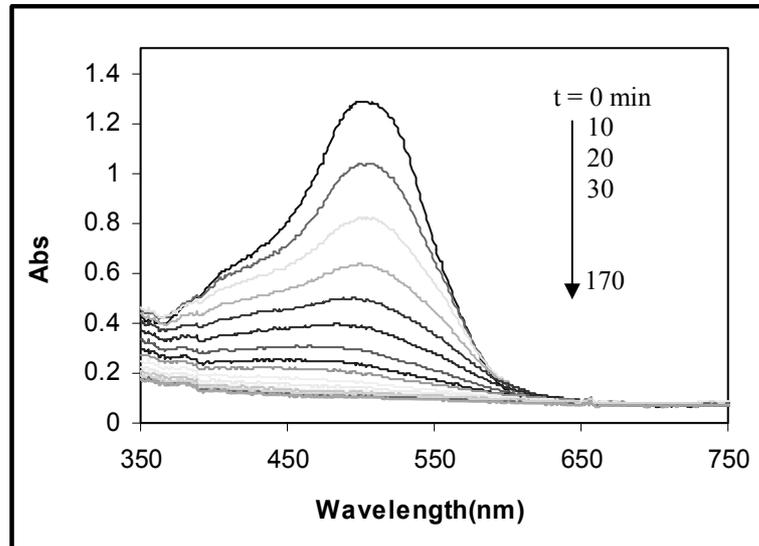


Fig. 5 – UV-Vis spectra of DR23 on photo-degradation (dye concentration = 60 ppm, catalyst amount = 4mg/L, H₂O₂ concentration = 450 ppm, pH = 6, T = 293 K, irradiation time = 170 min).

3. The effect of pH

pH is one of the main factors influencing the rate of degradation of some organic compounds in the photocatalytic process.¹⁵ It is also an important operational variable in actual wastewater treatment. Fig. 6 shows the photo-degradation of

DR23 at different pH from 2-12, which clearly shows the best results obtained in acidic solution, (pH = 6, $X = 90.53\%$). The charge of MWCNTs and its surface is presumably positively charged in acidic solution and negatively charged in alkaline solution. For the above reasons, dye that has a sulfuric group in its structure, which is negatively

charged, the acidic solution favors adsorption of dye onto the photocatalyst surface, thus the photo-degradation efficiency increases. There is also the photocatalytic degradation of DR23 in acidic solutions, which is due to the formation hydroxyl radical (OH^\bullet) as it can be inferred from H_2O_2 oxidation.¹⁶

4. The effect of initial DR23 concentration

The effect of initial concentration of DR23 on photo-degradation efficiency is shown in Fig. 7. The photo-degradation conversion of DR23 at first

increase, then decreases with an increase in the initial concentration of DR23. The presumed reason is that when the initial concentration of dye is increased, more and more dye molecules are adsorbed on the surface of MWCNTs. The large amount of adsorbed dye is thought to have an inhibitive effect on the reaction of dye molecules with photogenerated sites or hydroxyl radicals, which is due to the lack of any direct contact between them. Once the concentration of dye is increased, it also causes the dye molecules to adsorb light and the photons never reach the photocatalyst surface, thus the photo-degradation efficiency decreases.¹⁷

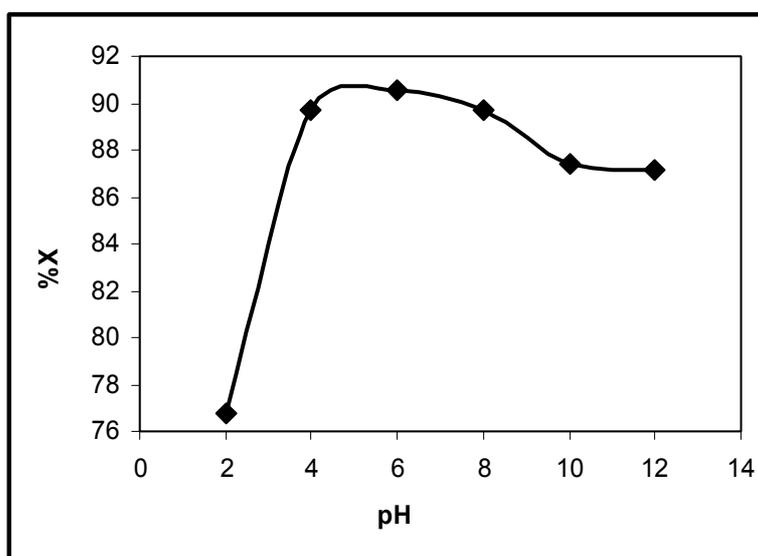


Fig. 6 – Effect of pH on photo-degradation of DR23 (dye concentration = 60 ppm, catalyst amount = 4 mg/L, H_2O_2 concentration = 450 ppm, $T=293$ K, irradiation time = 170 min).

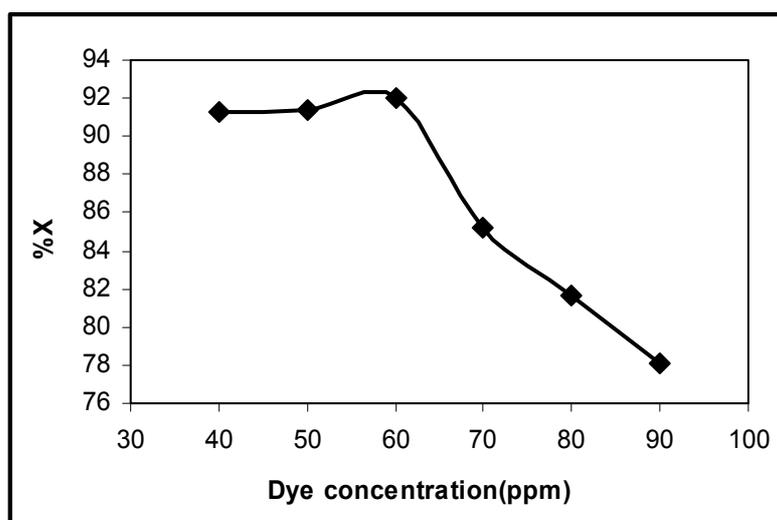


Fig. 7 – Effect of initial DR23 concentration on photo-degradation (catalyst amount = 4mg/L, H_2O_2 concentration = 450 ppm, pH = 6, $T=293$ K, irradiation time = 170 min).

5. The effect of catalyst amount

At this stage, the effect of different amounts of catalyst between 2 to 12 mg/L was tested. The results in Fig. 8 shows that increasing the catalyst amount to 4 mg/L reaction rate increased and with increasing amount of catalyst amount, reaction rate decreased. Because of reduced activity of photocatalytic in amount than 4 mg/L, which increases the photocatalytic phenomenon spread of light due to light rays with the catalyst dispersed in the solution occurred, and lost the number of photons of light energy and thus the amount photocatalytic reactions is reduced.¹⁸

6. The effect of H₂O₂ concentration

The results indicated that degradation of dye increases with increasing of H₂O₂ concentration is

shown in Fig. 9. This can be explained by the effect of the additionally produced hydroxyl radicals. When the H₂O₂ concentration increased to 450 ppm, decolorization after 170 min of irradiation could be achieved 92.97%. In higher concentrations than 450 ppm reduction in decolorization efficiency is observed. This indicates that the excess amount of H₂O₂ is decomposed without promoting further degradation or maybe due to recombination of hydroxyl radicals and also reaction of hydroxyl radicals with H₂O₂, the concentration of OH[•] and so decolorization efficiency is decreased. So the optimal amount of H₂O₂ concentration was 450 ppm.¹⁹

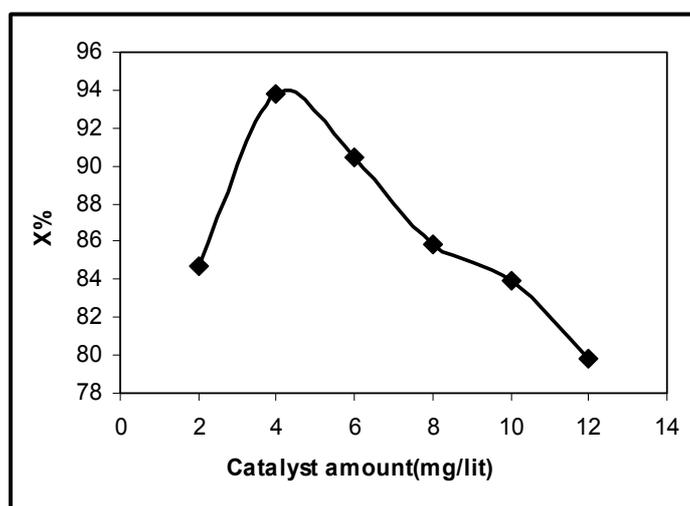


Fig. 8 – Effect of catalyst amount on photo-degradation of DR23 (dye concentration = 60 ppm, H₂O₂ concentration= 450 ppm, pH= 6, T=293 K, irradiation time= 170 min).

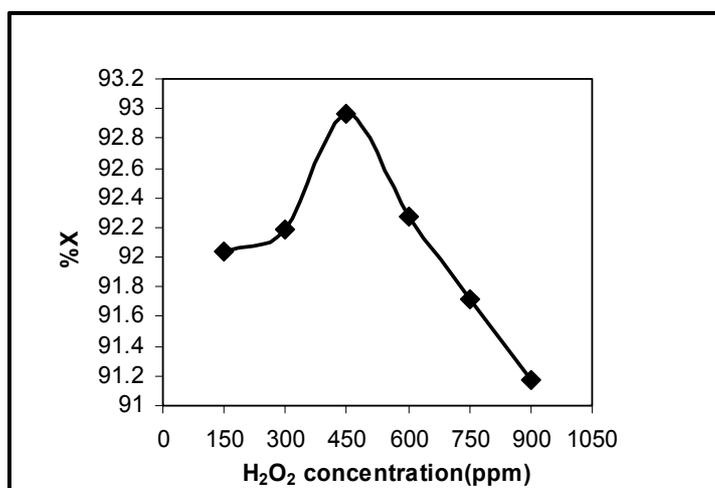


Fig. 9 – Effect of H₂O₂ concentration on photo-degradation of DR23 (dye concentration = 60 ppm, catalyst amount = 4 mg/L, pH= 6, T=293 K, irradiation time= 170 min).

7. The effect of UV irradiation, UV/H₂O₂ and UV/CNTs/H₂O₂

The effect of UV irradiation, UV/H₂O₂ and UV/CNTs/H₂O₂ on photo-degradation of DR23 are shown in Fig. 10. This figure indicates that in the presence of UV/CNTs/H₂O₂ 94% of dye was degraded at the irradiation time of 170 min while it was 48.7% for UV/H₂O₂. This was contrasted with 6.2% degradation for the same experiment performed under only UV irradiation. Adsorption of dye on CNTs is a process that also presents a low performance for dye removal from solution (1.7% of dye after 170 min of adsorption process in darkness) because of its relatively low affinity to the surface of CNTs. Considering that the hydrogen peroxide alone is not effective to oxidize dye in the colored wastewater sample, it needs to be activated by CNTs, which played a predominant role in its integrated treatment. It is observed that the simultaneous use of CNTs and H₂O₂ to a certain extent yielded a significant improvement of dye oxidation compared to that of the H₂O₂ oxidation alone. Hydrogen peroxide can be activated on the CNTs surface to generate hydroxyl free radicals.²⁰⁻²¹ The CNTs can be regarded to function as an electron-transfer catalyst involving the reduced (CNTs) and oxidized (CNTs⁺) catalyst states. The catalytic decomposition of H₂O₂ by CNTs involves

the exchange of a surface hydroxyl group on CNTs surface with a hydrogen peroxide anion (HO₂⁻) to generate peroxide on the surface, which then decomposes another H₂O₂ molecule producing oxygen and regenerating the CNTs active site.

8. Kinetics of photocatalytic degradation of DR23

Photocatalytic decomposition reaction kinetics of DR23 completely corresponds to the kinetic of pseudo-first-order model reaction.²² In the kinetic equation of pseudo-first-order, the relationship between concentration (*C*) and time (*t*) is as follows:

$$\frac{-dC}{dt} = k_{app}C \quad (2)$$

The integral equation is as follows:

$$\ln\left(\frac{C_0}{C}\right) = k_{app}t \quad (3)$$

In which *k_{app}* is the apparent pseudo-first-order rate constant (that is affected by dye concentration), and *t*, is the reaction time.

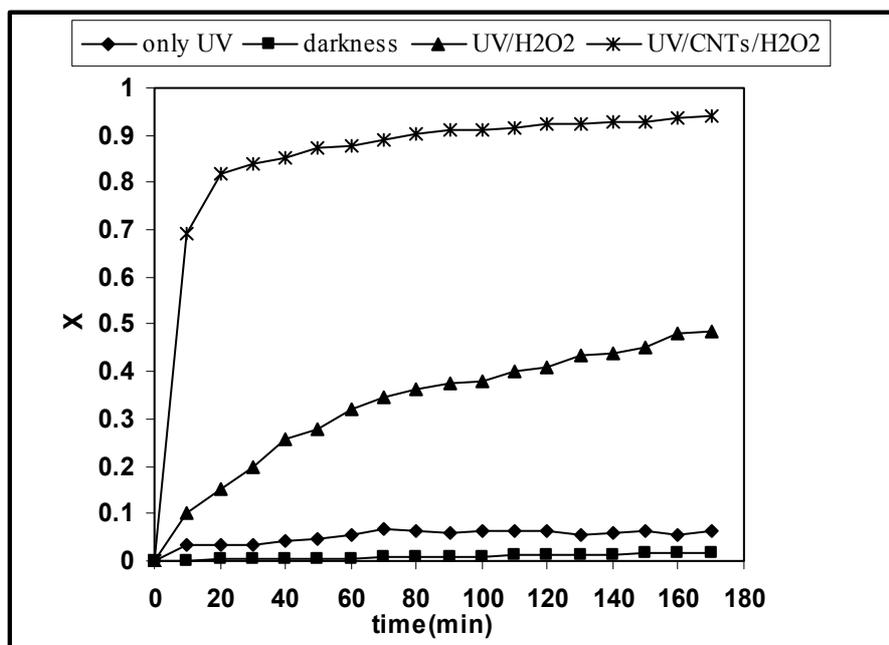


Fig. 10 – Effect UV irradiation, UV/H₂O₂ and UV/CNTs/H₂O₂ of DR23 on photo-degradation (dye concentration = 60 ppm, catalyst amount = 4mg/L, H₂O₂ concentration= 450 ppm, pH= 6, T=293 K, irradiation time= 170 min).

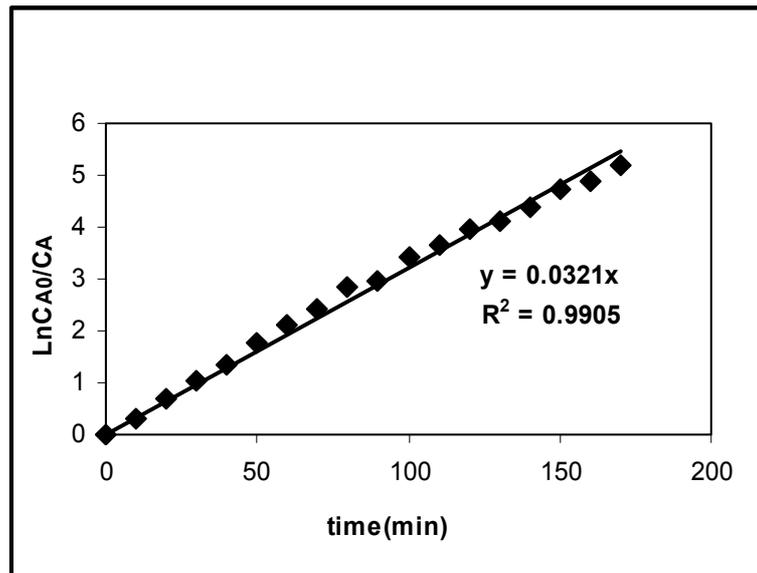


Fig.11 – Kinetics of photocatalytic degradation of DR23 (dye concentration = 60 ppm, catalyst amount = 4 mg/L, H₂O₂ concentration= 450 ppm, pH= 6, T=293 K, irradiation time= 170 min).

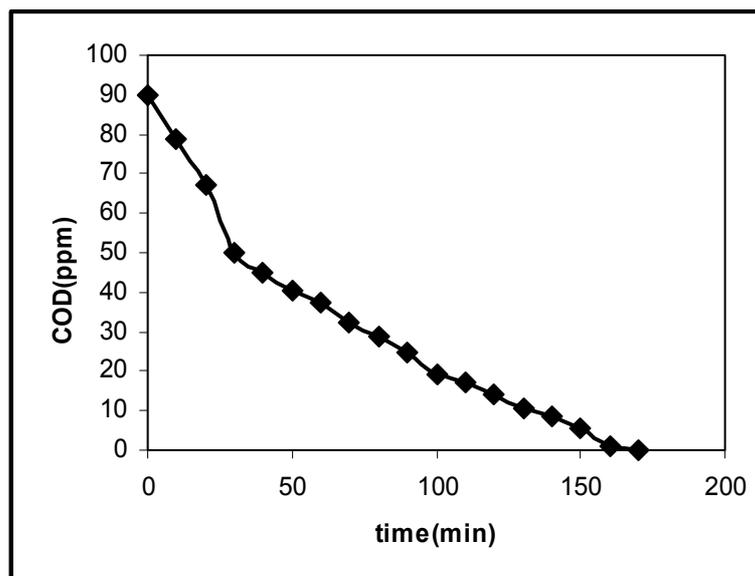


Fig.12 – COD removal of DR23 aqueous solution during the process (dye concentration = 60 ppm, catalyst amount = 4 mg/L, H₂O₂ concentration= 450 ppm, pH= 6, T=293 K, irradiation time= 170 min).

A plot of $\ln(C_0/C)$ versus t , in optimal condition for photocatalytic degradation of DR23 is shown in Fig. 11. The linear plot suggests that the photo-degradation reaction approximately follows the pseudo-first-order kinetics with rate coefficient $k = 0.0321 \text{ min}^{-1}$.

9. Photocatalytic mineralization of DR23

Mineralization can be defined as reaching the final degradation step of organic substances and

their intermediates under destructive treatment process. Organics due to the mineralization will be converted to CO₂ and H₂O. The process is able to mineralize organic pollutants content in water. The results of these experiments are shown in Fig. 12.

CONCLUSIONS

In this paper, MWCNTs particles were used as catalyst to degrade dye. Physical and chemical

characterization of catalyst was determined by SEM, TEM and FT-IR techniques. According to the literature, the results demonstrated that the MWCNTs particles have sufficient properties as a photocatalyst for degradation of dye. A batch photoreactor was used for degradation reaction. Various factors affecting in the degradation process such as: pH, catalyst amount, dye concentration and H₂O₂ concentration were analyzed and optimized. Kinetics of photocatalytic decomposition reaction was determined. Pseudo-first-order model reaction corresponds to the experiment data of photocatalytic degradation of dye. The results of COD measurements demonstrated that this process can be used for complete mineralization of DR23.

Acknowledgements: The author would like to gratefully acknowledge members of the Research Laboratory of Islamic Azad University, Toyserkan Branch, Toyserkan, Iran.

REFERENCES

1. L. Ai, C. Zhang, F. Liao, Y. Wang, M. Li, L. Meng and J. Jiang, *J. Hazard. Mater.*, **2011**, *198*, 282-290.
2. N. Bao, Y. Li, Z. T. Wei, G. B. Yin and J. J. Niu, *J. Phys. Chem. C*, **2011**, *115*, 5708-5719.
3. H. Zollinger, *Color Chemistry Synthesis, "Properties, and Applications of Organic Dyes and Pigments"*, third revised Edition, Wiley-VCH, 2003, p. 298.
4. C. M. Zhu, L. Y. Wang and L. R. Kong, *Chemosphere*, **2000**, *41*, 303-309.
5. T. Sauer, G. C. Neto and H. J. Jose, *J. Photochem. Photobiol. A: Chem.*, **2002**, *149*, 147-154.
6. N. Guettaï and H. Ait Amar, *Desalination*, **2005**, *185*, 439-448.
7. R. Gong, M. Li, C. Yang, Y. Sun and J. Chen, *J. Hazard. Mater.*, **2005**, *121*, 247-250.
8. S. S. Madaeni and Y. Mansourpanah, *Desalination*, **2004**, *161*, 13-24.
9. E. Guibal and J. Roussy, *React. Funct. Polym.*, **2007**, *67*, 33-42.
10. A. Bach and R. Semiat, *Desalination*, **2011**, *273*, 57-63.
11. A. R. Yeddou, B. Nadjemi, F. Halet, A. Ould-Dris and R. Capart, *Minerals Eng.*, **2010**, *23*, 32-39.
12. V. P. Santos, M. F. R. Pereira, P. C. C. Faria and J. J. M. Orfao, *J. Hazard. Mater.*, **2009**, *162*, 736-742.
13. X. M. Ren, C. L. Chen, M. Nagatsu and X. K. Wang, *Chem. Eng. J.*, 2011, *170*, 395-410.
14. G. Hejun, Z. Siyuan, C. Xiyuan, W. Xiaodong and Z. Liqiang, *Chem. Eng. J.*, **2013**, *223*, 84-90.
15. I. Peternel, N. Koprivanac and H. Kusic, *Water Research*, **2006**, *40*, 525-32.
16. J. Saien, M. Asgari, A. R. Soleymani and N. Taghavinia, *Chem. Eng. J.*, **2009**, *151*, 295-301.
17. A. Aleboyeh and Y. H. Moussa, *Dyes Pigments*, **2006**, *66*, 129-134.
18. M. J. Watts and A. T. Cooper, *J. of Solar Energy*, **2008**, *82*, 206-211.
19. N. Daneshvar, D. Salari and A. R. Khataee, *J. Photochem. Photobiol. A*, **2003**, *157*, 111-116.
20. T. A. Kurniawan and W. H. Lo, *Water Research*, **2009**, *43*, 4079-4091.
21. N. A. Klimentko, L. A. Savchina, T. V. Polyakova and I.P. Kozyatnik, *J. Water Chem. Technol*, **2009**, *31*, 92-97.
22. S. Qu, F. Huang, S. Yu, G. Chen and j. Kong, *J. Hazard. Mater.*, **2008**, *160*, 643-647.