



Removal of Direct Red Dye 23 from Water and Wastewater Using $S_2O_8^{2-}$ Oxidant Activated by UV Irradiation: An Investigation on the Operational Parameters

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Abstract

The photo-oxidative decolorization of Direct Red 23 (DR23), a textile dye which is suspected to be carcinogenic was investigated using peroxydisulfate activated by UV irradiation and heat in a batch photo-reactor at experimental conditions. A very simple analytical method, direct UV-vis spectrophotometric detection, was utilized for the progress of photo-oxidative decolorization of dye in aqueous medium. The effect of operational parameters namely initial peroxydisulfate concentration, pH and temperature of reaction, additional photo-catalyst on the decolorization rate was truly investigated. The results showed that use of UV/ $S_2O_8^{2-}$ system was a highly effective way to remove colored components from contaminated waters. Optimum conditions for maximum degradation was acidic pH (pH=2), temperature of 50°C with 7.5 mM of peroxydisulfate. Also, it was observed that dye degradation was enhanced using nano-TiO₂ glass beads as photo-catalyst and peroxydisulfate consumption was significantly reduced to achieve the same percentages of dye degradation which was observed in UV/ $S_2O_8^{2-}$ system at the same conditions.

Keywords: Advanced Oxidation Processes, Peroxydisulfate, UV irradiation, Direct Red 23, Immobilized nano-TiO₂.

Introduction

Different types of dyes are used in many industries such as textile, paint, ink, plastics and cosmetics. The textile industry utilizes about 10000 different mineral and organic dyes and pigments. The worldwide annual production of these dyes is over 7×10^5 tons.

Organic dyes came up as one of the many new chemicals which could be used in many industrial activities. Due to the extensive use of these dyes in industries, they have become an integral part of industrial effluent. In fact, of the 4.5×10^5 tons of organic dyes annually produced worldwide, more than 11% is lost in

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effluents during manufacture and application processes (50000 tons approximately) [1-3].

Dyes are mainly classified for their structure, source, color and method of application in color index, which has been continuously edited since 1924. Organic dye molecules consist of a the chromophore and there are about 20 classes of chromophores groups that include acridine dyes, azo dyes, arylmethane dyes, anthroquinone dyes, nitro dyes, xanthene dyes and the quinine-amine dyes, etc. The most common of which is the azo type that makes up to 60–70% of all textile dyestuffs produced. This dyestuff can be grouped as monoazo, diazo, triazo according to the number of azo bonds (-N=N-) in its structure. Their widespread use makes them as one of principal sources of contamination of used waters [3-6].

It has been well documented that some azo dyes are toxic and even mutagenic to living organisms in aquatic environment. The release of these colored wastewaters in the ecosystem is a dramatic source of aesthetic pollution, eutrophication and perturbation of aquatic life [6-8]. In addition, it is well known that soluble azo dyes when incorporated into the body are split into corresponding aromatic amines by liver enzymes and intestinal micro flora, which can cause cancer in human [9-10]. There for it is necessary to find an effective method to remove such organic compounds from industries effluents.

Over the last decade many different treatment

methods have been employed to removing pollutants from industrial and textile wastewater specially [3, 11-12]. The traditional processes for treatment of these effluents are insufficient to purify the important quantity of wastewaters after the different operations of textile dyeing and washing [3, 13-15]. Adsorption on activated carbon, enhanced coagulation, electro coagulation, electrochemical oxidation, flocculation, reverse osmosis and active sludge which have been widely employed to remove refractory pollutants from textile wastewaters, are fairly effective in removing pollutants with different success and costs. However, these techniques transform dyes in solution into solid forms, such that the waste must be expensively post-treated [16-18].

Advanced oxidation processes (AOPs) are alternative techniques of destruction of dyes and many other contaminating organics that based on the generation of very reactive species such as sulfate and hydroxyl radicals that are extraordinarily reactive species, they attack the most part of organic molecules with rate constants usually in the order of 10^6 – 10^9 $M^{-1}s^{-1}$ [15, 19]. AOPs generally involve used of high oxidation- potential sources that which is H_2O_2 , O_3 and $S_2O_8^{2-}$ recently, under irradiation of UV light for the oxidative degradation of contaminants [7, 13, 20-21]. However, there are limitations to the use of O_3 , such as the intensity of energy required to generate ozone, its pH sensitivity and its selectivity

for organic substrates. The ozonation process requires further research and development [10]. Also handling of the H_2O_2 is difficult and dangerous. Furthermore it is expensive (The best marketing of hydrogen peroxide have 30 percentage purity) [22]. On the other hand due to high reactivity of UV/ $S_2O_8^{2-}$ and high solubility of peroxydisulfate (persulfate or $S_2O_8^{2-}$), their application in wastewater treatment has recently been the focus of attention [13, 23-26]. Peroxydisulfate is a strong oxidant which has been used widely in the petroleum industry for the treatment of hydraulic fluids or as a reaction initiator in the petrochemical industry [13, 27].

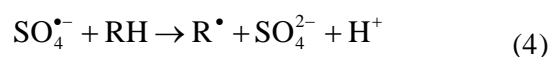
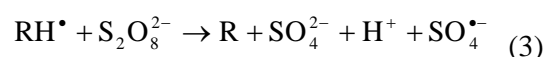
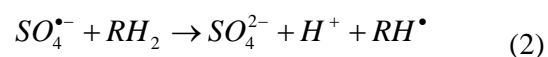
The use of peroxydisulfate as oxidant has some advantage: it is a strong oxidant (peroxydisulfate salt dissociates in water to form persulfate anions $S_2O_8^{2-}$ ($E_o = 2.01$ V)). In addition to its oxidation power, persulfate anion appears to be very stable at 20°C with half-lives of several months in aqueous phase. High aqueous solubility, relatively low cost, generation of high oxidizing radicals, non-selective reaction with organic pollutants and end products (sulfate anion SO_4^{2-}) make the peroxydisulfate oxidation a promising choice among the AOPs for the water treatment applications [26-27].

Three salts of the peroxydisulfate ion are commercially available: ammonium, sodium, and potassium. Ammonium peroxydisulfate is more accessible because of abundant and low cost of goods manufactured and sufficiently

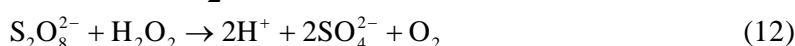
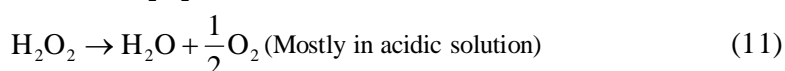
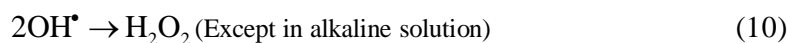
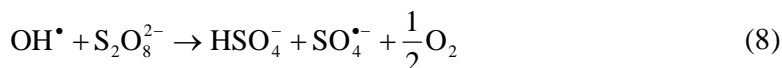
stable at or below ambient temperature (25°C), while stored in the solid form [28]. Therefore, Ammonium peroxydisulfate is preferred for use in this study as oxidant.

In spite of the fact that peroxydisulfate is a strong oxidant it usually requires higher reaction activation energy than other oxidants such as permanganate. It means that it is kinetically slow in reacting with many organics. Thermal or photochemical activated decomposition of $S_2O_8^{2-}$ ion to $SO_4^{\bullet-}$ radical has been proposed for acceleration of the process [29].

$SO_4^{\bullet-}$ radicals ($E_o = 2.68$ V) are among the strongest oxidants known, much stronger than oxidants commonly used in industry, such as permanganate ($E_o = 1.70$ V) and hypochlorous acid ($E_o = 1.49$ V). Among the known oxidants used in water treatment applications, only OH^{\bullet} have redox potentials ($E_o = 2.72$ V) close to the $SO_4^{\bullet-}$ [30]. The generation of $SO_4^{\bullet-}$ and subsequent destruction organic compound has been shown in equations 1-5 [22, 25]:



Also, available oxidants in the solution and their corresponding intermediates are indicated in equations 6-12 [13, 24]:



As can be seen in the above reactions, the oxidation process is begun by production of the sulfate and hydroxyl radicals. These radicals are powerful oxidizing agents which may attack the organic matters (R) in the contaminated water. It causes, ultimately, complete decomposition of toxic and bio-resistant compounds into harmless species (like CO_2 , H_2O , etc.). In the oxidation process, sulfate ions are generated as the final product, which leads to an increase in salt content of the effluent [22, 24-26].

To the best of our knowledge, this is the first time that UV/ $\text{S}_2\text{O}_8^{2-}$ process was employed in photooxidative decolorization of the textile dye, DR 23. Therefore, this study will attempt to summarize and highlight the effect

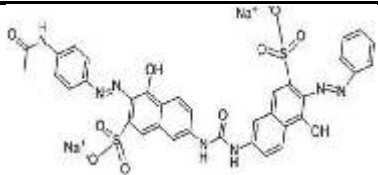
of a variety of conditions on photooxidative decoloration of DR23, such as concentration of dye, concentration of $\text{S}_2\text{O}_8^{2-}$, reaction pH, temperature and influence of utilizing glass bead nano- TiO_2 as photocatalyst on photochemical treatment of dye solution containing DR23 by UV/persulfate process.

Experimental

Materials and instrumental

Direct Red 23 which is a diazo dye used for dyeing of cotton, silk and cellulose fabrics was obtained from Alvan Sabet Company (Iran, Tehran) and was used without any further purification. Its structure and characteristics is given in Table 1. Also Figure 1 shows intense absorbance at 507 nm.

Table 1. Characteristics of DR 23 [31-32].

Molecular structure	Molecular Formula	Color Index Number	Type	λ_{max} (nm)	Molecular weight (g/mol)
	$\text{C}_{35}\text{H}_{25}\text{N}_7\text{Na}_2\text{O}_{10}\text{S}_2$	29160	Dianionic	507	813.72

Adjustment of pH of the dye solutions were carried out in a batch reactor with prior to degradation was carried out with 104.3744(cm) diameters. For providing NaOH or H₂SO₄ from Merck. Ammonium peroxydisulfate was also obtained from Merck. Distilled water was used for all solutions throughout this study. Experiments and above the sample exactly with constant distance from it which is 20cm.

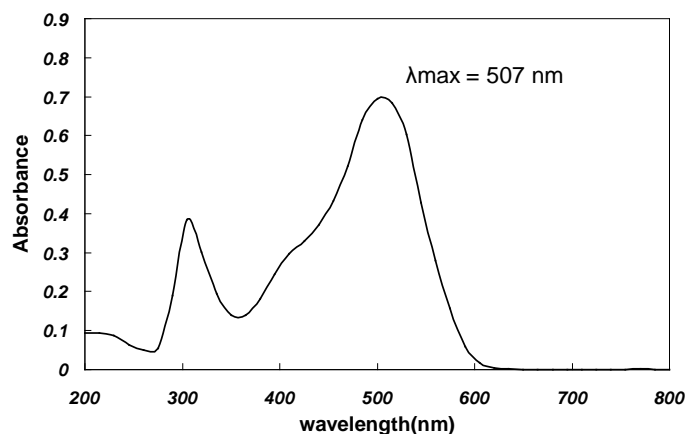


Figure 1. Absorption spectrum of Direct Red 23. [DR23] =20 ppm, pH 5.8.

The ballast and capacitor were connected in series with the lamp to avoid fluctuations in the input supply. Also, a thermostat (Lauda-RE 104) for temperature fixation and a pH meter (Metrohm, Swiss) for pH adjustment were utilized. In photocatalytic experiments, Immobilized nanopowder TiO₂ (Degussa P25) with BET: 50 m²g⁻¹ and particle size 21 nm on glass beads (0.5cm diameter) [15] was used as photocatalyst and were used in the reactor where glass beads allowed the reactor to agitate by a magnetic flea (Figure 2).

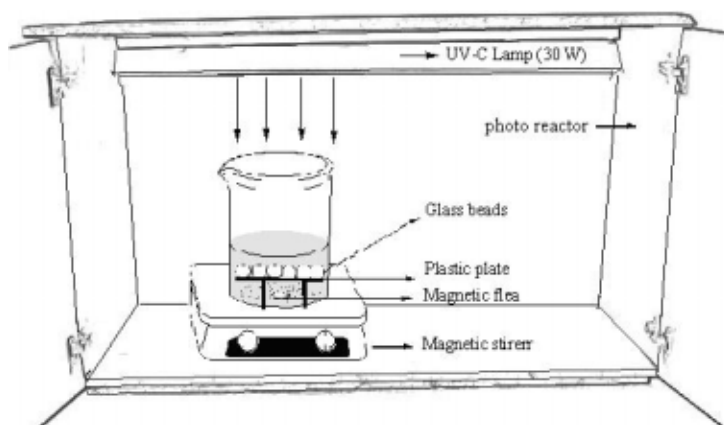


Figure 2. Schematic diagram of batch photoreactor.

procedures

Each experiment operated with 50ml of solutions in constant concentration of dye (20ppm) and desirable amounts of persulfate

in a pyrex reactor. The pyrex reactor included dye at desired temperature was irradiated immediately after addition of the persulfate to initiate the reaction (reaction time was 35 min). The pH of solution was 5.8 (the natural pH of the dye solution at the dye concentration employed). During irradiation, agitation was maintained to keep the solution homogeneous. To study the effect of operational parameters such as pH, temperature and persulfate concentration, other factors were considered as fixed and efficacy of the desired factor was investigated. Decolorization of dye solutions were checked and controlled by measuring the absorbance of dye solutions at the desired time intervals using a UV-vis spectrophotometer (Shimadzu UV-160) at $\lambda_{\max} = 507\text{nm}$ with a calibration curve based on the Beer-Lambert's law. The efficiency of color removal (R) was expressed as a function of time:

$$R = C / C_0 \quad (13)$$

Where " C_0 " is the initial absorbance value of DR23 and " C " is the absorbance value at time " t ". The operating conditions of all experimental test runs were summarized in each figure legend. The glass beads photo-catalysts of nano-TiO₂ were placed on the plate, which was 1cm above the bottom of pyrex reactor (Figure 2)

Results and discussion

Effect of UV/S₂O₈²⁻ in comparison with only S₂O₈²⁻ or only UV irradiation on DR23 decolorization.

Comparison of different conditions for degradation of DR23 (UV only, S₂O₈²⁻ only UV/S₂O₈²⁻) is shown in Figure 3. There is negligible degradation of color when UV irradiation was applied in the absence of S₂O₈²⁻. The same result obtained when S₂O₈²⁻ was utilized in the absence of UV irradiation. The results reveal that a considerable decrease in the concentration of the dye occurs when the sample was degraded by S₂O₈²⁻ under UV irradiation.

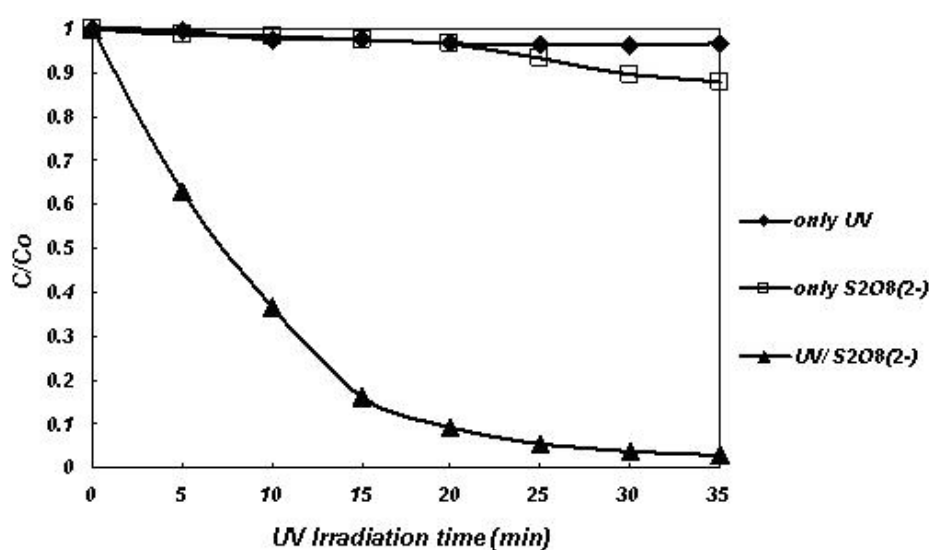


Figure 3. Comparison of degradation efficiency of UV only, S₂O₈²⁻ only, UV/ S₂O₈²⁻ system at the initial concentration of [Dye]=20ppm, [S₂O₈²⁻]=7.5mM, T= 25°C, pH 5.8.

Effect of persulfate concentration

The initial concentration of persulfate was found to be an important parameter for the photooxidative degradation of DR23. The change in the persulfate concentration versus time profile observed during the photooxidative decolorization of DR23 has been expressed in Figure 4. The increase

of initial $S_2O_8^{2-}$ concentration from 0.1 to 12.5 mM increases the efficiency of dye degradation. This is likely because more sulfate and hydroxyl radicals according to Eq. (1) and (6) are generated simultaneously and improved the photooxidative decolorization of DR23 [24, 33].

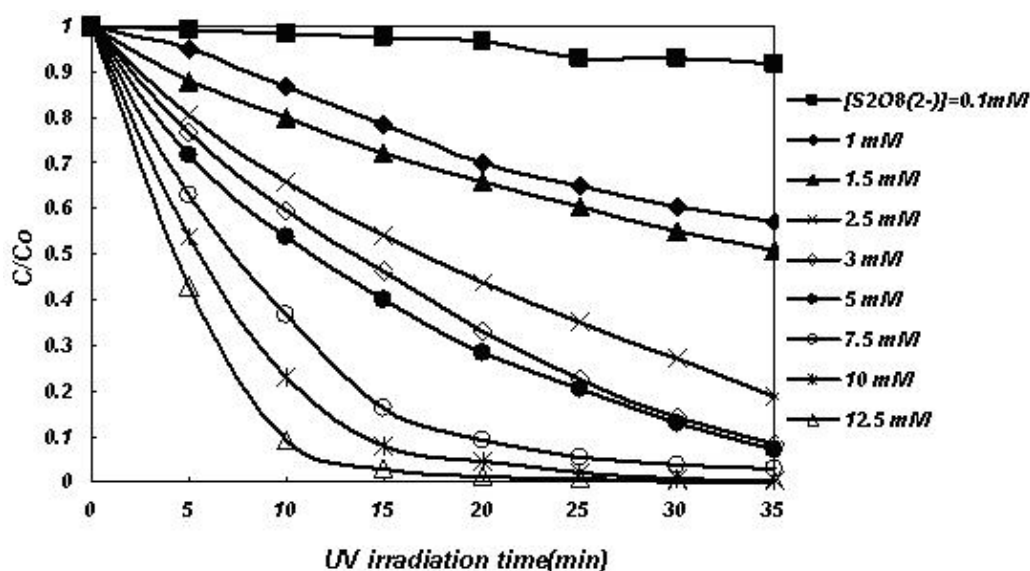


Figure 4. Influences of ammonium peroxydisulfate concentration on photooxidative degradation of DR23 at initial concentration of [Dye]=20ppm, T= 25°C, pH 5.8

Effect of initial dye concentration

The initial dye concentration has a remarkable influence on photo-oxidative degradation of DR23. To study the effect, dye concentration was changed from 5 to 40ppm while keeping the persulfate concentration constant (7.5mM). As shown in Figure 5 it can be seen that decolorization efficiency decreased as initial dye concentration increased. The presumed reason is that when the initial concentration of

dye is increased, the generated active radicals dye ratio decreases and the process efficiency reduces. Further, as the rate of photolysis of $S_2O_8^{2-}$ is strongly dependent on the UV light, as the dye concentration is increased, high dye concentration can reduce the UV light penetration into the depth of the solution which decreases the rate of generation of sulfate and hydroxyl radicals subsequently [34].

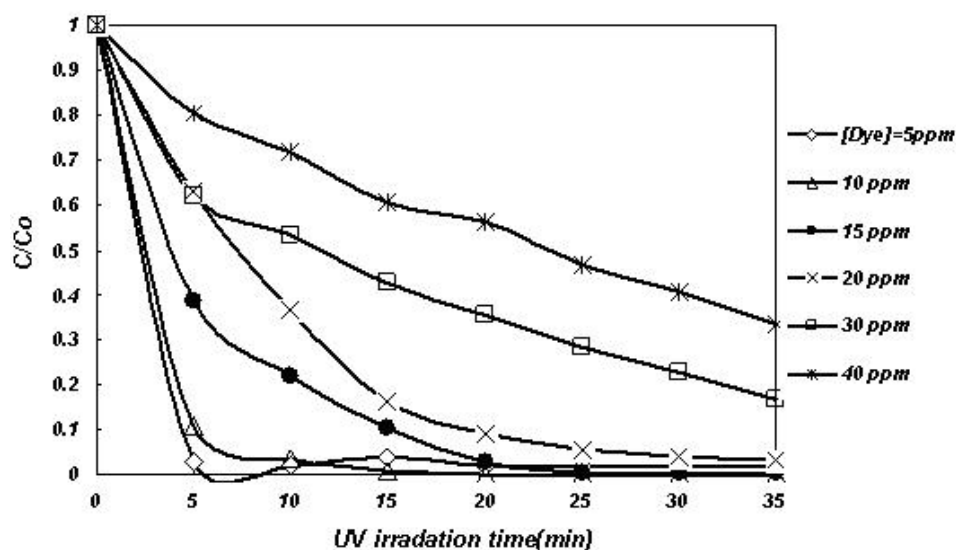


Figure 5. Influences of initial DR23 concentration on the photo-oxidative degradation efficiency at initial concentration of $[S_2O_8^{2-}] = 7.5 \text{ mM}$, $T = 25^\circ\text{C}$, $\text{pH} = 5.8$

Effect of initial pH

The wastewater from textile industries usually has a wide range of pH values. Generally, pH plays an important role both in the characteristics of textile wastewater and generation of active radicals [11, 35]. Hence, the photo-oxidative degradation of DR23 dye was studied in a pH range between 2 and 11 in constant concentration of dye (20 ppm) and peroxydisulphate (7.5 mM) at ambient room temperature. The pH of dye

solutions was adjusted by NaOH or H_2SO_4 before irradiation. Figure 6 shows the effect of pH on the decolorization rate of Direct Red 23. It can be seen that maximum decolorization efficiency is obtained at $\text{pH} = 2$ and in pH ranges of 4 to 11 the percentage degradation of dye is dropped. The inhibitory effect seems to be more pronouncing in the alkaline range (pH 9-11). For $\text{pH} = 2$, %96 and for $\text{pH} = 11$, %63.8 dye was degraded after 35 min.

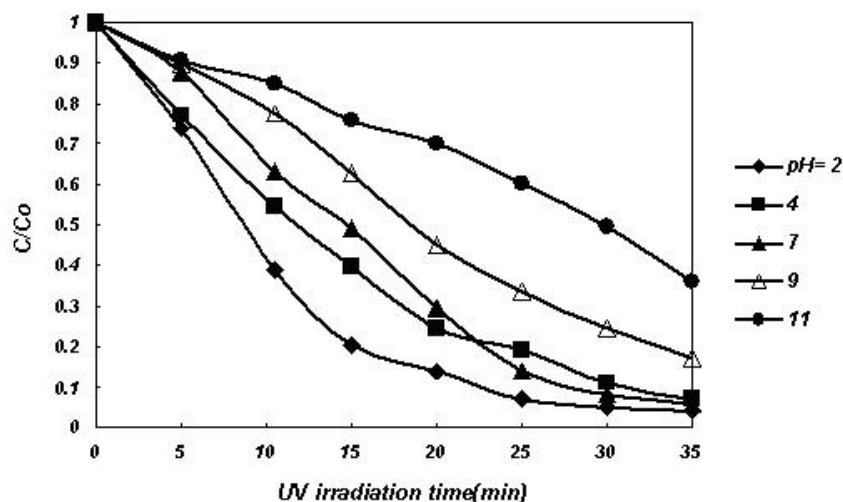
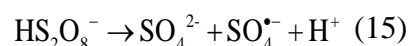
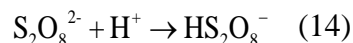
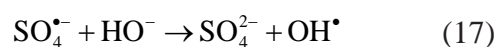
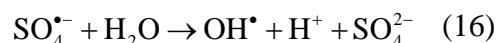


Figure 6. Effect of pH on the decolorization of DR23 under UV irradiation at initial concentration of $[\text{Dye}] = 20 \text{ ppm}$, $[S_2O_8^{2-}] = 7.5 \text{ mM}$.

The possible explanation for this behavior may be that under acidic conditions the breakdown of persulfate into sulfate free radicals can be further acid catalyzed as followed [36]:



Higher generation of acid catalyzed $\text{SO}_4^{\bullet-}$ can produce a rapid attack on oxidizable organic dye. On the other hand persulfate is known to be highly reactive at low pH ($\text{pH} < 3$) [37]. Therefore, the decolorization rates were highest at lower pH. Under neutral or basic pH conditions, $\text{SO}_4^{\bullet-}$ formed may undergo reactions with H_2O or OH^- in accordance with Eqs. (16, 17), respectively, to generate OH^\bullet [16]. Even though $\text{SO}_4^{\bullet-}$ can be converted to OH^\bullet , which exhibits a slightly higher redox potential than $\text{SO}_4^{\bullet-}$, that was indicated the presence of various ions in solution (e.g., SO_4^{2-}) may result in inhibition of the reactivity of OH^\bullet [25, 33, 36]. In alkaline or neutral solution SO_4^{2-} plays a role in scavenging OH^\bullet and slowing down the DR23 degradation rate as followed [16, 25]:



3.5. Effect of temperature

The effect of temperature was investigated in the range of 10 to 60°C with 20ppm of dye and 7.5mM of persulfate and natural pH. The results are summarized in Figure 7. Studies are revealed that increasing in temperature leads to enhancing dye degradation which is in accordance with standard Arrhenius behavior. The Arrhenius equation, $k=A \exp(-E_a/RT)$, where “A” is the frequency factor, “ E_a ” is the activation energy, “R” is the universal gas constant and “T” is the temperature in Kelvin indicating that increase the temperature lead to increase the “k” values thereby accelerating decolorization rate. So heat energy can activate persulfate to sulfate radicals more effectively [27]. Results are shown that changing the thermal activation is one of the ways to control the generation of sulfate radicals for destroying organic contaminants.

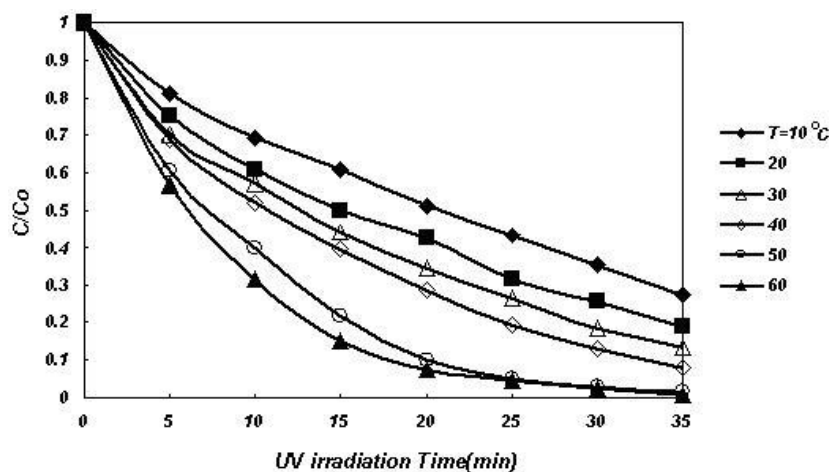
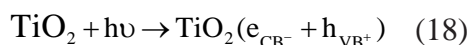


Figure 7. degradation rate of DR23 as a function of temperature at Initial concentration of [Dye]=20ppm , $[\text{S}_2\text{O}_8^{2-}] = 7.5 \text{ mM}$, $\text{pH} = 5.8$ in the UV/ $\text{S}_2\text{O}_8^{2-}$ systems.

3.6. Influences of glass bead nano-TiO₂ on DR23 degradation efficiency

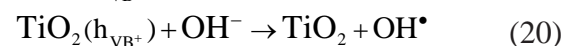
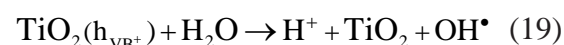
Photo-oxidative degradation was done at present of nano-TiO₂ as photo-catalyst. The TiO₂ that utilized in our study was immobilized TiO₂ nano-powder on glass beads instead of nano-TiO₂ particle suspended in solution to avoid two major problems: (i) The exponential of the light availability due to the scattering of UV light particles (ii) The difficulty in recycling the photo-catalyst. Thus, TiO₂ was immobilized on solid supports to solve these problems [15, 38].

Irradiation of TiO₂ by UV light excites TiO₂ and results in formation of electron-hole pairs as followed [15, 33]:

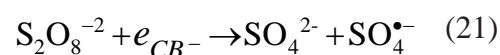


The positively charged holes react with water

or hydroxide ions to produce hydroxyl radicals, which are responsible for the destruction of organic dye [12, 25]:



On the other hand the persulfate anions can trap the photo-generated electrons of TiO₂, and generate strong oxidizing SO₄^{•-} according to the following reaction [4, 33]:



Also UV light can excite S₂O₈²⁻ to form sulfate radical (SO₄^{•-}) to significantly enhance the oxidation of contaminants [39].

The results from the degradation of DR23 using UV/S₂O₈²⁻/nano-TiO₂ system at the various temperature of reaction were summarized in Figure 8.

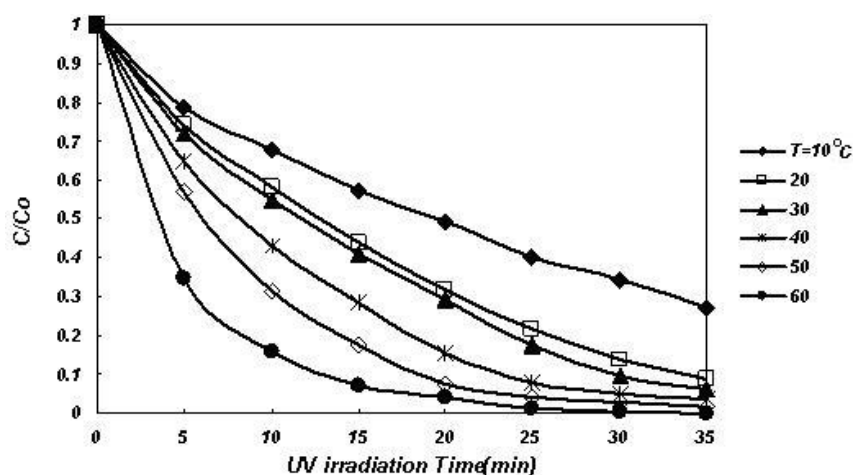


Figure 8. Influences of glass beads-nano-TiO₂ on photo-catalytic degradation of DR23 at different temperatures. [Dye]=20ppm, [S₂O₈²⁻]=2.5 mM, pH 5.8.

Figure 9 reveals that the decolorization efficiency in UV/S₂O₈²⁻/nano-TiO₂ system is equal or more slightly higher than decolorization efficiency in UV/S₂O₈²⁻ system at the same conditions, but with

consuming one of three amount of consumed persulfate at UV/S₂O₈²⁻ system. This makes the process being more economic and more environment friendly option for dye degradation.

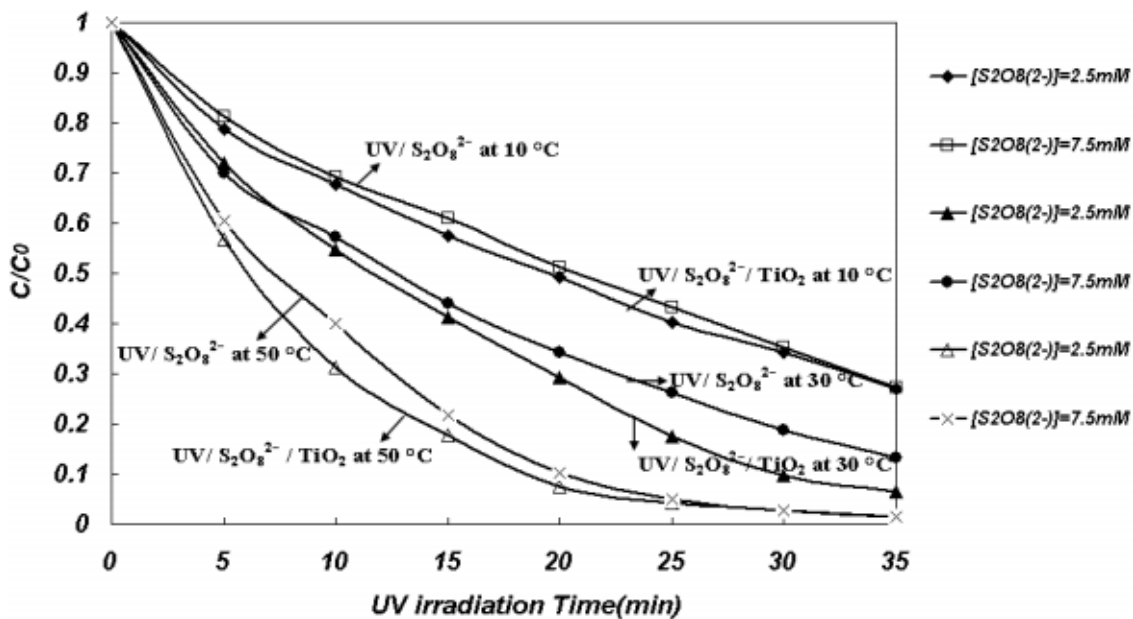


Figure 9. Comparison of UV/S₂O₈²⁻ system ([S₂O₈²⁻=7.5= [mM) versus UV/S₂O₈²⁻/nano-TiO₂ system([S₂O₈²⁻ 2.5=[mM) in decolorization and amount of peroxydisulfate at 10°C, 30°C and 50°C reaction temperatures.

Spectra of DR23 during oxidation by peroxydisulfate in spectra absorption of the dye solution at the Wavelength range 200–800 nm was investigated at different time intervals of irradiation which has been shown in Figure 10. The dye had a maximum absorption at 507 nm in aqueous solution in the UV–vis spectrum. During the decolorization studies, the change

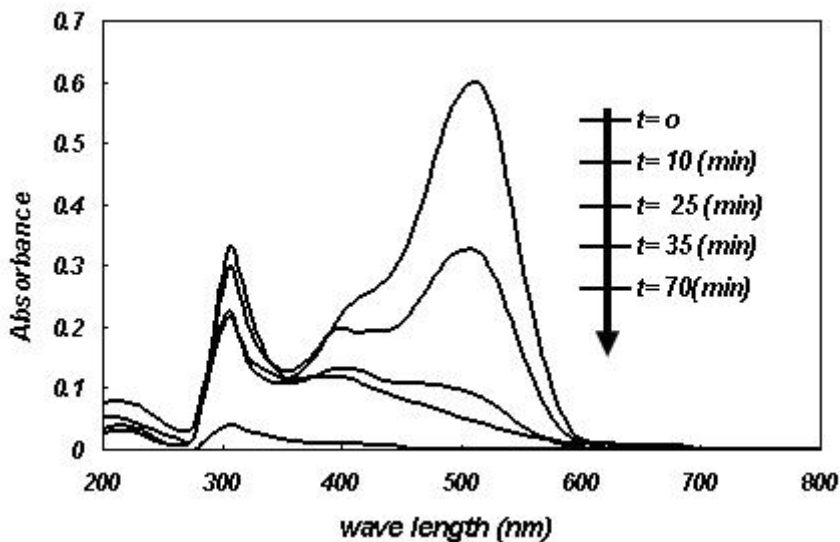


Figure 10. Absorption spectrums of DR23 with UV/ S₂O₈²⁻ at different time intervals of irradiation at initial concentration [Dye]=20ppm, [S₂O₈²⁻]=7.5= mM, T= 25°C, pH 5.8.

With a time elapse of 25min, the spectral height at 507nm decreased rapidly. This wavelength indicates the (-N=N-) bond of the dye which is the most active site for oxidation attack. Also the UV spectrum before and after degradation don't show any new peaks, no detectable intermediates were formed during the reaction.

Conclusion

In this study, photo-oxidative decolorization of Direct Red 23 dye in a batch photo-reactor that equipped with a UV-C lamp utilizing a very simple analytical method, direct UV-vis spectrophotometric detection, was investigated. The findings demonstrated that application of peroxydisulfate, along with UV irradiation, is an efficient, economical, environment friendly, fast and safe method for oxidative removal of DR23 at laboratory scale which is able to convert DR23 to minerals such as CO₂, H₂O and etc. within very short period of time.

Degradation rate of DR23 was shown to be dependent on the pH, solution temperature, initial dye and persulfate concentration. Obtained data were indicated initial S₂O₈²⁻ concentrations have promising effect on photo-degradation of DR23. The decolorization rate goes through a maximum when the concentration of S₂O₈²⁻ increases from 0.1 to 12.5mM. The reasonable concentration of S₂O₈²⁻ assigned 7.5mM and pH 2 was most

efficient pH for DR23 degradation. However satisfactory dye removal was achieved in the acidic to neutral pH range (2-7). Moreover photo-decay performance was shown to increase with increase the temperature of reaction. Higher temperature result in higher thermally generated (SO₄^{•-}) and higher percentage of dye degradation consequently. Also at the higher concentration of dye, the lower decolorization percentage would be accessed.

In this study, photo-oxidative degradation was promoted by utilizing nano-TiO₂ as photo-catalyst which had been immobilized on glass beads surfaces. It was found that the increasing photo-catalyst in UV/S₂O₈²⁻ system resulted in dramatic increase of dye degradation. In the UV/S₂O₈²⁻/nano-TiO₂-glass beads system amount of consumed peroxydisulfate in UV/S₂O₈²⁻ system can be accessed the similar result in dye decolorization at the same reaction temperatures so it causes to save 63% persulfate consumption approximately. Therefore using this technique may be a viable one for the treatment of large volumes of textile wastewaters. This is indicative the significant role of commercially, inexpensive, available catalysts with high photo-catalytic activity to more stable support substrates such as glass beads with high stability in the subsurface for photo-oxidative dye degradation by activated S₂O₈²⁻ oxidant.

Acknowledgements

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