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Hydroxyl Radical-Based Processes for Decolourization of Direct Blue 71: A Comparative Study

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Advanced oxidation processes are based on the generation of powerful oxidants such as hydroxyl radicals that are non-selective and much more powerful than other oxidants. Hydroxyl radicals are widely used to degrade organic products in industrial waste water, especially dye containing effluents. The objectives of this study were to investigate the hydroxyl radical-based processes for decolourization of direct blue 71. Decolourization of aqueous direct blue 71 using ultraviolet radiation and ultrasonic irradiation with and without hydrogen peroxide was investigated in a laboratory-scale batch photoreactor and sonoreactor with emphasis on the effect of various parameters on decolouration and degradation efficiency. The toxicity was also evaluated in acute toxicity studies using *Daphnia magna*. Results showed that, colour removal efficiencies by ultrasonic irradiation (US) and ultrasonic irradiation plus hydrogen peroxide (US/H_2O_2) processes were negligible. Almost complete disappearance of direct blue 71 after 5 min of irradiation in UV/H_2O_2 process was possible to achieve. The results clearly showed that dye examined was toxic to *Daphnia magna* and resulted in quite low LC_{50} value. The decolourization efficiency was found to increase with increasing H_2O_2 concentration, however, the marginal benefit became decreasing with further increasing of H_2O_2 due to the scavenging effect of excess H_2O_2. The rate of colour decay followed pseudo-first order kinetics with respect to the UV-visible absorption of the test dye during reaction.

Key Words: Sonolysis, Photolysis, Dye, Decolourization, Toxicity.

INTRODUCTION

Colour is the most obvious indicator of water pollution. The discharge of coloured wastes into streams not only affects their aesthetic nature but also interferes with the transmission of sunlight into streams and therefore reduces photosynthetic action. Thus, ecosystems of streams can be seriously affected if these effluents are not treated properly. Hence, contaminations due to dyes pose not only a severe public health concern, but also many serious environmental problems because of their persistence in nature and nonbiodegradable characteristics[1].

Particularly reactive azo dyes cause special environmental concern due to their degradation products such as aromatic amines which are considered highly carcinogenic[2]. They are characterized by the presence of at least one diazo group (-N=N-) bearing aromatic rings, dominates the worldwide market of dyestuffs with a share of *ca.* 70 %[3]. Reactive azo dyes released from textile dyeing plants are highly recalcitrant to conventional wastewater treatment processes. In fact, as much as 90 % of reactive dyes could remain unaffected after activated sludge treatment[4]. Therefore, alternative methods should be implemented for effective pollution abatement of dyed effluents. Several techniques, such as electrochemical degradation[5], advanced oxidation processes (AOPs)[6,7], AOP-biological treatment[8], adsorption[9], have been studied to removal azo dye wastewater.

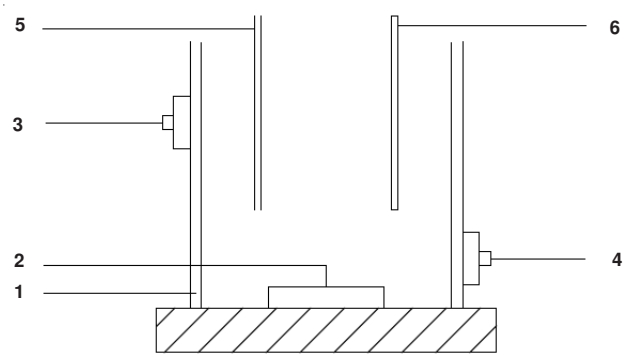
Advanced oxidation processes (AOPs) are based on the generation of powerful oxidants such as hydroxyl radicals that are non-selective and much more powerful than other oxidants[10]. Hydroxyl radicals are widely used to degrade organic products in industrial waste water, especially dye containing effluents[11]. Hydroxyl radicals have become the most important oxidants due to their high reactivity and lack of selectivity towards organic compounds[12]. The methods for generating these radicals are diverse, ranging from photocatalysis to sonochemistry. Besides photocatalysis and sonochemistry, utilization of Fenton process, ozonation, peroxone process, non-thermal plasma formed by electrical discharge is also reported in the literature[12]. Sonication is a relatively innovative advanced oxidation process based on the use of low to medium frequency (typically in the range 20-1000 kHz) and high energy ultrasound to catalyze the destruction of organic pollutants in waters. The chemical effects of ultrasound irradiation are the result of acoustic cavitation which is the formation and subsequent

collapse of micro-bubbles in a liquid[13,14]. When aqueous solutions are exposed to ultrasound, transient cavitations are formed due to compression and rarefaction of the bulk water. The cavitations collapse locally producing high pressure and temperature peaks (500 bar, 5000 K). Under these extreme conditions hydroxyl radicals and hydrogen atoms are formed by opening the H-O bond[13]. Another technology is photolysis. Direct photolysis has been always considered as one possible alternative because it is possible for molecules of most organic compounds to transform, to cleave bonds and even to undergo complete destruction in the presence of ultraviolet irradiation[15,16]. According to the literature review, no study was found to decolourize the direct blue 71 azo dye using low frequency (42 kHz, 170 W) sonochemical processes and UV radiation either alone or in conjunction with hydrogen peroxide. The aim of this study is to investigate the efficiency of low frequency ultrasound and ultraviolet light either alone or in conjunction with hydrogen peroxide for the degradation of direct blue 71. The effects of the key operating parameters such as pH, substrate initial concentration and hydrogen peroxide dosage on the decolourization and mineralization extents were also studied.

EXPERIMENTAL

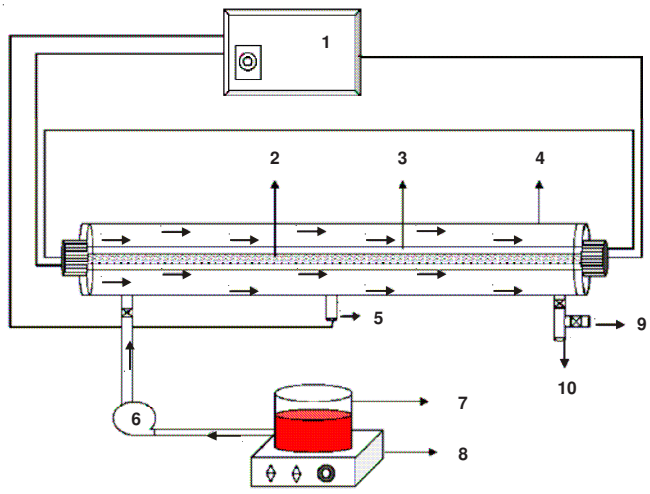
Direct blue 71 was obtained from Alvan Sabet dye manufacturing industry located in Hamedan, Iran and used without any purification. All other chemicals used in the experiments were obtained from Merck Chemical Co, Iran. All model solutions of dye were prepared using deionized water with the initial concentration of 30-70 mg L^{-1}. In each case, the reaction volume was 2500 mL and the pH value of the sample was adjusted to optimum value of each processes. The pH of each tested solution was adjusted to the required value with concentrated H_2SO_4 and NaOH solution. Sonication is achieved at frequency of 42 kHz (170 W) with an ultrasonic generator (Codyson CD-4820, China) with a piezoelectric transducer having a diameter of 5 cm fixed at the bottom of the vessel (Fig. 1). Ultrasonic energy dissipated in the reactor was set at 60 W. The apparatus is open to air. The sonochemical reactions were carried out for 3 h. The photodegradation studies were carried out in a batch reactor system. The photoreactor consist of a 2500 mL cylindrical stainless steel body. A 55 W low pressure mercury lamp (I = 50000 μW cm^{-2}, 909 mm long) surrounded by quartz jacket was located in the center of the reactor (Fig. 2). The photolysis reactions were carried out for 2 h. Samples were taken periodically from the reactors and analyzed immediately. The temperature of the reactor contents was maintained at 25 ºC. The concentration of dye in solution samples was determined at the maximum absorption wavelength with 10 mm glass cell using a double beam T80 UV/VIS spectrophotometer (PG Instruments Ltd). The maximum wavelengths λ_{max} (nm) for the dye studied was determined as 595 nm.

Acute toxicity of dye and the toxic effects of its degradation products after degradation processes were studied with *Daphnia magna* test according to standard methods[17]. Primary *Daphnia magna* was caught from their living site, then, one of them was cultured alone, after infants of primary *Daphnia*



1. Cooling water jacket
2. Transducer
3. Cooling water inlet
4. Cooling water outlet
5. Sampling tube
6. Thermometer

Fig. 1. Schematic diagram of sonoreactor



1. Transformator
2. Low pressure Hg UV lamp
3. Quartz jacket
4. stainless steel jacket
5. Photocell
6. Pump
7. Dye vessel
8. Shaker
9. Sampling tube
10. Outlet tube

Fig. 2. Schematic diagram of photoreactor

magna were used for culture in large amounts. Dilution water which was used for tests was groundwater. *Daphnia magna* was maintained in a 10 L glass vessel containing culture medium in a temperature-controlled condition of 22 ± 2 ºC and a 12/12 light-dark cycle. For running the experiment, 10 infants (age < 24 h) were exposed to the test volume of 100 mL in a 250 mL glass beaker. The initial concentration of dye was 70 mg L^{-1}. Experimental concentrations tested were 100, 50, 25, 12.5, 6.25 and 3.125 % of each effluent diluted with dilution water. After the setting periods of 24 and 48 h, LC_{50} values were calculated for toxicity tests by use of the special computer program [PROBIT][18]. Finally, for a certain comparison, the toxicity values were converted to toxic units. The toxic units of an effluent or mixture is equal to100 % divided by the LC_{50} of that effluent or mixture[19]. All experiments were run in triplicate to ensure reproducibility.

RESULTS AND DISCUSSION

The advanced oxidation process degradability of direct blue 71 was carried out under different initial concentrations. Initial results demonstrated that neither US nor US/H_2O_2 were able to appreciably decolourize direct blue 71 (70 mg L^{-1}). Figs. 3 and 4 show the degradation of direct blue 71 as function of time by ultrasonic irradiation with and without hydrogen peroxide. As can be seen, sonochemical decolouration proceeded very slowly leading to less than 14 and 25 % of direct blue 71 removal after 5 h by ultrasonic irradiation and ultrasonic irradiation plus hydrogen peroxide, respectively. It can also be observed from results that UV had its potential to degrade direct blue 71. More than 65 % decolouration was achieved after *ca.* 2 h at 70 mg L^{-1} of direct blue 71 (Fig. 5).

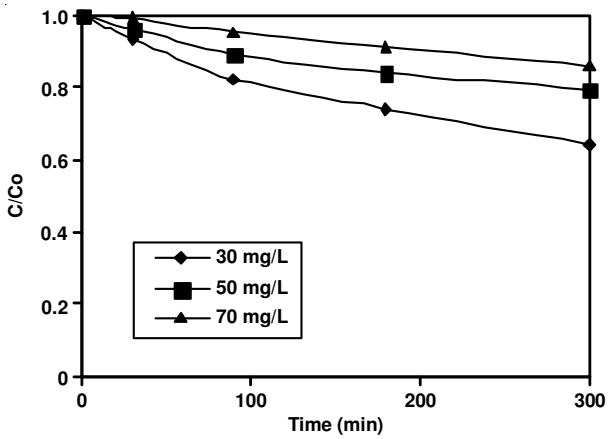


Fig. 3. Effect of ultrasonic irradiation in decolourization of direct blue 71 in different initial dye concentrations

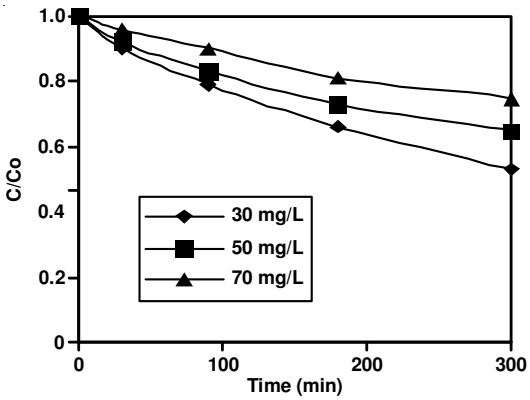


Fig. 4. Effect of ultrasonic irradiation plus hydrogen peroxide in decolourization of direct blue 71 in different initial dye concentrations

The poor effects of US alone on the decolourization efficiency may be attributed to the fact that low ultrasound frequencies hinder the development of hydroxyl radicals[20]. Hence, for direct blue 71, a non-volatile and highly soluble compound, reactions inside or in the vicinity of the bubble (where fast thermal decomposition and increased concentrations of radicals exist) are unlikely to occur to an appreciable extent and, therefore, its degradation will be driven by hydroxyl radical-mediated secondary activity in the liquid bulk. Thus US process generally demands a high contact time for significant degradation

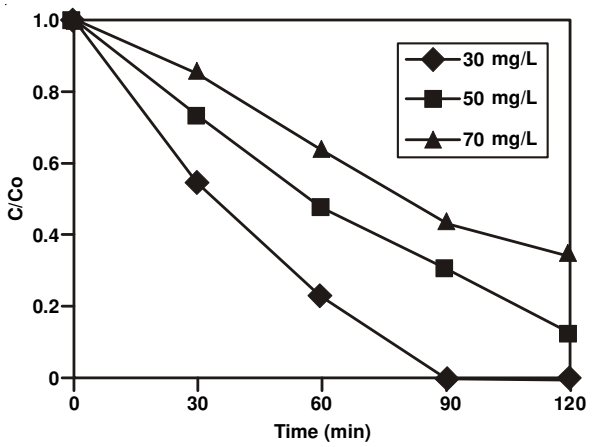


Fig. 5. Effect of ultraviolet radiation in decolourization of direct blue 71 in different initial dye concentrations

efficiency[21]. Instead UV light had high potential to produce the highly reactive hydroxyl. This would explain discrepancies in reactivity of direct blue 71 between sonochemical and photolytic reactions since the latter involve the participation of a more diverse range of reactive species (*i.e.*, radicals and electrons) than the former. In order to complete and rapid decolourization of direct blue 71 at the operating conditions the combination of UV with H_2O_2 was, therefore, necessary for the production of hydroxyl radicals to initiate the decolourization of concerning dye at a reasonable time scale even for the higher dye concentrations (Fig. 6). These results are in good agreement with other findings in literature. Aleboyeh *et al.*[22] showed combination of UV plus H_2O_2 in comparison with UV alone increases removal rates of acid orange 8 and methyl orange, 172 and 137 times, respectively. In this view, the UV radiation is combined with a powerful oxidant, H_2O_2, the degradation efficiency of the dye is significantly enhanced due to hydroxyl radical production caused by the photolysis of H_2O_2, as reported by other researchers[23]. This condition led to a rapid decolourization of direct blue 71 and more than 98 % decolourization of direct blue 71 after *ca.* 5 min. However, in the absence of H_2O_2, less than 7 % decolourization of direct blue 71 was obtained. Since H_2O_2 concentrations are important factors which influence on the decolourization rate of dye by UV photolysis in the presence of hydrogen peroxide, the series of experiments were conducted in order to optimize initial H_2O_2 concentration. For this purpose it was selected the hydrogen peroxide concentration of 10-50 mmol L^{-1} for above mentioned dye concentration. It can be seen the photodegradation efficiency increases with an increase in the amount of H_2O_2 concentration, up to the optimum value and then decreases when the H_2O_2 concentration is increased. This trend can be explained by the fact that H_2O_2 itself acts as an effective hydroxyl radical scavenger at concentrations that are specific for the pollutant in question. This is encountered during the destruction of not only dye but also many organic compounds as well[24]. It can be concluded that a H_2O_2 dose higher than 20 mM corresponds to an unprofitable consumption of H_2O_2. It has also been pointed out that the decolourization rates gradually decreased with increasing initial dye concentrations. Nevertheless, the efficiency of the

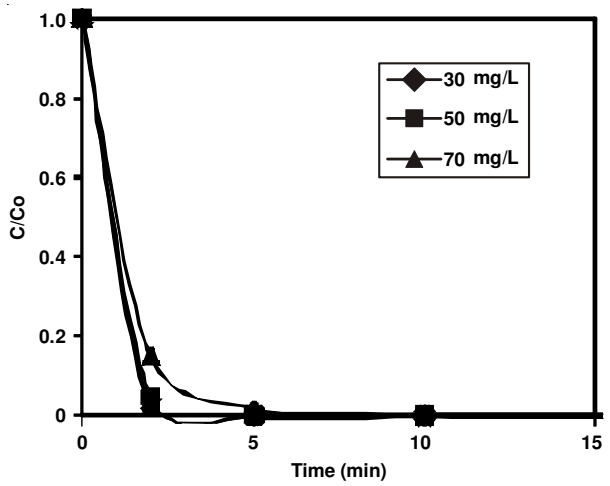


Fig. 6. Effect of ultraviolet radiation plus hydrogen peroxide in decolorization of direct blue 71 in different initial dye concentrations

process in terms of the amount of dye decolourized generally increased at higher initial concentrations. The presumed reason is that when the initial concentration of dye is increased, the competition between the dye intermediates and parent dye for hydroxyl radical became intense owing to the non-selective reactivity of hydroxyl radical. Additionally, in the US process with increasing initial dye concentration the cavities approached saturation[4]. The two factors contributed to a decreasing rate constant for the decolourization of dye with an increase in initial concentration.

As demonstrated in Table-1, the decolourization of dye solution by oxidation processes exhibit pseudo-first-order reaction kinetics. The pseudo-first-order rate constants (k) of decolourization obtained from the slope of -ln (C/C_0) *vs.* t (time) plots where C_0 and C are dye concentration at time zero and at time t, respectively. The rate of dye decolourization was dependent on dye initial concentration (C_0) and k decreased with increasing C_0. These results are in good agreement with other findings in literature[2,25].

TABLE-1
PSEUDO FIRST ORDER KINETIC VALUES FOR DEGRADATION OF DIRECT BLUE 71 AT DIFFERENT DECOLOURIZATION PROCESSES

Types of process		Direct blue concentration (mg L^{-1})		
		30	50	70
US	Rate constant (min^{-1})	0.0072	0.0039	0.0026
	Correlation coefficient	0.9800	0.9900	0.9600
US/H_2O_2	Rate constant (min^{-1})	0.0093	0.0071	0.0048
	Correlation coefficient	0.9700	0.9600	0.9700
UV	Rate constant (min^{-1})	0.0168	0.0095	0.0067
	Correlation coefficient	0.9900	0.9900	0.9600
UV/H_2O_2	Rate constant (min^{-1})	0.1423	0.1142	0.0942
	Correlation coefficient	0.9800	0.9700	0.9800

In further experiments, dye decolouration was carried out at various pH (4-11) during oxidation processes (data not shown). It is notable that decolouration depends strongly on the solution pH and is substantially reinforced at acidic conditions, while hindered at alkaline conditions. For instance, the extent of direct blue 71 decolouration (30 mg L^{-1}) after 1 h photolysis at pH values of 4, 7 and 11 was 77, 65 and 43 %, respectively. This acceleration is probably associated with the effect that under acidic pH, hydroxyl radical is the predominant reactive oxidant and under alkaline pH, hydroperoxyl radicals do not have as high oxidizing power as hydroxyl radical and also under extreme alkaline conditions, hydroxyl radical scavenging effects become more significant[26].

The evaluation of the dye toxicity was carried out for dye solutions before and after the decolourization processes with *D. magna*. Results showed that direct blue 71 was toxic to *D. magna* and resulted in quite low LC_{50} value. This means that the concentration values of the dye used is considered toxic to the aquatic environment and that colour removal is required. As can be seen in Table-2 the acute toxicity tests with *D. magna* showed lesser toxicity than parent form of dye after UV and US processes. However, UV process was more effective than US process in reducing dye toxicity. The toxicity level of dye solutions after US plus H_2O_2 and UV plus H_2O_2 processes were even higher than the toxicity level found for the dye solution without any colour removal treatment, indicating that even with a removal of 100 % of the dye direct blue 71 from the aqueous solution, an expressive mortality of the *D. magna* occurred. One possible reason for this increase in toxicity, after mentioned processes, could be due to the presence of dye degradation by products or surplus H_2O_2 in the effluents. Comparison of UV and UV plus H_2O_2 processes efficiency shown that both oxidation processes have led to complete dye elimination and there is no difference between UV and UV/H_2O_2 in terms of dye degradation results. However, in this special case it can be simply observed from Table-2 that there is a difference between UV and UV/H_2O_2 in terms of bioassay results. In other words, toxicity units decreased from 32.3 to 6.35 % after photolysis while it increased from 32.3 to 74 % after photolysis plus H_2O_2.

TABLE-2
ACUTE TOXICITY TOWARD *Daphnia magna* AFTER 48 h OF EXPOSURE

Test sample	LC_{50} (% v/v)	Toxicity unit
Parent dye	3.10	32.30
US effluent	4.56	21.92
US/H_2O_2 effluent	1.35	74.00
UV effluent	15.75	6.35
UV/H_2O_2 effluent	1.35	74.00

This point must also be noted that although the intermediate compounds have not been determined, they certainly have been produced and the existence of the toxicity in the samples after UV process with complete dye destruction should be related to the intermediates of the dye. On the other hand, because UV/H_2O_2 process is more efficient than UV process, the intermediates destruction is therefore more under the former process. Even if there is no difference between UV and UV/H_2O_2 processes in terms of intermediates destruction results, the results of bioassay should be the same in both processes. But, it is clear that toxicity unit increased after photolysis plus H_2O_2. In other words, it is concluded that another agent might have killed all bioindicators which is presumably due to the presence of the residual of H_2O_2 in samples. This

hypothesis was confirmed by measuring the amount of hydrogen peroxide and 2 to 4 mg L^{-1} of it was observed in the end of destruction process. This is not far from reality because in order to optimize initial H_2O_2 concentration, concentration interval was 10 mg L^{-1} and therefore, obtained optimum concentration of hydrogen peroxide may not be accurate. This means that there should be an optimum H_2O_2 concentration both for maximizing the dye degradation and for minimizing the toxicity increase. Accordingly, this is another point which worth to note for application of H_2O_2.

Conclusion

We have investigated the decolourization of direct blue 71 in aqueous solution by using several advanced oxidation processes: US, US/H_2O_2, UV and UV/H_2O_2. The experimental results indicate that the rate of decolourization is influenced by the initial concentration of dye, hydrogen peroxide dosage and pH. The decolourization efficiency proceeded very slowly when US and US/H_2O_2 processes are used. The experimental results demonstrated that the UV/H_2O_2 process could be a suitable pre-treatment method for complete decolourization for direct blue 71, once the optimum operating conditions are established. The decolourization efficiency was found to increase with increasing H_2O_2 concentration, however, the marginal benefit became decreasing with further increasing of H_2O_2 due to the scavenging effect of excess H_2O_2. The rate of colour decay followed pseudo-first order kinetics with respect to the UV-visible absorption of the test dye during reaction.

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