JRH
www.jrh.ir

Removal of reactive dyes from textile wastewater using sonochemical process: effective parameters study

Akbar Eslami[1], Ahmad Reza Yazdanbakhsh[2],
Mohammad Hassan Momayyezi[3]

Journal of Research & Health
Social Development & Health Promotion Research Center
Vol.5, No.2, Summer 2015
Pages: 184-192
Original Article

1. Assistant Professor of Environmental Health Department, Health Promotion Research Center, Shahid Beheshti University of Medical Sciences, Tehran, Iran
2. Associate Professor of Environmental Health Department, Health Promotion Research Center, Shahid Beheshti University of Medical Sciences, Tehran, Iran
3. **Correspondence to**: MSc Student of Environmental Health Department, Health Promotion Research Center, Shahid Beheshti University of Medical Sciences, Tehran, Iran
Tel/Fax: +98 353 5222032
Email: hassanmomayyezi@gmail.com

Received: 24 May 2013
Accepted: 8 Sep 2013

How to cite this article: Eslami A, Yazdanbakhsh AR, Momayyezi H. Removal of reactive dyes from textile wastewater using sonochemical process: effective parameters study. *J Research Health2015*; 5(2): 184-192.

Abstract
Large amounts of wastewater containing organic and inorganic chemicals from different sources enter the environment, each year. Given the importance of preserving public health and environment, efficient technologies like Advanced Oxidation Processes (AOP) should be noted. Ultrasound is an AOP and used as an efficient technology to remove pollutants in recent years. This study aimed to evaluate sonolysis for removing reactive dyes from textile wastewater. This experimental laboratory study utilized composite sampling from textile wastewater for 24 hours. First, raw wastewater characteristics were determined. Then, an undivided cell with a volume of 250 ml was used for 200 ml sample of textile wastewater to investigate the Sonochemical process. Given the variables, 48 samples were calculated. An ultrasonic bath (power=50 W, frequency=28 kHz) was used. The test results showed that the efficiency of dye removal is increased with decreasing pH and increasing catalyst concentration and retention time. Also, the optimal conditions for effective parameters on the process were obtained such as pH=2, air flow rate of 1 liter per minute, the catalyst concentration 3 mM and retention time 240 minutes at a frequency of 28 kHz and input voltage 50 W. Under these conditions, the efficiency of dye removal was obtained 42.5. According to the results, sonolysis (frequency=28 kHz and power=50 W) can be used as pretreatment to analyze resistant pollutants. Sonolysis is better to be used in combination with other advanced oxidation methods.

Keywords: Dye, Reactive, Oxidation, Ultrasound, Wastewater

Introduction
Large amounts of wastewater from domestic, agricultural and industrial sources enter the environment containing high concentrations of organic and inorganic chemicals such as hydrocarbon solvents, cyanide, dyes, heavy metals, and pesticides each year [1,2]. Toxicity, persistence and high concentration of pollutants cause many environmental and health effects. Water pollution is one of the biggest problems of these pollutants [3,4].

Industrial effluents are one of the main contaminants of the environment. Dye wastewaters are generated in various industries including textile, dyeing, pharmaceutical, food, cosmetics and health products, paper and leather and the like industries [5,6]. Dye effluents discharged of these industries have caused serious environmental problems. Water consumption in textile and dyeing industries varies between 25 and 250 cubic meters per ton of product depending on the type of product [6]. Studies show that approximately 40 million tons of textiles are produced in the world annually. The effluents generated by these industries are about 4 to 8 billion cubic meters per year and the most evident characteristic of textile industry effluents is that they contain dyes. About 700,000 tons of dyes, the most commonly used organic chemicals, are produced annually in textile industries, half of which are azo dyes. Over 2,000 azo compounds are listed in dye profiles. About 15% of dyes are wasted during dyeing and finishing processes and enter the environment through effluents. Azo compounds comprise the largest group of synthetic organic dyes [7-12]. Most dyes used in industries especially in the textile industry cannot be analyzed biologically due to the formation of robust complexes and also low BOD(biochemical oxygen demand): COD (chemical oxygen demand) ratio (usually less than 0.1). These dyes have a high molecular weight and aromatic rings and are toxic to microorganisms [13]. Therefore, the biological processes are not so effective for the treatment of effluents containing these dyes and conventional treatment processes such as adsorption, coagulation, flocculation and sedimentation are not also effective as these methods mainly generate solid waste that will eventually cause other environmental problems. Therefore, other treatment methods must be used [14,15]. Given the need for public health provision and environment conservation, efficient technologies in this field should be noted. Advanced oxidation processes (AOP) is one of these technologies.

In the final years of the twentieth century, AOP was noticed as the most efficient and powerful technology in various fields of environmental engineering to protect the environment from pollutants and as a key technology for future [8,16]. These methods act like free radicals, especially 0OH (reactions 1-3). These radicals can oxidize organic pollutants non-selectively and convert them into CO2, H_2O and inorganic mineral salts [20,21]. These processes have several advantages over other processes including complete degradation of pollutants, degradation of pollutants that cannot be absorbed or pollutants with low volatility. Mass transfer process is not like complete adsorption and aeration and only leads to transferring pollutants to another phase, so is may be need further treatment [17]. Sonochemical process is an AOP with a significant potential for the analysis of organic compounds. Many researchers have reported that ultrasonic irradiation process can analyze a variety of organic compounds such as phenol compounds, chloroaromatic compounds, carbon tetrachloride, pesticides, herbicides, benzene compounds, polycyclic aromatic hydrocarbons, and organic dyes [22,23].

Sonolysis is an effective method for degradation of pollutants and resistant compounds in the environment. Ultrasound waves degrade organic materials based on producing small bubbles through cavitation at low pressure section. High pressure and temperature are generated during the collapse and fall of bubbles that lead to the pyrolysis of organic materials and generating highly reactive radicals (reactions 1 to 3). The temperature is about 4,000 to 10,000 °K and the pressure is about 300 to 975 bars [17-19]. Oxidizer species are produced during sonolysis in an aqueous environment by splitting water molecules through pyrolysis. After H_2O splitting, other reactions depend on the presence of other species in the bubble gas phase. H_2O_2 is the main form produced by recombined reactions of radicals 0OH (reactions 4 to 12). 0OH and H_2O_2 are strong oxidizing agents with reduction potential of 2.8 and 1.77, respectively [24, 31].

This study aimed to evaluate effective parameters such as pH, air flow rate, ferrous ion concentration and retention time in dye removal from textile wastewater using the ultrasonic process.

Method

This research is an experimental laboratory study. First, the raw wastewater characteristics were determined in terms of COD, dye, EC, BOD5, and PH. Then, to investigate the Sonochemical process, an undivided cell with a volume of 250 ml was used for 200 ml sample of textile wastewater. Given the variables, 48 samples were calculated. To change the PH, sodium hydroxide and sulfuric acid 1 M were used. Ultrasonic bath (PARSONIC 2600S model) with the power of 50 W and frequency 28 kHz was filled by distilled water up to a certain level and the reactor was placed within ultrasonic machine. Before Sonochemical process, the sample was saturated for 10 min with air blown into it. The air required for injection into the cell is supplied by an air pump through a ceramic distributor. The inlet air is measured by a flow meter (Figure 1). Then a certain amount of ferrous ions (FeSO4. $7H_2O$, Merck, Germany) is added to the sample to combine with hydrogen peroxide to form hydroxyl radicals. The effect of factors such as PH, contact time, the amount of ferrous ions catalyst, and air flow rate was investigated by one factor at a time method to determine the percentage of dye removal. Dye concentrations were measured by ADMI (American Dye Manufacture Institute) using a Hach spectrophotometer (DR 5000).

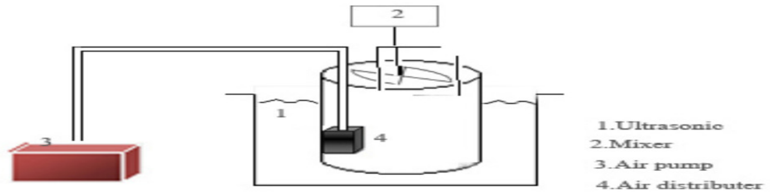


Figure 1 *Those of reactor Sonolysis*

Results

In Table 1 and Figure 1, the initial quality and visible absorption spectrum of dye from textile wastewater are presented. To evaluate the Sonochemical process, the effect of parameters such as PH, contact time, the

Table 1 *Initial Quality Textile Wastewater*

parameter	unit	mount
COD	mg/lit	1200
BOD5	mg/lit	100
BOD5/COD	%	3/8
pH	–	34/10
Electerical Conductivity	S/cmμ	4000
Color	ADMI	8850
Chlorine	mg/lit	520
Color Appearance	–	Black
Wavelength of maximum absorbance at 483nm		416/9

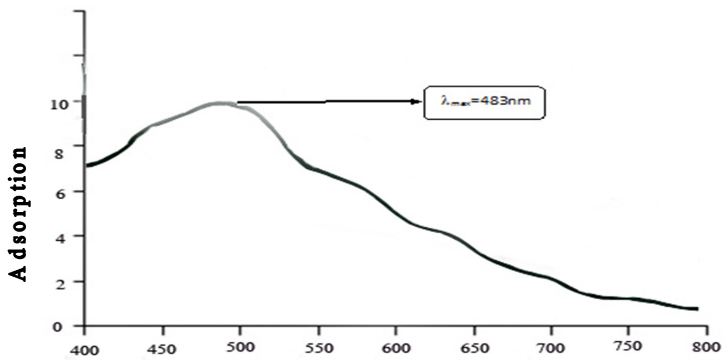


Figure 2 *absorption in the visible spectrum (400-700 nm) textile of raw wastewater*

amount of ferrous ions catalyst, and air flow rate were analyzed and the effect of these parameters was assessed on the dye removal efficiency. The evaluation of the dye removal efficiency in Sonochemical process is shown in Figures 1 to 5.

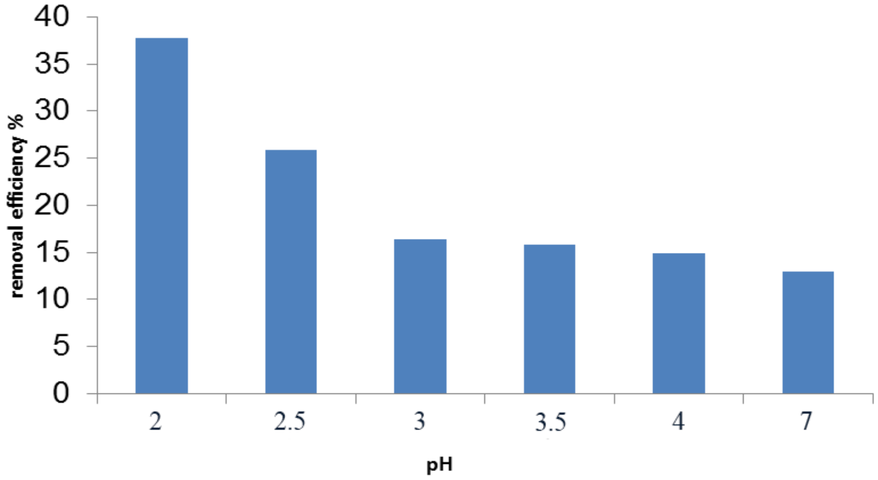
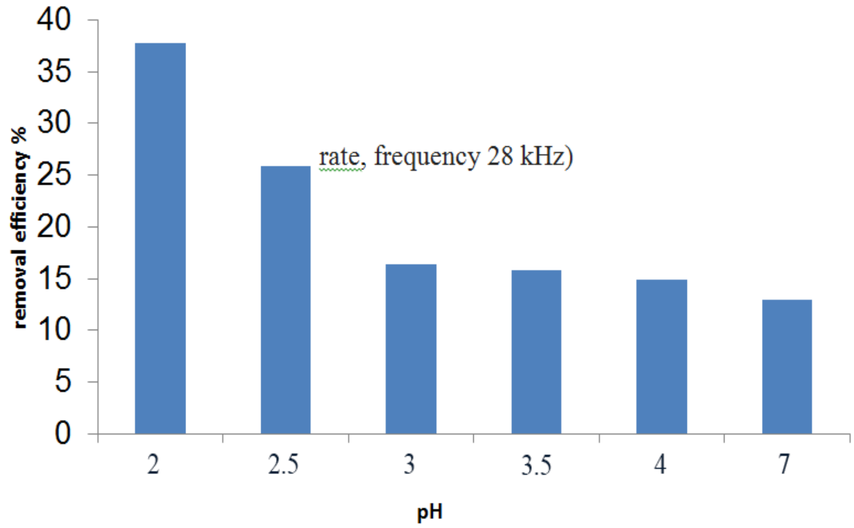


Figure 3 *Effect of pH on the color removal efficiency by sonolysis process in real textile wastewater (2 mM ferrous ion concentration, time of 240 minutes, 1.5 liters per minute of air flow*



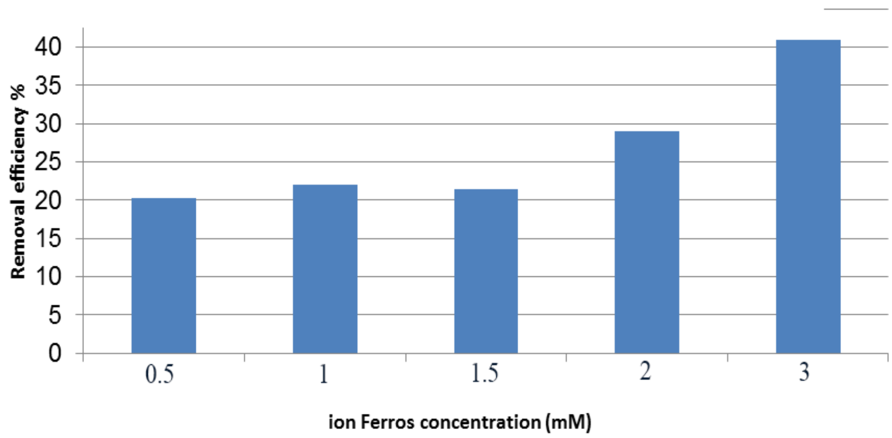


Figure 4 *Effect of ferrous ion concentration on color removal efficiency by sonolysis process in real textile wastewater (pH optimized 2-time of 240 minutes, the air flow rate of 1.5 liters per minute, a frequency of 28 kHz)*

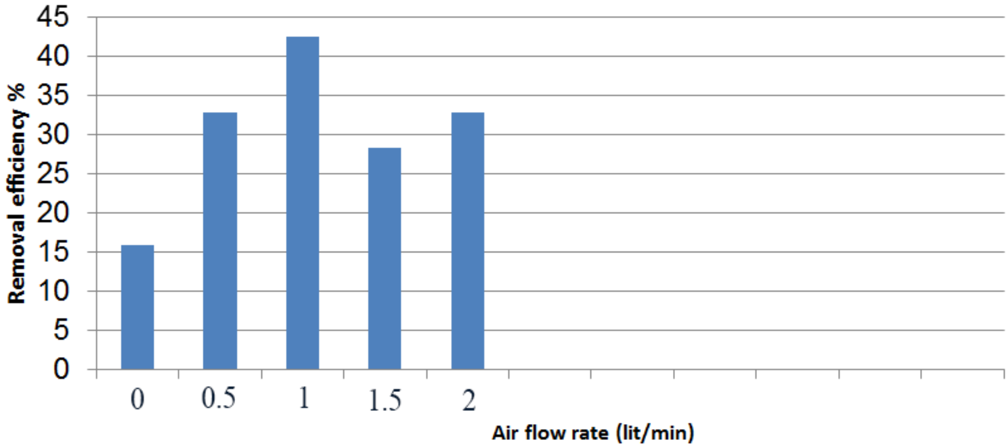


Figure 5 *Effect of flow on color removal efficiency by sonolysis process in real textile wastewater (pH optimum, 2, 3 mM ferrous ion concentration, time of 240 minutes, a frequency of 28 kHz)*

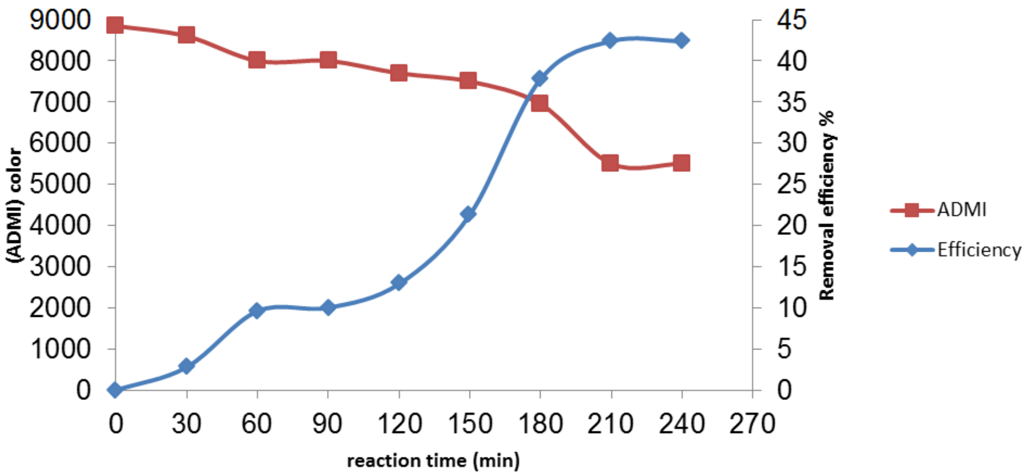


Figure 6 *Effect of reaction time on dye removal by actual of wastewater sonolysis process based on reactive dye in optimal conditions (2 = pH, ion concentration down to 3 mM, air flow rate of 1 liter per minute)*

Discussion

PH value is a critical parameter in the performance of the Sonochemical process; it plays an important role in the production of H_2O_2. The effect of PH was examined on the dye removal efficiency in PH values (2 to 7). Dye analysis is obviously affected by PH. As observed in Figure 2, acidic conditions accelerate the decolorization rate and the acceleration is due to the hydrogenation of negative charge of SO-3 in acidic environment ($SO^-_3 \rightarrow HSO_3^-$) (24). In Figure 2, the maximum efficiency is related to PH=2. Process efficiency in the dye removal is 37.8, 25.9, 16.38, 15.8, 14.9 and 13%, respectively at PH 2, 2.5, 3, 3.5, 4 and 7 while other variables remain constant.

A study conducted by Virendra Kumar et al. in 2011 to analyze the red dye 120 by the cavitation hydrodynamics showed that the lower PH increased decomposition rate, decomposition rate was much lower at PH=10, about 60% of decolorization and a 28% decrease in TOC was obtained at PH=2 [29]. At PH=2, the best conditions for generating hydroxyl radical is provided in Sonochemical process. A study conducted by Simona Wajhandi et al. in 2007 showed that decreased PH increased the efficiency of reactive black 5 dye removal [24].

Martins et al. conducted a study in 2012 on the decomposition of azure B dye in Mexico by sonochemistry and electro-Fenton. The results of this study showed that decreased PH to 2.5 increased dye removal efficiency and increased PH of 3 toward alkalinity decreased removal efficiency because iron was precipitated as oxyhydroxide [33].

Sonochemical process is less efficient in dye removal by increasing the PH to neutral because hydroxyl radical is an active and dominant oxidant under acidic conditions, but it does not have its maximum oxidizing power under alkaline conditions [24,30]. Also, most radical sweepers including CO_3^{-2} and SO_4^{-2} can be present at higher PH leading to a reduction in the amount of HO^0 radicals ultimately leading to the reduction in the rate of dye decomposition (24). Another study conducted by Maleki et al. in 2011 showed that low PH and a lower dye concentration is more suitable for decomposition [11].

In the Sonochemical process, hydrogen, hydroxyl and other radicals are produced through pyrolysis, and lead to dye decomposition. Radicals HO^0_2 and $^0O_2$, and the reaction of HO^0_2 with itself (reaction 14) are recombined and H_2O_2 is formed (reactions 13-15) that cannot decompose resistant pollutants by itself. So, ferrous ion is added to the reactor as a catalyst to react with hydrogen peroxide and produce hydroxyl radical (reactions 16, 17). According to Figure 3, dye removal efficiency is 20.3% at a concentration of 0.5 mM ferrous ions and 22%, 21.46%, 29% and 41% at concentrations of 1, 1.5, 2, and 3 mM, respectively. Removal efficiency was decreased at concentrations higher than 3 mM ferrous ions because of the sweeping property of ferrous ions to hydroxyl radical.

(13,14,15,16,17)

$$^{\circ}OH + ^{\circ}O_2^- \rightarrow OH^- + O_2$$

$$HO_2^{\circ} + HO_2^{\circ} \rightarrow H_2O_2 + O_2$$

$$HO_2^{\circ} + ^{\circ}O_2^- + H_2O \rightarrow H_2O_2 + O_2 + OH^-$$

$$Fe^{+3} + e^- \rightarrow Fe^{+2}$$

$$Fe^{+3} + H_2O_2 \rightarrow Fe^{+2} + H^+ + HO_2^0$$

A study conducted by Fernando Guzman et al. in 2011 showed that ferrous ions in led to a 32% increase of purple color removal from the aqueous environment in 180 minutes during sonolysis process [25].

Martins et al. conducted a study in 2012 on the decomposition of azure B dye in Mexico by sonochemistry and electro-Fenton. They concluded that ferrous ions catalyst is an important parameter in hydrogen peroxide activation, so it is effective on decomposition rate of organic compounds. In the absence of ferrous ions, dye removal was insignificant [33].

The inlet air flow rate to the reactor is an important parameter in the production of H_2O_2. The inlet oxygen reacts with H^+ and H_2O_2 is produced (reaction 18).

$$O_2 + 2H^+ + 2^{e-} \rightarrow H_2O_2 \quad (18)$$

Hydrogen peroxide is produced from strong oxidizers; however, this oxidizer reacts with ferrous ions added as a catalyst and hydroxyl radicals are produced which are very strong oxidizers [27]. A study conducted by Helal Uddin et al. in 2009 on the effect of nitrogen, oxygen, argon and air on sonolysis 2,4-dichlorophenol showed that dichlorophenol decomposition rate in the presence of oxygen, argon and air increased, respectively, and it had the lowest removal efficiency with nitrogen [34].

Color value changes over time are shown in Figure 5. The results of this study showed that the dye decomposition rate increased. As observed in the figure, the dye decomposition rate was high in 90 to 180 minutes. It can be said that the highest hydroxyl and hydrogen peroxide are produced at this time interval and hydrogen peroxide is converted into hydroxyl by adding ferrous ions. After this process, it will have a lower slope. Because of the power supply, energy consumption rate becomes important and the optimal time is 180 minutes. A study conducted by Wajhandi et al. in 2007 showed that increasing time increased the concentration of hydrogen peroxide leading to increased decomposition rate of reactive black 5 dye [24].

Another study conducted by Lee et al. in 2010 on the removal of cationic red X-GRL by sonolysis and electro-Fenton processes showed that from 80 minutes onward, a greater amount of H_2O_2 was produced at the ultrasonic frequency of 20 kHz and had a significant role on the dye removal. The highest removal efficiency in 180 minutes was obtained in ferrous ion concentration 5 mM, frequency 20 kHz, PH=3, the current density of 8.89 mA per square centimeter and dye concentration of 37.5 mg/L [2].

Ultrasound, like other advanced oxidation processes, is based on hydroxyl radical production with successive attacks on pollutant molecules. Another aim is complete mineralization of pollutants or converting them into less harmful compounds or with less chain, and then can be treated with a biological method. Given that Sonochemical process can decompose resistant compounds without producing sludge and also produce hydroxyl radicals, this process can be appropriate for pretreatment of wastewaters containing materials resistant to biodecomposition. Treatment with Sonochemical process has not yet been considered a large-scale treatment for chemical processes because ultrasound is high energy consumption and all cavitation energy produced is not attribute chemical and physical effects [32]. This process is better to be used combined with other advanced oxidation methods.

Conclusion

with regard to the results, the sonolysis process (frequency=28kHz, W=50w) can be used as a pretreatment for degradation of colored wastewater and refractory pollutants but have no acceptable efficiency for removal dye pollutants and therefore it must be used in hybrid with the other advanced oxidation processes.

Acknowledgements

This paper is a part of a Master's degree thesis for Environmental Health Engineering by Mohammad Hassan Momayezi, supervised by Dr. Akbar Eslami and the research project with the number of 10336-85-1-1391 in Shahid Beheshti University of Medical Sciences. Hereby, the authors greatly appreciate the cooperation and assistance provided by Water and Wastewater Chemical Laboratory in Health Faculty in Shahid Beheshti University of Medical Sciences, Mr. Aghayani and Ms. Mirshafieian.

Contributions

Study design: AS, MHM, ARY

Data collection and analysis: MHM

Manuscript preparation: AS, MHM

Conflict of interest

"The author declare that they have no competing interests."

References

1- Daneshvar N, Hejazi MJ, Rangarangy B, Khataee AR. Photocatalytic Degradation of an Organophosphorus Pesticide Phosalone in Aqueous Suspensions of Titanium Dioxide. *J Environ Sci and Health*2005;39(2): 285-96. [In Persian]

2- Hualiang Li HL, Qiang Yu, Zhong Li , Xin Feng, Bojie Yang. Effect of low frequency ultrasonic irradiation on the sonoelectro-Fenton degradation of cationic red X-GRL. *Chemical Engineering Journal*2010;160: 417-22.

3- Díaz-Cruz MS, Barceló D. Trace organic chemicals contamination in ground water recharge, Chemosphere. 2008; 72 (3): 333–42.

4- Mohapatra DP, Brar SK, Tyagi RD, Surampalli RY, Physico-chemical pretreatment and biotransformation of wastewater and wastewater sludge —fate of bisphenol A, *Chemosphere*2010; 78 (8): 923–41.

5- Lucas MS, Peres JA. Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation. *Dyes Pigm*2006;3: 236-44.

6- Ghaneiyan MT, Ehrampoosh M, Rahimi S, Ghanizade Q, Askarshahi M. Adsorption of Reactive Red 198 Dye on TiO2 Nano-particle from Synthetic Wastewater.Toloe behdashte. 2011; 4:59-70. [In Persian]

7- Ramalho PA, H.Scholze, Cardoso MH, Ramalho MT, Oliveira-Campos AM. . Improved conditions for the aerobic reductive decolorisation of azo dyes by Candida zeylanoides. *Enzyme and Microbial Technology*2002;31: 848-54.

8- Mahmoodi NM, Arami M. Bulk phase degradation of Acid Red 14 by nanophotocatalysis using immobilized titanium (IV) oxide nanoparticles. *Journal of Photochemistry and Photobiology*2006;182: 60-6. [In Persian]

9- Zhu C WL, Kong L, Yang X, Wang L, Zheng S, Chen F, Maizhi F, Zong H. Photocatalytic degradation of azo dyes by supported TiO2+UV in aqueous solution. *Chemosphere*2000;41: 303-9.

10- Wu C-H. Effects of sonication on decolorization of C.I. Reactive Red 198 in UV/ZnO system. *Journal of Hazardous Materials*2008;153: 1254-61.

11- Maleki A, Mahvi AH, Rezaee R. editor. Degradation of Reactive Red 198 using ultraviolet radiation and ultrasound waves in aqueous solution. 14 th congress national engineering health; 2011; Yazd2011. [In Persian]

12- Wang J, Jiang Y, Zhang X, et al. Investigation on the sonocatalytic degradation of acid red B in the presence of nanometer TiO2 catalysts and comparison of catalytic activities of anatase and rutile TiO2 powders, Ultrason. *Sonochem*2007;14 (5): 545–51.

13- Martinez-Huitle CA, Brillas E. decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. a general review, appl. catal. B Environ 2009;87:105-45.

14- Chao H YY, Xing FH, Larbot A. Influence of silver doping on the photocatalytic activity of titania films. *Appl Surf Sci*2002;200(1-4): 239-47.

15- Muruganandham M, Swaminathan M. Solar photocatlytic degradation of a reactive azo dye in TiO2-suspension. *Sol Energy Mater Sol Cel*2004;81: 439-57.

16- Behnejadi MA, Rabbani M, Modir N. Kinetic modeling of photocatalytic degradation and decolorization monoazo a color from textile industry in the process UV/TiO2. Ninth National Iranian Chemical Engineering Congress. 2005: 851-64.

17- Sina D. investigation potential combined technologies(photosonic and photooxidation) for destruction and reduce toxicity TCE Tehran: Tehran; 2011. [In Persian]

18- Ingale MN, Mahajani VV. Anovel way to treat refractory waste: sonication followed by wet air oxidation (SONIWO). *Technol , Biotechnol*1995;64: 80.

19- Marcio Inoue YM, Fumio Okada, Akihiko Sakurai, Ichiro Takahashi MS. Degradation of bisphenol a using sonochemical reactions. *Water Research*2008;42: 1379-86.

20- Pera-Titus M, García-Molina V, Baños MA, Giménez J, Esplugas S. Degradation of chlorophenols by means of advanced oxidation processes: a general review, Appl. *Catal. B Environ*2004;47 (4): 219–56.

21- Gogate PR, Pandit AB. A review of imperative technologies for waste water treatment I: oxidation technologies at ambient conditions, Adv *Environ Res*2004;8 (3–4): 501–51.

22- Lim M, Son Y, Yang J, Khim J. Addition of chlorinated compounds in the Sonochemical degradation of 2-chlorophenol, Jpn. *J Appl Phys*2008;47 (5 PART 2): 4123–26.

23- David B. Sonochemical degradation of PAH in aqueous solution. Part I: monocomponent PAH solution, Ultrason. *Sonochem*2009;16 (2): 260–65.

24- Vajnhandi S, Majcen Le, Marechal A. Case study of the Sonochemical decolouration of textile azo dye reactive Black 5. *Journal of Hazardous Materials*2007;141: 329-35.

25- Guzman-Duque F, Pettier C, Pulgarin C, Peũela G. Effects of Sonochemical parameters and inorganic ions during the Sonochemical degradation of crystal violet in water. *Ultrasonic's Sonochemistr*y2011; 18: 440-46.

26- Daneshvar N, Khataee AR. The modeling removal of blue color processes by H_2O_2 and UVC. Proceeding of the 9th Chemical Engineering Congress of Iran; 2009 Tehran, Iran. 2306-17. [In Persian]

27- Naddeo V, Belgiorno V, Ricco D, Kassinos D, Mantzavinosc D, Merica S. Ultrasonic degradation, mineralization and detoxification of diclofenac in water: optimization of operating parameters. Ultrasonic's Sonochemistry. 2009.

28- Kumar Saharan VP, Badve MB, Pandit A. Degradation of reactive red 120 dye using hydrodynamic cavitation. *Chemical Engineering Journal*2011; 178: 100– 7.

29- Bali U, Catalkaya E, Sengul F. Photodegradation of Reactive Black 5, Direct Red 28 and Direct Yellow 12 using UV, UV/H_2O_2 and UV/H_2O_2/Fe2+: a comparative study. *Journal of Hazardous Materials*2004; 114: 159-66.

30- Siddique M, Farooq R, Mehmood Khan Z, Khan Z, Shaukat SF. Enhanced decomposition of reactive blue 19 dye in ultrasound assisted electrochemical reactor. Ultrasonic's Sonochemistry 2011; 18: 190–6.

31- Y.G. Adewuyi, Sonochemistry in environmental remediation. 1. Combinative and hybrid sonophotochemical oxidation processes for the treatment of pollutants in water, Environ. *Sci Technol* 2005; 39 (10): 3409–20.

32- ChenV, Tang C. The photocatalytic degradation of reactive black 5 using TiO2/UV in an annular photoreactor. *Water Res*2004;38:2775-81.

33- Martinez SS, Velasco Uribe E. Enhanced Sonochemical degradation of azure B dye by the

electroFenton process. *Ultrasonics Sonochemistry*2012; 19: 174–8.
34- Helal Uddin MD, Hayashi S. Effects of dissolved gases and pH on sonolysis of 2,4-dichlorophenol. *Journal of Hazardous Materials*2009; 170: 1273–6.