Iran. J. Environ. Health. Sci. Eng., 2009, Vol. 6, No. 4, pp. 233-240

REDUCTION OF HUMIC SUBSTANCES IN WATER BY APPLICATION OF ULTRASOUND WAVES AND ULTRAVIOLET IRRADIATION

[1,2]A. H. Mahvi, *[3]A. Maleki, [3]R. Rezaee, [3]M. Safari

[1]School of public Health and Center for Environmental Research, Tehran University of Medical Sciences, Tehran, Iran
[2]National Instiute of Health Research, Ministry of Health , Iran
[3]School of Health, Kurdistan University of Medical Sciences, Sanandaj, Iran

Received 01 May 2009; revised 03 October 2009; accepted 23 October 2009

ABSTRACT

Humic substances mainly humic acids constitute the major fraction of natural organic matter in water supplies. They play an important role in the formation of harmful disinfection by products. Degradation of humic acids by means of ultraviolet radiation and ultrasonic irradiation processes was investigated in a laboratory-scale batch photoreactor equipped with an 300 W immersed-type medium-pressure mercury vapour lamp and sonoreactor with low frequency (42 kHz) plate type transducer at 170 W of acoustic power with emphasis on the effect of various parameters on degradation efficiency. Experiments were performed at humic acids initial concentrations varying between 2.5-10 mg/L. Oxidation of humic substances has been followed over time by measuring total organic carbon and UV absorbance in 254 nm and 436 nm. Initial results indicated a strong capacity of photolysis for degradation of humic substances. The results also showed that ultrasonic alone cannot be an efficient method for degradation of humic substances in comparison with UV process. The maximum degradation efficiency of humic substances after 90 min of irradiation, however, was only 5.7% and reached a maximum value of 9.5% after 300 min of irradiation. It was found that total organic carbon can be removed effectively by photolysis. It was also found that lower concentrations of humic substances favor the humic substances degradation. Also, the experimental results indicated that the kinetics of ultrasono-oxidation and photo-oxidation processes fit well by pseudo-first order kinetics.

Keywords: Humic acids, Ultraviolet radiation, Ultrasonic irradiation

INTRODUCTION

Natural organic matter (NOM) is a complex matrix of organic compounds present in natural surface water sources. Not only it does affect the odor, color and taste of water but it also affects several processes in drinking water treatment (Aoustin *et al.,* 2001). Concentrations of NOM in three rivers around Tehran are reported 8.53-12.9 mg/L (Zazouli *et al.,* 2007a). In another study the hydrophobic and hydrophilic fractions were about 41 and 59% (Zazouli *et al.,* 2007b). The presence of natural organic matter in water has been identified as one of the main contributors to the problems associated with the supply of potable drinking water (Parkinson *et al.,* 2001). Humic substances (HS) are the predominant type of natural organic matter present in ground and surface waters. On the basis of their solubility in water and as a function of pH, humic substances are generally classified into humic acids (HA), fulvic acids (FA) and humin (Uyguner and Bekbolet, 2005). Humic substances cause formation of disinfection by products (DBPs) such as chloroform, bromo-dichloromethane, etc., which are suspected carcinogenic compounds (Yıldız, *et al.,* 2008). Due to the harmful effects noted above, humic substances should be removed

---

*Corresponding author: *maleki43@yahoo.com*
Tel: +98 871 6626969, Fax: +98 871 6625131

from water (Yıldız, *et al.,* 2008).

However, NOM removal in conventional drinking water treatment processes is quite low, between 10 and 50% (Jacangelo *et al.,* 1995). Due to the presence of a wide variety of NOM and the necessity of the chemical disinfection process to protect the public health, many water utilities have to face the problem of disinfection by product DBPs formation.

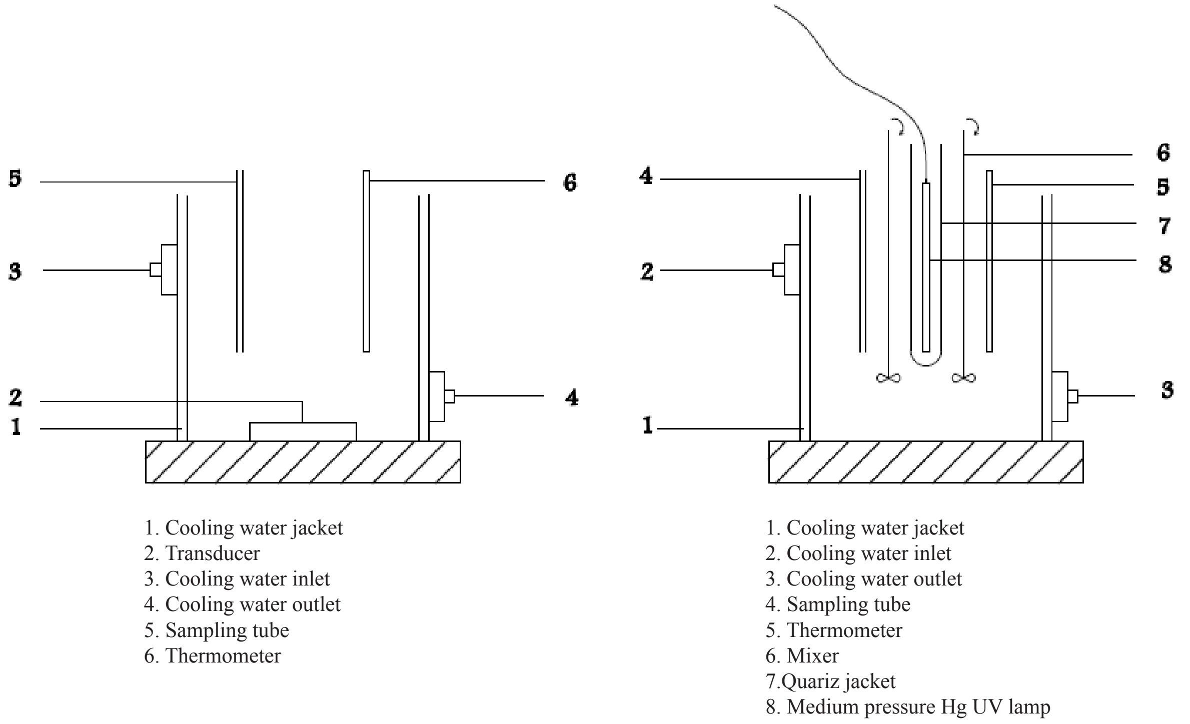
In the past two decades, advanced oxidation processes (AOPs) appear more appropriate for treating wastewaters containing organic substances (Mahvi *et al.,* 2009; Samarghandi *et al.,* 2007; Maleki *et al.,*2005). AOPs are defined as the processes that involve highly reactive species, specifically hydroxyl radicals (oxidation potential= 2.8 V) in sufficient quantities to oxidize the majority of complex organic chemicals in the water effluent (Mason and Lorimer, 2002). Hydroxyl radicals have become the most important oxidants due to their high reactivity and lack of selectivity towards organic compounds (Maleki *et al.,* 2007; Mason and Lorimer, 2002).

Sonication is a relatively innovative AOP based on the use of low to medium frequency (typically in the range 20–1000 kHz) and high energy ultrasound (US) 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 (Mahvi, 2009; Maleki *et al.,* 2007; Mason and Lorimer, 2002). In afew studies the efficiency of ultrasound has been determined in destruction of fungi and organic matters (Dehghani *et al.,* 2007a; Dehghani *et al.,* 2007b). 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 (Maleki *et al.,* 2007; Mason and Lorimer, 2002). 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 (UV) irradiation (Mahvi *et al.,* 2007). In addition, UV irradiation causes dissociation of the water molecule and formation of highly reactive hydroxyl radicals that attack and destroy the organic pollutants (Han *et al.,* 2004). Some research has been conducted to assess the sonochemical and photochemical destruction of humic substances in water. Chemat *et al.* reported 90% sonodegradation of natural and synthetic humic substances and 50% of TOC reduction within 60 min, respectively (Chemat *et al.,* 2001). Wang *et al.* showed that approximately 90% of the humic acid was oxidized within 1 h of irradiation when UV/quartz was used. However, oxidation of only 20% of humic acid was observed after 2 h irradiation when UV/Pyrex or sunlight was used as the light source (Wang *et al.,* 2000).

No study was observed for oxidation the humic substances using low frequency (42 kHz, 170 W) ultrasound wave and high intensity medium pressure (300 W) ultraviolet radiation. The purpose of this work was to compare the efficiency of low frequency ultrasound and high intensity medium pressure ultraviolet light for humic substances oxidation [measured by both means of UV_{254}, UV_{436} absorbance and total organic carbon (TOC)] in water.

MATERIALS AND METHODS

Humic acid purchased from Aldrich as sodium salt was used to simulate the organic matter in natural waters. All chemicals used for solutions were reagent grade and were used without further purification. All model solutions of humic acid were prepared using deionized water with the initial concentration of 2.5-10 mg/L. In each case, the reaction volume was 2500 ml and all of the experiments were conducted at pH=7. Sonication was 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.1a). Ultrasonic energy dissipated in the reactor was set at 60 W. Dimensions of ultrasonic bath were 262 cm×164 cm× 80 cm. Ultrasonic energy dissipated in the reactor was set at 1.6 W/cm^2 through the calorimetric method. The apparatus is open to air. The sonochemical reactions were carried out for 300 min. The photo-degradation studies were carried out in a batch reactor system (water depth was 10 cm). A 300 W medium pressure mercury lamp (I= 1400 μW/cm^2 through the radiometry method) surrounded by quartz jacket (20 cm length) was located in the center of the reactor. The lamp bandwidth was in the range of 210-250 nm (maximum emission at 247.3 nm). The photolysis reactions were carried out for 120 min. Samples were taken periodically from the reactors and analyzed immediately. The temperature of the reactor was maintained at 25±2 ºC with a water cooling jacket. After each run, the absorption of the supernatant was determined with 10 mm glass cell using a double beam spectrophotometer (PJ Instrument- T 80, England) at 436 nm (Color$_{436}$, 1/m) and 254 nm (UV$_{254}$, m^{-1}) for the evaluation of the kinetics of the sonolysis and photolysis degradation of humic substances. Total organic carbon was measured with a Shimadzu 5000A, total organic carbon analyzer. Source water parameters as pH, turbidity and total organic carbon (TOC) were also measured according to the Standard Methods (APHA, 1998). All experiments were run in triplicate to ensure reproducibility.



(a) (b)

Fig. 1. Schematic diagram of sonoreactor (a) and photoreactor (b)

RESULTS

Study on humic substances degradation was carried out for 2 and 5 h irradiation time in photolysis and ultrasonolysis processes, respectively. Tables 1 and 2 show the variation in concentration of humic substances with time in terms of Color_{436} and UV_{254}, turbidity and pH in photolysis and ultrasonolysis processes. Only 9.5% and 5% reduction in organic content of humic substances (UV_{254}) and color (Color_{436}) have been observed for 300 min ultrasonolysis of 10 mg/L humic substances solution, respectively. Instead 50.5% and 59% reduction in organic content of humic substances (UV_{254}) and color (Color_{436}) have been observed for 120 min ultrasonication of 10 mg/L humic substances solution, respectively. Table 3 shows the major calculated reaction rate coefficients. The experimental data from this study fitted well with pseudo-first order reaction rate equation. It was observed that the initial rate of ultrasonic degradation was high but later it reduced substantially. Figs. 2 and 3 show the removal of humic substances with respect to TOC during oxidation processes. As can be seen TOC was removed more efficiently by the UV than by the US processes. TOC concentration was reduced from 22.94 to 22.04 mg/L in 300 min ultrasonication and from 22.8 to 11.34 mg/L in 120 min photolysis at concentration of 10 mg/L humic substances.

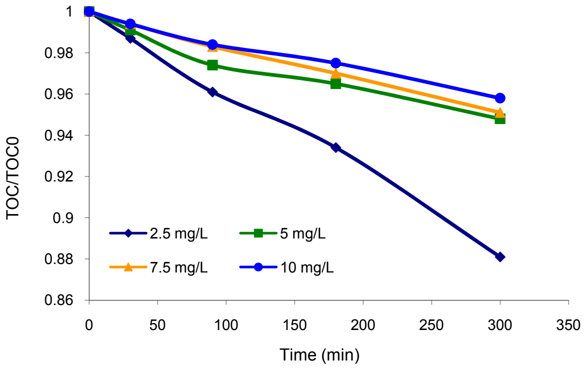


Fig. 2. Reduction of TOC vs. time for ultrasonodegradation of humic substances

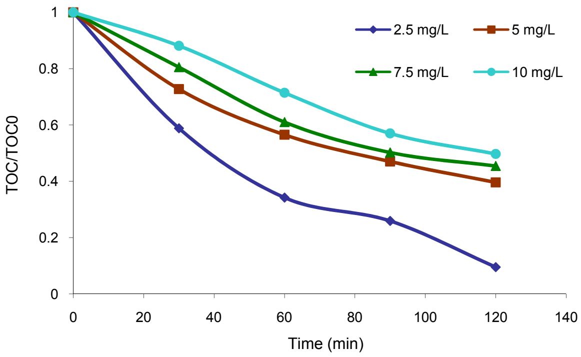


Fig. 3. Reduction of TOC vs. time for photodegradation of humic substances

DISCUSSION

The advanced oxidation of the humic substances at different initial concentrations in the range of 2.5-10 mg/L was investigated. Initial results demonstrated that ultraviolet radiation was able to appreciably degrade humic substances and ultrasound waves are the least efficient treatment in comparison with ultraviolet radiation. The efficiency of different treatment processes can be observed on the UV absorbance at 254 nm and 436 nm. Table 1 shows the degradation of humic substances as function of time. As can be seen, sonochemical degradation proceeded very slowly leading to less than 9.5% reduction in UV_{254} and 5 % reduction in Color_{436} after 300 min ultrasonication at 10 mg/L humic substances. It can also be observed from results that UV had its potential to degrade humic substances. More than 50.5% reduction in UV_{254} and 59 % reduction in Color_{436} were achieved after about 120 min at 10 mg l^{-1} of humic substances.

Table 1. Degradation efficiency of HS in terms of UV$_{254}$ and Color$_{435}$ by ultrasound wave

Concentration (mg/L)	**Time (min)**	**Initial characteristics**		**Secondary characteristics**			
		pH	**Turbidity (NTU)**	**pH**	**Turbidity (NTU)**	**UV$_{254}$ (Removal efficiency %)**	**Color$_{435}$ (Removal efficiency %)**
2.5	0	7	1.17	6.7[a]	1.3[a]	0	0
	30					1	10.2
	90					4	14
	180					6.5	17.5
	300					10.5	22
5	0	7	2.55	6.9[a]	2.6[a]	0	0
	30					1	3.5
	90					2.3	8.6
	180					3.16	12.2
	300					5.1	16
7.5	0	7	3.8	6.9[a]	3.84[a]	0	0
	30					0.5	2.3
	90					1.6	5.1
	180					2.8	7.8
	300					4.7	10.9
10	0	7	4.73	6.9[a]	4.9[a]	0	0
	30					0.5	2.1
	90					1.5	3.2
	180					2.5	4.4
	300					4.2	6.6

[a] after 300 min of reaction

The poor effects of US on the reduction efficiency of UV$_{254}$ and Color$_{436}$ may be attributed to the fact that low ultrasound frequencies hinder the development of hydroxyl radicals (Vinodgopal *et al.,* 1998). Naffrechoux et al. reported the changes of humic macromolecules induced by the ultrasonic waves are weak and probably concern only the molecular conformation. The main primary chemical process in the sonolysis of aqueous solutions is the thermal dissociation of water to hydrogen atoms and hydroxyl radicals (Naffrechoux *et al.,* 2003). They showed the hydrogen peroxide concentration continuously increases during US treatment of humic substances solution despite the low OH radicals quantity produced and the reactivity of humic substances with OH radicals seems quite limited (Naffrechoux *et al.,* 2003). Hence 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 efficiency (Ince and Tezcanli, 2001).

It can be also observed from Table 1 the initial turbidity value of the solution was increased by irradiation of US. This condition may be attributed to the fact that the effects of ultrasonication on the humic acids could be explained by two mechanisms. One is the chemical degradation of the humic acids in the cavitation bubbles by oxidation. The other is the physical aggregation of humic acid fragments. The main physical effect of powerful implosion of cavitation bubbles in the natural water is the fragmentation of the suspended solids. This effect is easily measurable by turbidity growth (Naddeo *et al.,* 2007).

A can be concluded from table 2 UV light had high potential to degrade humic substances. This may be because the main oxidant responsible for the oxidation of humic substances is the highly reactive hydroxyl radical that produce very much during the irradiation of solution using medium pressure mercury lamp (300 W). Also, UV radiation is strongly absorbed by humic substances, UV treatment of the substances solution leads to drastic changes of the molecules

(Naffrechoux *et al.,* 2003). This would explain discrepancies in reactivity of humic substances between ultrasonochemical 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.

Table 2. Degradation efficiency of HS in terms of UV_{254} and $Color_{435}$ by ultraviolet irradiation

Concentration (mg/L)	Time (min)	Initial characteristics		Secondary characteristics			
		pH	Turbidity (NTU)	pH	Turbidity (NTU)	UV_{254} (Removal efficiency,%)	$Color_{435}$ (Removal efficiency,%)
2.5	0	7	1.14	4.51[a]	0.9[a]	0	0
	30					41.6	62
	60					66.6	80.3
	90					75	87
	120					91.6	95
5	0	7	2.31	4.88[a]	1.71[a]	0	0
	30					27	37.2
	60					43.7	55.6
	90					53	68.6
	120					60	75.5
7.5	0	7	3.38	5.31[a]	2.1[a]	0	0
	30					19.2	24.2
	60					39	40.6
	90					50	56.7
	120					56.6	65
10	0	7	4.65	5.5[a]	2.31[a]	0	0
	30					12	15.8
	60					29	36
	90					43	49
	120					50.5	59

[a] after 120 min of reaction

It has also been pointed out that the humic substances reduction in terms of $Color_{436}$ and UV_{254} gradually decreased with increasing initial humic substances concentration (Table 1 and 2). Nevertheless, the efficiency of the process in terms of the amount of humic substances degraded generally increased at higher initial concentrations. The presumed reason is that when the initial concentration of humic substances is increased, the competition between the humic substances metabolites and humic substances for hydroxyl radical became intense owing to the non-selective reactivity of hydroxyl radical. Additionally, in the US process with increasing initial humic substances concentration the cavities approached saturation. The two factors contributed to a decreasing rate constant for the degradation of humic substances with an increase in initial concentration (Naddeo *et al.,* 2007).

The results showed that the pH of the initial solution decreased slightly during different treatment processes. The changes in the pH can possibly be attributed to the fact that, when the aqueous solution is irradiated by ultrasound, water vapor present in the ultrasound bubble is split to yield hydrogen and hydroxyl radicals. Naddeo et al. reported humic substances molecules present in the vapor phase or in the surrounding liquid of the collapsing bubbles are subject to direct attack by hydroxyl radicals, thus probably accelerating hydrolysis by several orders of magnitude in the presence of ultrasound. The acidic nature of humic substances such as humic acids is usually attributed to the ionization behavior of carboxylic and phenolic hydroxyl groups (Naddeo *et al.,* 2007; Joyce *et al.,* 2007).

The change in pH of the humic acid solution by ultrasonication implies that the ionization behavior of the acidic functional groups of humic acids in an ultrasound field could be modified (Naddeo *et al.,* 2007). Since, humic acids behave like weak acid polyelectrolytes with a relatively high pH buffering capacity, changes in the pH of the humic acids would probably not be evident, even when the acidic functional groups of the humic acid molecules change (Naddeo *et al.,* 2007).

$$r = -\frac{d[C]}{dt} = kC$$

Table 3. Pseudo-first-order rate constants for the different degradation processes at different initial HS concentration

Type of process		**Initial phenol concentration (mg/L)**			
		2.5	**5**	**7.5**	**10**
US	Rate constant (1/min)	0.0004	0.0002	0.0002	0.0001
	Correlation coefficient	0.99	0.97	0.99	0.99
UV	Rate constant (1/min)	0.0008	0.0036	0.0031	0.0026
	Correlation coefficient	0.97	0.95	0.95	0.93

As demonstrated in Table 3, the degradation of humic substances in terms of UV_{254} absorbance by oxidation processes exhibit pseudo-first-order reaction kinetics. The rate of disappearance of HS may be described by following equation:

Where, r, k and C are the reaction rate of HS, pseudo first order constant and HS concentration, respectively. The pseudo-first-order rate constants (k) of decolorization obtained from the slope of -ln (C/C_0) vs. t (time) plots where C_0 and C are humic substances concentration at time zero and at time t, respectively. The rate of humic substances degradation was dependent on initial humic substances concentration (C_0) and k decreased with increasing C_0.

The removal of the TOC of the humic substances for the both processes was determined. It was found that the ultraviolet radiation had more effects on the TOC removal from the aqueous solution in comparison to ultrasonic mineralization. An average of 50.2% reduction in TOC values occured during the photolysis of 10 mg/L humic substances. Also, the mineralization represented in terms of TOC reduction was increased with an increase of reaction time.

ACKNOWLEDGEMENTS

The authors are grateful for the financial support provided by Kurdistan University of Medical Sciences.

REFERENCES

Aoustin, E., Schafer, A. I., Fane, A. G., Waite, T. D., (2001). Ultrafiltration of natural organic matter. Sep. Purif. Technol., **22–23**: 63-78.

APHA., AWWA., WPCF., (1998). Standard Methods for the Examination of Water and Wastewater. 20th Ed., United Book Press Baltimore.

Chemat, F., Teunissen, P. G. M., Chemat, S., Bartels, P. V., (2001). Sono-oxidation treatment of humic substances in drinking water. Ultrasonics Sonochem., **8:** 247-250.

Dehghani, M.H., Mahvi, A.H., Jahed, G.R., Sheikhi, R.,(2007a). Investigation and evaluation of ultrasound reactor for reduction of fungi from sewage. Journal of Zhejiang University. Sci. B. **8** (7): 493-497.

Dehghani, M.H., Mahvi, A.H., Najafpoor, A.A., Azam, K.,(2007b). Investigating the potential of using acoustic frequency on the degradation of linear alkylbenzen sulfonates from aqueous solution. Zhejiang University: Science A 8 (9), pp. 1462-1468

Han, W., Zhu, W., Zhang, P., Zhang, Y., Li, L., (2004). Photocatalytic degradation of phenols in aqueous solution under irradiation of 254 and 185 nm UV light. Catal. Today., **90**: 319-324.

Ince, N. H., Tezcanli, G., (2001). Reactive dye stuff degradation by combined sonolysis and ozonation. Dyes and Pigments*,* **49**: 145-153.

Jacangelo, J. G., Demarco, J., Owen, D. M., Randtke, S. J., (1995). Selected processes for removing NOM. J. AWWA, **87**(1): 64-77.

Joyce, E., Phull, S. S., Lorimer, J. P., Mason, T. J., (2003). The development and evaluation of ultrasound for the treatment of bacterial suspensions. A study of frequency, power and sonication time on cultured Bacillus species. Ultrasonic Sonochem., **10**(6): 315-318.

Mahvi, A. H., (2009). Application of ultrasonic technology for water and wastewater treatment. Iran. J. Public Health, **38**: 1-17.

Mahvi, A. H., Ghanbarian, M., Nasseri, S., Khairi, A., (2009). Mineralization and discoloration of textile wastewater by TiO2 nanoparticles. Desalination, **239**: 309-316.

Mahvi, A. H., Maleki, A., Alimohamadi, M., Ghasri, A., (2007). Photo-oxidation of phenol in aqueous solution: Toxicity of intermediates. Korean J. Chem. Eng., **24**(1): 79-82.

Maleki, A., Mahvi, A. H., Mesdaghinia, A., Naddafi, K., (2007). Degradation and toxicity reduction of phenol by ultrasound waves. Bull. Chem. Soc. Ethiop., **21**(1): 33-38.

Maleki, A., Mahvi, A. H., Vaezi, F., Nabizadeh, R., (2005). Ultrasonic degradation of phenol and determination of the oxidation by-products toxicity. Iran. J. Environ. Health. Sci. Eng., **2**: 201-206.

Mason, T. J. and Lorimer, J. P., (2002). Applied Sonochemistry. Viley- VCH Verlag GmbH & Co., Weinheim.

Naddeo, V., Belgiorno, V., Napoli, R. M. A., (2007). Behaviour of natural organic mater during ultrasonic irradiation. Desalination, **210**: 175-182.

Naffrechoux, E., Combet, E., Fanget, B., Petrier. C., (2003). Reduction of chloroform formation potential of humic acid by sonolysis and ultraviolet irradiation. Water Res., **37**: 1948-1952.

Parkinson, A., Barry, M. J., Roddick, F. A., Hobday, M. D., (2001). Prelimanary toxicity assessment of water after treatment with UV-IR radiation and UVc/H_2O_2. Water Res., **35**: 3656-3664.

Samarghandi, M.R., Nouri, J., Mesdaghinia, A.R., Mahvi, A.H., Nasseri, S., Vaezi, F.,(2007). Efficiency removal of phenol, lead and cadmium by means of UV/TiO 2/H2O2 processes. Int Environ Sci and Technology **4** (1): 19-25.

Uyguner, C. S., Bekbolet, M., (2005). A comparative study on the photocatalytic degradation of humic substances of various origins**.** Desalination, **176**: 167-176**.**

Vinodgopal, K., Makogon, O., Kamat, P. V., (1998). Ultrasonic mineralization of a reactive textile azo dye, remazol black B. Water Res., **32**(12): 3646-3650.

Wang, G., Hsieh, S., Hong, C., (2000). Destraction of humic acid in water by UV light-catalyzed oxidation with hydrogen peroxide. Water Res., **34**: 3882-3887.

Yıldız, Y. S., Koparal, A. S., Keskinler, B., (2008). Effect of initial pH and supporting electrolyte on the treatment of water containing high concentration of humic substances by electrocoagulation. Chemical Engineering Journal, **138**: 63-72.

Zazouli, M.A., Nasseri, S., Mahvi, A.H., Mesdaghinia, A.R., Gholami, M.,(2007a). Study of natural organic matter fractions in water sources of Tehran. Pakistan Journal of Biolog Sci **10** (10): 1718-1722.

Zazouli, M.A., Nasseri, S., Mahvi, A.H., Mesdaghinia, A.R., Younesian, M., Gholami, M.,(2007b). Determination of hydrophobic and hydrophilic fractions of natural organic matter in raw water of Jalalieh and Tehranspars water treatment plants (Tehran). Applied Sci **7** (18): 2651-2655