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**TINIDAZOL ANTIBIOTIC DEGRADATION IN AQUEOUS  
SOLUTION BY ZERO VALENT IRON NANOPARTICLES  
AND HYDROGEN PEROXIDE IN THE PRESENCE OF  
ULTRASOUND RADIATION**

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*The purpose of this study was to investigate the efficiency removal of the antibiotic Tinidazol by hybrid system of ultrasonic/nZVI/H<sub>2</sub>O<sub>2</sub> (US/nZVI/H<sub>2</sub>O<sub>2</sub>) in aquatic environment. It examined the effect of variables such as concentration of antibiotic, nZVI and H<sub>2</sub>O<sub>2</sub>, frequency of US and pH. Also the performance of system in removal of COD and electrical energy consumed by the ultrasonic bath was investigated. Findings showed the best efficiency (93 %) for system in pH 3, concentration hydrogen peroxide of 1M, amount of 0,2 g of zero valent iron nanoparticles and 130 kHz radiation frequency. According to the results US/nZVI/H<sub>2</sub>O<sub>2</sub> method can be good performance in removal of antibiotics Tinidazol and similar pollutants.*

**Keywords:** tinidazol antibiotic, zero valent iron nanoparticles, hydrogen peroxide, ultrasound radiation

## **1. Introduction**

Antibiotics are dangerous pollutants in the aquatic environment due to its undesirable effects on aquatic live and humans. The problem may occur Due to presence of low concentrations of antibiotics in the environment, is developing of antibiotic resistant bacteria [1]. With increasing use of antibiotics in the world, the quality of drinking water for humans is significantly reduced. The majority of these contaminants have low biodegradability [2] and high toxicity [3], showing mutagenic and carcinogenic characteristics [4]. Tinidazol, a broad-spectrum antibiotic, is highly effective against gram-positive and gram-negative anaerobic pathogens as well as gram-positive aerobes and effectively used for the treatment of serious respiratory tract infections, serious skin and soft tissue infections, etc [5]. Different methods are used for wastewater treatment

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containing pharmaceutical compounds. Among these methods, advanced oxidation process (AOP<sub>s</sub>) seems to be more practical than other methods such as activated carbon adsorption, reverse osmosis and air stripping, because these techniques are only transferring pollutants from one phase to another without destroying them. Biological treatment is used for wastewater containing biodegradable substances and non-toxic materials [6]. AOP<sub>s</sub> such as ozonation, UV/H<sub>2</sub>O<sub>2</sub>, UV/O<sub>3</sub>, Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> and UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> Widely used to successfully in the degradation of organic compounds in industrial wastewater and groundwater [7]. Several studies have shown that this technology have good ability to oxidize organic pollutants to carbon dioxide and water [8]. Ultrasonic irradiation causes rapid degradation of chemical contaminants in water that has attracted much attention. Sonication of aqueous solutions motivates the formation and collapse of cavitation bubbles. During the collapse high temperature and pressure is created that causes the formation of chemical species such as H<sup>•</sup>, OH<sup>•</sup>, O<sup>•</sup> and H<sub>2</sub>O<sub>2</sub>. This phenomenon with high energy has led to the destruction of organic compounds in aqueous solutions. Degradation process may be carried out by two main mechanisms: direct pyrolysis in and around the collapsing bubbles and oxidation by OH<sup>•</sup> radicals [9, 10]. But it should be noted that the complete mineralization of pollutants is not possible by ultrasound alone. Because of the time scale and energy required to disperse is not cost effective economically. Therefore, the ultrasonic process is used more as a preoxidant step before the biological treatment. Organic compounds with large molecules are broken by ultrasonic, and then enter the biological treatment unit. Ultrasound is also used in combination with other technologies to increase the efficiency degradation. It can be noted that a combination of methods including sonochemical, sonophotochemical and sonoelectrochemical [11,12]. Iron in recent years zero valant iron nanoparticles have been considered due to high-efficiency removal of various contaminants such as heavy metals [13,14], chlorinated organic [15, 16], nitroaromatic compounds [17, 18], polybrominated diphenyl ethers [19, 20], nitrates [21, 22], pesticides [23, 24], dyes [25, 26], etc. Because of its small particle size, large specific surface area, high density and great intrinsic reactivity of reactive surface sites, nZVI gets good reliability for use in environment remediation [27, 28]. No much research has been done to remove the antibiotic Tinidazol (TN) in the aquatic environment. In this case can be pointed to a few case. Anna Zhu and et al were carried out on Tinidazol's separation and recovery from Tinidazol fermentation wastewater with nanofiltration (NF) membranes [29]. No study on removal of TN antibiotic in aqueous solution by US/nZVI/H<sub>2</sub>O<sub>2</sub> process has been reported. Therefore, it is important to

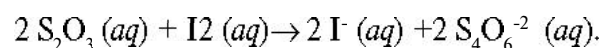
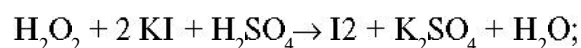
evaluate efficiency of this process in degradation of TN antibiotic in aqueous solutions. Recent study has examined the use of optimal conditions in the US/nZVI/H<sub>2</sub>O<sub>2</sub> process for removal of TN in the aquatic environment.

## 2. Experimental

**2.1. Reagents.** Tinidazol powder and methanol (HPLC grade  $\geq 99,9\%$ ) was purchased from "Sigma-Aldrich" (St. Louis, MO, USA) and acetone (HPLC grade  $\geq 99,98\%$  pure) from "Acros Organics Co", Belgium. Sulfuric acid, Sodium hydroxide, Potassium iodide, Sodium thiosulphate and Starch were prepared from CMC (Germany). H<sub>2</sub>O<sub>2</sub> (30 % w/w) was obtained from BDH Company and the Whatman filters were taken from Prolabo, France.

**2.2. Preparation of Zero iron nanoparticles.** The nZVI used this study was made according to the method described by Wang and Zang [30]. It was based on addition 0,16 M NaBH<sub>4</sub> aqueous solution dropwise under continuous stirring to 0,1 M FeCl<sub>3</sub>·6H<sub>2</sub>O aqueous solution. The nZVI formed was filtered and in pure water for disperse sonicated.

**2.3. Examination methods.** In this study Tinidazol as a selected antibiotic, with concentrations of 45; 80 and 100 mg/L, were added to the reactor includes different concentration of Zero valent Iron nanoparticles (0,06; 0,1; 0,2 g / L) and hydrogen peroxide (0,1; 0,5 and 1 M). Initial pH of Tinidazol solution was adjusted using hydrochloric acid and sodium hydroxide and measured (pHS-3B, Shanghai, China). Ultrasound treatments were conducted using ultrasound generator (Elma CD-4820, Germany) with 35 and 130 kHz frequencies and input power 500 W. Then, 5 ml of sample was extracted from the reactor outlet for the analysis of four 30-minute intervals over 150 min. Before injecting the sample into the HPLC, samples were passed through filters with a pore 0,2 microns. Detection of TN was conducted at 338 nm by HPLC. Residual hydrogen peroxide in samples was measured by potassium iodide method.



The results showed that hydrogen peroxide remaining in the sample output was not very impressive. All reaction was done in triplicate and results were reported this paper is average of them.

**2.4. Tinidazol analysis.** The most important physical and chemical properties of Tinidazol antibiotic (molecular formula  $C_8H_{13}N_3O_4S$ ; molecular weight – 247,28 g/mol; melting point –127,5 °C; water solubi – 0,008 mol/L) has been shown in Fig.1. Different concentrations of the antibiotic Tinidazol were determined by HPLC at a wavelength of 338 nm. The mobile phase was a mixture of 40 and 60% acetonitrile in 10 mM phosphate buffer with pH 7,5. The flow rate was 1,0 mL/min and injection of 20  $\mu$ l.

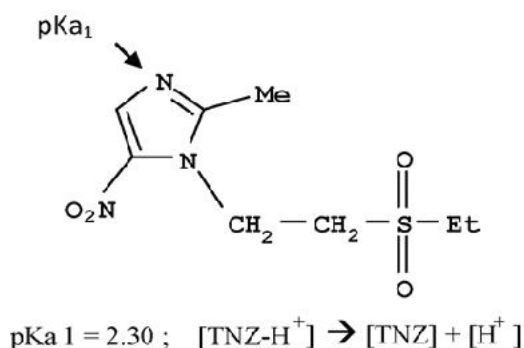
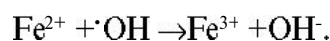


Fig. 1. Physical and chemical structure of Tinidazol.

### 3. Results and Discussion

**3.1. Effect of zero iron nanoparticles concentration.** The effect of zero iron nanoparticles concentration on TN removal was investigated. Results showed that with increasing zero iron nanoparticles dosages, removal efficiency increased. The most removal efficiency (43%) was obtained in 0,2 g/L zero iron nanoparticles concentration (Fig. 2). The cause of this increase can be attributed to increasing of sites for hydrogen peroxide decomposition and production of more reactive oxidants such as hydroxyl radicals. In other words we can say that with increasing nZVI dosage of the particles total surface area and adsorption increases on active sites [31 – 33]. It should be noted that a direct correlation between concentration of nZVI and removal efficiency is to a certain concentration and then there is not increasing, so there is an optimal dose for nZVI [34]. It attributed to the agglomeration of nZVI particles and the scavenging of hydroxyl radicals through undesirable reaction [35]:



**3.2. Effect of hydrogen peroxide concentration.** After determining the optimal concentration of zero valent iron nanoparticles ( $nZVI = 0,2 \text{ g/L}$ ,  $TN = 45 \text{ ppm}$ ,  $pH = 7$ ,  $US = 130 \text{ kHz}$ ) was examined the effect of hydrogen peroxide concentrations (0,1; 0,5 and 1 M) (Fig. 3). Result showed with increasing hydrogen peroxide concentration the removal efficiency increased (73 %). In advanced oxidation processes, goal is to produce hydroxyl radicals, which is much more hydroxyl radical production increases system efficiency. At higher concentrations of hydrogen peroxide increases production of hydroxyl radicals, this increases the removal of the antibiotic. But be careful that the concentration of hydrogen peroxide is not more than special because it is not seen to increase removal significantly. It is due to the scavenging effect of hydroxyl radicals and the inhibition of iron corrosion by hydrogen peroxide [36].

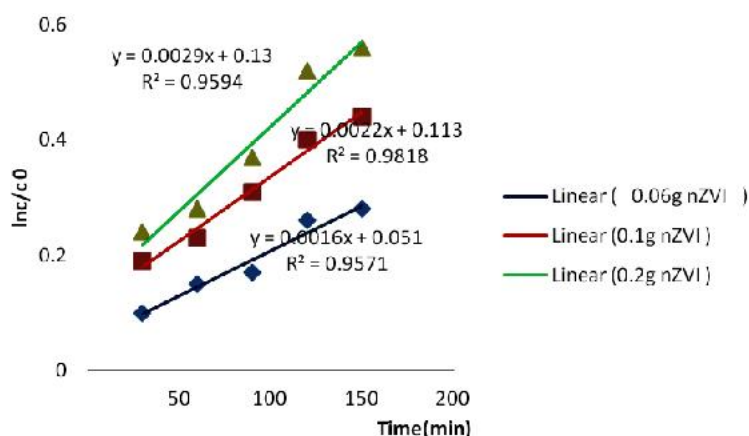


Fig. 2. Effect concentration of zero iron nanoparticle ( $1M H_2O_2$ ,  $TN = 45 \text{ ppm}$ ,  $pH = 7$ ,  $US \text{ frequency} = 130 \text{ kHz}$ ).

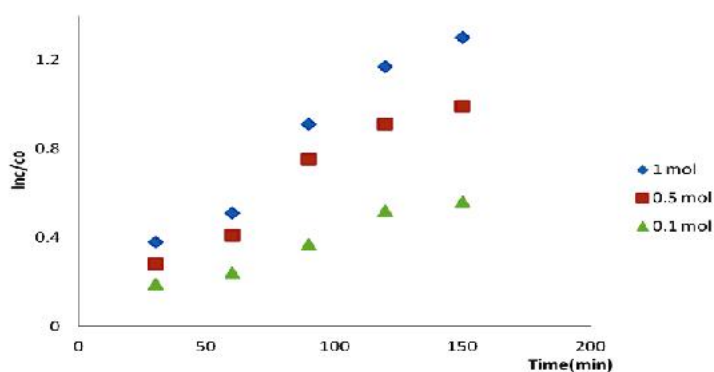


Fig. 3. Effect of concentrations of hydrogen peroxide ( $nZVI = 0,2 \text{ g/L}$ ,  $TN = 45 \text{ ppm}$ ,  $pH = 7$ ,  $US = 130 \text{ kHz}$ ) on Tinidazole removal efficiency.

Since the presence of excess hydrogen peroxide in the environment (surplus to requirements), In chemical reaction of  $H_2O_2$  radicals with the nanoparticle, hydroxyl ions produced, which is a less active than hydroxyl radicals and reduced the system efficiency [37]. In our experiment, the optimum concentration of hydrogen peroxide was obtained 1 M.

**3.3. Effect of initial pH.** pH is one of the most important factors that affect the performance of Fenton and Fenton-like processes. Studies have shown that acidic pH between 4 – 3 is the best range of pH for the Fenton reaction. Although some researchers believe the higher pH may also be significant reactivity. But at higher pH and alkaline environments  $H_2O_2$  decomposition reaction is slower and more limited [38].

This is due to its controlling role in the catalytic activity, stability,  $H_2O_2$  activity and iron species. Also, the oxidation ability of hydroxyl radicals in acidic conditions is stronger [39]. This study examined the effect of initial pH on the removal of TN, by US/ $H_2O_2$ /nZVI process in three different values of pH (3; 7 and 9) that the results are shown in Fig. 4. Decreasing pH, had a positive impact on US/ $H_2O_2$ /nZVI process in removal of TN. So that was observed the highest removal efficiency at pH 3.

**3.4. Effect of different frequencies.** In this section, the effect of different frequencies (35 and 130kHz) power of 500 watts was evaluated by ultrasonic bath without adding nano iron and hydrogen peroxide. The TN removal efficiency decreased with decreasing frequency from 130 kHz to 35 kHz (Fig. 5). Increasing the ultrasonic power will increase the energy of cavitation, lower the threshold limit of cavitation and enhance the quality of cavitation bubbles [40].

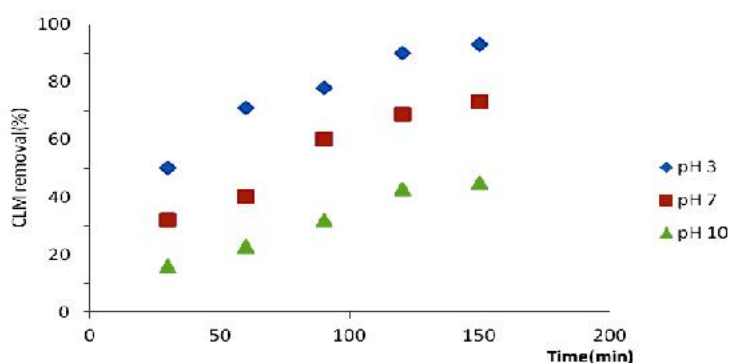


Fig. 4. Effect of pH ( $nZVI = 0,2 \text{ g/L}$ ,  $TN = 45 \text{ ppm}$ ,  $1M H_2O_2$ ,  $US = 130 \text{ kHz}$ ).

Therefore at higher frequencies, the reaction rate of hydroxyl radical (production of hydrogen peroxide and decomposition of antibiotics) is higher. The difference decomposition rate between these two frequencies is due to the low efficiency of production of hydroxyl radicals and possible less departure of these radicals from cavitation bubbles into the solution at a frequency of 35 kHz [41 – 43].

In other study Kim and et al similar results in degradation of dibenzothiophene by ultrasound have been obtained [44]. Therefore, 130 kHz selected as an optimum frequency.

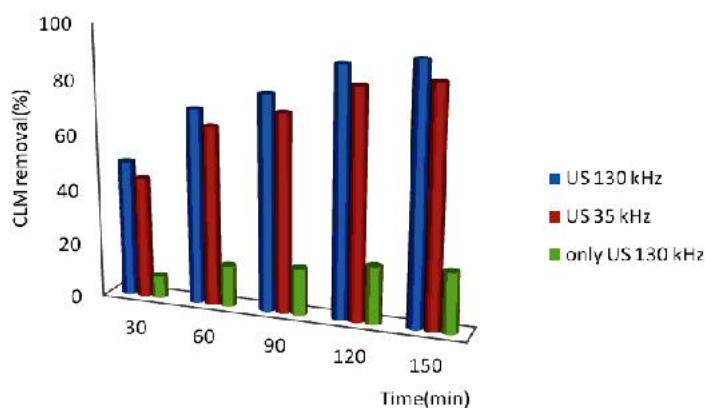


Fig. 5. Frequency effect ( $nZVI = 0,2 \text{ g/L}$ ,  $pH = 3$ ,  $TN = 45 \text{ ppm}$ ,  $1 \text{ M H}_2\text{O}_2$ ) on Tinidazol removal efficiency.

**3.5. Effect of Tinidazol initial concentration.** After determining the optimum dosage, frequency, and pH ( $nZVI = 0,2 \text{ g/L}$ ,  $TN = 45 \text{ ppm}$ ,  $1 \text{ M H}_2\text{O}_2$ ), the effect of different concentrations of selected antibiotic was studied in three concentrations (45; 80 and 100 ppm). Analysis showed increasing TN concentration in the reactor, removal efficiency decreased (Fig. 6). The hydroxyl radical production in a fixed condition will remain constant. Thus with increasing amount of the pollutants, because of hydroxyl radical reduction, the TN removal efficiency will decrease [45, 46].

**3.6. COD Removal efficiency.** Chemical oxygen demand (COD) was determined according to the Standard Methods [47]. When the sample contained  $\text{H}_2\text{O}_2$ , to reduce interference in COD determination pH was adjusted to above 10 to decompose  $\text{H}_2\text{O}_2$  to oxygen and water [48]. As is shown in the Fig. 7, COD decreased in optimum conditions of the combined systems used in this study. It can be found in similar studies [49].

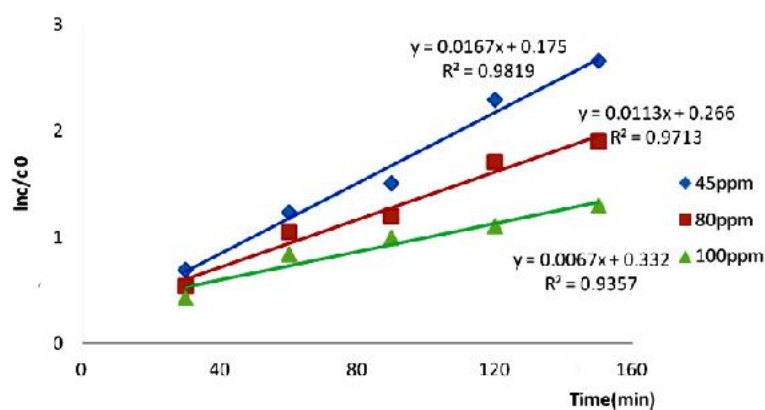


Fig. 6. Effect of Tinidazol concentrations ( $nZVI = 0,2 \text{ g/L}$ ,  $1 \text{ M H}_2\text{O}_2$ ,  $US = 130 \text{ kHz}$ ) in removal efficiency.

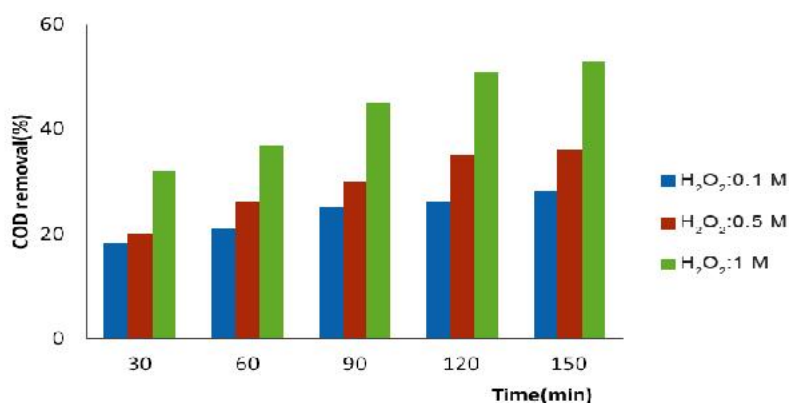


Fig. 7. Removal efficiency of COD ( $nZVI = 0,2 \text{ g/L}$ ,  $pH = 3$ ,  $TN = 45 \text{ ppm}$ ).

**3.7. Electrical energy consumed by the ultrasonic bath.** The amount of electrical energy (EE) consumed by the ultrasonic bath to selected antibiotic removal calculated from the following equation [48]

$$EE / O = \frac{P(t) / 3600) 3785}{V \log(C_0 / C)}$$

In which  $P$  is the lamp power (kW),  $t$  is the reaction time (s),  $V$  is the reactor volume (l),  $C_0$  and  $C$  are the Tinidazol initial and effluent concentration. Results are given in Table. As the results show, in optimal conditions, the electrical energy consumption is much less than other test conditions. The results also



showed that increasing of hydrogen peroxide concentration can be reducing electrical energy consumption. The significant reduction observed in pH = 3.

*Electrical energy consumption at ultrasonic bath with 500 W*

Time (min)	pH=7 H <sub>2</sub> O <sub>2</sub> =0,5 M C <sub>0</sub> =45 mg/L			pH=7 nZVI=0,2 g C <sub>0</sub> =45 mg/L			nZVI=0,2 g H <sub>2</sub> O <sub>2</sub> = 1 M C <sub>0</sub> =45 mg/L		nZVI=0,2 g H <sub>2</sub> O <sub>2</sub> = 1 M pH=3	
	nZVI(g)			H <sub>2</sub> O <sub>2</sub> (%)			pH		C <sub>0</sub> (mg/L)	
	0,06	0,1	0,2	0,1	0,5	1	3	10	80	100
30	94,6	47,3	35,3	37,3	31,4	26,6	12,6	54,0	16,5	21,0
60	126,1	74,1	63,0	75,7	42,0	34,4	14,2	5,8	16,8	21,0
90	141,9	89,9	70,9	70,9	35,4	29,1	17,4	70,9	21,8	59,4
120	137,6	89,0	68,8	68,8	38,7	30,2	15,1	8,6	20,4	31,5
150	157,6	99,5	78,8	85,9	43,9	33,7	156,6	75,7	23,0	31,5

#### 4. Conclusions

This study is aimed to investigate the antibiotic Tinidazol removal by the hybrid process of US/nZVI/H<sub>2</sub>O<sub>2</sub> under different conditions.

Results showed that the system was most efficient at lower Tinidazol concentrations as a selected antibiotic in acidic conditions and 0,2 g/L concentration of zero iron nanoparticles, 1 M H<sub>2</sub>O<sub>2</sub> and maximum contact time. The results can be shown that each factor involved in the US/nZVI/H<sub>2</sub>O<sub>2</sub> combined process have the important role in the promotion of process. Hydroxyl radicals in this study had a major role in the removal of the antibiotic Tinidazol. Presence of both zero Iron nanoparticles and hydrogen peroxide was critical to formation of ion exchange and energetic hydroxyl radicals. From this findings can be concluded that US/nZVI/H<sub>2</sub>O<sub>2</sub> combined process is efficient for removing Tinidazol and similar antibiotic.

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## References

- [1] *Walter M.V., Vennes J.W.* //Appl. Environ. Microbiol. – 1985. – **50**. – P. 930–933.
- [2] *Richardson M.L., Bowron J.M.* //J. Pharm. Pharmacol. – 1985. – **37**. – P. 1–12.
- [3] *Kummerer K., Al-Ahmad A., Mersch-Sundermann V.* // Chemosphere. –2000. – **40**. – P. 701–710.
- [4] *Bendesky A, Menendez C., Ostrosky-Wegman P.* //Rev. Mutat. Res. – 2002. – **511**. – P. 133–144.
- [5] *Liu C.-M., Chen Y.-K., Yang T.-H., Hsieh S.-Y., Hung M.-H., Lin E.T.* //J. Chromatogr., **B**.– 1997. – **696**. – P. 298.
- [6] *Emad S. Elmolla, Malay Chaudhuri* //Desalination. – 2010. – **256**. – P. 43–47.
- [7] *Ming-Chin Chang, Hung-Yee Shu, Hsin-Hung Yu.* //J. Hazard. Materials., **B**. – 2006. – **138**. – P. 574–581.
- [8] *Venkatadri R., Peters R.W.* // Hazard. Materials. – 1993. – **10**. – P. 107–149.
- [9] *Drijves D., Van Langenhove H., Beckers M.* //Water Res. – 1999. – **5**. – P. 1187–1194.
- [10] *Jiang Y., Petrier C., Waite T.D.* //Ultrason. Sonochem. – 2002. – **9**, N3. – P.163 – 168.
- [11] *Wu C., Liu X., Wei D., Fan J.* //Water Res. – 2001. – **35**, N16. – P. 3927–3933.
- [12] *Trabelsi F., Lyazidi H.A., Ratsimba B., Wilhelm A.M., Delmas H., Fabre P.L.* //Chem. Eng. Sci. – 1996. – **51**. – P. 1857–1865.
- [13] *Dickinson M., Scott T.B.* //J. Hazard. Materials. – 2010. – **178**. – P. 171–179.
- [14] *Celebi O., Uzum C., Shahwan T., Erten H.N.* //Ibid. – 2007. – **148**. – P. 761–767.
- [15] *Qiu X.H., Fang Z.Q.* //Progress in Chem. (in Chinese). – 2010. – **22**. – P. 291–297.
- [16] *Song H., Carraway E.R.* //Appl. Catal., **B**. – 2008. – **78**. – P. 53–60.
- [17] *Zhang X., Lin Y., Chen Z.* //J. Hazard. Matererials. – 2009. – **165**. – P. 923–927.
- [18] *Zhang X., Lin Y.M., Shan X.Q., Chen Z.L.* //Chem. Eng. J. – 2010. – **158**. – P. 566–570.
- [19] *Li A., Tai C., Zhao Z., Wang Y., Zhang Q, Jiang G. Hu J.* //Environ. Sci. and Technol. – 2007. – **41**. – P. 6841–6846.
- [20] *Shih Y.H., Tai Y.T.* //Chemosphere. – 2010. – **78**. – P. 1200–1206.
- [21] *Wang W., Jin Z.H., Li T.L., Gao H.Z.S.*// Ibid.– 2006. – **65**. – P. 1396–1404.

- [22] *Shin K., Cha D.K.* //Ibid. – 2008. – **72**. – P. 257–262.
- [23] *Joo S.H., Feitz A.J., Waite T.D.* // Environ. Sci. and Technol. – 2004. – **38**. – P. 2242–2247.
- [24] *Elliott D.W., Lien H.L., Zhang W.X.* //J. Environ. Eng. – 2009.– **135**. – P. 317–324.
- [25] *Fan J., Guo Y., Wang J., Fan M.* //J. Hazard. Materials. – 2009. – **166**. – P. 904–910.
- [26] *Lin Y., Weng C., Chen F.* //Purif. Technol. – 2008. – **64**. – P. 26–30.
- [27] *Nurmi J.T., Tratnyek P.G., Sarathy V., Baer D.R., Amonette J.E., Pecher K., Wang C., Linehan J.C., Matson D.W., Penn R.L., Driessen M.D.* // Environ. Sci. and Technol. – 2005. – **39**. – P. 1221–1230.
- [28] *Wei Y.T., Wu S.C., Chou C.M., Che C.H., Tsai S.M., Lien H.L.* //Water Res. – 2010. – **44**. – P. 131–140.
- [29] *Zhu A., Zhu W., Wu Z., Jing Y.* //Ibid. – 2003. – **37**. – P. 3718–3732.
- [30] *Wang C.B., Zhang W.X.* //Environ. Sci. and Technol. – 1997. – **31**. – P. 2154–2156.
- [31] *Ramirez J.H., Maldonado-Hdar F.J., Perez-Cadenas A.F., Moreno-Castilla C., Costa C.A., Madeira L.M.* //Appl. Catal., B. – 2007. – **75**. – P. 312–323.
- [32] *Daud N.K., Hameed B.H.* //J. Hazard. Materials. – 2010. – **176**. – P. 938–944.
- [33] *Liao Q., Sun J., Gao L.* //Colloids Surf. Physicochem. Eng. Aspects . – 2009. – **345**. – P. 95–101.
- [34] *Lejin Xu, Jianlong Wang* //J. Hazard. Materials. – 2011. – **186**. – P. 256–264
- [35] *Zhou T., Li Y.Z., Ji J., Wong F.S., Lu X.H.* //Purif. Technol. . – 2008. – **62**. – P. 551–558.
- [36] *Xue X.F., Hanna K., Abdelmoula M., Deng N.S.* //Appl. Catal., B. – 2009. – **89**. – P. 432–440.
- [37] *Ghauch .A, Baydoun H, Dermesropian P.* //Chem. Eng. J. – 2011. – **172**. – P. 18– 27.
- [38] *Sedlak D., Andren A.* //Environ. Sci. and Tecnol. – 1991. – **25**. – P.1419–1427
- [39] *Ranjit P.J.D., Palanivelu K., Lee C.S.* //Korean J. Chem. Eng. – 2008. – **25**, N1. – P. 112–117.
- [40] *Jiang Y., Petrier C., Waite T.D.* //Ultrason. Sonochem. – 2002. – **9**. – P. 317–323.
- [41] *Lesko T.M.* Chemical Effects of Acoustic Cavitation / Ph.D. Thesis, California Institute of Technology. – Pasadena, California, 2004.
- [42] *Mason T.J., Newman A.P., Phull S.S.* Sonochemistry in water treatment, Division of chemistry, Coventry University, Coventry CV1 5FB, 1994.
- [43] *Wu C., Liu X., Wei D., Fan J., Wang L.* //Water Res. – 2001. – **35**, N16. – P. 3927–3933.

- [44] *Kim I.K., Huang C.P., Chiu P.C. //Ibid. – 2001. – 35, N18. – P. 4370–4378.*
- [45] *Jing Fan, Yanhui Guoa, JianjiWang, Maohong Fan. //J.Hazard. Materials. – 2009. – 166. – P. 904–910.*
- [46] *Zhang Hui, Duan Lijie, Zhang Yi, Wu Feng. //J. Dyes and Pigments. – 2005. – 65. – P. 39–43.*
- [47]. *APHA, AWWA, WPCF, Standard Methods for the Examination of Water and Wastewater, 18th ed., American Public Health Association, American Water Works Association, Water Pollution Control Federation. – Washington, DC, USA, 1992.*
- [48] *Talinli I., Anderson G.K. //Water Res. – 1992. – 26. – P. 107–110.*
- [49] *Etmollaa E. S., Chaudhuria M., Eltoukhyb M.M. //J. Hazard. Materials. – 2010. – 179. – P.127–134.*

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