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DETERMINATION OF THE ULTRASONIC EFFECTIVENESS IN ADVANCED WASTEWATER TREATMENT

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ABSTRACT

Ultrasonic technology may be used for water and wastewater treatment as an advanced oxidation process. Application of this technology, leads to the decomposition of many organic compounds during cavitation process. In this study, the efficiency of ultrasonic in advanced treatment of municipal wastewater has been investigated by use of an ultrasonic bath. COD and BOD_5 tests were used as the indicators of organic matter concentrations and three detention times for treatment were appointed at 10, 30 and 60 minutes. Two frequencies of 35 and 130 kHz for sonication were used. Results indicated that sonication can reduce 25% to 30% of COD in less than 60 minutes. Also, it was indicated that suspended COD was mainly converted to soluble COD during sonication. The rate of hydrogen peroxide production and thus the efficiency of treatment were higher at 130 kHz, but this efficiency was not much increased by prolonging sonication time. In other words, maximum efficiency was achieved at the initial time of sonication. Furthermore, no considerable change in nutrients concentration was detected and pH variations of samples were negligible (<0.3). In contrast, significant temperature change occured which was about (18-20)^oC increase in 60 minutes. However, this temperature change had no considerable effect on treatment efficiency.

Key words: Ultrasonic, organic matter, capitation, secondary effluent treatment

INTRODUCTION

Biological treatment is the most commonly applied method for treatment of wastewaters. However, biological treatment can be inhibited by bacteriotoxic or persistent pollutants present in wastewater (Lifka *et al*., 2003). As a result, this technology may be incapable of reducing the levels of contaminants below which they are not considered as a potential threat to public health. Therefore, new technologies that offer significant improved levels of treatment or constituent reduction need to be tested and evaluated (Metcalf and Eddy, 2003). Advanced oxidation processes (AOPs) are used to oxidize organic constituents found in wastewater that are difficult to degrade biologically. AOPs typically involve the generation and use of hydroxyl free radical as a strong oxidant to destroy compounds (Metcalf and Eddy, 2003). Ultrasonic technology (as an AOP) has been used for water and wastewater treatment (Naffrechoux *et al*., 2000). Ultrasound (US) was defined as the sound of a frequency that is beyond human hearing above 16 kHz. The ultrasound energy which has been used in sonochemistry is in the distinct ranges of 16-1000 kHz i.e. power ultrasound (Zheng, 2004). Ultrasonic irradiation of aqueous solutions can result in the growth and collapse of gas bubbles (cavitation) so producing high transient temperatures and pressures, which leads to the formation of free radicals (^oOH , ^oOOH) via thermal dissociation of water and oxygen. These radicals penetrate into water and oxidize dissolved organic compounds. Hydrogen peroxide (H_2O_2) is formed as a consequence of ^oOH and ^oOOH radicals recombination in the outside of the cavitation bubble (Langenhore, 1998; Jang *et al*., 2002; Visscher *et al.*, 2004). Three regions, gas phase, inerfecial region surrounding the cavitation bubble, and the bulk solution are present during cavitation (Laughrey *et al*., 2001). High-volatile compounds diffuse more easily into the cavitation bubbles and hence are degraded mainly through pyrolytic reactions. The aquasonolytic degradation

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of low volatile pollutants by ^{o}OH radicals takes place in the surrounding water (Lifka *et al*., 2003). The concentration of HO^{o} at a bubble interface can be as high as 4×10^{-3} M, witch is 10^{8}-10^{9} times higher than that in the other advanced oxidation processes (Crittenden *et al*., 2004). Furthermore, there are no additives introduced into the ultrasonic system and no by products generated by ultrasonic technology. Therefore, there are no anticipated environmental concerns associated with this technology (Buchholz *et al*., 1998). In contrast to many other processes which are negatively affected when suspended solids of effluent increase, US efficiency may even improve by increase of turbidity or suspended solids (Manson and Lorimer, 2002). Although the technology has been shown to be feasible on a small scale, the commercialization of sonolysis is still a challenge, due to the high energy requirement of the process (Crittenden *et al*., 2004).

Many studies have been performed on sonolytic degradation of different compounds and related factors which affect the rate of decomposition. Francony and Petrier showed that the rates of reactions involving hydroxyl radicals (H_2O_2 formation and phenol degradation) have a maximum value at 200 kHz compared with lower and higher frequencies (20, 500 and 800 kHz) (Francony and Petrier, 1997). Goel and co-workers recognized that decomposition rates of non-volatiles were lower than volatiles (Goel *et al*., 2004). Study of the effect of temperature revealed that the destruction rate of 1,2-DCA (dichloroethane) is almost independent of temperature (in the range of 15-30^{o}C) (Kruger *et al*., 1999). Treatment of raw sewage by sonuv (combined sonication and UV irradiation) in 90 min was not effective to mineralize the organic matter. A significant reduction of COD was observed after 4h of sonuv treatment (Naffrechoux *et al*., 2000). Ultrasonic can decompose other organic substrates such as chlorinated hydrocarbons, pesticides, phenol, explosives such as TNT, and esters, and transform them into short-chain organic acids, CO_2 and inorganic ions as the final products. The time for complete degradation ranges from minutes to hours (Haffmann *et al*., 1996). The main purpose of this study was to determine the efficiency of sonication process in treatment of secondary effluent municipal wastewater.

MATERIALS AND METHODS

Sampling

Secondary effluent samples were collected from two sewage treatment plants, Ghods and Shoosh sites, in Tehran. Activated sludge biological treatment is used in both treatment plants. Sampling was performed between 8-10 am in the spring of 2005. In order to determine the effect of ultrasonic on wastewater constituents, individual samples were taken for organics and nutrient treatment. Samples had been taken after secondary clarification (before chlorination) and sent for analysis in less than one hour.

Treatment

The wastewater samples were treated in an ultrasonic bath with the characteristics shown in Table 1. 500mL beakers were used for this purpose and each sample was treated in three sonication times of 10, 30 and 60 minutes. Thereupon, the treatability tests had been performed in batch system.

Table 1: Characteristics of ultrasound apparatus

Elma TI-H-5, Germany	
Dimensions	250 cm ×130 cm ×150 cm
Frequencies	35 and 130 kHz
Transducer	Two piezoelectric transducers
Input power	500 W
The energy dissipated in the reactor	25 W/cm^2
Capacity	3.7 L

Analyses

Samples were analyzed before treatment for determination of: total COD (TCOD), suspended COD, soluble COD (SCOD), total BOD_5 ($TBOD_5$), suspended BOD_5, soluble BOD_5 ($SBOD_5$), pH, temperature, total suspended solids(TSS), total phosphorous (TP) and total Kjeldal nitrogen (TKN). After sonication, samples were analyzed for determining COD (TCOD, suspended COD and SCOD), BOD_5 ($TBOD_5$, suspended BOD_5 and $SBOD_5$), pH and temperature. All the analyses were performed according to the procedures described in the Standard Methods (APHA, 2005). Temperature

and pH were measured by a thermometer and a pH meter, respectively. Producible H_2O_2 was analyzed by a Hatch Model Kit.

Interferences and their removal

In this study, some increase in COD was detected for all samples after sonication. Reduction of COD was possible in the initial sonication times (during 10 and 30 min), however, at longer times (60 min), it raised often to 1.3 times of the initial COD. This effect which was not recorded in the previous studies may be attributed to the radicals and H_2O_2 formation (H_2O_2 was detected after sonication). Two methods can be recommended for removal of this interference. By one way, COD formation by radicals and H_2O_2 can be measured and then the result is substracted from total COD. But, by the second way it is necessary to remove interferences (radicals and H_2O_2). Regarding the volatile characteristic of radicals and H_2O_2, removal of these chemicals is possible after 20-30 min maintaining in ambient air, and this way was considered as a simple method to omit this interference. Thus, a same period of 30 min was used and COD of all samples had been determined after this period. OH radicals may also interfere with BOD_5 determination by increasing dissolved oxygen of samples. A same method was again used for removal of this interference.

RESULTS

Effect of ultrasound on organic matter

Results showed that US reduces BOD_5 of secondary effluent (Fig. 1). But sanitation time had no considerable effect on the efficiency of this treatment ($p>0.05$). Suspended BOD_5 was removed completely (near 100%). However, soluble BOD_5 was increased in some cases, may be because of suspended BOD conversion to soluble forms. As COD concentrations were much more than BOD_5 concentration, the effect of ultrasound on organic matter oxidation has been studied by use of COD results. In this study, the efficiency of total COD removal was determined to be 17-28% (Tables 3 and 4). The effects of US on soluble and suspended COD have also been determined. As shown, removal of suspended COD is better accomplished than SCOD. Two reasons may be mentioned: suspended COD may be really better affected by US and/or this form may be converted to SCOD by US treatment. To find the reason, an extra experiment has been performed after preparation of a new special sample by first removing the SCOD and then adding TSS which had the inorganic nature in concentration equal to the original samples (namely about 10 mg/L). Results which can be seen in Fig.1 indicated that there is no considerable difference (such as the high difference between total and soluble COD, shown in the previous Figure) between these two types of COD, and treatment efficiencies are relatively similar. This means that suspended COD has converted to SCOD during sonication. Similar to suspended COD, the removal of suspended BOD is better accomplished than SBOD.

Effect of sonication time on organic matter

Tables 3 and 4 show the effect of sonication time on the efficiency of organics removal. Much of the COD decomposition was accomplished in the initial sonication time and the efficiency of this decomposition was not much increased by increasing time. For example, this efficiency was 20% in 10 min (Table 3: COD=49.2 mg/L and f=130 kHz) and was only increased 3.5% and 5% after 30 and 60 minutes, respectively. But, the effect of time was significant ($p<0.01$).

Table 2: H_2O_2 formation (in mg/L) in distilled water during US process

Sonication time (min)	Frequency (kHz)	
	35	130
30	1	2.5
60	2	5
120	4	10

Effect of ultrasound frequency

As shown in Fig.2, better decomposition of secondary effluent organics has been performed at 130 kHz compared with the lower frequency

Table 3: Efficiency of Percentage COD Removal by Ultrasound at 35 kHz Frequency

Time (min)	sample 1			sample 2			sample 3		
	TCOD	Suspended COD	SCOD	TCOD	Suspended COD	SCOD	TCOD	Suspended COD	SCOD
	44.9	8	36.9	49.2	8.5	40.7	58.2	9.4	48.8
10	16.7	75	4.1	16.6	74.1	4.6	15.9	75.5	4.4
30	21.1	87.5	6.7	19.3	89.4	4.6	19.6	87.2	6.6
60	24.8	93.8	9.8	24.1	94.1	9.5	23.6	93.6	10.1

COD (mg/L)

Table 4: Efficiency of percentage COD removal by ultrasound at 130 kHz frequency

Time (min)	sample 1			sample 2			sample 3		
	TCOD	Suspended COD	SCOD	TCOD	Suspended COD	SCOD	TCOD	Suspended COD	SCOD
	44.9	8	36.9	49.2	8.5	40.7	58.2	9.4	48.8
10	20.4	63.8	11	20.4	64.7	11.2	18.5	67.0	9.2
30	23.9	80	11.7	24.2	82.4	12.1	23.2	80.8	12.1
60	28.2	87.5	15.3	27.3	89.4	14.3	26.7	90.4	14.4

COD (mg/L)

($p<0.05$). The efficiency of treatment in 60 minutes sonication at the frequency of 35 kHz was about 24%, but it raised to about 28% at 130 kHz frequency. H_2O_2 formation at 130 kHz frequency was about 2.5 times higher than that at the frequency of 35 kHz (Table 2). It should be noted that ^{o}OH radicals formation and thus H_2O_2 formation in distilled water is less than that of the effluent, but due to absence of organics in distilled water much of these radicals remain and so H_2O_2 measurement in distilled water may better demonstrate the radical formation. The effect of US frequency on suspended COD can be seen in Fig.3. In contrast to TCOD, the removal efficiency of suspended COD was better at the frequency of 35 kHz, may be because of formation of finer bubbles and therefore more intensive collapse of these bubbles at lower frequencies.

Effect of ultrasound on nutrients

Nitrogen and phosphorous are among the most important pollutants in secondary effluent which should be removed by wastewater treatment. In this research, the effect of ultrasonic on these pollutants has been determined by TKN and TP analyses. The concentrations of TKN in the initial effluent samples were as low as 3.6-6.5 mg/L. It was revealed that 45-60 min sonication had no detectable effect on these low concentrations of TKN. Also, it should be noted that these two frequencies had no significant effect on total phosphorous concentration (initial concentrations were always < 4.2-5 mg/L). It is noteworthy that the concentrations of both nutrients in the initial effluents were low .

Effect of ultrasound on pH

The ultrasound had no considerable effect on pH of samples, and the little change occurred was insignificant ($p>0.05$).

Effect of ultrasound on temperature

In an ultrasonic reactor, the temperature increases with sonication if it is not controlled. In this research, temperature increase in 60 min was about 18-20 ^{o}C and it is due to cavitation. The increase in

temperature in 35 kHz frequency was about 2-3 °C more than in 130 kHz frequency, but this difference was not significant ($p>0.05$). Besides, by preserving a constant temperature during sonication (through use of an ice bath) it was detected that temperature increase of samples during ultrasound had no considerable effect on COD removal by itself. In general, increase of temperature can increase or sometimes decrease the degradation rate.

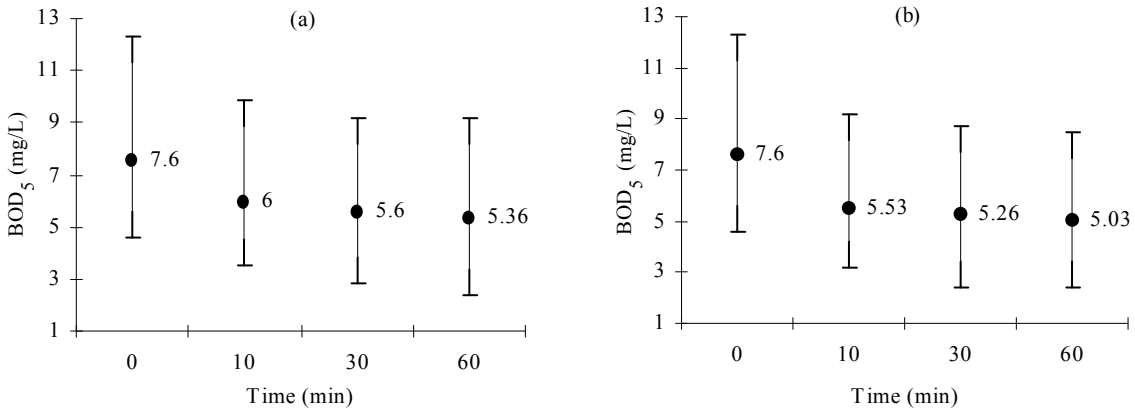

Fig. 1: BOD_5 variations of different effluent samples at two frequencies: (a: 35 kHz and b:130 kHz)

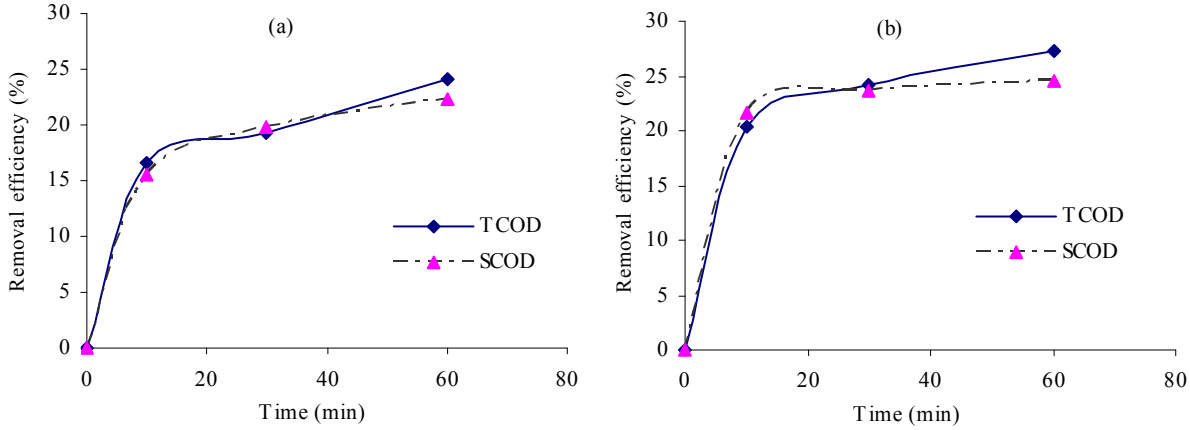

Fig. 2: TCOD and SCOD removal efficiency by ultrasound at two frequencies: (a:35 kHz and b:130 kHz)

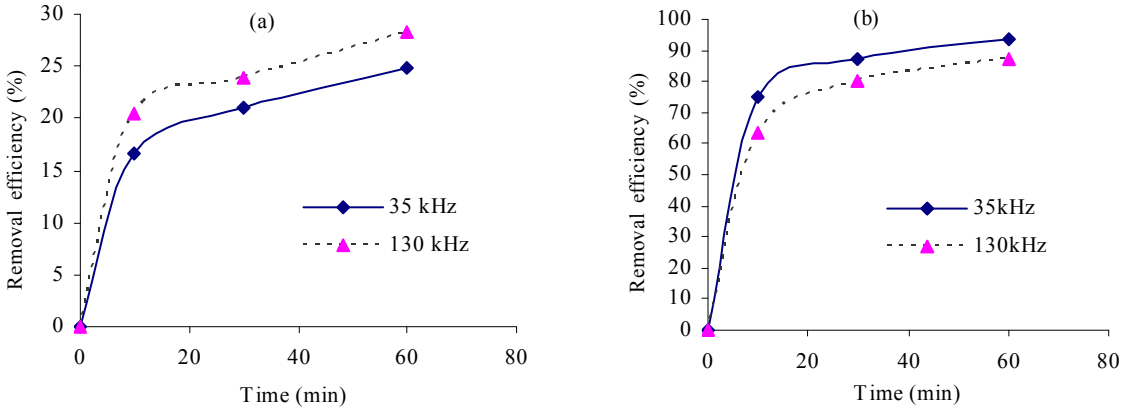

Fig. 3: TCOD removal efficiency by ultrasound at two frequencies
(a: TCOD= 44.9 mg/L and b: suspended COD=8 mg/L)

DISCUSSION

Treatment of secondary effluent by ultrasonic can reduce about 30% of the remained organics in these effluents. This treatment efficiency is probably the result of organics characteristics. Most of the organics in secondary effluent are low-volatile. Besides, it is predictable that most of the remained matter in effluent have hydrophilic characteristics. Therefore, it is probable that the main mechanism of organics removal is treatment by ^{o}OH radicals in bulk solution. Pollutants which decompose in this region are less degradable by ultrasound than pollutants which decompose in gas phase. Besides, secondary effluent contains different organic compounds with specific characteristics. Thus, each have different behavior in treatment by ultrasonic. Moreover, these different compounds may interfere with the decomposition process of eachother and deteriorate or enhance the ultrasonic treatment. Inorganic matter can affect the decomposition of organics too. Sometimes, treatment by US covnerts complex organics to much smaller compounds and it is obvious that much sonication times are needed for complete demineralization. Often, relative conversion of organics suffices for meeting much of the requirements. As these simple compounds have organic nature, the effect of treatment can not be detected by routine tests of COD and BOD_5 and in other words, by these tests it is difficult to show the effect of ultrasound on organics decomposition. For example, in sono-oxidation of humic acids (Chemat *et al.*, 2001), complete degradation of these compounds occured in 60 minutes whereas, reduction of TOC was only 40%. Suspended COD has converted to SCOD during sonication. Previous works on SCOD of wastewater sludge confirm our result about conversion of suspended COD to SCOD.

For example, one of the previous studies showed considerable increase of SCOD of sludge after sonication such that the SCOD was reported to increase from 620 mg/L to 2100 mg/L after 2.5 minutes and to 4200 mg/L after 10 minutes (Gronroos and Hyllonen, 2005). The mechanical shear forces caused by ultrasonic may be the dominant factor for the disintegration enhancement (Mao *et al.*, 2004). In a few studies (Pandit *et al.*, 2001), the low improvement of efficiency versus time has been attributed to the degasification effect of ultrasound. Degasification of solution leads to increase in cavitation threshold and thereby to reduction in efficiency. Besides, most of the decomposable organics by ultrasound are removed in initial sonication time and the remained fraction of organics may be less removable. Suspended solids are also effective in the process of cavitation and their reduction may lead to increase cavitations threshold. Ultrasonic can reduce TSS, but in this study the TSS of effluent samples were low (less than 8 mg/L) and this concentration reached to less than 2 mg/L after 60 minutes.

It is expected and also reported that the rate of degradation of organic compounds increases with the increase in frequency of sonication, although, the effect of frequency is somewhat system specific (Goel *et al*., 2004). The optimal frequency for aquasonolysis of high-volatile pollutants ranges between 300 and 800 kHz. The generation of ^{o}OH radicals and the degradation of low-volatile pollutants by oxidation is optimal at frequencies of approximately 200 kHz (Lifka *et al*., 2003). As decomposition by ^{o}OH radicals is expected to be the main mechanism for sonolysis of the organics present in the secondary effluent, it can be accepted that meeting the better efficiency at 130 kHz frequency is due to better formation of ^{o}OH radicals in bulk solution. Results of H_2O_2 measuring in distilled water in these two frequencies (Table.3) can be considered as the conformation for this claim.

Sonochemical treatment of various organics generated low molecular weight carboxylic acids. Simultaneously, water decomposes to ^{o}H and ^{o}OH radicals. ^{o}OH radicals react with organics, and remained hydrogen may produce acidic compounds hence pH drop may result. But, these effects are not considerable in real samples, because water has bufferic characteristics. However, more work is needed to confirm these results. In a previous study (Kruger *et al*., 1999), sonication of 1,2 DCA solution in deionized water has resulted in pH drop, but, in groundwater the pH has raised from 6.2 to 7. Presence of carbonate system in natural waters was reported to be the reason of this phenomenon.

Finally, it is concluded that treatment of secondary effluent organics by ultrasonic seems not very efficient but it should be noted that the efficiency of many other advanced treatment processes is not much higher. On the other hand, not much higher efficiency is always needed at this stage. Finally, if we consider the disinfection capability of this method, we can expect much better position for this technology. According to a research accomplished in our country, the efficiency of this method was determined to be as much as more than two logs for total coliforms disinfection (Dehghani, 2005) and this is an outstanding advantage for accepting US in the process of secondary effluent treatment.

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