PRETREATMENT OF BIOCIDE CONTAINING WASTEWATERS BY ADVANCED OXIDATION PROCESSES

by

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ABSTRACT

Biocide is an antimicrobial agent used in various industrial applications to control the bacterial growth that leads to environmental, ecological and toxicological problems in water. The discharge effluents from manufacturing, production and industrial applications contain complex and diverse groups of chemicals. These effluents are hard to treat by conventional treatment methods because of the inhibitive effect of biocides on bacterial growth in biological treatment process.

Advanced Oxidation Processes (AOPs) have the ability to generate short-lived, powerful hydroxyl radicals (•OH) that readily attack and destroy contaminants in wastewaters.

The purpose of the study was to investigate the most suitable process (or processes) and its optimal operating conditions for the pre- or post-treatment of hexahydrotriazine (HHT) containing wastewaters (in an ultrasonic bath operated individually, sequentially (before an ultrasonic probe) or simultaneously with an advanced oxidation process (AOP)).

It was found that a low power ultrasonic bath alone was an ineffective method for sufficient degradation of HHT to render biodegradability or organic matter destruction, but its sequential operation with an ultrasonic probe, or simultaneous operation with photo-Fenton process were very effective, particularly for enhancing the biodegradability of the solution. The synergy was the result of increased mass transfer rates and OH radical formation under ultrasonic irradiation.

ÖZET

Biyosit doğal ortamda çevresel, ekolojik ve toksikolojik pek çok probleme yol açan endüstriyel uygulamalarda bakteriyel büyümeyi engellemek için kullanılan bir anti mikrobiyal ajandır. Endüstriyel kullanımlardan olduğu kadar üretimden sürecinden de deşarj edilen biyosit içerikli atıksular çeşitli kimyasallar içermektedir. Biyosit içeren atıksuların geleneksel arıtma yöntemleri ile arıtımı biyositlerin biyolojik proseslerde bakteri inhibisyonu neden olması ile oldukça zordur.

İleri Oksidasyon Prosesleri (İOP), atıksulardaki kirleticileri kısa ömürlü ve güçlü hidroksil radikalleri (•OH) oluşturmakta ve sudaki kirleticileri parçalamaktadır.

Bu çalışma, hexahydrotriazine (HHT) içeren atıksuların arıtımında ultrases ve ultrases banyosunun prob ile sıralı ve çeşitli ileri oksidasyon prosesleri ile eş zamanlı uygulandığı kombinasyonları test ederek en uygun proses ve işletme şartlarının belirlenmesini içermektedir.

HHT’nin biyolojik parçalanabilirliğinin artması ve organik madde gideriminde düşük güçteki ultrases banyosunun etkili olmadığı ancak banyonun ultrases probu ile sıralı veya UV/Fenton ile eşzamanlı yürütülen uygulamalarında oldukça etkili olduğu görülmüştür. Bu uygulamalar özellikle biyolojik parçalanabilirliğin arttırılmasında başarılı olmuştur. Sinerjik etki artan kütle transferi ve OH radikallerine bağlıdır.

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1. INTRODUCTION

A biocide is an antimicrobial agent used in various industrial applications to control bacterial growth that lowers production yields and product quality, reduces aesthetic and economic value of products, destroys plants and crops, and causes damage to materials, products and manufacturing processes (Horst K, 2005).

The use of less frequent doses with higher concentrations of biocide in industrial applications is much more effective than low level frequent doses (IWRC, 2003). However, biocide application results in high residual in wastewater. Biocides are also released to wastewater during production and manufacturing operations, ending up in sewage treatment facilities.

Biocides are inherently toxic, frequently difficult to degrade, persistent in the natural environment, and capable of accumulating in a variety of matrices causing contamination. The presence of biocides in water and wastewater leads to environmental, ecological and toxicological problems. The primary difficulty in applying conventional treatment methods to biocide containing wastewaters is the inhibitive effect of biocides on bacterial growth in biological treatment process. Therefore, research on alternative and feasible treatment methods that can be integrated with conventional treatment facilities is highly important.

In view of the wide range of potentially different fate, behavior and toxicity of biocides, this dissertation is limited to the effects of hexahydrotriazine which is a common biocide-widely used in metal cutting industry for the prevention of bacterial activity.

In this regard, the research was aimed to investigate the treatment effectiveness of different advanced oxidation processes (AOPs) on the ultimate or pretreatment of hexahydrotriazine (HHT) to allow its direct discharge into natural water and/or to improve its biodegradability for treatment in biological systems. The test processes consisted of Fenton, photo-Fenton, ultrasound and various combinations thereof. In addition, the effectiveness of hydrogen peroxide and heating were investigated as potential means of HHT destruction. The performance of the processes was tested by monitoring the reduction in total organic carbon and chemical oxygen demand as well as the improvement in the biodegradability of the biocide solution.

2. THEORETICAL BACKGROUND

2.1. The Use of Biocides

The presence of bacterial pathogens in the field and workplace lowers production yields and product quality, causes damage to materials, products and manufacturing processes (Horst K, 2005). Biocides are active substances and preparations containing one or more active substances, which destroy, prevent the action of, or otherwise exert a controlling effect on any harmful organism by chemical or biological means (Directive 98/8/EC, 1998). The use of biocides reduces the costs of maintenance and repairs, thus, the use of biocides (inhibitors of bacterial activity) is very common in the protection of goods particularly leather, textiles (and their auxiliaries), cosmetics, cleaners, lubricants, metal working fluids, coolants, detergents, polymers, plastics, rubber, paper, cardboard, building materials, cement, tiles, masonry, concrete, pigment preparations, paint formulations, adhesives and sealants against microbial attack (Mike, 2003; Jurgen, 2004).

2.1.1. The Biocide Industry

The biocide industry is divided into three groups:

i. manufacturers of the active ingredients.
ii. suppliers that sell ready to use biocides made by mixing the active ingredients with other additives or carrier fluids. Most of these second group companies not only sell biocides but also provide full water treatment services to users. The range of services provided includes chemical analysis of the water to be treated, assistance in getting regulatory approval to use the product, dosing recommendations, and actual operation of the water treatment system (Veil et al., 1997). During the study on biocide treatment patterns, fouled fluids are treated with a commercial biocide at various concentrations and frequencies while microorganism populations are monitored. For all biocide-application

rates tested, the efficiency of antimicrobial control is found to vary widely with treatment pattern (IWRC, 2003).

iii. independent consultants who provide a full range of water treatment services to users but do not sell or provide any biocide products (Veil et al., 1997).

2.1.2. Classification of Biocides

Most biocides are synthetic, but a class of natural biocides derived from bacteria and plant also exists. Synthetic biocides may either be in form of a pesticide (e.g. fungicides, herbicides, insecticides, algicides, molluscicides, miticides and rodenticides) and an antimicrobial agent (e.g. germicides, antibiotics, antibacterials, antivirals, antifungals, antiprotozoals and antiparasites). Biocides are classified either as oxidizing biocides or non-oxidizing biocides, the difference being the following (IWRC, 2003):

2.1.2.1. Oxidizing Biocides. Exist mostly as chlorine or bromine compound, and form hypochlorous acid (HOCl) or hypobromous acid (HOBr) in water. Sodium hypochlorite and chloroisocyanurate are common forms of chlorine biocide. HOBr is an effective microbiocide over a wider pH range than is HOCl. Other oxidizing biocides that do not rely on chlorine or bromine as an active agent include ozone and hydrogen peroxide (Veil et al., 1997).

2.1.2.2. Non-oxidizing Biocides. Numerous non-oxidizing chemicals are used as either primary biocides or as supplements to oxidizing biocide applications. One product that is widely used for control of zebra mussels and other organisms is quaternary ammonium salts (quats). Some other non-oxidizing biocides used include glutaraldehyde, isothiazoline, triazines, organo-tin compounds, dodecylguanidine hydrochloride (DGH), carbamates, methylene bis-thiocyanate (MBT), and dibromonitrilopropionamide (DBNPA) (Veil et al., 1997).

2.1.3. Biocide Application in Metal Working Fluids

Metal working fluids (MWFs) are known as coolants, cutting oils, lubricants, and machining fluids. These lubricate and cool metalworking operations by reducing friction and carrying away heat. MWFs are also used to wash away waste metal chips. Microbial contamination is very common in metal working fluids due to the presence of nutrients and food material such as spoiled oil that support bacterial growth (IWRC, 2003; Carmody et al., 1990). As a result, bacterial control is very important to sustain long life of metal working fluids. Biocides used in metalworking fluids can be classified either as formaldehyde-releasing agents (containing condensates of formaldehyde) or others (Whittaker, 1997). The health hazards of metal working fluids depend on the presence of additives and contaminants, as well as the type of fluid (Whittaker, 1997).

Typically used concentration of biocide is 0.15 % in the working solution (Haskoning, 1995). The most commonly used materials in the synthesis of biocides for metalworking fluids are (Baumann, 1996):

- aldehydes (triazine, oxazolidine)
- fatty acid ester
- heterocyclic substances with N,O,S (benzotrialzole, thiazole)
- boron compounds

2.1.4. Hexahydrotriazine Biocide

Hexahydrotriazine (HHT) is an antimicrobial, and formaldehyde-release biocide used as an industrial preservative to control slime forming bacteria and fungi in adhesives, fuels, oil storage tanks, metalworking fluids, paints, slurries, rubber products, and industrial processing chemicals (EPA, 1997). HHT is commonly used in MWFs as preservatives at mass ratios of 0.1–0.15% (Fekete et al., 2006). The chemistry of hexahydrotriazines has been in the literature since 1800's when it was recognized that ammonia formed trimeric compounds with aldehydes. Most synthetic routes to HHT in the literature employ aqueous solvent systems. HHT belongs to reactive group(s) of amines, alcohols and polyols. Derivatives of HHT are saturated nitrogen/oxygen heterocycles, which inhibit the growth of gram-negative bacteria (that are the primary colonizers of commercial fluids) via the production of formaldehyde (Fekete et al., 2006; Cameochemicals, 1992). N,N,N-substituted hexahydro-1,3,5-triazines are cyclic ligands containing three nitrogen atoms as coordination sites. N,N,N-Functionalized hexahydro-1,3,5-triazines are easily accessible by reaction of primary amines and formaldehyde (Brunner et al., 1998).

HHT has a similar range of activity to that of formaldehyde. Aqueous solutions of hexahydrotriazine hydrolyze to form free formaldehyde (CH_2O) and monoethanolamine ($(CH_2CH_2OH)NH_2$). The pH and temperature of the solution determines the amount of free formaldehyde release. As a general rule, the lower the temperature, the lower the amount of formaldehyde released (BASF, 2004).

The chemical structure of HHT is represented in Figure 2.1, and the properties are as the following:

Molecular Weight : 219.28134 (g mol^{-1})
Molecular Formula : $C_9H_{21}N_3O_3$
H-Bond Donor : 3
H-Bond Acceptor : 6
Rotatable Bond Count : 6

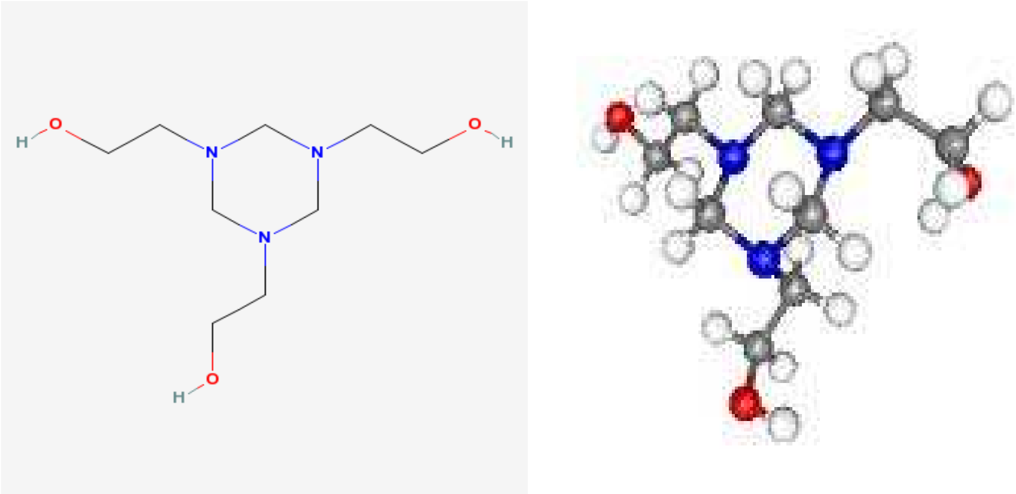

Figure 2.1. The chemical structure of HHT (BASF, 2004).

There are three derivatives of HHT as shown in Table 2.1.

Table 2.1. Hexahydrotriazine derivates placed in EPA list (EPA, 2002).

CAS Number	Chemical Name	Structural Class
91–78–1	s-Triazine, hexahydro-1,3,5-triphenyl	Hexahydrotriazine
6281–14–7	1,3,5-Tricyclohexylhexahydro-s-triazine	Hexahydrotriazine
68083–44–3	1,3,5-Triazine, hexahydro-1,3,5-tris(2-methylphenyl)- trihydrochloride	Hexahydrotriazine

Formaldehyde, the hydrolysis product of HHT, is highly soluble in water, alcohol, and other polar solvents. It has solubility in water up to 550 g L^{-1} at 25 ^{o}C. Concentrations as high as 95 % in water are obtainable if suitable temperatures are maintained. In dilute aqueous solutions, formaldehyde exists almost exclusively in the hydrated gem-diol form, (equation 2.1) while at higher concentrations formaldehyde forms other species, such as methylene glycol, glycol, polyoxymethylene and hemiformals (BASF, 2004; NICNAS, 2006).

$$CH_2O + H_2O \leftrightarrow CH_2(OH)_2 \qquad (2.1)$$

Hydrolysis products of two commercial HHT-based biocides are presented in Figure 2.2.

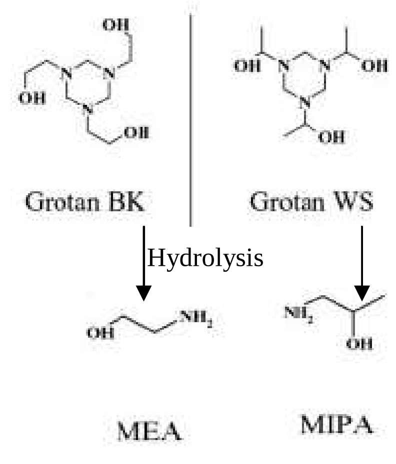

Figure 2.2. Hydrolysis Products of HHT based biocides (Grotan BK and WS).

2.1.4.1. Destruction of Formaldehyde. Destruction of formaldehyde is described as follows:

Oxidation and Mineralization:

Formaldehyde undergoes mineralization in the presence of hydrogen peroxide via the following reaction sequence (Moussavi et al., 2002):

$$HCHO + H_2O_2 \rightarrow HCOOH + H_2O \tag{2.2}$$

$$HCOOH + H_2O_2 \rightarrow CO_2 + 2\ H_2O \tag{2.3}$$

In addition to oxidation by H_2O_2, the intermediate product, formic acid, may also undergo oxidative destruction by advanced oxidation processes via the hydroxyl radical with a reaction rate constant of $1 \times 10^9\ M^{-1}\ s^{-1}$ (Buxton, 1998; Rodriguez, 2003).

Photolysis:

Aqueous photolysis of formaldehyde is not a common destruction pathway. Formaldehyde exists entirely as a hydrate in natural water which does not absorb sunlight in water solution. On the other hand, the atmospheric photolysis half life of the formaldehyde varies from 1.25 to 6 hours. The maximum light absorption is approximately 300 nm and significant absorption extends to approximately 360 nm in the gas phase (Howard et al., 1991).

2.1.4.2. Health Effects and Environmental Impacts of HHT and Formaldehyde. HHT is acutely toxic via oral and inhalation routes, and both HHT and formaldehyde are corrosive resulting in acute dermal toxicity and primary eye and skin damage (EPA, 1997). HHT demonstrates toxicity to both cold and warm freshwater fish and to birds, and is slightly toxic to freshwater invertebrates on acute basis. Thus, HHT is classified in Toxicity Category I and II by US EPA (EPA, 1997). In addition to these ecological and human health effects, 1,3,5-Hexahydrotriazines are important building blocks in high-explosive compounds (Ghandi et al., 2006).

Formaldehyde releasers pose risks on human health since they have sensation effect of allergic contact dermatitis, and they have been recognized as skin and lung irritant (Fekete et al., 2006). Formaldehyde shows mutagenic activity in bacterial and mammalian cell culture test systems but the test is negative in whole animal systems (Imbus, 2003). Formaldehyde is toxic to a range of micro-organisms and kills viruses, bacteria, fungi, and parasites when used at relatively high concentrations. Unicellular micro-organisms appear to be most sensitive to formaldehyde at acute lethal concentrations ranging from 0.3 mg L^{-1} to 22 mg L^{-1} (NICNAS, 2006).

Limited degradation data for formaldehyde are available. Hydrolysis is not a degradation pathway because formaldehyde does not contain any hydrolysable groups. At low concentrations, formaldehyde is readily biodegradable, with 90% degradation reported in closed bottle tests (at 2-5 mg L^{-1}) after 28 days and sewage micro-organisms are inhibited at 30 mgL^{-1} (NICNAS, 2006). Because of its high toxicity, the permissible exposure limit for formaldehyde is 0.75 mg L^{-1} according to regulatory standards, and 41.1µg L^{-1} in drinking water (Moussavi et al., 2002).

2.2. Treatment of Formaldehyde Containing Wastewater

The existing research on destructive processes for formaldehyde containing wastewater involves conversion of formaldehydes to non-toxic compounds (raising temperature to around 80 ^{o}C by the condensation of formaldehyde to formose sugars promoted) in the presence of lime (Moussavi, et al., 2002). In addition, chemical coagulation, electrochemical oxidation (Han et al., 2007), alkalinization followed by heat treatment (Weisenfeld, 1998), dielectric discharge systems (Chang and Lee, 1995), catalytic oxidation using precious metals (Smith, 1997) and aerobic or anaerobic biochemical oxidation (Qu and Bhattacharya, 1997; Hidalgo et al., 2002; Laopaiboon and Smith, 2003; Eirora et al., 2006) are potential methods of formaldehyde destruction in water.

More recently, treatability of formaldehyde by AOP has gained significant attention, particularly by methods using heterogeneous catalysts with TiO_2 and TiO_2–H_2O_2 (Arana et al., 2003) and homogenous AOPs with UV/H_2O_2, Fenton and photo-Fenton (Kajitvichyanukul et al., 2006). The literature shows that photo-Fenton process is the most effective method for formaldehyde degradation providing total mineralization and detoxification (Kajitvichyanukul et al., 2006).

Based on the effectiveness of AOPs for formaldehyde destruction, the following section is devoted to a review of advanced oxidation processes.

2.3. Advanced Oxidation Processes

Advanced Oxidation Processes (AOP) are based on the insitu generation of very powerful oxidizing agents such as hydroxyl radicals, which are highly effective for removing refractory organics from water and effluents of wastewater (Güyer et al., 2004). Once hydroxyl radicals are generated, they may attack directly or indirectly via the generation of strong oxidants, e.g. hydrogen peroxide. Advanced oxidation processes can be classified into four groups as described in the following section.

2.3.1. Homogenous AOPs

2.3.1.1. Photochemical Homogenous. Photochemical homogenous advanced oxidation processes are described as follows:

1) Direct Photolysis (UV Irradiation):

Photolysis involves the interaction of light with molecules to bring about their dissociation into fragments. If the absorption of a photon by a molecule is to cause photolysis, the photon energy must be exceeding the energy of the bond to broken (Solarchem, 1994). If and only if both of the following conditions are met, an organic molecule can undergo photolysis (Parsons, 2004):

i. light energy is absorbed by the molecule to produce an electronically excited state molecule
ii. chemical transformations of the excited state are competitive with deactivation processes

In the photochemical reactions, hydroxyl radicals may be generated by water photolysis as shown in equation 2.4 (Rodriguez, 2003):

$$H_2O \rightarrow H\bullet + OH\bullet \qquad (2.4)$$

The most common sources of UV light are continuous wave low pressure mercury vapor lamps (LP-UV), continuous wave medium pressure mercury vapor lamps (MP-UV), and pulsed-UV (P-UV) xenon arc lamps. Both LP-UV and MP-UV mercury vapor lamps produce a series of line outputs, whereas the xenon arc lamp produces continuous output spectra (Kommineni et al., 2000). The 253.7 nm radiation (LP-UV) has proven efficient for remediation of water contaminated with pollutants of various chemical structures, such as unsaturated chlorinated aliphatics and aromatics, nitroso-derivatives (Parsons, 2004). The characteristics of typical low pressure UV lamps are shown in Table 2.2.

Table 2.2 Characteristic of typical low pressure (LP) UV lamps (Parsons, 2004; Solarchem, 1991).

Characteristics	**Low Pressure UV Lamp**
Emission	Monochromatic (85-90% at 253.7 nm)
Peak Output Wavelength	253.7 nm
Arc Length	40-75 cm
Operating Temperature	40-60 ^{o}C
Life Time	8000-10000 hours
Light Intensity	Low

2) Photolysis of Hydrogen Peroxide:

The UV/ H_2O_2 system generates •OH by photolyzing the peroxide HO-OH bond with UV light below 300 nm (Yao and Mill, 1994). Generation of •OH by UV photolysis of H_2O_2 is described by the following reaction:

$$H_2O_2 + h\nu \longrightarrow 2\,\bullet OH \qquad (2.5)$$

Low pressure mercury vapor UV lamps with a 254 nm peak emission are typically used to produce UV radiation, but these lamps may not be the best choice for a UV/H_2O_2 process because the maximum absorbance of UV radiation by H_2O_2 occurs at about 220 nm and because the molar absorption coefficient of H_2O_2 at 254 nm is low. If low-pressure mercury lamps are used, a high concentration of H_2O_2 is needed in the medium to generate sufficient •OH because of the low molar absorption coefficient. High concentrations of H_2O_2, HCO_3^- and CO_3^{-2} may scavenge the •OH, making the UV/H_2O_2 process less effective due to the production of radical intermediates, •OH, $HO_2\bullet$, $\bullet O_2^-$, and $\bullet CO_3^-$ as shown in reactions 2.6-2.9.

$$\bullet OH + H_2O_2 \longrightarrow H_2O + HO_2\bullet \qquad (2.6)$$

$$\bullet OH + HO_2^- \longrightarrow \bullet O_2^- + H_2O \qquad (2.7)$$

$$\bullet OH + HCO_3^- \longrightarrow H_2O + \bullet CO_3^- \qquad (2.8)$$

$$OH + CO_3^{-2} \longrightarrow HO^- + \bullet CO_3^- \qquad (2.9)$$

To overcome this limitation, some AOP technology vendors use high intensity, medium-pressure, broad band UV lamps; others use high intensity, xenon flash lamps whose spectral output can be adjusted to match the absorption characteristics of H_2O_2 or another photolytic target (EPA, 1998).

3) Photolysis of Ozone:

Combined application of UV and ozone results in a net enhancement of organic matter degradation due to direct and indirect production of $OH^{\cdot}$ radicals upon ozone decomposition and H_2O_2 formation respectively (Güyer et al., 2004). UV photolysis of O_3 in water to yield H_2O_2, which in turn react with UV radiation or O_3 to form $^{\cdot}OH$ are shown in equation 2.10-2.14 (Akata and Gurol, 1992).

$O_3 + hv + H_2O \rightarrow H_2O_2 + O_2$ (2.10)

$H_2O_2 + hv \rightarrow 2 \bullet OH$ (2.11)

$2O_3 + H_2O_2 \rightarrow 2 \bullet OH + 3O_2$ (2.12)

$O_3 + hv \rightarrow O_2 + O(^1D)$ (2.13)

$O(^1D) + H_2O \rightarrow 2 \bullet OH$ (2.14)

4) Photo-Fenton Process:

A combination of hydrogen peroxide and UV radiation with Fe^{+2} or Fe^{+3} oxalate ion, the so-called photo–Fenton process produces more hydroxyl radicals than the conventional Fenton method or photolysis, thus promoting the rates of degradation of organic pollutants. Figure 2.3 shows the reaction pathways for the process starting with the primary photo-reduction of the dissolved Fe^{+3} complexes to Fe^{+2} ions followed by the Fenton's reaction and the subsequent oxidation of organic matter.

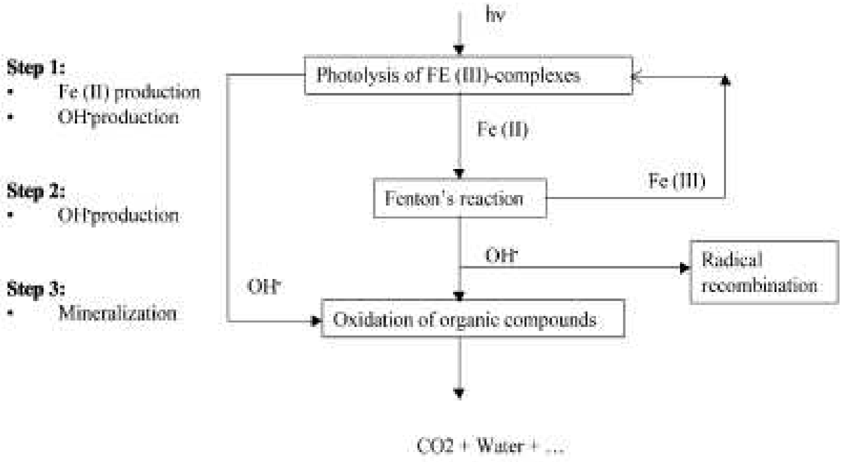

Figure 2.3. Reaction pathways of the photo-Fenton process (Gogate and Pandit, 2003).

2.3.1.2. Non-Photochemical HomogenousAOPs. Non-photochemical homogenous advanced oxidation processes are described as follows:

1) Ozone:

O_3 is selective in its reaction with organic substances and might also decompose in water to generate $OH^{\cdot}$ radicals (Akata and Gürol, 1992). The reaction mechanism of ozone in water is as follows:

$$2O_3 + H_2O \rightarrow \bullet OH + O_2 + H_2O \qquad (2.15)$$

The stability of dissolved ozone is directly affected by the pH of the medium and concentration of radical scavengers (Staehlin and Hoigne, 1982). Molecular O_3 is the major oxidant at acidic pH and reacts directly by electrophilic attack, where as less selective and faster radical reaction oxidation (mainly •OH) becomes predominant at pH>7 as a consequence of OH^- accelerated O_3 decomposition (Glaze et al., 1987).

2) Ozone and Hydrogen Peroxide:

H_2O_2 reacts with O_3 only in its ionized form and the reaction is as follows:

$$O_3 + H_2O_2 \rightarrow \bullet OH + O_2 + HO_2 \qquad (2.16)$$

In order to achieve effective pollutant removal, particularly in the presence of radical scavengers, the dose of hydrogen peroxide must be increased. However, H_2O_2 in the excess of the optimum dose may inhibit because of following reaction (Ince et al., 2001).

$$H_2O_2 + \bullet OH \rightarrow HO_2\bullet + H_2O \qquad (2.17)$$

$$HO_2\bullet + \bullet OH \rightarrow OH^- + H_2O\bullet \qquad (2.18)$$

3) Fenton Process:

In Fenton process, reaction between dissolved Fe^{+2} and H_2O_2 in acidic aqueous solution leads to oxidation of Fe^{+2} to Fe^{+3} and form the highly reactive hydroxyl radical ($OH^{\cdot}$) (equation 2.19-2.24).

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^- \quad (2.19)$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{+2} + \bullet O_2H + H^+ \quad (2.20)$$
$$Fe^{+2} + \bullet OH \rightarrow OH^- + Fe^{+3} \quad (2.21)$$
$$H_2O_2 + \bullet OH \rightarrow \bullet O_2H + H_2O \quad (2.22)$$
$$Fe^{+2} + \bullet O_2H + H^+ \rightarrow Fe^{3+} + H_2O_2 \quad (2.23)$$
$$Fe^{3+} + \bullet O_2H \rightarrow Fe^{+2} + O_2 + H^+ \quad (2.24)$$

For maximum efficiency of the Fenton process, at least the stoichiometric amounts of ferrous ion and hydrogen peroxide must be added both of which at high concentrations are scavengers of hydroxyl radicals (equation 2.21-2.21) (Parsons, 2004, Hunter, 1991). In addition, for maximum efficiency, pH should be at $3 \leq pH < 5$ (Namkung et al., 2007; Torres et al., 2007; Barbunski and Filipek, 2001). Fenton's reagent is commonly made by mixing $FeSO_4$ and H_2O_2 in at optimum ratio.

4) Ionizing Radiation:

This process is based on the chemical changes produced by the absorption of radiation of sufficiently high energy to induce ionization of atoms and generation of excited species. Gamma irradiation and electron beam techniques are the most common commercial radiation sources. Gamma irradiation with $Cobalt_{60}$ and electron beam irradiation with electron accelerators are the most widely preferred radiation techniques (Cooper et al, 1998; McKeown et al., 1998).

2.3.2. Heterogenous Photocatalysis

Heterogeneous photocatalysis is a process involving the use of metal semiconductors to decompose environmental contaminants by means of light induced reactions. Semiconductors are solids that have electrical conductivities between those of conductors and insulators (Hasan, 1999). The process involves generation of conduction band electrons and valence band holes by UV irradiation of semiconductor materials such as TiO_2, strontium titanium trioxide, and zinc oxide (ZnO). TiO_2 is commonly used in commercial AOP applications because of its high level of photoconductivity, ready availability, low toxicity, and low cost (Bahar, 1997). The primary photocatalytic mechanism is believed to proceed as follows (EPA, 1998):

$$TiO_2 + hv \rightarrow e^-_{CB} + h^+_{VB} \qquad (2.25)$$

At the TiO_2 surface, the holes react with either H_2O or OH^- from waste dissociation to form •OH as follows:

$$h^+_{VB} + H_2O \rightarrow \bullet OH + H^+ \qquad (2.26)$$

$$h^+_{VB} + OH^- \rightarrow \bullet OH \qquad (2.27)$$

2.3.3. Ultrasonically – Induced Advanced Oxidation Processes

Ultrasound is defined as any sound of frequency above which the human ear has no response (Mason and Dietmar, 2002). Ultrasound is the part of the sonic spectrum which ranges from about 20 kHz to 10 MHz and can be roughly subdivided into three main regions: (1) low frequency or conventional power ultrasound (20-100 kHz), (2) medium frequency or “sonochemical effects” ultrasound (300 kHz-1 MHz), and (3) high frequency or diagnostic ultrasound (2-10 MHz) (Ince et al., 2001).

Sonochemistry can be defined as chemistry induced by intense pressure waves in a liquid medium. The chemical effects of ultrasound fall into three areas: homogeneous sonochemistry of liquids, heterogeneous sonochemistry of liquid-liquid or liquid-solid systems, and sonocatalysis (which overlaps the first two) (Mason et al., 1990).

Unique and extreme conditions are generated by ultrasonic waves in liquid media and this medium is remarkably suitable for ‘high-energy chemistry’. These extremes promote the oxidative destruction of target contaminants via free radical reactions and provide an excellent medium for their thermal decomposition in the gas phase (Ince et al., 2001). Ultrasonic irradiation of liquids produces excessive energy for chemical reactions due to the physical phenomena that create the conditions necessary to drive chemical reactions. The most important of these is acoustic cavitation. It is the formation, growth and violent collapse of bubbles formed by coupling the pressure waves of ultrasound with a liquid (Hua and Hoffmann, 1996; Mason et al., 1990).

The phenomenon of acoustic cavitation consists of at least three stages: 1) nucleation, 2) bubble growth (expansion), and 3) implosive collapse. The first stage is a nucleated process, by which cavitational nuclei are generated from microbubbles trapped in microcrevices of suspended particles within the liquid. In the bubble growth stage, the bubbles grow and expand in a manner restricted by the intensity of the applied sound wave. The third stage occurs only if the intensity of the ultrasound wave exceeds that of the “‘acoustic cavitational threshold”. At this condition, the microbubbles overgrow to the extent where they can no longer efficiently absorb energy from the sound environment to sustain them and implode violently. The temperatures and pressures within a collapsing microbubble can reach values as high as 4200-5000 K and 200-500 atm respectively (Ince et al., 2001).

Two types of cavitation are known: stable and transient. Stable cavitation means that the bubbles oscillate around their equilibrium position over several refraction/compression cycles. These stable bubbles are formed by power ultrasound and they have enough time to expand. In transient cavitation, the bubbles grow over one (sometimes two or three) acoustic cycles to double their initial size and finally collapse violently. Transient bubbles are formed by the application of medium frequency ultrasound and they do not have enough time to grow to form large bubbles. Transient cavitation (Figure 2.4) induces the implosive collapse of gas and vapor bubbles and thus generates transient “hot-spots’’ with local temperatures and pressures thought to be several thousand degrees Kelvin and hundreds of atmospheres (Margulis and Dmitrieva, 1982). The pressures and temperatures developed in transient cavitations are much higher than found in stable cavitations because in stable cavitation phenomena there is lots of time for the diffusion of dissolved gases and vapors into the bubble. Therefore this collapse has a “cushion effect” (Ince et al., 2001).

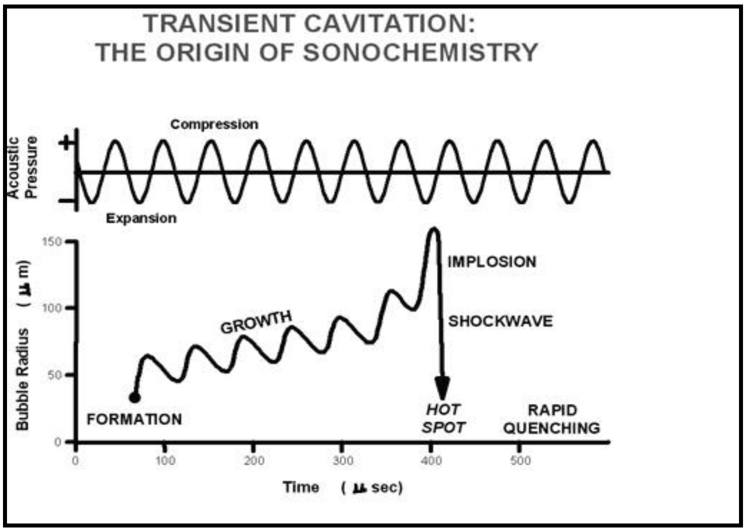

Figure 2.4. Transient cavitation: the origin of sonochemistry (Suslick, 1994).

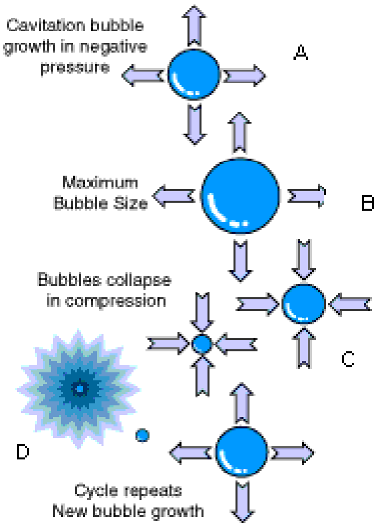

Figure 2.5. Formation, growth and implosion of a cavitation bubble (Variclean, 2001).

During phase A, numerous gas bubbles are formed in the liquid and these bubbles expand during time. The formation of gas bubbles is the start of cavitation. During the second phase of ultrasonic compression (phase B), the enormous pressure exerted on the expanded bubble causes the compression of the bubble (phase C) until the bubble implodes violently generating intense localized temperatures and pressures (phase D). The collapse becomes so rapid compared to the time it takes water to diffuse through the bubble interior that excess vapor becomes trapped inside. As the excess vapor is compressed by the collapse, the contents reach several thousand Kelvin and the trapped vapor is largely dissociated. In the case with water, it is the creation of hydroxyl radicals (•OH) from the hot vapor that is often of interest in applications (Mark et al., 1998; Gong and Hart, 1998; Storey and Szeri, 2002).

There are three potential reaction sites of a collapsing bubble for chemical reactions in ultrasonically irradiated liquids; (i) the cavitation bubble itself (the gaseous phase inside the bubble), (ii) the interfacial sheath between the gaseous bubble and the surrounding liquid and (iii) the surrounding liquid, the solution bulk as shown in Figure 2.6.

To undergo a reaction inside the bubble where extreme conditions exist, a substrate must be easily expelled from the solution, either because of a low degree of salvation and/or a relatively high volatility with respect to the solvent. In water and aqueous solutions, the predominant phenomenon is the sonolysis of the O-H bond, which occurs in the gas phase of the bubble (Henglein, 1991). Reactions in the interfacial region correspond to an indirect mechanism in which sonolysis of the solvent in the bubble or a volatile solute constitutes a first step. The sonolysis occurs with preferential hydroxylation and subsequent oxidations induced by the hydroxyl radical. The third site where a reaction can take place is the solution itself. Substrates reacting at this site are non-volatile or strongly solvated compounds, with no special tendency to migrate towards the bubble boundary.

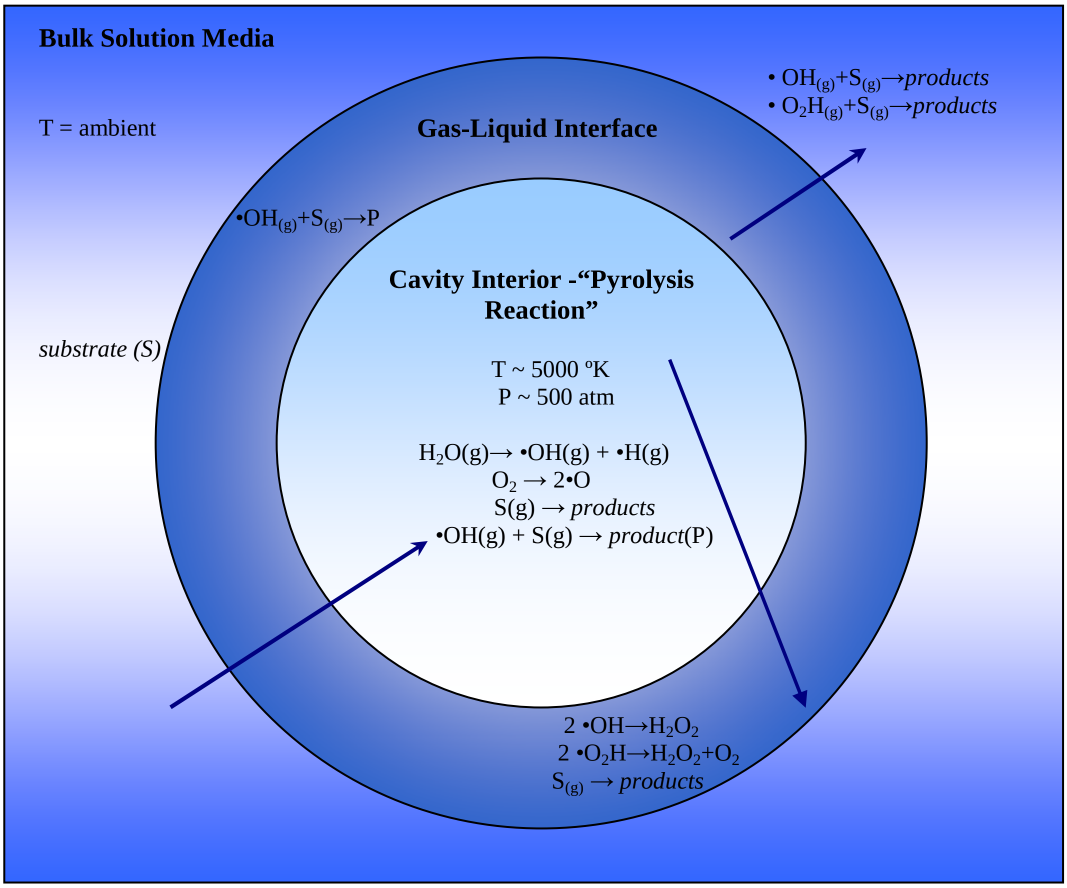

Figure 2.6. Possible sites of chemical reactions in homogeneous reaction media (Ince et al., 2001).

The hydroxyl radicals generated by water sonolysis may either react in the gas phase or recombine at the cooler gas-liquid interface and/or in the solution bulk to produce hydrogen peroxide and water as shown in the following equations (Ince et al., 2001; Riesz and Mason, 1991; Fischer et al., 1986; Wu et al., 1992):

H_2O + **)))** $\rightarrow \bullet OH + \bullet H$ (pyrolysis) (2.28)

$\bullet OH + \bullet H \rightarrow H_2O$ (2.29)

$2\bullet OH \rightarrow H_2O$ (2.30)

$2\bullet OH \rightarrow H_2O_2$ (2.31)

$2\bullet H \rightarrow H_2$ (2.32)

If the solution is saturated with oxygen, peroxyl and additional hydroxyl radicals are formed in the gas phase (due to the decomposition of molecular oxygen), and the recombination of the former at the cooler sites (interface or the solution bulk) produces more hydrogen peroxide, as shown (Ince et al., 2001; Makkino et al., 1982; Petriér et al., 1994):

$$O_2 + \bullet H \rightarrow \bullet O_2H \tag{2.33}$$
$$O_2 +))) \rightarrow O + O \tag{2.34}$$
$$O + H_2O \rightarrow \bullet OH + \bullet OH \tag{2.35}$$
$$\bullet O_2H + \bullet O_2H \rightarrow H_2O_2 + O_2 \tag{2.36}$$

Nonlinear bubble implosions play a major role at lower frequencies, whereas higher flux rates (mass transport) of solutes and radicals influence chemical reactivity at higher frequencies (Kanthale et al., 2008).

The main factors that affect ultrasonic cavitation are (Martin and Ward, 1993):

i. the intensity of the ultrasound field (i.e., the frequency and amplitude of radiation)
ii. the physical properties of the water (e.g., viscosity, surface tension, and vapor pressure)
iii. the temperature
iv. the presence of dissolved gas

The degradation efficiency of organic compounds is related to their hydrophobicity: the greater the hydrophobicity, the more efficiently they can be destroyed. Sonolysis alone does not achieve the target of total degradation particularly in the case of hydrophilic compounds since it is difficult for them to transfer to hydrophobic regions of the cavitation bubbles, where most of the degradation occurs (Wu et al., 2000).

Sonication has proved to be an efficient hybrid method for the pre-treatment and post-treatment of hydrocarbon contaminated water, being successfully applied in labscale for the degradation of aliphatic, aromatic, polycyclic aromatic and halogenated hydrocarbons, azo dyes and for some pesticides (Ioan et al., 2006).

Methods of Catalyzing Sonochemical Reactions:

1) UV Irradiation:

A considerable increase in the rate of organic compound destruction is observed when ultrasonic irradiation is combined with ultraviolet radiation. The effect is due to the synergy of photodecomposition and sonodecomposition (Sohmiya, 1999; Kidak et. al., 2007; Wu et al., 2000; Wu et al., 2001). In addition, the use of UV light shorter than 200 nm produces O_3 from atmospheric O_2 and may enhance the sonophoto decomposition thus further enhancing the rate of decomposition (Naffrechoux et al, 2000).

2) Hydrogen Peroxide:

The addition of H_2O_2 also enhances the rate of organic matter degradation under ultrasonic cavitation via decomposition of H_2O_2 in the bubbles to form $OH\cdot$ radicals. Another possibility is that H_2O_2 oxidizes the selected compound directly. The operating pH, intensity of turbulence existing in the reactor, the state (whether molecular or ionic) and nature (hydrophobic or hydrophilic) of the pollutant and sometimes its concentration are the crucial factors to be analyzed before combination of ultrasound with hydrogen peroxide (Lin et al., 1996; Visscher and Langanhove, 1998; Teo et al., 2001; Parag et al., 2007).

3) Ozone:

When water is ozonated simultaneously with ultrasonic irradiation, ozone undergoes thermal decomposition in collapsing bubbles, generating additional OH radicals as follows (Güyer et al., 2004):

$H_2O\ ))) \rightarrow \bullet OH + \bullet H$ (2.37)

$O_3\ ))) \rightarrow O_2(g) + O\ (^3P)(g)$ (2.38)

$O\ (^3P)(g) + H_2O(g) \rightarrow 2\ \bullet OH$ (2.39)

4) Ferrous and Ferric Iron:

The addition of ferrous and ferric ions in proper molar ratios to H_2O_2 is also very effective in catalyzing ultrasonic reactions (Seo et al., 2007; Ioan et al., 2006; Torres et al., 2007; Neppolian et al.; 2003, Lin et al., 2000).

2.4. The Impact of Water Quality Parameters on Advanced Oxidation Processes

There are many water quality parameters that may impact the effectiveness of any particular AOP. The presence of alkalinity, natural organic matter, nitrites and other inorganics can limit the effectiveness of AOPs upon their scavenging of hydroxyl radicals that would otherwise be used to destroy target compound (Kommineni et al., 2000; Gültekin, 1999). Nearly all dissolved organic compounds present in the source water will serve to reduce the removal efficiency of the target compound by consuming •OH. The hydroxyl radical is nonselective and, thus, can be exhausted by the presence of organic or inorganic compounds other than the contaminants of concern. Both carbonate and bicarbonate will scavenge hydroxyl radicals to create carbonate radicals which, in turn may react with other organic or inorganic compounds present (Kommineni et al., 2000). The reaction for the scavenging of hydroxyl radicals by bicarbonate ions is shown by equation 2.40.

$\bullet OH + HCO_3^- \rightarrow CO_3\bullet + H_2O$ (2.40)

Any constituent present in water that adsorbs UV light will reduce the formation of hydroxyl radicals. Nitrates and nitrites adsorb UV light in the range of 230 to 240 nm and 300 to 310 nm and consequently, high nitrate (>1 mg L^{-1}) or high nitrite (>1 mg L^{-1}) concentrations limit the effectiveness of UV technologies (Solarchem, 1994; Kommineni et al., 2000).

Phosphate and sulfates have the potential to scavenge hydroxyl radicals. However they are extremely slow in reacting with hydroxyl radical, and their scavenging effect can usually be neglected for ozone, peroxide, and UV systems (Kommineni et al., 2000).

The presence of Iron (II), Copper(I), Magnase(II), and other reduced metals in combination with hydroxyl radicals may lead to the formation of metal-organic complexes and permanganate. In addition, the presence of iron (absorptivity 200 to 400) and other scaling agents may result in fouling of UV lamps (Solarchem, 1994; Kommineni et al., 2000).

Turbidity lowers the transmittance of the source water, and thus lowers the penetration of UV irradiation into the source water. The presence of solids also implies adsorption of organics on solid surfaces (Solarchem, 1994; Kommineni et al., 2000).

2.5. Literature Review of Biocide Treatment

Barbunski et al., (2001) investigated the efficiency of Fenton’s reaction on pesticide containing triazine derivatives. They found that the increase of hydrogen peroxide dose (above 1 gdm^{-3}) was followed by a very efficient degradation of pesticides and a decrease in the BOD_5/COD ratio. The decrease in BOD_5/COD ratio observed under high dose of H_2O_2 was concluded as the faster BOD_5 decrease than that of COD. They found that H_2O_2 in Fenton’s reagent was largely decomposed to react with the biodegradable components of the biocide. The best results were achieved within a Fe^{+2}: H_2O_2 molar ratio of 1:3-1:2 at pH 3.0-3.5.

Nick et al., (1992) investigated the photolysis of triazine herbicides at 253.4 nm using a Sterisol low pressure Hg lamp in quartz cells. They found that the quantum yields were within 0.018-0.099 range, and hydroxylated triazine derivatives were major photodegradation products. It was observed that at low fluencies, less than 5% of the triazines were transformed and in the presence of H_2O_2, the atrazine decay was six times faster than UV photolysis.

Prado et al., (2008) studied the sonochemical degradation of triclosan, an antimicrobial agent, at 80 kHz frequency. They found that the ionic strength of the sample had a beneficial effect on the degradation. Sonochemical degradation in urban runoff was about twice as fast as that in deionized water, due to the presence of dissolved solids that facilitated the formation of acoustic cavities.

Alaton, I. (1999), has investigated the degradation of a textile biocide (active ingredient: 2,4,40-trichloro-20-hydroxydiphenyl ether) using Fenton and photo-Fenton processes. The highest COD removal was obtained with 5 m M Fe^{2+} in the ‘‘dark’’ Fenton process, making up a $Fe^{2+}:H_2O_2$ ratio of 1:4. In the presence of UVA irradiation, the COD removal increased from 37% to 80% after 30 min treatment of the biocide effluent. However, no further increase in COD removal was obtained upon extension of the irradiation time, resulting in 81% COD removal after 60 min irradiation.

3. MATERIALS AND METHODS

3.1 Materials

3.1.1. Biocide

Protectol HT (1,3,5-Tris-(2-hydroxyethyl)-1,3,5-hexahydrotriazine, Molecular Weight: 219 g mol^{-1}, Molecular Formula: $C_9H_{21}N_3O_3$) in 78 % purity was obtained from BASF (Istanbul). The chemical structure of the compound is given in Figure 2.1.

3.1.2. Hydrogen Peroxide, $FeSO_4.7H_2O$, NaOH

Reagent grade hydrogen peroxide (35 %, w/v), and $FeSO_4.7H_2O$ were obtained from Merck (Istanbul) and used as Fenton' reagents. Reagent grade NaOH (1N) from Merck (Istanbul) was used for pH adjustment.

3.1.4. $K_2Cr_2O_7$, $HgSO_4$, Ag_2SO_4, H_2SO_4, Potassium Hydrogen Phthalate (KHP)

$K_2Cr_2O_7$, $HgSO_4$, Ag_2SO_4, and H_2SO_4 were used as COD reagents (digestion and sulfuric acid). Potassium Hydrogen Phthalate (KHP) was used to prepare KHP standard for COD, TOC calibration and H_2O_2 analysis.

3.1.5. KH_2PO_4, K_2HPO_4, $Na_2HPO_4.7H_2O$, NH_4Cl, $MgSO_4.7H_2O$, $CaCl_2$, $FeCl_3.6H_2O$, $MnSO_4.4H_2O$

Reagent grade KH_2PO_4, K_2HPO_4, $Na_2HPO_4.7H_2O$, NH_4Cl was used for phosphate buffer solution for BOD analysis. Reagent grade $MgSO_4.7H_2O$, $CaCl_2$, $FeCl_3.6H_2O$ and $MnSO_4.4H_2O$ from Merck (Istanbul) were used for the chemical reagent preparation of BOD_5 analysis.

3.1.6. Ammonium Molybdate Tetrahydrate, KI, NaOH

Reagent grade ammonium molybdate tetrahydrate, KI, and NaOH from Merck (Istanbul) were used for H_2O_2 analysis.

3.1.7. Catalase

Catalase from Micrococcus Iysodeikticus was purchased from Fluka (Istanbul) to remove H_2O_2 residual in solution before analysis of COD, BOD_5, and TOC of HHT solution. Catalase has 176340 u mL^{-1} activity. (1 u corresponds to the amount of enzyme which decomposed 1 µ mol H_2O_2).

3.1.8. Instrumental Equipment

pH Meter: A Metler Toledo pH meter was used to monitor the pH.

Chemical Oxygen Demand (COD) Reactor: A Hach COD reactor was used to heat the samples before spectrometric analysis by a DR/2010 model spectrophotometer.

Dissolved Oxygen (DO) Meter: A WTW Oxi 330 Portable Oximeter with WTW Cellox Probe was used to determine dissolved O_2 of the samples.

Total Organic Carbon (TOC) Analyzer: TOC was monitored by a Shimadzu TOC-V CSH Analyzer.

Spectrophotometer: A Unicam – Heλios-Alpha/Beta Double Beam Spectrophotometer was used to determine the amount of I_3^- in H_2O_2 analysis.

Mixers: A Velp Scientifica Magnetic Stirrer was used to mix the sample solutions.

Gravimetric Balances: A Scaltec SBA 31 was used to weight the biocide in the sample solutions.

3.2. Methods

3.2.1. Set up and Procedure

3.2.1.1. Experimental Set- up. Ultrasonic, UV and hybrid reactors used in the study are described in the following sections.

Ultrasonic Reactors:

Two different ultrasonic reactors were used in the batch experiments.

1) A 20 kHz Probe Inserted Reactor:

The system consisted of a 100 mL glass cell surrounded by a water-cooling jacket to keep the reactor at constant temperature (25 ± 0.5 °C), a probe type transducer with tip area of 1.13 cm^2, and emitting ultrasonic waves at 20 kHz, and a 180 W generator (Bandelin Sonoplus HD2200). The horn was submerged 3 cm from the top of a reaction cell, which had an effective volume of 80 mL. The power was adjusted to 30 %. The power density in reaction cell was 0.17 W mL^{-1}. The system was mounted in a polyurethane isolating material to prevent excessive noise. A photographic view of the reactor is presented in Figure 3.1.

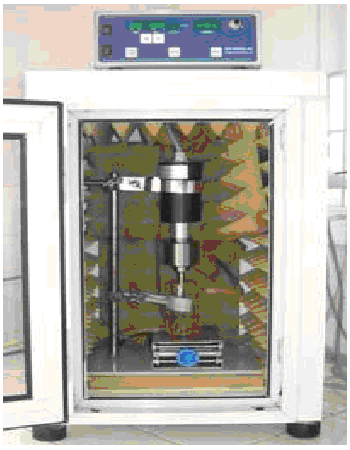

Figure 3.1. Photographic view of the ultrasonic probe type reactor.

2) Ultrasonic Bath Reactor:

Individual and sequential bath experiments were carried out in a stainless steel rectangular tank with dimensions 24x10x10 cm and value of 2 L (BANDELIN-Sonorex Super RK 102 H). The bath was operated at 35 kHz, 480 W peak output and 58 W input power with one transducer attached underneath the flat base. The power density in the tank was 0.058 W mL^{-1}. A 250 mL glass reactor filled with 100 mL of the test solution was suspended in the positioning cover, and the power density in the reactor was 0.039 W mL^{-1}. A schematic view of the ultrasonic bath is presented in Figure 3.2.

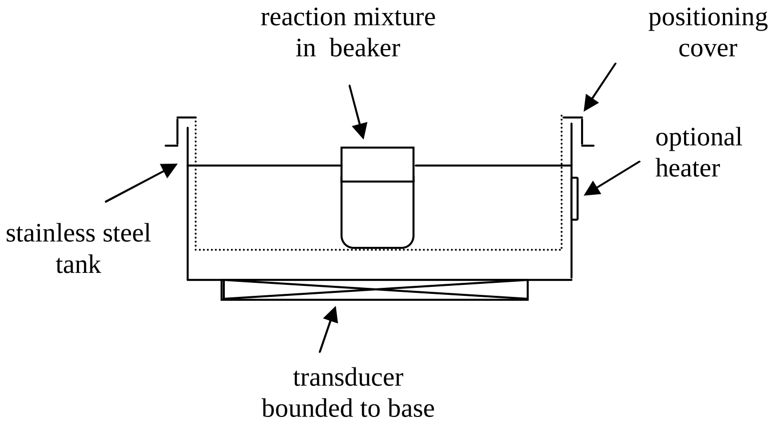

Figure 3.2. The schematic representation of the US bath reactor.

UV and Hybrid (UV/US Bath) Reactors:

1) UV Column Reactor:

A UV column reactor was used to investigate the photolytic degradability of the test biocide. The reactor was made of a two liter plexy glass batch column with a magnetic stirrer to provide a homogeneous mixture. The light source was a low-pressure mercury UV lamp (16.7 Watts m^{-2}), emitting monochromatic light at 253.7 nm.

The lamp was placed in a quartz tube, and immersed along the central axis of the column. A schematic view of the reactor is presented in Figure 3.3.

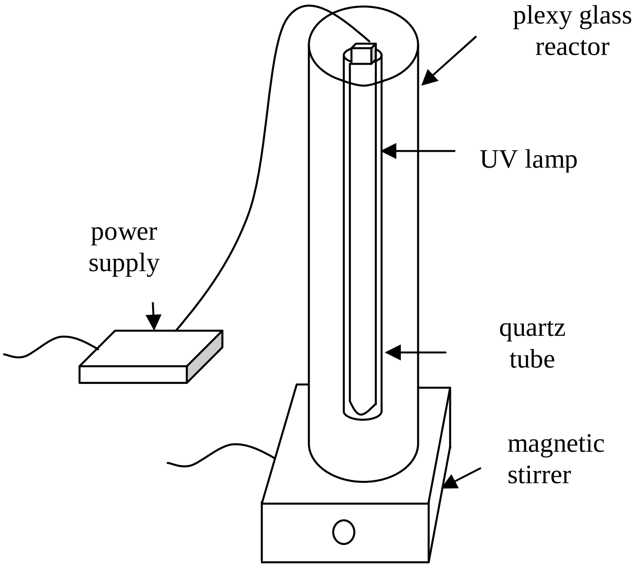

Figure 3.3. Schematic view of UV column reactor.

2) Hybrid Reactor (UV/US Bath):

A hybrid UV-US reactor was used to evaluate the combined effect of ultrasound and ultraviolet irradiation. The system consisted of an ultrasonic bath equipped with four low-pressure mercury UV lamps (1.56 Watss m^{-2}), emitting monochromatic light at 253.7 nm. The lamps were located at the top of the reactor with a perpendicular distance of 9 cm from the surface of solution. A schematic view of the hybrid reactor is given in Figure 3.4.

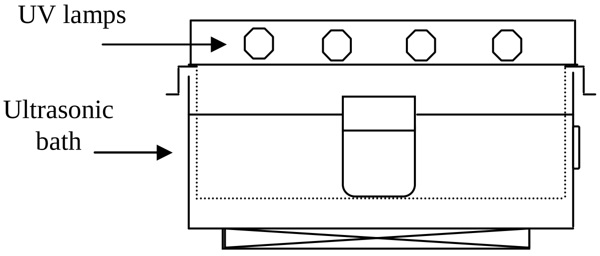

Figure 3.4. Schematic view of UV/US reactor.

3.2.1.2. Experimental Procedures. Experimental procedures are described as follows:

Preparation of Test Solutions:

Fresh samples of the test biocide (hexahydrotriazine-HHT) were prepared daily as 0.05 M in distilled water. Each sample was mixed with a magnetic stirrer for five minutes to provide homogeneity.

Test Processes:

1) Fenton (FE):

Fenton experiments were carried out in 100 ml flasks following pH adjustment to 3.0 with 15 N H_2SO_4. Fenton reagent was prepared from $FeSO_4$ and H_2O_2 as Fe^{+2}:H_2O_2= 1:10 by M. The test molar ratios of H_2O_2 to HHT were 1:1, 3:1, 6:1 and the concentrations of Fe^{+2} was adjusted in accordance. The reaction vessel was covered with aluminum foil to avoid photochemical reactions. The test solution was mixed with a magnetic stirrer at all times. The residual iron and hydrogen peroxide were removed from solutions before analysis of COD, TOC and BOD_5. The precipitate was allowed to settle for thirty minutes and filtered through a 0.45 μm syringe filter. The pH of the supernatant was then adjusted to 7.0, and catalase was added in order to remove the residual H_2O_2. The samples were analyzed for pH, T, BOD_5, COD, and TOC before and after the experiment.

2) Photolysis:

Direct photolysis of HHT was tested in the UV column reactor (UV1) filled with 0.05 M HHT during three hours contact time. The samples were analyzed for pH, T, BOD_5, COD, and TOC before and after the experiment.

3) Sonolysis:

Bath:

A 250 ml glass reactor filled with 100 mL of the test solution (0.05 M HHT) was immersed in the bath filled with 1 liter water. The experiments were run in open (US1) and closed modes in order to test the effects of evaporation and heating. In closed system (US2) experiments, the surface of the reactor was covered with a transparent oven bag (Koroplast- resistant to 200 ^oC). The pH of the solutions in both modes was adjusted to 3.0, 7.0, and 10.0 with 15 N H_2SO_4 and 1 N NaOH. The contact time in closed tests was four and eight hours and that in open tests was four hours. The samples were analyzed for pH, T, BOD_5, COD, and TOC before and after the experiment.

The Probe(UP)**:**

The experiments were run at two distinct pH, namely 3.0 and 10.0. 0.05 M HHT solutions were sonicated for 30 min. The samples were analyzed for pH, T, BOD_5, COD, and TOC before and after the experiment.

4) Combined Sonolysis and Photolysis(U2/UV):

The test solutions of 0.05 M HHT were sonicated for four and eight hours in the presence of UV irradiation in the hybrid reactor described in section 3.2.1.1. The pH of the test solutions was adjusted to 3.0, 7.0 and 10.0. The samples were analyzed for pH, T, BOD_5, COD, and TOC before and after the experiment.

5) Sono-Fenton Reactor(U2/FE):

The test solutions of 0.05 M HHT were sonicated in the presence of Fenton reagent (Fe^{+2}:H_2O_2= 1:10, H_2O_2:HHT = 1:1, 3:1, 6:1) for four and eight hours. The samples were analyzed for pH, T, BOD_5, COD, and TOC before and after the experiment.

6) Sono-Photo-Fenton Reactor(U2/FE/UV):

A 100 ml sample (0.05 M HHT) was injected into the glass reactor immersed in the ultrasonic bath. The bath and UV lamps were turned on after the addition of Fenton’s reagent (Fe^{+2}:H_2O_2= 1:10, 1:1, 3:1, 6:1 as H_2O_2:HHT by M) and pH adjustment. The samples were sonicated for four and eight hours. The samples were analyzed for pH, T, BOD_5, COD, and TOC before and after the experiment.

7) Sequential Processes:

The test solutions of 0.05 M HHT tested in U2 for four hours and in U2/V reactor for four or eight hours at pH=3.0, 7.0 and 10.0 were then sonicated by UP for thirty minutes. Samples were analyzed for pH, T, BOD_5, COD, and TOC before and after the experiment.

8) Additional Processes:

Oxidation by H_2O_2:

The experiments were performed in 100 mL test samples containing 0.05 M HHT at pH=3. Various quantities of H_2O_2 (1:1, 3:1, 6:1 as H_2O_2:HHT by M) were added into the test solutions and allowed to react for four hours. The residual H_2O_2 was removed after pH adjustment to 7.0. Samples were analyzed for pH, T, BOD_5, COD, and TOC before and after the experiment.

Heating:

The test solution (0.05 M HHT) was heated to 100 ^{o}C at pH=10.0 in order to evaluate evaporation and temperature effect on HHT degradation. Samples were analyzed for pH, T, BOD_5, COD, and TOC before and after the experiment.

3.2.2. Analytical Methods

3.2.2.1. Chemical Analysis. Chemical analyses used in the study are described as follows:

Chemical Oxygen Demand (COD): COD was determined in accordance with the Standard Methods of water and wastewater analysis (AWWA, 1992) via ignition to 150 ^oC followed by monitoring of the absorbance at 600 nm.

Biochemical Oxygen Demand (BOD_5): The 5 day BOD was determined by the dilution method described in the Standard Methods of water and wastewater analysis (AWWA, 1992) using an acclimated seed.

Total Organic Carbon (TOC): TOC was determined by a TOC analyzer operating in the non-purgeable organic carbon (NPOC) mode. The instrument was calibrated by standard solutions of KHP (10-1000 ppm). Samples were acidified with HCl to pH 1-2 and purged for 1.5 min prior to injection with instrument grade air to ensure that all carbonate, bicarbonate and carbonic acid are removed as carbon dioxide (in gas form) from the solution. All samples were measured in triplicate.

H_2O_2: H_2O_2 was analyzed by the standard iodide method based on the production of I_3^- by the reaction of H_2O_2 with of ammonium molybdate tetrahydrate and potassium hydrogen phthalate (Klassen et al., 1994). The absorbance of I_3^- was measured spectrophotometrically at 351 nm.

All analysis was run in three parallel samples.

3.2.2.2. Physical Analysis. Physical analyses used in the study are described as follows:

1) Ultrasonic Power:

The ultrasonic power density in solution was determined by using the calorimetric method based on the assumption that all of the energy delivered to the system is dissipated as heat. The power dissipiated (P_{diss}) in a reaction mixture is expressed by:

$$P_{diss} = \left(\frac{dT}{dt} \right)_{t=0} MCp \tag{3.1}$$

where Cp is heat capacity of water. M is mass of water, and $\left(\frac{dT}{dt} \right)_{t=0}$ is the initial slope of the temperature rise of the reaction mixture versus time (Teo et al., 2001; Mason and Dietmar, 2002).

2) Optimization of reactor position in the US bath:

The reaction vessel should be located in the bath such that maximum sonochemical effects are achieved. An ultrasonic wave will have positions of maximum amplitude at multiples of half wavelength of sound in the medium (Mason and Dietmar, 2002). From equation 3.2, the wavelength of the ultrasound in water will be about 3.75 cm (v: velocity of sound, 1500 m s^{-}, f: frequency of transducer, 35000 cycles per second, λ: wavelength of the ultrasound in the water). It is expected that maximum effects occur at vertical intervals of 1.87 cm from the base. For this reason, the reaction vessel was placed 2 cm above the bottom of the bath which was filled with one liter of distilled water. A large piece of aluminum foil was placed horizontally in order to determine the horizontal position of the reactor. The reaction vessel was placed on the red line shown in the Figure 3.5.

$$v = f\lambda \tag{3.2}$$

Figure 3.5. Position of the reaction vessel.

3) UV Light Intensity:

The intensity of the light source was determined by a chemical actinometer. The actinometer consisted of a well-oxygenated aqueous solution containing potassium peroxodisulphate (0.01 mol L^{-1}) and tert-butanol (0.1 mol L^{-1}) which upon irradiation with 254 nm light produced sulphuric acid. Upon photolysis of this solution, hydrogen ions (H^+) were generated whose formation could be followed with a pH meter. The drop in pH as a function of irradiation time was recorded. The quantum yield of H^+ formation is defined as the ratio of the number of H^+ ions formed per the number of photons absorbed. When the pH data were converted into $[H^+]$ (pH = -log $[H^+]$), and then plotted versus the irradiation time, a linear relationship was obtained.

The quantum yield of H^+ formation ($\Phi (H^+)$) is expressed by equation 3.3.

$$\Phi (H^+) = \frac{[H^+] \text{ x } N_L \text{ x } V_{tot} \text{ x } 10}{t \text{ x } I_{abs} \text{ x } M} \tag{3.3}$$

where Vtot denotes the total volume (cm^3) of the solution in the reactor, M is the surface area of the solution (cm^2), t is the irradiation time and I_{abs}/N_L (N_L, Avogadro number) is the absorbed fluence rate in terms of Einsteins m^{-2} s^{-1}. $[H^+]/t$ value was obtained from the slope of $[H^+]$ vs. t plot. Absorbed fluence rate was calculated by using the constant values of $\Phi (H^+)$, M and Vtot. A reference value of 1.8 was used for $\Phi (H^+)$. Incident fluence rate was calculated by equation 3.4.

$$I_{abs} = I_o \left(1 - 10^{-\varepsilon.c.l}\right) \qquad (3.4)$$

where I_{abs} is the absorbed photon fluence rate, Io is the incident photon fluence rate, l is the pathlength, ε and c are the molar extinction coefficient (20 dm^3 mol^{-1} cm^{-1}) and concentration of potassium peroxodisulphate (0.01 M), respectively (Mark et al., 1990).

4. RESULTS AND DISCUSSION

4.1. Composition of the Test Sample

The composition of the raw test sample as determined in the laboratory is summarized in Table 4.1. The molar concentration of the solution was estimated based on 78 percent hexahydrotriazine. The test solution was alkaline with pH=10.0 ± 0.4 at 25 ^{o}C.

Table 4.1. The composition of the test solution.

Parameters	Value
HHT concentration (M)	0.05
HHT concentration (mg L^{-1})	10950
COD (mg L^{-1})	16650
BOD_5 (mg L^{-1}) dilution factor=1/3000	8350
BOD_5/COD	0.52±0.1
TOC (mg L^{-1})	5320
pH	10.4

4.1.1. Theoretical Oxygen Demand

The theoretical oxygen demand of HHT was found using the following oxidation reactions:

$$C_nH_aO_bN_c + (n+(a/4)-(b/2)-(3/4)c)O_2 \rightarrow n\ CO_2 + (n+(a/2)-(3/2)c)\ H_2O + cNH_3 \qquad (4.1)$$

$$C_9H_{21}O_3N_3 + 10.5\ O_2 \rightarrow 9\ CO_2 + 6\ H_2O + 3\ NH_3 \qquad (4.2)$$

Accordingly, 336 g O_2 is used by 1 mol HHT for complete oxidation, and thus 16800 mg L^{-1} O_2 is used by 0.05 M HHT. This is close to the value of chemical oxygen demand (COD) found in the laboratory (16650 mg L^{-1}).

4.1.2. Total Organic Carbon (TOC)

The total organic carbon of HHT is 9x12=108 g/mol, and so 5400 mg L^{-1} TOC exists in 0.05 M HHT. This value is close to the value found in the laboratory (5320 mg L^{-1}).

4.1.3. Biodegradability

The 5 day BOD of the test sample varied with two parameters:

i. dilution factor
ii. date of analysis

The variations in BOD_5 by those two parameters are shown in Table 4.2 and Table 4.3. The BOD_5/COD of solution by date of analysis was found as 0.52±0.1.

Table 4.2. BOD_5 variation by dilution factor.

Dilution Factor	**BOD_5 (mg L^{-1})**
1/3000	9021
1/300	60
1/30	0
1/15	0

Table 4.3. BOD_5 variation by date of analysis (dilution rate=1/3000).

Date	**BOD_5 (mg L^{-1})**
27.04.2008	9225
05.05.2008	8295
11.06.2008	9995
18.07.2008	8570

Table 4.3 shows that biodegradability increases with dilution, suggesting that high concentrations of HHT inhibit the growth of sewage bacteria in closed bottle tests.

Assuming that the inhibition is due to formaldehyde release upon hydrolysis, the fraction of formaldehyde at various pH and temperature are given in Table 4.4.

Table 4.4. Formaldehyde release in solution at various pH and temperature (BASF,2004).

T (^{o}C)	**% Formaldehyde**		
	pH=3.0	pH=7.0	pH=10.0
20	4.7	2.2	1.4
>37	4.2	2.2	1.8

In accordance, the concentration of formaldehyde in the test solution at various pH and temperature are as given in Table 4.5.

Table 4.5. Formaldehyde concentration in the test solution.

T (^{o}C)	**Formaldehyde (mg L^{-1})**		
	pH=3.0	pH=7.0	pH=10.0
20	514	241	153
>37	459	241	197

The results show that formaldehyde release in acidic pH is much larger than at neutral and alkaline pH. It is reported that the growth of sewage microorganisms is inhibited by 30 mgL^{-1} formaldehyde (NICNAS, 2006). Thus, the test sample was toxic to sewage microorganisms at 0, 1/15 and 1/30 dilution fractions, but non toxic at higher dilution rates. The dilution factor for BOD_5 analysis was selected as 1/3000 in the rest of the study.

4.2. Determination of Process Parameters

4.2.1. H_2O_2 Yield

The quantity of H_2O_2 in an ultrasonic reactor is an indicator of the cavitation intensity. The yield of H_2O_2, which is an indirect measure of OH radicals, was measured by the standard iodide method described in section 3.2.2.1. The absorbance of I_3^- was measured spectrophotometrically at 351 nm, and was converted to concentration. The amount of H_2O_2 in the ultrasonic bath and the glass reactor in it are given in the Table 4.6

Table 4.6. Hydrogen peroxide concentration in the bath and immersed reactor.

H_2O_2 concentration (mg L^{-1})	
The bath	**Immersed reactor**
0.751	0.168

The data shows that the effect of cavitation inside the glass reactor was nearly five times lower than that in the bath.

4.2.2. Ultrasonic Power Density

The results of calorimetric analysis showed that the power density was 0.039 W mL^{-1} in the immersed glass reactor, 0.058 W mL^{-1} in the bath and 0.17 W mL^{-1} in probe reactor. The temperature rise with time in reaction vessel, ultrasonic bath and probe reactor is represented in Figure 4.1 and 4.2.

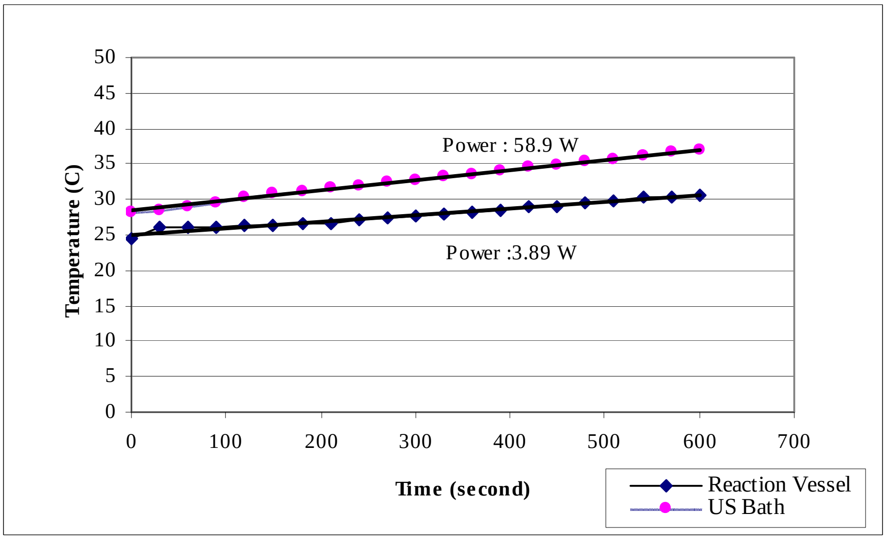

Figure 4.1. The temperature rise with time in ultrasonic bath and reaction vessel (both filled with distilled water).

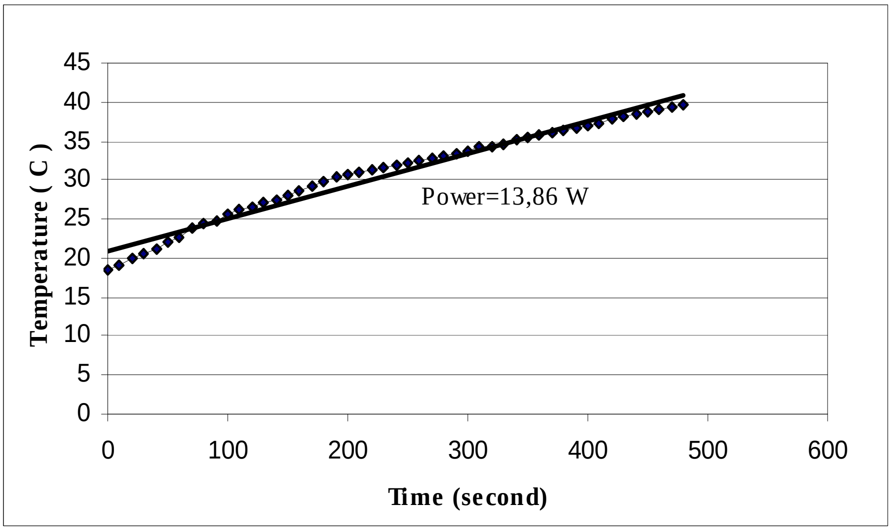

Figure 4.2. The temperature rise with time in ultrasonic probe (filled with distilled water).

4.2.3. Light Intensity

The light intensity was measured by peroxodisulphate/tert-butanol chemical actinometer as described in section 3.2.2. The drop in pH was converted into the increase in H^+ concentration and then plotted versus the irradiation time as shown in Figure 4.3 (a) hybrid reactor (HR) and (b) for the UV column reactor (UV1).

The slopes of the straight lines in the Figure 4.3 provide the absorbed fluence as 3.31×10^{-6} Einsteins m^{-2} s^{-1} (1.56 Watts m^{-2}) in the hybrid reactor and 3.54×10^{-5} Einsteins m^{-2} s^{-1} (16.7 Watts m^{-2}) in the UV column reactor. The efficiency of light absorbtion was found as 98 % in hybrid and 37 % in the UV column reactors.

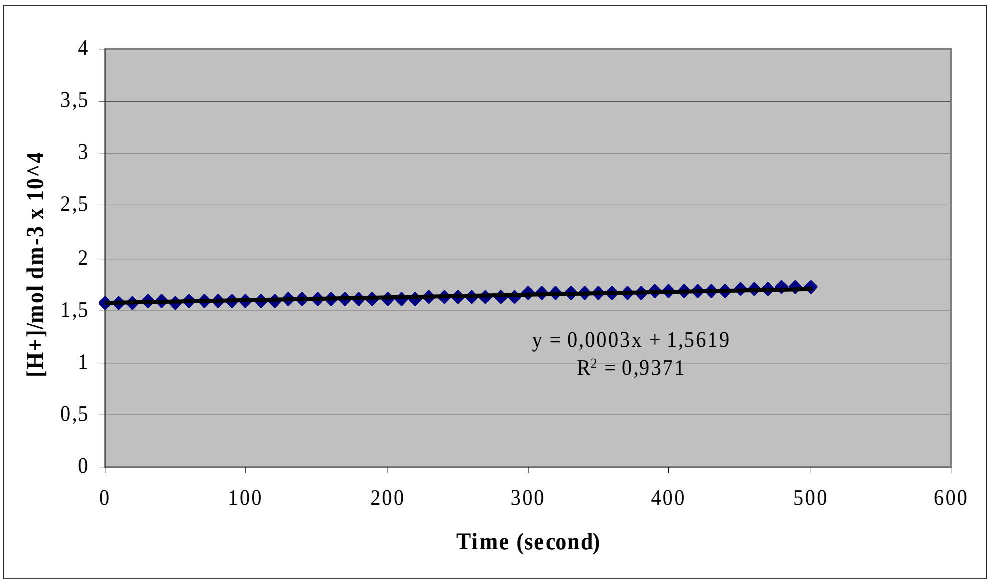

Figure 4.3. (a) Variation of H+ concentration with time in the HR.

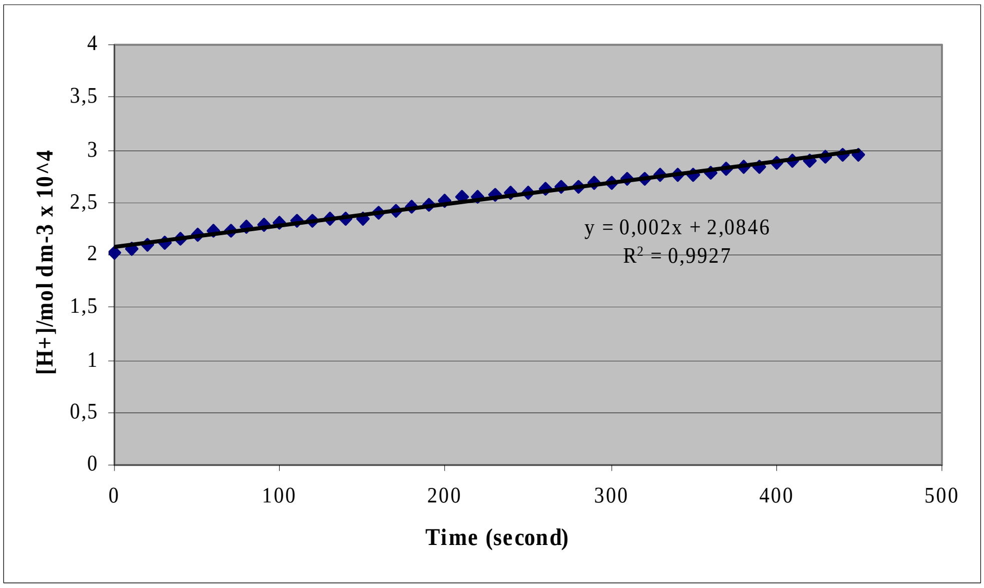

Figure 4.3. (b) Variation of H^+ concentration with time in the UV1.

Table 4.7. Comparison of hybrid and UV column reactors for light intensity.

Reactor	Incident fluence rate (Einsteins $m^{-2} s^{-1}$)	Intensity (Einsteins $m^{-2} s^{-1}$)	Efficiency %
UV-Column	9.59×10^{-5}	3.54×10^{-5}	37
UV-US (hybrid)	3.37×10^{-7}	3.31×10^{-7}	98

4.3. Sonication of HHT in the Ultrasonic Bath

Bath experiments were conducted in open bath (US1) and closed bath (US2) as described in section 3.2.2.1. The test samples were sonicated in a glass reactor immersed in bath for 4 h and 8 h at pH=3.0, 7.0 and 10.0. Variations in temperature, pH and water quality parameters are given in the following sections.

4.3.1. Temperature Variations

Most of the energy delivered into the solution by sonication is dissipated as heat. Variations of temperature in the ultrasonic bath after 4 h sonication with the experimental conditions are summarized in Table 4.8. It was found that maximum heat was dissipated at pH=10.0 when the reactor was covered and heat dissipation was lowered when the cover was removed.

Table 4.8. Variations in temperature in US1 and US2 reactors after 4 h.

Conditions		**T (°C)**	
System	**pH**	**t=0**	**t=4 h**
US1	3.0	20.4	56.7
	7.0	20.7	54.9
	10.0	20.6	55.3
US2	3.0	25.1	77.6
	7.0	25.3	71.8
	10.0	24.9	78.2

The effect of time on heat release was further investigated in the closed reactor in the bath for 8 h sonication. The results are summarized in Table 4.9.

Table 4.9. Variations in temperature in US2 after 8 h sonication of HHT.

pH	**T (°C)**	
	t=0	**t=8 h**
3.0	21.1	75.4
7.0	21.0	61.8
10.0	21.3	67.5

It was found that temperature increase was not directly related to the time of sonication as the average raise in temperature after 4 h and 8 h sonication was 53.3 ^{o}C and 44.2 ^{o}C, respectively.

4.3.2. pH Variations

pH variations in the ultrasonic bath after 4 h and 8 h sonication under open and closed atmospheres are summarized in Table 4.10 and Table 4.11.

Table 4.10. Variations in pH in US1 and US2 after 4 h sonication of HHT.

System	**pH**	
	t=0	**t=4**
US1	3.05	3.22
	7.06	6.83
	9.99	9.54
US2	3.08	3.65
	7.13	6.81
	9.97	9.11

Table 4.11. Variations in pH in US2 after 8 h sonication of HHT.

System	**pH**	
	t=0	**t=8 h**
US2	3.01	3.60
	7.21	7.11
	10.02	9.14

It was found that changes in the final pH of the solutions were not significantly influenced by the initial conditions, such as contact time and closed/open modes.

4.3.3. Variations in Water Quality Parameters

The results of bath experiments conducted in covered and uncovered bath are discussed in the following sections for open and closed conditions separately.
1) Open System:

The performance of the system in reducing organic pollution is tabulated in Table 4.12.

Table 4.12. 4 h performance of US1 reactor for organic matter degradation.

pH	**% Reduction**		
	COD	**TOC**	**COD/BOD$_5$**
3.0	34	14	41
7.0	38	21	30
10.0	32	7	34

The observed improvement in the quality of the sample must be due to cavitation effects, particularly the production of OH radicals and H_2O_2. It is important that value of BOD_5 increased except at pH=7.0, and the maximum COD and TOC abatement was observed at pH=7.0 with the formation of a clear dark red color in the solution. This must be due to the formation of a colored complex.

The change in BOD_5/COD ratio after 4 h sonication is summarized in Table 4.13. It was found that maximum improvement in BOD_5/COD ratio was attained at pH=3.0.

Table 4.13. Alterations in BOD_5/COD in US1 reactor after 4 h sonication of HHT.

pH	**BOD_5/COD**	
	t=0	**t=4 h**
3.0	0.53	0.90
7.0	0.50	0.71
10.0	0.54	0.82

2) Closed System:

The performance of the system in reducing organic pollution is tabulated in Tables 4.14 and Table 4.15.

Table 4.14. 4 h performance of the US2 for organic matter degradation.

pH	**% Reduction**		
	COD	**TOC**	**COD/BOD_5**
3.0	25	8	30
7.0	17	12	13
10.0	15	6	23

Table 4.15. 8 h performance of the US2 for organic matter degradation.

pH	**% Reduction**		
	COD	**TOC**	**COD/BOD_5**
3.0	27	16	24
7.0	25	14	21
10.0	17	7	8

It was found that the degree of COD and TOC removal was slightly increased at all pH levels when the contact time was increased to 8 h. The maximum COD removal occurred at pH=3.0 in closed bath, whereas the maximum in the open reactor occurred at pH=7.0. However, maximum TOC removal in the closed bath occurred at pH=7.0 after 4 h contact time; it was also the maximum in the open system. The removal efficiency of the system is presented in Figure 4.4 and Figure 4.5.

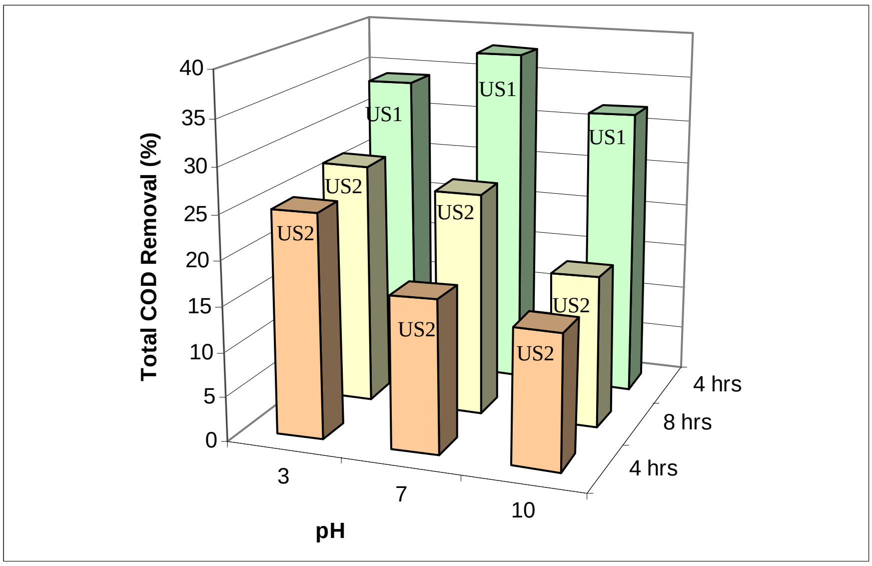

Figure 4.4. Relative COD removal in US1 and US2 reactors at various contact times and pH.

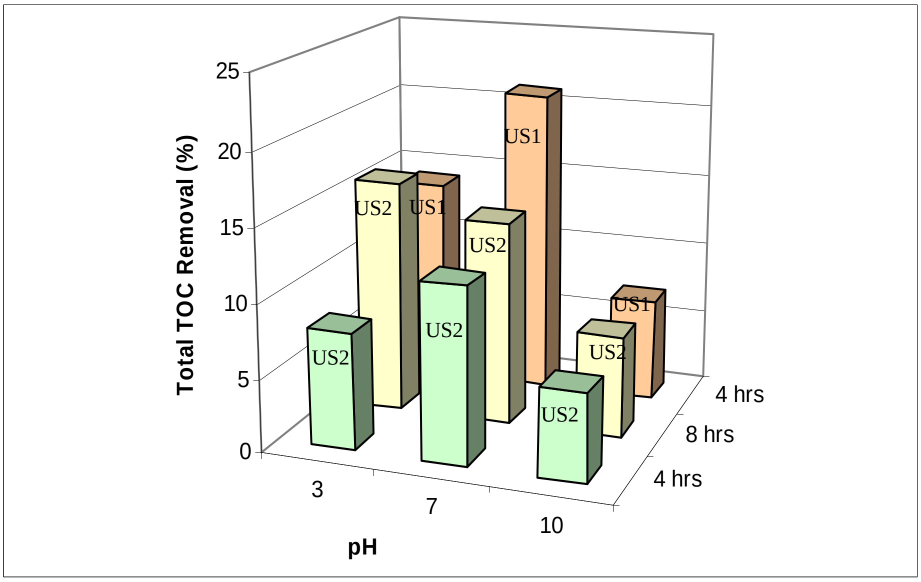

Figure 4.5. Relative TOC removal in US1 and US2 reactors at various contact times and pH.

However, the improvement in biodegradability of the sample was inversely related to sonication time. A summary of BOD_5/COD ratio in the closed system after 4 h and 8 h sonication is given in Table 4.16.

Table 4.16. Alterations in BOD_5/COD ratio in US2 after 4 h and 8 h sonication.

pH	**BOD_5/COD**	
	t=0	**t=4 h**
3.0	0.59	0.84
7.0	0.63	0.73
10.0	0.61	0.79
pH	**t=0**	**t=8 h**
3.0	0.59	0.78
7.0	0.61	0.78
10.0	0.60	0.65

It was observed that maximum degradation and maximum increase in BOD_5/COD ratio took place at acidic pH, but minimum degradation was at pH=7.0 for 4 h sonication and pH=10.0 for 8 h sonication.

The differences in the removal efficiencies at closed and open systems may be due to the temperature differences. It was found that temperature increased to ~56±1.1 ^{o}C in the uncovered reactor and to ~75±3 ^{o}C in the covered reactor in 4 hours. However, the temperature in the closed reactor was ~68.2±7 ^{o}C after 8 h sonication. Lower efficiency of the closed reactor after 4 h and 8 h must be due to its higher temperature. The effects of increased temperature in reactors are the following (Jiang et al, 2006):

i. decrease the energy of cavitation,
ii. lower the threshold limit of cavitation,
iii. reduce the quantity of the dissolved gas, and
iv. increase the vapor pressure

In addition to the temperature effect, the CO_2 intake from the surface of the solution in open system may lead to CO_3^{-2} radical formation by the conversion of CO_2 to CO_3^{-2} in solution. Although carbonates consume OH radicals by reaction 4.3, the formation of CO_3^{-2} radicals after reaction may enhance the oxidation of organics.

$$CO_3^{-2} + OH^{\cdot} \rightarrow HO^{-} + \bullet CO_3^{-2} \tag{4.3}$$
$$\bullet CO_3^{-2} + \text{organics} \rightarrow \text{products} \tag{4.4}$$

Moreover, the volume of the test solution was reduced by 12 ml after 4 h sonication in the open bath. Hence, higher level of COD and TOC removal in the open bath reactor is also due to loss of some volatile oxidation by product upon evaporation. The loss of the solution by evaporation was prevented in closed system and the volume was fixed.

4.4. Heating and Cooling of HHT

The solution was heated to 100 ^{o}C and then cooled to room temperature in order to evaluate the effect of evaporation and temperature on COD and TOC abatement of the test sample. The results are tabulated in Table 4.17.

Table 4.17. Effect of heating/cooling on the degradation of HHT.

Conditions	**% Reduction**		
	COD	**TOC**	**COD/BOD$_5$**
Heating, T=100.2	-21	-	8
Cooling, T=21.5	39	7	25

It was found that heating first led to an increase in COD but cooling of the effluent subsequently resulted in 39 % COD removal (relative to raw sample). The results indicate that HHT undergoes chemical changes by both heating/cooling operations. The reduction in TOC must be due to evaporation of the volatile hydrolysis components of the biocide. The unexpected COD increase by heating may be due to enhanced hydrolysis of the compound.

4.5. Sonication of HHT in the Ultrasonic Probe Reactor

The ultrasonic probe reactor (UP) was used to evaluate the effect of higher ultrasonic power (0.17 W mL^{-1}) on the degradation of HHT at 20 ^{o}C. pH dependent performance of the reactor for organic matter degradation is presented in Table 4.18.

Table 4.18. Impact of pH on the degradation of HHT by the UP.

pH	**% Reduction**		
	COD	**TOC**	**COD/BOD$_5$**
3.0	21	19	30
10.0	11	10	23

It was found that significant COD and TOC removal was achieved within 30 min contact time but efficiency was much larger at pH=3.0. This can be explained by the fact that sonochemical decay, especially with -OH, -NH$_2$, -COOH groups, is largely enhanced by acidification (Wu, 2005). In addition, maximum H$_2$O$_2$ formation takes place at pH=3.2 and the yield decreases as pH is increased (Jiang et al., 2002). Besides, HHT is most hydrolysable in acidic conditions and converted to formaldehyde. The highest TOC abatement at both pH=3.0 and pH=10 was achieved in probe reactor among all processes discussed in the previous sections (open/closed baths).

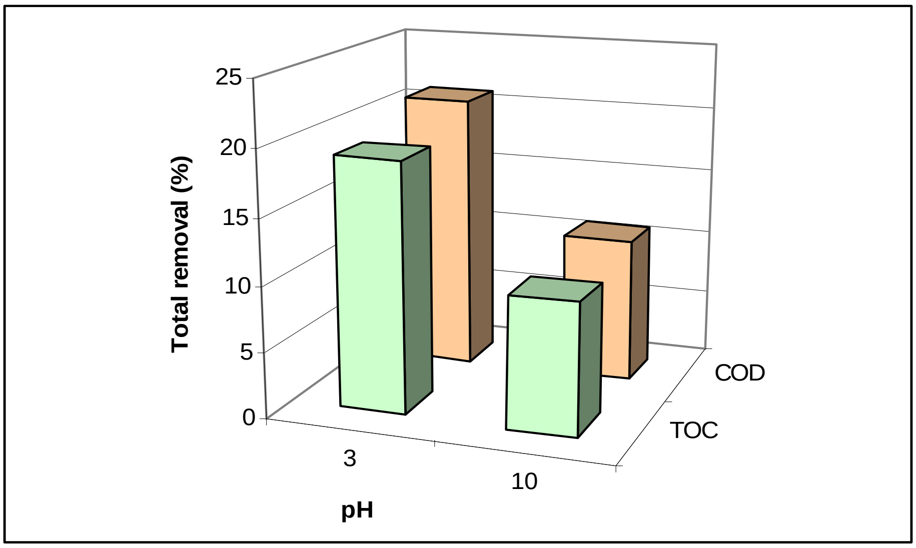

Figure 4.6. COD and TOC reduction by the UP after 30 min.

The ratio of BOD_5 to COD after 30 min sonication is shown in Table 4.19. It was found that the degree of improvement was influenced by pH, with nearly 43 % increase at pH=3.0 and 30 % increase at pH=10.0

Table 4.19. Alterations in BOD_5/COD by 0.5 h sonication at UP.

pH	**BOD_5/COD**	
	t=0	**t=0.5**
3.0	0.53	0.76
10	0.60	0.78

4.6. UV Irradiation of HHT

The following discussion is about the effects of UV irradiation with and without ultrasound on the degradation of HHT. Single UV experiments were run in the column reactor, and in the hybrid reactor with US switch shut down.

4.6.1. UV Column Reactor (UV1)

The results for 60 min, 120 min, and 180 min irradiation in the column reactor are given in Table 4.20.

Table 4.20. The effect of time on degradation of HHT solution at pH=10.0.

Time (min)	**% Reduction**		
	COD	**TOC**	**COD/BOD_5**
60	6	4	26
120	10	6	34
180	15	7	40

The data show that photolysis can be a degradation pathway for HHT if at least 180 min of contact with $3.54x10^{-5}$ Einsteins m^{-2} s^{-1} (16.7 Watts m^{-2}) is allowed. The biodegradability of the test solution increased from 0.57 to 0.77 in 1 h, to 0.80 in 2 h and to 0.86 in 3 h contact time.

4.6.2. Hybrid Reactor (UV/Ultrasonic Bath)-HR

The reactor was operated first by turning the US switch off (UV2) and secondly by turning both switches on (US2/UV). When the US switch was off no degradation was observed at pH=7.0, 2 % degradation of COD was observed at pH=3.0 and 8 % degradation of COD was observed at pH=10.0.

When US switch was turned on the performance was still lower than that of US Bath (closed) after 4 h and 8 h operation. The efficiency of the system for organic matter degradation is tabulated in Table 4.21.

Table 4.21. Performance of the US2/UV after 4 h and 8 h sonication.

Time	**pH**	**% Reduction**		
		COD	**TOC**	**COD/BOD$_5$**
4 h	3.0	11	5	19
	7.0	6	2	3
	10.0	14	7	31
8 h	3.0	20	14	30
	7.0	17	9	17
	10.0	37	21	29

The degradation of HHT improved when the contact time was extended from 4 h to 8h. However the lower efficiency achieved by adding UV lamps to US2 may be due to the following:

i. hindrance of light transmission by the vapor accumulated between the cover material and the surface of the test solution.
ii. absorbtion of UV light by covering material
iii. absorbtion of UV light by SO_4^- (added for pH adjustment) and $-NH_2$ (a hydrolysis product of HHT).
iv. inefficiency of the light source and reactor geometry.
v. excess temperature increase in solution (~80±4.5 °C).

The highest TOC and COD reduction was achieved at pH=10.0. Additionally, maximum improvement in BOD_5/COD ratio achieved at pH=10.0 in 4 h reaction.

4.7. Sequential Operations

4.7.1. Ultrasonic Bath (US2) followed by Ultrasonic Probe (UP)

The experiments consisted of sonication of the test sample in the US Bath (Step 1) followed by sonication of the effluent in the US Probe reactor (Step 2). Experimental conditions and composition of the effluent are schematically presented in Figure 4.7.

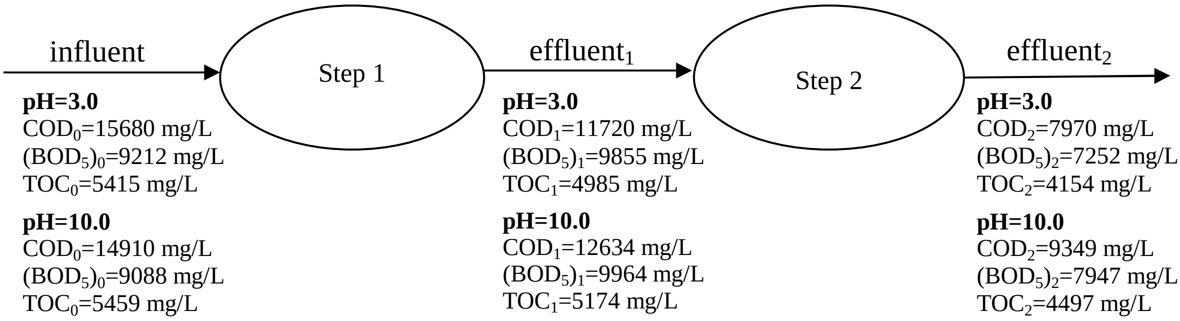

Figure 4.7. A scheme of the consecutive operation of US bath and probe reactor.

It was found that consecutive operation improved both COD and TOC reduction in the HHT solution. The performance of the sequential operation is summarized in Table 4.22. The highest degradation of HHT was attained at pH=3.0.

Table 4.22. Performance of consecutive operation (4 h US bath + 30 min probe reactor).

System	**pH**	**% Reduction**		
		COD	**TOC**	**COD/BOD$_5$**
Step 1 **(4 h sonication)**	3.0	25	8	30
	7.0	17	12	14
	10.0	15	6	23
Step 2 **(4.5 h sonication)**	3.0	32	18	35
	7.0	20	12	16
	10.0	26	9	28

Relative fractions of COD and TOC elimination after the first and second step operations are presented in Figure 4.8 and Figure 4.9, respectively.

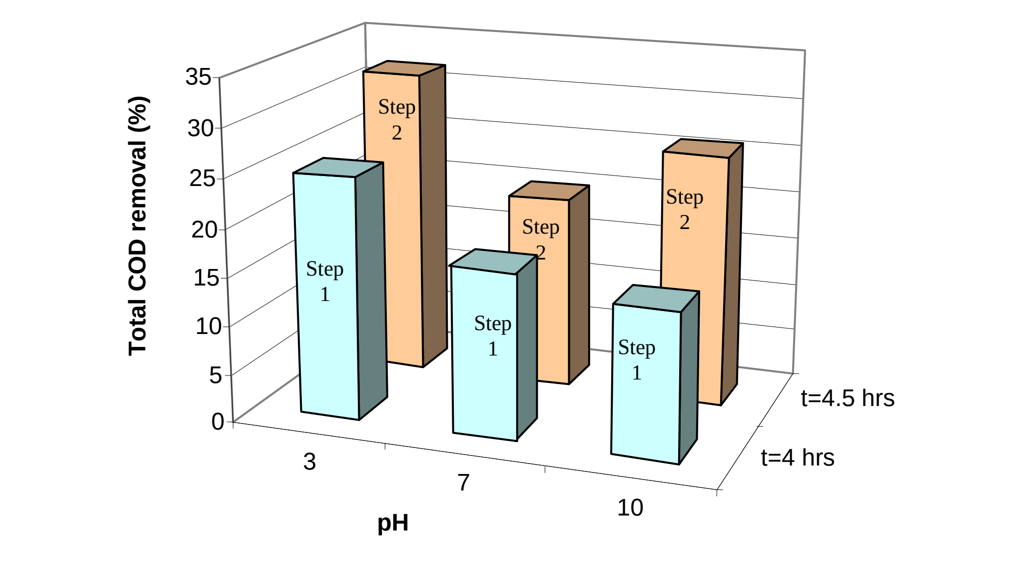

Figure 4.8. COD removal in sequential process of closed bath and probe reactor.

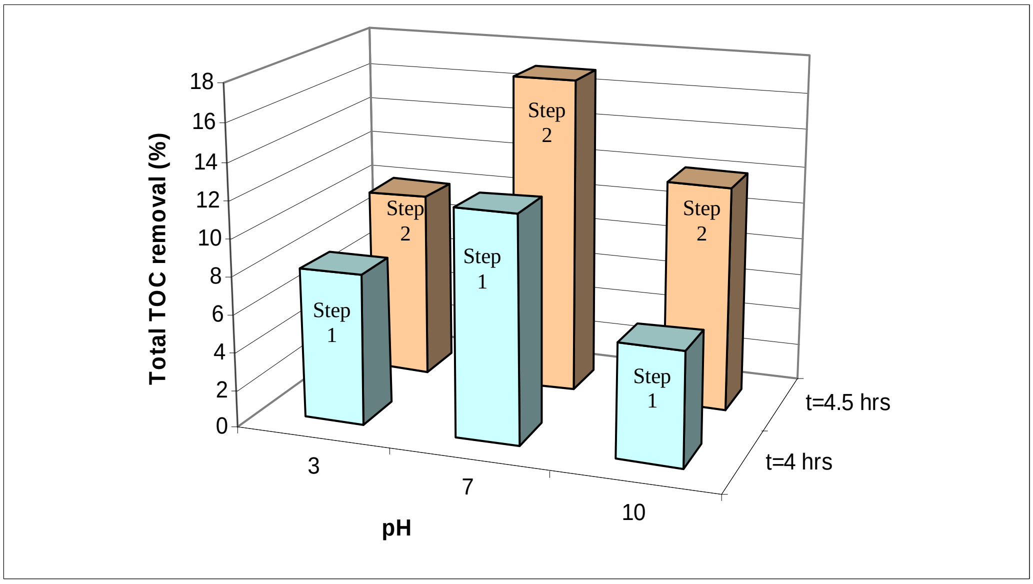

Figure 4.9. TOC removal in sequential process of closed bath and probe reactor.

The effect of the consecutive operation on BOD_5/COD is shown in Table 4.23. It was found that maximum BOD_5/COD ratio was achieved at pH=3.0 in the effluent if Step 2.

Table 4.23.Alterations in BOD_5/COD ratio in consecutive operation.

System	**pH**	**BOD_5/COD**	
		t=0	**t=4**
Step 1 **(4 h sonication)**	3.1	0.59	0.84
	7.1	0.63	0.73
	10.0	0.61	0.79
Step 2 **(4.5 h sonication)**	3.7	0.84	0.91
	6.8	0.73	0.75
	9.1	0.79	0.85

4.7.2. Hybrid Reactor and Ultrasonic Probe

The effluents of the hybrid reactor (Step 1: US2/UV) treated for 4 h at pH=3.0 and 10.0 was further processed ultrasonic probe reactor (Step 2: UP) for 30 min. The results of the sequential application are summarized in the Table 4.24.

Table 4.24. Sequential treatment performance by US2/UV (4 h) + UP (30 min).

System	**pH**	**% Reduction**		
		COD	**TOC**	**COD/BOD$_5$**
Step 1 (4 h sonication)	3.0	11	5	19
	10.0	14	7	31
Step 2 (4.5 h sonication)	3.0	20	7	6
	10.0	22	9	16

It was found that sonication of the HR effluent for 30 min in the UP significantly enhanced COD removal. The application was not effective for increasing the ratio of BOD$_5$/COD.

4.8. Oxidation by Hydrogen Peroxide

The effect of H_2O_2 addition on the degradation of HHT was investigated by inputting various doses of H_2O_2 (1:1, 3:1, 6:1 M:M HHT). The results are given in Table 4.25.

The results show that oxidation by hydrogen peroxide can be slightly effective only at high doses of the reagent.

Table 4.25. Influence of H_2O_2 dose on the degradation of HHT in 4h at pH=3.0.

H_2O_2 dose (M/M HHT)	**% Reduction**		
	COD	**TOC**	**COD/BOD_5**
1	12	10	8
3	13	14	29
6	18	19	35

4.9. Oxidation by Fenton and Sono-Fenton Processes

Investigation of the Fenton process was run in the absence and presence of ultrasonic irradiation and UV light using the bath (covered) reactor for 4 h.

4.9.1. Fenton without Ultrasound (FE)

Fenton reagent (FE) was added on molar basis as 1:10 (Fe:H_2O_2) and the dose was varied to obtain mass ratios of 40, 800 and 1800 mg FE g^{-1} HHT. The pH of the solution was kept at pH=3.0. The results are given in Table 4.26.

Table 4.26. Impact of FE reagent dose on the degradation of HHT after 4 h at pH=3.0.

FE dose (mgFE/ gHHT)	**% Reduction**		
	COD	**TOC**	**COD/BOD_5**
40	35	33	-
800	37	36	-
1800	58	22	2

The tests showed that Fenton’s reagent is effective for reducing the COD of the sample and the effect is enhanced as the dose is increased. However, total TOC removal was lower at excess doses of the reagent. Relative variations of COD and TOC removal are presented as bars in Figure 4.10.

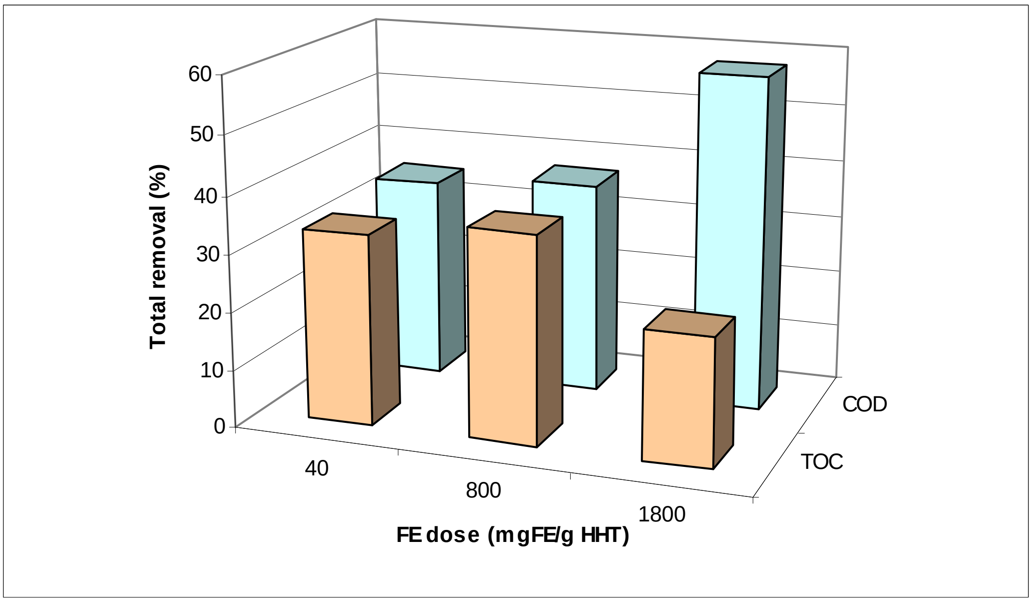

Figure 4.10. Relative COD and TOC removal by FE dose after 4 h at pH=3.0.

It was also found that Fenton process was ineffective for improving the biodegradability of the HHT because the BOD_5/COD ratio decreased at all doses of the reagent. This is due to faster BOD_5 reduction than COD reduction as a consequence of the reaction of hydrogen peroxide with the biodegradable components of HHT (Barbunski et al., 2001).

4.9.2. Fenton with Ultrasound (US2/FE)

The reagent doses were kept the same as in the Fenton process without ultrasound. The results are summarized in Table 4.27.

Table 4.27. Impact of US2/FE on HHT degradation after 4 h at pH=3.0.

FE dose **(mgFE/g HHT)**	**% Reduction**		
	COD	**TOC**	**COD/BOD$_5$**
40	35	30	-
800	45	39	-
1800	53	45	-

The tests showed that Fenton's reagent is effective for reducing the COD and TOC of the sample and the effect is enhanced as the dose is increased. Relative variations of COD and TOC removal are presented as bars in Figure 4.11.

It was also found that Fenton with ultrasound process was ineffective for improving the biodegradability of the HHT because the BOD$_5$/COD ratio decreased at all doses of the reagent. This is due to faster BOD$_5$ reduction than COD reduction as a consequence of the reaction of hydrogen peroxide with the biodegradable components of HHT (Barbunski et al., 2001).

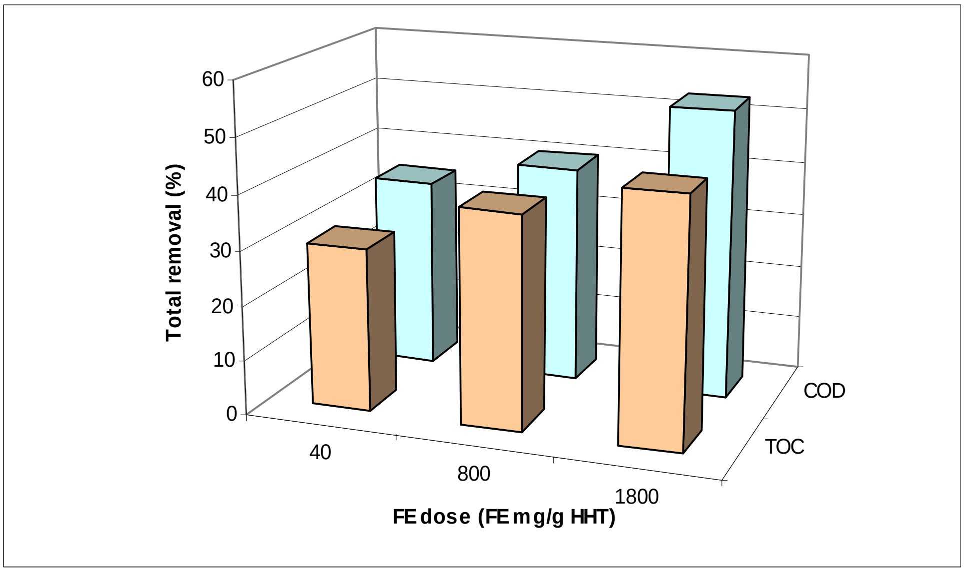

Figure 4.11. Relative COD and TOC removal by FE dose in US2/FE after 4 h at pH=3.0.

4.9.3. Fenton with Ultrasound and UV light (US2/FE/UV)

The process was run in the US bath with the UV lights (1.56 Watts m-^{2}) turned on. Dosing of Fenton reagent was the same as in the previous experiments. The results are summarized in Table 4.28 and presented in Figure 4.12 as bars.

Table 4.28. Impact of UV added Sono-Fenton process on HHT degradation after 4 h.

FE dose (mgFE/g HHT)	**% Reduction**		
	COD	**TOC**	**COD/BOD$_5$**
40	32	21	18
800	45	44	11
1800	48	47	12

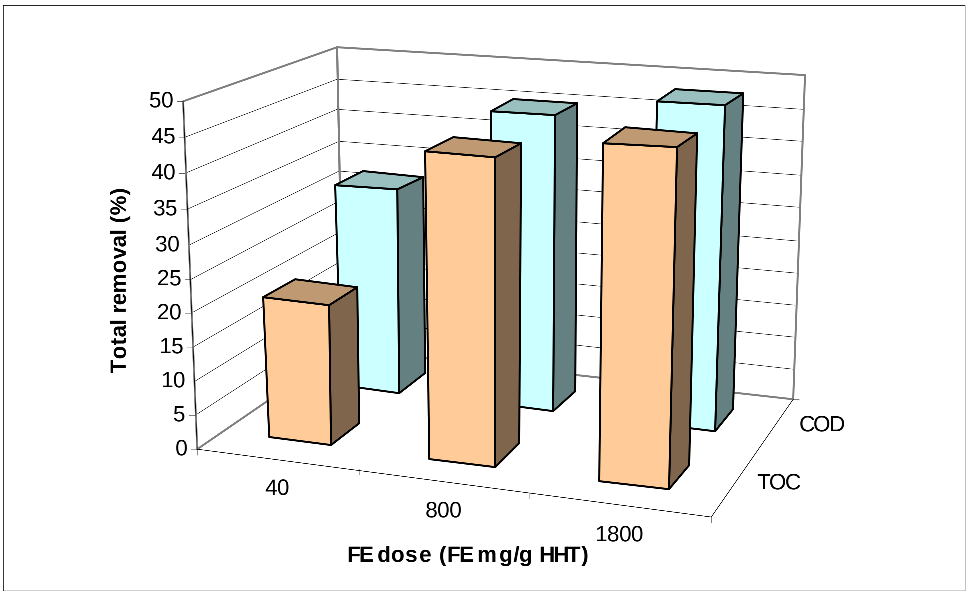

Figure 4.12. Relative removal of COD and TOC by US2/FE/UV after 4 h reaction at pH=3.0.

It was found that irradiation of the solution by low intensity UV radiation produced a remarkable enhancement in the degradation of HHT. Total COD and TOC reduction in 4 h was 48 % and 47 %, respectively at the maximum dose of the Fenton’s reagent. The data also showed that very high doses of the reagent did not bring significant advantage in COD and TOC abatement.

In addition, the process rendered more than 30 % increase in the BOD_5/COD ratio at the lowest dose of the reagent as shown in Table 4.29.

Table 4.29. Alterations in BOD_5/COD ratio in US2/FE/UV after 4 h reaction at pH=3.0.

FE dose (mgFE/g HHT)	**BOD_5/COD**	
	t=0	**t=4 h**
40	0.64	0.78
800	0.62	0.70
1800	0.58	0.66

5. COMPARATIVE EVALUATION OF THE TEST PROCESSES

A list of all chemical processes, their operating conditions and the relative efficiencies is given in Table 5.1 and Table 5.2, respectively. In addition, relative treatability of HHT at pH 3 by each process is presented in Figure 5.1 (a) and 5.1 (b) for total COD elimination and mineralization, respectively.

Table 5.1. List of test processes and operating conditions.

Process description	**Contact time (h)**	**pH**	**Reagent Dose**
1. Single-Step			
U1(US Bath open)	4	3, 7, 10	_
U2(US Bath closed)	4, 8	3, 7, 10	_
UP (US Probe)	0.5	3, 10	_
UV1 (UV Column)	1, 2, 3	10	_
UV2 (Hybrid-without US)	4	3, 7, 10	_
U2/UV (Hybrid/UV)	4, 8	3, 7, 10	_
H-H_2O_2	4	3	1:1, 3:1, 6:1 (M:H_2O_2:M HHT)
FE (Fenton)	4	3	40, 800, 1800 (mg FE/g HHT)
U2/FE (US bath/Fenton)	4	3	40, 800, 1800 (mg FE/g HHT)
U2/FE/UV (Hybrid/Fenton)	4	3	40, 800, 1800 (mg FE/g HHT)
2. Consecutive	Contact time (h)	pH	Reagent Dose
U2+UP	4 + 0.5	3, 10	_
U2/UV+UP	4 + 0.5	3, 7, 10	_

Table 5.2. Relative efficiencies of the test processes for HHT degradation (C_0 =0.05 M).

Process	pH	Time (h)	Reagent Dose	% Reduction		
				COD	TOC	COD/BOD_5
U1	3.0	4.0	_	34	14	41
	7.0			38	21	30
	10.0			32	7	34
U2	3.0	4.0	_	25	8	30
	7.0			17	12	13
	10.0			15	6	23
	3.0	8.0	_	27	16	24
	7.0			25	14	21
	10.0			17	7	8
UP	3.0	0.5	–	21	19	30
	10.0			11	10	23
UV1	10.0	1.0	_	6	4	21
		2.0		10	6	29
		3.0		15	7	34
UV2	3.0	4.0	_	2	0	0
	7.0			0	0	0
	10.0			8	0	3
U2/UV	3.0	4.0	_	11	5	19
	7.0			6	2	3
	10.0			14	7	31
	3.0	8.0	_	20	14	30
	7.0			17	9	17
	10.0			37	21	29
H_2O_2	3.0	4.0	(M:M HHT)			
			1:1	12	10	8
			3:1	13	14	39
			6:1	18	19	35
FE – Fenton	3.0	4.0	(mg:g HHT)			
			40:1	35	33	-
			800:1	37	36	-
			1800:1	58	22	2
U2/FE	3.0	4.0	(mg:gHHT)			
			40:1	35	30	-
			800:1	45	39	-
			1800:1	53	45	-
U2/FE/UV	3.0	4.0	(mg:gHHT)			
			40:1	32	21	18
			800:1	45	44	11
			1800:1	48	47	12
U2+UP	3.0	4.5	_	32	18	35
	7.0			20	12	18
	10.0			26	9	28
U2/UV+UP	3.0	4.5	–	20	7	6
	10.0	4.5		22	9	16

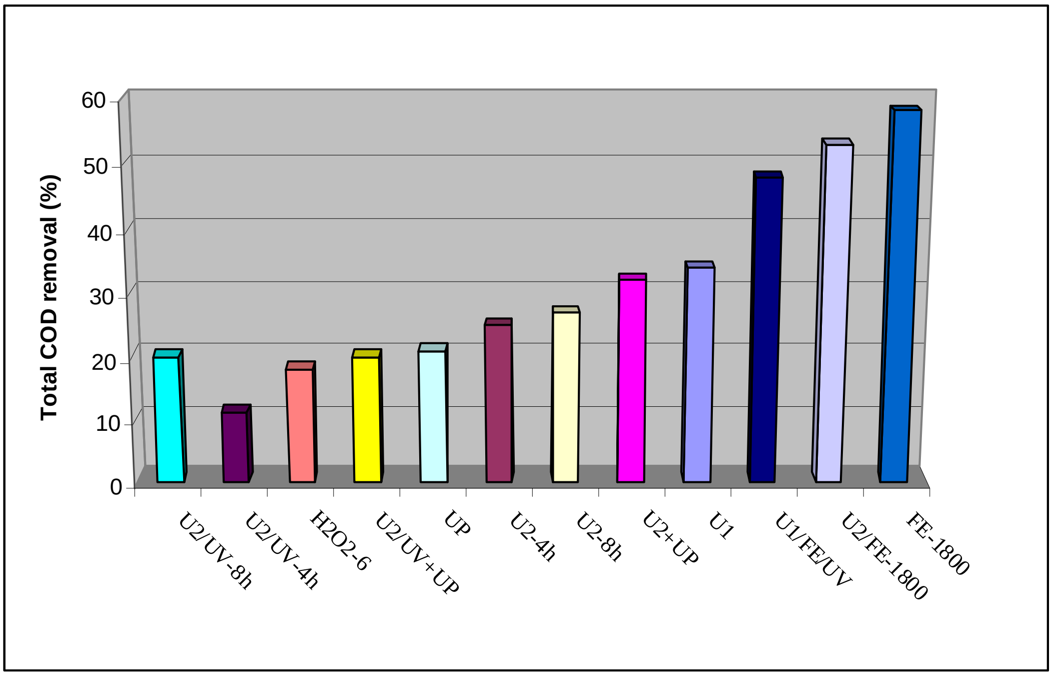

Figure 5.1. (a) Relative effectiveness of the test processes for total COD removal (pH=3.0).

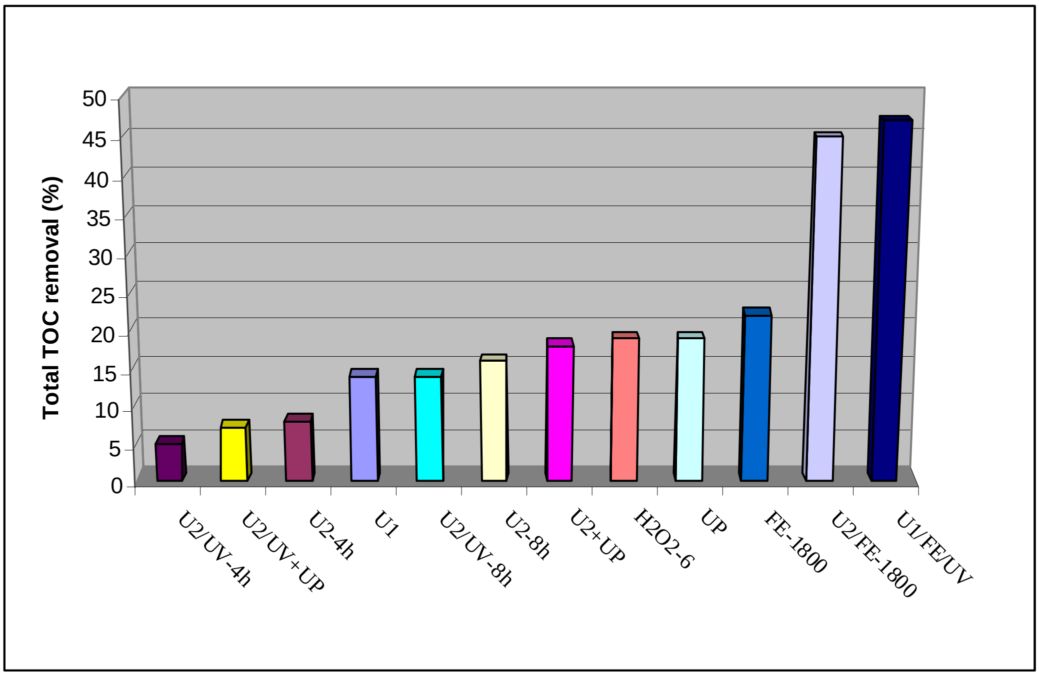

Figure 5.1. (b) Relative effectiveness of the test processes for mineralization (pH=3.0).

The data show that the best two processes for COD and TOC elimination are “Sono-Photo-Fenton” (U1/FE/UV) and “Sono-Fenton” (U2/FE) operated at pH 3.0 for 4 h at a Fenton’s reagent dose of 1800 mg g^{-1} HHT. On the other hand, the two best processes for biodegradability enhancement is sonication in the bath for 4 h at pH 3.0 during atmospheric contact (U1), and reaction with H_2O_2 (dose = 3:1 by M) for 4 h at pH 3 (H_2O_2).

6. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

The research presented here is about the treatability of formaldehyde-based biocides such as hexahydrotriazine (HHT) in an ultrasonic bath operated individually, sequentially (before an ultrasonic probe) or simultaneously with an advanced oxidation processes (AOP). The objective was to select the most suitable process and its optimal operating conditions for the pre- or post-treatment of HHT containing wastewaters.

It was found that the most important control parameter in all test systems was pH, and treatability was generally favored at acidic pH due to easier hydrolysis of the compound at this condition (to release formaldehyde). Reactor temperature was also a crucial parameter, as uncontrolled raises in temperature (when the bath was closed to atmospheric contact to avoid evaporation and splashing of the solution) lowered the performance of the processes and altered pH effects. In addition, contact time and reagent dose (H_2O_2, Fenton's) were critical parameters affecting the efficiency of the processes.

In general, it was found that a low power ultrasonic bath alone was not effective for acceptable level of COD and TOC elimination in HHT solutions, but was effective for increasing the biodegradability when operated at acidic pH and atmospheric contact. The effectiveness of the bath was significantly enhanced when it was operated sequentially before sonication with an ultrasonic probe, or simultaneously with UV irradiation and Fenton process. The synergy was the result of OH radical formation and increased mass transfer rates. A more specific summary of the conclusions is given in the following:

1) Maximum enhancement in BOD_5/COD ratio (or biodegradability) was obtained:
    - At pH 3 in the bath when operated individually under "open" and "closed" conditions, and when operated simultaneously with Fenton's reaction and UV irradiation.

   - At pH 10 in the bath when operated with UV irradiation followed by sonication by the probe. Lowered biodegradability at pH 7 was attributed to the formation of a colored complex.

2) Maximum COD removal was obtained:
   - At pH=3.0 and 7.0 in the bath under “closed” and “open” conditions, respectively.
   - At pH=3.0 in the probe reactor.
   - At pH=10 in the hybrid reactor (operated with UV irradiation).
3) Maximum mineralization was obtained:
   - At pH=7.0 in open and closed baths operated for 4 h.
   - At pH=3.0 in closed bath operated for 8 h and in the probe reactor.
   - At pH=10 in the hybrid reactor.
   - At pH 3.0 in the sequential operation.
4) Operation of the bath for 8 h enhanced the efficiency of the hybrid reactor for COD and TOC reduction, and for biodegradability enhancement at pH 3 and 7.
5) The bath was more effective when operated at “open” conditions, due to lower temperatures, volatilization (of some intermediate products) and the intake of CO_2 leading to the formation CO_3 radicals, which is a powerful oxidizing agent.
6) Higher mineralization was possible in the probe reactor operated for 30 min than in the bath operated for 4 h. The difference was attributed to the larger power effectiveness of the probe ($0.17\ W\ mL^{-1}$ vs $0.039\ W\ mL^{-1}$) and cooling of the probe reactor to 20 ^{o}C at all times.
7) Photolysis was not an alternative degradation pathway for HHT under the applied UV intensity ($3.31x10^{-6}$ Einsteins $m^{-2}\ s^{-1}$), as 2 %, 0 % and 8% improvement was observed in COD reduction at pH=3.0, 7.0, 10.0, respectively after 4 h reaction in the hybrid reactor. Photolysis can be considered only if the intensity of UV irradiation is significantly increased and the lamp is inserted axially through the center of the reactor.
8) Sequential application of the probe after closed bath improved COD and TOC reduction by 1.3 and 2.2 fold, respectively and led to 1.3 fold biodegradability enhancement, but the efficiency was lower than that of the open individual bath application for 8 h.

9) Fenton reaction was the most effective pathway for HHT degradation in terms of COD and TOC reduction, but not for biodegradability enhancement due to inhibition of sewage bacterial growth by excess Fe^{+2} and H_2O_2.

The recommendations for future work:

The study has shown that hexahydrotriazine-based biocides are non-biodegradable and require advanced treatment operations either to enhance their biodegradability before discharge to sewage treatment operations, or to convert them to non-toxic intermediates after treatment in biological systems. Hence, more extensive research involving advanced techniques (e.g. adsorption, membrane separation, ozonation) or biotechnological methods (e.g. generation of microorganisms that are capable of metabolizing the biocide) is required to propose alternative methods for the ultimate treatment of HHT containing process effluents or waste streams.

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