Treatment of ibuprofen containing industrial first wash-water by ozonation, sonication, ozonation/H_2O_2, ozonation/sonication, and sonication/H_2O_2

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ABSTRACT

Ibuprofen (IBP) is one of the most prescribed drugs. It has been shown that IBP resist physicochemical wastewater treatment (Gagnon and Lajeunesse 2008). Also, IBP has a known negative effect on algae (Brown et al. 2007). This research focused on removal of aqueous IBP using five different oxidative techniques: ozonation, ozonation with hydrogen peroxide, ozone with sonication, sonication with hydrogen peroxide and sonication alone. IBP and chemical oxidation demand (COD) removals were monitored for experiments performed over a range of operating conditions: pH (4 to 7), temperature (5 to 25ºC), applied ozone dose (8 to 16 mg/L) and applied power 5 watts. Solutions of 5 mg/L IBP were treated in a custom-designed semi-continuous 900-mL reactor. The design allowed the application of ozone and ultrasounds from the bottom of the reactor either separately or simultaneously. A synergic effect was observed for the combined treatment O_3/sonication. This might be explained by the higher mass transfer of ozone in the solution observed in presence of ultrasounds. Although H_2O_2 significantly increased the IBP removal when used in combination with O_3, the addition during sonication did not result in increased IBP removal. Four transformation products were detected as new peaks on the HPLC chromatograms. Oxo-ibuprofen, 4-acetylbenzoic acid, 4-ethybenzaldehyde and oxalic acid were identified as products using LC/MS. COD analyses indicated low degrees of mineralization in the range of 11 to 41%. The highest IBP and COD removals of 95% and 41% were obtained with O_3/H_2O_2 performed at 15ºC and pH 7. Optimized parameters for each technique were applied to IBP contained in first wash-water produced at an ibuprofen processing plant (Wyeth, St-Laurent, Quebec, Canada). The industrial first wash water had an IBP concentration of 582ppm. All experiments with first-wash-water were compared to results obtained in a synthetic solution of equivalent IBP concentration in pure water. For all oxidation techniques, a higher IBP removal was obtained in the wash-water and the highest IBP removal of 16% was obtained with O_3/H_2O_2. To the author's knowledge, this project was the first study comparing all these techniques and considering the treatment of first wash-water of an industrial plant.

SOMMAIRE

L'ibuprofène (IBP) est un des composés pharmaceutiques les plus prescrits. L'IBP résiste au traitement physico-chimique des eaux usées (Gagnon and Lajeunesse 2008). L'IBP a également été identifié comme ayant des effets négatifs sur des algues (Brown et al. 2007). Cette recherche s'est concentrée sur l'élimination de l'IBP aqueux par cinq techniques d'oxydation dont l'ozonation, l'ozonation couplée au peroxyde d'hydrogène, l'ozonation couplée à la sonification, la sonification couplée au peroxyde d'hydrogène et la sonification seule. La diminution d'IBP et la demande chimique en oxygène ont été déterminées pour chaque technique oxydative opérées sous les paramètres d'opération suivants : pH (4 à 7), température (5 à 25ºC), dose d'ozone (8 à 16 mg/L) et puissance de sonication (0-5 Watts). Une solution de 5 ppm d'IBP a été traitée dans un réacteur semi continu de 900 mL conçu pour ce projet. Le design de ce réacteur permet au bas du réacteur l'alimentation d'ozone et l'émission d'ultrasons, séparément ou simultanément. Un effet synergique a été observé lorsque l'ozone est combiné à la sonification. Cette synergie peut être expliquée par l'augmentation du transfert de masse de l'ozone dans la solution due au champ d'ultrasons. L'ajout de H_2O_2 a augmenté significativement l'élimination d'IBP lorsque combiné avec l'ozone. L'addition durant la sonification a démontré aucun effet. Quatre produits de transformation ont été identifiés par LC/MS : oxo-IBP, acide 4-acetylbenzoïque, 4-athylbenzaldehyde et l'acide oxalique. Les analyses de COD ont indiqué un degré de minéralisation allant de 11 à 41%. L'élimination la plus significative d'IBP et de COD a été de 95% et 41%, obtenu lors du traitement avec l'O_3/H_2O_2 à une température de 15ºC et un pH de 7. Les paramètres optimaux pour chaque technique d'oxydation ont été appliqués à une eau de premier lavage d'un procédé industriel de comprimés d'ibuprofène fourni par Wyeth, St Laurent, Québec, Canada, ayant une concentration d'IBP de 582 ppm. Une plus grande élimination d'IBP a été obtenue dans l'eau de lavage comparativement à une solution synthétique de même concentration et ce, pour chaque technique étudiée. La plus importante élimination d'IBP dans l'eau de lavage, d'une valeur de 16%, a été obtenue avec le traitement d'O_3/H_2O_2. Selon l'auteur, cette étude constitue une première comparaison systématique de ces techniques et la première étude du traitement d'une première eau de lavage industrielle.

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1. Introduction

Water pollution is a known problem. They're a conscientious about the fact that water is a fundamental resource and a necessity for life. Water contamination can affect individual species, but also biological communities.

The presence of pharmaceuticals in water is a problem, which has concerned the scientist community for a few decades. Pharmaceutical consumption, and thus production, has greatly increased for the last two centuries (Bond 2003). The human body only absorbs a small part of these pharmaceuticals or these are transformed into metabolites sometimes similar to their original compound.

A part of these drugs consumed by millions of people get into the environment after excretion. This is the main way that pharmaceutical products contaminate water, but it is not the only way. Pharmaceutical companies also release large amounts of pharmaceutical compounds legally along with their wastewater. Yearly, in the U.S.A., manufacturers legally release at least 271 million pounds of pharmaceuticals in wastewater (Donn et al. 2009). No estimate of yearly release is available for Canada but the situation is the same in Canada considering that as in the U.S.A., there are no regulations in regarding the discharge of pharmaceuticals in sewage. This problematic could lead to more severe regulations in the future years for the pharmaceutical processing plants. The pharmaceuticals companies have to rapidly identify the best ways to treat the wastewaters in order to control/minimize the discharge of pharmaceuticals in sewage systems.

This research focuses on non-steroidal anti-inflammatory drugs (NSAID), more specifically ibuprofen, which is widely used and produced in large quantities. Ibuprofen has a known effect on algae (Brown et al. 2007). It has been shown that ibuprofen and its metabolites resist physicochemical wastewater treatment and the biological treatment seems to transform the ibuprofen into the same metabolites (Gagnon and Lajeunesse

2008). The necessity of additional treatment or pre-treatment of industrial wastewater is obvious. Consumption of ibuprofen is very common in a lot of countries (Hudec et al. 2008) so its production is also considerable. The amount of ibuprofen released into the environment by the drug makers should be reduced to decrease the total amount of this drug in the environment.

Some experiments have been done with different treatments, such as with ozonation sonication and hydrogen peroxide, to determine the efficiency of these techniques at removing IBP. This project focused on the comparison of the efficiency of these three techniques, applied separately or in combination to remove ibuprofen from a wash-water stream produced at an IBP processing plant. The main objective of this Masters project was:

> To identify which of ozonation, ozonation/H_2O_2, ultrasound (US) removal, ozonation/US and US/H_2O_2 is the most appropriate treatment method for the removal of ibuprofen from a first wash-water produced by an ibuprofen processing plant (Wyeth, St-Laurent, Quebec, Canada). Each method was evaluated based on their efficiency to remove ibuprofen.

The literature review presented in section 2 starts with an overview of the impact of the pharmaceutical products on the environment and the effect of ibuprofen on the environment. The studies already done to remove this compound and more specifically the studies using techniques of interest: ozonation, sonication and hydrogen peroxide are discussed. The setups used to study these techniques are also discussed. The following section describes analytical techniques that were used to measure the chemical oxygen demand (COD), the amount of hydrogen peroxide in water, the quantity of ozone in water, the concentration of ibuprofen and the power dissipated by the frequency transducer.

For this project**,** a reactor able to perform sonication, ozonation and addition of hydrogen peroxide, both separately or simultaneously, was designed and built. This reactor allowed

comparison of the efficiencies of these techniques (either alone or in combinations). The design of this reactor is described in section 4. Section 5 discusses the results of the experimental plan while conclusions and recommendations are provided in the last section of the thesis.

2. Background

2.1 Pharmaceuticals in our environment

About two decades ago pharmaceutical products (PP) were recognized as contaminants of emerging interest and were identified as contaminants not efficiently removed during conventional wastewater treatment. The presence of pharmaceutical products in treated municipal wastewater gives an idea of the extent of the problem. In 2007, researchers registered 3000 pharmaceutical products and transformation products present in this type of water (Schultz and Furlong 2008). The biological activity of these compounds can lead to negative effects on the ecosystems such as diminution of the total number of species because of the high levels of bioaccumulation (Fent et al. 2006). In some cases the transformation products are even more detrimental than the pharmaceuticals and contribute to the toxic effects on the environment. For example, some studies showed that transformation products of carbamazepine and bronopol are more toxic than their parent compound (Cui et al. 2010) (Kosjek and Heath 2008). Currently, many studies have been conducted to determine the occurrence of pharmaceuticals in waters all around the world and to investigate their fate in river and wastewater treatment plants (Kolpin et al. 2002; Brun et al. 2006; Chen et al. 2006; Gagné et al. 2006; Lishman et al. 2006; Servos et al. 2007; Yargeau et al. 2007; Araujo et al. 2008; Besse and Garric 2008; Comeau et al. 2008; Gagnon and Lajeunesse 2008; Siemens et al. 2008; Loganathan et al. 2009). Some studies also tried to evaluate the risk associated with pharmaceuticals in the aquatic ecosystems and identify the pharmaceutical products degraded into toxic compounds when passing into a sewage or wastewater treatment plant. (Pérez and Barceló 2007).

2.2 Sources of pharmaceutical contamination

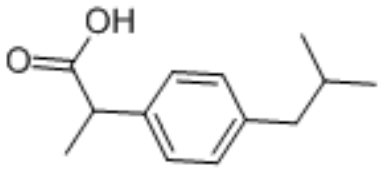
Active pharmaceutical products present in surface waters enter the environment by many routes. The principal source of contamination is through human consumption. When a drug is administered to a person, the human body may metabolize as less as 10% of this compound, therefore up to 90% of a drug administered may end up into the environment unchanged (Ferrari et al. 2003). Also, 50% of the metabolites formed in the human body are very similar to the initial compound and may remain bioactive (Farré et al. 2008). Pharmaceuticals can also come directly from the disposal of unused and expired drugs and from effluents of the pharmaceutical industry sent to municipal sewage without any treatment. For specific industries, such as for the pulp and paper industry and the petroleum industry, there are some regulations on the quality of their effluent, but until now, no regulations govern the pharmaceutical industries wastewater effluents other than the basic parameters such as the chemical oxygen demand (COD), biological oxygen demand on five day (BOD_5), the mineral content including water hardness, the amount of suspended matter and the pH of the water (Gouvernement du Quebec 2002). In fact, pharmaceuticals are organic compounds, which are recognized as harmless to human health if administered properly. However, little is known about the fate of these products in the environment and in engineered systems. The risk associated with pharmaceuticals in the environment has yet to be fully assessed. Now that the presence and persistence of these compounds in the environment have raised significant concerns, we can expect that rules and regulations going to be implemented soon to control pharmaceutical concentrations in industrial effluents. Pharmaceutical companies must be pro-active in identifying ways to treat their effluents.

2.3 Pharmaceutical of interest

One of the most prescribed categories of drugs is the non-steroidal anti-inflammatory drug (NSAID). Approximately 40% of the environmental studies assessing the presence of pharmaceutical products in water include this class of drug (Mompelat et al. 2008). The pharmaceutical of interest for this research is ibuprofen, which falls under this category. Ibuprofen is the second most studied drug in all the wastewater treatment plants

with a frequency of approximately 20% (Miège et al. 2009). The most studied technology to remove this compound was ozonation (Esplugas et al. 2007). The following figure represents the structure of the ibuprofen molecule.

Figure 1 : Structure formula of ibuprofen



A recent study showed that Montreal wastewater treatment does not efficiently eliminate this compound (Gagné et al. 2006). The following table shows data obtained from wastewater treatment plants (WWTP) and municipal sewage treatment plants (MSTP) in Canada and a few other countries. These data show the important quantities of ibuprofen released in the environment along with treated municipal wastewater.

Table 1 : Influent/ effluent concentrations and percentage of removal for various sewage and wastewater treatment plants around the world

Country	Treatment plant	Mean influent concentration (µg/L)	Mean effluent concentration (µg/L)	% removal	Reference
Canada	WWTP over Thames rivers	8.45	0.384	80-90	(Lishman et al. 2006)
	WWTP of Montreal		0.786		(Gagné et al. 2006)
	WWTP of Windsor		0.176		(Servos et al. 2007)
Germany	WWTP		0,37	74-94	(Ternes 1998)
Switzerland	WWTP over Lake Greifense		0,18	75-90	(Tixier et al. 2003)
USA	MSTP (Southern California)		0,79		(Loraine and Pettigrove 2006)

Furthermore, ibuprofen is found to be enough persistent in the environment to show pharmacological effects on aquatic fauna (Brown et al. 2007). The IBP half-lives have been estimated in wastewater but varied significantly from one study to another: 1-2 day (Kosma et al. 2010) and 10 hours (Gros et al. 2010). Another problem associated with this PP is the synergic effect with the other pharmaceutical compounds present in the environment. In the algae and fish, synergetic effects were observed with some NSAIDs including ibuprofen, clofibric acid and carbamazebine. This mixture of compounds led to an increase in toxicity higher than expected when observing the EC_{50} on *Daphnia* (Cleuvers 2003). Ibuprofen is sold as an enantiomer molecule. It was shown that the two chiral molecules don't have the same rate of removal. One of them degrades more rapidly under anaerobic conditions while the other degrades more rapidly under aerobic condition (Matamoros et al. 2009). This study also suggests that these two enantiomers degrade into different compounds depending on the molecule structure. These results indicate that the ratio of the two-ibuprofen molecular structures can also influence the IBP removal at a specific step in a WWTP.

The two major human metabolites produced are the hydroxyl-ibuprofen (OH-IBP) and the carboxyl-ibuprofen (CB-IBP) (Zwiener and Frimmel 2003). These two compounds, having similar structure to ibuprofen, were found in the wastewater treatment effluents and are also not efficiently removed during wastewater treatment (Stumpf et al. 1999). OH-IBP is found in greater quantity than the CB-IBP. It was also found that biological wastewater treatment also transforms ibuprofen into OH-IBP during aerobic removal while under anoxic condition, ibuprofen degrades to CB-IBP (Quintana et al. 2005; Pérez and Barceló 2007; Farré et al. 2008).

2.4 Ibuprofen transformation products

Another problem associated with ibuprofen is the toxicity of some known transformation products issued from thermal removal and removal by reagent like $KMnO_4$, H_2O_2 and K_2CrO_7. In a study conducted in 2002, at least 13 products issued from these oxidations were reported (Caviglioli et al. 2002) and of these products two were recognized as toxic;

4-isobutylacetophenone (4IBAP) and 1-(4–isobutylphenyl)-1-ethanol. The latter molecule is an intermediate in the conversion of ibuprofen into 4IBAP. The molecular structures of these two compounds are shown in the following figures. In addition, Zorita et al. showed that 4IBAP was present in the influent of a wastewater treatment plant in Sweden (Zorita et al. 2009).

Figure 2 : Structure formula of 1-(4–isobutylphenyl)-1-ethanol

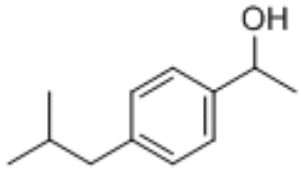
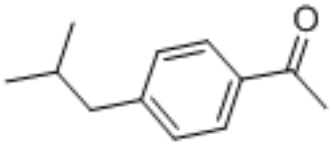


Figure 3 : Structure formula of 4-isobutylacetophenone (4IBAP)



Some work on ibuprofen removal was done by (Caviglioli et al. 2002) in order to identify the mechanism of transformation of IBP in presence of different oxidants. Other researchers also investigated its removal in order to identify the advanced oxidative technology offering the highest IBP removal potential (Wert et al. 2009). It is however important to consider that the removal of a PP by different advanced oxidation processes (AOP's) involved different types and amounts of oxidants such as hydroxyl radical and ozone and that these can lead to different transformation products having different toxicity.

Some empirical equations for the removal of IBP by ozonation were developed to model the removal behaviour of IBP (Huber et al. 2003). In one study, IBP was shown to degrade slowly with ozone similarly as *para*chlorobenzoic acid (pCBA). In this work, the removal of pCBA was also monitored and was used as a probe to demonstrate that ibuprofen degraded by radical hydroxyl exposure (Huber et al. 2003). At the moment,

most pharmaceutical transformation products present in the effluent of advanced oxidative treatments (AOT) have yet to be identified.

Also, considering the low efficiency of the primary and secondary wastewater treatment approaches to remove ibuprofen, as presented in the previous section, researchers have started to investigate advanced treatment methods as described in the following section.

3. Review of advanced treatment approaches

Since a few decades, some researches were done with different technologies, which can potentially oxidize aqueous ibuprofen directly or from hydroxyl radical. The optimal goal of these applications is to degrade the pharmaceutical and organic compounds into CO_2 and inorganic ions. These technologies include ozonation, ozonation coupled with peroxide, ultraviolet process, the Fenton process, the oxidation with Fe (VI), the ultrasonic treatment and the electrochemical process.

Common AOP processes weren't experimented with pure ibuprofen like ozonation in presence of a catalyst and ozone and ultrasound together. A list of all research focusing on the removal of ibuprofen in pure water or other matrix is shown in the following table.

Table 2 : Oxidation processes studied for the removal of ibuprofen

Process	Reference	Type of water	% removal	Operating parameters (tr = Reaction time)	Comment
Ozonation	(Gagnon and Lajeunesse 2008)	Wastewater	48-82%	Ozone dose : 3.6-15	-Detection of transformation products wasn't performed but with the result obtained, the amount should be significant
Ozonation/peroxide	(Zwiener and Frimmel 2000)	Drinking Water Treatment Plant (DWTP)	70%	tr=10 min, C_{03}=1 mgL^{-1}, C_{H202}=0.5 mgL^{-1}	-Detection of transformations products wasn't performed but with the result obtained, the amount should be significant
Ultraviolet process	(Yuan et al. 2009)	Mix of pharmaceutical in pure water	24%	pH=7, UV=1272 mJ/cm^2	-Poor level of efficiency
UV/H_2O_2 Process	(Yuan et al. 2009)	Mix of pharmaceutical in pure water	42%	pH=7, 1nM H_2O_2 UV=40mJ/cm^2	-Poor level of efficiency
Electro-Fenton process (solar)	(Skoumal et al. 2009)	IBP in pure water	86%	pH=3, tr=3 h, E/V=4.3 kWh/m^3	-High amount energy required for industrial application - High persistent transformation products formed - Complete mineralization of IBP
Oxidation of the drug with Fe (VI)	(Sharma and Mishra 2006)	IBP in pure water	-	-	-The half lives may not be practical to apply Fe(VI) in removing ibuprofen in water
Ultrasonic treatment	(Méndez-Arriaga et al. 2008)	IBP in pure water	98%	pH=3, tr=30min P=80 W	-High level of transformation product formed
Chlorine dioxide treatment	(Huber et al. 2005)	DWTP, lake, groundwater and ibuprofen in pure water	≈0%	-	-Ibuprofen doesn't react with applied chlorine dioxide amount
Electrochemically process	(Ciríaco et al. 2009)	IBP in pure water	100%	pH=6.47, tr=6 H	-High amount energy required for industrial application -Decrease of 48 to 92% TOC

When observing the previous table**,** it is difficult to compare the efficiency of the various approaches studied in order to select one for study at larger scale and there is clearly a lack of information about the formation of transformation products during removal. Some techniques presented earlier are very expensive for operation at large scale and there are processes, which do not work with ibuprofen. Currently, some researches (Zwiener and Frimmel 2000; Yuan et al. 2009) have considered a combination of oxidation processes to ensure that ibuprofen is completely removed from wastewater. Some processes are better producers of hydroxyl radicals than others. As discussed before, it is known that ibuprofen, similarly to other compounds, degrades more rapidly with hydroxyl radicals compared to ozone on its own.

It is important to note that when dealing with a multi-organic component matrix, which consists of several organic compounds, some of these compounds can be easily degraded with ozone alone. If ibuprofen is present in this matrix, it may degrade more efficiently when ozone is coupled with another oxidant, which leads to a higher production of selective hydroxyl radicals. Only little research shows comparison of ibuprofen removal between ibuprofen in pure water solution and a multi-organic component matrix solution.

In the following section, the important results of previous research related to AOP processes pertinent to this project are reviewed. First, ozonation is discussed, since it is the most common treatment studied for removal of PP's. Also, ozonation coupled with hydrogen is presented. It is important to note that although the Fenton process is the most frequently used approach to produce hydroxyl radicals at the industrial level (Esplugas et al. 2007), this method is not part of the scope of this project. The technique based on sonication, also known to produce a large amount of hydroxyl radical, is instead considered in the following section. Lastly, the results of the few studies coupling these processes, sonication/ozonation and sonication/hydrogen peroxide, are summarized.

3.1 Ozonation and Ozonation coupled with H_2O_2

Studies on ozonation of ibuprofen showed that conventional ozonation (O_3 only) does not efficiently degrade ibuprofen and its derivative compounds (Zwiener and Frimmel 2000). This resistance to removal by O_3 might be explained by its oxidized state provided by its functional groups (hydroxyl and carboxylic moieties) which are more sensitive to (•OH) hydroxyl radical than O_3 (Zwiener 2007). It was shown that the limited availability of hydroxyl radicals in the initial stage of the ozonation makes ibuprofen difficult to degrade (Wert et al. 2009). During ozonation, ibuprofen starts to degrade mainly after the instantaneous ozone demand (IOD) period is complete. This IOD period is defined as the period when O_3 gets dissolved in water and during which less •OH radicals are present.

The pH is also an important factor considering that the production of hydroxyl radicals from the decomposition of ozone is higher at alkaline pH's (Oh et al. 2007). This study showed that a change in pH from 5 to 7 can have a significant effect on the percentage of removal of ibuprofen. The following table illustrates the percentage of removal for the same initial ozone concentration at different pH levels.

Table 3 : Removal percentages at different pHs for an initial IBP concentration of 10 µM in pure water (Oh et al. 2007)

pH	Percentage of removal	Ozone concentration
5	10%	0.4mg/L
7	95%	0.4mg/L

By measuring the difference of dissolved organic compound (DOC) at the beginning and at the end of an experiment, it is also possible to evaluate the degree of mineralization during the oxidative process experiment. For example, in the ozonation removal experiment of Oh et al. 2007, 95% removal of ibuprofen was achieved but only a decrease of less than 10% of the DOC was observed. Also it was shown that the

transformation products of ibuprofen subjected to ozonation are less hydrophobic and have a higher polarity (Oh et al. 2007).

Ozonation coupled with hydrogen peroxide helps to produce more hydroxyl radicals and achieve a better removal of ibuprofen compared to ozonation alone (Wert et al. 2009). A small fraction of ozone concentration is converted into hydroxyl radicals in a batch reactor. The important operating parameters for ozonation and for O_3/H_2O_2 studied in previous experiment with a batch reactor are:

- pH
- Concentration of ozone
- Concentration of hydrogen peroxide
- Temperature
- Initial amount of ibuprofen
- Reaction time

The following table summarizes experiments performed to remove ibuprofen by ozonation and ozonation coupled with hydrogen peroxide. These results showed that ozonation, applied alone of in conjunction with H_2O_2, remove less ibuprofen.

Table 4 : Experiments performed on the removal ibuprofen by ozonation

Process	Reference	Types of water	% Removal	Operation parameters	Comment
Ozonation	(Huber et al. 2003)	DWTP	41%	tr=10 min, C_{03}=2 mgL^{-1}, C_0=0.5 μM, pH=8	-Detection of transformations products wasn't performed but formation is expected
	(Gagnon and Lajeunesse 2008)	Municipal Wastewater	48-82%	Ozone dose : 3.6-15	
	(Zwiener and Frimmel 2000)	DWTP and distilled water	12% (distillate)	tr=10 min, C_{03}=1 mgL^{-1}, C_0=2 ugL^{-1}, pH=2	
	(Wert et al. 2009)	WWTP water	≈20%	tr≤10 min, C_0=75 ngL^{-1}, C_{03}=2.5 mgL^{-1}, pH=7.1	
	(Oh et al. 2007)	DWTP and pure water	95%	tr=12 min, C_0=10 μM, C_{03}=0.4 mgL^{-1} pH=7	- DOC drop of 10% mean that some transformation products are formed
Ozonation Hydrogen Peroxide	(Huber et al. 2003)	DWTP and lake water	84%	tr=10 min, C_{03}=2 mgL^{-1} C_{H2O2}=0.7 mgL^{-1}, pH=8	-Detection of transformations products wasn't performed but formation is expected
	(Zwiener and Frimmel 2000)	DWTP	70%	tr=10 min, C_{03}=1 mgL^{-1}, C_{H202}=0.5 mgL^{-1}, pH=2	

3.2 Sonication and sonication coupled with H_2O_2

When water or organic compounds are exposed to ultrasonic irradiation, the propagation of the ultrasonic waves leads to a phenomenon called cavitations. This phenomenon is occurring at frequencies of 20 kHz or above. With successive cycles of exposure to rarefaction and compression zones, "cavitations bubbles" are formed and grow until they become unstable and implode. At this time the sudden collapse releases a significant of heat flow creating what is called "hotspots". Within these "hotspots" the temperature and pressure reaches values as high as 2000-5000ºC and 200atm, respectively (Ince and Tezcanlí 2001). Under these conditions water dissociates in two radicals:

$$H_2O +))) \rightarrow \bullet OH + \bullet H \quad [1]$$

Following this, the radical hydrogen combines with oxygen to form perhydroxyl radical:

$$\bullet H + O_2 \rightarrow \bullet OOH \quad [2]$$

Both perhydroxyl and hydroxyl radicals can then form hydrogen peroxide:

$$2\bullet OH \rightarrow H_2O_2 \quad [3]$$

$$2\bullet OOH \rightarrow H_2O_2 + O_2 \quad [4]$$

In the work done by Mendez and al. (Méndez-Arriaga et al. 2008), it was shown that a 98% removal of ibuprofen was achieved in 30 minutes of sonication (power of 80 W, a frequency of 300 kHz, initial concentration of 21ppm, pure water). However, the COD analysis indicated a low degree of mineralization suggesting the accumulation of transformation products in the ultrasonic reactor. After 120 minutes of ultrasound treatment, a decrease of COD of only 8% was observed. The important parameters to consider during sonication are the following.

- Ultrasonic frequency

- Power applied
- Temperature
- Amount of dissolved gas in the solution
- pH
- Initial concentration of ibuprofen
- Treatment time

It was shown that the rate of hydroxyl radicals formation increases for a 20, 200 and 500 kHz transducer of similar diameter and same applied power, but the rate stays stable for further increase of frequency between 500 and 800 kHz (Isariebel et al. 2009). Lower frequencies are desired because it is easier to operate and design a sonoreactor in these conditions than higher frequencies. The cost of the piezotransducer is higher and the security of operation is worst at highest frequency. Based on literature, the optimal frequency to degrade pharmaceutical is expected to be between 200 and 500 kHz, which was the lower frequency with significant removal reported (Isariebel et al. 2009). Few studies on sonication of ibuprofen and other NSAID showed good results from removing these particles. The following table shows the parameters used to degrade NSAID pharmaceuticals.

Table 5 : Sonication parameters used to study the removal of NSAID

Parameter	Ibuprofen	Paracetamol
Frequency (kHz)	300	574
Power (W)	80	32
pH	3	-
Time to reach complete removal	≈ 1h	8h
Temperature(ºC)	25	20
Type of water	pure water	pure water
Kinetic order	Higher than first order	Pseudo fist order
Initial Concentration	21 mgL^{-1}	25 mgL^{-1}
Reference	(Méndez-Arriaga et al. 2008)	(Isariebel et al. 2009)

The experiments conducted by Méndez-Arriaga are, to the author's knowledge, the only published study on removal of ibuprofen by sonication and she concludes that ultrasound can remove IBP completely but transformation products were formed. .Only few other studies on sonication of pharmaceuticals in water have been published ((Emery et al. 2005; Hartmann et al. 2008; Sanchez-Prado et al. 2008)). Klavarioti reported that approximately only 4% of the research on removal of pharmaceuticals in water were based on sonication (Klavarioti et al. 2009). Addition of hydrogen peroxide to sonication is also not a well-studied process; no reference was found of pharmaceutical removal experiment with this application. What is expected to happen during this treatment, as suggested by (Behnajady et al. 2008) is the formation of perhydroxyl radicals as the result of the reaction of hydrogen peroxide with hydroxyl radicals, as presented below:

$$H_2O_2 + OH \rightarrow \bullet OOH + H_2O \quad [5]$$

Furthermore, it has to be noted that OH radicals tend to concentrate at the surface of the bubbles formed due to cavitations while H_2O_2 tends to remain in the bulk of the solution (Merouani et al. 2010) The diffusion of the OH radicals to the bulk being low, another reaction may play a significant role. In presence of ultrasound, H_2O_2 may dissociate into two hydroxyl radicals according to the following reaction:

$$H_2O_2 +))) \rightarrow 2\bullet OH \quad [6]$$

The addition of hydrogen peroxide during sonication of solutions containing pharmaceuticals hasn't be experimented, but the increase OH radicals formation is expected to contribute to the removal of aqueous pharmaceuticals.

3.3 Ozone coupled with sonication

No research has been conducted on removal of pharmaceuticals using ozone coupled with sonication. However, research on degrading reactive dyestuff was performed (Ince and Tezcanlí 2001; He et al. 2007; Song et al. 2007) and confirmed the potential of this approach to remove aqueous organic compounds. From these examples in literature, it was shown that the same parameters studied for ozonation and sonication alone influence the removal rate. A potential benefit of combining these oxidation processes is the increase of ozone mass transfer in water engendered by the ultrasound. When increasing the power applied to the system, the gas diffusion coefficient is higher (Ince and Tezcanlí 2001). Another potential benefit is the formation of hydrogen peroxide during sonication at a sufficiently power which may also contribute to the removal of the compound as previously described in the 3.2 section.

3.4 Characteristics of setups used

Different types of setups can be used to investigate the removal of pharmaceutical products in water by the following processes; ozonation, ozonation with hydrogen peroxide feed, sonication, sonication with ozonation and sonication with hydrogen

peroxide. The reactors used to perform those experiments and the investigation methods to study pharmaceutical products removal are often very different from one research to another and results obtained can hardly be compared. Therefore, those two aspects constitute the focal point of this section. Also, there are more reactor design options when combining two removal methods such as ozonation and sonication.

SEMI-BATCH OZONE REACTOR - Some experiments with ozone were done in a semi batch reactor where ozone was fed continuously into the reactor by a diffusion system. Ozone can be sent by a sparger (Vogna et al. 2004) or from the bottom of the reactor by a diffusion plate (Zwiener and Frimmel 2000; Rodayan et al. 2010). The objective is to disperse a maximum of ozone inside the reactor to reach homogeneity in concentration. In this case, the quantity of ozone in the gas stream entering and leaving the system can be measured in order to determine the amount of ozone transferred to the system after a certain time (the dose of ozone). Either from pure dry oxygen or dry air supplied by a compressed gas cylinder can generate the ozone. In some cases, hydrogen peroxide was also added continuously at given ozone/H_2O_2 ratios.

BATCH OZONE REACTOR - Batch reactors were used to study pharmaceutical removal during ozonation. Water containing a known concentration of dissolved ozone was mixed in glass bottles with solutions of pharmaceutical products (Huber et al. 2003).

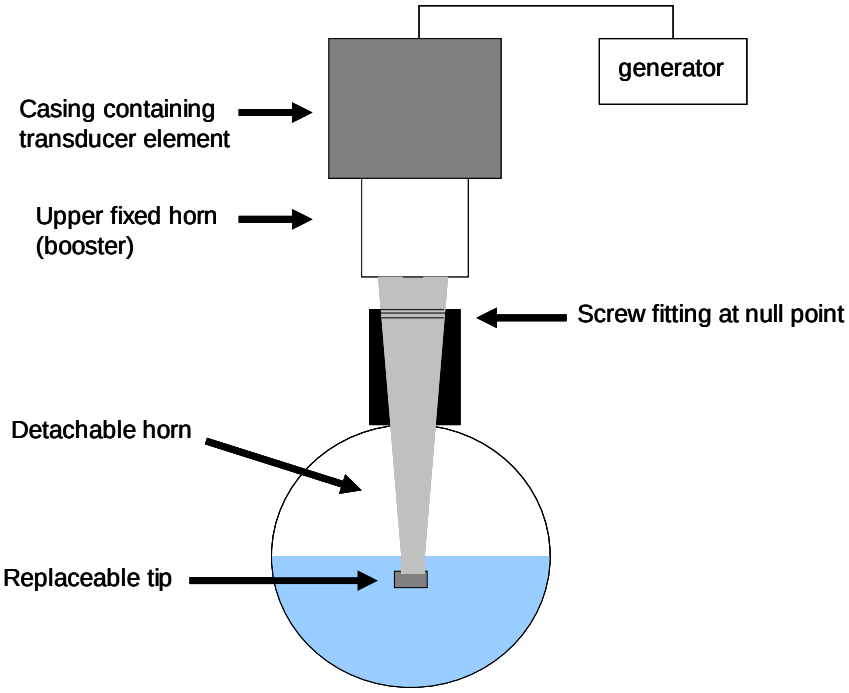
OZONE PILOT PLANT SETUP - In the case of ozone investigation, some analyses were done using an ozonation pilot plant treating municipal sewage treatment plant (MSTP) effluents (Ternes 1998). In these experiments, the system was run in the continuous mode of operation and samples were taken in the effluent and the influent of the ozonation step treating a fraction of the effluent of the MSTP

OZONE / HYDROGEN PEROXIDE SETUP - In some experiments, an amount of Hydrogen peroxide was used at different mass percentages of the ozone amount. Hydrogen peroxide was then first introduced into the system and, once the desired quantity of dissolved

ozone was reached, the pharmaceutical solution was added (Zwiener and Frimmel 2000; Huber et al. 2003; Yu et al. 2006).

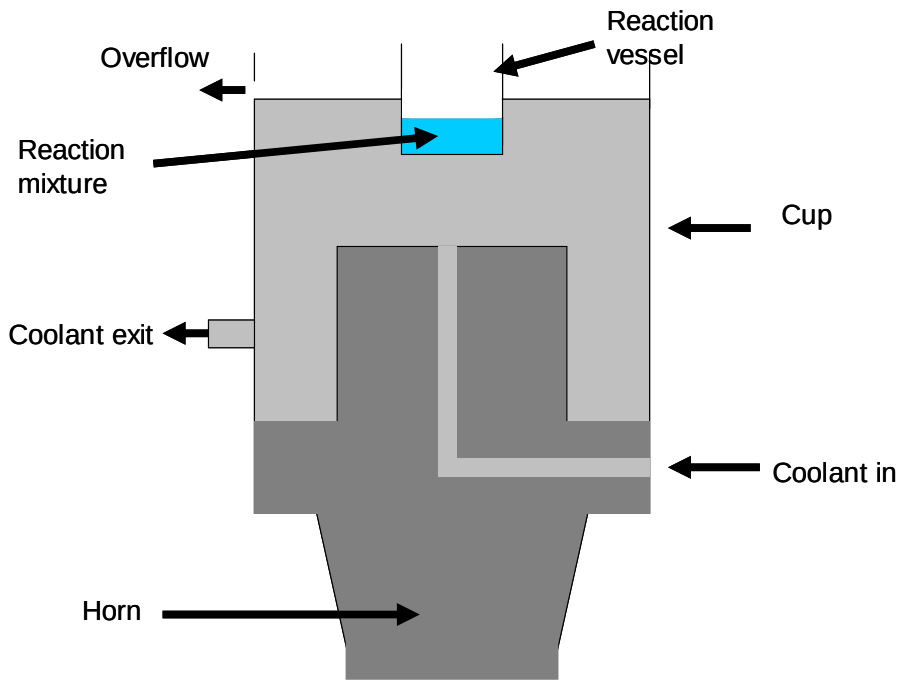
SONOREACTOR - Sonoreactors used to study the removal of pharmaceuticals products differ significantly from one research to another. Chowdhury and Viraraghavan reviewed the various kinds of setups used (Chowdhury and Viraraghavan 2009). The principal ones consisted of a submerged sonication probe, a cup-horn setup and a batch sonicator. The cup-horn setup is a mixed method of the two other setups. Pétrier, Zhang and Emery (Petrier et al. 1994; Zhang and Hua 2000; Emery et al. 2005) did some experiments with a horn or probe system. The principle of the probe system is to introduce it into the solution in order to sonicate pharmaceutical products. The next figure shows a schematic of a probe system.

Figure 4 : Schema of a probe system



The cup-horn setup work also with a horn, but in that case, the sample is not in direct contact with ultrasound emission. They're a liquid between the horn and the reaction vessel. The next figure is a schema of cup-horn design.

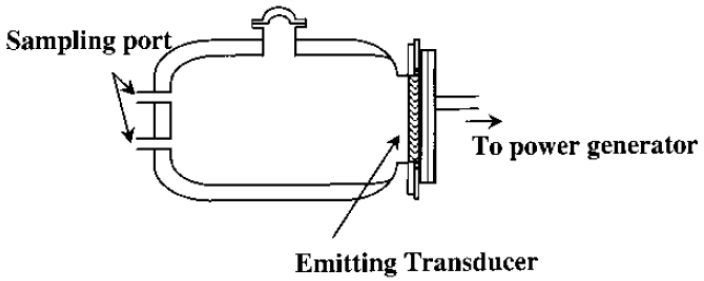
Figure 5 : Schema of cup-horn system



For sonication experiments, a piezoelectric transducer such as the ones used in ultrasonic bath is used to convert an electrical signal into a mechanical signal. Recent experiments with sonication and sonication coupled with ozone were performed using homebuilt bath equipped with one large cylindrical piezoelectric transducer at the bottom of a jacketed reactor (Mason 1992).

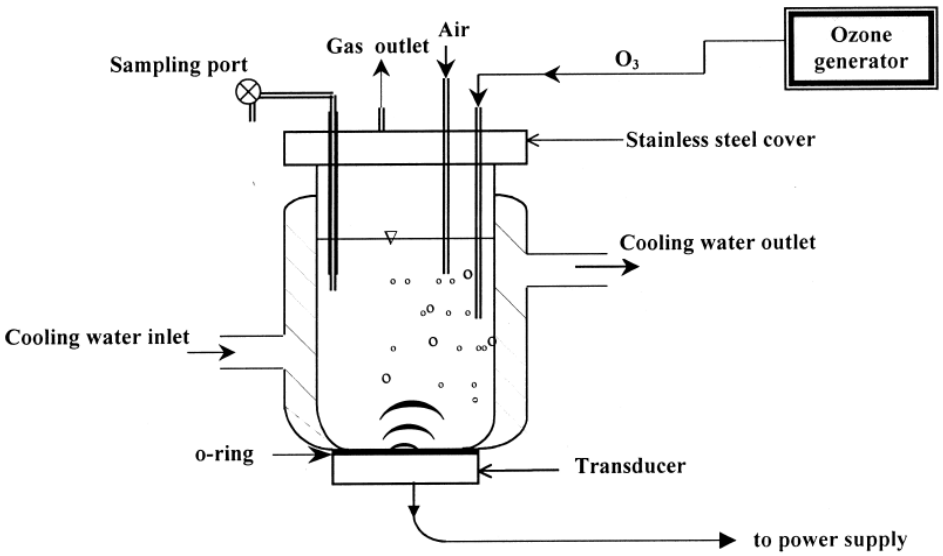
The advantage of this configuration based on only one piezotransducer at the bottom is the presence of a more regular acoustic field because one of the single ultrasound sources emitted from a flat surface. With this setup, it is possible to operate at different powers and to control temperature using a circulating fluid. Some similar reactors were designed with a vertical piezotransducer (Hung and Hoffmann 1999), no increase performance as yet be observed. The only experiment performed at large-scale was conducted with a vertical sonoreactor having a volume of 250 Litre (Son et al. 2009). The following figure show a vertical sonoreactor design.

Figure 6 : Vertical piezotransducer sonoreactor design (Mason 1992)



SONICATION-OZONATION SETUP - For the experiments combining ozonation and sonication, reactors such as ultrasonic bath type were mostly used. Ozone was send continuously and measured in doses of mg dissolved per litre. The following figure illustrates the ozone/sonication setup used by Ince et al. (2001).

Figure 7 : Setup of ozonation/sonication with a piezotransducer at the bottom (Ince and Tezcanlí 2001)



In literature, many reactors send ozone by a sparger at the top and send ultrasounds with a piezoelectric transducer at the bottom of the reactor. Setups seen by previous researchers studying ozone/sonication treatments are similar to the reactor showed in the

figure 4 (Ince and Tezcanlí 2001; Tezcanli-Guyer and Ince 2003; Torres et al. 2007; Gogate 2008; Méndez-Arriaga et al. 2008). Other experiments were done with a reactor that used a probe system to send ultrasounds from the top of the reactor and ozone, by a diffuser (Weavers et al. 2000; He et al. 2007) as in the figure 6**.** Ultrasound is sent in a radial direction rather than by the flat surface discussed earlier. Other reactor designs are possible with the different sonication setup combine with an ozone process.

Figure 8 : Ozonation/sonication setup with probe system (He et al. 2007)

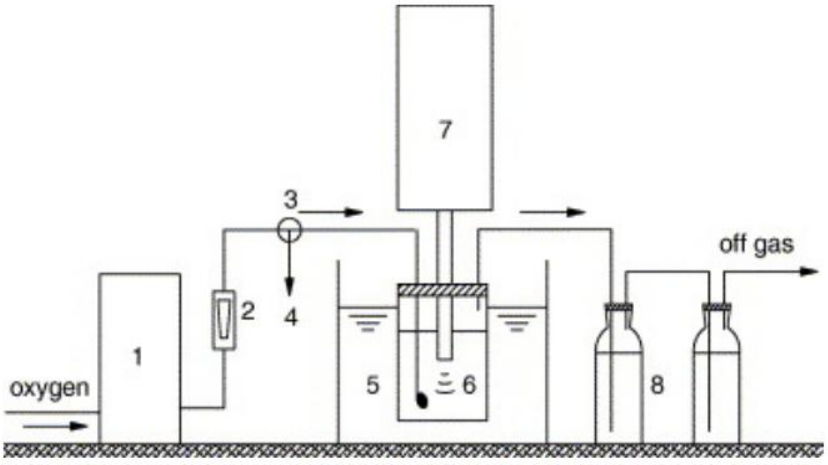


Fig. 1. The experimental set-up: (1) ozone generator; (2) rotameter; (3) three-way valve; (4) to input ozone gas detection; (5) temperature-controlled bath; (6) reactor; (7) ultrasonic generator; (8) absorption bottle.

SONICATION-HYDROGEN PEROXYDE SETUP - Experiments involving sonication with hydrogen peroxide are less frequent than other experiments discussed earlier. From literature (Merouani et al. 2010; Nalini Vijaya Laxmi et al. 2010; Wang et al. 2010), the reactors used to perform this experiment are the same as those presented for sonication; the probe system, the homemade sonoreactor or the ultrasonic bath. Hydrogen peroxide is set at different concentrations in the reactor for each test performed, thus showing the effect of H_2O_2 on sonication. For many setups, a continuous system would be difficult to design because of the impedance shift when increasing the reactor volume in time.

It is certain that other reactor designs are possible, especially in the case of the ozonation and sonication mixed setup. Those presented are the most common, but it is easy to imagine other possibilities, like a reactor sending ozone by the bottom with an annulus porous ring. The setups seen previously are the most common to monitor the removal of pharmaceutical products with the ozonation and sonication techniques. Many studies can be coupled with other removal processes as those discussed earlier in order to reach a higher removal of the pharmaceutical (Madhavan et al. ; Oh et al. 2007).

4. Objectives

From previous information it was observed that no investigation was done with sonication mixed with another method to remove IBP. Also, comparison of results is difficult due to the various setups and conditions used and transformation products have never been investigated with these oxidation techniques, including ozonation and sonication. Investigation on treatment of first wash water of pharmaceutical plants has never studied as a way to mitigate the release of pharmaceuticals into sewage and thus into the environment.

As a result, the objectives of the theses was first to perform an investigation of these oxidation methods for the removal of IBP in pure water in order to determine the optimal operating parameters and identify the most promising oxidative method for the removal of IBP amongst the following: ozonation, ozonation/H_2O_2, ultrasound (US) removal, ozonation/US and US/H_2O_2. The objective was then to apply these results to the treatment of a first wash-water produced at an ibuprofen processing plant (Wyeth, St-Laurent, Quebec, Canada). Each method was evaluated based on its efficiency to remove ibuprofen.

5. Reactor design

5.1 General description

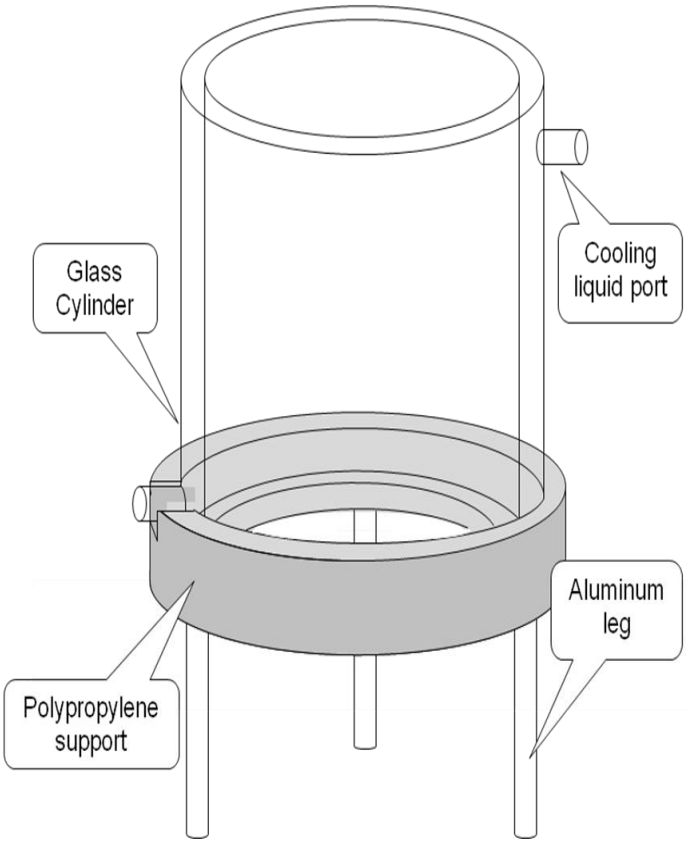
Experiments were performed using a 1-L reactor designed and built in-house to allow the operation of the same system in each oxidation mode taken separately or in combination (sonication, ozonation and hydroxyl peroxide addition) in order to provide a basis of comparison of the results. The body of the reactor, showed in Figure 7, was made of glass cylinder, open at the top and bottom, and jacketed to control the temperature using a circulating fluid provided by a thermostatic bath (Lab Companion RW-1025G). All the materials used to build the reactor are ozone resistant.

The dimensions of the reactor were determined according to the requirements to fit at its bottom the piezoelectric transducer of desired capacity (W/cm^2) and the porous metal plate to supply the ozone. The reactor was set on a polyethylene support with aluminum legs of 6 in, providing the required space below the reactor for the electrical box connected to the piezoelectric. The following table indicates the dimensions of the reactor:

Table 6: Dimensions of the designed reactor

Dimensions	**Value**
Height	20cm
Internal diameter	8cm
Cooling water volume	895mL

Figure 9: Main structure of the reactor

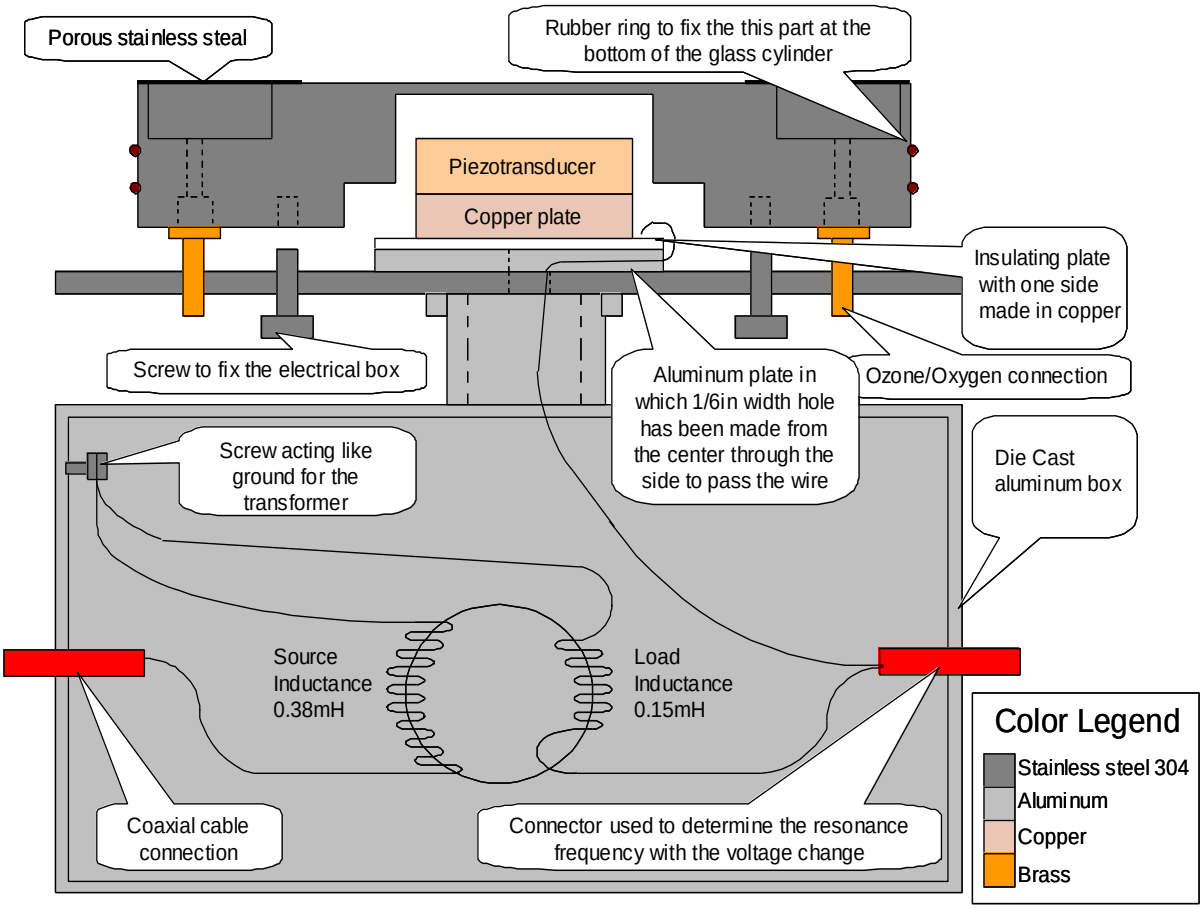


The bottom of the reactor was made of a grade 304 stainless steel disk. This piece was inserted inside the glass cylinder and was held in position by two rubber rings. The piezoelectric transducer disk (Sensortech Inc.) was placed at the center below the thin part (1 mm thickness) of the stainless steel disk. The piezoelectric disk was connected to an electrical system composed of a transformer (Discuss in section 5.2), an amplifier (Amplifier Research #75A250) and a function generator (RACAL-DANA model F64). The ozone was fed by the bottom of the reactor through an annulus disk made of porous stainless steel (Mott Corporation 2 um) and having a contact surface with water of 11.5 cm^2. Four barb hoses (5/16 inch diameter) distributed evenly around the ring supplied the ozone into the annulus compartment below the porous metal plate.

The electrical part of the reactor was placed inside a die-cast rectangular aluminium box screwed at the bottom of the reactor. A circular insulated plate with a copper face was put

directly below the piezoelectric transducer. A wire was connected to the copper surface then to the transformer in the electrical box. An aluminum disk with a hole, allowing a passage for the electrical wire, was placed between insulated plates and the main structure. The electrical box was connected to the amplifier with a coaxial cable. This cable prevented the dispersion of the electrical field. There was security precautions taken to prevent any accidents because of the high voltage reached in the transformer inside the box. To determine exactly the value of the resonance frequency, a connection was made to the wire in the box between the transformer and the piezotransducer. This wire was connected to an input plug outside the box to which an oscilloscope can be connected. The following figure shows the bottom of the reactor with its electrical setup related to the piezotransducer.

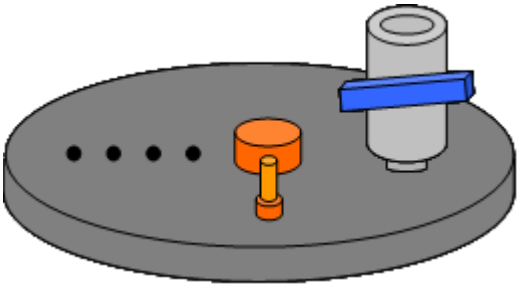
Figure 10: Bottom part of the reactor



The oxygen/ozone flow rate fed to the reactor was measured using a rotameter (Matheson U002). The OZOMAX generator, model OZO4VTT was fed with dry oxygen (purity 99.994%) to produce the required O_3/O_2 mixture. Because the flow rate produced by the ozone generator was higher than needed, a splitter was used to divert some of the ozone gas mixture produced. The required gas flow was sent to the reactor to a rotameter and a damper used to prevent flow rate shock variations (often when starting ozonation). The damper consisted of an Erlenmeyer capped with a rubber stopper.

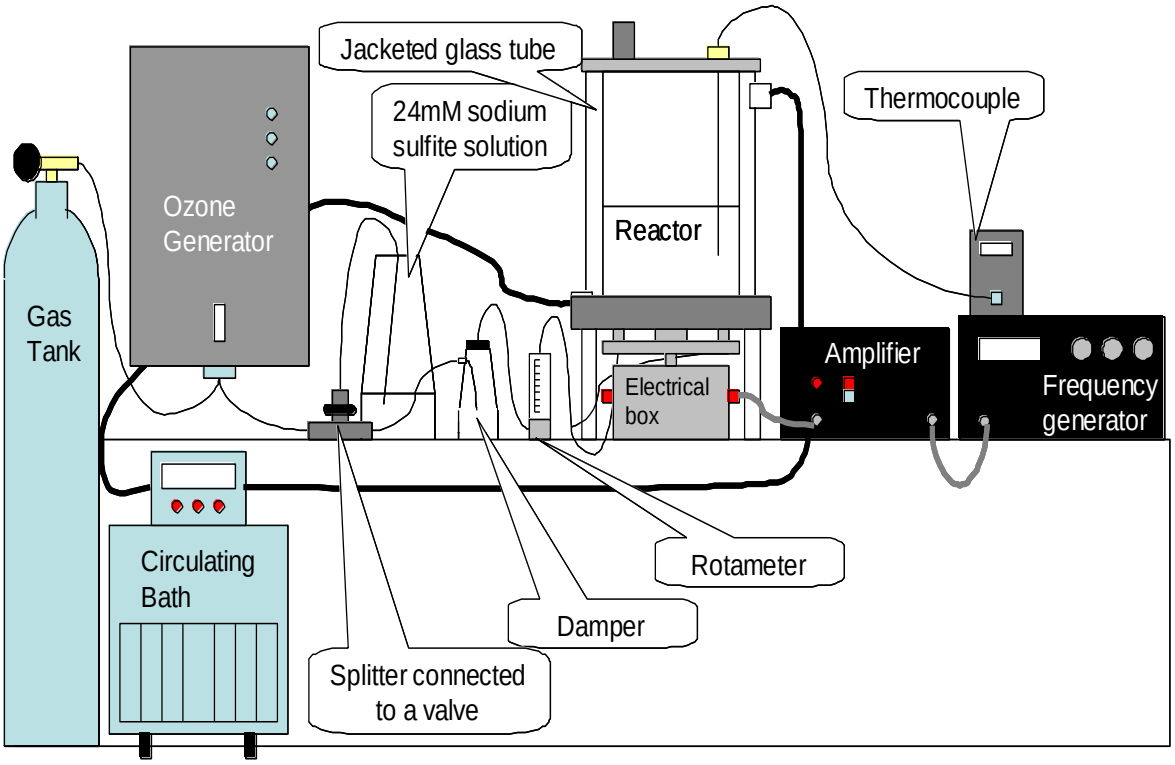
The lid of the reactor, also made of stainless steel 304, had holes having different functions. A sampling port allowed sampling directly from the bulk of the solution halfway into the height of the solution. Another hole allowed evacuating the off gas to prevent pressure build-up and to determine the residual concentration of ozone using an ozone analyzer (Model UV-100). A hydrogen peroxide brass connector, fitted to a third hole, allowed the addition of H_2O_2 15 cm below the top of the reactor, exactly halfway into the solution. The hydrogen peroxide was fed by a peristaltic pump (Cole-Palmer MasterFlex). Four 1/16 inch diameter holes were aligned on the radius of the top of the reactor in order to determine the temperature profile along the longitudinal and radial axis with a thermocouple (Omega HH11 probe T300E). A last hole was made in the center of the lid for the mixer used to obtain uniform mixing in the reactor, if necessary. The following figure presents the top of the reactor.

Figure 11 : Top of the reactor



During the experiment, the reactor was placed in the fume hood while the other components were placed on the bench top. The following diagram shows the various components of the experimental setup.

Figure 12 : Schematic of the setup used



5.2 Electrical design of the reactor

The piezoelectric transducer used in this project was made with BM400 (Lead Zircon ate Titanate, Sensortech Inc.). The main resonance harmonic of the ceramic alone is 261.6 kHz. The main characteristics of the piezotransducer were the following:

Table 7 : Characteristics of the piezotransducer

Characteristics	Value
Elasticity modulus	12.5×10^{-12} m^2/N
Density	7.6 g/m3
Wavelength	261.6 kHz
Thickness	7.7 mm
Capacitance	2563 pF
Resistance	18 ohm
Area	15.2 cm^2

The piezotransducer was a resistant and capacitive circuit (RC). To send ultrasounds, a transformer or an inductance was necessary in order to have a resistive, capacitive and inductive circuit (RCI), which would resonate in order to transform electric energy into mechanical energy. An RCI circuit is resonant at its maximum, if the capacitance effect equals the inductance effect.

The "Maximum power theorem" says that the power is highly transferred when the impedance of the source is equal to the impedance of the load. To match perfectly the load to the source, the impedance, which is composed of the resistance and reactance, must be equal to its opposite sign. In the system, the source was an amplifier with a 50-ohm resistive and the load was the piezotransducer. There was no reactance value in the impedance sources; so it was important that the reactance generated by the inductance correspond well to the capacitor value in the internal circuit. With the following formula, the capacitive reactance generated by the piezotransducer was calculated:

$$Z = \frac{j}{2\pi f C} \qquad [5]$$

With the formula of reactance generated by the inductance, it is now possible to match this value:

$$Z = 2\pi f L \qquad [6]$$

From the piezotransducer characteristic, the calculated inductance was 0,15mH. With this principal characteristic it was possible to build a transformer, which would match the impedance of the source and the load.

Some factors are important to choose the correct core to build a transformer. For a resonant circuit, a core with a high Q value is important. The Q value is the efficiency of a core to maintain the energy. The Q value depends on the material and the size of the core. With this information it was possible to find the core corresponding to the Henri number of interest and the turn coil number we needed to reach it in the reference table of Amidon Corporation (APPENDIX 3). The coil used to make the transformer was chosen according to the amount of current passing through it. If the coil chosen did not have enough current capacity it would have heated when current was sent to it. The following formula was used as to have a current approximation in the coil:

$$I = \sqrt{\frac{P * Q}{\Omega * L}} \qquad [7]$$

Where

I = current (RMS amps)

P = Power (Watts) = 50 Watts

Q = circuit Q (dimensionless) = 100

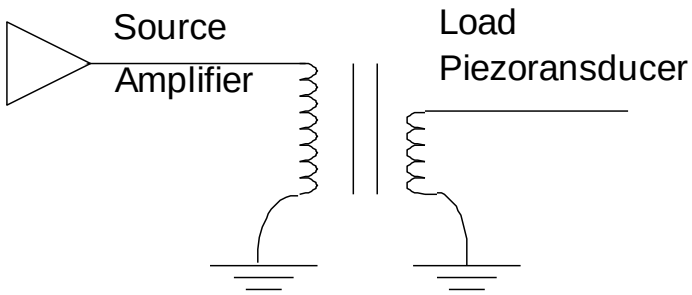
Ω = 2 x Pi x Frequency = 2 x 3.14 x 250 x 10^3

L = Coil Inductance (Henries) = 150 x 10^-6

The approximate current was around 4,6AMP. In the table of standard (APPENDIX 4) wire it is now possible to find the adequate BWG wire corresponding to this current. The

wire used to make the coil was 20AWG. The transformer inside the electrical box is made using the following schema:

Figure 13 : Electrical schema of a transformer



Two inductors fixed on a same core can represent a transformer. One was connected to the amplifier and the other one was connected to the piezotransducer. The source inductance was determined by this formula:

$$\frac{Z_S}{Z_L} = \frac{L_S}{L_L} \qquad [8]$$

Where:

Z_s = source side impedance

Z_l = load side impedance

L_s = source side inductance (which correspond to a turn number in Amidon table)

L_l = load side inductance (which correspond to a turn number in Amidon table)

The value calculated for L_S is 0,39mH. After some tests with different sizes and materials**,** a core was chosen. The different material and core tested are presented in (Section 6.1.1).

6. Methodology

6.1 Experimental plan

The experimental work was divided in three main parts listed below and described in the following paragraphs.

PART I – Design and optimization of reactor setup

PART II – Optimization of the treatment conditions in pure water

PART II – Case study: Treatment of Wyeth first wash-water

In PART I. A reactor that could be operated under sonication or ozonation mode either separately or simultaneous, with or without the addition of hydrogen peroxide, was designed. The ozone flow rate, the power transfer to the reactor and the volume of solution were optimized in order to obtain stable operation and measurable ibuprofen removal.

In PART II, the treatment conditions (see next section) were optimized for the five different AOP studied to obtain a maximum removal of ibuprofen. These processes were ozonation, ozonation with H_2O_2, sonication, sonication with ozonation and sonication coupled with hydrogen peroxide.

In PART III, first wash-water was obtained from Montreal's Wyeth plant processing IBP. The solution was characterized for its ibuprofen content, pH, COD, solid content; dissolved and total and a mineral analysis. Optimal operating conditions identified in PART II for each oxidative treatment were used to evaluate the performance of the treatment methods for the removal of ibuprofen in this more complex matrix. The main ingredients of ADVIL pills are presented in APPENDICE 3.

6.1.1 Optimization of operating parameters

The various operating parameters listed in Table 8 were optimized for the removal of ibuprofen as measured after 10 and 20 minutes of treatment. In all experiments, samples collected at times 0, 10 and 20 minutes were quenched with 0.1mL of 24mM sodium sulfite (Na_2SO_3, CAS# 7757837). The following paragraphs described the rational for the selection of these ranges of operation for the optimization.

Table 8 : Parameters studied with each experiment

Advance oxidation setup	Ozone dose (mg/L)	Time (min)	pH	Temperature (c)	Power (W)	Hydrogen peroxide flow rate (% of ozone flow rate)	Hydrogen peroxide amount (mg/L)	Number of experiments*
Ozone	8, 12, 16		5, 7,10	5, 15, 25	-	-	-	6
Ozone + Hydrogen peroxide	8, 16		-	-	-	25, 35, 45	-	3
Ozone + sonication	9, 17		4, 7	5, 15, 25	0.5, 3.4, 3.75, 4.8, 5.0	-	-	10
Sonication		10, 20	4, 7	5, 15, 25	0.5, 3.4, 3.75, 4.8, 5.0	-	-	10
Sonication + hydrogen peroxide		10, 20	-	-	-	-	3.5, 8, 16, 24, 50	5

* Each experiment was run in triplicates

OPTIMIZATION OF PH: The pKa of IBP being 4.9, pH values lower and higher than the pKa were selected for the optimization. When changing the pH, the temperature was set to 15˚C, the ozone dose was 8 and 16 mg/L for ozonation, the power was 4.8W during sonication and no hydrogen peroxide was added.

OPTIMIZATION OF THE TEMPERATURE: Ozonation, ozonation/sonication and sonication processes were tested at 3 different temperatures to determine the effect of temperature on IBP removal. The temperatures were chosen according to literature (Zwiener and Frimmel 2000; Huber et al. 2003; Oh et al. 2007; Méndez-Arriaga et al. 2008) indicating that at lower temperature**,** ozone dissolution increases. These experiments were performed at pH 7, an ozone dose of 8 and 16 mg/L for ozonation, a power of 4.8W for sonication and without hydrogen peroxide.

OPTIMIZATION OF POWER: The power range studied was from 0.5W to 5W. The different value corresponds to the amplifier gain. 5W was also the limit of power reached with the amplifier used. This power applied was calculated by calorimetry (Mason et al. 1992) by recording the temperature increase of the same volume of water For these experiments, temperature was kept at 15˚C, pH of 7 was used, no ozone and hydrogen peroxide were added.

OPTIMIZATION OF HYDROGEN PEROXIDE CONCENTRATION: Experiments combining the use of ozone and hydrogen peroxide had already been performed to study the removal of IBP in a batch reactor. Therefore, only the hydrogen peroxide flow rate was investigated here in the semi-continuous reactor. The hydrogen peroxide flow rate was fixed at the value used by Huber et al. 2003. Ratios of 25%, 35%, 45% of hydrogen peroxide flow rate over ozone flow were tested. Ozone and hydrogen peroxide were sent continually to the reactor. These experiments were performed at a temperature of 15ºC and a pH of 7 and an ozone dose of 8 and 16 mg/L.

The range of hydrogen peroxide concentration added initially during sonication was chosen to obtain an equivalent amount added to the reactor over 20 min of operation of the ozone/H_2O_2 performed in a semi-continuous mode of operation. Sonication with hydrogen peroxide experiment wasn't performing in semi-continuous because the volume addition changed the resonance frequency due to impedance mismatch. After 20 min of operation of O_3/H_2O_2 process, an amount of 3.5 mg/L of H_2O_2 was sent into the reactor. Previous results on sonication with H_2O_2 showed performance increase at a higher H_2O_2 concentration like 50 mg/L to 1000 mg/L (Merouani et al. 2010; Nalini Vijaya Laxmi et al.), but because great effects were identified for O_3/H_2O_2 process at low concentration, H_2O_2 amount of the same order was chosen (3.5, 8, 16, 24, 50). For experiments combining sonication with hydrogen peroxide, the temperature was set to 15˚C, pH to 7 and power to 4.8W.

6.2 Preparation of the solutions

6.2.1 Pure ibuprofen solution preparation

One litre of stock solution of 100ppm ibuprofen (MP Biomedical, LLC) was made in reverse osmosis water. PH of the solution was adjusted at pH 9 with sodium hydroxide (50%w/w, NaOH) in order to dissolve ibuprofen. The solution was mixed for at least 12 hours to ensure complete dissolution of ibuprofen. For storage, the IBP solution was maintained at 5˚C in the dark for less than 3 weeks. The stock solution was diluted to 5 mg/L prior to each experiment and pH was adjusted with sodium hydroxide (50%w/w, NaOH) or formic acid (88%) to reach the desired pH for the experiment.

6.2.2 Industrial first wash-water characterization

The ibuprofen-containing first wash-water was obtained from the company Wyeth Canada (now part of Pfizer) located in the St-Laurent quarter of Montréal. This wash-water is normally sent directly to municipal sewage without any treatment. The characterization of this solution included pH, chemical oxygen demand (COD), metal content and suspended solid concentration. A Hach Digital Reactor Block 200 (DRB

200), a Hach spectrophotometer DR/2500 and COD digestion vials (0 to 15,000 mg/L) were used to measure the COD concentration. Analysis of the metal content was performed with inductive coupled plasma (ICP) to determine the concentration of the following elements: Zinc, Iron, Copper, Manganese, Titanium, Cobalt, Cadmium, Calcium and Magnesium. Ingredients of the tablets manufactured by Wyeth are presented in APPENDIX 1.

6.3 Operation procedure

6.3.1 Ozonation procedure

For experiments using ozone, 500mL of 5ppm IBP solution was introduced into the reactor and brought to the desired temperature using the circulating bath prior to collecting the sample at time 0. Once the oxygen flow rate from the cylinder is stabilized, the ozone generator was set at 32.5 SCFH and turned on and the rotameter at the entrance of the reactor was set at 35 CCM. The pressure was of the oxygen gas tank was fixed at 8 PSI.

The flow rate was continuously monitored to ensure that ozone was sent to the reactor at a constant flow. Sampling was done using a 10-mL pipette (Fisherbrand) at time 0 and after 10, 15, 20 minutes of ozonation**,** which correspond to ozone doses of 8, 12 and 16 mg/L with the flow rate fixed. Samples were collected in vials containing 0.1mL of 24mM of sodium sulfite (Na_2SO_3, CAS# 7757837) solution in order to quench the residual ozone. After 20 minutes, the ozonation was stopped and IBP solution was drained into 5mL of 24mM of sodium sulfite solution. Thereafter the solution was disposed of in the appropriate waste containers. Finally the reactor was rinsed with osmosis water 3 times and dried for 20 minutes by introducing air into the sparger. Samples were stored at 4˚C in the dark and were analyzed within 15 days.

6.3.2 Ozonation/H_2O_2 procedure

For this oxidation method, the procedure described in the previous section was followed and a peristaltic pump (Cold-palmer Masterflex) was used to send the H_2O_2 solution through a tube (Saint-Gobin, 06409-14 Tygon) connected to a stainless steel straw attached to one of the lid ports. Hydrogen peroxide solution was sent at a constant flow rate of 1.2mL/min. The volume percentage of the solution was varied (0.016% to 0.029%) in order to obtain the proper concentrations to be tested. A mixer (Fisher Scientific, Dyna-mix) was used to ensure that the hydrogen peroxide was dispersed uniformly into the solution.

After having removed the initial 10-mL sample, ozone and peroxide hydrogen were sent simultaneously to the reactor and 10-mL samples were collected after 10 and 20 minutes. All samples were collected in vials containing 0.1mL of 24mM of sodium sulfite (Na_2SO_3, CAS# 7757837) solution in order to quench radicals. Samples were stored at 4˚C in the dark and were analyzed within 15 days.

6.3.3 Sonication procedure

For the sonication experiments, 300mL of 5ppm IBP solution was introduced into the reactor. The volume was decreased slightly as compare to the ozonation experiments in order to obtain an adequate power/volume ratio resulting in measurable IBP removal, The temperature kept constant using the circulating bath. The frequency was set at 241.4 kHz and the power was adjusted at the desired level. A 5-mL sample was collected at time 0, prior to starting the sonication. After 10 minutes, 5mL of the solution was removed, and rapidly the frequency was readjusted to 243.6 kHz to match the new impedance associated with the decreased solution volume. After 20 minutes another 5-mL sample was taken, and the frequency generator and the amplifier were switched off. All samples were collected in vials containing 0.1mL of 24mM of sodium sulfite (Na_2SO_3, CAS# 7757837) solution in order to quench the radicals. Samples were stored at 4˚C in the dark and were analyzed within 15 days.

6.3.4 Ozone/Sonication procedure

For the experiments coupling sonication and ozonation, 300mL of 5ppm IBP solution was introduced into the reactor. The temperature was kept constant using the circulating bath. The frequency generator was set at 241.4 kHz. When the oxygen flow rate to the generator is stable, the ozone generator was adjusted at 32.5 SCFH and the rotameter at the entrance of the reactor was set at 30 CCM. The pressure of the oxygen gas tank was fixed at 8 PSI. A 5-mL sample was collected at time 0 prior to turning on the ozone generator at the same time as the amplifier, previously adjusted at the desired power. After 10 minutes, 5mL of the solution was removed, and rapidly the frequency was readjusted to 243.6 kHz to match the new impedance associated with the decreased volume. After 20 minutes, another sample was taken, and the frequency generator and the amplifier were switched off. All samples were collected in vials containing 0.1mL of 24mM of sodium sulfite (Na_2SO_3, CAS# 7757837) solution in order to quench ozone and radicals. Samples were stored at 4˚C in the dark and were analyzed within 15 days.

6.3.5 Sonication/Hydrogen peroxide procedure

Sonication experiments performed in presence of hydrogen peroxide procedure were performed using the procedure described in the previous section. The difference was when making the 300mL IBP solution; an amount of hydrogen peroxide (3% H_2O_2 standard solution, Sigma) was introduced.

6.4 Analytical techniques

Various analytical methods described in the following sections were used to characterize the first wash-water, to measure the initial concentration and residual ibuprofen concentrations in the samples in order to determine efficiency of removal of each treatment method as well as to detect transformation products and determine their nature whenever possible.

6.4.1 Chemical oxygen demand

The chemical oxygen demand (COD) was measured to have an idea of the amount of residual organic compounds remaining in solution after the different treatments (ie. Indication of the degree of mineralization). An HACH Digital Reactor Block 200 (DRB 200), an HACH spectrophotometer DR/2500, and COD Digestion Reagent Vials Ultra low range (0 to 40 mg/L), Low Range (0 to 150 mg/L) and High range (0 to 1500 mg/L) were used to measure COD concentrations. The standard method #2540D, presented in APPENDIX 2, was followed.

6.4.2 Total organic carbon

Due to the high risks of interferences in the COD analysis by H_2O_2 produce or used in some techniques, the total organic carbon (TOC) was used to measure the degree of mineralization of the samples collected during the experiments performed at high ibuprofen concentration and with Wyeth fist-wash water. The apparatus used for these analyses was located at École des Technologies Supérieures de Montréal, in the laboratory of Dr Robert Haussler. An Apollo 9000 combustion TOC analyzer form Teledyne Tekmar was used to perform those analyses.

6.4.3 Dissolved Ozone concentration

To Indigo method (Standard method for examination of water and wastewater 4500-O_3 ozone residual) was used to measure the amount of O_3 dissolved in the water. This method was preferred over the direct analysis with a UV spectrophotometer due to the interferences caused by other compounds present in the samples. The standard method is presented in APPENDIX 2.

6.4.4 Percentage of ibuprofen removal

To optimize and compare the efficiencies of each advanced oxidation approach studied, the percentages of ibuprofen removal were determined for each conditions tested. The

initial and residual concentrations of ibuprofen were measured by high performance liquid chromatography (HPLC) following the method described below. The percent removal was then determined from these measurements and using the following equation:

$$Percent\ removal = \frac{(C_o - C_f)}{C_o} * 100 \quad [9]$$

The concentration of ibuprofen was determined using an Agilent 1100 Series HPLC after filtration using 13 mm syringe filters (PVDF, 0.22μm, Fisherbrand), adjustment of the pH to a value of 9 and mixing over 24 hours. The HPLC method developed is presented in Table 10.

Table 9: HPLC method used to measure the concentration of ibuprofen

Operating condition	**Value**
Column	Zorbax Eclipse XDB-C18 (4.6mm X 250mm, 5μM) Serial number: USN009976
Guard column	Eclipse XDB-C18 (4.6mm X 2.5mm, 5 μM Serial number: USUQA01791
Mobile Phase	A = 20mM Ammonia Acetate in water pH 3 adjusted using formic Acid B = Methanol C = Water
Flow Rate (mL/min)	0.7
Gradient	0 min = 60%B, 3%A 2 min = 67%B, 3%A 4 min = 74%B, 3%A 6 min = 81%B, 3%A 8 min = 88%B, 3%A 10 min = 95%B, 3%A 12 min = 97%B, 3%A 25 min = 97%B, 3%A
Detector	254 nm
Temperature of the column (˚C)	40
Post time (minutes)	5
- Injection Volume for high concentration curve 1-50ppm (μL) - Injection Volume for low concentration curve 0.01-1ppm (μL)	15μL 100μL

The retention time of IBP using this method developed in-house was 13.9 min and the limit of detection (LOD) was calculated to be 0.1 mg/L. To determine the limit, different small concentrations were tested with the method at the higher injection volume. The

smallest value, at which IBP can be monitored, represents this limit of detection. The limit of analysis (LOA) was considered to be 3 times higher than the LOD and equal to 0.3 mg/L. The method could have been improved to lower the limit of analysis but this level met the needs of this investigation.

Two different calibration curves, 0.1 to 10ppm and 5 to 100ppm, were used to determine the quantity of ibuprofen in the samples. These calibration curves along with a typical HPLC chromatogram for an IBP solution are presented in the APPENDIX 6.

6.4.5 Applied ozone dose

The rate of ozone applied to the solution (mg/L) was determined by measuring the rate of ozone production (mg/min) obtained in the same operating conditions. The rate of ozone production was measured by bubbling the same flow rate of O_3/O_2 gas in a gas-washing bottle containing 200mL of 2% potassium iodide and following the oxidation-reduction titration method using sodium thiosulfate and potassium iodide (KI). All the steps of this method are shown in APPENDIX 2. Knowing the rate of ozone production, the following formula indicates the dose of ozone applied for different ozonation time and volume of solution.

$$Ozone\ \ dose(mg/L) = \frac{Ozone\ \ time(\min) * ozone\ \ \ production(mg/\min)}{Volume(L)} \qquad [10]$$

6.4.6 Identification of transformation products

The analysis of the transformation products produced during the oxidation processes was achieved by liquid chromatography (HPLC) and mass spectrometry (MS). The HPLC used is the same as the one described in section 6.4.4. MS analyses were done using an LC/MS/MS of the model QTRAP 5500 from AB Sciex Instruments. First, fractions of products detected by HPLC were collected using the HPLC method previously described and using a fraction collector. The analyses of the fractions were performed at Trent

University (Ontario) by comparison with standards of compounds identified as potential transformation products of IBP based on literature. Fractions collected were analyzed by MS/MS in negative and positive modes and compared to the spectra of the potential transformation products of IBP previously reported in literature. Various transformation products were reported to be formed during oxidation processes using $KMnO_4$, H_2O_2 and K_2CrO_7 (Caviglioli et al. 2002). Some of these products were selected for comparison based on their reported importance or toxicity or because of their HPLC retention times being similar to new peaks observed on our HPLC chromatograms. These selected compounds were: 4-isobutylacetophenone (4IBAP), 1-(4–isobutylphenyl)-1-ethanol, oxo-ibuprofen, hydroxyl-ibuprofen, 4-ethylbenzaldehyde, 4-acetylbenzoic acid and oxalic acid.

6.4.7 Hydrogen peroxide concentration

To measure the amount of hydrogen peroxide formed during sonication a method based on Chai et al. experiments was applied (Chai et al. 2004). This method for rapid determination of hydrogen peroxide is based on the rapid reaction between ammonium molybdate and hydrogen peroxide. This molybdate salt concentration can be observed at a wavelength of 350nm. To quantify a small amount of hydrogen peroxide, 6 different concentrations of hydrogen peroxide were mixed with a solution of 5mL of 2.4mmol/L of Ammonium molybdate and 0.5 mol/L of H_2SO_4. Those H_2O_2 quantities are 2, 4, 8, 12, 16 and 20uL of a standard solution of H_2O_2 (3%). These hydrogen peroxide quantities were plotted with their specific absorbance at 350nm on the UV-spectrometer to form a standard curve. The concentration of hydrogen peroxide can be determined by the following equation.

$$C\left(\frac{g}{L}\right) = \frac{Slope}{V_{sample}(mL)} \times Absorbance_{(350nm)} \qquad [11]$$

6.4.8 Amount of power transferred to the solution

To measure the amount of power dissipated into the reactor**,** a calorimetric method was used. The ultrasonic power transferred to the system over a period of time results in a difference of temperature (ΔT). The difference of temperature over time can be measured with a thermocouple and knowing the mass (M) of the solution as well as its heat capacity (Cp) it is possible to correlate this temperature difference to the power transferred to the system using the following equation:

$$Power = \frac{\partial T}{\partial t} C_p M \qquad [12]$$

The power dissipated into the reactor was sometime not enough accurate to determine the energy transferred because it was not necessarily uniform in the entire reactor. Therefore, in this case we had to calculate the intensity of power produced by the area of ultrasonic source like in the following equation:

$$Intensity\left(\frac{W}{cm^2}\right) = \frac{Power(W)}{Surface\ of\ \ piezoelectric\ transducer(cm^2)} \qquad [13]$$

To compare this parameter with other experiments, there exists a standard measurement of irradiation (W/cm^2) intensity which measures this parameter in $100cm^3$ of water at 30˚C (Mason et al. 1992).

7. Results and discussion

7.1 Optimization of the operation of the US/O_3 reactor

7.1.1 Permanent Piezotransducer fixation to the reactor

The first sonication experiments were conducted using Vaseline (LEVER POND'S) to ensure a contact between the piezotransducer and the stainless steel plate in direct contact with the solution. Vaseline is known to be a good sound wave conductor but the efficiency of the power transfer was low, probably because of the heating of the Vaseline, and this resulted in low transfer efficiencies as shown by the high return lost presented in Table 11.

This table shows the results obtained with an Agilent Vector Network Analyzer for the operation of the reactor at different frequencies (around the resonance frequency of the material of 260.6 kHz) and volumes of water. The lower the return loss value, the less power is reflected to the source. That means that when impedance is matching well, the return loss value is lower.

Table 10 : Resonance frequency results obtained with Vector Network Analysis at different frequencies and volume of water using Vaseline

Frequency (KHz)	Return Loss (dB)	Impedance (Ohms)	
		R	jX
500mL Water			
259	-4	323	-9
253	-4	206	-5
252	-5	180	-35
700mL Water			
248	-	-	-
253	-	-	-
750mL Water			
232	-4	-	-
248	-5	-	-
252	-5	-	-
Without Water (test 1)			
252	-5	174	11
246	-5	159	-73
Without Water (test 2)			
230	-4	126	-102
247	-5	171	-148
252	-5	189	4

From that analysis, the low return loss shows that energy transfer to the water was not that high. Considering that a return loss lower than -10 dB is normally obtained in a piezotransducer application with an acceptable energy transfer, the high values of -4 and -5 dB indicated low efficiencies and a drop of the resonance frequency of the system compared to the resonance frequency of the piezotransducer alone. It was also noted that the resonance frequency of the system was continuously changing because of the change in viscosity of Vaseline during the treatment due to the increase in temperature. When reaching the resonance frequency, a meniscus is formed at the center of the water surface. A few times, the frequency had to be readjusted by more than 5 kHz to maintain the meniscus created by the acoustic field.

To avoid these problems, the piezotransducer was glued to the plate with a silver conductive epoxy (MG Chemicals #8331). This type of glue was chosen for its good conductive properties. Better return losses, in the -13 to -16 ranges were measured for the system having a glued piezotransducer.

7.1.2 Transformer optimisation

Another way to increase the energy transfer is to perform the network analysis in order to find the best inductor to match the impedance of the system. Inductors of different sizes and materials were tested to obtain a core that would not heat and would generate more cavitations in the water. The core materials tried were made of iron powder or ferrite (FT) based. The inductor FT-140-61 used to perform the Network Analysis test of the reactor with Vaseline fixation (Table 11) caused an impedance mismatch and didn't offer optimal conditions. The following table presents the different inductors and transformers tested and their different characteristics. Henry numbers and Q values were measured using a GR1650A impedance bridge.

Table 11: Characteristics of the cores tried for optimization of energy transfer

Number	Serial Number	Material	Suppliers	Type of device	Henry (uH)	Q	Turn
1	TK5123-ND	-	Digi-key	Inductor	390	-	-
2	811-2078-ND	-	Digi-key	Inductor	150	-	-
3	M9995-ND	-	Digi-key	Inductor	150	-	-
2	FT-240-43	FT-43	Amidon corp.	Inductor	155	15	12
3	FT-140-43	FT-43	Amidon corp.	Inductor	150	-	12
4	FT-240-61	FT-61	Amidon corp.	Inductor	155	14	31
5	FT-140-61	FT-61	Amidon corp.	Inductor	154	41	34
6	FT-240-61	FT-61	Amidon corp.	Inductor	150	-	30
7	FT-240-43	FT-43	Amidon corp.	Transformer	367	18	18
					171	28	12
8	FT-140-61	FT-61	Amidon corp.	Transformer	375	28	48
					178	18	38

After many tests with inductors, some tests with transformers were performed and an important performance increase was visually observed. The core selected was FT-240-43 for the transformer. Network analyses with this transformer were performed and show better impedance match. The impedance values obtained are presented in the next section (6.1.3). Transformer optimization can still be done, but the accessibility of the Network analyser was limited. This apparatus was the only known to calculate impedance at this frequency range.

7.1.3 Resonance frequency analysis

An analysis with an Agilent Vector Network Analyzer was done on the reactor when the piezotransducer is fixed with silver epoxy. The following graph shows the main resonance frequencies and their corresponding return losses for different reactor water volumes.

Table 12: Resonance frequency result with Vector Network Analysis on different water volume sonoreactor with piezotransducer fixed with silver epoxy

Frequency (kHz)	Return Loss (dB)	Impedance (Ohms)	
		R	jX
Without Water			
240	-16	-	-
280ml Water			
232	-5	-	-
256	-6	-	-
240	-13	-	-
285ml Water			
244	-9	-	-
239	-11	-	-
244	-4	-	-
290ml Water			
244	-12	-	-
295ml Water			
241	-11	-	-
241	-16	-	
300ml Water			
239	-9	80	6
248	-6	180	-
260	-3	175	-

This analysis allows having an accurate frequency value for different reactor operation volume. When changing the volume of the reactor, global impedance of the system changes. Also it was determined that when removing 1mm in height of solution (5mL)

from the reactor**,** the resonance frequency shifts 2 kHz more. It shows that the system was very sensitive and a study of the kinetic was difficult in those conditions.

From these results, the frequency was initially fixed at 241 kHz. The volume of solution in the reactor corresponding to this frequency was 295ml because it included the initial 5mL removal of standard solution. When the other sample of 5mL was taken after ten minutes, the frequency was rapidly fixed to 244 kHz to match the impedance and increase the energy transfer.

7.1.4 Temperature distribution with sonication experiment

In order to ensure that temperature increased uniformly in the reactor during sonication experiments, the radial and axial temperature profiles were measured inside the reactor using three thermocouples (Omega). Measurements made every 2 minutes over a period of 30 minutes of operation at 5W, pH 7 and 20˚C indicated a uniform temperature in both the axial and radial directions.

7.1.5 Ozone flow rate adjustment

After the experiment with UV-analyzer it was concluded that no repeatable data was obtained with this apparatus. The level of ozone was higher than the limit of this apparatus. Using the KI titration method (Standard method #2350E) to calculate the ozone flow rate**,** it was possible to fix it. Repeatable data were obtained for flow rate and ozone dissolved with indigo method.

For all the experiments using ozone, the pressure was fixed to 10 BAR and the gas flow meter fixed on the ozone generator was fixed to 32.5 SCFH. The gas splitter was adjusted and kept at the same position. The flow rate to the reactor was set to 35CCM for the ozone experiment and the ozone with sonication experiment. Triplicates show an ozone flow rate of 0.395mg/s. The Ozone/sonication experiment was set to a flow rate of 30CCM because the solution volume used was set to 300mL for a better sonication

efficiently. In order to try to get similar doses, the flow rate was fixed to this rate. Again, triplicates show ozone flow rate of 0.261mg/s.

With formula 10 in sections 5.4.4 it was possible to calculate the ozone dose for the ozone and O_3/H_2O_2 experiments with 500mL volume and a flow rate of 0.395 mgO_3/s. For ozone/sonication experiment, ozone dose is calculated with a volume of 300mL with a flow rate of 0.261mg/s.

7.2 Characteristics of the Industrial first wash-water

Each characteristic was determined as the average of the values obtained for 3 different samples of the solution obtained from Wyeth. COD test performed on the wash-water diluted with reverse osmosis water at a volume ratio of 1/16 and using High range vials (0 to 1500 mg/L) indicated a COD level of 19,408 mg/L.

The average suspended solid concentration based on the standard method #2540D was 612 ± 37mg/L. The average pH value of the wash-water was 5.2 at room temperature.

From the ICP analysis, the concentration of cobalt, manganese, titanium and chrome were below the detection limit of 0.01ppm. Calcium and magnesium were the most abundant metals but these may come from the tap water used to wash the tanks rather than from the ibuprofen formulation. Iron oxide and titanium oxide are listed as ingredient use in the formulation but their concentration in the wash-water was very low. The following table indicates the concentration of the metals detected.

Table 13 : Metals concentration in the Wyeth first wash-water (ppm)

	Mg	Ca	Fe	Ti	Co	Cu	Zn	Mn	Cr
Average	13.5	40.5	0.2	0.0	0.0	0.3	0.1	0.0	0.0

The average concentration of IBP in the wash-water was 583ppm, based this time on 6 samples rather than three. It was expected that this value was close to the limit of saturation of IBP in water because it very difficult to reach the same value with a solution

of pure water and IBP. Analyse of the second wash-water showed that the concentration of IBP in this solution was lower than the LOD value. The first wash was sufficient to remove IBP from the industrial mixer.

Because of the high organic concentration calculated by the COD analysis and the high level of certain metals, it was decided to dilute the sample on the $1/10^{th}$ to perform HPLC analyse. Analyse of TOC shown that Wyeth first wash had 2740±641mg/L of TOC. The IBP contributed to about 21% of this TOC level. Analyse was done using a dilute solution on the $1/25^{th}$ in order to fit on the concentration range of the apparatus.

7.3 IBP and COD removal by the different AOP's

7.3.1 IBP removal during ozonation

The experiment performed with a 5 mg/L ibuprofen solution prepared with reverse osmosis water for three different temperatures three different pHs and three different ozone doses gave the results presented in the following figures**:**

Figure 14: IBP removal by ozonation at various pHs and ozone doses at a temperature of 5°C

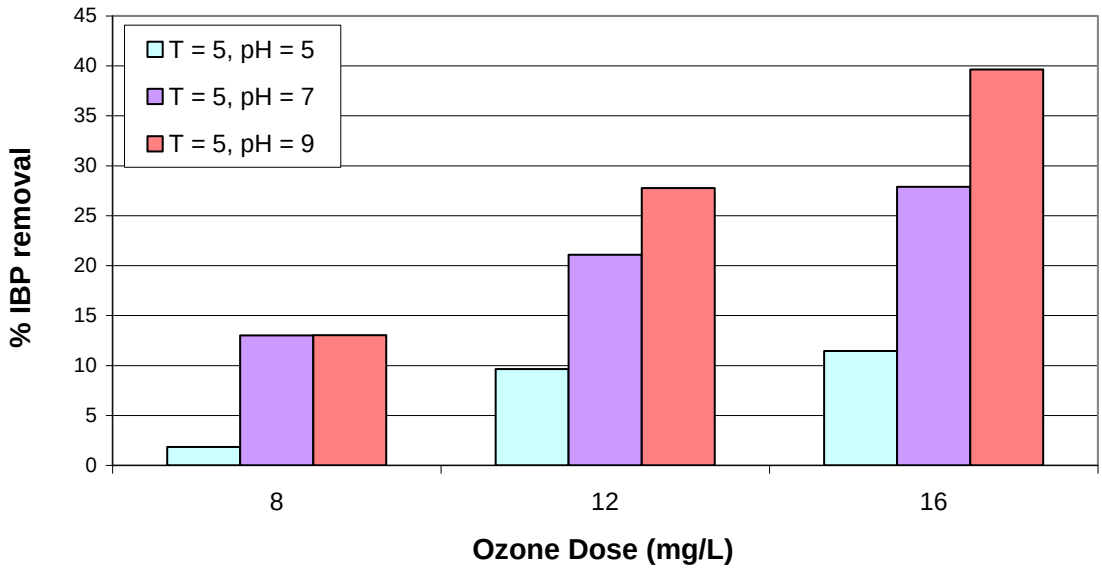
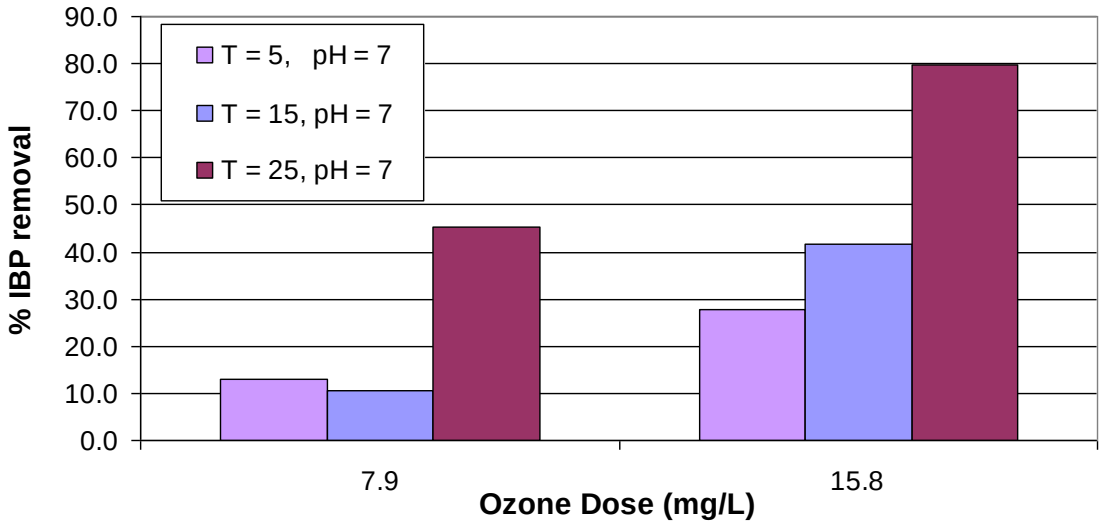


Figure 15: IBP removal by ozonation at various temperatures and ozone doses at a neutral pH



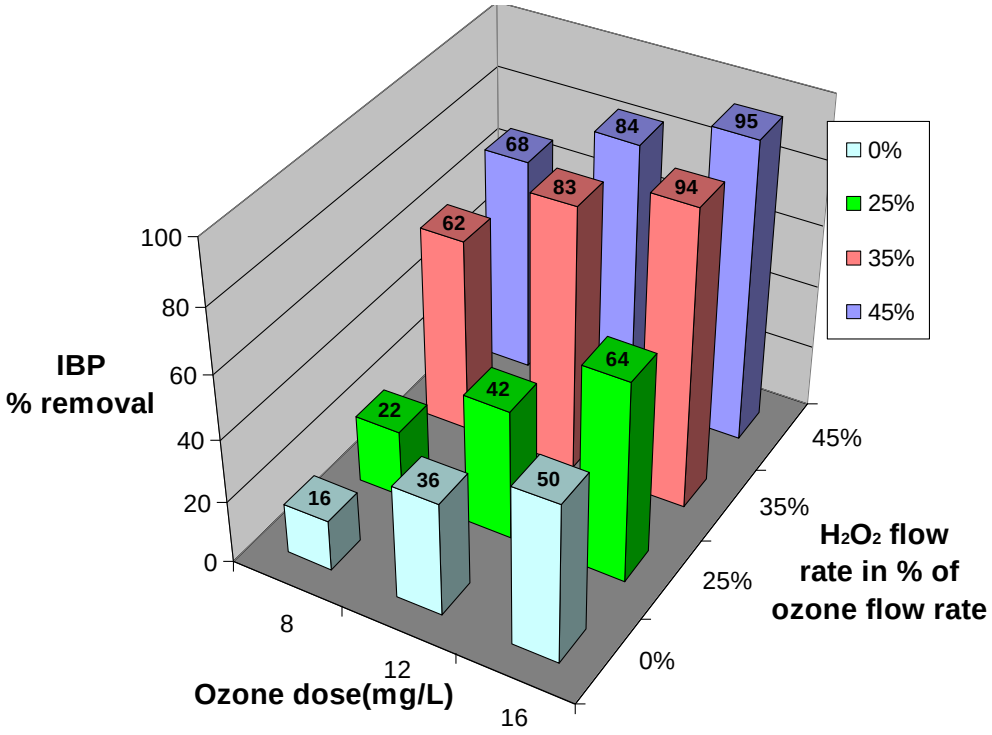
The increase in pH from 5 to 9 resulted in higher ibuprofen removals. The pKa of IBP being 4.9, ibuprofen is mostly in its anion state and is more reactive at higher pHs (Hoigné and Bader 1983) explaining the higher removals of IBP observed in this work using alkaline solutions and reported in the literature (Oh et al. 2007). Another factor contributing to the higher removals observed at higher pHs if the increased instability of ozone in alkaline solution leading to the formation of more •OH (Muthukumar et al. 2005).

The increase in temperature usually leads to a faster kinetics of reaction and thus higher removals within a given period of time. However, the solubility of ozone decreasing with temperature may have led to lower removals. The results obtained indicated an increased removal at higher temperatures suggesting that the effect on the kinetics of the reaction was more significant that the effect on the solubility of ozone within the range of temperature studied. Those values obtained for temperature analysis were similar to those obtained in literature (Huber et al. 2003) in which second order rate constants was determined with IBP in pure water solution.

7.3.2 IBP removal during ozonation in presence of H_2O_2

The removals obtained for experiments conducted using different ozone doses coupled with various ratios of hydrogen peroxide are summarized in the figure below.

Figure 16: IBP removal by ozonation at different ozone doses and hydrogen peroxide ratios at neutral pH and 15°C



These results indicated an increased removal at higher ozone doses and similar removal profiles as a function of the H_2O_2 addition for all ozone doses tested. The increase in the ratio of H_2O_2/O_3 was beneficial up to 35% after which, the addition of more hydrogen peroxide add no significant effect on the ibuprofen removal. This increased performance may be explained by the fact that more ozone molecules were converted into OH radicals in presence of H_2O_2 and the fact that IBP reacts faster with OH• (Zwiener and Frimmel 2000). These results obtained with the addition of 35% H_2O_2 can be compared to a value reported in literature by (Huber et al. 2003) which indicated that an amount of hydrogen peroxide of 35% of the ozone concentration can double the removal of ibuprofen. In this

present study, ozone alone removed 36% of the ibuprofen at pH 7. 15˚C and ozone dose of 12 mg/L of O_3 while the addition of hydrogen peroxide at a ratio of 35% of the ozone flow led to a removal of 83% an increase of a factor of three. The larger effect of hydrogen peroxide observed in this study as compared to literature (Zwiener and Frimmel 2000; Huber et al. 2003) might be explained by the continuous dosage of H_2O_2 along with ozone rather than the initial addition to the H_2O_2 dose. The results showed that there was a small increase on IBP removal when operated in semi-continuous than operated in batch like it was previously shown in Huber's results.

7.3.3 IBP removal during sonication

Results obtained using the different levels of power treatment time, temperature and pH are summarized in Figure 15, 16 and 17. Similarly to the results reported by Méndez-Arriaga et al. 2008 for the removal of approximately 26% of IBP was obtained with a power of 20W by sonication. When the power was increased, a higher IBP removal was observed. This might be explained by a larger amount of OH radicals formed in presence of more intense cavitations generated at higher power (Figure 16). As expected, a longer treatment time resulted in higher removal in all conditions tested (Figures 16. 17 and 18).

Figure 17 : IBP removal by sonication at different power and treatment times at neutral pH and 15°C

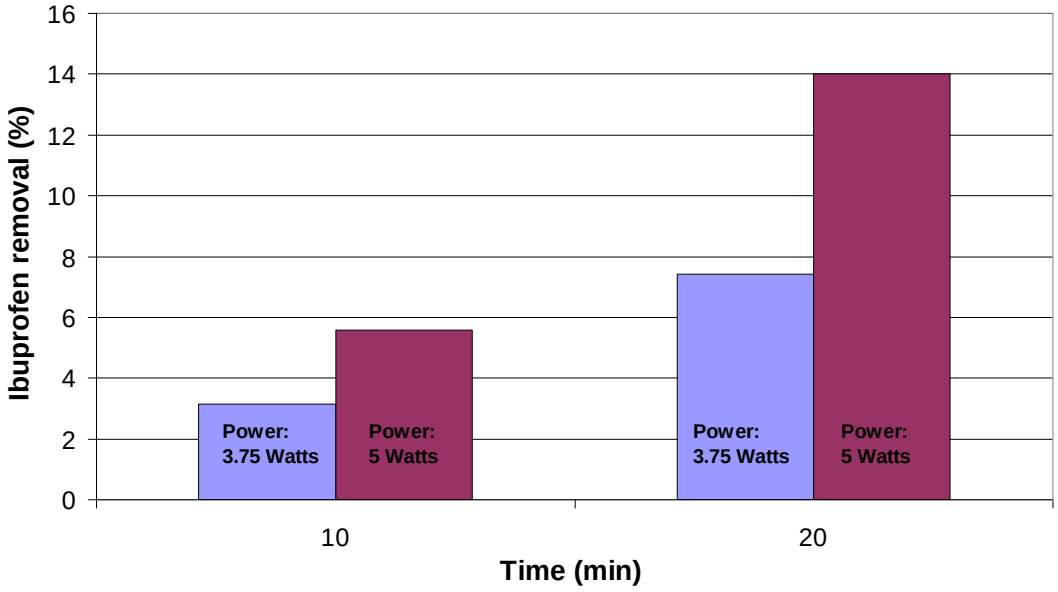
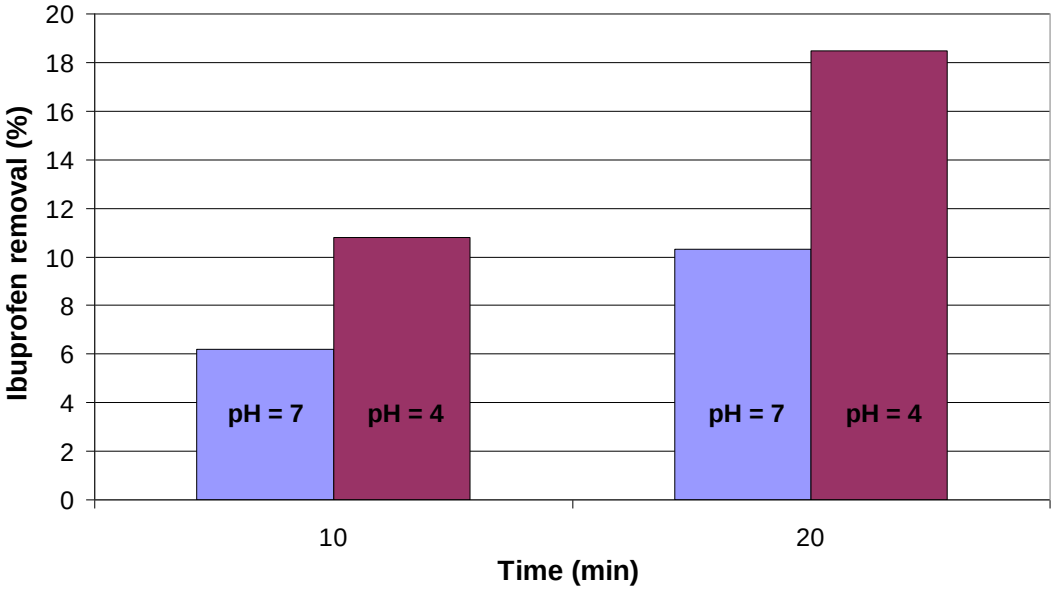


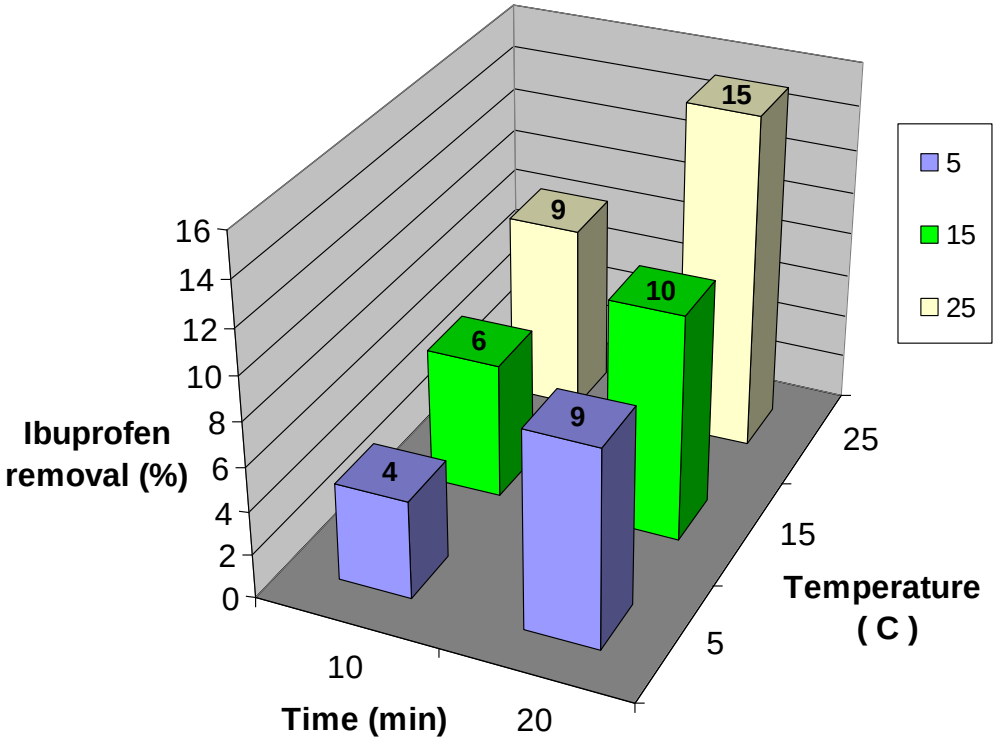
Figure 18 : IBP removal by sonication at different pHs and treatment times at a power of 5W and 15°C



The previous figure (Figure 16) shows that IBP removal increased when sonication was performed at a lower pH. This trend is opposite to the one obtained with O_3 and can be explained as follows. With sonication, IBP is most probably mainly removed at the surface of the cavitations bubbles where extreme conditions of temperature and pressure are created. Studies in literature reported that the highest concentration of OH radicals are observed at the surface of the cavitations bubbles (Méndez-Arriaga et al. 2008) and that that only 10% of the OH radicals are dissolved in the bulk of the solution (Goel et al. 2004). When the pH is lower than the pKa, IBP becomes more hydrophobic and tends to accumulate near the cavitations bubbles were higher its have probability of reacting with the OH radicals.

A slight increase in IBP removal was observed when the temperature was raised from 5 to 25°C (Figure 18). However, the effect of temperature during sonication was less pronounced than the one observed during ozonation. This trend is probably due to various factors such as changes in surface tension, gas solubility, viscosity of the solution and reaction kinetics, which can have opposite effect on the removal of IBP. There is also no report in the literature on the impact of temperature on the removal of pharmaceuticals during sonication.

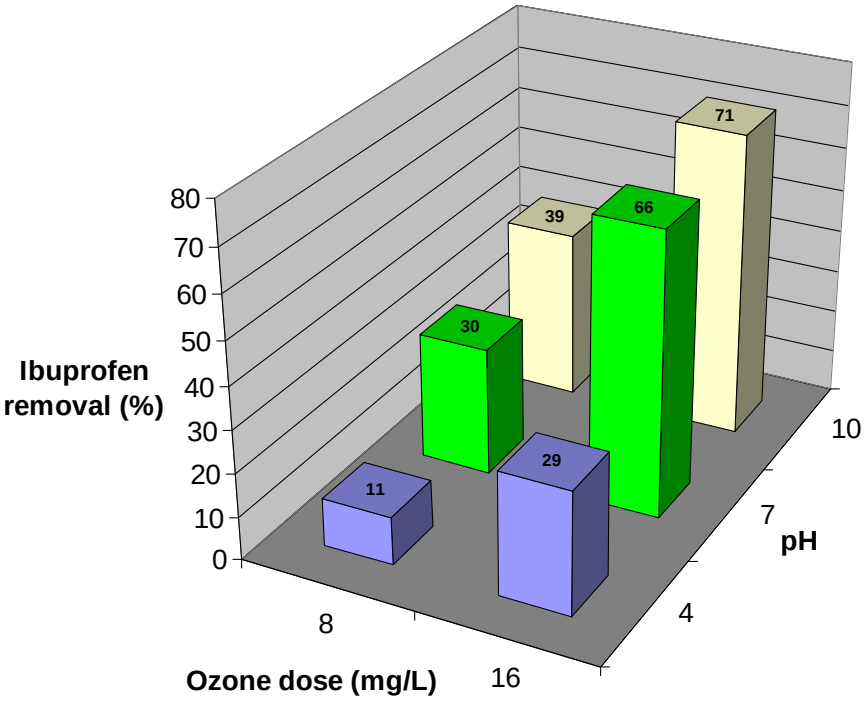
Figure 19 : IBP removal by sonication at different temperatures at neutral pH and power of 5 W



7.3.4 IBP removal during ozonation/sonication

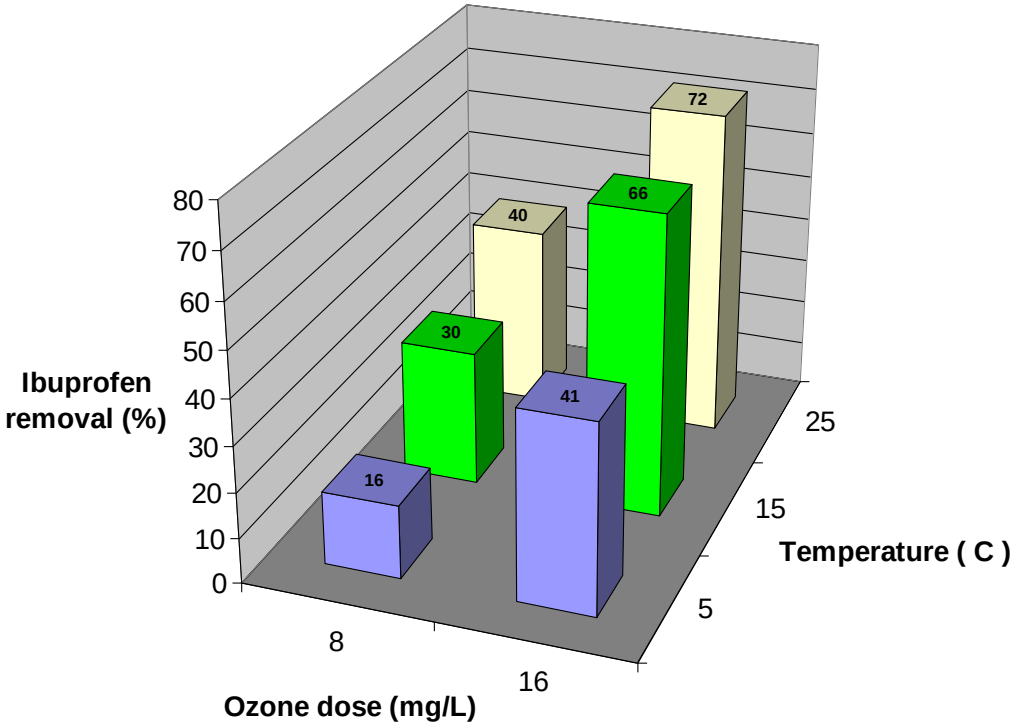
Figure 18, 19 and 20 summarized the first results ever reported on the removal of IBP during an oxidation process combining ozonation and sonication. The effect of pH on the combined process shown in Figure 19 was similar to the one observed during ozonation and this, at both ozone doses tested. This indicates that over the range of conditions tested the dominant removal mechanisms were associated with ozonation, which is favoured at higher pH's rather than the mechanisms associated with sonication for which a higher pH is detrimental. It must however be noted that a different trend might be obtained if a higher power could be applied to the system.

Figure 20 : IBP removal by ozonation/sonication at different pHs and ozone doses at a power of 5 W and 15°C



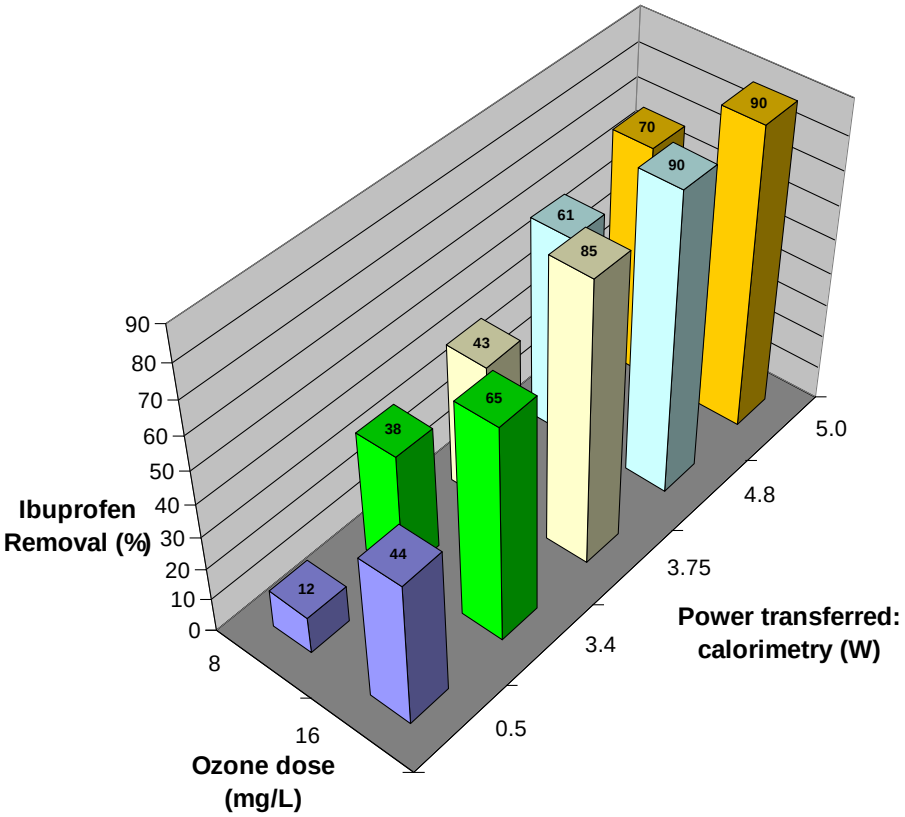
The results obtained for an increase of temperature reported in Figure 20 indicated trends similar to the ones observed using ozonation or sonication alone for the reasons described in the previous sections.

Figure 21 : IBP removal by ozonation/sonication at different temperatures and ozone doses at a power of 5 W and neutral pH



When increasing the power sent to the piezoelectric transducer, a higher ibuprofen removal was obtained (Figure 20). This is in accordance with experiments performed to study the removal of IBP to 25% to 100% when increased the power from 20W to 80W during sonication separately (Méndez-Arriaga et al. 2008). The experiments performed in the current study also indicated that the removal of IBP seems to reach a plateau after a certain level of power. This observation had also been reported for the removal of aminophenol during 30 min at 25˚C, pH 11, O_3 dose of 5.3 g/h and with different small applied energy density (0.1 to 0.3W/mL) (He et al. 2007). This phenomenon might be explained by a degassing effect associated with higher power resulting in a lower concentration of ozone in the solution. This effect might be dominant over the effect of the higher cavitations bubbles temperature that would be formed at a higher power and should lead to higher IBP removal.

Figure 22 : IBP removal by ozonation/sonication at different powers and ozone doses at neutral pH and 15°C



Removals obtained with ozonation/sonication (e.g. 65% at an ozone dose of 17mg/L and power of 3.4 W) were significantly higher than the removals obtained for each oxidative method applied separately (17% and 24%. respectively) under the same conditions). It was hypothesised that this synergetic effect might be due either to 1) the formation of hydrogen peroxide, known to occur during sonication, which would enhance the removal by ozonation or 2) an increase mass transfer of ozone into the solution due to sonication The following experiments were performed to verify both hypotheses.

A 300-mL water solution at a temperature of 15˚C and. a pH of 7 was subjected to sonication at 4.8W over 120, 180 and 300 minutes to determine the amount of hydrogen peroxide produce during sonication. Using the ammonium molybdate test described in the methodology section, it was shown that less than 3.993E-07 mg of H_2O_2/L. corresponding to the limit of detection of the method was formed during the treatment.

Considering that this value was much lower than those concentrations used in the ozonation experiments in presence of hydrogen peroxide (0.0988 mg/L) it is unlikely than the presence of such a low concentration of hydrogen peroxide had an effect of the mechanisms of removal associated with the ozonation.

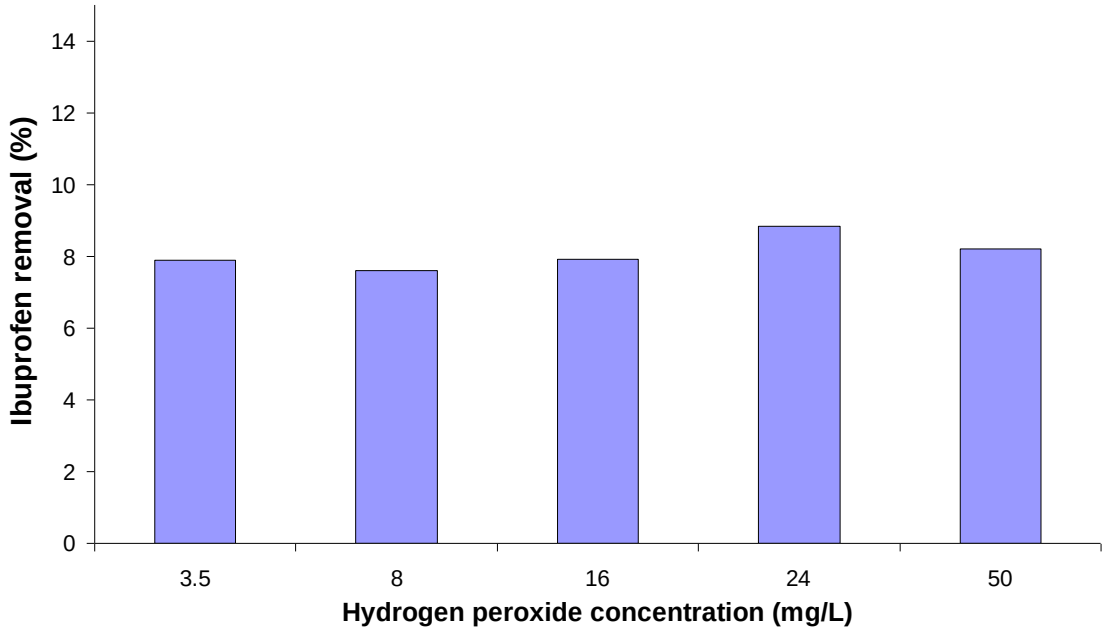
The amount of ozone dissolved in water after 20 minutes operations for ozonation and ozonation/sonication experiments was calculated with the indigo method described in the methodology section. Experiment was done in pure water at pH 7, power of 5 W and a temperature of 5˚C. Triplicates of this experiment can't prove that mass transfer of ozone was increased during ozonation/sonication treatment because the values obtained were not significantly different.

A known effect of oxygen on sonication was the increase in OH radical formation. Because the gas sent to the reactor was mainly composed of oxygen, an experiment at a pH level of 7 and temperature of 15˚C was done with an oxygen flow rate of 35 CCM. The triplicate of this experiment shows that oxygen was not sufficient to increase the hydroxyl radicals in the reactor. Oxygen was probably not able to dissolve enough in these operation conditions to make a difference on IBP removal. Also the power sent to the system was important, but maybe with a stronger power, an oxygen effect would be observed.

7.3.5 IBP removal during sonication in presence of H_2O_2

From Figure 22 summarizing the results obtained during sonication performed using different level of hydrogen peroxide, it can be seen that hydrogen peroxide did not have a significant effect on the removal of IBP. Considering that ibuprofen is known to react strongly with hydroxyl radical (Wert et al. 2009). These results suggest that over the range of hydrogen peroxide concentration tested, no significant increase in the formation of OH radicals was obtained.

Figure 23 : IBP removal after 20 minutes of sonication for different hydrogen peroxide concentrations at neutral pH, 5W and 15°C



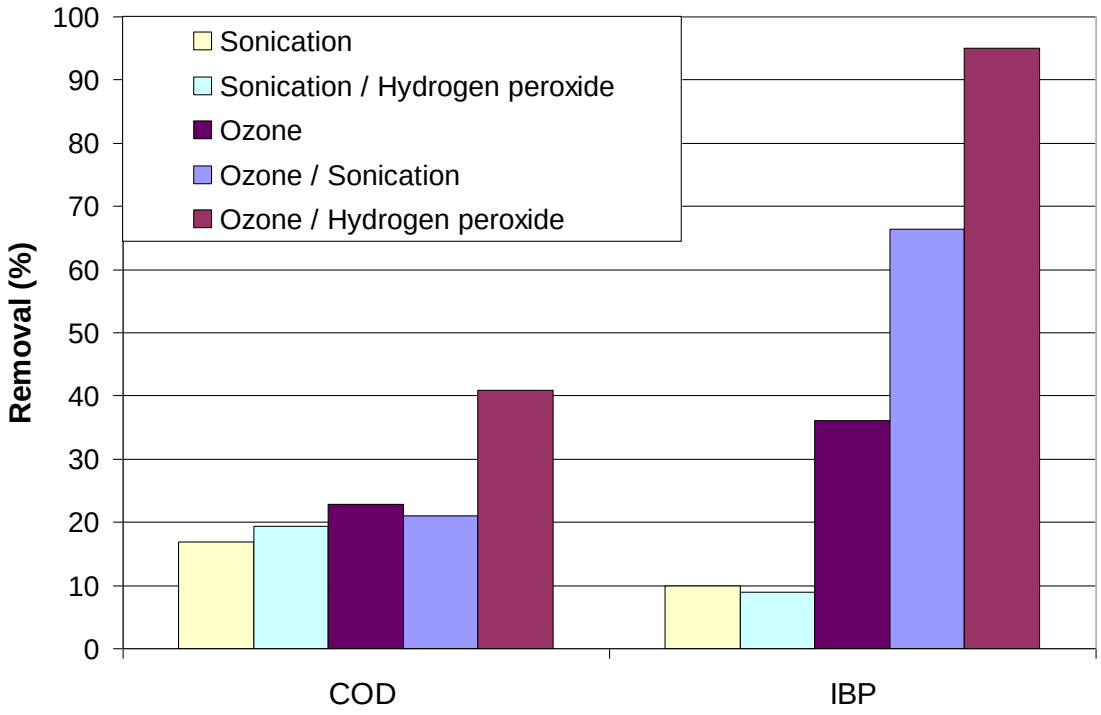
At these concentrations of H_2O_2, no effect on IBP removal was observed probably because H_2O_2 was all dissolved in the bulk, and it was close to the cavitations bubbles where IBP was degraded. Other experiments reported in literature (Merouani et al. 2010; Nalini Vijaya Laxmi et al. 2010) indicated an influence of H_2O_2 on removal but larger H_2O_2 concentrations were used: Merouani used 50-1000ppm and Nalini used 10-250ppm of H_2O_2. Maybe with a larger H_2O_2 concentration OH radical can go closer to the cavitations bubbles and can react with H_2O_2.

7.3.6 Comparison of the AOP's

As seen in the previous sections, the optimal operating parameters for better IBP removal were different for the various AOP studied indicating that various removal mechanisms were in action and suggesting that different transformation products were possibly formed. In order to compare the efficiencies of the AOPs, 20-minutes experiments were performed at the common treatment conditions of neutral pH and temperature of 15°C,

corresponding to common wastewater conditions. The COD and IBP removals obtained are presented in Figure 23.

Figure 24 : COD and IBP removals obtained for each AOP operated over 20 minutes at neutral pH and 15°C



Interestingly similar COD removals were obtained for all oxidation approaches used expect when hydrogen peroxide was added during ozonation. This approach led to an almost doubled COD removal. These results indicate that the best COD and IBP removals were obtained using ozonation in presence of hydrogen peroxide. This may be explained by the larger amount of OH radicals formed. The following table present the different %COD and %IBP removals obtained with ozonation/hydrogen peroxide performed at different ratio of hydrogen peroxide that should also contribute to the formation of OH radicals.

Table 14 : COD and IBP removal for different hydrogen peroxide flow rate at 15˚C. pH 7 and a ozone dose of 16 mg/L

Hydrogen peroxide flow rate in % of ozone flow rate	% COD removal	% IBP removal
0%	23	41
25%	53	64
35%	40	94
45%	41	95

These results indicate that although hydrogen peroxide did increase IBP and COD removal, above a certain level of H_2O_2, the removals were not increasing any further. These low levels of COD removal strongly suggest that transformation products were formed and that part of these might be persistent. Increasing the amount of ozone used resulted in higher ratios of COD/IBP removal suggesting that the transformation products formed were sensitive to ozone.

Sonication was the approach with which the ratio of COD\IBP removal was the highest. This is surprising considering that Mendez et al. 2009 reported for sonication a low TOC removal compared to IBP removal. This might be explained by the fact that water sonication is known to produce a large amount of OH• (Gogate 2008), which are less selective and may lead to greater removal of the products formed. IBP is also known to react greatly with hydroxyl radical (Wert et al. 2009) and reaction between IBP and hydroxyl radicals is certainly a dominant removal mechanisms during sonication.

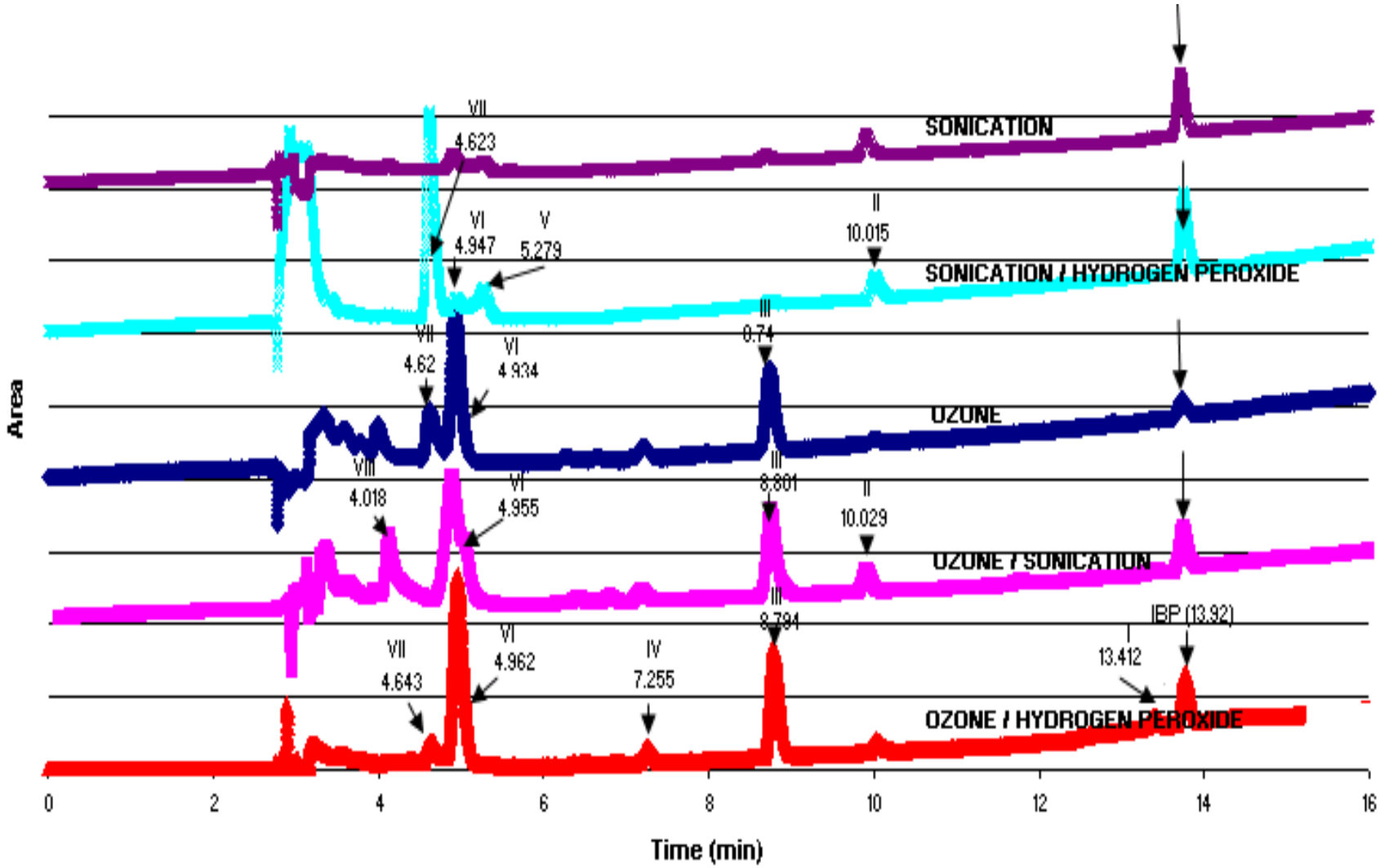
The ozonation and ozonation/sonication experiments had similar COD removals while ozonation/sonication had higher IBP removals. It is possible that the amount of OH• was higher with ozonation/sonication, but not enough to degrade the transformation products formed. The IBP removal obtained during ozonation/sonication experiments was a little

higher than the summation of removals obtained by ozonation and sonication performed separately, indicating a synergetic effect between the two oxidative approaches. Previous results indicated that ozonation alone is more efficient when IBP is in its anions state (IBP^-) while sonication allows a better removal when IBP is not in its anions state. The experiments presented in Figure 23 were done at a pH level of 7 so it is probable that there was a certain amount of IBP^- and IBP in the solution because of the proximity to its pKa value.

7.4 Transformation products formed in AOP's

During HPLC analysis, several transformation products were observed as new peaks on the chromatograms of the samples analyzed for each oxidative approach studied. Figure 25 shows the different transformation products detected for each technique. Products were detected at a wavelength of 254 nm with the exception of product I and VI, which were detected at 220 nm and 254 nm.

Figure 25 : HPLC chromatograms of the samples collected for each AOPs studied



Product VI is the product that was observed at a higher peak area using all ozonation approaches. An higher extend of formation seemed to occur depending on the techniques used. Some products like products I, III, IV seemed to be more abundant after ozonation than after sonication. In general, lower peak areas were observed for all peaks detected in the samples subjected to sonication and sonication/hydrogen peroxide indicating that these oxidative approaches probably enhance the removal of the transformation products formed. These results were in accordance with COD value obtained, which showed higher %COD to %IBP removal ratios with these two techniques. On the other hand, product V seemed to be specific to sonication and was not detected in samples treated by ozonation.

Transformation products I, II, III, IV, VI, VII and VIII were collected in vials using the fraction collector on the HPLC. Although transformation products of IBP formed during ozonation and sonication had never been reported, the fractions collected were to be compared to a list of transformation products reported in literature to form during oxidation of IBP by heat treatment, hydrogen peroxide, $KMnO_4$ and $K_2Cr_2O_7$ (Caviglioli et al. 2002; Skoumal et al. 2009). Potential transformation products were compared with the fractions based on their HPLC retention times and their MS spectra. To account for the effect of the sample matrix on the products HPLC retention times, samples were spiked with the potential transformation products, one compound at a time, prior to HPLC analysis. The chromatograms obtained by this analysis are presented in Appendix 5. The list of the products, which were compared to transformation products, is presented in the following table.

Table 15 : Product investigated as transformation products

Products
4-IBAP
Oxalic Acid
4-ethylbenhaidehyde
4-ethylbenzoic acid
1-hydroxyl Ibuprofen
1-Oxo Ibuprofen
Acetic Acid
Formic Acid

Product III collected at a retention time of 8.7 was shown to have a similar MS spectral to that of oxo-ibuprofen (O-IBP). The retention time of this product spiked into the sample also matched and supported the identification of the nature of this new peak.

Product VI having a retention time of 4.9 min had a similar MS spectral to oxalic acid although the retention time of oxalic acid spiked in the sample had a retention time of 2.9 min. Other HPLC peaks collected as fractions and analyzed by MS were also showed to contain some oxalic acid. These results clearly indicated that oxalic acid was formed during the oxidation of IBP although it probably did not correspond to Product VI.

Product VII was also collected at a retention time of 4.6 and had a similar MS spectral to that of 4-acetylbenzaldehyde acid. Comparison of the HPLC retention times showed that 4-acetylbenzaldehyde acid and product VII had the same retention times. It can be concluded that this product, was 4-acetylbenzaldhyde acid.

Product VIII collected at an HPLC retention of 4 min had MS spectra comparable to that of 4-ethylbenzaldehyde although the retention time of this product spiked into the sample was determined to be 10 min. However, the formation of this product can be further supported by the generation of a cherry odour during the treatment of the IBP-containing solution, especially during the treatment of the industrial first wash water.

The toxic product 4IBAP reported in literature during oxidation of IBP by NaOH was not identified as one of the fractions collected (Caviglioli et al. 2002). However, the retention time of this product spiked into the samples indicated that this product elute as the same retention time as IBP. Unfortunately, no fraction had been collected at this retention time and further analysis is now required to confirm or infirm the formation of this product during ozonation and sonication.

The following table summarizes the identification of the transformation products formed during ozonation and sonication. All MS Spectrum of standards and samples are presented in APPENDIX 7.

Table 16 : Transformation products identified during oxidation reactions of IBP by ozonation and sonication

Products	Similar HPLC retention time	Identification by MS spectral	Peak identification
1-oxo-ibuprofen	X	X	III
oxalic acid		X	
4-acetylbenzoic acid	X	X	VII
4-ethylbenaldehyde		X	

7.5 Case study: Treatment of Industrial First-Wash Water

The optimal parameters determined for each treatment approach in the previous sections, and summarized in Table 17, were used to study the treatment the industrial ibuprofen--containing wash-water obtained from Wyeth.

Table 17 : Optimum parameters for the different AOPs

Advance oxidation setup	pH	Temperature (˚C)	Power (W)	Hydrogen peroxide flow rate (% of ozone flow rate)
Ozone	10	25	-	-
Ozone + hydrogen peroxide	10	25	-	45
Ozone + sonication	10	25	5	-
Sonication	3	25	5	-

In order to compare the results obtained with the complex matrix of the industrial water to the treatment of IBP contained in pure water, all conditions listed in Table 17 and studied in the previous sections were repeated using a 600ppm IBP solution in pure water. Triplicates were done for each treatment approach and results are summarized in Table 22. Large variations in the degree of removal (up to 50% in few cases) were observed for the treatment of these solutions having IBP concentrations close to the limit of solubility. The percentage of IBP removal for sonication experiments with 600ppm IBP solution was not consistent. Those results were probably inconsistent because the pH was adjusted at 3 for sonication experiments, which affected the solubility and measurable concentration of IBP. In fact, some precipitate was observed after adjustment of the pH of the solution prepared in water.

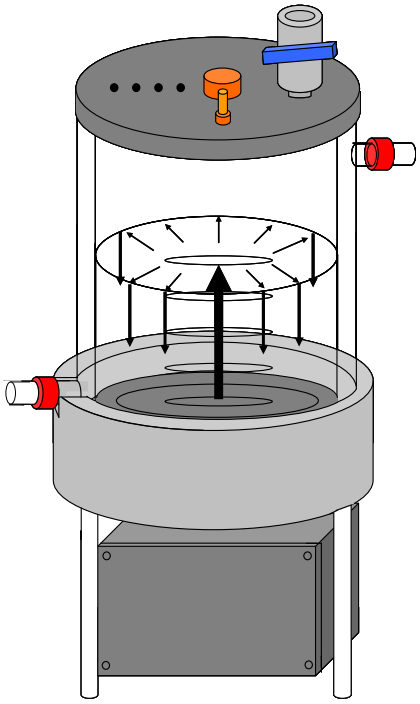
Table 18 : IBP removal obtained with the optimized parameters for each treatment applied to pure water (600ppm) and the industrial wash water

	O_3	O_3/H_2O_2	O_3/SONO	SONO
IBP removal after 20min (pure water solution)	4.5%	9.0%	6.2%	-
IBP removal after 20min (Industrial first wash water)	12.9%	16.1%	11.9%	8.5%

However, comparison of the treatment methods (AOPs) applied to pure water having a concentration of IBP of 600ppm indicated again that the highest IBP removal was obtained with O_3/H_2O_2 followed by O_3/sonication. The IBP removals obtained in the industrial first wash-water were higher than the results obtained using the pure water IBP solution in all of the conditions tested. It is hypothesized that this difference is due to the presence of minerals in the industrial first wash-water. A study conducted by Rodayan et al. also showed that higher pharmaceutical removals were observed in municipal wastewater than in pure pharmaceutical solutions (Rodayan et al. 2010). These higher removals may be due to the presence of other constituents such as minerals, which may influence the mass transfer of ozone and/or its solubility or may contribute to the formation of radicals.

Some interesting observations were also made during sonication of the wash water. The presence of suspended solid formed a fluidizing bed inside the reactor, a phenomenon not observed with the pure water IBP solution. The suspension was most probably composed of cornstarch; the first ingredient of the Wyeth ADVIL pills, as presented in APPENDIX 1. The movement of the suspended solids in the reactor is represented in the following figure. This may have contributed to the dispersion of IBP in the solution.

Figure 26 : Suspended particles motion during sonication of Wyeth first wash-water

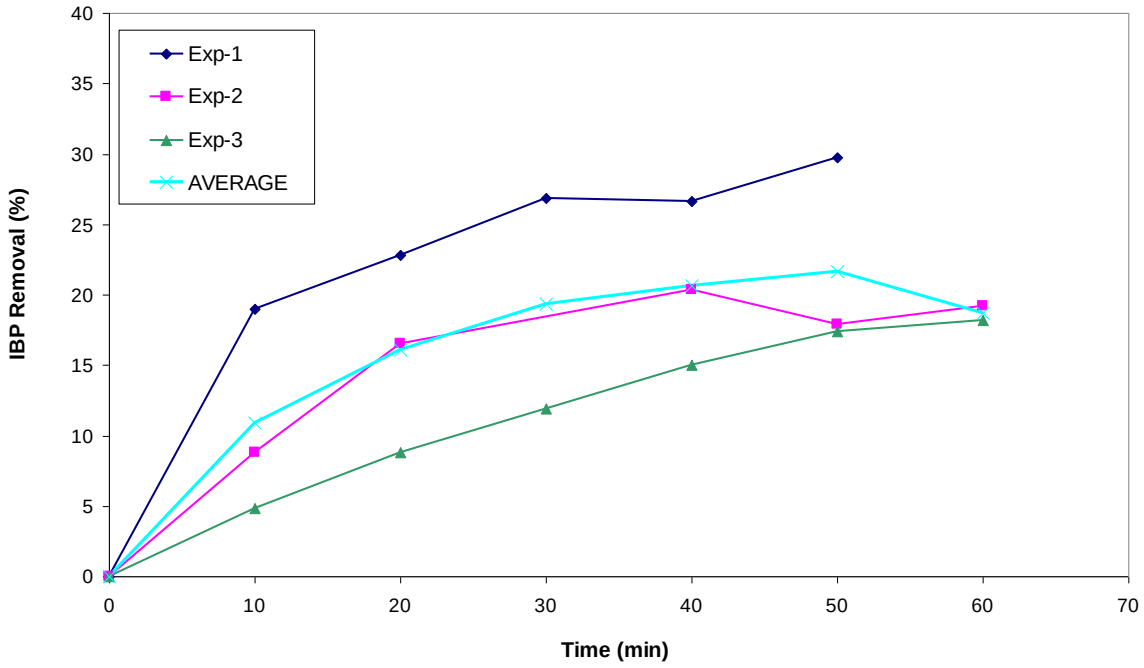


Another observation during ozonation/sonication experiments was the formation of two phases. When oxygen/ozone mixture was sent to the system two phases appeared: one opaque layer of suspended solids at the top, and at the bottom, a clear liquid phase. The phase containing suspended solids decreased in thickness until equilibrium was reached which was after approximately 7 minutes of operation.

7.5.1 Extended treatment of wash-water

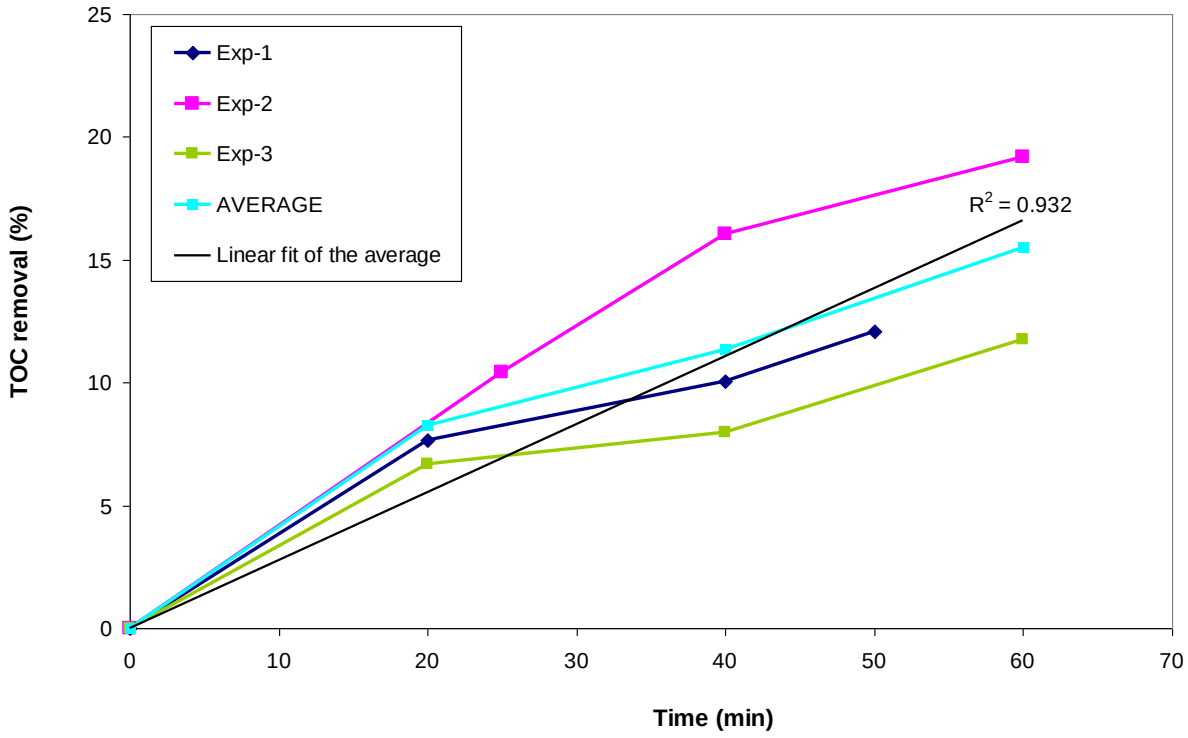
Extended treatments of the wash-water were also performed using the oxidative method identified as the most efficient: ozonation/hydrogen peroxide using the conditions listed in Table 21. Figure 29 present the results of three replicates of treatment performed over one hour. These experiments showed that the decrease in IBP concentration was not linear as initially expected but rather started to plateau after about 50 minutes.

Figure 27 : IBP removal during a one hour O_3/H_2O_2 treatment of the industrial first wash-water at the conditions listed in table 17



One reason, which may explain this trend, is the formation of transformation products. At a certain point, the transformation products amount in the solution can be important enough that the O_3 and OH radicals preferentially degrade the transformation products rather than the parent compound, IBP. To determine if the transformation products formed during O_3/H_2O_2 treatments were also degraded, TOC analyses were done and results are reported in the following figure.

Figure 28 : TOC removal during a one hour O_3/H_2O_2 treatment of the industrial first wash-water at the conditions listed in table 17



These results show that the TOC removal did not reach a plateau and continued to increase almost linearly over time as indicated by a R^2 closer to 1. As previously mentioned, the transformation products formed during O_3/H_2O_2 treatment probably starts, after a certain point, to react with the oxidants (OH radicals and ozone). This may explain the continuous removal of TOC observed even though the IBP removal started to plateau.

8. Conclusion

The majority of the parameters studied influenced the oxidation processes studied for their capacity to remove IBP. Performance of ozone, ozone/H_2O_2 and ozone/sonication experiments were higher at increased pH, temperature and ozone dose. Sonication performance was higher when the pH was decreased; the temperature and reaction time were increased. No hydrogen peroxide was formed during sonication at the ultrasound power studied, so the major part of increased performance of ozone/sonication experiment is probably due to an increase of O_3 dissolution in water. The processes involving ozonation showed great results, which can be applied to the treatment of industrial waters. Four of the products formed during removal of IBP by ozonation, ozonation with H_2O_2, sonication and ozonation/sonication were identified as 1-oxo-ibuprofen, oxalic acid, 4-acetylbenzoic acid and 4-ethylbenaldehyde. Further analyse should be done in order to determine the residual toxicity of these products and to determine the nature of the other transformation products not identified yet.

The removal method, which shows the highest removal of IBP and COD in a solution of pure IBP in water and in the first wash water, was ozone with H_2O_2. This method has now to be tested at a larger scale in order to evaluate its potential for industrial applications.

The characteristics of such an industrial first wash-water were assessed for the first time. The levels of removal obtained during the treatment of this solution were significantly higher than the ones obtained during the treatment of a pure solution of similar concentration. This shows the importance to perform experiments with actual industrial wastes rather than synthetic solutions. To the author's knowledge, these were the first experiments reported on the treatment of such a waste. This work helped to characterize this type of waste and demonstrated the potential of oxidative treatment to mitigate the discharge of pharmaceuticals into sewage by pharmaceuticals processing plants.

9. Limitations of this study

Due to the time required to design, build and optimized the reactor setup, the experimental plan was designed based on parametric studies rather than a factorial design. This means that the interactions between the parameters varied were unfortunately not investigated during this study.

No kinetic data were obtained for the different oxidation process studied due to time constraints and experimental limitations. In order to perform a kinetic analysis of the removal of IBP during sonication, many samples would have to be collected over a short period of time at the start of the reaction. However, the reduction in volume from the initial 300mL associated with the removal of each 5-mL sample would result in a change of impedance of 3 kHz; therefore leading to an impedance mismatch and a continuously decreasing power transfer efficiency. It would be impossible with the current setup to maintain constant conditions over time in order to determine an initial rate of reaction.

The use of a small-scale system rendered the system sensitive to small changes in the settings of the oxygen tank pressure as well as the ozone generator. It was noted that very small differences in the pressure of the oxygen tanks (such as 8-12 psi) resulted in significantly higher ozone flow rate and thus higher IBP removal. Great care had to be taken in order to obtain reproducible results.

Various interferences with COD analysis were observed especially with the use of hydrogen peroxide. Various controls had to be performed. Standards of hydrogen peroxide were made using the same concentration of H_2O_2 used during the experiment in order to monitor the COD increase (interference) generated by H_2O_2.

Lastly, larger variations were observed in the experiments performed at higher concentration of IBP and with the wash water from Wyeth. Experimental protocols might have to be revised to minimize the risk of precipitation of IBP during the experiments in order to improve the reproducibility of the results.

10. Suggestions for future work

10.1.1 Improvement of the setup

Two aspects of the setup should be improved to facilitate the operation of the reactor under reproducible and stable conditions. A flow meter and an ozone analyser should be added in order to continuously monitor and control the ozone flow rate fed to the reactor. A control system should be added to automatically adjust the resonance frequency according to the level of water into the reactor in order to minimize the impedance mismatch and maintain a stable and efficient energy transfer. With these changes, higher reproducibility would be obtained and additional studies such as a kinetic study could then be performed.

10.1.2 Future research directions

Sonication in presence of a catalyst could be considered as a way to increase the efficiency of removal. Some catalysts such as soluble iron or titanium dioxide were shown to increase the removal of 2-chloro-5-methyl phenol during sonication at 33 kHz, at a power of 1255 W and temperature varied from 15 to 20˚C (Nalini Vijaya Laxmi et al.) It was shown that 25% more removal was obtained with titanium dioxide. Addition of soluble iron during sonication increased the removal of Rodamine B (Merouani et al. 2010)

The reactor design can be modified to allow a continuous mode of operation. The sonoreactor used in this study was operated in a semi-continuous or batch mode but Mason showed that type of reactor can be design for continuous operation (Mason 1992). Experiments performed on a larger scale may also provide insight on the industriousness of this approach coupling ozonation and sonication or hydrogen peroxide to treat industrial waters.

A more thorough analysis should be done on the transformation products formed. Many IBP transformation products have yet to be identified. In addition, the stability,

persistence and toxicity of these products have to be determined in order to assess the risks for the environment and public health associated with these products.

11. References

Araujo, L., J. Wild, et al. (2008). "Determination of anti-inflammatory drugs in water samples, by in situ derivatization, solid phase microextraction and gas chromatography-mass spectrometry." Talanta 75(1): 111-115.

Behnajady, M. A., N. Modirshahla, et al. (2008). "Ultrasonic degradation of Rhodamine B in aqueous solution: Influence of operational parameters." Journal of Hazardous Materials 152(1): 381-386.

Besse, J.-P. and J. Garric (2008). "Human pharmaceuticals in surface waters: Implementation of a prioritization methodology and application to the French situation." Toxicology Letters 176(2): 104-123.

Bond, M. T. (2003). "Pharmaceuticals in U.S. Health Care: Determinants of Quantity and Price." Journal of Economic Perspectives Vol. 16: pp. 45-66.

Brown, J. N., N. Paxéus, et al. (2007). "Variations in bioconcentration of human pharmaceuticals from sewage effluents into fish blood plasma." Environmental Toxicology and Pharmacology 24(3): 267-274.

Brun, G. L., M. Bernier, et al. (2006). "Pharmaceutically active compounds in Atlantic Canadian sewage treatment plant effluents and receiving waters, and potential for environmental effects as measured by acute and chronic aquatic toxicity." Environmental Toxicology and Chemistry 25(8): 2163-2176.

Caviglioli, G., P. Valeria, et al. (2002). "Identification of degradation products of Ibuprofen arising from oxidative and thermal treatments." Journal of Pharmaceutical and Biomedical Analysis 30(3): 499-509.

Chai, X. S., Q. X. Hou, et al. (2004). "Rapid determination of hydrogen peroxide in the wood pulp bleaching streams by a dual-wavelength spectroscopic method." Analytica Chimica Acta 507(2): 281-284.

Chen, M., K. Ohman, et al. (2006). "Pharmaceuticals and endocrine disruptors in wastewater treatment effluents and in the water supply system of Calgary, Alberta, Canada." Water Quality Research Journal of Canada 41(4): 351-364.

Chowdhury, P. and T. Viraraghavan (2009). "Sonochemical degradation of chlorinated organic compounds, phenolic compounds and organic dyes - A review." Science of The Total Environment 407(8): 2474-2492.

Ciríaco, L., C. Anjo, et al. (2009). "Electrochemical degradation of Ibuprofen on Ti/Pt/PbO2 and Si/BDD electrodes." Electrochimica Acta 54(5): 1464-1472.

Cleuvers, M. (2003). "Aquatic ecotoxicity of pharmaceuticals including the assessment of combination effects." Toxicology Letters 142(3): 185-194.

Comeau, F., C. Surette, et al. (2008). "The occurrence of acidic drugs and caffeine in sewage effluents and receiving waters from three coastal watersheds in Atlantic Canada." Science of The Total Environment 396(2-3): 132-146.

Cui, N., X. Zhang, et al. (2010). "Toxicity profile of labile preservative bronopol in water: The role of more persistent and toxic transformation products." Environmental Pollution In Press, Corrected Proof.

Donn, J., M. Mendoza, et al. (2009). "Tons of released drugs taint US water." PhysOrg.org(Associated Press Writers).

Emery, R. J., M. Papadaki, et al. (2005). "Extent of sonochemical degradation and change of toxicity of a pharmaceutical precursor (triphenylphosphine oxide) in water as a function of treatment conditions." Environment International 31(2): 207-211.

Esplugas, S., D. M. Bila, et al. (2007). "Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents." Journal of Hazardous Materials 149(3): 631-642.

Farré, M. l., S. Pérez, et al. (2008). "Fate and toxicity of emerging pollutants, their metabolites and transformation products in the aquatic environment." TrAC Trends in Analytical Chemistry 27(11): 991-1007.

Fent, K., A. A. Weston, et al. (2006). "Ecotoxicology of human pharmaceuticals." Aquatic Toxicology 76(2): 122-159.

Ferrari, B., N. Paxéus, et al. (2003). "Ecotoxicological impact of pharmaceuticals found in treated wastewaters: study of carbamazepine, clofibric acid, and diclofenac." Ecotoxicology and Environmental Safety 55(3): 359-370.

Gagné, F., C. Blaise, et al. (2006). "Occurrence of pharmaceutical products in a municipal effluent and toxicity to rainbow trout (Oncorhynchus mykiss) hepatocytes." Ecotoxicology and Environmental Safety 64(3): 329-336.

Gagnon, C. and A. Lajeunesse (2008). Persistence and fate of highly soluble pharmaceutical products in various types of municipal wastewater treatment plants. WIT Transactions on Ecology and the Environment.

Goel, M., H. Hongqiang, et al. (2004). "Sonochemical decomposition of volatile and non-volatile organic compounds--a comparative study." Water Research 38(19): 4247-4261.

Gogate, P. R. (2008). "Treatment of wastewater streams containing phenolic compounds using hybrid techniques based on cavitation: A review of the current status and the way forward." Ultrasonics Sonochemistry 15(1): 1-15.

Gouvernement du Quebec, D. d., environnement et parc (2002). "Eaux Usees."

Gros, M., M. Petrovic, et al. (2010). "Removal of pharmaceuticals during wastewater treatment and environmental risk assessment using hazard indexes." Environment International 36(1): 15-26.

Hartmann, J., P. Bartels, et al. (2008). "Degradation of the drug diclofenac in water by sonolysis in presence of catalysts." Chemosphere 70(3): 453-461.

He, Z., S. Song, et al. (2007). "p-Aminophenol degradation by ozonation combined with sonolysis: Operating conditions influence and mechanism." Ultrasonics Sonochemistry 14(5): 568-574.

He, Z., S. Song, et al. (2007). "C.I. Reactive Black 5 decolorization by combined sonolysis and ozonation." Ultrasonics Sonochemistry 14(3): 298-304.

Hoigné, J. and H. Bader (1983). "Rate constants of reactions of ozone with organic and inorganic compounds in water--II: Dissociating organic compounds." Water Research 17(2): 185-194.

Huber, M. M., S. Canonica, et al. (2003). "Oxidation of Pharmaceuticals during Ozonation and Advanced Oxidation Processes." Environmental Science & Technology 37(5): 1016-1024.
Huber, M. M., S. Korhonen, et al. (2005). "Oxidation of pharmaceuticals during water treatment with chlorine dioxide." Water Research 39(15): 3607-3617.
Hudec, R., M. Kriska, et al. (2008). "Comparison of NSAID Consumption in slovakia, Finland and Norway." Bratisl lek listy 109: 370-373.
Hung, H.-M. and M. R. Hoffmann (1999). "Kinetics and Mechanism of the Sonolytic Degradation of Chlorinated Hydrocarbons: Frequency Effects." The Journal of Physical Chemistry A 103(15): 2734-2739.
Ince, N. H. and G. Tezcanlí (2001). "Reactive dyestuff degradation by combined sonolysis and ozonation." Dyes and Pigments 49(3): 145-153.
Isariebel, Q.-P., J.-L. Carine, et al. (2009). "Sonolysis of levodopa and paracetamol in aqueous solutions." Ultrasonics Sonochemistry In Press, Corrected Proof.
Klavarioti, M., D. Mantzavinos, et al. (2009). "Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes." Environment International 35(2): 402-417.
Kolpin, D. W., E. T. Furlong, et al. (2002). "Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: A national reconnaissance." Environmental Science and Technology 36(6): 1202-1211.
Kosjek, T. and E. Heath (2008). "Applications of mass spectrometry to identifying pharmaceutical transformation products in water treatment." TrAC Trends in Analytical Chemistry 27(10): 807-820.
Kosma, C. I., D. A. Lambropoulou, et al. (2010). "Occurrence and removal of PPCPs in municipal and hospital wastewaters in Greece." Journal of Hazardous Materials 179(1-3): 804-817.
Lishman, L., S. A. Smyth, et al. (2006). "Occurrence and reductions of pharmaceuticals and personal care products and estrogens by municipal wastewater treatment plants in Ontario, Canada." Science of the Total Environment 367(2-3): 544-558.
Loganathan, B., M. Phillips, et al. (2009). "Contamination profiles and mass loadings of macrolide antibiotics and illicit drugs from a small urban wastewater treatment plant." Chemosphere 75(1): 70-77.
Madhavan, J., F. Grieser, et al. "Combined advanced oxidation processes for the synergistic degradation of ibuprofen in aqueous environments." Journal of Hazardous Materials In Press, Corrected Proof.
Mason, T. J. (1992). "Industrial sonochemistry: potential and practicality." Ultrasonics 30(3): 192-196.
Mason, T. J., J. P. Lorimer, et al. (1992). "Quantifying sonochemistry: Casting some light on a [`]black art'." Ultrasonics 30(1): 40-42.
Matamoros, V., M. Hijosa, et al. (2009). "Assessment of the pharmaceutical active compounds removal in wastewater treatment systems at enantiomeric level. Ibuprofen and naproxen." Chemosphere 75(2): 200-205.
Méndez-Arriaga, F., R. A. Torres-Palma, et al. (2008). "Ultrasonic treatment of water contaminated with ibuprofen." Water Research 42(16): 4243-4248.

Merouani, S., O. Hamdaoui, et al. (2010). "Sonochemical degradation of Rhodamine B in aqueous phase: Effects of additives." Chemical Engineering Journal 158(3): 550-557.

Miège, C., J. M. Choubert, et al. (2009). "Fate of pharmaceuticals and personal care products in wastewater treatment plants - Conception of a database and first results." Environmental Pollution In Press, Corrected Proof.

Mompelat, S., B. LeBot, et al. (2008). "Occurrence and fate of pharmaceutical products and by-products, from resource to drinking water." Environment International In Press, Corrected Proof.

Muthukumar, M., D. Sargunamani, et al. (2005). "Statistical analysis of the effect of aromatic, azo and sulphonic acid groups on decolouration of acid dye effluents using advanced oxidation processes." Dyes and Pigments 65(2): 151-158.

Nalini Vijaya Laxmi, P., P. Saritha, et al. (2010). "Sonochemical degradation of 2chloro-5methyl phenol assisted by TiO2 and H2O2." Journal of Hazardous Materials 174(1-3): 151-155.

Oh, B. S., H. Y. Jang, et al. (2007). "Role of ozone for reducing fouling due to pharmaceuticals in MF (microfiltration) process." Journal of Membrane Science 289(1-2): 178-186.

Pérez, S. and D. Barceló (2007). "Application of advanced MS techniques to analysis and identification of human and microbial metabolites of pharmaceuticals in the aquatic environment." TrAC Trends in Analytical Chemistry 26(6): 494-514.

Petrier, C., M. F. Lamy, et al. (1994). "Sonochemical degradation of phenol in dilute aqueous solutions - comparison of the reaction rates at 20-kHz and 487-kHz." Journal of Physical Chemistry 98(41): 10514-10520.

Quintana, J. B., S. Weiss, et al. (2005). "Pathways and metabolites of microbial degradation of selected acidic pharmaceutical and their occurrence in municipal wastewater treated by a membrane bioreactor." Water Research 39(12): 2654-2664.

Rodayan, A., R. Roy, et al. (2010). "Oxidation products of sulfamethoxazole in ozonated secondary effluent." Journal of Hazardous Materials In Press, Corrected Proof.

Sanchez-Prado, L., R. Barro, et al. (2008). "Sonochemical degradation of triclosan in water and wastewater." Ultrasonics Sonochemistry 15(5): 689-694.

Schultz, M. M. and E. T. Furlong (2008). "Trace Analysis of Antidepressant Pharmaceuticals and Their Select Degradates in Aquatic Matrixes by LC/ESI/MS/MS." Analytical Chemistry 80(5): 1756-1762.

Servos, M. R., M. Smith, et al. (2007). "The presence of selected pharmaceuticals and the antimicrobial triclosan in drinking water in Ontario, Canada." Water Quality Research Journal of Canada 42(2): 130-137.

Sharma, V. and S. Mishra (2006). "Ferrate(VI) oxidation of ibuprofen: A kinetic study." Environmental Chemistry Letters 3(4): 182-185.

Siemens, J., G. Huschek, et al. (2008). "Concentrations and mobility of human pharmaceuticals in the world's largest wastewater irrigation system, Mexico City-Mezquital Valley." Water Research 42(8-9): 2124-2134.

Skoumal, M., R. M. Rodríguez, et al. (2009). "Electro-Fenton, UVA photoelectro-Fenton and solar photoelectro-Fenton degradation of the drug ibuprofen in acid aqueous

medium using platinum and boron-doped diamond anodes." Electrochimica Acta 54(7): 2077-2085.
Son, Y., M. Lim, et al. (2009). "Investigation of acoustic cavitation energy in a large-scale sonoreactor." Ultrasonics Sonochemistry 16(4): 552-556.
Song, S., M. Xia, et al. (2007). "Degradation of p-nitrotoluene in aqueous solution by ozonation combined with sonolysis." Journal of Hazardous Materials 144(1-2): 532-537.
Stumpf, M., T. A. Ternes, et al. (1999). "Polar drug residues in sewage and natural waters in the state of Rio de Janeiro, Brazil." The Science of The Total Environment 225(1-2): 135-141.
Ternes, T. A. (1998). "Occurrence of drugs in German sewage treatment plants and rivers." Water Research 32(11): 3245-3260.
Tezcanli-Guyer, G. and N. H. Ince (2003). "Degradation and toxicity reduction of textile dyestuff by ultrasound." Ultrasonics Sonochemistry 10(4-5): 235-240.
Torres, R. A., F. Abdelmalek, et al. (2007). "A comparative study of ultrasonic cavitation and Fenton's reagent for bisphenol A degradation in deionised and natural waters." Journal of Hazardous Materials 146(3): 546-551.
Vogna, D., R. Marotta, et al. (2004). "Advanced oxidation of the pharmaceutical drug diclofenac with UV/H2O2 and ozone." Water Research 38(2): 414-422.
Wang, N., L. Zhu, et al. (2010). "Sono-enhanced degradation of dye pollutants with the use of H2O2 activated by Fe3O4 magnetic nanoparticles as peroxidase mimetic." Ultrasonics Sonochemistry 17(1): 78-83.
Weavers, L. K., N. Malmstadt, et al. (2000). "Kinetics and Mechanism of Pentachlorophenol Degradation by Sonication, Ozonation, and Sonolytic Ozonation." Environmental Science & Technology 34(7): 1280-1285.
Wert, E. C., F. L. Rosario-Ortiz, et al. (2009). "Effect of ozone exposure on the oxidation of trace organic contaminants in wastewater." Water Research In Press, Corrected Proof.
Yargeau, V., A. Lopata, et al. (2007). "Pharmaceuticals in the Yamaska River, Quebec, Canada." Water Quality Research Journal of Canada 42(4): 231-239.
Yu, Y.-h., J. Ma, et al. (2006). "Degradation of 2,4-dichlorophenoxyacetic acid in water by ozone-hydrogen peroxide process." Journal of Environmental Sciences 18(6): 1043-1049.
Yuan, F., C. Hu, et al. (2009). "Degradation of selected pharmaceuticals in aqueous solution with UV and UV/H2O2." Water Research In Press, Accepted Manuscript.
Zhang, G. and I. Hua (2000). "Ultrasonic degradation of trichloroacetonitrile, chloropicrin and bromobenzene: design factors and matrix effects." Advances in Environmental Research 4(3): 219-224.
Zorita, S., L. Mårtensson, et al. (2009). "Occurrence and removal of pharmaceuticals in a municipal sewage treatment system in the south of Sweden." Science of The Total Environment 407(8): 2760-2770.
Zwiener, C. (2007). "Occurrence and analysis of pharmaceuticals and their transformation products in drinking water treatment." Analytical and Bioanalytical Chemistry 387(4): 1159-1162.

Zwiener, C. and F. H. Frimmel (2000). "Oxidative treatment of pharmaceuticals in water." Water Research 34(6): 1881-1885.

Zwiener, C. and F. H. Frimmel (2003). "Short-term tests with a pilot sewage plant and biofilm reactors for the biological degradation of the pharmaceutical compounds clofibric acid, ibuprofen, and diclofenac." The Science of The Total Environment 309(1-3): 201-211.

APPENDIX 1

Table 19 : Inductance-turns chart, Ferrite Toroids material (Amidon Corp)

MATERIAL #43

turns count > core number		A_L*	10	20	30	40	50	60	70	80	90	100
			Inductance in millihenries									
FT-23	-43	188	.018	.075	.169	.300	.470	.677	.921	1.20	1.52	1.88
FT-37	-43	420	.042	.168	.378	.672	1.050	1.510	2.060	2.69	3.40	4.20
FT-50	-43	523	.052	.209	.471	.836	1.300	1.880	2.560	3.35	4.24	5.23
FT-50A	-43	570	.057	.228	.513	.912	1.430	2.050	2.790	3.65	4.62	5.70
FT-50B	-43	1140	.110	.456	1.030	1.820	2.850	4.100	5.590	7.30	9.23	11.4
FT-82	-43	557	.056	.224	.503	.894	1.400	2.010	2.740	3.58	4.53	5.59
FT-114	-43	603	.060	.241	.543	.965	1.510	2.170	2.950	3.86	4.88	6.03
FT-140	-43	953	.095	.380	.857	1.520	2.380	3.430	4.660	6.09	7.71	9.52
FT-240	-43	1239	.123	.494	1.110	1.970	3.090	4.440	6.050	7.90	9.96	12.3

MATERIAL #61

turns count > core number		A_L*	10	20	30	40	50	60	70	80	90	100
			Inductance in millihenries									
FT-23	-61	24.8	.002	.010	.022	.040	.063	.089	.122	.159	.201	.248
FT-37	-61	55.3	.006	.022	.050	.088	.138	.199	.271	.354	.448	.553
FT-50	-61	68.8	.007	.028	.062	.110	.172	.248	.337	.440	.557	.688
FT-50A	-61	75.0	.008	.030	.068	.120	.186	.270	.366	.480	.608	.750
FT-50B	-61	150.0	.015	.060	.135	.240	.375	.540	.735	.960	1.220	1.500
FT-82	-61	73.3	.007	.029	.066	.117	.183	.264	.359	.469	.594	.733
FT-114	-61	79.3	.008	.032	.071	.127	.198	.285	.389	.508	.642	.793
FT-114A	-61	146.0	.015	.058	.131	.233	.365	.526	.715	.934	1.180	1.460
FT-140	-61	140.0	.014	.056	.126	.224	.350	.504	.686	.896	1.130	1.400
FT-240	-61	171.0	.017	.068	.154	.274	.428	.616	.838	1.090	1.390	1.710

MATERIAL #67

turns count > core number		A_L*	10	20	30	40	50	60	70	80	90	100
			Inductance in millihenries									
FT-23	-67	7.9	——	.003	.007	.013	.020	.028	.038	.051	.064	.079
FT-37	-67	19.7	.002	.008	.018	.032	.049	.071	.097	.126	.160	.197
FT-50	-67	22.0	.002	.009	.020	.035	.055	.079	.108	.141	.178	.220
FT-50A	-67	24.0	.002	.020	.033	.038	.060	.086	.112	.154	.194	.240
FT-50B	-67	48.0	.005	.019	.043	.077	.120	.173	.235	.307	.389	.480
FT-82	-67	22.4	.002	.009	.020	.036	.056	.081	.110	.143	.181	.224
FT-114	-67	25.4	.003	.010	.023	.041	.064	.091	.124	.163	.206	.254
FT-140	-67	45.0	.005	.018	.041	.072	.118	.162	.220	.288	.365	.450
FT-240	-67	53.0	.005	.021	.048	.084	.133	.199	.260	.339	.430	.530

MATERIAL #68

turns count > core number		A_L*	10	20	30	40	50	60	70	80	90	100
			Inductance in millihenries									
FT-23	-67	7.9	——	.003	.007	.013	.020	.028	.038	.051	.064	.079
FT-23	-68	4.0	——	.002	.004	.006	.010	.014	.020	.026	.032	.040
FT-37	-68	8.8	——	.006	.008	.014	.022	.032	.043	.056	.071	.088
FT-50	-68	11.0	.001	.004	.010	.018	.028	.040	.054	.070	.089	.110
FT-50A	-68	12.0	.001	.005	.011	.019	.030	.043	.059	.077	.097	.117
FT-82	-68	11.7	.001	.005	.011	.019	.029	.042	.057	.075	.095	.117
FT-114	-68	12.7	.001	.005	.011	.020	.032	.046	.062	.081	.123	.127

* A_L value in mh/1000 turns

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SECTION II: FERRITE CORES

Ferrite Cores are available in numerous sizes and several permeabilities. Their permeability range is from 20 to more than 15,000. They are very useful for resonant circuit applications as well as wideband transformers and they are also commonly used for RFI attenuation. We can supply sizes from 0.23 inches to 2.4 inches in outer diameter directly from stock.

Ferrite toroidal cores are well suited for a variety of RF circuit applications and their relatively high permeability factors make them especially useful for high inductance values with a minimum number of turns, resulting in smaller component size.

There are two basic ferrite material groups: (1) Those having a permeability range from 20 to 800 μ_i are of the Nickel Zinc class, and (2) those having permeabilities above 800 μ_i are usually of the Manganese Zinc class.

The Nickel Zinc ferrite cores exhibit high volume resistivity, moderate temperature stability and high 'Q' factors for the 500 KHz to 100 MHz frequency range. They are well suited for low power, high inductance resonant circuits. Their low permeability factors make them useful for wide band transformer applications as well.

The Manganese Zinc ferrites, having permeabilities above 800 μ_i, have fairly low volume resistivity and moderate saturation flux density. They can offer high 'Q' factors for the 1 KHz to 1 MHz frequency range. Cores from this group of materials are widely used for switched mode power conversion transformers operating in the 20 KHz to 100 KHz frequency range. These cores are also very useful for the attenuation of unwanted RF noise signals in the frequency range of 20 MHz to 400 MHz and above.

A list of Ferrite toroids, including physical dimensions, A_L values, and magnetic properties will be found on the next few pages. Use the given A_L value and the equation below to calculate a turn count for a specific inductance.

$$N = 1000\sqrt{\frac{\text{desired 'L' (mh)}}{A_L\ \text{(mh/1000 turns)}}} \qquad L(\text{mh}) = \frac{A_L \times N^2}{1{,}000{,}000} \qquad A_L(\text{mh/1000 turns}) = \frac{1{,}000{,}000 \times \text{'L' (mh)}}{N^2}$$

N = number of turns L = inductance (mh) A_L = inductance index (mh)/1000 turns)

To improve voltage breakdown, coatings of ferrite cores are available for the F, J, W and H materials. Typical coatings are parylene C, Gray Coating and Black Lacquer. Parylene C coating has a thickness of 0.5 mils to 2 mils with a voltage breakdown of 750V. Gray coating has a thickness of 4 mils to 8 mils with voltage breakdown of 500V. Black Lacquer coating has a thickness of 0.5 mils to 2 mils with no increase in voltage breakdown.

All items in this booklet are standard stock items and usually can be shipped immediately. Call for availability of non-stock items.

- **For standard stocking items of Inductors, Chokes, Transformers and other wound ferrites, please see section V.**
- **For custom design of Inductors, Chokes, Transformers or Special Coil Windings, please call or fax your specifications today.**
- **Amidon provides engineering designs, prototyping and manufacturing. Low to high volume production capability with the most competitive pricing.**

APPENDIX 2

Table 20 : Standard table of AWG gauge wire

AWG gauge	Conductor Diameter Inches	Conductor Diameter mm	Ohms per 1000 ft.	Ohms per km	Maximum amps for chassis wiring	Maximum amps for power transmission
1	0.2893	7.34822	0.1239	0.406392	211	119
2	0.2576	6.54304	0.1563	0.512664	181	94
3	0.2294	5.82676	0.197	0.64616	158	75
4	0.2043	5.18922	0.2485	0.81508	135	60
5	0.1819	4.62026	0.3133	1.027624	118	47
6	0.162	4.1148	0.3951	1.295928	101	37
7	0.1443	3.66522	0.4982	1.634096	89	30
8	0.1285	3.2639	0.6282	2.060496	73	24
9	0.1144	2.90576	0.7921	2.598088	64	19
10	0.1019	2.58826	0.9989	3.276392	55	15
11	0.0907	2.30378	1.26	4.1328	47	12
12	0.0808	2.05232	1.588	5.20864	41	9.3
13	0.072	1.8288	2.003	6.56984	35	7.4
14	0.0641	1.62814	2.525	8.282	32	5.9
15	0.0571	1.45034	3.184	10.44352	28	4.7
16	0.0508	1.29032	4.016	13.17248	22	3.7
17	0.0453	1.15062	5.064	16.60992	19	2.9
18	0.0403	1.02362	6.385	20.9428	16	2.3
19	0.0359	0.91186	8.051	26.40728	14	1.8
20	0.032	0.8128	10.15	33.292	11	1.5
21	0.0285	0.7239	12.8	41.984	9	1.2
22	0.0254	0.64516	16.14	52.9392	7	0.92
23	0.0226	0.57404	20.36	66.7808	4.7	0.729
24	0.0201	0.51054	25.67	84.1976	3.5	0.577
25	0.0179	0.45466	32.37	106.1736	2.7	0.457
26	0.0159	0.40386	40.81	133.8568	2.2	0.361

Reference : http://www.powerstream.com/Wire_Size.htm

APPENDIX 3

Advil Tablets, Caplets, Gel Caplets

Directions
Adults and children over 12: Take 1 or 2 tablets, caplets or gel caplets every 4 hours as needed. Do not exceed 6 tablets, caplets or gel caplets in 24 hours, unless directed by a physician. Children 12 and under should use Children's Advil.

• **Caution**
Keep out of reach of children. This package contains enough medicine to seriously harm a child.

Warning
Do not take Advil if taking acetylsalicylic acid (ASA) or other products containing ibuprofen, or if allergic to ASA, salicylates or anti-inflammatory drugs, or any of its ingredients. Consult your physician before taking Advil if you have peptic ulcers, high blood pressure, heart, kidney or liver disease, any other serious disease, or are taking any other drug. Do not take Advil if you are pregnant or nursing a baby, unless directed by a physician. Consult your physician if the pain or fever persists for more than 5 days. Do not exceed the recommended dose unless advised by a physician.

If abdominal pain, heartburn, nausea or vomiting, bloating, diarrhea or constipation, ringing or buzzing in the ears, nervousness, sleeplessness, dizziness, any change in vision, fluid retention, itching, skin rashes or any other side effect or unexplained symptom develops while taking Advil, discontinue use immediately and contact a physician. In case of overdose, call a Poison Control Centre or a doctor at once even if there are no symptoms.

Tablets and Caplets Non-medicinal Ingredients
acetylated monoglycerides, beeswax, carnauba wax, corn starch, croscarmellose sodium, ethoxyethanol, iron oxides, lecithin, microcrystalline cellulose, parabens, pharmaceutical glaze, pharmaceutical shellac, povidone, pregelatinized starch, silicon dioxide, simethicone, sodium benzoate, sodium lauryl sulfate, stearic acid, sucrose, titanium dioxide.

Gel Caplets Non-medicinal Ingredients
corn starch, croscarmellose sodium, FD&C red No. 40, FD&C yellow No. 6, gelatin, glycerin, hypromellose, iron oxides, medium chain triglycerides, pregelatinized starch, propyl gallate, propylene glycol, silicon dioxide, sodium lauryl sulfate, stearic acid, titanium dioxide, triacetin.

Advil Extra Strength Caplets

Directions
Adults and children over 12: Take 1 caplet every 4 hours as needed. Do not exceed 3 caplets in 24 hours, unless directed by a physician. Children 12 and under should use Children's Advil.

• **Caution**
Keep out of reach of children. This package contains enough medicine to seriously harm a child.

Warning
Do not take Advil if taking acetylsalicylic acid (ASA) or other products containing ibuprofen, or if allergic to ASA, salicylates or anti-inflammatory drugs, or any of its ingredients. Consult your physician before taking Advil if you have peptic ulcers, high blood pressure, heart, kidney or liver disease, any other serious disease, or are taking any other drug. Do not take Advil if you are pregnant or nursing a baby, unless directed by a physician. Consult your physician if the pain or fever persists for more than 5 days. Do not exceed the recommended dose unless advised by a physician.

If abdominal pain, heartburn, nausea or vomiting, bloating, diarrhea or constipation, ringing or buzzing in the ears, nervousness, sleeplessness, dizziness, any change in vision, fluid retention, itching, skin rashes or any other side effect or unexplained symptom develops while taking Advil, discontinue use immediately and contact a physician. In case of overdose, call a Poison Control Centre or a doctor at once even if there are no symptoms.

Non-medicinal Ingredients
corn starch, croscarmellose sodium, hydroxypropyl methylcellulose, iron oxides, lecithin, pharmaceutical shellac, polyethylene glycol, pregelatinized starch, silicon dioxide, simethicone, sodium lauryl sulfate, stearic acid, talc, titanium dioxide.

Advil Liqui-Gels® and Extra Strength Liqui-Gels®

Advil Liqui-Gels (200 mg) Directions
Adults and children over 12: For migraine headaches, take 1 or 2 Liqui-Gels at the first sign of symptoms and every 4 hours as needed. For all other uses, take 1 or 2 Liqui-Gels every 4 hours as needed. Do not exceed 6 Liqui-Gels in 24 hours, unless directed by a physician. Children 12 and under should use Children's Advil.

Advil Extra Strength Liqui-Gels (400 mg) Directions
Adults and children over 12: For migraine headaches, take 1 Extra Strength Liqui-Gel at the first sign of symptoms and every 4 hours as needed. For all other uses, take 1 Extra Strength Liqui-Gel every 4 hours as needed. Do not exceed 3 Extra Strength Liqui-Gels in 24 hours, unless directed by a physician. Children 12 and under should use Children's Advil.

• **Caution**
Keep out of reach of children. This package contains enough medicine to seriously harm a child.

Warning
Do not take Advil if taking acetylsalicylic acid (ASA) or other products containing ibuprofen, or if allergic to ASA, salicylates or anti-inflammatory drugs, or any of its ingredients. Consult your physician before taking Advil if you have peptic ulcers, high blood pressure, heart, kidney or liver disease, any other serious disease, or are taking any other drug. Do not take Advil if you are pregnant or nursing a baby, unless directed by a physician. Consult your physician if the pain or fever persists for more than 5 days. Do not exceed the recommended dose unless advised by a physician.

If abdominal pain, heartburn, nausea or vomiting, bloating, diarrhea or constipation, ringing or buzzing in the ears, nervousness, sleeplessness, dizziness, any change in vision, fluid retention, itching, skin rashes or any other side effect or unexplained symptom develops while taking Advil, discontinue use immediately and contact a physician. In case of overdose, call a Poison Control Centre or a doctor at once even if there are no symptoms.

Advil Liqui-Gels (200 mg) Non-medicinal Ingredients
FD&C green No. 3, gelatin, polyethylene glycol, polyvinyl acetate phthalate, potassium hydroxide, propylene glycol, purified water, sorbitan, sorbitol, titanium dioxide.

Advil Extra Strength Liqui-Gels (400 mg) Non-medicinal Ingredients
gelatin, iron oxide, lecithin, medium chain triglycerides, polyethylene glycol, polyvinyl acetate phthalate, potassium hydroxide, propylene glycol, purified water, sorbitan, sorbitol.

APPENDIX 4

Iodometric titration (standard method #22350E)

1. Measure a bottle of 200 ml of distilled water containing 2% of potassium iodide.
2. Experiment are run 20 to 40 after which 10mL of 1N sulfuric acid were added to the bottle
3. A titration is executed with a solution of 0.1 N sodium thiosulfate until a yellow color had been reach.
4. When yellow color appears, a 2mL of a 5% starch solution is added like indicator.
5. The production of ozone per minute can be calculated by the following formula:

Ozone Production (mg/min) = (A)*N*24/T

Where :

A= mL of titrant for bottle A

N= Normality of $Na_2S_2O_3$

T = time of ozonation (min)

Indigo method

Preparation of the stock solution

1. Take 500mL of pure water and put it in a 1L flask
2. Put 1mL of phosphoric acid in the 1 L flask
3. Mix the solution
4. Add 770mg of potassium indigo trifulfonate into the 1 L flask
5. Fill to 1 L volumetric flask
6. Mix the solution

The stock solution is stable for 3 months if is kept in obscurity

Standard solution

1. Measure 20mL of stock solution and put it in 1 L flask
2. Put 10 g of sodium dihydrogen phosphate into the flask
3. Put 7mL of concentrated phosphoric acid into the flask
4. Fill the solution to the mark with the desired sample

The following formula was used to determine the quantity of ozone dissolved

$$C_{O3}\ (mg/O_3/L) = ((A_b*V_T)_{blank}-(A_S*V_T)_{sample}))/(f*V_S*b)$$

Where:

A_b: Absorbance of blank

A_S: Absorbance of sample

f: 0.42

$V_{T(Blank):}$ Total volume of blank = 100mL

$V_{T(Sample):}$ Total volume of sample plus indigo solution (mL)

V_S: Sample volume

B : Path length of cell (1cm)

COD Standard method protocol

1. Turn on the COD reactor and select the appropriate COD program, 150˚C with a 2 H countdown
2. Close the safety shield in front of the reactor and allow it to pre-heat to 150˚C
3. Choose the correct digestion vials based on the expected COD range and choose one to use as an experimental blank
4. Pipette 2mL of sample into vial (200-1500 mg/L) or 2mL of pure water for the standard
5. Cap the vials and invert the vials several time to mixed them
6. Put the vials into the COD reactor during 2 H
7. After the vials passed to the COD reactor and they are cold, Take the Touch HACH Program and select the program to used based on the COD range vials
8. Clean the exterior of the vials and place the blank into the apparatus
9. Tare the apparatus with the blank
10. Put other vials one by one into the apparatus

REFERENCE: HACH program User manual

APPENDIX 5

Figure 29 : HPLC Chromatogram of IBP

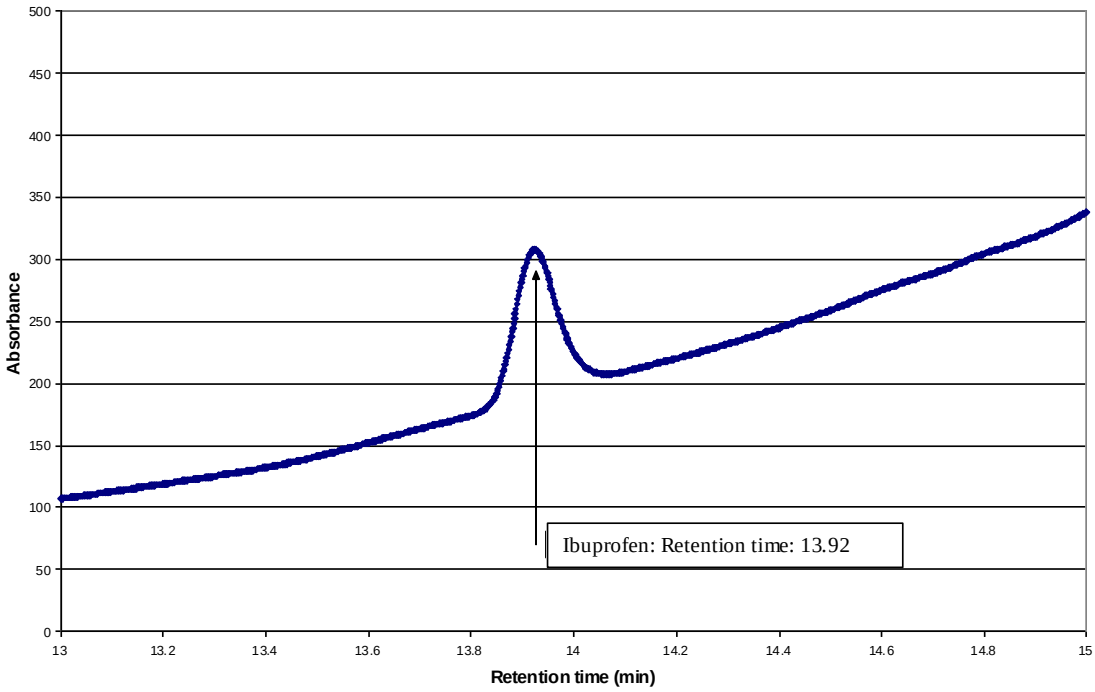


Figure 30 : HPLC Calibration curve for low IBP concentration

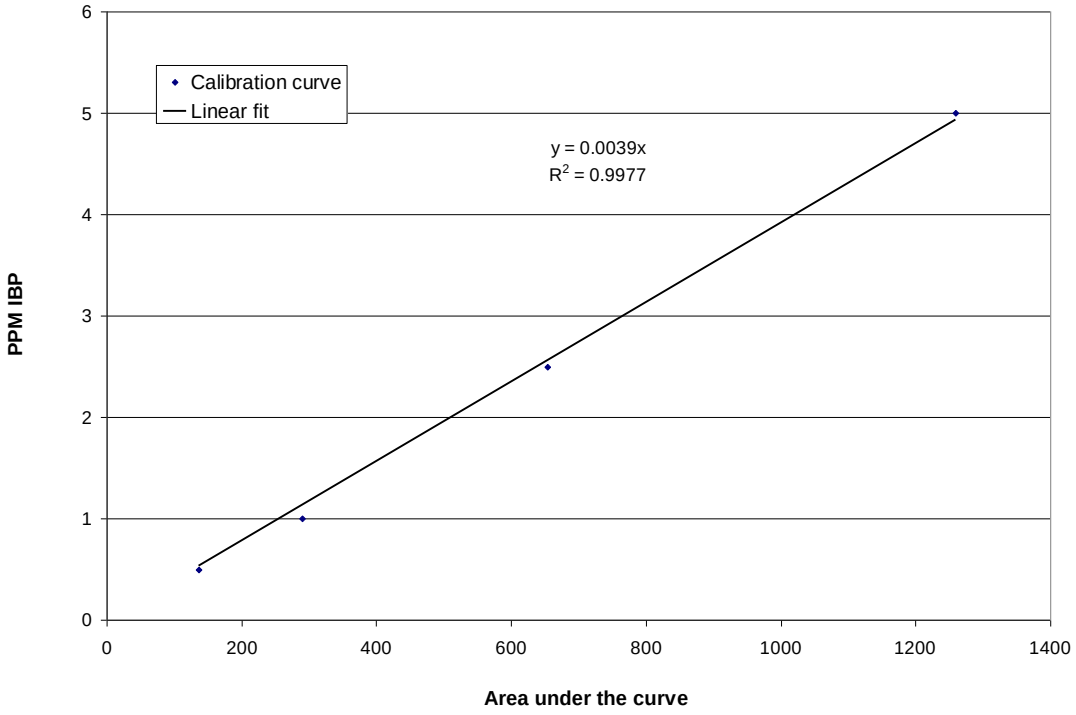
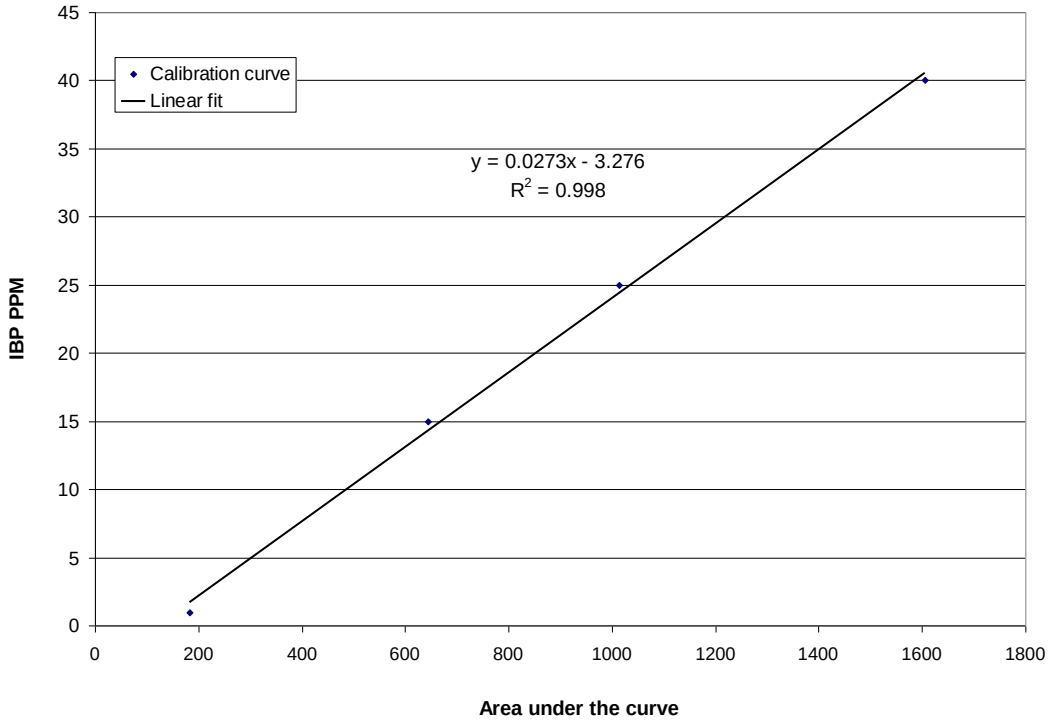


Figure 31 : HPLC calibration curve of IBP for high concentration



APPENDIX 6

Figure 32 : 5ppm standard of potential products mixed 50%/50% with transformation product solution from oxidative experiment

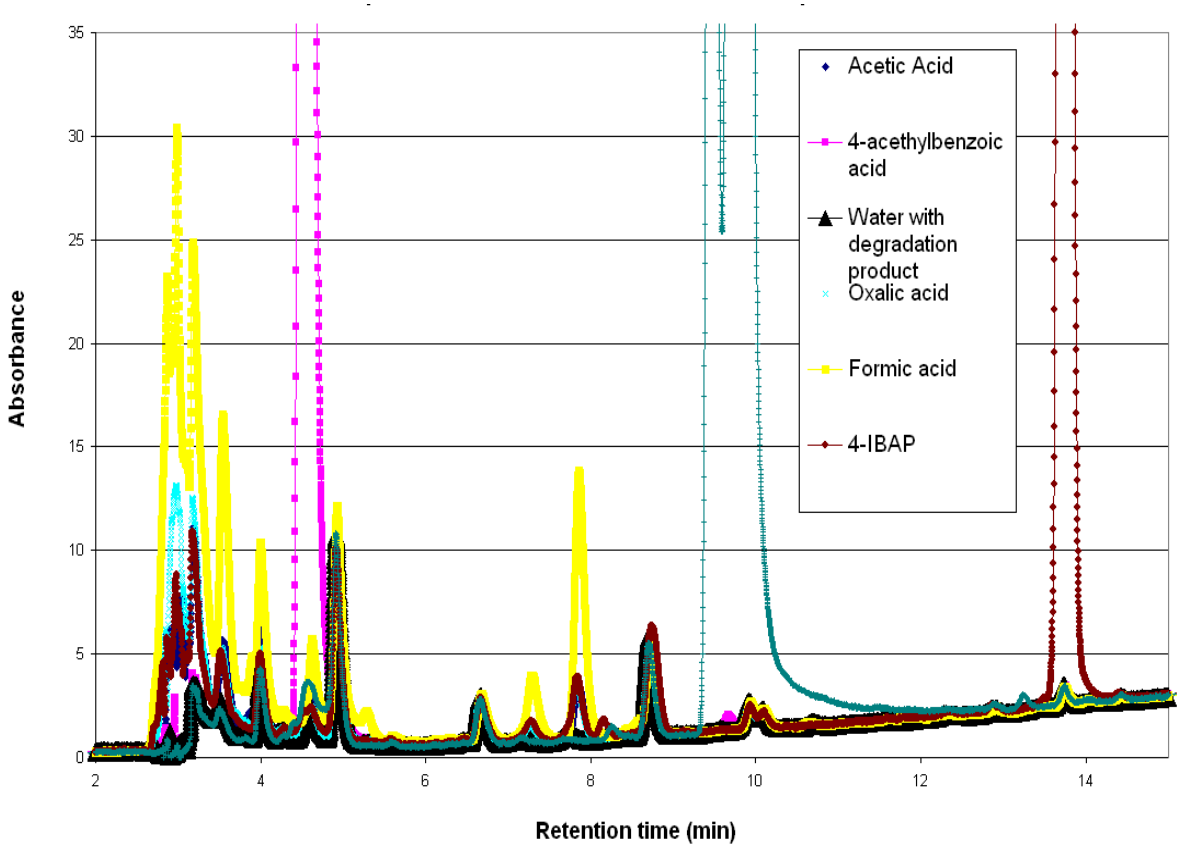
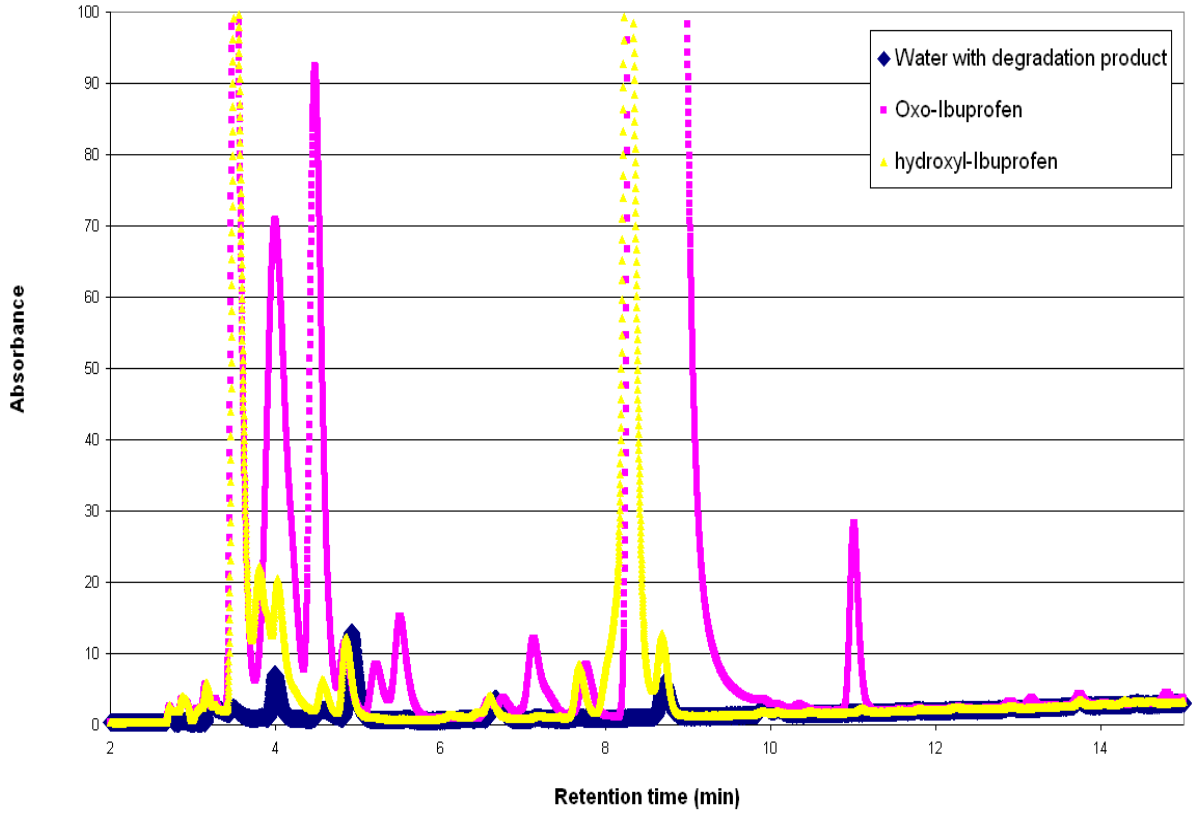


Figure 33 : 0.5ppm standard of potential products mixed 50%/50% with transformation product solution from oxidative treatment



APPENDIX 7

Figure 34: MS spectral of a standard of 4-ethylbenhaldehyde

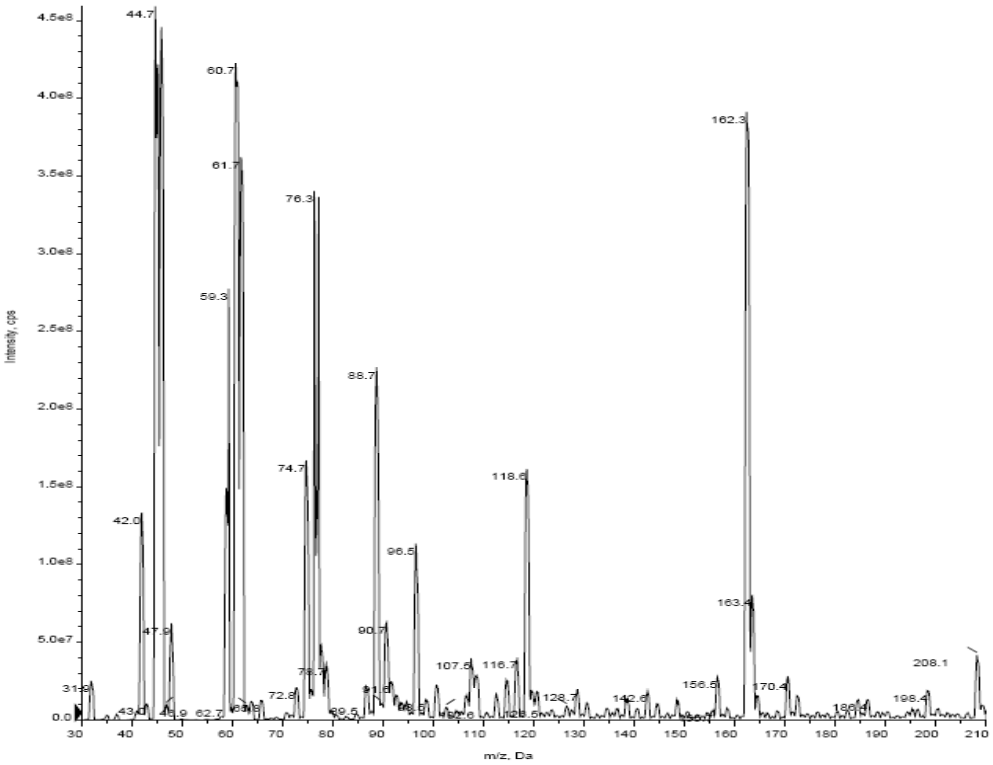


Figure 35: MS spectral of a standard of 4-ethylbenhaldehyde

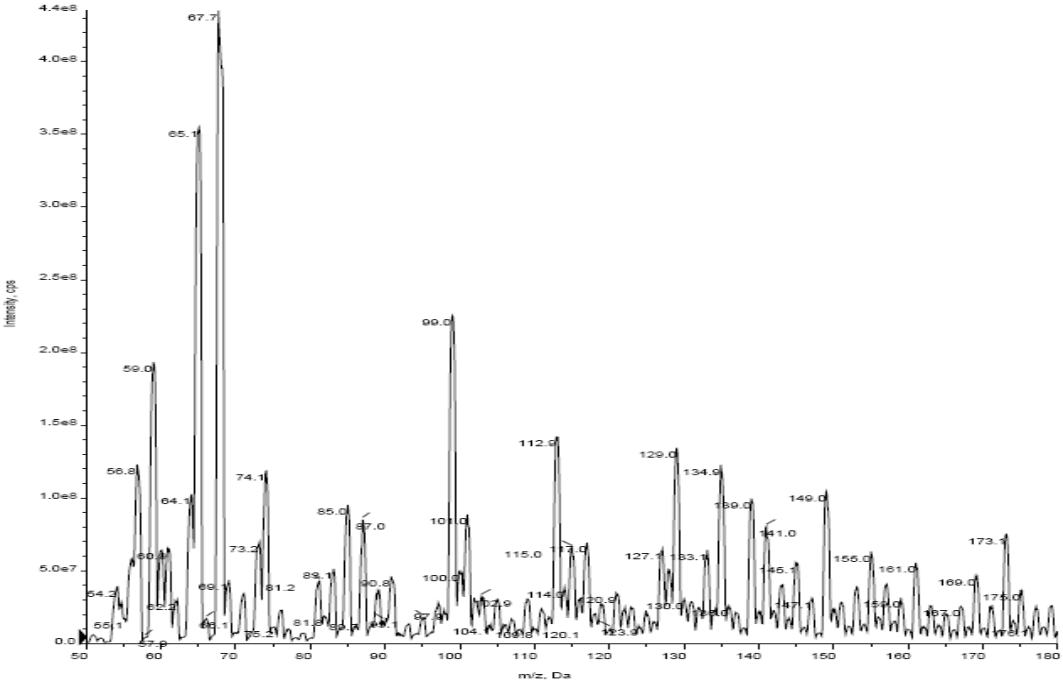


Figure 36: MS spectral of a standard of 4-isobutylacetophenone

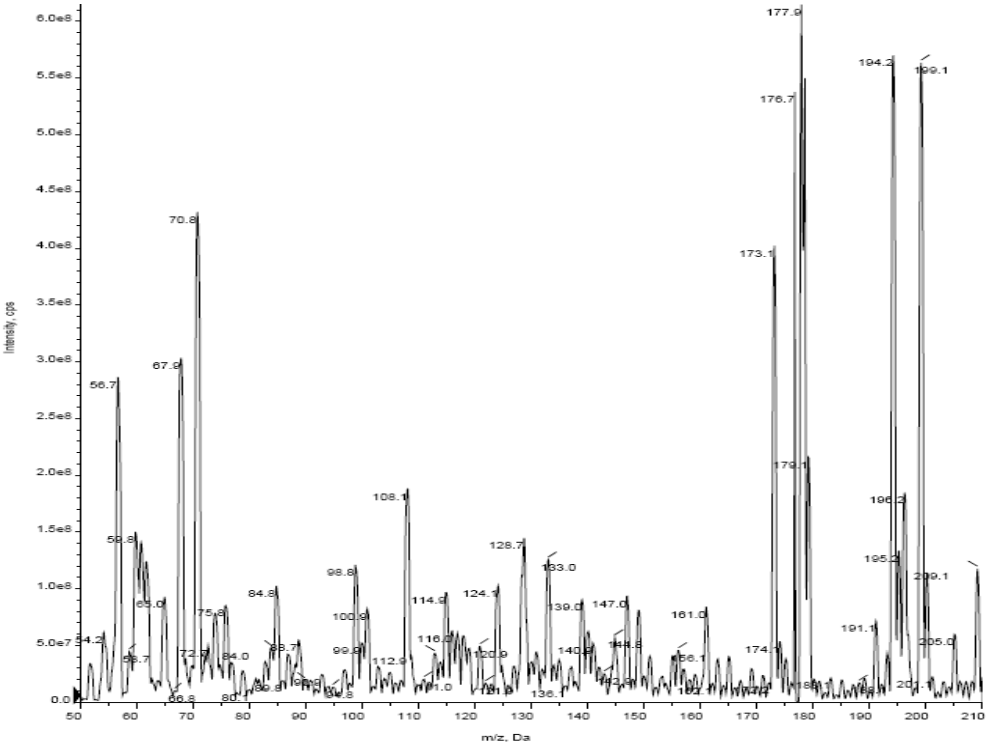


Figure 37 : MS spectral of s standard of oxalic acid

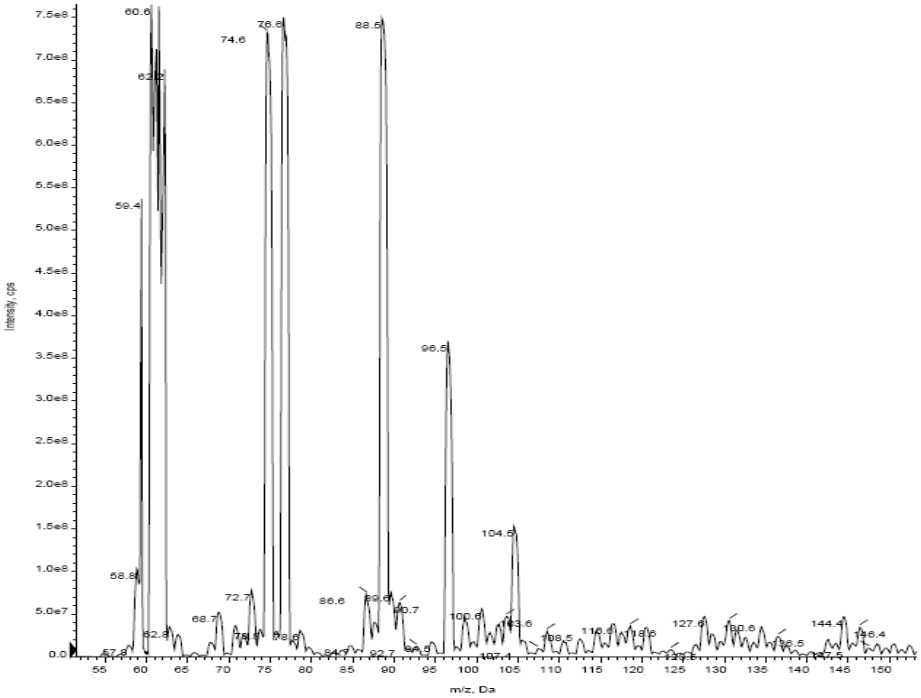


Figure 38 : MS spectral of a sample collected at 4.62 min

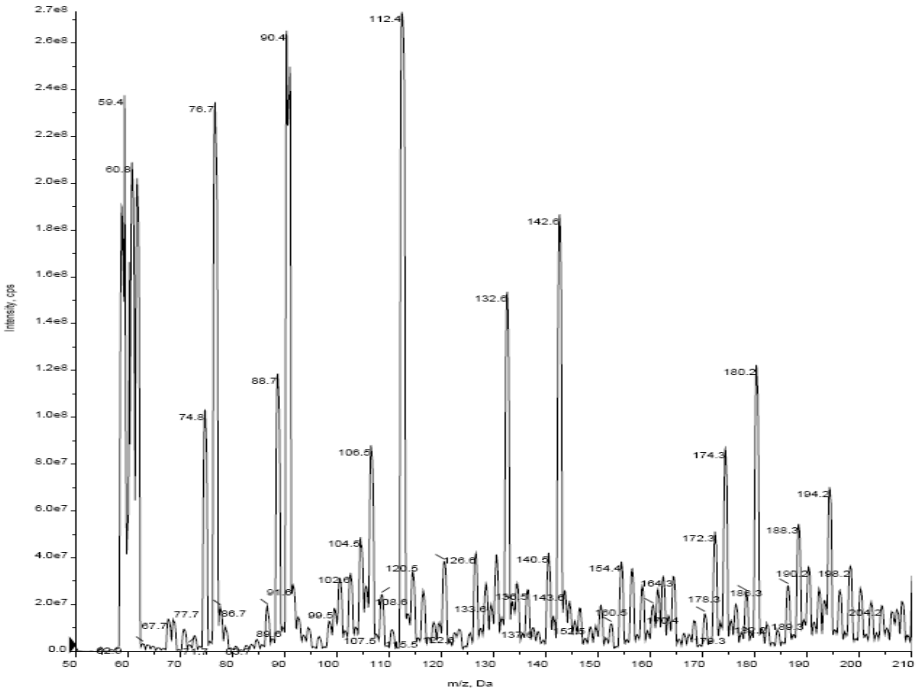


Figure 39 : MS spectral of a sample collected at 13.2 min

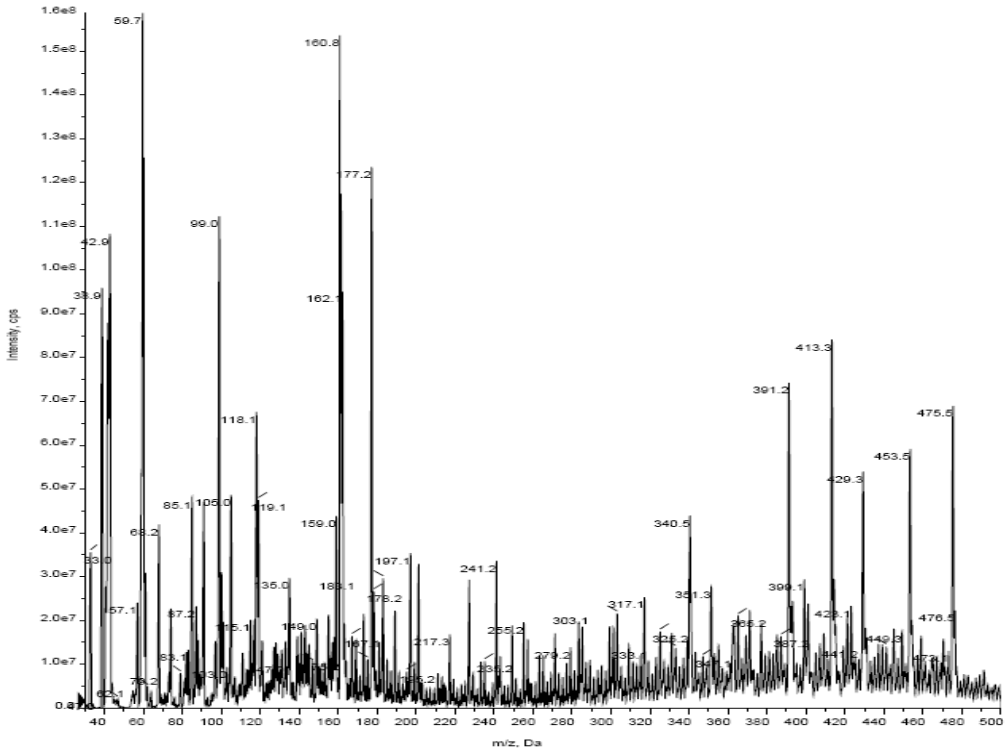


Figure 40 : MS spectral of a sample collected at 8.5min