DEGRADATION OF METHYL ORANGE USING ULTRASONIC IRRADIATION: ENHANCED WITH ADSORPTION USING NEWSPAPER

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ABSTRACT

Nowadays, the type of dye being released by textile industry is named by azo dyes. There are many researchers has used the technique of ultrasonic irradiation to degrade the dyes pollutant. In this study, the ultrasonic irradiation simultaneous with adsorption method using newspaper will apply to degrade methyl orange solution. The ultrasonic bath cleaner (50 - 60 kHz) was used to degrade methyl orange with and without the presence of low cost adsorbent which is newspaper waste at initial concentrations 10 mg/l to 100 mg/l, initial pH 1 to pH 12, also temperature at 30^oC to 80° C and contact time from 20min to 120 min. The newspaper used was cut into small size in range 4mm to 5mm. The absorbance value of Methyl orange (MO) solution before and after the degradation process was analyzed using UV-Vis Spectrophotometer. Maximum of 11% degradation achieved on the effect of initial concentration study. For initial pH effect, maximum of 24 % degradation was achieved at pH 1.Also maximum 11% degradation achieved for the study on the effect of temperature. Degradation percentage was increased in increasing of time. Maximum 12% degradation was achieved at up to 120 min contact time. By using ultrasonic bath cleaner, we can conclude that degradation can be achieved using ultrasonic irradiation method simultaneous with adsorption method. The percentage degradation was increased with the increased of temperature and time. However percentage degradation was decreased with increased of initial concentration. The pH value brought some pattern into degradation percentage. The ability of newspaper sorbent in order to degrade methyl orange solution in the presence of ultrasonic irradiation indicated that such sorbent could be employed as low cost alternatives to commercialize like as activated carbon in wastewater treatment for the removal of color and dyes.

ABSTRAK

Pada hari ini, jenis bahan pewarna yg selalu dilepaskan dari sistem buangan air industry tekstil ialah jenis "azo". Terdapat banyak penyelidik yang telah menggunakan teknik iradiasi ultrasonik untuk penyahwarnaan larutan bahan buangan pewarna.Dalam kajian ini,teknik irradiasi ultrasonik digunakan serentak dengan teknik serapan oleh suratkhabar di aplikasikan untuk mengurangkan kepekatan larutan bahan pewarna yang dinamakan "methyl oren". Pembersih takungan ultrasonik (50 - 60 kHz) digunakan untuk mengurangkan kepekatan larutan methyl oren dengan dan tanpa kehadiran suratkhabar yang mana surat khabar adalah ejen serapan yang murah harganya pada nilai kepekatan awal, nilai keasidan awal juga pada masa dan suhu yang pelbagai.Suratkhabar telah dikerat menjadi kecil kepada saiz dalam lingkungan 4 hingga 5 milimiter.Nilai absorban bagi larutan methyl oren, sebelum dan selepas proses penyahwarnaan dianalisa menggunakan alat UV-Vis spectrofotometer.Maksimum 11% penyahwarnaan dicapai untuk kajian kesan kepakatan awal larutan.Untuk kajian kesan nilai keasidan awal larutan, maksimum 24% penyahwarnaan telah dicapai pada keasidan 11. maksimum 11% penyahwarnaan dicapai untuk kajian kesan suhu.Penyahwarnaan meningkat dengan peningkatan masa.Maksimum 12% penyahwarnaan dicapai apabila masa sehingga 120 minit.Dengan meggunakan alat pembersih takungan ultrasonik, dapat disimpulkan bahawa penyahwarnaan dapat dicapai meggunakan teknik radiasi gelombang ultrasonik bersama teknik serapan.Peratusan penyahwarnaan meningkat dengan kenaikan suhu dan masa.Namun, peratusan penyahwarnaa menurun dengan peningkatan kepekatan awal larutan.Keasidan awal telah mempengaruhi peratusan penyahwarnaan dengan corak tertentu. Kemampuan serapan suratkhabar dalam proses penyahwarnaan larutan pewarna oren dengan kehadiran radiasi gelombang ultrasonik, menunjukkan bahawa suratkhabar boleh diaplikasikan peggunaannya sebagai bahan serapan alternatif yang murah yang boleh dikomersialkan seperti bahan karbon aktif dalam bidang rawatan air buangan dan penyahwarnaan larutan bewarna.

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LIST OF SYMBOLS

Hz	-	Hertz
kHz	-	Kilohertz
L	-	Liter
MHz		Megahertz
mg	-	Milligram
ml	-	Milliliter
min	-	Minute
mm	-	Millimeter
nm	-	nanometer
⁰ C	-	Degree Celsius
sec	-	Second
kg	-	Kilogram
Κ	-	Degree Kelvin
m	-	Meter

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Nowadays, variety industries from textile industries and paper industries widely involved in the issues of the contaminated of water from their dyes effluent. The major sources of dyes in the environment are effluents from the textile industry. Textile industries consume over 700 00 tons of dyes annually and use up to 1 liter of water per kg of dye processed and are third largest polluters in the world, the problem being aggravated by the inefficiencies of the dye houses (Cecil Clifford, 2006). Even dyes make our world beautiful, but they bring us pollution. The colored waters of industrial effluents are unattractive because they account significant concentrations of pollutants so that they become the sources of increasingly acute complaints. Dye wastewater usually consists of a number of contaminants including acids, bases, dissolved solids, toxic compounds, and colored materials. Usually, the type of dye being released by textile industry is named by azo dyes. Many researchers have been conducted to solve this environmental problem. Several methods have been used for the removal of dyes from effluents, including physical, chemical, and biological processes. These methods are based on the decolorization by oxidation processes, photo decomposition, microbiological, electrochemical decomposition, precipitation, coagulation flocculation and adsorption. There are also many researchers has used the technique of ultrasonic irradiation to degrade the dyes pollutant (Hugo Destaillats et al., 2003). In this study, the ultrasonic irradiation simultaneous with adsorption using newspaper method will apply to degrade methyl orange solution.

1.2 Research Background

1.2.1 Dye

Dye in environment closely related to the textile industry. The increasing of dyes in the environment is due to the demanding towards the textile industry. The world population growth gives an impact to the textile industry which we can see that the demanding toward textile industry also increased. Actually, not all the dye is fixed to the fiber during the dyeing process. The reactive dyes used for cotton have the poorest fixation rate, most colored effluent problems arise from dyeing cotton with reactive dyes. Azo dyes account for 60 - 80% of the dyes consumed in textile processing (Mendez-Paz *et al.*, 2004). The delivery of color onto fabric is not an efficient process and up to 40 % of the dyes are lost during the dyeing process (Stolz A, 2001; Pearce *et al.*, 2003; Moreira *et al.*, 2004). The percentage of unfixed dye is depending the dye types itself and also the fiber type used as shown in Table 1.1.

Table 1.1: Percentage of unfixed dye for different dye types and application

 (Adapted from Entec UK Ltd, 1997)

Fibre	Dye Type	Unfixed dye (%)
Wool and Nylon	Acid dyes/reactive dyes for wool	7 - 20
	Pre-metalized dyes	2 - 7
	After chromes	1 – 2
Cotton and viscose	Azoic dyes	5 - 10
	Reactive dyes	20 - 50
	Pigment	1
	Vat dyes	5 - 20
	Sulphur dyes	30 - 40
Polyester	Disperse	8-20
Acrylic	Modified basic	2 - 3
Polypropylene	Spun dyed	N/A

Textile and dyestuffs wastewater are characterized by their highly visible color, high chemical oxygen demand (COD), suspended solids and alkaline pH (9 - 11) (Manu *et al.*, 2002). Azo dyes constitute a major part of all commercial dyes

employed in a wide range of processes in the textile, paper, food, cosmetics, and pharmaceutical industries. They are characterized by the presence of the azo group as shown at Figure 1.1 which is attached two substituent, mainly benzene or naphthalene derivatives, containing electron-withdrawing and/or electron-donating groups (Hugo Destaillats *et al*, 2000]. Example of color characterized as azo dyes are Reactive red 2, Methyl orange, Acid red 1, Acid red 73, Acid red 249, Acid orange 7, Acid blue 113, Acid brown 75, Acid green 20, Acid yellow 42, Acid mordant brown 33, Acid Mordant Yellow 10 and Direct Green 1. In this study, methyl orange which is one of the azo dyes was used as sample to be degrading using the ultrasonic irradiation method.

Azo dyes are by far the most important and versatile classes of dyes which have been studied and used more than any other class (Stolz A, 2001). They are water-soluble synthetic organic compounds possessing the characteristic -N=N-, which links the chromophore and auxochrome to form colored molecules of great structural diversity. Generally azo dyes contain between one and three azo linkages, linking phenyl and/or naphthyl rings that are usually substituted with some combination of functional groups including triazine amino, chloro, hydroxyl, methyl, nitro and sulphonate (Bell *et al*, 2000). Azo dyes exist in the trans form in which the bond angle is ca. 120°. The nitrogen atoms are sp^2 hybridized and the designation of A and an E group is consistent with colour index (C.I.) usage (Colour index, 1971).



Figure 1.1: Azo chromophore

Typical properties of an azo dye are the groups which A represents electron accepting substituents particularly hydroxyl and amino groups, while E represents electron withdrawing groups such as halogens and carboxylic groups. Dyes without any substituents that carry only aromatic groups such as benzene are known as carboxylic azo dyes while those with heterocyclic groups are referred to as heterocyclic azo dyes (Hunger K, 2003). The fact that the azo bond can link together various chromophores and auxochromes illustrates the enormous structural diversity that is possible with azo dyes leading to a wide spectrum of shades, mainly within the scale of red.Unfortunately, the disadvantage limiting their function is that none of the azo dyes are Green (Rys, P. and Zollinger, H, 1972).Table 1.2 showed the azo dye structure and their wavelength.

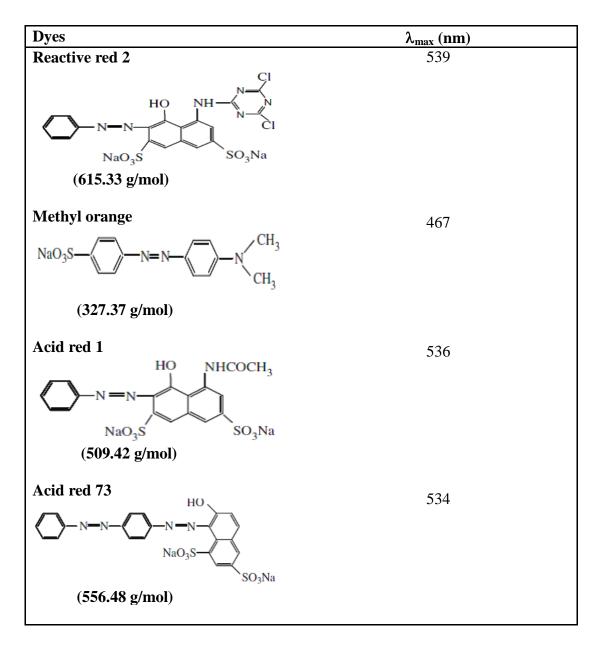


 Table 1.2: The azo dye structure and wavelength.(M. Li et al,2007)

1.2.2 Ultrasonic Irradiation

Ultrasonic irradiation has been investigated for the destruction of aqueous organic and inorganic pollutants (L.K.Weavers et al., 2000; E.Psillakis et al., 2004). The term sonochemistry describes all chemical processes in which ultrasonic irradiation is involved. The substrate molecules can undergo degradation by two different main pathways depending on their chemical nature: pyrolytic reactions inside the cavitation bubbles or oxidation by hydroxyl radical in the bulk medium (M. Joseph et al., 2000). Sonochemistry proceeds because the passing of acoustical waves of large amplitude, called finite amplitude waves, through solutions causes cavitation. Cavitation can be generated when large pressure differentials are applied in a flowing liquid (hydrodynamical cavitation), or by means of an electromechanical transducer, piezoelectrical or magnetostrictive, in contact with the fluid (acoustical cavitation). Sonochemical destruction is particularly effective for volatile substrates as these solutes can be directly combusted within the gas phase of the hot collapsing cavitation bubbles. The effect of ultrasonic irradiation on removal organic contaminants from aqueous solutions can be explained physically or chemically. Physically, the ultrasonic waves can clean surface of solid particles, reduce the particle size and increase mass transfer (J. Yano et al., 2005). Chemically, when ultrasonic waves are irradiated into an aqueous solution, cavitations occur. The violent collapse of the cavitations bubbles results in a hot spot, which has an extremely high temperature and pressure (T.J. Mason et al., 1991; J. Rae et al., 2005). The hot spot enables the generation of OH radicals.

$$H_2O(g) \longrightarrow \bullet H(g) + \bullet OH(g)$$
 (1.1)

1.2.3 Ultrasonic Irradiation with Adsorption Method

The ultrasonic irradiation method can be combined with other method in other to increase the effectiveness of the degradation process toward the pollutant. In this paper, the removal of contaminants in aqueous solution by the application of ultrasound is combining with the adsorption technical by the solid material. The adsorption is an effective, low cost and low energy consuming process. Its use in water purification has already widely been accepted. Decolourisation of azo dyes is a result of two mechanisms; (1) adsorption onto a solid matrix and (2) ion exchange as a result of differential charges between dyes and the matrix. These two mechanisms are influenced by physical-chemical factors such as dye-sorbent interaction, sorbent surface area, particle size, temperature, pH and contact time. However, combination of ultrasound and adsorption process, to our knowledge has not been explored well before in the field of environment. By the simultaneous use of ultrasound and adsorption, the mass transfer rate of adsorbate from the bulk solution to the surface of adsorbent, which usually limits the efficiency of adsorption process, can be largely enhanced. The solid phase as a sorbent used in this work was cellulosic materials such as newspaper. The basic ingredients that make up the cellulosic materials are cellulose, hemi-cellulose, lignin, and additives. The percentage of components is different from one kind to another one. The chemical composition is related to the chemical treatment applied on the wood for preparation of paste. In the case of newspaper, the chemical treatment is negligible and therefore the composition of the newspaper is approximately the same as the wood. It means that it contains cellulose (39–41%), hemi-cellulose (30–37%), lignin (20–27%), and other chemicals (2-4%) (M.H. Entezari et al., 2006).

1.3 Problem Statement

Effluent discharge from textiles and dyestuff industries into water bodies and waste water treatment systems is currently causing significant health concerns. The decolourization of textile waste water is one of the significant problems as the dye will be visible even at low concentration. It is also a problem because of these dye compounds in wastewater ordinarily contain one or several benzene ring and cannot be decomposed easily in chemical and biological. Most of the dyes are found to be resistant to normal treatment process as they are designed to resist chemical and photochemical degradation (H. Destaillats *et al.*, 2000). Majority the azo dyes contained azo group, formic acid, caustic soda, metallic compounds, and sodium

nitrate. If this unwanted compound introduce to the human daily life continuously it will course major problem and will be resulting in the health diseases of human.

In the last few years, environmental legislature about the appearance of color in discharges, combined with increasing cost of water in the industrial sector has made treatment and re-use of dying effluents increasingly attractive to the industry. Dye waste waters enter the environment from manufacturers and consumers (i.e. textile, leather and food industries) usually in the form of dispersion or a true solution (Seshadri *et al.*, 1994) and often in the presence of other organic compounds originating from operational processes. Color is the first contaminant to be recognized in textile waste water and has to be removed before discharging into water bodies or onto land (Banat *et al.*, 1996). The presence of small amounts of dyes in water (even < 1 ppm) is highly visible and it affects the aesthetic merit, causes significant loss in luminosity and any increase in the temperature will greatly deplete the dissolved oxygen concentration in waste water. This results in subsequent alteration of the aquatic ecosystem (Moreira *et al.*, 2004).

As mentioned in introduction part, there are many method can be use to degrade dyes in water before enter the environment. All the techniques are effective for color removal but are energy intensive and introduce chemicals which are not wanted in the first place. They also concentrate the pollutants into solid or liquid side streams which require additional treatment or disposal thus escalating cost of effluent treatment (Bell et al., 2000; Robinson S, 1969; Shaw et al., 2002). To lower the cost of wastewater treatment, many researchers have focused on finding nonconventional alternative adsorbents. Non-conventional adsorbents or so-called lowcost adsorbents are generally referred to non-hazardous waste produced from industry, agriculture, and biosorbents. In particular, the use of newspaper waste in adsorption system has been drawn attention from some researchers because: (1) it is abundantly available; (2) news paper waste are readily to be used and do not require a complex pretreatment step or activation process before applications; (3) regeneration of these adsorbents may not be necessary (unlike activated carbon, where regeneration is essential); and (4) less maintenance and supervision are required for the operation of the adsorption process. Nevertheless, use of these cheap alternatives for wastewater treatment remains limited due to both insufficient documentation in real wastewater systems and the necessity of post-usage disposal. Utilization of newspaper waste for the treatment of wastewater is a win–win strategy because it not only converts the waste into a useful material but it also saves on disposal costs.

1.4 Objectives

The proposed research was studied to achieve the following objectives:

- (i) To determine the optimum condition for degradation of methyl orange solution using low cost method by the combination of ultrasonic irradiation and adsorption method with newspaper.
- (ii) To enhanced the degradation process of methyl orange solution using the application of simultaneous ultrasonic irradiation method with the adsorption using newspaper method

1.5 Scopes of Study

In order to achieve the objectives, the following scopes have been identified.

- (i) Study and compare the degradation of methyl orange solution process at different initial concentration in range 10mg/l to 100mg/l, initial pH value in range 1 to 12, also at different system temperature in range 30^oC to 80^oC and last is in different of contact time between 20 minutes to 120 minutes.
- (ii) Using the newspaper as adsorbent in ultrasonic irradiation combined with adsorption method in order to lowering the cost of degradation method.

1.6 Research Contributions

The degradation of methyl orange using the simultaneous of ultrasonic irradiation and adsorption with newspaper are beneficial to the environment and society. There are several benefits which are:

- (i) Contribute to the society in preventing the community from any harm and danger chemical for instance water.
- (ii) Preserving and protecting environment.
- (iii) Reduce the cost and energy consumption needed to degrade the dyes effluent.

CHAPTER 2

LITERATURE REVIEW

2.1 The Basis of Color in Dyes

Dyes are characterized in accordance with their capacity to absorb the energy of a particular part of the electromagnetic radiation to which the human eye is sensitive (Rys, P. and Zollinger H, 1972). Dyestuffs give color to the material onto which they have been anchored, by selectively retaining some of the wavelengths out of the light falling upon the surface. However, there are only a few organic molecules that possess this property of absorbing light selectively (Trotman, E.R, 1990). Therefore if a dye absorbs strongly at the red end of the spectrum, the light which is reflected is of a bluish hue.

Wavelength of	Absorbed light	Visible color
Light absorbed(nm)	X7* 1 /	
400 - 435	Violet	Yellowish Green
435 - 480	Blue	Yellow
480 - 490	Greenish Blue	Orange
490 - 500	Bluish Green	Red
500 - 560	Green	Purple
560 - 580	Yellowish Green	Violet
580 - 595	Yellow	Blue
595 - 605	Orange	Greenish Blue
605 - 750	Red	Bluish Green

 Table 2.1: Color absorbance spectrums (Adapted from Trotman, 1990, pg254)

A colored compound is built up from three subsystems, namely aromatic groups called chromophores which are characteristically electron accepting molecules and secondly, nucleophiles commonly referred to as auxochromes. These are electron withdrawing and contain substituted groups like amino, hydroxyl, sulfonic and carboxylic groups. The third constituent of a typical coloured compound is a system of conjugated double bonds that joins the chromophore and auxochrome to form a colour specific compound known as a chromogen (Wallace, T.H, 2001). Besides supplementing the chromophore in the production of colour, they also enhance solubility of the dye and increase its affinity towards fibers (Trotman, E.R, 1990). Both auxochromes and chromophores shift the higher wavelength absorption bands of the conjugated system to longer wavelengths (bathochromically) and both can be classified empirically in order of increasing bathochromic effect on a particular conjugated system (Rys, P. and Zollinger, H, 1972).

2.2 Textile effluent and waste water

Textile industries consume large volumes of water and chemicals during wet processing of textiles. The chemical reagents used during manufacture and processing are diverse in chemical composition ranging from inorganic compounds to polymers and organic products (Banat *et al.*, 1996; Juang *et al.*, 1996). By design the majority of dyes are recalcitrant so that they can confer color onto the designated materials (Plumb *et al.*, 2001) and resist fading on exposure to sweat, soap, water, light or oxidizing agents (Banat *et al.*, 1996; Robinson *et al.*, 2001).

Dye waste waters enter the environment from manufacturers and consumers (i.e. textile, leather and food industries) usually in the form of dispersion or a true solution (Seshadra *et al.*, 1994; Bell *et al.*, 2000) and often in the presence of other organic compounds originating from operational processes. Color is the first contaminant to be recognized in textile waste water and has to be removed before discharging into water bodies or onto land (Banat *et al.*, 1996; Kumar *et al.*, 2005). The presence of small amounts of dyes in water (even < 1 ppm) is highly visible and it affects the aesthetic merit, causes significant loss in luminosity and any increase in the temperature will greatly deplete the dissolved oxygen concentration in waste

water. This results in subsequent alteration of the aquatic ecosystem (Moreira *et al.*, 2004).

The removal of color from textile waste water is often more important than the removal of the soluble colorless organic substances which usually contribute to the major fraction of Biochemical Oxygen Demand (BOD). Methods for the removal of BOD from most of these effluents are fairly well established (Banat *et al.*, 1996; Sponza and Isik, 2002; Pearce *et al.*, 2003). On the other hand textile waste waters exhibit low BOD to COD ratios (< 0.1) indicating their difficulty to bioremediate or breakdown (Pagga and Brown, 1986). On the whole, textile waste water is characterised by unfixed dyes, organic pollutants (much higher than regular domestic waste water), large amounts of COD (organic compounds), high conductivity due to salts, high amounts of sulphide and heavy metals due to chlorinated bleaching agents and halogen, sulphur or heavy metal dyes.

2.3 Dye Effluent Treatment Methods.

Effluents from textile industries are the most expressive from an ecological and physiological perspective (Parac-Osterman D *et al.*, 2004). In order to achieve satisfactory and acceptable quality levels that allow recycling of textile waste water, removal of dyes and related compounds is very crucial. Based on the fact that azo dyes constitute the largest percentage of textile dyes, most treatment methods are based on the decolorization of azo dyes (Raghavacharya, C, 1997). Currently the main operational methods used in treatment of textile waste water involve physical and chemical processes (Shaw and C.B, 1997). There are several factors that determine the technical and economic feasibility of each dye removal technique. These include; dye type, composition of the waste water, dose and cost of required chemicals, operational costs, environmental fate and handling costs of generated waste (Van Der Zee, F.P. and Villaverde S, 2005). Each dye removal technique has its limitations and one individual process may not be sufficient to achieve complete decolorization. To overcome this problem, dye removal strategies involve a

combination of different techniques (Raghavacharya C, 1997). Table 2.2 showed the summaries of some textile effluent treatment method in term of the advantages and disadvantages.

Table 2.2: Advantages and disadvantages	s textile effluent treatment method (Cecil
Clifford Zvandada Mutambanengwe, 2006))

Physical/Chemical Methods	Advantages	Disadvantages
Fenton's reagent	Effective decolorization of both soluble and insoluble dye	Sludge regeneration
Ozonation	Applied in gaseous state; no alteration of volume	Shot half life
NaOCl	Initiates and accelerates azo bond cleavage	Release of aromatic amines
Photochemical Cucurbituril	No sludge production Good sorption capacity for various dyes	Formation of bi – products High operating cost
Electrochemical destruction	Breakdown compounds are non hazardous	High cost of electricity
Activated carbon	Good removal of a variety of dyes	Very expensive to operate
Peat	Good adsorbent due to cellular structure	Specific surface areas for adsorption are lower than activated carbon
Wood chips	Good sorption capacity for acid dyes	Requires long retention times
Silica gel	Effective for basic dye removal	Side reactions prevent commercial application
Membrane filtration	Removes all dye types	Concentrated sludge production
Ion exchange	Regeneration; no adsorbent loss	Not effective for all dyes
Irradiation	Effective oxidation at lab scale	Requires a lot of dissolved O ₂
Electro kinetic coagulation	Economical feasible	High sludge production

2.4 Ultrasound

Ultrasound occurs at a frequency above 16 kHz, higher than the audible frequency of the human ear, and is typically associated with the frequency range of 20 kHz to 500 MHz. The frequency level is inversely proportional to the power output. Low-intensity, high frequency ultrasound (in the megahertz range) does not alter the state of the medium through which it travels and is commonly used for nondestructive evaluation and medical diagnosis. However, high-intensity, low-frequency ultrasound does alter the state of the medium and is the type of ultrasound typically used for sonochemical applications.

The chemical and mechanical effects of ultrasound are caused by cavitation bubbles which are generated during the rarefaction, or negative pressure, period of sound waves. During the negative-pressure cycle, the liquid is pulled apart at sites containing some gaseous impurity (nucleation sites), forming a void. The chemical effects of ultrasound have been attributed to the collapse of both stable and transient cavitational events. Stable cavities oscillate for several acoustic cycles before collapsing, or never collapse at all. Transient cavities, conversely, exist for only a few acoustic cycles.

Some authors have concluded that the cavitational effects of ultrasound are not due to a single cavitational event but are due instead to events occurring within a cloud of bubbles (Atchley *et al.*, 1988). Neppiras (1980) explains that when bubbles are in a cloud, the collapse is more violent because it initiates at the outermost layers of the cloud and then propagates inward. This type of collapse occurs when the bubbles expand in phase (approximately) with the driving frequency on the tension half-cycle.

2.5 Factor affecting cavitations

The ambient conditions of the reaction system can greatly influence the intensity of cavitation, which directly affects the reaction rate and/or yield. These conditions include the reaction temperature, irradiation frequency, acoustic power, and ultrasonic intensity. Other factors which significantly affect the cavitational intensity are the presence. Each of these factors is described in detail below.

2.5.1 Ambient Temperature.

Contrary to chemical reactions in general, an increase in the ambient reaction temperature results in an overall decrease in the sonochemical effect. The decrease is a result of a sequence of events. First, as the reaction temperature is raised, the equilibrium vapor pressure of the system is also increased. This leads to easier bubble formation (due to the decrease of the cavitation threshold); however, the cavitation bubbles which are formed contain more vapors. \Vapor reduces the ultrasonic energy produced upon cavitation because it cushions the implosion in addition to using enthalpy generated in the implosion for the purposes of condensation. In general, the largest sonochemical effects are observed at lower temperatures when a majority of the bubble contents is gas (L. H. Thompson and L. K. Doraiswamy, 1999).

In certain reaction systems, an optimum reaction temperature may lead to more favorable results. In such systems, an increase in temperature will increase the kinetic reaction to a point at which the cushioning effect of the vapor in the bubble begins to dominate the system. However, increasing the temperature was also simultaneously decreasing the intensity of cavitation, thus reducing the amount of free radicals produced within the bubble. It was speculated that these free radicals were required for the degradation reaction to occur and that they diffuse from the vapor cavity to the gas-liquid film where reaction ensues. As the rates of the counter diffusing reactants became comparable, a further increase in temperature had little or