# DEGRADATION OF METHYLENE BLUE USING ULTRASONIC IRRADIATION: A COMPARISON OF ULTRASOUND WITH AND WITHOUT SALT (SODIUM CHLORIDE)

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## ABSTRACT

In this research, the objectives are to determine the best conditions for the degradation of methylene blue and at the same time studying the effects of Sodium Chloride (NaCl) when added to a dye solution that being degraded via ultrasonic irradiation method. Environmental violations caused by poorly treated textile effluents have caused major problems towards aquatic life and the stability of the aquatic ecosystem in rivers or lakes. Methylene blue is a basic dye that is commonly used in textile industries. This research project is designed to degrade methylene blue using ultrasonic irradiation with and without the addition of salt by manipulating key parameters such as the temperature of the dye solution in the range of 40 $^{o}$C – 80 $^{o}$C, the initial concentration of dye samples at 4 mg/L - 20 mg/L, the time of for methylene blue to be degraded (15 minutes – 120 minutes) and the pH value (pH 1.61 – pH 12.35) of the dye solution while being degraded under ultrasonic irradiation. The results for the experiment showed that methylene blue is best degraded at 80 $^{o}$C, 4 mg/L and 90 minutes with the pH value of 12.35, where the percentage of degradation for the 100 ml dye solution was at 86.28%. When the experiment was repeated with the addition of salt (NaCl), to the solution was degraded at 87.80%. It can be concluded that the treatment of waste water containing methylene blue can be degraded by using ultrasonic irradiation and the efficiency of this method can be improved with the addition of salt into the methylene blue solution.

# ABSTRAK

Tujuan kajian ini adalah untuk menentukan keadaan terbaik bagi degradasi metilen biru dan pada masa yang sama mempelajari kesan natrium klorida (NaCl) apabila ditambah ke dalam larutan pewarna yang mengalami degradasi melalui kaedah iradiasi ultrasonik. Sikap tidak bertanggungjawab pembuangan sisa tekstil yang tidak dirawat telah menyebabkan masalah besar terhadap kehidupan air dan kestabilan ekosistem perairan di sungai atau tasik. Metilen biru merupakan pewarna alkali yang umum digunakan dalam industri tekstil. Projek ini direka untuk mengdegradasikan metilen biru dengan menggunakan iradiasi ultrasonik dengan dan tanpa penambahan garam dengan memanipulasi parameter - parameter seperti suhu larutan pewarna dalam lingkungan 40 $^{o}$C - 80 $^{o}$C, kepekatan awal sampel pewarna pada 4 mg/L - 20 mg/L, masa untuk metilen biru untuk didegradasikan (15 minit - 120 minit) dan nilai pH (pH 1.61 - pH 12,35) larutan pewarna yang dirawat menggunakan irradiasi ultrasonik. Data eksperimen menunjukkan bahawa biru metilen menunjukkan bacaan terbaik apabila didegradasi pada 80 $^{o}$C, 4 mg/L dan 90 minit dengan nilai pH 12.35, di mana peratusan degradasi untuk metilen biru pada 100 ml adalah 86.28%. Ketika percubaan diulangi dengan penambahan garam (NaCl), penyelesaian itu meningkat pada 87,80%. Dapat disimpulkan bahawa pemprosesan air sisa yang mengandungi metilen biru boleh dirawat dengan menggunakan iradiasi ultrasonik dan kecekapan kaedah ini dapat dipertingkatkan dengan penambahan garam ke dalam larutan biru metilen.

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| | | |
|---|---|---|
| Hz | - | Hertz |
| kHz | - | Kilohertz |
| L | - | Liter |
| OH● | - | Reactive free radicals / hydroxyl ions |
| mg | - | Milligram |
| ml | - | Milliliter |
| min | - | Minute |
| nm | - | nanometer |
| $^{0}C$ | - | Degree Celsius |
| sec | - | Second |
| kg | - | Kilogram |
| K | - | Degree Kelvin |
| m | - | Meter |

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# CHAPTER 1

# INTRODUCTION

## 1.1 Brief Introduction and Research Background

As far as the world is concerned about environmental violations that are happening around the world today like global warming, natural habitats destructions or air pollutions, the problems with water pollutions also comes to mind. This research revolves around the concerns of wastewaters containing untreated dyes that are released to the environment by irresponsible industrial activities. Recent studies have shown that it is believed the widespread disposal of industrial wastewater containing organic dyes onto land and water bodies has led to serious contamination in many countries worldwide where, about 1–20% of the total global production of dyes is lost during the dyeing process and is released into the environment as textile effluent (Fang Han *et al.*, 2009).

A study on the degradation of methylene blue by means of ultrasonic irradiation (with and without the addition of salt) will be conducted as methylene blue is a type of dye and is used in textile industries for various applications. Water contamination by methylene blue and similar dyes is a major concern because the release of colored waters into the ecosystem is a source of aesthetic pollution, also causing perturbation to aquatic life (Fla´vio Andre´ Pavan *et al.*, 2007). Problems that arises from dye wastewaters has encourage scientists and engineers from all sorts of fields to work together creating methods to treat wastewaters containing dye effluents more effectively. Conventional methods for treating dye-containing wastewater include biological treatment, froth flocculation, adsorption, chemical oxidation, hyper-filtration, coagulation, (Julide Yener *et al*., 2008).

Based on the experimental results of various investigators, ultrasonic degradation of volatile compounds probably occurs via oxidation at the hot bubble–liquid interfacial regions by highly reactive free radicals (OH●) or occurs inside collapsing bubbles predominantly by direct pyrolysis. The destruction rates of volatile contaminants are expected to be dependent on chemical and physical conditions inside the bubbles and to be linked to their physical and chemical properties, particularly their hydrophobic and volatile nature (Yi Jiang, 2002).

In sonolysis of water containing hydrophilic compounds such as textile dyes, hydroxyl radicals are generated only by water fragmentation in the collapsing bubbles, and oxidative dye destruction is possible if the radicals are effectively ejected into the solution bulk. The efficiency of OH● diffusion into the aqueous phase is related to system parameters such as frequency, reactor geometry, presence of cavitations nuclei, and the ambient conditions (T.J. Mason & C.M. Cordemans, 1998).

Sonochemical engineering of solid–liquid processes is an emerging field in environmental processes for removing of different pollutants more importantly this field of science has the potential to be used in wastewater systems more effectively. Acoustic cavitation derived from ultrasonic irradiation of a liquid provides unusual and unique conditions which are different from those of conventional methods (M. H. Entezari and Z. Sharif Al-Hoseini, 2006). The use of ultrasound in degradation of dyes and other pollutants has developed in recent decades and has been applied in various scales to treat wastewater that contains dyestuff (M. Inoue et al., 2006).

Although treating wastewater with the knowledge of Sonochemistry using ultrasonic irradiation has been around for a few years now, more studies and research are still needed to improve the method. The sonochemical degradation of a variety of chemical contaminants in aqueous solution has already been investigated where substrates such as chlorinated hydrocarbons, pesticides, phenols, explosives such as TNT, and esters are transformed into short-chain organic acids, $CO_2$, and inorganic ions as the final products (Michael R. Hoffmann et al., 1996). This research hopes to help the world of science more about how to treat wastewater containing a dye such as methylene blue with a little knowledge of sonochemistry.

## 1.2 Problem Statement

Problems about dyestuffs industries and also textile industries not being able to treat their waste effluents from their plants properly have been highlighted as a major concerns for environment experts. Looking at current technologies that are available to treat wastewaters containing dyes, many of them are effective has been used widely between these industries to treat wastewaters. The processes developed consist in decolorizing by photocatalytic oxidation, microbiological or enzymatic decomposition and adsorption on inorganic or organic matrices (Robinson *et al*., 2002). But, not all industries apply these technologies within their plants or water treatment system to treat their effluents. Most of the factors leading to these irresponsible actions are because of the expensive cost to treat wastewater. The most commonly used method is by means of adsorption, for this purpose the material used has been activated carbon but, due to the relatively high operating costs, such as regeneration of the used adsorbent had limited application on a larger scale (Robinson *et al*., 2002; Al-Degs *et a*l., 2001; Guo *et al*., 2003).

**Table 1.1:** Advantages and disadvantages of the methods used for dye removal from industrial effluent (Adapted from T. Robinson et al., 2001).

| Physical/Chemical Method | Advantages | Disadvantages |
|---|---|---|
| Fenton Reagent | Effective Decolorization | Sludge generation |
| Ozonization | No Change in Effluent Volume | Short half-life (20 min) |
| Cucurbituril | Good Sorption capacity for dyes | High Cost |
| Electrochemical | Non-hazardous end products | High cost of electricity |
| Activated Carbon | Highly Effective for Various Dyes | Very Expensive |
| Ion Exchange | No absorbent loss | Not effective for all dyes |

From Table 1.1, activated carbon, the most widely used adsorbent, remains an expensive adsorbent and has high regeneration cost while being exhausted. Not all methods are actually up to the task of treating dyes in wastewaters. Those tasks that are actually effective backfire with their expensive cost of equipment and materials used. Therefore, there is a need to find a more cheaper and effective method of treatment so that dyestuff industries as well as textile industries are able to treat their problematic effluents effectively without worrying about the cost for the process for water treatment so much.

Effluents of textile dyeing processes are intensely colored and contaminated with high concentrations of chemical oxygen demand (COD), suspended and dissolved salts and traces of recalcitrant material that are hard to be treated. If improperly processed, these effluents not only deteriorate the aesthetics of receiving waters and may hinder the penetration of oxygen, but also create a significant threat to life forms upon hydrolysis of some dyes in the wastewater to form harmful toxic products. Thus, the reason for the presence of dye residuals in wasted effluents is that some dyes have poor exhaustion capacities such that an important fraction of them is ultimately discharged with spent dyebaths (G. Tezcanli-Guyer and N.H. Ince, 2003).

## 1.3 Objectives

To ensure a successful research, the objectives below are going to be achieved.

(i) To determine the best conditions for the degradation of methylene blue using ultrasonic irradiation.

(ii) To study the effects of the addition of salt (Sodium Chloride, NaCl) towards the ultrasonic irradiation method.

## 1.4 Scope of the Research

Scopes has been identified for this experiment to make sure that the objectives can be achieved without any deviation.

(i) Studying the effect of temperature (40 $^{o}$C – 80 $^{o}$C), the effect initial concentration (4 mg/L – 20 mg/L), the effect of time of degradation (15 minutes – 120 minutes) and the effect of pH value of the dye solution (pH 1.61 – pH 12.36) towards the percentage of degradation of 100 ml methylene blue dye solution.

(ii) Studying the effect of the addition of salt (Sodium Chloride, NaCl) by comparing the efficiency of ultrasonic irradiation with and without the addition of salt.

## 1.5 Research Contribution

This research about the degradation of methylene blue using ultrasonic irradiation will contribute a significant amount of information for 3 major elements which are:

(i) A contribution to Science; This research will give certain insight about the relation between an ultrasonic wave frequency and the degradation of a wastewater solution. Moreover, the study of thermal conditions and pH value of a dye wastewater solution during ultrasonic irradiation would create more interest in creating a more efficient way to curb pollution problems regarding dyes in wastewaters.

(ii) A contribution to Society; This research will be able to protect the society from being exposed to dangerous toxic waste in dye wastewaters. By having a dye wastewater solution to be degraded to an extent where the treated water that is released back to the environment is clean and safe, this will ensure clean water reaches the society.

(iii) A contribution to the environment; Mother Nature's water has already been badly damaged by various irresponsible acts by men itself; information from this research would then help tackle the wastewater problems regarding untreated dyes. A more efficient way making sure cleaner water is produced after treatment will ensure a better preserved environment in the future.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Dyes

### 2.1.1 Basic Dyes

A dye can generally be described as a colored substance that has an affinity to the substrate to which it is being applied. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber (Dye, n.d.).

Basic dyes such as methylene blue that will be used in this research are widely used in textile industries. Basic dye is a class of dyes, usually synthetic, that act as bases, and which are actually aniline dyes. Their color base is not water soluble but can be made so by converting the base into a salt. The basic dyes, while possessing great tinctorial strength and brightness, are not generally light-fast; therefore their use in the dyeing of archival materials is largely restricted to those materials not requiring this characteristic. Basic dyes were at one time used extensively in dyeing leather, mainly because they are capable of combining directly with vegetable-tanned leather without the use of a mordant. Basic dyes show virtually no migration in acrylic fibers under normal dyeing conditions, compatibility is of major importance in selecting dye combinations with optimum level dyeing behavior (Kvavadze E. *et al*., 2009).

A basic dye is a stain that is cationic (positively charged) and will therefore react with material that is negatively charged. The cytoplasm of all bacterial cells have a slight negative charge whengrowing in a medium of near neutral pH and will therefore attract and bind with basic dyes. Some examples of basic dyes are crystal violet, safranin, basic fuchsin and methylene blue. It's applied to wool, silk, cotton and modified acrylic fibres. Usually acetic acid is added to the dyebath to help the take up of the dye onto the fibre. Basic dyes are also used in the coloration of paper. Basic dye is a class of dyes, usually synthetic, that act as bases, and which are actually aniline dyes. Their color base is not water soluble but can be made so by converting the base into a salt. The basic dyes, while possessing great tinctorial strength and brightness, are not generally light-fast; therefore their use in the dyeing of archival materials is largely restricted to those materials not requiring this characteristic. Basic dyes were at one time used extensively in dyeing leather, mainly because they are capable of combining directly with vegetable-tanned leather without the use of a mordant. Basic dyes show virtually no migration in acrylic fibers under normal dyeing conditions, compatibility is of major importance in selecting dye combinations with optimum level dyeing behavior (Dyestuff: Basic Dyes, n. d.).

Basic dyes possess cationic functional groups such as $-NR^{3+}$ or $=NR^{2+}$. The name 'basic dye' refers to when these dyes were still used to dye wool in an alkaline bath. Protein in basic conditions develops a negative charge as the -COOH groups are deprotonated to give $–COO^{-}$. In an electric field the chromophore ion travels to the cathode or negative pole; it is positively charged. Generally forms salts with negatively charged (acidic) substances in tissue (chromatin, ergastoplasm, cartilage matrix, some granules). Affinity for such dyes is called basophilia. Basic dyes perform poorly on natural fibres, but work very well on acrylics (Basic Dye, n. d.).

### 2.1.2 Methylene Blue

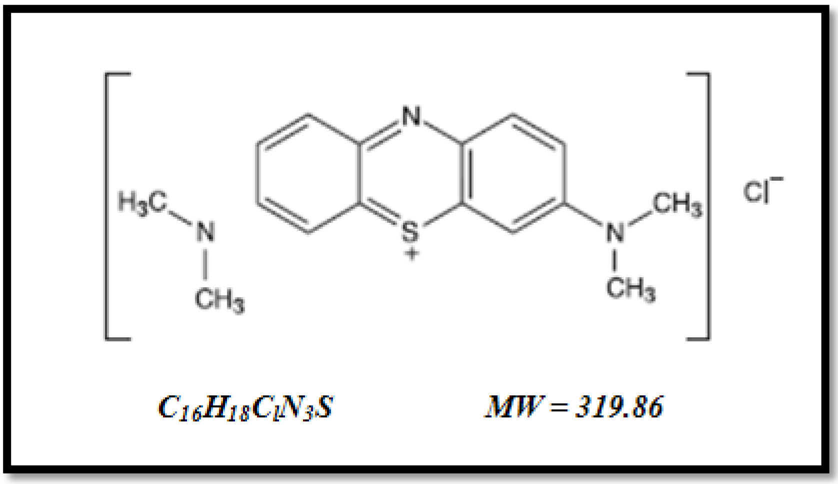


**Figure 2.1:** Details of Methylene Blue

Methylene blue (or MB) is a basic aniline dye with the molecular formula $C_{16}H_{18}N_3SCl$. At room temperature, it appears as a solid, odorless, dark green powder that yields a blue solution when dissolved in water. It has many uses in a number of different fields. For instance, chemists use it to detect oxidizing agents and biologists use it to stain tissue samples and detect nucleic acids. In medicine, it is used as a treatment for various illnesses and disorders, including methemoglobinemia, schizophrenia, kidney stones, and herpes infections. In aquaculture, it is used to prevent freshwater fish eggs from being infected by bacteria and fungi. Methylene blue has been reported to be used as a dye for temporary hair colorants, cotton, wool, leather, and paper (Methylene Blue, n.d.). In this research, methylene blue will be treated as a pollutant in waste water. The study of sonochemistry is still new and using the knowledge from this area of study to treat chemical pollutants is still ongoing.

## 2.2 Sonochemistry

In chemistry, the study of sonochemistry is concerned with understanding the effect of sonic waves and wave properties on chemical systems. The chemical effects of ultrasound do not come from a direct interaction with molecular species. Studies have shown that no direct coupling of the acoustic field with chemical species on a molecular level can account for sonochemistry or sonoluminescence. Instead, sonochemistry arises from acoustic cavitation: the formation, growth, and implosive collapse of bubbles in a liquid. This is demonstrated in phenomena such as ultrasound, sonication, sonoluminescence, and sonic cavitation.

The attractiveness of sonochemistry in environmental engineering seems to stem from three major facts. Firstly, sonochemistry can cause real chemical changes to a solution without the necessity of adding any other compounds. Secondly, sonochemistry is often conducted at low or ambient temperatures and pressures; thus, no heating or pressurization is required. These two features simplify enormously the design and operation of reactors. Thirdly, in many cases, the peculiar nature of sonochemical reactions offers alternative pathways, providing a faster or environmentally safer degradation of contaminants. The last 20 years witnessed a dramatical increase in the amount of scientific work in the field of sonochemistry, joined by the development of new and more powerful instrumentation. Some sonochemical syntheses have also been successfully scaled up to plant size, providing convenient advantages such as lower operation costs and shorter times of operation compared to traditional techniques. The present challenge for sonochemists and acoustical physicists in the field of environmental remediation is to provide cost-effective sonochemical solutions to large-scale problems (Leighton T. G., 1992).

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).

Cavitation consists of the formation of bubbles in a solution. These bubbles generally start very small, and grow in diameter by joining together until they become buoyant enough to escape the solution. At some point in this growth, they become resonant, which means that their diameter is such that their bubble wall motion is completely determined by the acoustical wave. The coupling of the bubble wall movements with the acoustical field is a complex physical and chemical phenomenon on the microscale (lengths are on the order of micrometers and times of oscillation are in the microsecond range), which triggers a series of processes that yield chemical reactions and light emission (sonoluminescence) (M. A. Margulis and I. M. Margulis, 1999). In a sonochemical reactor, the energy input is focused on small hot spots of the solution (i.e., the cavitation bubbles), instead of heating the whole system. This provides localized, highly extreme reaction conditions.

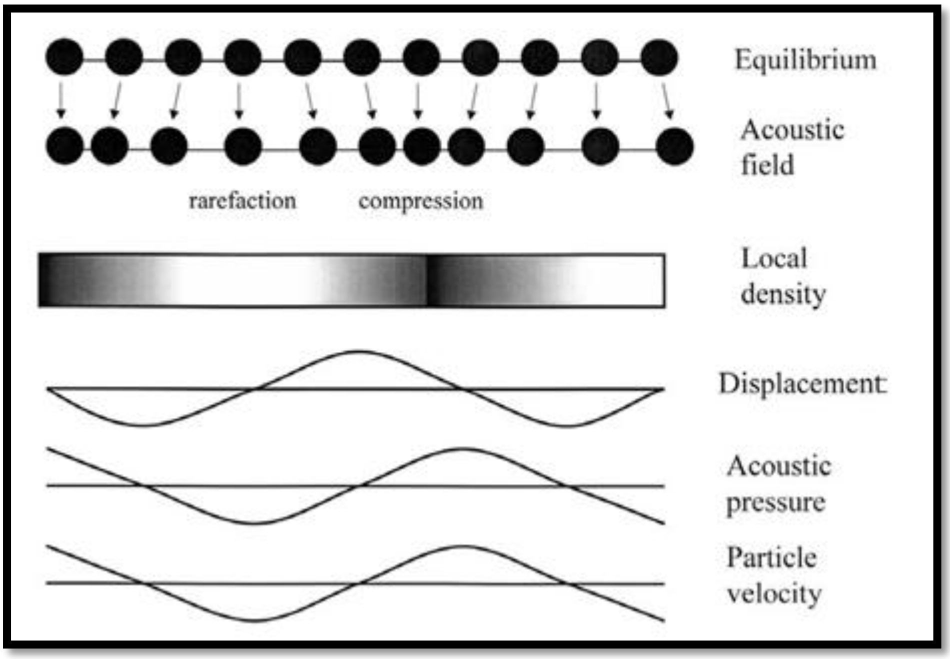


**Figure 2.2:** Propagation of a one-dimensional ultrasound wave (Brennen CE. 1998).

The chemical effects of ultrasound on liquids have been studied for many years. Most of these studies, however, have dealt with the sonolysis of water. The primary products are $H_2$ and $H_2O_2$ other high-energy intermediates have been suggested, including $HO_2$, $H^+$, $OH^-$ and $e^-$ (aq). Many studies regarding ultrasonic irradiation of dye solutions demonstrate definitively the generation of $H^+$ and $OH^-$

during ultrasonic irradiation, even with clinical sources of ultrasound (Jun Wang *et al*., 2009). The effectiveness of ultrasound upon liquids is closely related to many parameters. Experimental parameters that are always manipulated to study the efficiency of ultrasonic degradation of dye chemicals are *temperature*, *initial concentration* of dyes in water solutions, *time* for ultrasonic degradation to take place and *pH value* for the dye solution (H. Destaillats and M. R. Hoffmann, 2003). In addition, there are some reported researches that has added salt to the dye solution to improve the degradation of dye pollutants using ultrasound (S. Findik & G. Gunduz, 2007).

## 2.3 Effects of the Addition of Salt on a Liquid Solution

### 2.3.1 Effect of Salt on Liquid – Liquid Intermolecular Forces

In any type of liquid there is the existence of intermolecular forces that holds the molecules together, mainly hydrogen bonding types of forces. When salt is added to such a system, this will introduce ionic forces that affect the equilibrium of the bonds. Basically, the ions are solvated, and part of the water molecules in the solution become unavailable for the solution, and they are "salted out" from the aqueous phase (G. R. Santos *et al*., 2000).

### 2.3.2 Effect of Salt on Degradation Rate of Treated Water

There have been studies that researched on the effects of salt on polluted aqueous solution that is undergoing treatment with addition of salts by means of oxidation process (J. D. Seymour and R. B. Gupta, 1997). It was proven that the addition of salts actually increases the degradation rate of the pollutants in the aqueous solution. In a different research that was studying the effects of the addition of salts such as NaCl, $CaCl_2$ and $NaHCO_3$ to a dye (Acid Blue 25) containing solution while undergoing ultrasonic irradiation, the result showed a similar result where the degradation rate of the dye increases with the addition of salt (Houria Ghodbane & Oualid Hamdaoui, 2008).

### 2.3.3 Effect of Salt on Hydrophobic Characteristic of a Solution

On a different scale from this research, it has been founded out that the effects of salt addition such as sodium chloride (NaCl), ammonium chloride ($NH_4Cl$), and guanidinium chloride (GdmCl) on strength and dynamics of hydrophobic interactions in an aqueous solution actually extends the lifetime of hydrophobic associations by reducing water diffusivities and enhancing the structuring of water. The hydrophobic interactions upon salt additions are thus modified on a delicate balance due to the complex interplay of various molecular interactions. It was futher explained that the hydrophobic interaction is reduced by NH4Cl ions, which results from their reduction of structural fluctuation, enhanced by GdmCl ions, the effect of which is ascribed to their ability of making large salvation shells, and slightly enhanced by NaCl (Takatoshi Fujita *et al*., 2007).

## 2.4 Effects of Temperature on a Liquid Solution

### 2.4.1 Effect of Temperature on Liquid Phase Kinetic Energy

Temperature is a measure of the average energy of motion, or kinetic energy, of particles in matter. When particles of matter such as liquids, move faster or have greater mass, they carry more kinetic energy, and the material appears warmer (will then indicates higher temperature readings) than a material with slower or less massive particles (Temperature n.d.). In an indirect relation, when heat is added to a process (heat is added to a solution while undergoing ultrasonic degradation) the temperature of the liquid solution will increase and the kinetic movement of the particles within the studied solution will also increase. According to Ira N. Levine

(2008), in the context of thermodynamics, it is also referred to as thermal energy and the transfer of thermal energy is commonly referred to as heat. Heat always flows from regions of higher temperature to regions of lower temperature. While the particles making up a gas are too small to be visible, the jittering motion of pollen grains or dust particles which can be seen under a microscope, known as Brownian motion, results directly from collisions between the particle and air molecules. In the kinetic energy per degree of freedom, the constant of proportionality of temperature is 1/2 times Boltzmann constant. In addition to this, the temperature will decrease when the pressure drops to a certain point. This result is related to the equipartition theorem.

### 2.4.2 Effects of Temperature on Degradation Rate on Treated Water

With an increase in the temperature, the initial degradation rate will be increased for a dye solution that is being degraded by ultrasonic irradiation (Houria Ghodbane and Oualid Hamdaoui, 2008). In addition, based on the research of Nan Wang *et al* (2010), the relationship between the catalytic activity of $Fe_3O_4$ MNPs (magnetite magnetic nanoparticles) towards the degradation of a dye and the influence of temperature was studied. The research founded out that the degradation of the dye is improved as temperature was increased.

## 2.5 Effects of Dye Concentration during Ultrasonic Degradation

There are some researches that have studied the degradation of methylene blue while manipulating the initial concentration of the dye before the degradation process. One of the findings stated that lower concentration of the methylene blue solution was found to be better for the degradation of methylene blue (W. S. Kuo & P. H. Ho, 2001). The research used a photocatalytic decolorization system equipped with immobilized $TiO_2$ and illuminated by solar light was used to remove the color of wastewater, although the method of the study is different from this research, the theory of degradation of methylene blue by manipulating the initial concentration is quite similar. In a different study, according to Shiying Zhang *et al.* (2007), when studying the photocatalytic oxidation of methylene blue that was performed in the presence of suspended $TiO_2$ (Titanium dioxide) fibers prepared by a properly two-step method in an air-sparged tube reactor, the photocatalytic process was influenced by the initial concentration of methylene blue. The study founded out that methylene blue degrades better when in lower concentrations.

## 2.6 Effects of pH Value on Dye Solution during Ultrasonic Degradation

Because methylene blue is considered a basic dye, the degradation of this dye solution in acidic pH would not show considerable influence. From a previous research (L. M. Ma et. al., 2003), a significant decrease in concentration of methylene blue occurred in the alkaline solution (pH 10–12) by using a Fe/Cu (Iron / Copper) bimetallic plant system. Moreover, according to Qi Xiao *et al.* (2007), the photocatalytic degradation of methylene blue under visible light irradiation showed that increasing the pH value of the dye solution, the photocatalytic degradation efficiency increased. There is also a study that mentioned low pH (ranging from pH 1.00 – pH 9.00) methylene blue solutions reduced the color degradation efficiency by means of Solar Photocatalytic treatment (W. S. Kuo and P. H. Ho, 2001).

## 2.7 Effect of Time of Degradation on Dye Solution

It has been shown from various researches regarding the degradation of pollutants in a waste water sample or a dye solution that the amount of substances being degraded increases along with the time of degradation process to take place. A study done by Marcio Inoue *et al.* (2006), reported that when degrading substances (Rhodamine B and Orange II dyestuff solution) using sonochemical reactions at ultrasonic frequencies 118, 224, 404 and 651 kHz, the concentration degradation plot were linear within the given reaction time. Similarly, other studies from previous researches (Cao *et al.*, 1999; Deng *et al.*, 2000; Ghauch *et al.*, 2001) reported that during the degradation of the dye solution with the presence of Fe (iron), the degradation rate follows the first-order reaction law which will then shows that the degradation of the dye increases along time. In the same way, Shiying *et al.* (2007) by means of photocatalytic oxidation, the degree of methylene blue degradation is increasing with reaction time length with the addition of suspended $TiO_2$ (Titanium dioxide) fibers.