

**ADVANCED OXIDATION PROCESSES FOR DECOMPOSITION OF SOLID  
SLUDGE FORMED VIA HERBAL TREATMENT OF TEXTILE EFFLUENT**

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## **ABSTRACT**

The real time textile effluents having high chemical oxygen demand (COD), are potentially pollutant, because of their large volume and refractory nature. Biological processes generally are not capable to remove the pollutants present in the textile effluents. Advanced Oxidation Processes (AOPs) can produce a total mineralization, transforming recalcitrant compounds into inorganic substances or partial mineralization, transforming them into more biodegradable substances. In this study, solid sludge, formed as a result of addition of herbal coagulant in the real time textile effluent, and the filtrate are treated with two major AOPs such as ultrasound cavitation and ozonation process for the decomposition of solid sludge as well as removal of COD from the filtrate obtained from effluent to less than  $150\text{mg L}^{-1}$ . The US cavitation process and ozonation process is carried out at five different pH from 2-10. US power is varied in the range of 50-250 W and ozone flow rate varied in the range of 2-6  $\text{g h}^{-1}$ . The sludge decomposition and COD removal at these conditions are studied in this investigation.

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The variation in the COD level of the real time textile effluent, filtrate obtained after the TMLR addition, ozone treated filtrate at various conditions.The pH of sludge water is varied as 2 (a),4 (b), 6.6(c), 8.8 (natural pH of filtrate) (d), and 10 (e).

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wavelength used is 315 nm.

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Variation in the PL intensity in the visible range as a function of ozonation time The graphs are associated with 3-aminophthalate formed as a result of  $O_2^{\bullet-}$ -trapping by luminol. The optimum ozone flow rate has been chosen and pH varied as 2 ( $O_3$  flow rate= 6 g h<sup>-1</sup>) (a), 4 ( $O_3$  flow rate= 6 g h<sup>-1</sup>) (b), 6 ( $O_3$  flow rate= 5 g h<sup>-1</sup>)(c), 8.8 ( $O_3$  flow rate= 3 g h<sup>-1</sup>) (d), and 10 ( $O_3$  flow rate= 2 g h<sup>-1</sup>) (e).The excitation wavelength used is 350 nm.

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## **LIST OF ABBREVIATIONS**

AOPs	Advanced oxidation processes
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
EC	Emerging contaminants
EDCs	Endocrine disrupting compounds
IBP	Ibuprofen
HC	Hydrodynamic cavitation
PL	Photoluminescence
TA	Terephthalic acid
TOC	Total organic carbon
US	Ultrasound
UV	Ultraviolet
VSS	Volatile suspended solids

# CHAPTER-1

## INTRODUCTION

The generation of uncontrollable amounts of sludge from wastewater treatments plants has been caused by the rapid rise of industrialization and urbanization in the 21<sup>st</sup> century. New types of hazardous organic compounds are continuously being generated from industries and are released into the water system. In most parts of the world, increases in population, the use of huge quantities of fertilizers and pesticides in modern agriculture, the expansion of food processing industry and the growth of other industrial processes contribute to the volume of sewage and waste water. The availability of fresh water is a great concern for our world, specifically for the safe drinking water and agriculture usages of our exponentially growing population. Water pollution occurs when undesirable effluents disperse in a water stream and hence water quality is adversely affected. The primary recognizable contaminant in a wastewater is color, because even a very small amount of synthetic dyes in water ( $< 1$  ppm) are highly visible, affecting the aesthetic merit, transparency and gas solubility of water bodies. They impede photosynthesis and aquatic animals growth by absorbing and reflecting sunlight that enters the water. In addition, depending on the concentration and duration of exposure, they may have acute or persistent impacts on organisms.

Environmental pollution is one of the major and most urgent problems of the modern world. Industries are the greatest polluters, while the textile industry generating high liquid effluent pollutants due to the large quantities of water used in the fabric processing. Wastewater differing in composition is produced in these industries. Other industries such as paper, pulp mills, distilleries, dyestuff, and tanneries are also producing highly colored wastewaters. The

highest amounts of watery waste and dye effluents are discharged from the dyeing process in the textile sector, with strong persistent color and a high biological oxygen demand, both of which are unattractive and unsustainable. Asian economies, among others, heavily rely on the textile industry. Around 80000 tons of all created dyes and pigments are consumed in India, which accounts for the majority of the world's dye stuff consumption. The synthetic dye containing industrial effluents block sunlight from entering rivers, which negatively impacts the photosynthetic process of aquatic flora and, in turn the food source for aquatic organisms. Additionally, a thin layer of discharged dyes that can form on the surface of receiving waters can reduce the amount of dissolved oxygen, which has an impact on aquatic fauna.

Textile wastewaters are known to be highly resist to biodegradation under both natural and wastewater treatment plant conditions. However several methods are in practice to treat wastewater. Effective and efficient treatment techniques before the discharge of used water in the environment are need of the hour. Both organic and inorganic pollutants present in the wastewater are removed by a set of chemical treatment methods. Various methods like photocatalysis, adsorption, oxidation processes, and surfaceplasmon resonance are used in wastewater treatment. Among various chemical processes for used water, the oxidation process is broadly employed and known as the advanced oxidation processes (AOPs). In this process for water purification, an adequate amount of hydroxyl radicals ( $\bullet\text{OH}$ ) are generated and this notion was later expanded to sulfate radicals ( $\text{SO}_4\bullet^-$ ), superoxide radicals ( $\text{O}_2\bullet^-$ ), and hydroperoxyl radicals ( $\bullet\text{OOH}$ ) oxidative processes. Apart from the degradation of organic and inorganic pollutants, AOPs are also been studied for the pathogen and pathogen indicators in activation. The recalcitrant organic pollutants present in the wastewater can be swiftly degraded by the

strong oxidants and hence AOPs have been considered as the one of the efficient technologies for the wastewater treatment.[1]

The AOPs have gained exceptional recognition concerning the advancement of wastewater treatment technologies for the two decades. Some of the methods, including photocatalysis, Fenton treatment, cavitation, and ozonation have been utilized for the breakdown of recalcitrant organic contaminants at the pilot scale. Research has been done on both the homogenous and heterogeneous AOPs in the wastewater treatment domain. Catalysts or activators such as  $\text{TiO}_2$ ,  $\text{ZnO}$ , UV/visible light, various oxidants such as  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ , etc. are employed to stimulate AOPs. At the time of activation, AOPs produce  $\bullet\text{OH}$  and other radicals which react with organic composites in the proximity of dissolved  $\text{O}_2$  of solvent media. Absolute mineralization of organic colorants can be achieved by employing dynamic AOPs.

Nano photocatalyst application can be employed for wastewater treatment. The photocatalytic AOP could commence the intricate chain reactions and there is also a chance of generation of uncolored organic intermediates and the generated intermediates sometimes become poisonous. Some of the semiconductors like  $\text{TiO}_2$ ,  $\text{CdS}$ ,  $\text{ZnO}$ , and  $\text{WO}_3$  have been widely used as photocatalysts. Biodegradation are considered as the most suitable methods for demolishing the noxious compounds in natural water. Pesticides, phenols, aromatic hydrocarbons, etc. can be degraded by using the microbes, and thereby the pollutants are eliminated. Studies have revealed that the integration of biological methods with the chemical oxidation processes will enhance the efficiency of degradation of contaminants and lower the operating costs.

Fundamental to the Fenton process is the Fenton reaction, which generates  $\bullet\text{OH}$  at atmospheric pressure and room temperature. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and ferrous ions ( $\text{Fe}^{2+}$ )

are called Fenton reagents. The classic Fenton reaction occurs when these two reagents are brought into contact in aqueous solution at acidic pH. The ferrous ion initiates and catalyzes  $\text{H}_2\text{O}_2$  decomposition, and results in the generation of highly reactive  $\bullet\text{OH}$ . Meanwhile, the generated ferric ion could be reduced by excess  $\text{H}_2\text{O}_2$  to ferrous ion enabling an effective cyclic mechanism for ferrous regeneration. The photo-Fenton process is another modification of the classic Fenton process that has been brought to the actual practice of industrial effluent treatment. By combining Fenton reagents and UV/vis irradiation, the photoreduction of  $\text{Fe}^{3+}$  could facilitate  $\text{Fe}^{2+}$  regeneration and simultaneously promote  $\bullet\text{OH}$  generation through the Fenton reaction. Additional amount of  $\bullet\text{OH}$  could also be generated through the direct photolysis of  $\text{H}_2\text{O}_2$ . As a result, photo-Fenton achieves a higher oxidation rate and efficiency than the classic Fenton process). In addition, there are remarkable reductions of total iron usage and ferric sludge formation in the photo-Fenton process. The disadvantages of Fenton process include the relatively high cost of  $\text{H}_2\text{O}_2$  and the high amount of ferric sludge produced in the neutralization step of the treated solution before disposal.

Cavitation is also an effective method of disinfection of water. Complete oxidation of hardly degradable organic contaminants, including pharmaceuticals, organic dyes, insecticides, phenol and its derivatives was observed when using hybrid processes: hydrodynamic or acoustic cavitation combined with the Fenton process, ozonation, hydrogen peroxide, UV irradiation, catalysts, and persulfate. Ultrasound is particularly effective in surface decontamination where the cleaning action is induced by cavitation collapse near a surface. One of the major goals in wastewater treatments is the removal of chemical pollutants. They pollutants are may be of from agricultural origin, for example pesticides, or from industry (effluent released from chemical factories or stormwater run-off). The cavitation effects which are the basis of the sonochemical

actions are also the reasons for the extremely effective of ultrasound to degas liquids. Ultrasonic cavitation is also employed for the sludge decomposition which is of great concern. Sonochemical water treatment shows great promise particularly in the areas of decontamination, degassing and the dispersion of solids.

Ozonation process has been widely applied in water and wastewater treatment, such as for disinfection, for degradation of toxic organic pollutants. During catalytic ozonation, catalysts can promote O<sub>3</sub> decomposition and generate active free radicals, which can enhance the degradation and mineralization of organic pollutants.

In the present thesis, the ultrasound cavitation and ozonation process are used for sludge decomposition and COD removal of real time textile effluents.

The outline of the present thesis as follows:

- A brief literature survey has been provided in the chapter-2 where the available reports related to the present study have been reviewed.
- The major objectives of the thesis are described in the chapter-3.
- The materials and methods has been discussed in the chapter-4
- The obtained results have been presented and discussed in the chapter-5.
- The present work has been concluded in the chapter-6.
- References have been listed at the end of the thesis.



## CHAPTER -2

### LITERATURE REVIEW

#### 2.1. Advanced Oxidation Processes (AOPs)

AOPs are the set of processes which involve in-situ generation of  $\bullet\text{OH}$  having very high oxidative potential (standard oxidation potential = 2.80 V) and responsible for the degradation of organic contaminants present in the wastewater. AOPs are known to be the most efficient method for water decontamination because of their ability to mineralise the organic pollutants rapidly as compared to the traditional treatment technologies. AOPs are classified broadly into three groups. They consist of photochemical, non-photochemical, and hybrid process [1].

##### 2.1.1. Photochemical methods

This method includes UV oxidation, UV/H<sub>2</sub>O<sub>2</sub>, photo-Fenton and the photocatalysis process.

##### **Ozone-UV radiation (O<sub>3</sub>/UV)**

In O<sub>3</sub>/UV process, photolysis of ozone resulting in producing oxygen atoms and molecular oxygen. Ozone absorbs UV radiation at 254 nm producing H<sub>2</sub>O<sub>2</sub> as an intermediate which then decomposes to hydroxyl radicals ( $\bullet\text{OH}$ ).

##### **Photo-Fenton and Fenton-like systems**

When  $\text{Fe}^{3+}$  ions are added to  $\text{H}_2\text{O}_2/\text{UV}$  process, it is called photo-Fenton type oxidation. At pH 3, the  $\text{Fe}(\text{OH})^{2+}$  complex is formed because of the acidic environment.



### **Photocatalytic oxidation**

The photo-excitation of a semiconductor by the absorption of electromagnetic radiation, often but not exclusively in the near UV region, is the basis of photocatalysis. When exposed to UV irradiation, photons possessing sufficient energies excite the semiconductor material to produce the conduction band electrons and valence holes. The charge carriers are able to induce reduction or oxidation respectively. At the surface of  $\text{TiO}_2$  nanoparticles, these may react with absorbed species. Holes possess an extremely positive oxidation potential and should be able to oxidize almost all chemicals. Even the one-electron oxidation of water resulting in the formation of hydroxyl radicals should be energetically feasible.



### **Hydrogenperoxide-UV radiation ( $\text{H}_2\text{O}_2/\text{UV}$ )**

The direct photolysis of  $\text{H}_2\text{O}_2$  leads to the formation of  $\bullet\text{OH}$ .

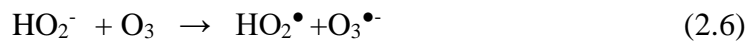
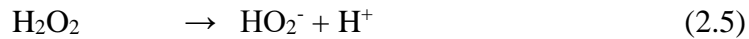


#### 2.1.2. Non-photochemical methods

These are the methods for generating  $\bullet\text{OH}$  without using light energy. Peroxone process and Fenton system are included in this category.

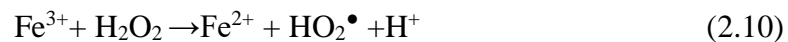
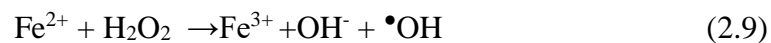
### **Ozone + hydrogenperoxide ( $\text{O}_3/\text{H}_2\text{O}_2$ ) – (Peroxone)**

The peroxone process is an efficient catalytic system for the degradation of refractory pollutants in the wastewater. It involves a radical chain mechanism based on the ozone decomposition initiated by the hydroperoxide anion ( $\text{HO}_2^-$ ). The synergistic effect of  $\text{O}_3$  with  $\text{H}_2\text{O}_2$  promotes the production of  $\bullet\text{OH}$  radicals [1].



### **Fenton process**

In the Fenton process, ferrous and ferric ions take part in the reaction with  $\text{H}_2\text{O}_2$  and generate different radicals under mild acidic condition.



AOPs are reliable for the treatment of wastewater to check the various water quality parameters, including chemical oxygen demand (COD), biochemical oxygen demand (BOD), odour, and bacterial or microbial disinfection. AOPs have been used for targeting

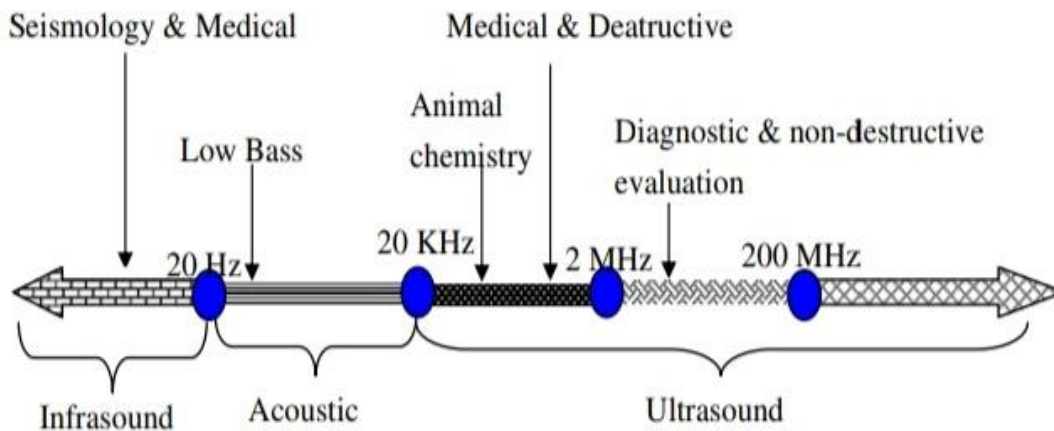
numerous types of pollutants such as complex aromatic rings containing organic compounds, emerging contaminants (EC), endocrine disrupting compounds (EDCs) from pharmaceutical industries, and waste discharge from clinical. AOPs such as photocatalysis and photo-Fenton have been proposed as tertiary treatments for urban effluents due to their ability to detoxify wastewater streams containing persistent contaminants. Treatment by activated sludge is more efficient and less expensive for removing high concentrations of organic compounds. The advantages of AOPs include their small footprint and easy integration with other treatment processes. The non-biodegradable substances that persist after biological treatment can be removed. AOPs can be used to partially degrade toxic compounds for obtaining effluents with more biodegradables prior to the biological process [2].

## 2.2. Ultrasonication

Ultrasonication (US) is an effective mechanical pre-treatment method to enhance the biodegradability of the sludge and it would be very useful to all wastewater treatment plants in treating and disposing sewage sludge. The degree of disintegration depends on the sonication parameters and also on sludge characteristics, therefore the evaluation of the optimum parameters varies with the type of sonicator and sludge to be treated [3]. Sonolysis is one of the most recent AOP techniques, where ultrasound irradiation is used as a tool to produce  $\bullet\text{OH}$  via the pyrolysis of water. Therefore, this method is considered as a green method to eradicate toxic water pollutants without using or producing any exterior chemicals in the water system. However, energy is required for the acoustic cavity of bubbles that were produced from ultrasound irradiation. The acoustic bubble formation is controlled significantly by altering the

power and frequency that were applied in the form of ultrasound as the parameter to control the degradation rate of pollutants [1].

Ultrasound is the transmission of sound energy in the form of pressure waves at frequencies above the limit of human hearing which is about 16 kHz. Based on the frequency, the three important regions are classified as -power ultrasound (20-100 kHz), high frequency ultrasound (100 kHz–1 MHz), and diagnostic ultrasound (1–500 MHz) [3]. Applications of power ultrasound usually include ultrasonic plastic soldering and metal welding, ultrasonic machining, cell disruption, ultrasonic cutting and drilling. High frequency ultrasound is employed in dermatology; assessment, diagnosis and management of many dermatologic conditions. Real time imaging, morphological and physiological aspects of skin are also obtained using high frequency ultrasound. The ultrasound ranging from 1 MHz to 10 MHz is used in different fields like animal navigation and communication, detection of cracks or flaws in solids and underwater echo location, fetal scanning, and detection of pelvic abnormalities, treating benign and malignant tumours [3]. Diagnostic ultrasound is used to visualise subcutaneous body structures including tendons, muscles, joints, vessels and internal organs.



**Fig. 2.1.** Diagram of sound range

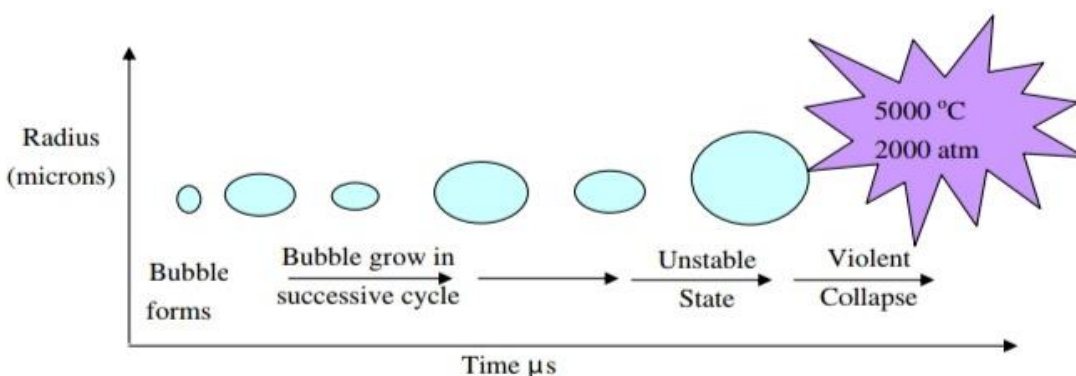
### 2.2.1. Ultrasound Cavitation

Cavitation is the process of formation, growth, and violent collapse of cavities in a liquid. Acoustic cavitation can be thought of as a means to concentrate the energy of a uniform sound field at a finite number of locations.

The energy release during a cavitation can be quite large. Bubble collapse conditions can create localized temperatures from 2000 to 5000 K, and pressures from 1,800 to 3,000 atm. Conditions during the US cavitation are sufficient to split water to produce  $\bullet\text{OH}$  (sonochemistry) or excite gases inside the bubble to emit light (sonoluminescence). When a bubble collapses near a solid surface, a jet with a velocity of up to  $300 \text{ ms}^{-1}$  is formed. This localized high-speed jet could mechanically damage nearby solid surfaces. At some distance away from the site of bubble collapse, other physical and mechanical effects such as the acoustic

shockwaves, microstreaming, and emission of sound and light are observed. These effects could also contribute to disinfection.[4]

When the ultrasound wave propagates in sludge medium, it generates compressions and rarefactions, the compression cycles exert a positive pressure on the liquid by pushing the molecules together and the rarefaction cycle exerts a negative pressure by pulling the molecules from one another. Because of this excessively large negative pressure, microbubbles are formed in the rarefaction regions. These microbubbles grow in successive cycles and reaches to an unstable diameter that collapse violently producing shockwaves (temperature of around 5000°C and pressure of 2000 atmospheres at a lifetime of few microseconds) [3].

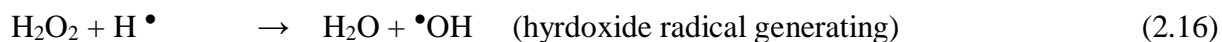
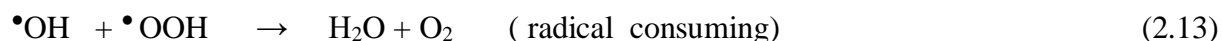
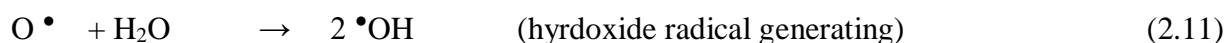


**Fig. 2.2.** Development and collapse of the cavitation bubble.

The microbubbles generated by pressure pulses inside the liquid act as small reactors, reaching an extreme pressure-temperature (P-T) conditions during short periods of time and generating highly oxidant radicals such as  $\bullet\text{OH}$ . This chemical behaviour is analogous to that of AOP. The cavitation induced by the ultrasound has proven efficient, reliable, and easy to optimize. Hydrodynamic cavitation (HC) can be studied as a valuable alternative to the US cavitation. Recently, few researchers have studied the role of different additives on degradation

of various organic pollutants using the cavitation processes [5]. It is observed that the phenomenon of cavitation gives rise to a number of interesting physicochemical effects which can be employed to isolate and oxidize contaminants in water.

The sequence of chemical reactions responsible for the radical generation under the US cavitation conditions are as follows [6].



### 2.2.2. Mechanical effects of US

- (i) The mechanical effects of ultrasound, such as particle disruption, are more pronounced at lower ultrasound frequencies.
- (ii) Long-chain polymers may be degraded by the mechanical action of ultrasound and the degradation rate is larger for polymers with higher molecular mass.
- (iii) Sonochemical and sonomechanical effects are not necessarily correlated, that is, higher sonochemical effects may not translate to larger sonomechanical effects. This shows that the mechanical effects of ultrasound may operate through different pathways than the chemical effects [4].



The combined effect of cavitation and magnetic stirring with the AOPs has been studied. The different parameters like pH, ultrasound irradiation time and dosage of hydrogenperoxide have been examined. The samples were treated by two different approaches by varying these parameters. In the first approach, wastewater was treated in the presence of cavitation using ultrasound probe sonicator and in the second approach in the presence of magnetic stirring by using a magnetic stirrer. In both the cases, the suspended total organic carbon (TOC) was measured before and after varying the parameters to ensure the destruction of organic pollutants present in the wastewater sample. The experimental results show that the combination of cavitation and  $H_2O_2$  gives a higher reduction in the suspended TOC values of tannery wastewater than with the addition of only hydrogen peroxide [7].

Ultrasound increased the degradation of Ibuprofen from 30 to 98% in 30 min. The  $\bullet OH$  was observed to be the active oxidative species on IBP. IBP destruction by sonolysis used 300 kHz and 80W of applied power leading to 98% destruction in 30 min. pH values, above its pKa, reduces the degradation rate of IBP compared to the results obtained in an acidic media where the most favourable condition for the degradation was observed [8].

### 2.3.Ozonation

Ozonation has been applied vibrantly as an advanced oxidation technology, particularly in field research for tackling industrial wastewater. This process deals with the two-phase (gas-liquid) reaction, where the two important species such as  $O_3$  and  $\bullet OH$  are used as efficient tools for the treatment purposes. The  $O_3$  that has been used as a source decomposes via a series of

chemical reactions. The main advantage of this process is that it is predominant at low pH, which may be an electrophilic nature that helps in the disintegration of the organic complexes. However, a higher pH favours the decomposition of  $O_3$  molecules into free radical ( $O_2$ ,  $HO_2^\bullet$ , and  $^\bullet OH$ ), although  $O_3$  shows strong oxidizing characteristic with the standard oxidation potential of 2.07V [9].

As an effective and promising disinfectant,  $O_3$  shows a better performance than chlorine disinfectant (such as free chlorine, chlorine dioxide, and chloramines) even  $^\bullet OH$ . Ozonation is an oxidizing technique which converts more toxic arsenite to less toxic arsenate by utilizing ozone molecules. Almost complete oxidation is possible through this method. More the initial concentration of pollutants, more the time of consumption. pH is also an important parameter. The highly acidic condition favours effective arsenite oxidation. The arsenic removal with ozone dosage  $0.56 \text{ mgs}^{-1}$  by varying an initial pollutant concentration from 50 to  $200 \mu\text{g L}^{-1}$  and found N90% of oxidation in 25 min [10]. Ozone can decompose to oxygen by split to radical such as  $^\bullet OH$ ,  $OH_3$ ,  $OH_4$ , and superoxide ( $O_2^\bullet$ ). The radicals generated are highly oxidative enough to react with various organic substances. The researchers demonstrated that the rate of decomposition of ozone is correlated with temperature, pH, and concentration of organic and inorganic compounds [11].

The ozonation has a benefit for the complete oxidation of volatile suspended solids (VSS) by a combination of partial sludge oxidation with subsequent biological oxidation. A comparison with mechanical and thermo-chemical sludge mass reduction methods shows that the mass reduction potential of ozonation is presently higher [12]. The ozonation can reduce colour in the wastewater more than 90% for the reaction time of 6 hours. When ozone gas is transferred into water, the dissolved ozone reacts with the organic and inorganic compounds including

pathogens. Ozone can react with the organic compounds at double bond of carbon, nitrogen, and aromatic rings destroying these bonds. In the beginning of the first two hour of reaction, the decolourization is potentially less and the colour is still remained because of the complexity of various types of intermediate molecules. As a result, the ozone generator could not produce enough ozone to react with the polluted water [5]. When the ozone dose is increased, the colour, COD, and DOC removal efficiency is increased. The oxidation activity of radicals might be limited by the presence of scavengers, which causes an incomplete degradation of organics [13].

The short lifetime of ozone is the most important and noteworthy point that made this method expensive and highly energy sensitive. In this context, these are considered as major drawbacks of process specifically for the real applications in the pharmaceutical wastewater treatment method [1]. The influence of ozone dosages and environment for four different types of pharmaceutical compounds (diclofenac, carbamazepine, sulfamethoxazole, and trimethoprim) has been investigated [14].

Ozone is used for water and wastewater treatment due to its strong oxidative properties. During the sludge ozonation, because of the complex composition of sludge, ozone decomposes itself into radicals and reacts with the whole matter (soluble and particulate fractions, organic or mineral fractions). If activated sludge is exposed to low dose ozone at less than 0.02 g O<sub>3</sub> per gram of TS, ozone firstly destroys the floc, leading to the disruption of the compact aggregates [15]. Moreover, by applying ozone dose at 0.05 g O<sub>3</sub> per gram of TS, the soluble COD increased linear with the ozonation time during the first 105 min and then stagnated, probably because of the balance of sludge lysis and mineralization, showing that too long time was unnecessary. Extra ozone dose or long treatment time resulted in mineralization of dissolved organics and should be avoided.

## CHAPTER – 3

### MAJOR OBJECTIVES

- Formation of sludge from industrial effluent using herbal (organic) coagulant supplied by Eco Health Products PVT LTD, Chennai.
- Decomposition of sludge by using ozonation and ultrasound cavitation.
- Identify the optimum parameters such as pH, US power, ozone flowrate for the maximum decomposition of sludge
- To identify whether ozonation or ultrasound cavitation is better technique for sludge decomposition.
- Monitor the COD levels of the filtrate (obtained after addition of coagulant), treated using US and O<sub>3</sub>.
- Identify the optimum parameters such as pH, US power, ozone flowrate for the maximum COD removal.
- To identify whether ozonation or ultrasound cavitation is better technique for sludge COD removal

## CHAPTER-4

### MATERIALS AND METHODS

#### 4.1 Materials

Following chemicals were used in the as received condition without any further purification.

1. Sodium hydroxide (NaOH, pellets, 97 % SDFine – Chem. Ltd., Mumbai, India)
2. Terephthalic acid (TA,  $C_6H_4(CO_2H)_2$ , 98% Sigma-Aldrich Chemicals, Bangalore, India)
3. Luminol (5-Amino-2,3-dihydrophthalazine- 1,4 - dione) from Merck Specialties Pvt. Ltd., Mumbai, India)
4. Hydrochloric acid (HCl, 35 wt%) from Ranbaxy Fine Chemicals Ltd., India
5. The herbal coagulant TMLR (Ecohealth Products Pvt. Ltd, Chennai)
6. The real time textile effluent (Karnataka State Garments Washing Owners Association)
7. Sulphuric acid( $H_2SO_4$ , 98 %) from Emcure pharmaceuticals, Pune,Maharashtra,India
8. Ferrous Ammonium Sulphate ( $(NH_4)_2Fe(SO_4)_2(H_2O)_6$  from Emcure pharmaceuticals, Pune,Maharashtra,India
9. Pottassium dichromate( $K_2Cr_2O_7$ ) from Merck KGaA Darmstadt, Germany
10. Ferrous sulfate( $FeSO_4$ ) from Merck life science private limited, Vikhroli,Mumbai
11. 1,10- Phenanthroline monohydrate( $C_{12}H_8N_2.H_2O$ ) from Merck KGaA Darmstadt, Germany

## 4.2 Methods

### 4.2.1. Sludge formation

100 ml of real time textile effluent, with an initial pH of 8.9, was taken in a 250 ml beaker. Three drops of the TMLR reagent were added to the effluent and followed by magnetic stirring (magnetic stirrer, C MAG HS 7, IKA, Germany) for 15 minutes. The effluent is then kept for 60 min without stirring for the settling of sludge. The clear filtrate on the top were separated out using dropper and centrifuged( Hettich EBA 20, Sigma-Aldrich, India) at 2100 rpm for 10 min. Sludge settled on the bottom of beaker is transferred to a petridish and dried in an oven at 80<sup>0</sup> C for 12 h( Labline Instruments, Kochi, India).

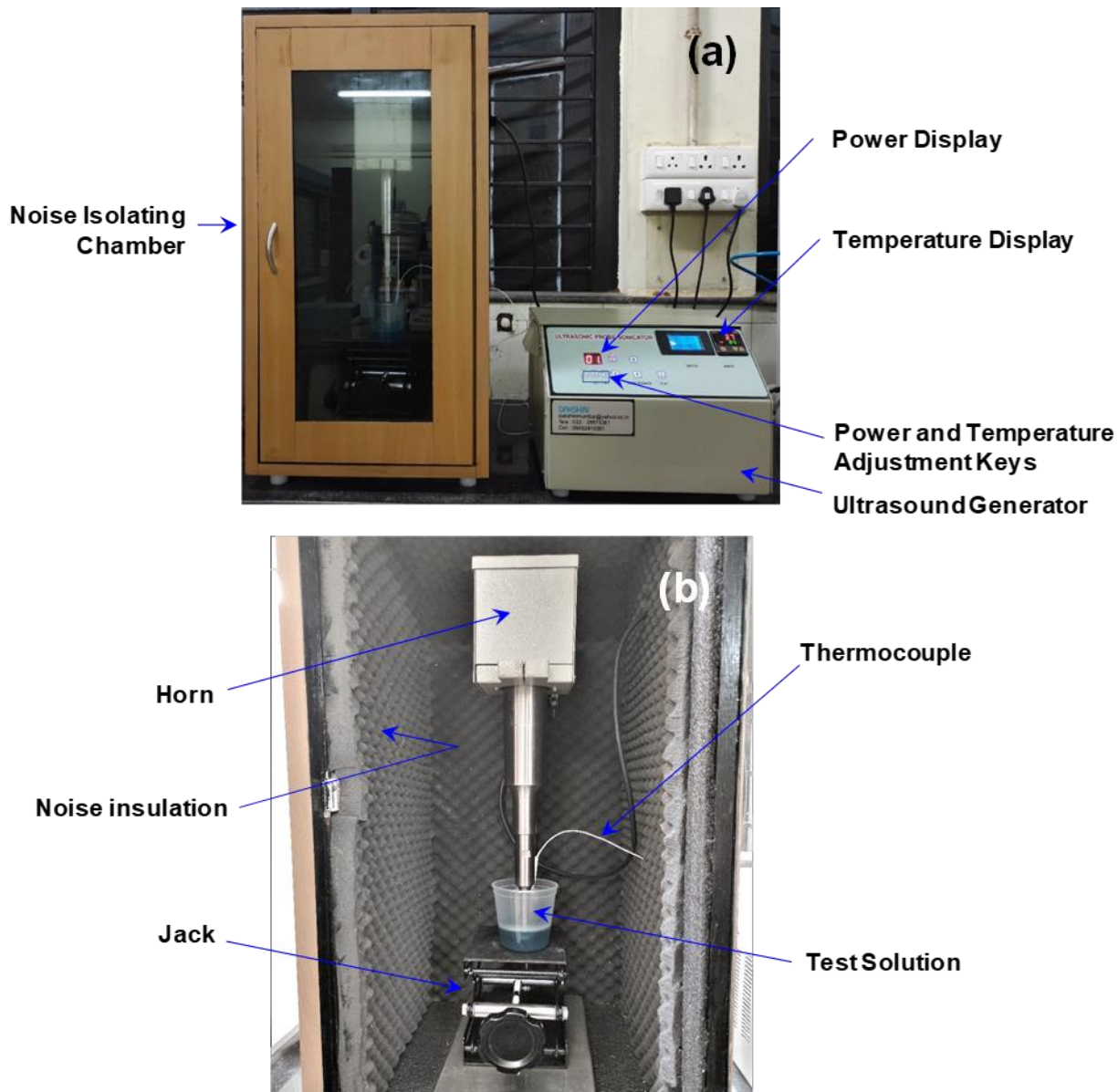
### 4.2.2. Decomposition of solid sludge using US

An ultrasound probe sonicator is used for ultrasonic treatment of sludge. The sonicator consists of a horn which is mounted on the stand and connected to the US processor(DP 250, Dakshin, Mumbai, India)which generates the US waves having the frequency of  $22 \pm 2$  kHz which are in turn dissipated into the solution through the stainless steel sonicator probe having the tip diameter of 12 mm. Initially, 100 ml distilled water in a plastic beaker. The beaker is then

placed on a jack inside the noise isolating chamber. A thermocouple was dipped inside the beaker to measure the temperature which was displayed on the control panel and the cut-off temperature was set at 85° C. The height of jack is adjusted till the probe dipped inside the solution. For the decomposition of sludge using US cavitation, an average weight of approximately 0.05 g of dried sludge is transferred to the beaker. The US wave was passed through the sludge containing beaker at the initial temperature of 32° C with an automatic power ON and OFF duration of 25 and 5 s. The total time of US cavitation experiment was kept constant at 72 min so that the cumulative power ON and OFF periods were 60 and 12 min respectively. The US power was varied within the range of 50–250 W at the interval of 50 W. After 72 min, the sludge containing water inside the beaker is centrifuged and about 15 ml of the filtrate is collected for COD measurement and compared with the COD of the distilled water. The remaining sludge inside the beaker along with the residue in centrifuging tube is transferred to a petridish and dried in an oven at a temperature of about 80° C for 12 h. After drying, the weight of the sludge is again measured. From the difference between the weight of the sludge before and after US treatment, the percentage of decomposition of sludge using US cavitation can be calculated by the Equation.

$$\% \text{ of weight loss} = \frac{(\text{Initial weight} - \text{final weight}) \times 100}{\text{Initial weight}} \quad (4.1)$$

The experiment was repeated by changing the pH of distilled water varied in the range of 2-10 which was adjusted by using HCl and NaOH stock solutions and corresponding weight loss and COD measurements were analysed.



**Fig-4.1** Digital photographs showing the US probe sonicator with closed (a) and opened (b) door of noise isolating chamber



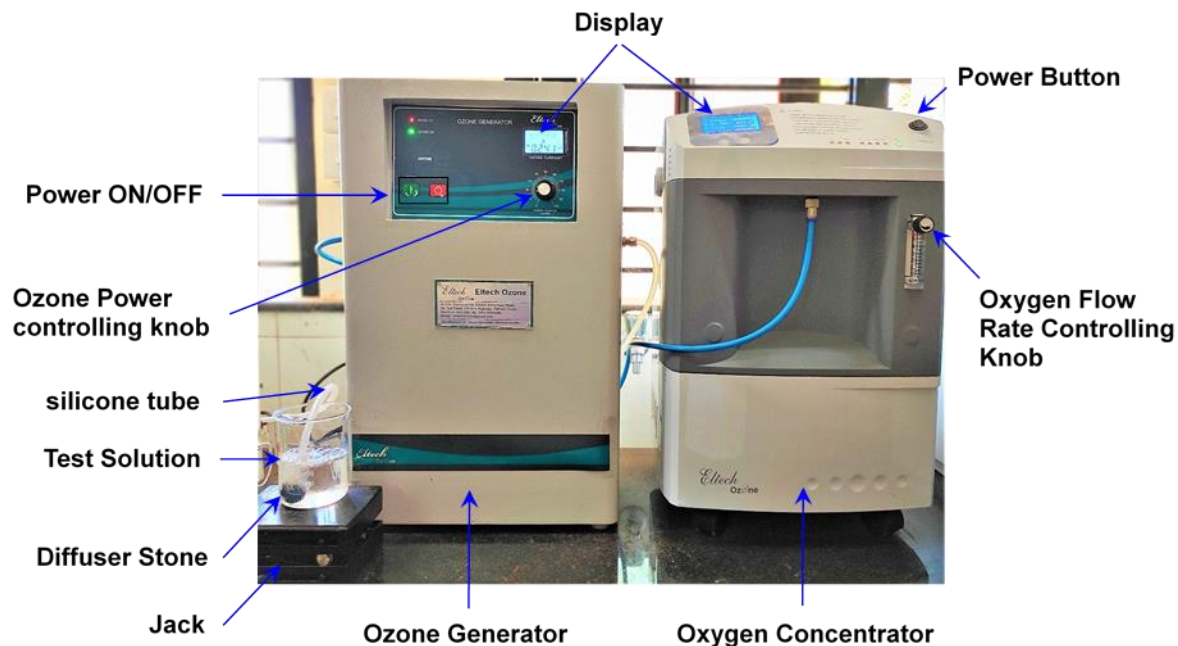
#### 4.2.3. Decomposition of solid sludge using ozonation

An ozone generator purchased from Eltech ozone, Mumbai, India is used for ozonation. It consists of an oxygen concentrator which converts an atmospheric air into 92% O<sub>2</sub>. The flow rate of O<sub>2</sub> produced as an output can be adjusted within the maximum range of 1–5 L min<sup>-1</sup> which is flown through the O<sub>3</sub> generator. The ozone generator converts the pure O<sub>2</sub> to O<sub>3</sub> via an electric discharge method. The O<sub>3</sub> flow rate, as an output, can be adjusted within the range of 2–6 g h<sup>-1</sup> by using an appropriate combination of O<sub>3</sub> power and O<sub>2</sub> flow rate which are provide in the table no.

**Table 4.1.** The combination of the values of O<sub>3</sub> power and O<sub>2</sub> flow rate used for obtaining the required O<sub>3</sub> flow rate.

<b>O<sub>3</sub> power (%)</b>	<b>O<sub>2</sub> flow rate (L min<sup>-1</sup>)</b>	<b>O<sub>3</sub> flow rate (g h<sup>-1</sup>)</b>
50	1	2
50	2	3
60	2	4
60	3	5
70	3	6

100 ml of distilled water is taken in a 250 ml plastic beaker and a measured weight of an average of about 0.05 g of dried sludge is added to the plastic beaker. The generated O<sub>3</sub> gas was continuously bubbled into the sludge water for 60 min by allowing it to pass through the diffuser stone connected at the end of silicone tube. After one hour, the sludge containing water is centrifuged and 15 ml of the filtrate is centrifuged and collected for COD measurement and the remaining sludge and filtrate is taken in a clean and dry petridish. It is then placed in the oven at a temperature of about 80° C. The same experiment is conducted with distilled water having pH range from 2-10. After drying, the weight of the sludge is again measured. From the difference between the weight of the sludge before and after ozone treatment, the percentage of decomposition of sludge using ozone cavitation can be calculated. The experiment was repeated by changing the pH of distilled water varied in the range of 2-10 which was adjusted by using HCl and NaOH stock solutions and corresponding weight loss and COD measurements were analysed.



**Fig.4.2** Digital photograph showing the O<sub>3</sub> Generator

#### 4.2.4. COD removal of TMLR treated filtrate using US

Initial COD of the filtrate is measured. The upper filtrate obtained after sludge formation using TMLR is treated with ultrasound cavitation for the removal of COD. 100 ml of the filtrate, with an initial pH of 8 is taken in a plastic beaker and placed on a jack inside the noise isolating chamber. The US cavitation experiment were conducted as per the procedure described in section 4.2.2. except here, there is no addition of sludge. After 72 min, 15 ml of the treated filtrate is collected for COD analysis. The experiment was conducted at different power varied from 50-250 W at different pH varied in the range of 2-10.

#### 4.2.5. COD removal of TMLR treated filtrate using ozonation

The upper filtrate obtained during sludge formation is also treated with ozonation for the removal of COD. Initial COD of the filtrate is measured. 100 ml of the filtrate, with an initial pH of 8 is taken in a beaker. The ozone probe is dipped inside the solution. The ozonation of TMLR treated filtrate were conducted as per the procedure described in section 4.2.3. except here, there is no addition of sludge. After 60 min, 15 ml of the treated filtrate is collected for COD analysis. The experiment was conducted at ozone flow rate varied from 2-6 g h<sup>-1</sup> at different pH varied in the range of 2-10.

#### 4.2.6. Radical - trapping

A trapping substance called TA was utilized to find the existence of hydroxyl radicals ( $\bullet\text{OH}$ ). All of the radical trapping studies were carried out in distilled water with the proper quantity of NaOH added in order to completely dissolve the TA. The initial concentrations of TA and NaOH were 0.058 g L<sup>-1</sup> ( $3.4 \times 10^{-4}$  M) and 0.08 g L<sup>-1</sup> ( $2 \times 10^{-3}$  M). The  $\bullet\text{OH}$  trapping experiments for the ultrasound cavitation process were carried out under test conditions similar to those in section 4.2.2, with the exception that 10 ml aliquots were periodically collected during the sonication off period after each sonication time of 10 min for a total cumulative sonication time of 60 min. The test settings for the ozonation treatment were virtually identical to those described in section 4.2.3, with the exception that 10 ml aliquots were periodically collected after 10 min time intervals for a total of one hour of ozonation. The aliquots were immediately analysed via the photoluminescence (PL) spectrophotometer (Cary Eclipse, Varian,

The Netherlands). The production of 2-hydroxyterephthalic acid, which has a distinctive peak at 425 nm at an excitation wavelength of 315 nm, is caused by the trapping of free OH radical by TA. The concentration of OH radical produced under the specified test conditions is qualitatively evaluated as the PL intensity.

A chemiluminescent probe called luminol was employed to find the produced superoxide radical ( $O_2^{\bullet-}$ ). For this distilled water was first mixed with  $0.4 \text{ gL}^{-1}$  of NaOH and  $0.278 \text{ gL}^{-1}$  of luminol for dissolution. The remaining processes for this treatment approach were identical to those previously outlined for the OH radical trapping. The intensity of the 3-aminophthalate (AP) peak, which exhibits a distinctive broad PL peak typically located at 420 nm at an excitation wavelength of 350 nm, is taken as a measure of the generated concentration of  $O_2^{\bullet-}$ . The luminol molecules react with the generated  $O_2^{\bullet-}$  radicals to form 3-aminophthalate (AP).

#### 4.2.7. COD Measurements

The degradation of the organic matter was monitored in terms of COD. The distilled water containing sludge, treated with ultrasound cavitation and ozonation are taken for COD measurement. For US cavitation the sludge water is treated with five different powers of sonicator varied from 50-250 W and five different pH varied from 2-10 is taken for COD measurement. Similarly, the upper filtrate treated with five different powers and five different pH is used for COD. For ozonation the sludge water and upper filtrate is treated under five different ozone flow rate from  $2-6 \text{ g h}^{-1}$  and five different pH varied from 2-10 is taken for COD measurements

To analyze the COD values for a particular sample, samples are added to the COD digestions vials, which are kept in the digester block. At a time six samples can be kept in the

digester, out of which five being wastewater sample and remaining one being a blank sample. Two blanks were also prepared by adding all the reagents except the sample solution (instead of sample 20 ml of distilled water was added). One blank was kept for digestion along with the test solutions (hot blank) and the other was kept at normal room temperature (cold blank). 10 ml of sample for analysis and blank samples were individually mixed with 10 ml of 0.25 N potassium dichromate solution ( $K_2Cr_2O_7$ ) followed by 20 ml of sulphuric acid ( $H_2SO_4$ ). After attaining uniform mixing, the contents were transferred to the COD cell tests, then the cells were sealed with caps and placed in the COD digester which was then allowed to get heated (150 °C) up to 2h. After digestion, solutions were cooled and completely transferred into conical flasks. About 2-3 drops of Ferroin was added as the indicator and titrated against approximately 0.125 N Ferrous ammonium sulphate (FAS) solution. The end point was identified by the colour change from greenish-blue and the end point of titration being wine-red. Volume of FAS required for each titration is noted and the COD was calculated using the equations below.

$$\text{Normality of FAS} = \frac{\text{Normality of Potassium dichromate} \times \text{volume of potassium dichromate}}{\text{Volume of FAS}} \quad (4.2)$$

$$\text{COD} = \frac{\text{Normality of FAS} \times (A-B) \times 8000}{\text{Volume of sample taken}} \text{ mg L}^{-1} \quad (4.3)$$

Where,

A- Volume of FAS used for blank

B- B- Volume of FAS used for sample

C- 8000- equivalency of oxygen to 1000 ml

## CHAPTER – 5

### RESULTS AND DISCUSSION

#### 5.1. Decomposition of solid sludge using US

##### 5.1.1. Determination of weight loss (%) of solid sludge after US treatment

The percentage of decomposition of solid sludge with US cavitation at different initial distilled water pH varied from 2-10 for different US power of 50-150 W. The percentage weight loss at different US power for different pH is shown in the table 5.1– 5.5.

**Table 5.1** Weight loss (%) of solid sludge at pH 2 after ultrasound cavitation of power varied from 50-250 W

No	US power (W)	Initial weight (g)	Final weight (g)	Weight loss (%)
1	50	0.0520	0.0344	33.80
2	100	0.0466	0.0312	33.00
3	150	0.0485	0.0322	31.50
4	200	0.0497	0.0354	28.70
5	250	0.0510	0.0382	25.00

**Table 5.2** Weight loss (%) of solid sludge at pH 4 after ultrasound cavitation of power varied from 50-250 W

No	US power (W)	Initial weight (g)	Final weight (g)	Weight loss(%)
1	50	0.0576	0.0393	33.27
2	100	0.0596	0.0398	33.22
3	150	0.0589	0.0438	25.00
4	200	0.0455	0.0323	29.00
5	250	0.0557	0.0350	37.00

**Table 5.3** weight loss (%) of solid sludge at neutral pH (6.6)after ultrasound cavitation of power varied from 50-250 W

No	US power (W)	Initial weight (g)	Final weight (g)	Weight loss (%)
1	50	0.0541	0.0219	59.50
2	100	0.0487	0.0220	54.82
3	150	0.0428	0.0297	30.60
4	200	0.0493	0.0288	30.62
5	250	0.0502	0.0291	42.00



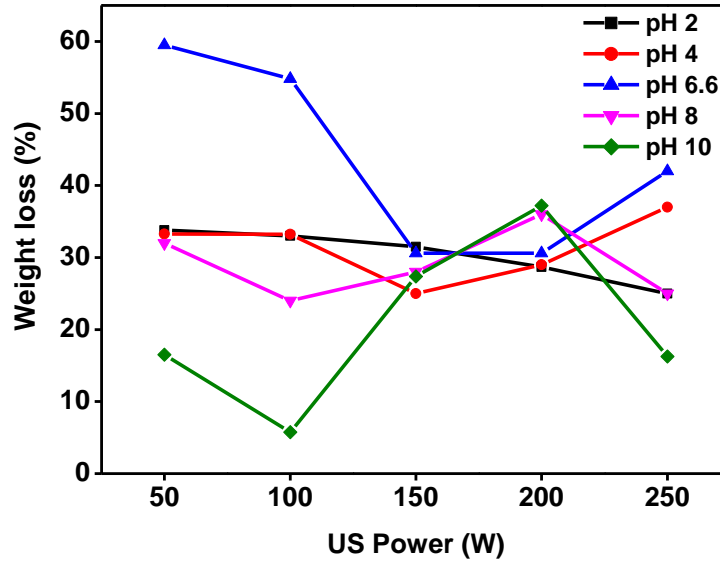
**Table 5.4** Weight loss (%) of solid sludge at pH 8 after ultrasound cavitation of power varied from 50-250 W

No	US power (W)	Initial weight (g)	Final weight (g)	Weight loss(%)
1	50	0.0718	0.0487	32.00
2	100	0.0457	0.0346	24.00
3	150	0.0624	0.0447	28.00
4	200	0.0500	0.0320	36.00
5	250	0.0606	0.0452	25.00

**Table 5.5** Weight loss (%) of solid sludge at pH 10 after ultrasound cavitation of power varied from 50-250 W

No	US power (W)	Initial weight (g)	Final weight (g)	Weight loss(%)
1	50	0.0363	0.0303	16.52
2	100	0.0574	0.0541	5.74
3	150	0.0508	0.0369	27.36
4	200	0.0324	0.0324	37.20
5	250	0.0304	0.0304	16.25

The maximum percentage of weight loss was observed at neutral pH at a power of 50 W. It was about 59.50% and the minimum weight loss is observed at pH 10 at 100 W power and it was about 5.74%. A graph is plotted with US power along X axis and percentage of weight loss along Y axis shown in Fig 5.1. Here the percentage of weight loss of sludge at five different pH, that is from 2-10 is noted.

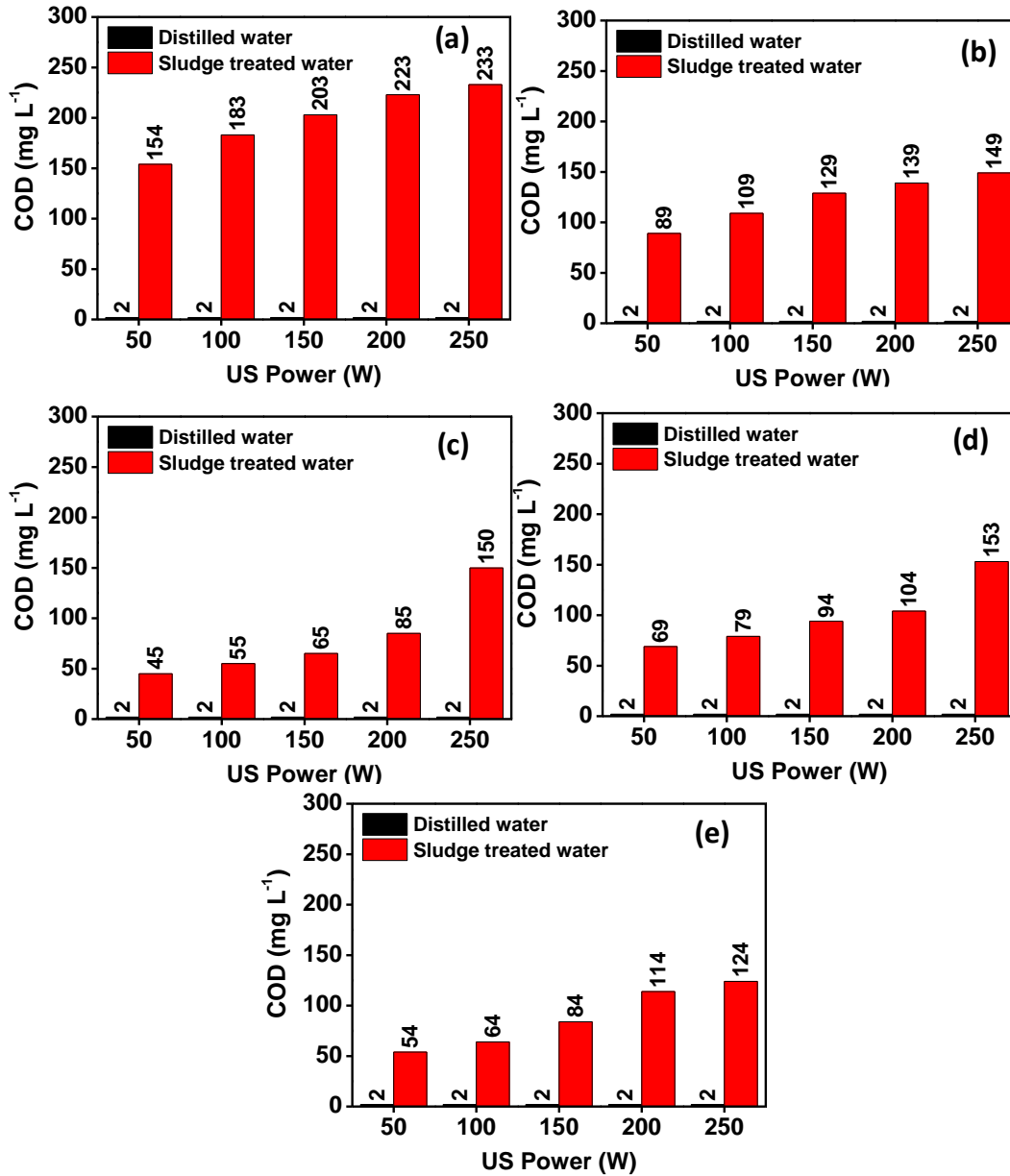


**Fig 5.1** Weight loss (%) of sludge at different US power and different pH

#### 5.1.2. Comparison of COD of Distilled water with US treated sludge water.

The COD of distilled water was found to be  $2 \text{ mgL}^{-1}$ . Sludge water (distilled water after the addition of sludge) after the treatment US cavitation at different initial distilled water pH

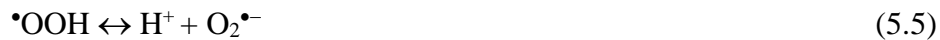
varied from 2-10 for different US power of 50-150 W are taken for COD measurement and the results are shown in figure 5.2.



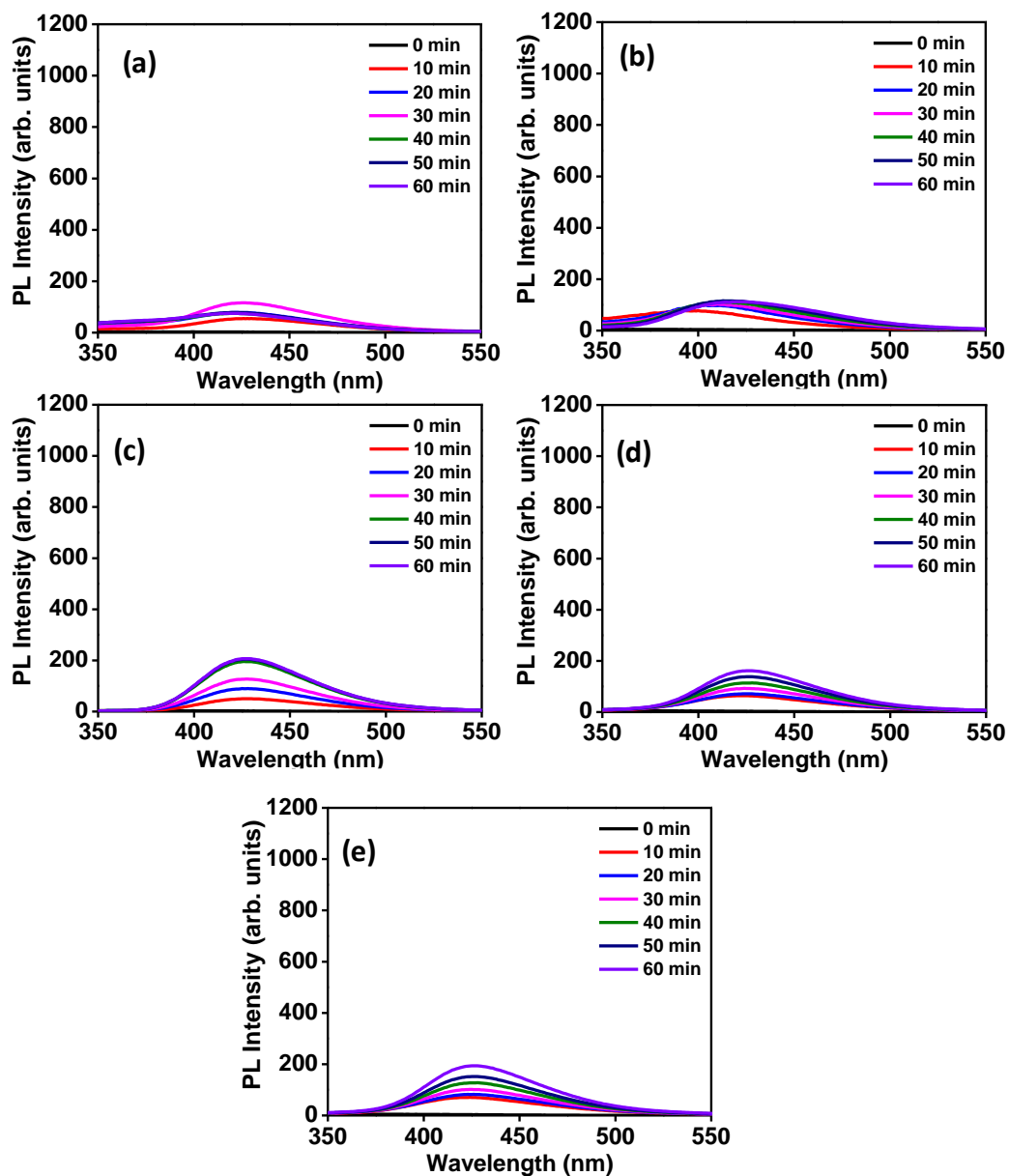
*Fig. 5.2 Comparison in the COD values of distilled water and sludge water obtained after US treatment for five different initial solution pH as the US power varies from 50-250 W. The pH is varied as 2 (a), 4 (b), 6.6 (c), 8 (d), and 10 (e).*

Sludge containing water is treated at different initial distilled water pH varied from 2-10 for different US power of 50-150 W are shown in the Fig.5.2. The COD is found to be increasing with increase in power of US, where highest COD removal were obtained at lowest US power of 50 W, which is the optimum US power for the solid sludge removal. At highly acidic pH that is at pH 2 the value of COD is high, the amount of COD removal increases when the pH value increases from 2 to 6.6 (neutral) where highest COD removal was obtained. When the pH is increased to the alkaline region (pH=6.6 to 10), the removal of COD decreased. The optimum parameters for the COD removal in the solid sludge decomposition using US cavitation are at the neutral pH and at an US power of 50 W.

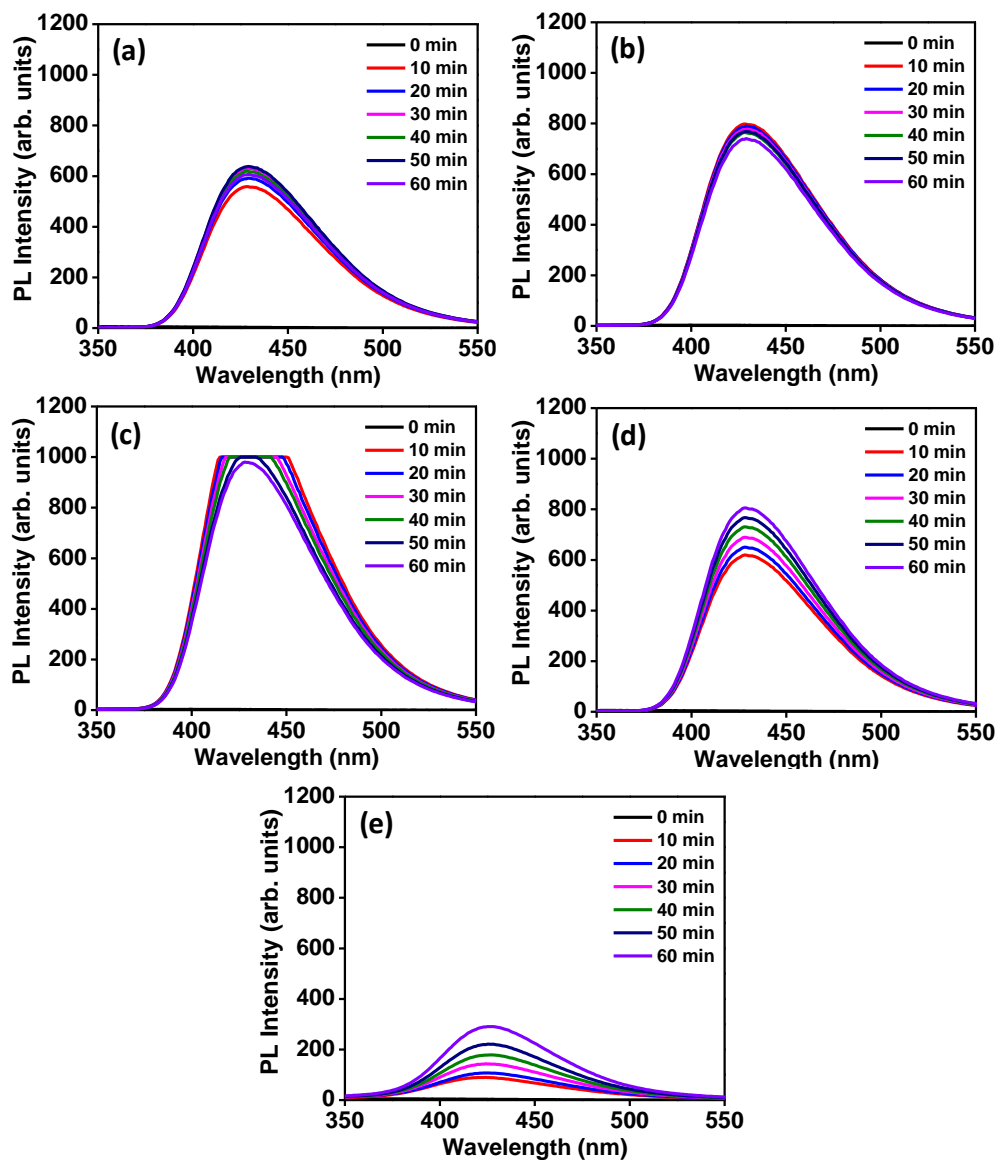
When ultrasound wave propagates in aqueous solution, it generates compressions and rarefactions. These US waves nucleate microbubbles around the dissolved gas molecules which expand during the rarefaction of acoustic cycle. These microbubbles grow in successive cycles and reaches to an unstable diameter that collapse violently producing short lived hot spots which are the microscopic regions of very high temperature (5000 K) and pressure 1000 atm. This phenomenon is called acoustic or ultrasound cavitation which results in the thermal dissociation (pyrolysis) of  $H_2O$  molecule into  $\bullet H$  and  $\bullet OH$ . The hydroxyl radicals are often held responsible for the COD removal. The sequence of chemical reactions responsible for the radical generation under the US cavitation conditions are presented in the Eqs. (5.1) - (5.10). (Note: In Eqs (5.1) and (5.2), “ $\bullet$ ”) represents the US wave travelling through an aqueous solution).



From the Eqs. 5.1 to 5.10, the major radicals generated here are  $\text{H}^\bullet$ ,  $\bullet\text{OH}$ ,  $\text{O}^\bullet$ ,  $\bullet\text{OOH}$ , and  $\text{O}_2^{\bullet-}$ . The radicals except  $\bullet\text{OH}$  and  $\text{O}_2^{\bullet-}$  are found to be quenched which may also give produce  $\bullet\text{OH}$  and  $\text{O}_2^{\bullet-}$  in the reactions. So the major COD removal can be attributed to the presence of  $\bullet\text{OH}$  and  $\text{O}_2^{\bullet-}$ . To understand the mechanism of removal of COD for the US treated sludge water,  $\bullet\text{OH}$  and  $\text{O}_2^{\bullet-}$  radical-trapping experiments were conducted and the results are shown in the Figs 5.3 and 5.4.



*Fig. 5.3* Variation in the PL intensity in the visible range as a function of sonication time, associated with 2-hydroxyterephthalic acid formed as a result of  $\bullet\text{OH}$  trapping by TA. The US power is fixed at 50 W and pH varied as 2(a), 4(b), 6.6(c), 8(d), and 10(e). The excitation wavelength used is 315 nm.



**Fig. 5.4** Variation in the PL intensity in the visible range as a function of sonication time, associated with 3-aminophthalate formed as a result of  $O_2^{\bullet-}$ -trapping by luminol. The US power is fixed at 50 W and pH of the solution is varied from 2 (a), 4 (b), 6.6 (c), 8 (d), and 10 (e). The excitation wavelength used is 350 nm. (Note: the peaks in the graph are truncated on the upper side due to very high concentration  $O_2^{\bullet-}$  which is beyond the detection limit of PL spectrophotometer used in this investigation).

The maximum sludge decomposition using ultrasound cavitation is obtained at 50 W US power. By analyzing the Fig 5.3, it is observed that, even though hydroxyl radical formation occurs at all pH, the intensities of the peaks are almost comparable. This confirms that the change in pH did not affect the  $\bullet\text{OH}$  concentration produced at an US power of 50 W. From the Fig. 5.4, the amount of  $\text{O}_2^{\bullet-}$  produced at 50 W were found to be varied with the change in initial distilled water pH. The amount of radical produced were increased with the initial solution pH changed from 2-6.6 (neutral). The maximum amount  $\text{O}_2^{\bullet-}$  were observed at neutral pH. Further increase in initial solution pH from 6.6 to 10 showed a decrease in the  $\text{O}_2^{\bullet-}$  radical concentration. This is in agreement with the results obtained during sludge decomposition using ultrasound cavitation, the maximum sludge decomposition occurs at neutral pH, under US power of 50 W, where the amount of  $\text{O}_2^{\bullet-}$  found to higher. Hence the maximum sludge decomposition can be attributed to the presence of  $\text{O}_2^{\bullet-}$ .

## 5.2 Decomposition of solid sludge using ozonation

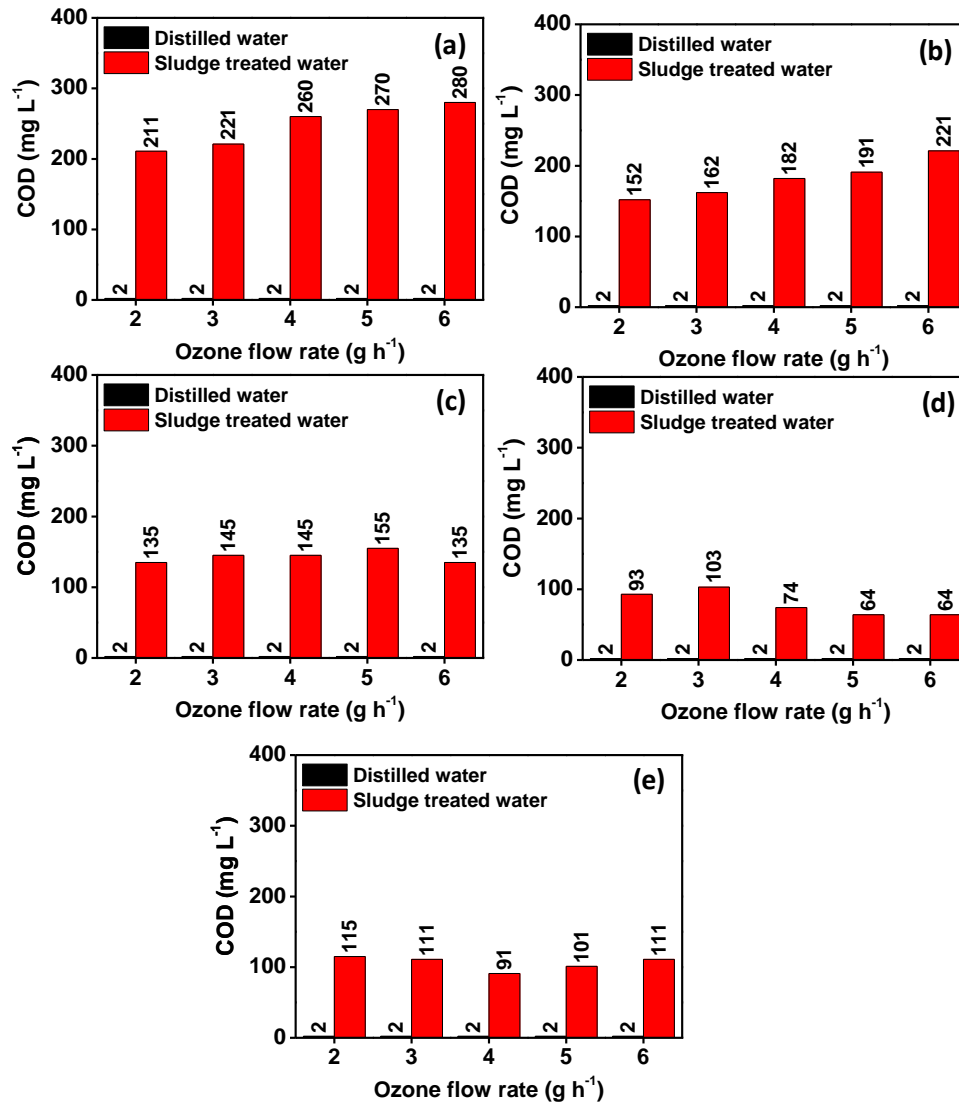
### 5.2.1. Determination of weight loss (%) of solid sludge after $\text{O}_3$ treatment

The solid sludge treated with ozone at different ozone flow rate varied from 2-6  $\text{g h}^{-1}$  were examined for measuring the final weight. However, the sludge remained after the ozone treatment were negligible amount and very much difficult to measure and therefore weight loss (%) of solid sludge after the ozonation treatment is considered to be almost 100%.



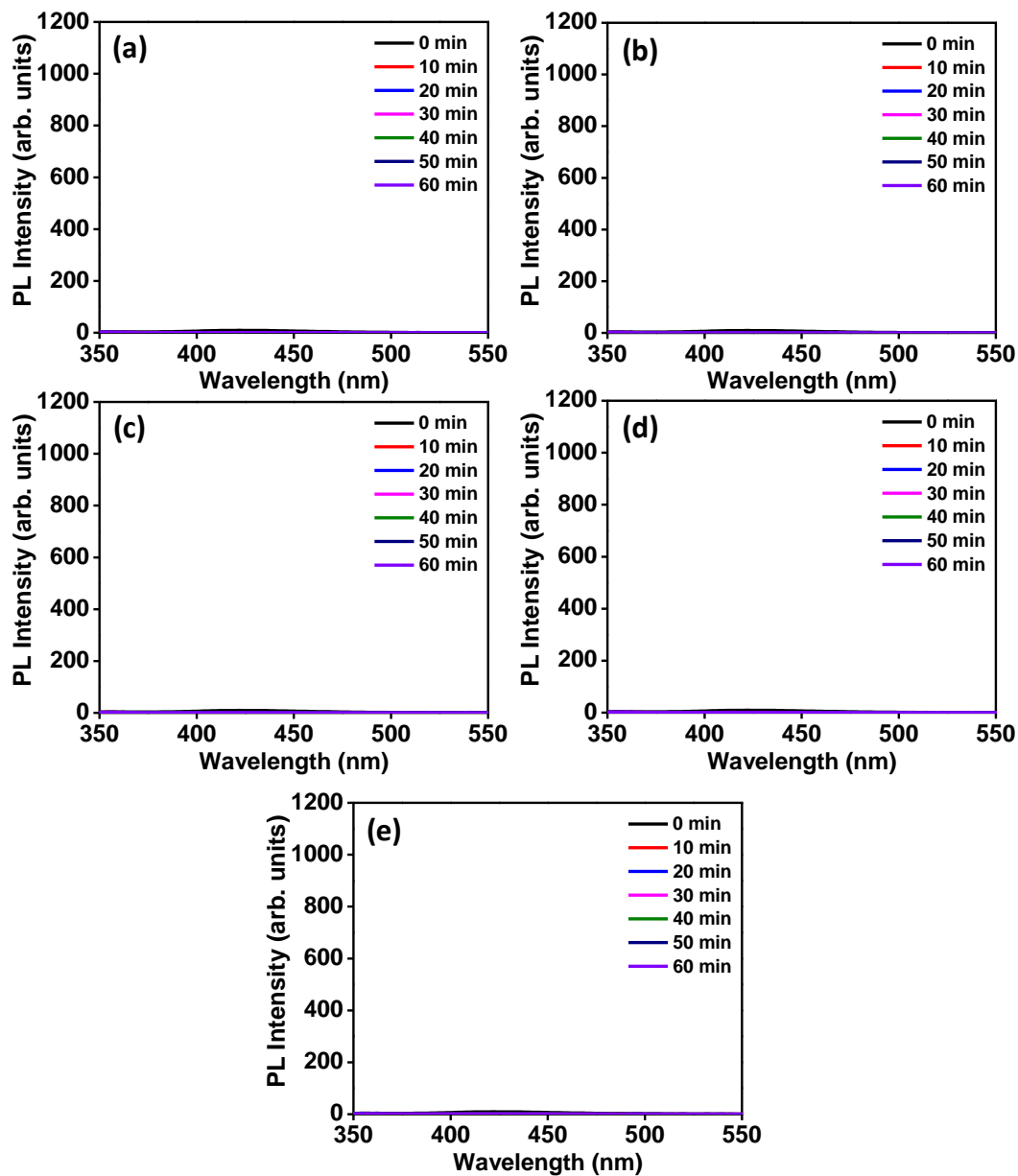
### 5.2.2. Comparison of COD of distilled water with ozone treated sludge water

The sludge containing water is treated at different pH varied from 2-10 at different ozone flow rate of 2-6 g h<sup>-1</sup> are shown in Fig5.5.

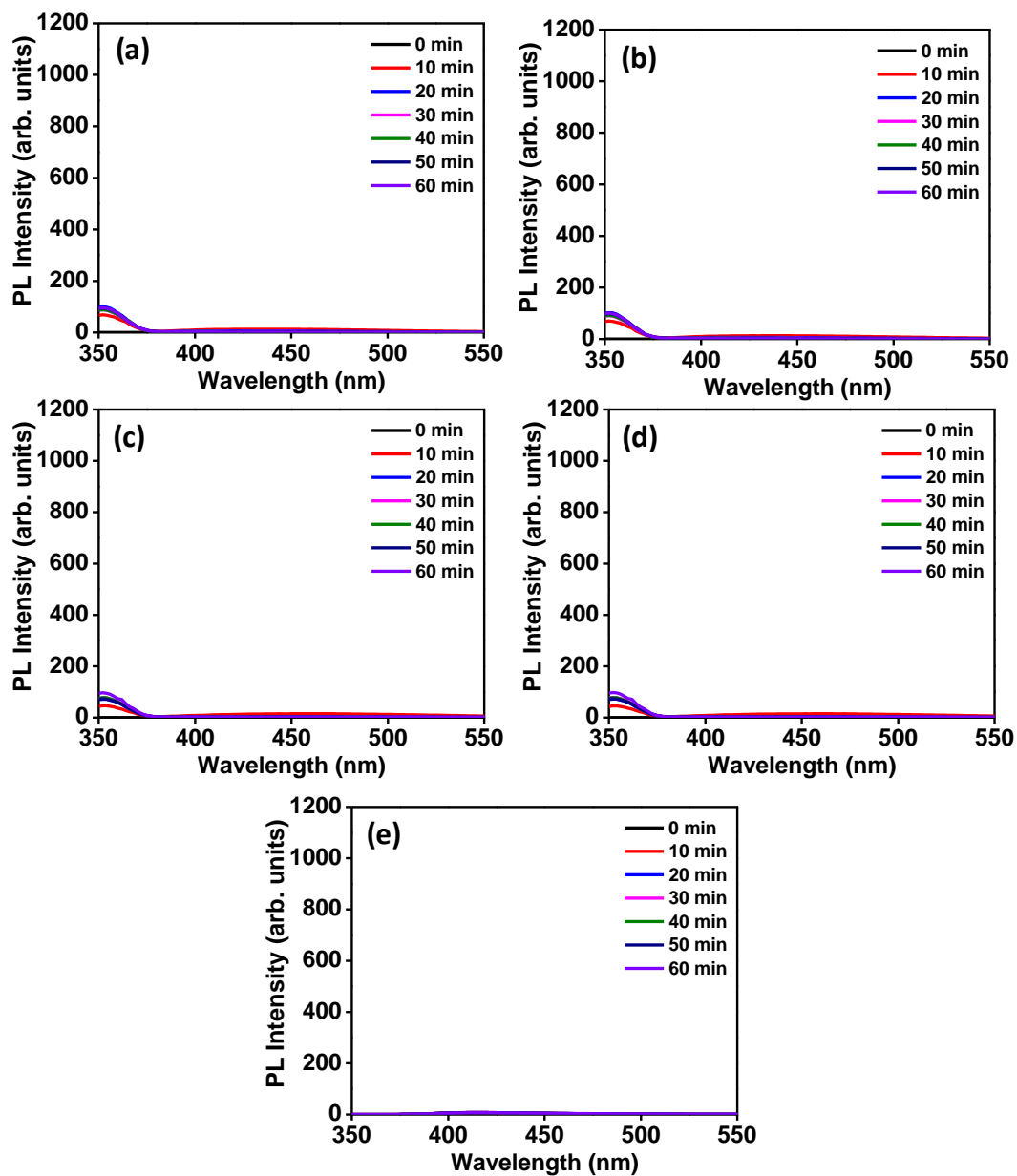


*Fig. 5.5. Comparison in the COD values of distilled water and sludge water obtained after O<sub>3</sub> treatment for five different initial solution pH for the optimum ozone concentration in each case. The pH is varied as 2 (a), 4 (b), 6.6 (c), 8 (d), and 10 (e).*

The COD is found to be increasing with increase in ozone flow rate at highly acidic conditions (pH= 2 to 4), where highest COD removal were obtained at lowest ozone flow rate 2 g h<sup>-1</sup>. When the pH is increased from pH=4 to 6.6 (neutral), the value of COD removal was increased and the removal efficiency was almost comparable for the different ozone flow rates. The increases in pH from 6.6-10decreases the COD removal,but the COD values are almost comparable irrespective of increase in pH and ozone flow rate. The maximum COD removal is obtained at neutral pH (6.6) at an ozone flow rate is 6 gh<sup>-1</sup>.Ozone can react with the target molecules either via direct pathway (direct reaction with aromatic compounds via electrophilic, nucleophilic or cycloaddition reactions) or indirect pathway (radical pathway). Direct pathway reactions are very specific, and hence, the reaction rates are very low for many organic/inorganic species. Indirect pathway proceeds via the radical generation, which results in the formation of highly non-selective radicals such as •OH, O<sub>2</sub>•<sup>-</sup>,O•<sup>-</sup>,O<sub>3</sub>•<sup>-</sup>and hydroperoxyl (•OOH) which can be ascribed to the degradation of both the organic and inorganic species.To understand the mechanism of removal of COD for the ozone treated sludge water, radical-trapping experiments, were conducted and the results are provided in the Figs 5.6 and 5.7.



*Fig. 5.6 Variation in the PL intensity in the visible range as a function of ozonation time, associated with 2-hydroxyterephthalic acid formed as a result of  $\bullet\text{OH}$  trapping by TA. The optimum ozone flow rate has been chosen and pH varied as 2 (a), 4 (b), 6.6 (c), 8 (d), and 10 (e). The excitation wavelength used is 315 nm.*



*Fig. 5.7 Variation in the PL intensity in the visible range as a function of ozonation time, associated with 3-aminophthalate formed as a result of  $O_2^{\bullet-}$ -trapping by luminol. The optimum ozone flow rate has been chosen and pH of the solution is varied from 2 (a), 4 (b), 6.6 (c), 8 (d), and 10 (e). The excitation wavelength used is 350 nm.*

The  $\bullet\text{OH}$  and  $\text{O}_2^{\bullet-}$ -trapping results are presented in Figs. 5.6. and 5.7. It is surprising to note that none of the two radicals are detected within the ozonation time of 10–60 min. Hence, the COD removal via the ozonation process could not be ascribed to the formation and attack of  $\bullet\text{OH}$  and  $\text{O}_2^{\bullet-}$ . Nevertheless, a blue fluorescence is observed for short time immediately after flowing the  $\text{O}_3$  gas through an aqueous solution for the ozonation time of less than 5 sec is attributed to the formation of 3-aminophthalate which is a result of trapping  $\text{O}_2^{\bullet-}$  by luminol which strongly suggests the generation of  $\text{O}_2^{\bullet-}$  and their quenching in less than first 5 sec of ozonation time. For a highly alkaline ozonation treatment condition, [16], [17] proposed the indirect mechanism of radical generation involving the following sequence of chemical reactions from (5.10) to (5.15).

The reaction of  $\text{O}_3$  under acidic pH is a direct attack mechanism which does not involve the presence of any radicals. Hence under the pH 2 and 4, the radical generation are not possible which is in accordance with the trapping results obtained in Figs. 5.6 (a) and (b) and 5.7 (a) and (b). Under neutral and alkaline conditions, the possible reactions of  $\text{O}_3$  in the aqueous solution are given below in the Eqs (5.10) to (5.15).



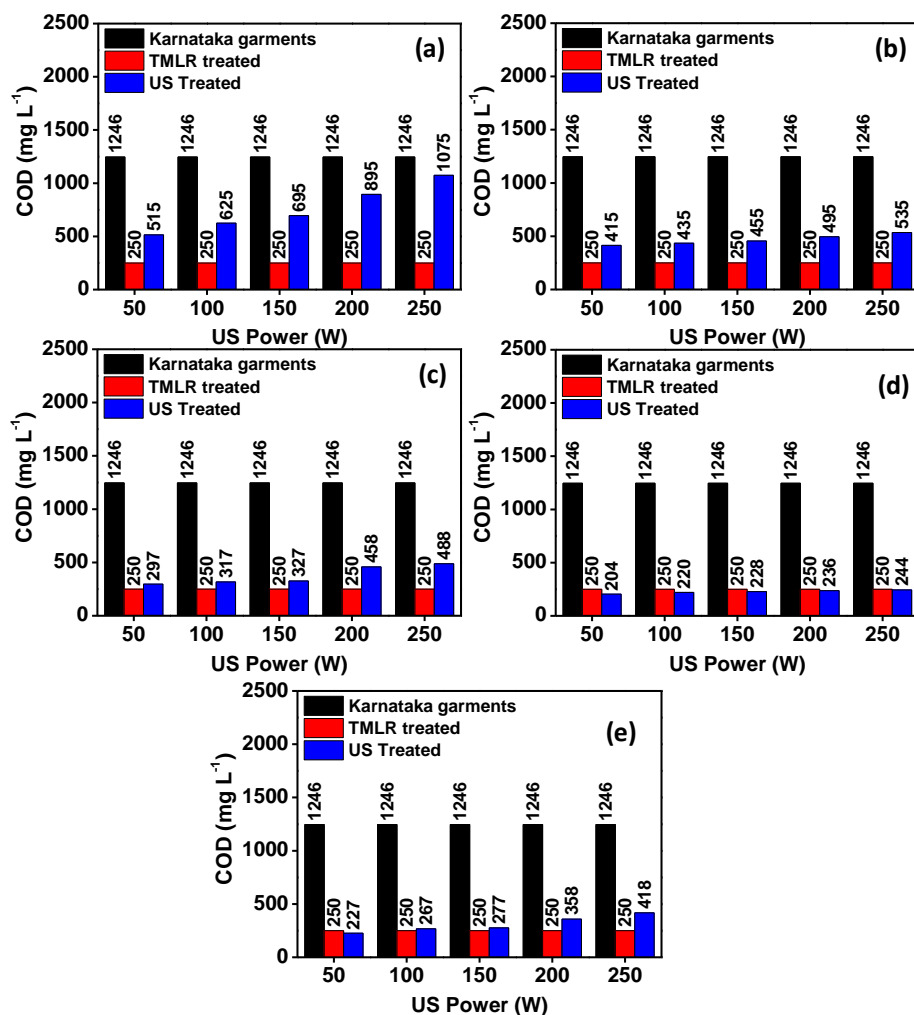
The above sequence of chemical reactions suggests that under the high  $O_3$  flow rate combined with neutral or alkaline condition, both  $O_2^{\bullet-}$  and  $\bullet OH$  are generated Eqs. (5.11) and (5.14) and quenched immediately by  $O_3$  Eqs. (5.12) and (5.15). This is in agreement with the absence of radical species as observed in the results of radical-trapping experiments as presented in Figs. 5.6 (c)-(e) and 5.7 (c)-(e). Hence, the  $O_3$ , utilized in this investigation, is sufficiently high enough not only to generate these radicals but also to quench them immediately subsequent to their formation. It is further noted that the  $\bullet OOH$  are also generated during the formation of  $O_2^{\bullet-}$  and the quenching of  $\bullet OH$ , Eqs. (5.11) and (5.15). As a consequence, in the absence of highly reactive  $O_2^{\bullet-}$  and  $\bullet OH$ , the COD removal as observed during the ozonation treatment can be ascribed to the possible attack of predominantly  $\bullet OOH$ .

### 5.3 COD removal of TMLR treated filtrate using US

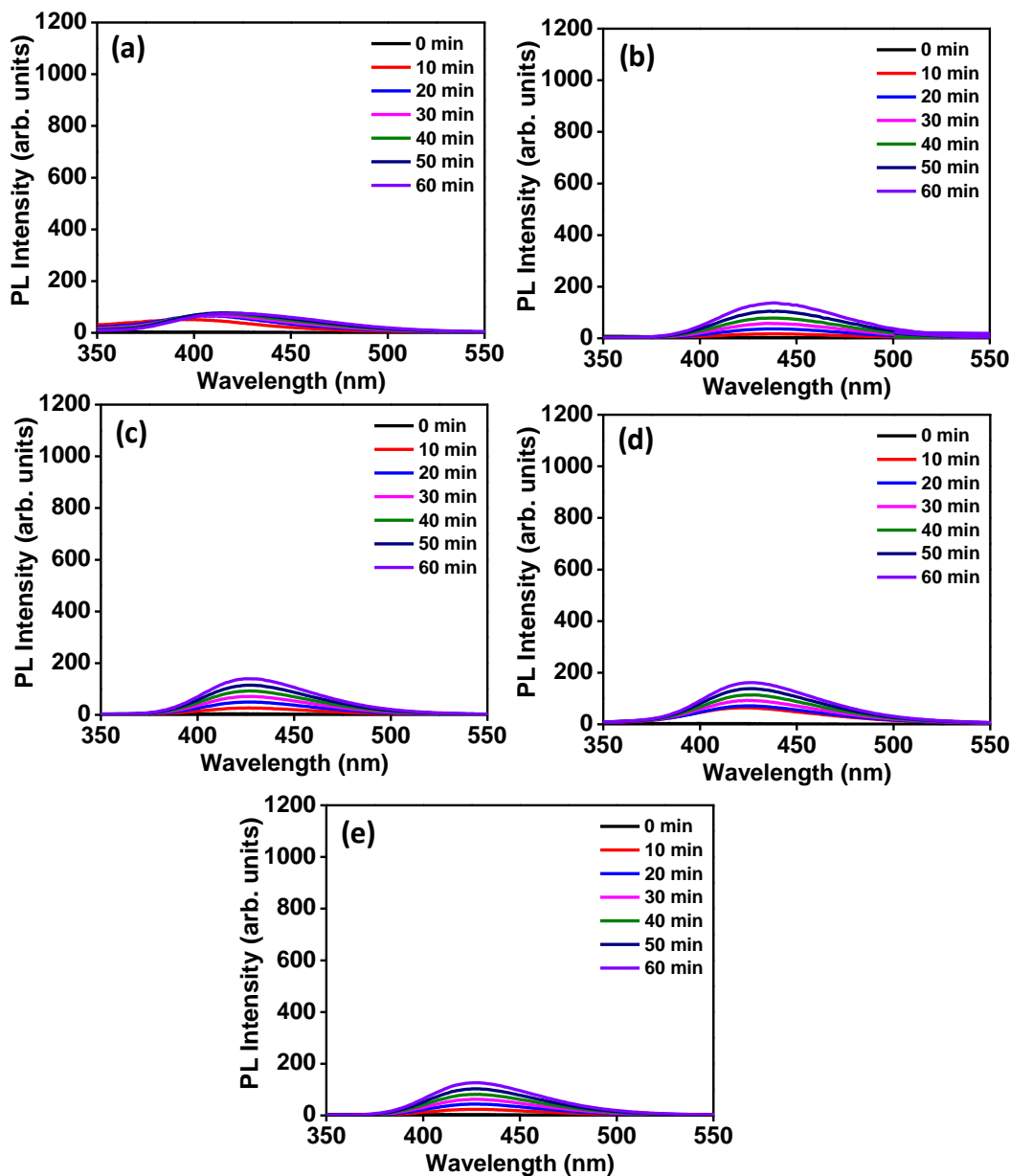
The variation in the COD level of the real time textile effluent, filtrate obtained after the TMLR addition, US treated filtrate at various conditions were examined and shown in the Fig 5.8. The initial COD value of real time textile effluent is  $1246 \text{ mgL}^{-1}$ . After the treatment with the TMLR, the COD value of filtrate is reduced to  $250 \text{ mgL}^{-1}$ . The filtrate obtained after the TMLR addition is treated using US at different pH varied from 2-10 at different US power of 50-150 W. The COD is found to be increasing with increase in power of US, where highest COD removal were obtained at lowest US power of 50 W, which is the optimum US power for the treatment of filtrate.

At highly acidic pH (pH 2), the value of COD is observed to be very much high. The amount of COD removal increases when the pH value increases from 2 to 8.8 (natural pH)

where highest COD removal was obtained. When the pH is increased to further alkaline region (pH=10), the removal of COD decreased. The optimum parameters for the COD removal in the solid sludge decomposition using US cavitation are at the neutral pH and at an US power of 50 W. To understand the mechanism of removal of COD for the US treated filtrate,  $\bullet\text{OH}$  and  $\text{O}_2\bullet^-$  radical-trapping experiments were conducted and the results are shown in the Figs. 5.9 and 5.10.

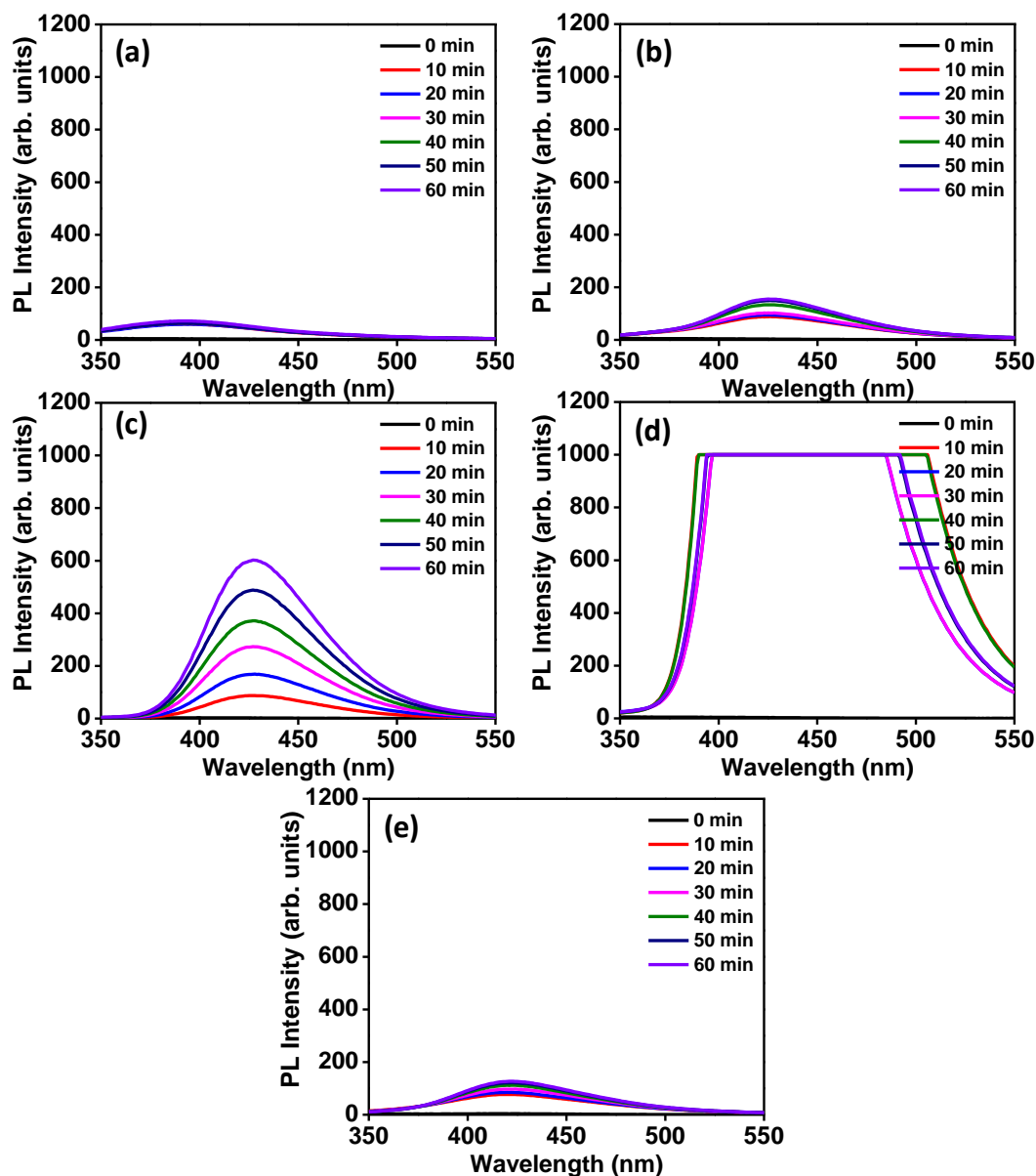


**Fig 5.8** The variation in the COD level of the real time textile effluent, filtrate obtained after the TMLR addition, US treated filtrate at various conditions. The pH of filtrate is varied as 2 (a), 4 (b), 6(c), 8.8(natural pH of filtrate) (d), and 10 (e).



*Fig. 5.9. Variation in the PL intensity in the visible range as a function of sonication time, associated with 2-hydroxyterephthalic acid formed as a result of  $\cdot\text{OH}$  trapping by TA. The US power is fixed at 50 W and the pH of filtrate is varied as 2 (a), 4 (b), 6(c), 8.8 (natural pH of filtrate) (d), and 10 (e). The excitation wavelength used is 315 nm.*



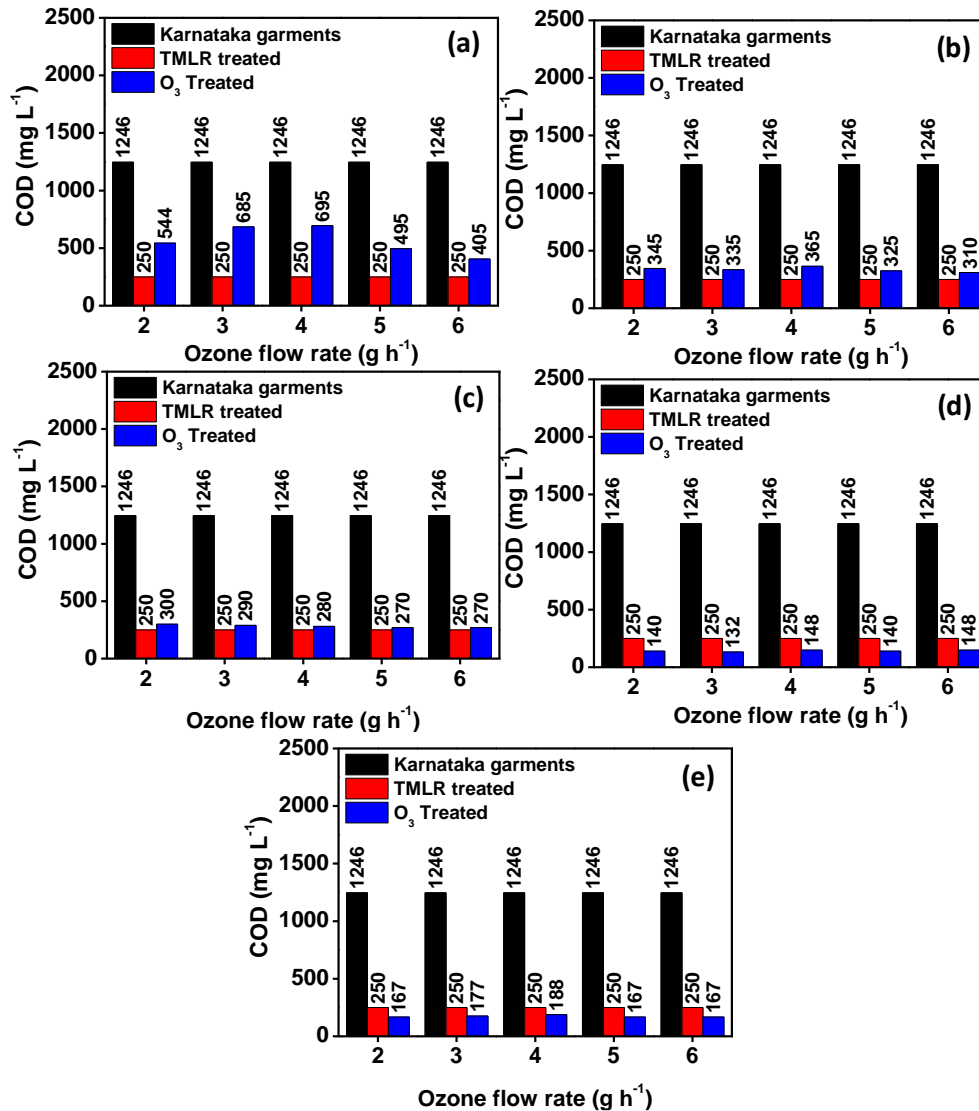


*Fig. 5.10. Variation in the PL intensity in the visible range as a function of sonication time, associated with 3-aminophthalate formed as a result of  $O_2^{\bullet-}$ -trapping by luminol. The US power is fixed at 50 W and the pH of filtrate is varied as 2 (a), 4 (b), 6(c), 8.8 (natural pH of filtrate) (d), and 10 (e). The excitation wavelength used is 350 nm. (Note: the peaks in the graph are truncated on the upper side due to very high concentration  $O_2^{\bullet-}$  which is beyond the detection limit of PL spectrophotometer used in this investigation).*

The maximum COD removal using ultrasound cavitation is obtained at 50 W US power. By analyzing the Fig 5.9, it is observed that, even though hydroxyl radical formation occurs at all pH, the intensities of the peaks are almost comparable. This confirms that the change in pH did not affect the  $\bullet\text{OH}$  concentration produced at an US power of 50 W. From the Fig. 5.10, the amount of  $\text{O}_2^{\bullet-}$  produced at 50 W were found to be varied with the change in initial filtrate solution pH. The amount of radical produced were increased with the initial solution pH changed from 2-8.8 (natural pH). The maximum amount  $\text{O}_2^{\bullet-}$  were observed at natural pH. Further increase in the filtrate solution pH from 8.8 to 10 showed a decrease in the  $\text{O}_2^{\bullet-}$  radical concentration. This is in agreement with the results obtained during COD removal of filtrate using ultrasound cavitation, the maximum COD removal occurs at natural pH of 8.8, under US power of 50 W, where the amount of  $\text{O}_2^{\bullet-}$  found to higher. Hence the maximum COD removal can be attributed to the presence of  $\text{O}_2^{\bullet-}$ .

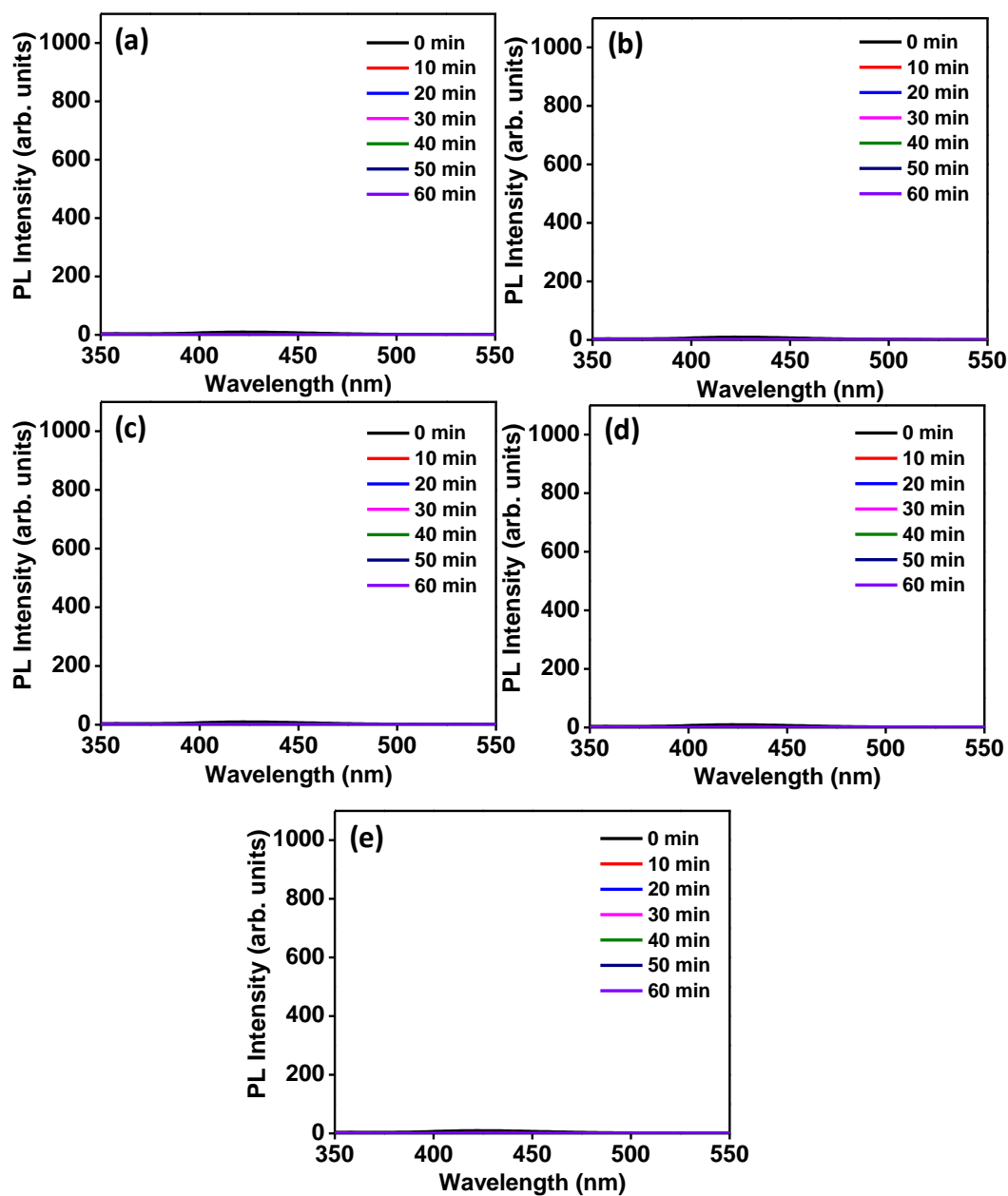
## 5.4 COD removal of TMLR treated filtrate using ozonation

The variation in the COD level of the real time textile effluent, filtrate obtained after the TMLR addition, ozone treated filtrate were examined and shown in the Fig 5.11.

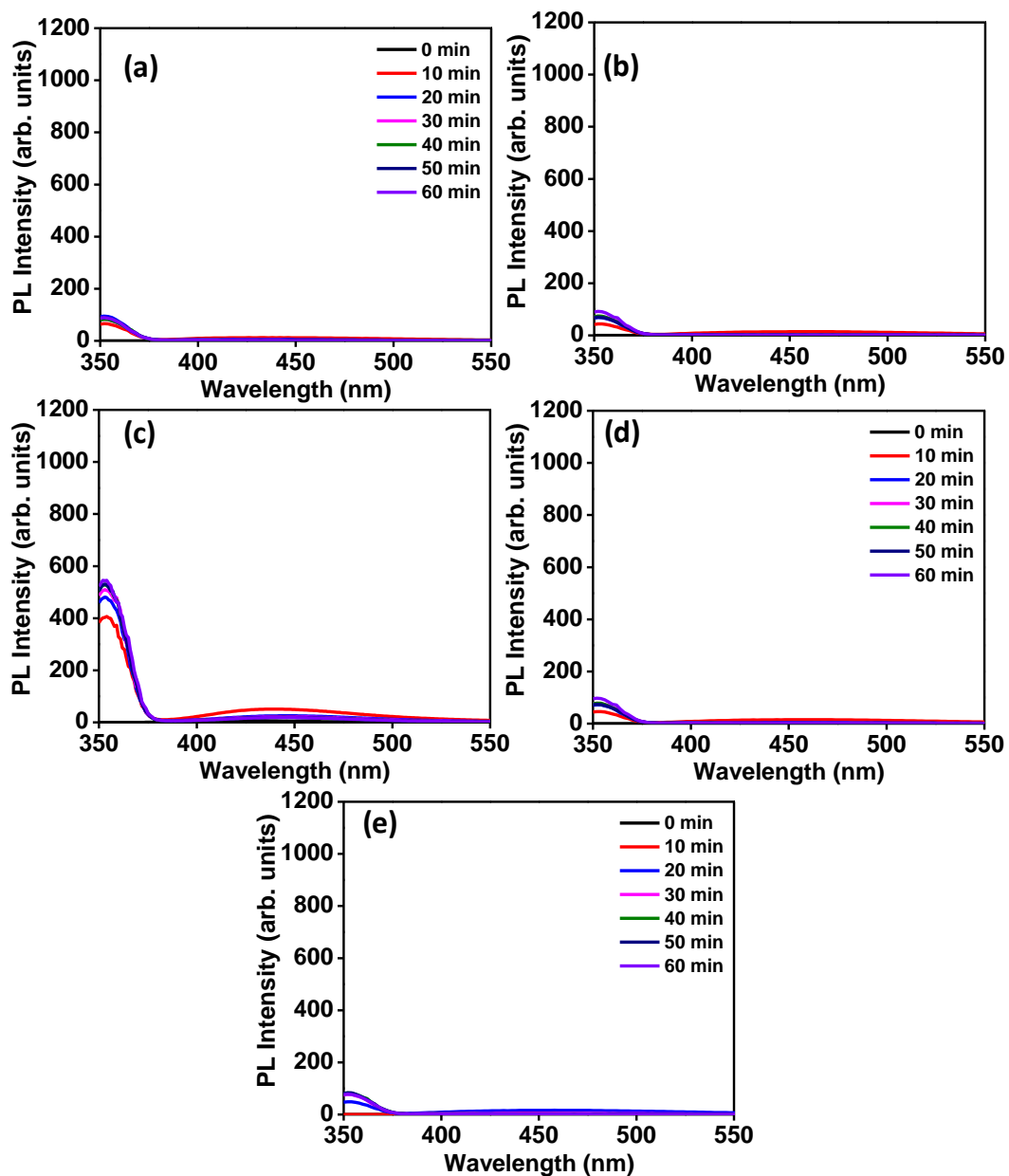


**Fig 5.11.** The variation in the COD level of the real time textile effluent, filtrate obtained after the TMLR addition, ozone treated filtrate at various conditions. The pH of sludge water is varied as 2 (a), 4 (b), 6.6(c), 8.8 (natural pH of filtrate) (d), and 10 (e).

The initial COD value of real time textile effluent is  $1246 \text{ mgL}^{-1}$ . After the treatment with the TMLR, the COD value of filtrate is reduced to  $250 \text{ mgL}^{-1}$ . The COD values of the TMLR added filtrate treated with ozone at five different flow rates ( $2\text{-}6 \text{ g h}^{-1}$ ) for five different pH (2-10) are given in the fig 5.11. While analyzing the removal of COD of filtrate by treating with ozone, it was observed that the COD values at each pH condition showed comparable results when the oxygen flowrate is varied from  $2\text{-}6 \text{ g h}^{-1}$ . The maximum reduction in COD is observed at natural pH (8.8) and at the ozone flow rate  $3 \text{ g h}^{-1}$ . At this condition the COD value is  $132 \text{ mg L}^{-1}$ . The COD values below  $150 \text{ mg L}^{-1}$  are advisable to use. At the natural pH of the filtrate, considerable reduction in COD is observed at all ozone flow rates. The COD is reduced below  $150 \text{ mg L}^{-1}$  under the all ozone flow rate ( $2\text{-}6 \text{ g h}^{-1}$ ) at natural pH. To understand the mechanism of removal of COD for the  $\text{O}_3$  treated filtrate, radical-trapping experiments, were conducted at the optimum  $\text{O}_3$  flow rate at each pH where maximum COD removal is observed and the results are provided in the Fig 5.12 and 5.13.



**Fig.5.12.** Variation in the PL intensity in the visible range as a function of ozonation time. The graphs are associated with 2-hydroxyterephthalic acid formed as a result of  $\bullet\text{OH}$  trapping by TA. The optimum ozone flow rate has been chosen and pH varied as 2 ( $\text{O}_3$  flow rate =  $6 \text{ g h}^{-1}$ ) (a), 4 ( $\text{O}_3$  flow rate =  $6 \text{ g h}^{-1}$ ) (b), 6 ( $\text{O}_3$  flow rate =  $5 \text{ g h}^{-1}$ ) (c), 8.8 ( $\text{O}_3$  flow rate =  $3 \text{ g h}^{-1}$ ) (d), and 10 ( $\text{O}_3$  flow rate =  $2 \text{ g h}^{-1}$ ) (e). The excitation wavelength used is 350 nm.



**Fig.5.13.** Variation in the PL intensity in the visible range as a function of ozonation time. The graphs are associated with 3-aminophthalate formed as a result of  $O_2^{\bullet-}$  trapping by luminol. The optimum ozone flow rate has been chosen and pH varied as 2 ( $O_3$  flow rate=  $6 \text{ g h}^{-1}$ ) (a), 4 ( $O_3$  flow rate=  $6 \text{ g h}^{-1}$ ) (b), 6 ( $O_3$  flow rate=  $5 \text{ g h}^{-1}$ ) (c), 8.8 ( $O_3$  flow rate=  $3 \text{ g h}^{-1}$ ) (d), and 10 ( $O_3$  flow rate=  $2 \text{ g h}^{-1}$ ) (e). The excitation wavelength used is 350 nm.

The reaction of  $O_3$  under acidic pH is a direct attack mechanism which does not involve the presence of any radicals. Hence under the pH 2 and 4, the radical generation are not possible which is in accordance with the trapping results obtained in Figs. 5.12 (a), (b) and 5.13 (a), (b). Under neutral and alkaline conditions, the possible reactions of  $O_3$  are given in the Eqs 5.11 to 5.16. These chemical reactions suggest that under the high  $O_3$  flow rate combined with neutral or alkaline condition, both  $O_2^{\bullet-}$  and  $\bullet OH$  are generated Eqs. (5.12) and (5.15) and quenched immediately by  $O_3$  Eqs. (5.13) and (5.16). This is in agreement with the absence of radical species as observed in the results of radical-trapping experiments as presented in Figs. 5.6 (c)-(e) and 5.7 (c)-(e). Hence, the  $O_3$ , utilized in this investigation, is sufficiently high enough not only to generate these radicals but also to quench them immediately subsequent to their formation. It is further noted that the  $\bullet OOH$  are also generated during the formation of  $O_2^{\bullet-}$  and the quenching of  $\bullet OH$ , Eqs. (5.11) and (5.15). As a consequence, in the absence of highly reactive  $O_2^{\bullet-}$  and  $\bullet OH$ , the COD removal as observed during the ozonation treatment can be ascribed to the possible attack of predominantly  $\bullet OOH$ .

## CHAPTER -6

### CONCLUSION

The herbal (organic) coagulant TMLR is effective for the formation of sludge from real time textile effluent. The two major AOPs such as ultrasound cavitation and ozonation are used for solid sludge decomposition and COD reduction filtrate of real time textile effluent. The optimum parameters for the sludge decomposition using US cavitation are obtained at neutral pH at power of 50 W which is attributed to the generation and attack of  $O_2^{\cdot-}$ . The optimum parameters for the sludge decomposition using ozonation process are obtained at neutral pH at an ozone flow rate of  $6\text{ g h}^{-1}$ . This can be attributed to the generation and attack of  $\bullet OOH$ .

While monitoring the COD level of the real time effluent, filtrate (obtained after addition of organic coagulant TMLR), and the US and  $O_3$  treated filtrate, the optimum parameters for COD removal using US cavitation are obtained at natural pH of the filtrate (pH=8.9) under US power of 50 W and the optimum parameters for COD removal by ozonation process is at natural pH of the filtrate (pH=8.9) with an ozone flow rate of  $3\text{ g h}^{-1}$ . The COD removal is achieved via the generation and attack of  $O_2^{\cdot-}$  for US cavitation process; while the COD removal using  $O_3$  process is achieved via the generation and attack of  $\bullet OOH$ . On comparing the two techniques, ozonation process is better for sludge decomposition and COD removal than US cavitation. The COD value of filtrate is maximum reduced to  $132\text{ mg L}^{-1}$  by ozonation process.



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