International Academic Journal of Advanced Pure & Applied Science Research
ISSN: 5280-5269 | Volume 9, Issue 9 | September, 2023 | pages 8 – 52
DOI: 22294428314252727799 2
Double Blind Peer Reviewed International Research Journal
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Ozonation of Remazol Brilliant Blue R in Semi-Batch Reactor

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Abstract: *Textile wastewater that contain dyes has serious problem when it release to the environment. Advance oxidation processes has proven to be a promising treatment technique for textile wastewaters. The six classes of dyes listed in the environmental Protection Agency because of their toxic and hazardous effects on health and environment such as (1) Azoic dyes, (2) Basic dyes, (3) Disperse dyes, (4) Acid dyes, (5) Direct dyes and (6) Fiberre reactive dyes. Remazol Brilliant Blue R (RBBR) is one of the group of Azo dye which is used and applied to fabric which include nylon, wool and silk etc. In this study Ozonation was used to investigate the treatment of aqueous dye solution, which is Remazol Brilliant Blue R (RBBR). The effect of pH on ozonation was studied. 100 mg/L of aqueous solution of RBBR was treated by Ozonation and catalytic Ozonation under three different pH value 3, 7 and 10. Adsorption test was also carried out to observe the interaction between the solid catalyst and RBBR. Result indicated that the removal of RBBR by Ozonation only observed under pH 10 is more efficient than pH 3 and 7. The application of solid CuO catalyst the first order reaction rate constant to 0.35 min*$^{-1}$ *at pH 10 condition and for pH 3 and 7 no change of application was observed.*

Keywords: *Ozonation, Catalytic Ozonation, Advance Oxidation Process, RBBR.*

INTRODUCTION

CHARACTERISTICS OF TEXTILE WASTEWATERS AND TARGET CONTAMINANT

The need of manufacturing of textile production around the globe today has rapidly increased. Statistics show that, due to global textile production, the textile industry in the world produced 140.84 million tons approximately in the year 2012, when relating with 2008 statistical analysis show that there is additional of 25.7% (Zhu, 2012). The world textile manufacturing industry growing on and on at the rate of 6.5% in future (Xu and Jiang, 2009). Today, China is one of the world largest country in the production of textile products globally that has about 79.29 million tons of textile production in the year 2012, with 56.3% of world production (Huang, et al., 2017).

The significant sector of the world economy today is the textile industry where it mostly located in many countries around the world such as Pakistan, China, Malaysia, India, and Bangladesh. Poland, employment in the year 2014 in textile industry reached about 114 thousand people, with the profit of about 3.85 billion euro (statistics for companies employing additional than 9 employees, clothing and textile sector) (Lucyna Biliriska et al., 2016).

Figure 1.1Global textile industry dominated in China and India

(Fibre 2 Fashion, 2017)

Textile industries are one of the major cause of water pollution observed in environmental sources (B. Neppolian et al., 2002).Large amount of water is consumed and therefore polluted during the manufacturing in textile industry (Figure 1.2). More than 100,000 dye structure were synthesized, over 0.7 million tons of different dyestuff used in different industries such as paper, textile, cosmetics, and pharmaceutical industry, provide in a year (Yamjala et al., 2016). About 7000 compounds required huge amount of water (Hessel, et al. 2007).

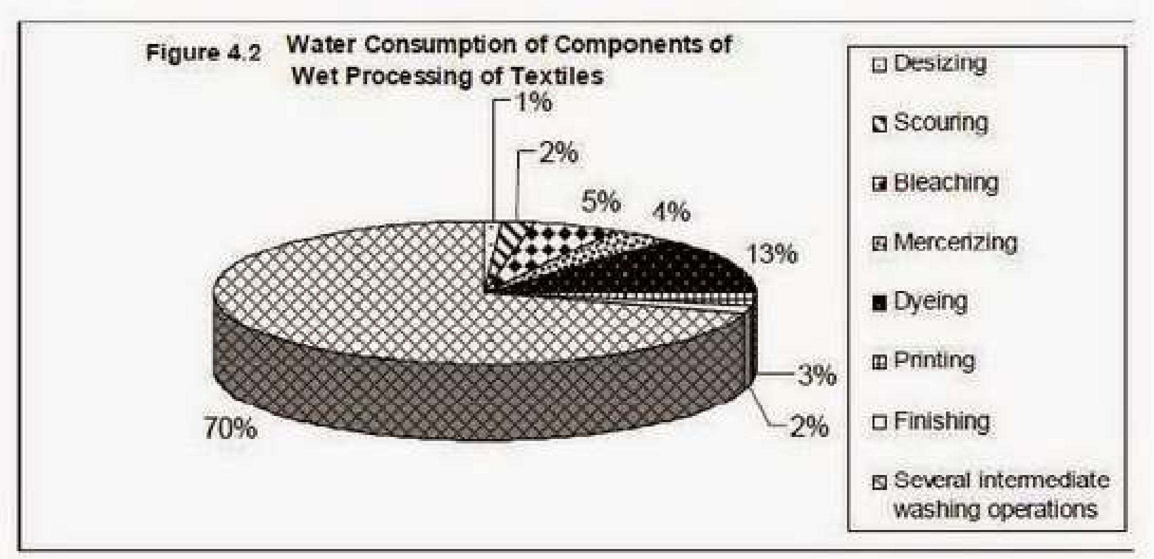


Figure 1.2 Water consumption in textile industries

(Textile Learner, 2017)

Huge quantities of textile industry are usually produces wastewater that is been characterized by high chemical oxygen demand (COD), strong color and highly fluctuating pH. General characteristics of textile wastewater are given in Table 1.1.

Table 1.1 Textile industry wastewater characteristics (Textile Learner, 2017)

Parameters	Standard effluent	Cotton	Synthetic	Wool
pH	5.5-9.0	8.0-12	7.0-9.0	3.0-10
BOD	30-350 ppm	150-750 ppm	150 – 200 ppm	5000 – 8000 ppm
COD	100-250 ppm	200-2400 ppm	400-650 ppm	10.000-20.000 ppm
TS	1500-2100 ppm	2100 – 7700 ppm	1060 – 1120 ppm	10.000 – 15.000 ppm

1–15% of finishing and dyeing processes is lost during its released into wastewater (Daneshver et al., 2015). Dye effluent contains chemicals that can be categorized as teratogenic and carcinogenic to the various living organisms (Daneshvar et al., 2003).

Teratogenic is explained asthe effects of an ecological agent on the fetus or embryo because of its chemical or physical characteristics as well as some numerous other factors such as dose, path, and dimension of exposure, the growing period at which the experience occurs; the genetic weakness of the mother and fetus or; and the existence and natural surroundings of concurrent experiences [Wilson (1977), Brent (2001)].

Teratogenic experiences during prenatal growth effect disruptions regardless of the progressive point or site of achievement. Most operational defects triggered by teratogenic contacts arise throughout the embryonic duration, which is when critical growing measures are compelling place and the fundamentals of organ structures are being recognized Gilbert (2003). Unlike organ systems which is having a different episodes of weakness to exogenous agents.

Congenital malformations can be caused by three factors: 1) genetic factors (chromosomal abnormalities as well as single gene defect); 2) environmental factors (drugs, toxins, infectious etiologies, mechanical forces) and multifactorial etiologies which include the combination of environmental and genetic factors. Teratogenic agents are the cause of about 7% of congenital malformations. A teratogenic agent is a chemical, infectious agent, physical condition or deficiency that, on extreme exposure, can disrupt fetal morphology or subsequent function. Teratogenicity is dependent on the ability of the agent to cross the placenta. The embryo is more vulnerable to teratogenic agent during the period of rapid differentiations. The development stage of the embryo determines the susceptibility of the teratogen.

Carcinogenic might be explained as the ability of the substance to cause damage to the genome or to the disorder caused in the cellular metabolic process. Numerous radioactive substances are considered as carcinogens, but their carcinogenic nature is attributed to the radiation they emit. Carcinogenicity is also associated with synthetic chemicals. Carcinogens are not always toxic but they tend to bio accumulate and their effect is gradual and harmful. There are several natural carcinogens which are produce by some fungus and some and some certain viruses. Co-carcinogens are chemicals which do not always cause cancer on their own, but can induce the activity of other carcinogens in causing cancer. Textile dyes are regarded as carcinogenic chemicals.

In general production of fabric, materials and chemicals, used for production of fabric, cause ecological balance and decline. The chemicals which are being used in textile products can cause health risk (Hatch 1984). They can develop over the skin, or into digestion (Golka et al., 2004). Allergic reactions can also cause from the textile materials (Hatch and Maibach 1995). Textile materials can be mutagenic and carcinogenic (Moll and Malliand 1991; Busk and Ahlbarg. 1982, and Esancy et al. 1990; Myslak et al., 1991) Textile effluents are also teratogenic which their presence may result with malformations in the development of fetus.

The textile dyes can be classified in to many ways and depending on different functions which can be used in textile dyeing process. The classification is:

1. Azoic dyes: Azo group containing (N=N) dye molecules.
2. Disperse dyes: Smallest dye molecules that contain anthraquinone (aromatic organic compound) or azo benzene (two phenyl rings attached to N=N) group in its structure.
3. Acid dyes: Dyes having aromatic structure and connected to sulphuric, carboxylic or phenolic organic acid.
4. Direct dyes (substantive): Molecules that are water soluble and contains azo structures.

5. Basic dyes: Dye molecules having amino functional group which is responsible for positive charge.
6. Fiberre active dyes: Dye molecules that are attached on fiber and not easily removed.
7. Sulfur dyes: Molecules that contain di-sulphide (S-S) connections in their molecular structure.
8. Oxidation dyes: Dye molecules that have aromatic structure having common chemical character as diamines, aminophenols and phenols.
9. Vat dyes: This classification can contain all dyes that are processed in a vat.
10. Optical brighteners: Dye molecules that can absorb UV-light.
11. Mordant (chrome) dyes: The molecules that are used for fixation for other molecules.
12. Pigments: the molecules that react in the presence of light.
13. Developed dyes: The molecules having azo dyes characteristics that can be further processed.
14. Solvent dyes: Molecules that can be dissolved in organic solvents and can give color for different materials.

Among all, the first six groups have been listed in Environmental Protection Agency Toxic Substances list because of their hazard effects to health and the environment.
One of the most significant type of textile industrial dyes is Remazol Brilliant Blue R (RBBR). It is used and applied to fabric which include wool, nylon and silk to produce a varieties of bright hues and colourfast. The RBBR dye is not focusing only on textile industry it require some other dyeing process such as printing and paper on other principal substrates which include inks and leather (Nomalzutul et al., 2016).

RBBR has a chemical formula $C_{22}H_{16}N_2Na_2O_{11}S_3$ with 626.54 g/mol molecular weight. It is the one that highly have stable anthraquinone aromatic structure as shown in Figure 1.3. Some of its physico-chemical properties are given in Table 1.2.

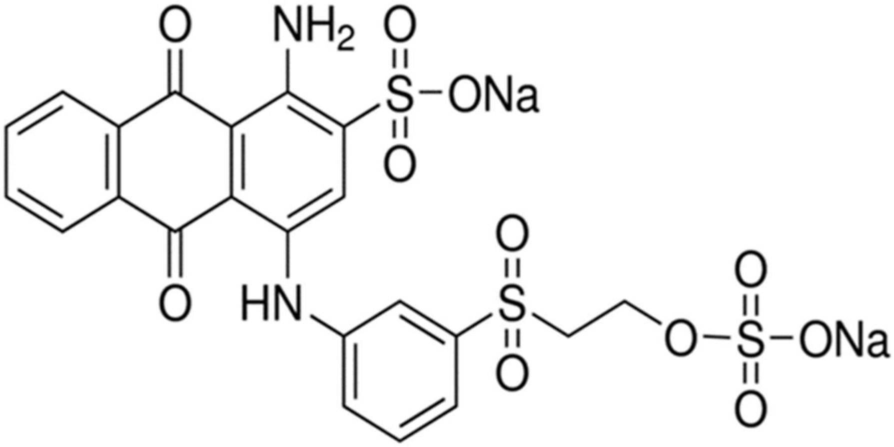


Figure 1.3 Molecular structure of Remazol Brilliant Blue R (RBBR)

Table 1.2 some physico-chemical properties of RBBR (Normaizatul et al., 2016)

Properties	Values
Molecular formula	$C_{22}H_{16}N_2Na_2O_{11}S_3$
Molecular weight	626.54 mol^{-1}
Maximum wavelength	590nm
Water solubility ($mg.L^{-1}$ 25°C)	314.4 mg/L
Vapor pressure (25°C)	$3.41x10^{-27}$ mmHg
EC_{50} green algae	68.154 $mg.L^{-1}$

Water solubility is the amount of substance to be dissolved in water to give a saturated solution under controlled temperature and pressure. It is measured in mg/L. The weight of a substance (in milligram) that will dissolve in one litre of water (L). Low water solubility less than 10 mg/L, moderate water solubility 10 – 1000 mg/L, High water solubility more than 1000 mg/L. RBBR molecule has low-moderate water solubility.

Vapour pressure is the pressure at which water vapour is in thermodynamic equilibrium with its condensed stage. This value shows the ability of a molecule to transfer to the gaseous state. RRBR molecule has too low vapour pressure showing that it cannot be volatilized easily from environmental matrices after its discharge to nature.

EC_{50} is the effective concentration of a molecule to effect 50% of a living population. Low EC_{50} value indicates that there is serious toxicity possessing chemicals whereas; higher values represent the chemical is not toxic. RBBR molecule possesses moderate-high toxicity.

TREATMENT OF TEXTILE WASTEWATERS

Dye wastewaters have low BOD/COD ratio. Biodegradable organics are the degradable pollutants in waste water that needs to treated prior to discharge into aquatic environment; however if untreated and discharge into aquatic environment it can lead to depletion of natural oxygen; and also they are measured in-terms of COD and BOD.

Biological Oxygen Demand is applied to water and wastewater to remove organic pollutant biologically takes 5 days (BOD_5) it include the determination of Dissolved Oxygen (DO) applied by microorganism. Therefore BOD is used to measure biodegradable organic carbon in wastewater, the amount of Oxygen required by microorganism while stabilizing (transform of organic pollutant into non-toxic or hazardous ends products).

However, since BOD is a bioassay procedure is significant that the environmental condition to be suitable for living organism. Therefore, the BOD test result can be determine by the size of the wastewater treatment facilities, determine how to measure the accuracy of some treatment process and also to determine the people complaining the wastewater release without permit.

Chemical Oxygen Demand is providing knowledge regarding the contamination power of wastewater that can be chemically degradable. COD is constantly higher than BOD in the process of water and wastewater treatment. Microorganism is not capable of breaking all kind of organic carbon. Why because of this reasons (1) organic material that is hard to handle biologically for example lignin, can be handled chemically. (2) Some organic matter perhaps exposed to the microorganisms if utilized in BOD test. (3) An inorganic material that is eliminated by dichromate improve the rate of organic comfortable of a sample.

Subsequently, the COD charges can extremely be utilized only if there is inorganic material in water. By every sign COD test hold, one principal benefit is that, be performed in 2 hours only associated by BOD within 5-days or further than that. To reduce the COD test time more expansion was added to 15 min time.

Different biological treatment processes should be proposing, for instants in respect of biological nutrient that is more vital to separate using COD. The key separation is soluble and particle COD. Hence, in the biological treatment experiments, the division of the solvent and particle remain separated to charge the treatable wastewater. The division done is included, (1) regularly biodegradable colloidal and particulate COD (2) fixed biodegradable solvent COD, (3) non-biodegradable colloidal and particulate COD, (4) non-biodegradable soluble COD. The fixed biodegradable soluble COD is the one that has already divided into complex COD which can be acidifying to volatile fatty acid.

Interaction between BOD and COD

Interaction exists within the BOD and COD is within the content of the ratio of domestic wastewater between 0.3 to 0.8 which can be show in Table 1.3. When the ratio of BOD/COD is 0.5 or bigger than that, the wastewater can be simply treated biological method therefore when ratio is less than 0.3 the waste maybe consider as toxic compounds that can be treated chemically.

Table 1.3 Comparison of BOD/COD Ration of various parameter used to characterize wastewater (Metcalf and Eddy, fourth edition).

Type of wastewater	BOD/COD Ratio
Untreated	0.3 - 0.8
After primary settling	0.4 - 0.6
Final effluent	0.1 - 0.3

BOD test is limit only when the concentration is highly active, there is need of pre-treatment when considering hazardous or toxic substance, and it only measure biodegradable organic substance, BOD also take much time to get the result. From the above all limitation the most important one is that of 5-days test time may or may not be equal with the soluble organic matter which is used presently.

The manufacturing dyeing method of wastewater that led various artificial color that recognizes the effluents on several parameters. This involves the physical characteristics such as turbidity, color, dissolved and suspended particles etc. nevertheless Chemical characteristics which introduce the effluent of Azo dyes, basic dyes, acidic dyes and complex dyes etc. moreover, wastewater is competent and slightly improved in treatment. Colour profluent can be developed by Oxygenation or aeration. Decolourization strength be accomplished by removal of nitrogen-nitrogen bonds, this can simply be performed in the appearance of NO and NO_2 radicals

pH is an essential parameter used in every experiment is used to express the intensive of the Acid and Alkaline condition in a solution. Usually, used to express the concentration of hydrogen ion which is also express as the negative logarithm. The effluent of wastewater may affect the concentration of natural water. For the treatment of wastewater effluent that release in to the environment the suitable pH for the treatment of such waste is ranging from 7 to 9 approximately. It determine by colour measurement of paper and solution to different colour standard. It can also express as

$$pH = -log_{10}\,[H^{+}]$$

Total solid or maybe total suspended solid (TSS): Total suspended solids (TSS) are known to be particles that are greater than 2 microns and observed in the water column. Dissolved solid that are less than 2 microns that area normally separate; is considered dissolved solid. More so, suspended solids are formed up of both inorganic matters. Though bacteria and algae can also donate to the total solids concentration.

Moreover, TSS is the measure of the entire suspended, colloidal and dissolved solid in a water sample; and they are increasing the temperature of water since they adsorb extra energy from light. Total solids can be prepared by drying of the water sample. The water is dried at a distinct temperature (103 – 105 ^{0} C) and the residue taken is concentrated and the measured as the total solids. Total solid in a water is essentially characterized into total suspended solid (TSS), Total dissolve solids (TDS) and Settleable solid (SS).

Carbon is the major element of the organic materials discovered in wastewater. It is biodegraded by the microorganisms in activated sludge below anaerobic positions, in an anoxic environment and also in the aerated portion of a biological step (nitrification zone). Furthermore, microorganisms apply the carbon mixtures to form cell structures and to generate power for their growth. Carbon mixtures (in water/ wastewater) are limited as BOD_5 or TOC, COD.

Nitrogen inflow of wastewater processing plants, nitrogen application to be present in it organically bonded structure and also as ammonium nitrogen; nevertheless, when the biological wastewater processing, organic N is transformed to NH_4-N by the bacteria in the initiated sludge. Moreover, the NH_4-N and the NH_4-N from the inflow is transformed to nitrite which in change is turned, to nitrate (nitrification). Although, any mixtures (nitrogen are not biodegraded in the activated sludge; this type of nitrogen are changed in anoxic positions (an aerobic condition) to basic nitrogen (denitrification). Usually, nitrogen composites are measured as NH_4-N, NO_2-N, NO_3-N and TN (total nitrogen).

The phosphorus load in the inflow of a wastewater treatment plant is in combination (made-up) of orthophosphate-phosphorus (PO_4-P), organic phosphorus compounds polyphosphates. In summation, they give the sum parameter 'total phosphorus' (Ptot). More so, during biological wastewater treatment, polyphosphates and organically attached phosphorus are converted to orthophosphate. The P demand of the organisms is due to the special role of phosphorus in their energy for metabolism. P is required to form the cell membrane and DNA. Some of the phosphorus in wastewater is eliminated biologically. The remaining ones can be eliminated by chemico-physical phosphate precipitation.

A broad variety of persistent organic pollutants (POPs) chemicals, are usually developing from distinct group or classes of specific chemicals (for instance, 209 another PCBs, changing from one to extra by a level of chlorination and change positions). Hence, POPs are rigid in the environment for controlling large lives both in the air and soils or sediments. Though, there is no consent agreement about the long life continuation for the duration refractory. But, POPs would become a half-life duration of the practice or extra decades in soil and in the atmosphere. POPs are classic 'water-hating' and 'fat-loving' chemicals, i.e. hydrophobic and lipophilic. In water systems and soils, they wall strongly to solids, notably organic material, withdrawing the aqueous form. Also barrier into lipids in organisms slightly than entering the aqueous setting of cells and enhance saved in a fatty membrane.

Most usually found poisonous heavy metals in wastewater are Cadmium Arsenic, Lead, Mercury while the few common: Copper, Chromium, Nickel, and Zinc. A principal cause of heavy metal in wastewater are Manufacturing causes: e.g. metal finishing and plating, Printed board production, semiconductor production, textile dyes; though Road flows and Landfills. Many heavy metals remain vital trace parts for individuals, animals, and plants in less quantity. Though, higher amounts cause serious and persistent toxicity and it is associated with training disabilities, cancers and also death at any levels Moreover, heavy metals possess inhibitory impacts toward the biological treatment process at the wastewater processing plants.

Table 1.4 Heavy metals permissible limit in waterSource. R. Pehlivan et al. (2012)

Parameter	Who (Drinking water)	EPA 2009 (Drinking Water)	EU 98/83/EC (Drinking Water)	TS 266 and RG25730 (Spring water)
Al^{3-}	0.1	0.2	0.2	0.2
Fe^{3+}	0.3	0.3	0.2	0.2
As^{3+}	0.01	0.01	0.01	0.01
Ag^{3+}	0.005	0.1	X	X
Hg^{2+}	0.001	0.002	0.001	0.001
Co^{2+}	X	X	X	X
Cd^{2+}	0.003	0.005	0.005	0.005
Cr^{3+}	0.05	0.1	0.05	0.05
Pb^{2+}	0.01	0.015	0.01	0.01
Ni^{2+}	0.02	X	0.02	0.02
Ti^{4+}	X	0.002	X	X
Ba^{2+}	0.7	2.0	X	X
Mn	0.5	0.05	0.05	0.05
Zn^{2+}	0.01	5	X	X
Cu^{2+}	2.0	1.3	2.0	2.0
Se^{4+}	0.01	0.05	0.01	0.01
Sb^{3+}	0.005	0.006	0.005	0.005
U^{3+}	0.015	0.03	X	X
Tubidity	5 NTU	0.3 NTU	1 NTU	1 NTU

Surface water are coloured by organic materials like tannic acids, humic and fulvic. They resulted from the decomposition of vegetables materials and are usually related to compound like phenol that have carbon-carbon bond. Ozone break organic double bond very fast and the colour will remove rapidly.

The issue of industrial toxic waste treatment is very important in recent period of time. The factory that produce chemicals, especially which release large quantity of hazardous materials in to the environment. This waste comes in the processes of dilution, are not sufficiently by anti-pollution measure. Because it has high concentration aspect when consider as toxic. Therefore ozone is used in the treatment of toxic waste to attack all the harmful pollutant. Ozone in this have additive advantage in this treatment that prove the removal of toxic.

The toxic which know as heavy metals from industrial effluents such as cyanides, heavy metals that are presence in water in the system of complex mixtures in water. Ozone reacts to changeover the metals to the highest reaction stage that are normally generate less soluble oxides, which is simple to remove by filtration. Also there are some metals such as copper, manganese, lead, zinc etc. can all be treated the same way. Generally ozone reacts on this heavy metals to generate hydroxide or metallic oxide that can simply be precipitate off and remove from water. Ozone here used to remove or eliminate heavy metals which produce from many industrial effluents.

Advantages of ozone:

1. Ozone can react with deferments variety of organic compounds which contain organic-by products

2. Ozone is a strong Oxidant that is available in the treatment of aqueous solutions and gaseous mixture.

3. After Ozone oxidizes, it decomposes into Oxygen.

4. Ozone in gaseous phase is a promising deodorizer for a different of odorous materials.

5. Safe to handle because it cannot be stored and, therefore must be generated and used on site.

Disadvantages of ozone:

1. Higher equipment, operational cost and maintenance.

2. Ozonation provides no disinfection residual to prevent or inhibit regrowth.

3. Ozone is less soluble in water, compared to chlorine.

4. Toxicity and fire hazards issues are associate with the ozone generator.

Physical processes such as adsorption process, coagulation, filtration and flocculation are engaged in treating textile wastewaters. This technique gives a huge quantity of sludge, not really effectual and costs a lot of money (Holker et al. 2014, Robison et al. 2001, Vandevivere et al. 1998, Anjneyudu et al., 2005).

Ground waters and surface waters are both comprised of dissolved and suspended constituents. Coagulation and flocculation are both engaged to isolate suspended solids from waste waters. Flocculation and coagulation are hinged on certain criteria such as charge, density, particle size(s) and form. In water, when suspended solids come together, they repel each other due to the negative charge they possess and the same kind of surface charge they exhibit. Due to this, suspended solids will continue in suspension and will not cluster with each other and settle out of water unless flocculation and actual coagulation is ultimately employed. The repeling stops the particles from combining enabling them to remain in a suspended state. Flocculation and coagulation take place in sequential order delibrately to shatter the forces balancing the particles in suspension bringing about smashing of the particles and formation of flocs which eventually settles and is then extracted from the water. Flocculation and coagulation are methods to cater to industrial and domestic waste water in order to eradicate suspended particles from the water.

A Coagulation is a process whereby a chemical known as Coagulant is added into a sample containing suspenden solid so as to cause the suspendent solid to settle down. The suspendent solids contained Similar charges (negative chages), which prvent them from coming together to form setteble solids. The negative charge effects of the suspended solids (ss) can be neutralize by the additional of chemical known as coagulant which has a chage opposite to that of the suspendent solids.

More so, the neutralization of the negative charges by the coagulant allows the smaller perticles to come together thereby becoming heavier enough to settle.

Flocculation: is a process that involve a show or gentle mixing stage and this increases the particle size from non – visible (submicroscopie) to visible solids in a sample. The micro floes particles collide with one another resulting into a bond formation producing pinflocs which is larger and visible. With the additional of supplemented inorganic or organic polymers, the size of the flocs build due to the additional collision and interface and hence microflocs are formed.

The coagulation and fluclation are usually applied before the physical separation processe in the wastewater treatment processes.

Most common chemical substances (reagents) are: organic and/ or mineral coagulants (basically aluminium salt, iron, and organic polymers), flocculation additives such as activated carbon, talcum and activated silica Etc.

The advanced oxidation processes (AOPs) was proposed in 1980s as a potable water treatment process (Glaze et al., 1987). This process involved the generation of hydroxyl radicals ($OH^{\cdot}$) and their subsequent interaction with the organic contaminants thereby influencing the water purification. These hydroxyl radicals generated are powerful and one of the most acceptable oxidizing agents when AOPs are to be used for the treatment of water and wastewaters. The AOPs treated water and wastewaters are less or even non-toxic products and hence a proper solution for the wastewater treatment (Huang et al., 1993).

The AOPs are considered to be two steps processes that involved the production of an oxidant (such as hydroxyl radicals) and then the reaction of these radicals with the organic contaminants. More so, in the water treatment applications, the AOPs is a subsection of the processes that involved ozone (O_3), hydrogen peroxide (H_2O_2) and/or UV light. However, with regards to this work the AOPs will be applied to a more general group of processes that include titanium (iv) oxide (TiO_2) catalysis, cavitation, E-beam irradiation as well as Fento's reaction. Indeed, all the aforementioned processes can successfully generate the hydroxyl radical that subsequently remove the organic contaminants. In general, the effectiveness of AOPs is proportional to its ability to generate hydroxyl radical. Though a number of processes mentioned above may have other mechanism for the removal of organic contaminants.

The system of an AOP is controlled by the emanating contaminant concentration, victim influent contaminant concentration, wanted current speed, and background water characteristic parameters such as pH, bromide application, and alkalinity. The principal system parameters for AOPs comprises; the chemical dosages and the rates including other chemicals, and also reactor contact time, and reactor form. The proper dosages, rates, and contact form are water-specific and processing scenario-specific and are normally measured within pilot studies using the water matrix of interest.

There are many advantages of AOPs over conventional methods. For instance the oxidation of the organic compounds to carbon dioxide (CO_2) and water H_2O with no sludge production and hence may not require another process for the destruction or treatment of the sludge. Equally, APO is much better when compared with other methods (such as biological process) in the treatment of the refractory pollutants (Baczkaj and Fermandes, 2017). Additionally, AOP is a treatment process that can be used in water and wastewaters with less organic loads, ppb that contain dissolved organic compounds. On the other hand the AOP is not cost effective due to the involvement of ozone, electrical energy and ultraviolet. As a result of this issue therefore, there is need to explore other alternative wastewater treatment methods (Mota et al., 2009, Poyatos et al., 2010, Sayen and Nejati 2007, M. Litter, 2005).

Commonly used advance Oxidation processes that are applied in industrial wastewater applications are Fenton's process, Ozonation and UV irradiation (Olivia et al., 2006).

Hydrogen peroxide and iron (II) react to form Fenton's reagent (an unstable iron-oxide complex) that subsequently generate hydroxyl radicals (Fenton, 1894). The reaction is shown below:

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-}$

$Dye + OH^{\bullet} \rightarrow CO_2 + H_2O$ + other products

Ozone is a strong oxidant that decompose radicals under alkaline conditions. Nevertheless, both ozone and radicals have the oxidizing potential of dye molecules. The reaction pathway is represented below:

$O_3 + H_2O \rightarrow 2HOO^{\bullet}$

$O_3 + HOO^{\bullet} \rightarrow OH^{\bullet} + 2O_2$

UV irradiation exits catalysts in aqueous phases and as a result, radicals are formed as represented below:

$H_2O_2 + hv \rightarrow 2OH^{\bullet}$

$H_2O_2 \rightarrow HO_2^{-} + H^{+}$

$HO_2^{-} + hv \rightarrow OH^{\bullet} + O^{\bullet -}$

Vilhunen et al., (2010). Reported that when H_2O_2 solution reacts with UV irradiation there will be energy from the light where it will break the bonds and subsequently generate HO^{*} as the following mechanisms are shown below:

$H_2O_2 + hv \rightarrow 2HO^{*}$

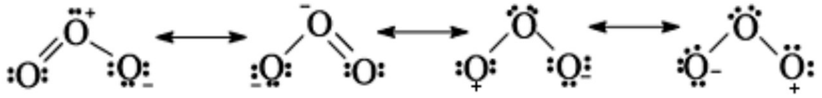
Similarly, when UV react with H_2O_2/O_3, it generates HO^* and can efficiently influence the amount of degradation as revealed by Kusic et al., (2006), the mechanisms is revealed below:

$O_3+H_2O_2 +hv \rightarrow 3O_2+ 2HO^*$

The name Ozone was formed from the Greek word "Ozein" by Schonbein 1785; where it was described as smelling since 1840. Just few scientist found around the odor of Ozone in 1785. Furthermore, Schonbein further, explains that ozone destroys potassium iodine and produce iodine ions in a solvent.

(Saltuk, P., 2008) confirms that ozone is a strong gas that is unstable, the investigation more prove that ozone has odor features and It is a blued color gas; though is extremely difficult to perceive the color when is produced from wastewater/water processing applies at fewer concentrations levels. Ozone decomposes in an aqueous mechanism to oxygen fast though, this transfers on the quality of the contaminants and concentration level.

The structure of ozone is presented below as discussed in the literature as a hybrid of the four canonical forms (Rip G and Aharon Netzer 1982).



Ozonation process is commonly used in various industries and known for centuries in the use of disinfection purposes based on it oxidative properties. Furthermore; It can be employed in Wastewater Treatment, Drinking Water purification, Odour Removal, Air Purification, color Removal and in Removal of pesticides among others.

Ozone is a strong oxidant (Oxidant are the reactant that removes from other reactants. Example ozone, nitric acid and hydrogen peroxide, Oxidation is the loss of an electron).Which oxidizes pollutants by two different oxidative species. There are two different oxidative ways in Ozonation which are the direct or indirect way. A direct way of Ozonation (acidic pH conditions) is done by the ozone molecule and indirect oxidation way occurs as the outcome of decomposition of ozone which at the end forms hydroxyl radicals (Dong, et al., 2008).

Hydroxyl radicals' production was described to developed ozone breakdown by existing type on catalyst cover (Park et al 2004, Zhang et al., 2008). from the different site, the outcome of catalytic based on the adsorption on surface of the catalyst and changed reflection on the surface was reported in three complex processes in the study of (Hardren et al., 2003) as (i) adsorption of target substance on the catalyst surface, moreover oxidation with aqueous ozone, (ii) ozone adsorption on the catalyst surface, resistance of bonded ozone particles with the aqueous target mixtures and (iii) adsorption of the ozone and target substances, then the catalyst reaction on the surface. Truly, from any of the cases, aqueous Ozonation reactions will be used into consideration. Beltran et al (Beltran et., al 2005).

The hydroxyl radicals can be produced by combining chemicals and improving the pH solution to be used during Ozonation (Salome et., al 2006, Meamtu et al., 2002, Hordem, et al., 2003). Ozone decomposition at basic conditions is given.

$O_3 + OH^- \rightarrow O_2^* + HO_2^*$ (Alkaline pH)

$O_3 + HO_2^* \leftrightarrow 2O_2 + HO^*$

$2HO_2^* \rightarrow O_2 + H_2O_2$

$O_3 + OH^* \rightarrow O_2 + HO_2^* \leftrightarrow O_2^* + H^+$

The above Ozonation mechanism reaction clearly shows that increasing pH value will yield increased hydroxyl radical generation.

(Chu and Ma, 2000) investigated that the ozone ruled oxidation process at low pH the hydroxyl radical displays more important impact at high pH. As the result of the gradual flow of decomposition (i.e., the reaction of O_3 with less abounding OH^-) at low pH, O_3 make up in the aqueous phase to a higher intensity (that is the powerful O_3 saturation concentration at less pH). Moreover, owing to the impact of OH^- with the reaction of O_3 of more great reactions happens at greater pH, the time of concentration of the formation of more hydroxyl radicals are generated while the O_3 in water is overcome at greater pH.

Certain interactions limit the color discharge in the aqueous phase by the following conditions: (1) hydroxyl radical is governed the oxidation process at greater pH position, and (2) the molecule of O_3 dominated the oxidation process at less pH condition. The oxidation capacity of hydroxyl radical meaningfully exceeded that the molecule of ozone (Shu et al., 2005).

AIM OF THE STUDY

The aim of this study is listed below

→ Study RBBR removal by Ozonation under different initial RBBR concentration.
→ Study RBBR removal by Ozonation under different pH conditions.
→ Monitor mineralization.
→ Apply CuO to check the effects on Ozonation process.

LITERATURE REVIEW

In literature review, various researchers have been investigated in different articles on the removal or degrade the Remazol Brilliant Blue R molecule from the aqueous solution.

Recently there is a global concern on the increase of wastewater generation owing to the high industrial activity from dye (textile) industries (K.K. Panda and A.P. Mathews 2014). Similarly, Akmar N et al., (2016). Reported that textile industry are sources of wastewater, and argues that the treatment of wastewaters from textile industries has been the current problem of wastewater management. Furthermore, dyes in combination of other organic pollutants, dyes bring additional problems for the environment when participate in the natural waters, nonetheless wastewaters containing dyes may overload the self-purification mechanism or may even reduce photosynthetic process if not prevented. This is known to have a carcinogenic impact on the ecosystem (Aznier M 2010).

Sequel to the discovery of refractory compounds that are toxic and carcinogenic among other problems in water supplies has leads to the concern for the improvement of the current technologies and the development of new techniques to cover these persistent organic pollutants in water reported by Osma et al., (2010). Various dyes, drugs, pharmaceutical products and synthetic organic chemicals are not captured by the current treatment processes and discharged to surface waters. The new oxidation methods using ozone, UV photons, supercritical water, electron beam irradiation, ultrasound irradiation and non-thermal plasmas were being developed or perhaps improved to tackle this problem Hoeben W et al., (1999). Among the advanced oxidation processes, ozone has been attaining acceptance as an oxidant either by itself alone or in combination with UV or hydrogen peroxide to produce hydroxyl radicals for oxidation of persistent organics and the decontamination of water supplies.

Mostly, volatile dyes are comprises of an efficient groups similar to azo, phthalocyanine, anthraquinone, formazane, and oxazine as chromophore. Throughout the process of dyeing, under an intensive heat in alkaline environments, a dye's volatile locations act in response with a well-organized sets of fiber. Although a huge portion of the theoretical reactive dye is misused since in the procedure of dyeing volatile dye is hydrolyzed to a certain level and some of the volatile dyestuff are deactivated via this hostile hydrolysis reaction. Associated with additional peroxides, volatile dyes symbolize plain toxins (Pearce et al., 2003). One of the major problem of environmental problem is complete removal of dyes even in a very low amount in the dye industries. Therefore, removal of dyes from textile dyeing wastewaters is a major environmental problem and complete dye removal is necessary because dyes will be visible even at very low concentrations (Kannan smith. 2001: Golob smith. 2005). Several techniques have been considered for treating dye wastes, established on physical and chemical methods, in addition to their mixtures, such as coagulation electro flotation, electro kinetic coagulation, precipitation, oxidation, ozonation, adsorption and biosorption. Selcuk (2005) the coagulation/flocculation method is widespread use for pre-treating of dyes waste water, foremost, and post-treatment. Though, in removal of dyes and organic materials comprising of coagulation and sedimentation, pre-treatment process is needed. Polymeric coagulants is progressively used for water treatment plant for waste water, swimming pool water, drinkable water and so on (Joo et al., 2007), amongst which polyaluminium chloride (PAC), a polymerized usage of alum, is repeatedly used. PAC has demonstrated itself as a resourceful coagulant particularly aimed at removal of biological materials existing in water, independent from their source and difficult structure (Dimzoski smith 2006). The aim of this study was to examine the application of PAC as a coagulant/flocculant for the elimination of textile dyes in Wastewater treatment, and to control the ideal of coagulation situations for wastewater pre-treatment. Present work describes the PAC as inorganic coagulant for the adsorption of Remazol Brilliant Blue R dye (C. I. 61200).

Ozone holds significant oxidation potential of 2.08 that is higher than chlorine which holds significant oxidation potential of exactly 1.36, being essentially reported by F. Erol and T.A. Özbelge (2008*)* and ozone does not generate chlorinated disinfection by-products which remain toxic and carcinogenic. Consequently, the possibilities for application of ozone oxidation technology remains crucial owing upon its huge technological practicability. W.T. Shin et al., (2000); reported that, within the group of oxidation methods, ozonation has demonstrated to be a promising technique for the color extraction in textile industrial wastewaters. Moreover, within the ozonation process, ozone molecules hastily and selectively strike and attack unsaturated bonds of chromophores ending toward some quick extraction of color W.T. Shin et al., (2000).

Notwithstanding, specific oxidation process concerning dye molecules creates certain ozonation by-products, which is difficult to oxidize with ozone molecules totally, these comprise organic acids, aldehydes, and ketones among others. Sequentially, the mineralization remains measured based on the chemical oxygen demand (COD) and total organic carbon (TOC) or some modifications cannot be accomplished adequately (H. Einaga, S. Futamura 2004). M. Meamtu et al., (2002) and M. Hassan et al., (2006); authenticates the stability concerning ozonation side-products via further oxidation with ozone, owing to the fact that the low solubility couple with low stability of ozone within water and again, the tremendously huge cost of ozone production demand special utilization of an advanced oxidation technology for huge treatment capability.

Moreover, advanced oxidation processes (AOPs) occurred due to the production of hydroxyl radicals which remain highly strong than ozone and also catalytic Ozonation implying one example of these processes investigated widely. Catalytic Ozonation analysis are categorized based on two sections such as heterogeneous and homogeneous which for homogeneous catalytic Ozonation process investigates transition metals like Cu(II), Cr(III), Co(II), Ag(II), Mn(II), Cd(II), Fe(II), Ni(II), Zn(II) involved utilization as homogeneous solutions within an Ozonation mechanism M. Meamtu et al., (2002).

Nevertheless, since heterogeneous catalytic Ozonation investigations are conducted by utilizing metal oxides, and also those metals which rely upon metal oxides. In a north shell, synthesized catalysts were utilized considering the catalytic Ozonation reasons; despite MnO_2, TiO_2, SiO_2, Al_2O_3 and also any metals or metal oxides lıke Ru, Pt, Fe_2O_3, Pd, Co, Cu, Pb, etc. as reported by M. Meamtu et al., (2002).

Furthermore, Park, J. et al., (2004) state that catalytic ozonation wıth synthesized catalysts together with some natural catalysts, were also used during the ozonation of organic materials in water. The study furthermore examines catalytic ozonation using natural goethite in the treatment of para-chlorobenzoic acid. They further reported that positive impact on this Fe-based catalyst in the oxidation of para-chlorobenzoic acid; and they recommend a pH-dependent catalytic mechanism based on surface reaction, bulk reaction, and reactions taking place at catalyst–liquid interface. They noted radical generation with the interaction of ozone and catalyst surface. Several researchers have conducted numerous studies and have been made for the catalytic ozonation of organics in either homogeneous or heterogeneous phase with numerous various catalysts.

Studies were conducted by Cooper, and R. Burch, (1999): published that, degradation doxalic acid to be 85%, 88%, and 87% in catalytic ozonation with Fe_2O_3/Al_2O_3, Al_2O_3, TiO_2/Al_2O_3, respectively. For similar circumstances, the target acid degradation only 15% was completely achieved by ozone alone. Similarly, Ernst et al. (2004) observed that, the catalyst effect on the Ozonation of oxalic, succinic and salicyclic acids by use of Al_2O_3. Nevertheless, in non-buffered circumstances, the starting DOC was decreased at 90% in catalytic Ozonation than the 20% in Ozonation solely.

Shuang Song, et al., (2007) investigated that the effects of Operational Parameters on the decolourization of C.I. Reactive Blue 19 in aqueous solution by Ozone enhanced electrocoagulation. In the study the initial pH was 10.0, and the initial dye concentration of 100 mg/L and the ozone flow rate of 20 mL/min, were they reported that over, 96% of the color was removed after 10 min; so also the total organic carbon (TOC) removal was over 80% as the experiment was observed under the temperature of 30 ˚C. However, the degradation of anthraquinon dye C.I Reactive Blue 19 in aqueous solution by Ozonation; also shows that, detoxification was observed following the biodegradability enhancement by the increasing BOD/COD ratio of 0.15 to 0.33 after 10 minutes of Ozonation (Fanchiang and Tseng, 2009).

Enes Sayan and M.Esra (2008); reviewed the Optimization study using response surface method on the decolourization of Reactive Blue 19 from aqueous solution by ultrasound. The research shows that the utilization of ultrasonic irradiation remained advantageous for decolourization of RB 19 of an aqueous solution through adsorption. Furthermore, the decolourization of RB 19 remained accomplished at maximum conditions utilizing ultrasound, activated carbon and combined ultrasound/activated carbon as a distinct percentage of 36%, 91%, and 99.9%, sequentially. The research further presumes that the dye intensity, time and activated carbon concentration are essential to processing parameters influencing the decolourization performance.

Nur Azimah Jamalluddin and Ahmad Zuhairi Abdullah, (2010) review that reactive dye degradation by combined Fe(III)/TiO_2 catalyst and ultrasonic irradiation on the effect of Fe(III) loading and calcination temperature; in their investigations, Fe(III)/TiO_2 were synthesized employing a Sol-gel procedures including the addition of tetrabutyl–or tatitanate (TBT) into the solution of ethanol at room temperature. Specific investigation showed that aeration produces a meaningful improvement to the reaction rate and stated that 96% of RB4 extraction could be achieved with the mixture of 0.4 Fe (III)/TiO_2 and aeration amount underneath ultrasonic irradiation.

T.Y. Chen, et al, (2009). Study the application of Ozone on the decolourization of reactive dyes – orange-13 and Blue 19. In 14 L reactor use in the research and prepared with a gas provider at the bottom to spare the ozone/air stream within the water remaining dealt with in the research, furthermore the pH 3 and 10 was effective in the decolourization of Blue 19 and Orange 13 strongly within the duration of 30 min with ozone rate of 2.66 g/h. Furthermore, the result demonstrated that decolourization of colors Orange-13 and Blue-19 with various ozone measurements exist independently as shown under standard conditions. Similarly, the result shows that more strong decolourization was seen at 2.7 or 4.0g/h over 1.3g/h of O_3.

Mohammad A. N.K, et al., (2015) investigate the removal of reactive blue 19 dye by sono, photo and sonophotocatalytic oxidation using visible light and reported that 90% degradation was achieved within 120 min as revealed by the GCMS results the reactive blue 19 (20 mgL^{-}1) during the studies.

Dutta, et al., (2016) investigated that rapid reductive degradation of azo and anthraquinone dyes by nanoscale zero-valent iron. In their studies the reactive dyes was used, Remazol brilliant orange 3RID (RBO 3RID) and reactive blue MR (RBMR), P initial pH value of dye concentration were measured with the pH of (2-12), 80% of dyes removal was achieved within the first 15 min of reaction.

Ahmed M.A and Altrozi. R (2010). Investigated that the Optimization of preparation conditions for mangosteen peel-based activated carbons for the removal of Remazol Brilliant Blue R using response surface methodology. According to their investigation they used with MP activated carbon to treat carbon dioxide gasification with the preparation of physiochemical method. The effect of temperature on CO_2 activation on temperature, CO_2 activation on time and KOH ration was also studies to remove the percentage RBBR with the used of activated carbon. The important aspect in any of the experimental design was identified from the analysis of variance. The conditions that resulted for MP activated carbon under the temperature of 828 ˚C within the period of 1h and IR of 3.0.accouding to their study the RBBR removal was achieved in 80.35% and 20.76% with activated carbon respectively.

Sathishkumar, et al., (2001). Study the utilization of agro industrial waste jatropha curcas pods as a carbon for removal of Remazol brilliant blue R, they examine the removal of RBBR by activated carbon within the range of 2h. Also investigate that the effect of pH values between 1 and 8 the dye adsorbed on JCPAC in the maximum of pH 3. In their result they found that 90% of RBBR dye absorption by 0.2g of jotropha pods activated carbon, also showed that the jotropha pods activated carbon is finally achieved more than absorption for the degradation of reactive dye RBBR in aqueous solution.

Ahmed, M.A and Alrozi, R; (2011) examined the optimization of rambutan peel based on the activated carbon preparation condition for the removal of RBBR, was examined through the application of absorption and effective treatment technique of the degradation of the contaminant of water and wastewaters are further researched. 0.3g of RPAC combined with the aqueous dyes solution concentration of RBBR dye extract utilizing double UV-vis spectrophotometer. Based on their investigation, RBBR extraction and RPAC were observed varying from 28.78% to 80.93% and 13.67 to 21.83% sequentially. The result revealed that 88.7% of entire removal of RBBR and RPAC are removed respectively.

Normaizatul A, R et al., (2016) studied the investigation of the remazol brilliant blue R removal using Agricultural waste, according to the experiment conducted the concentration of dye from the initial is 500mg/L and the result showed that they achieved more than 90% of the removal of remazol brilliant blue R, and also result that lime peels act as adsorbents for good function in the removal of remazol brilliant blue R.

Chun He, et al, (2016). Examine the evaluation of sono-electrocoagulation for the removal of reactive blue 19 by ultrasound. In the research, the stock solution of RB 19 was introduced by dissolving in deionized water and also diluted the wastewater fixation to (99% in immaculateness). They noted that electrochemical technique in any of the submersed of 50cm^2 ozone, a special research was completely prepared in a batch electrochemical reactor using 2000ml limit and also was well blended to mix the solution homogeneously when run and use approximately 60 min. Result prove that the anode impedance increased throughout the EC Process but was lessen despite the sono-EC process. The result also illustrates that weight film can be dislodged from the anode used by ultrasound and that lead to more creation of coagulant metals by the electrode.

Mohammad Abdul N.K, et al., (2015). Studies the removal of reactive blue 19 by sono, photo and Sono photocatalytic oxidation. Recognized that the artificial utilized were all achieved with the utilization of deionized water and the investigation was focused on varying pH level from 3-11 and unique ultrasound power (40-100). In their research, the result showed that the reactive blue 19 was removed by 90% in the span of 120 min. The result accomplished that the rate of color depleted was degraded with expanded absorption of color in all of the approaches and keep up the catalyst fixed.

Siddique, et al, (2010). Study the decomposition of reactive blue 19 dye in ultrasound assisted electrochemical reactor. In their research, the RB 19 dye was established from the stock solution of 20, 40, 60, 80 and 100 mg/L. Additionally, they noted that at different pH level ranging between

3-9, the different ultrasonic frequencies (20-80 KHZ) with the used of 50mg/L for 120min at color absorption. Furthermore, the primary concentration of pH test was applied to examine the results of the color focus from the beginning. In the research, the result illustrates that the rate of disintegration progressed with the pH increase from acidic to basic form 67.6% of the most advanced breakdown was analyzed at the pH 8. The additional result showed that if the value of pH shift from 2-8, dissolution rate will expand.

Zhiqiao He, et al., (2008). Investigate the mineralization of C.I Reactive Blue 19 by Ozonation combined with Sonolysis; Performance Optimization and degradation mechanisms. They examined the various forces of operational parameters that involved the principal concentration of color, the thickness of ultrasonic energy, pH and Ozone measurement, which oxidized the Total Organic Carbon (TOC). The result illustrates the mineralization of O_3/US note that regular extraction rate of TOC was oxidized at 3.4×10^{-4}, 5.9×10^{-3}, and 8.4×10^{-3} min^{-1} for US, O_3 and O_3/US utterly. And they further concluded that combination of two technique for AOP showed that synergistic was expanded in all of the mineralization rates.

Siddiqu, et al, 2013 investigate that degradation of synergistic effects of Combining Ultrasound with Fenton process. The study showed that RB19 Stock Solution arranged in 1 gram of color associated to the unification of each experiment of 25 mg/L (4×10^{-5} mol/L), sulphuric acid and sodium hydroxide utilized to change the pH of the color formation. According to the investigation, they noted the greatest degree of decoloration of approximately 78% was detected in the copulated ultrasound and $H_2O_2/FeSO_4$ without ultrasound. Moreover, show that using ultrasound can develop the action of the $H_2O_2/FeSO_4$ so that the exploratory parameter was analyzed to look at the source of the influence.

Saltuk and Tulay A. 2009 studied the comparison of non – catalyst and catalytic Ozonation process of three different aqueous single dye solutions with respect to powder copper sulfide catalyst. The study investigates that Ozonation and Catalytic Ozonation analysis was carried in a 1L semi-batch reactor at a several initial ozone application of gas on the pH of 3, 7 and 10. All noted that the charge of RBBR and AR-151 aqueous solution also the TOC discharge of about 90% of aqueous dyes been discharge and were detected in the reactant Ozonation by CuS since various colors only at pH 10. The outcome shows that TOC discharge at the limit of 80min by 123%, 65% and 58% in the treatment of 100mg/L RBBR, RB 5 and AR-151 aqueous solutions, was absolutely discharged at pH3.

Mahbubul Hassan and Christopher J. (2002). Investigate the feral – catalyzed ozonation of aqueous dye in the bubble-column reactor. According to the study, an aqueous solution of colors was used at a part of the study of decolourization colors by ozone inside the sight of feral. Ozonation studies were performed in a semi-continuous method in 1.51 end or limit. Outcome shows that feral improved in the decolourization potency for EYMR, moreover after the 60s of ozonation 91% of dyes was strongly eliminated, though within that period only 59% of color elimination was accomplished by sole ozone. Also in the situation of HRD5BN color for around 90s of ozonation in the appearance of feral the elimination of dyes performance only 93% were accomplished out feral and it was only 84%.

Though, some basic application of ozone in the treatment of wastewater is restricted at instant due to the nearly huge cost of Ozonation.

Table 2.1 Summary of the process efficiencies used in literature

Process	Efficiency	Reference
Catalytic ozonation	88 % dye removal	C. Cooper, and R. Burch, (1999).
Sono. photo and sonophotocatqlytic	90% dye removal	Khan,et al;(2015).
Sono Electrocoagulation	97% 0f Rb 19 removal	Chun et al ;(2016).
Catalytic Ozonation	98.9% removal	Erol, et al ;(2008).
Non- catalyst and catalytic Ozonation	65% removal	Saltuk and Tulay A, (2009).
Ultrasound assisted electrochemical reactor	90% removal	Siddqu et al ;(2011).
Ozone enhanced electro coagulation	96% removal	Song et al; (2008)
Ozonation	95% removal	Fanchiang and tseng (2009).
Ultrasound irradiation	90% removal	Jamalluddin and Abdullah (2011).
Ultrasound	99.9% removal	Sayan and Edecan (2008).
Feral catalyzal Ozonation	93% removal	Mahbubul Hassan and Christopher J (2002).
Applicaton of Ozone	83% removal	Chen et al; (2009).
Ultrasound with Fenton process	78% and 50% removal	Siddique et al; (2014).
Ultrasound process	56.6% removal	Vajnhandl S. and Le Marechal (2005).
Adsorption process	95% removal	Sathislkumar p. et, al; (2012).
Coagulation Process	97.01% removal	Li et al; (2016).
Absorption process	74% removal	Isah A. et al; (2015).
Ozonation	88.7% removal	Ahmed, M. A and Alrozi R, (2011).

Advanced oxidation processes (AOP) are technologies based on the generation of highly reactive species, the hydroxyl radicals, used in oxidative degradation procedures for organic compounds dissolved or dispersed in aquatic media. These processes are promising alternatives for decontamination of media containing dissolved recalcitrant organic substances, which would not be efficiently removed by conventional methods. Therefore, Advance Oxidation Process (AOPs) are promising to be used for textile dye effluent according the results summarized in the literature.

MATERIALS AND METHODS

MATERIALS

Remazol Brilliant Blue R, sodium thiosulphate ($Na_2S_2O_3$, 97%), were supplied from Merck KGaA 64271 Darmstadt Germany, potassium iodide (KI, 99%, supplied from Sigma Aldrich and purchased from Tin Muhendislik Turkey.), sulfuric acid (96% purity), sodium chloride (NCl, 99.5% for analysis), sodium carbonate (99.9% purity), sodium bicarbonate, potassium hydrogen phthalate (99.5% purity), hydrochloric acid (HCl, 37%, analytical grade), copper oxide, were all the products of Merck and purchased from Dorhan Medical, North Cyprus. Distilled water supplied from Sartorius 61316 and purchased from Sartonet, Turkey. OPAL 400 bench type of ozone generator was obtained from Tin Mühendislik, Turkey.

METHODS

KI Method for Gaseous Ozone Measurement

The reaction between the iodide ions with the ozone gas lead to formation of iodine based on the following reaction:

$O_3 + 2I^- \rightarrow I_2 + O_2 + OH^-$

The amount of iodine produced directly related with the concentration of ozone gas and determined through the titration with the sodium thiosulfate:

$2S_2 O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

Reagents

The following are the reagent used in the measurement of gaseous ozone concentration using KI method:

1. KI solution: 20 g of potassium Iodide (KI) were dissolved in 1000 ml of water to make a 0.1205M KI solution.

2. Starch indicator: 0.5 g of starch was added to 100 ml of distilled water.

3. 1N H_2SO_4: 13.6 ml of stock H_2SO_4 solution was place in a 500 ml of volumetric flask and diluted with distilled water.

4. 0.1M of Na_2SO_4: 1.5811 g of sodium thiosulfate ($Na_2S_2O_3$) was added to a 100 ml volumetric flask and diluted with distilled water.

Procedure

200 ml KI solution was transferred into an Erlenmeyer flask and exposed to ozone for 1 minute. After that the KI solution was titrated with sodium thiosulfate. This procedure repeated three times. Titration set up is given in Figure 3.1.

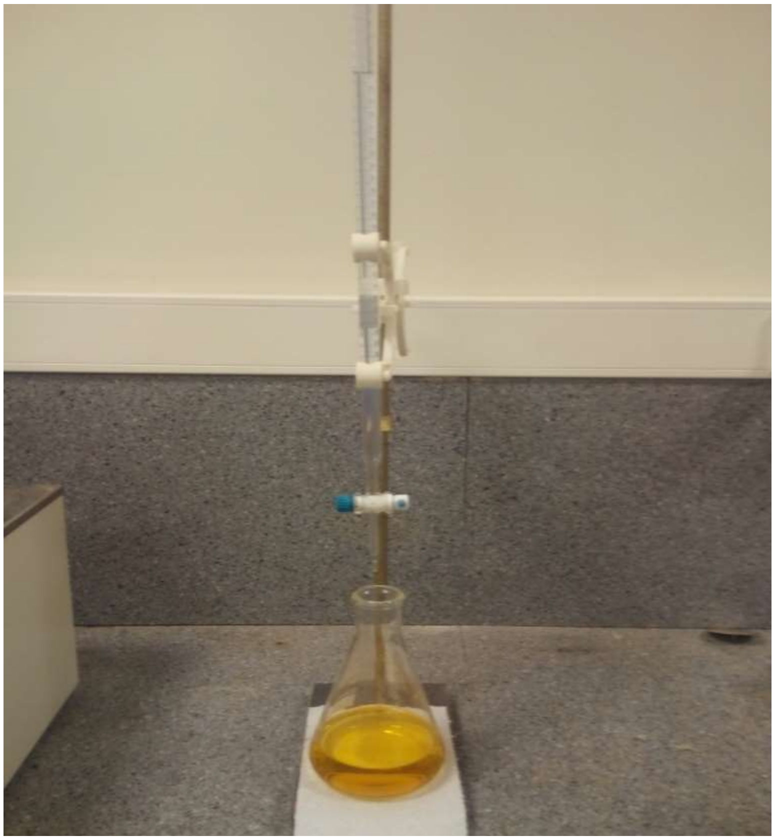


Figure 3.1 Titration setup for gaseous ozone measurement

Calculation

The Concentration of gaseous ozone was calculated by the used of the following equation:

$$\frac{M\ O_3}{L} = \frac{A \times M \times 24000}{ml\ sample} \qquad \text{Equation.1}$$

Where A is the volume of $Na_2S_2O_3$ consumed in the titration of the KI solution, M is the molarity of $Na_2S_2O_3$, which was 0.1M.

The consumed volume of the titrant is given in Table 3.1 and the gaseous ozone concentration calculation was made for each test. The average concentration was found as 24.76 $mg.L^{-1}$.

Table 3.1 Gaseous ozone measurement (25˚C ± 0.5).

Titrant consumed (ml)	Gaseous ozone concentration (mg L^{-1})
1.9	22.8
2.4	28.8
2.2	26.4
1.9	22.8
1.8	21.6
2.9	34.8
2.4	28.8
2.3	27.6
2.8	33.6
1.8	21.6
2.0	24.0
2.1	25.2
1.8	21.6
1.7	20.4
2.2	26.4
1.9	22.8
2.2	26.4
2.1	25.2
2.1	25.2
1.9	22.8
2.0	24.0
2.4	28.8
2.1	25.2
2.3	27.6
2.0	24.0
2.2	26.4
2.3	27.6
2.0	24.0
2.1	25.2
2.2	26.4
1.9	22.8
2.2	26.4

RBBR CONCENTRATION MEASUREMENT

The concentration of RBBR was determined by Schimadzu UV-2450 spectrophotometer (Figure 3.2). Standard RBBR solutions were prepared from 1000 mg.L^{-1} stock solution and the absorbance readings were recorded at 600 nm wavelength. The calibration curve is shown in Figure 3.3 and the data is represented in Table 3.2.

Figure 3.2 Schimadzu UV-2450 type of UV-visible spectrophotometer

RESULTS

MODELLING OF REACTION KINETICS

Changes in RBBR concentration by time have been conducted in semi-batch reactor. A constant dose of ozone gas was continuously added to the solution during the reaction whereas there was no other input or output of mass in/from the reactor. Based on these conditions the reaction rate can be expressed as follows:

$$\frac{dC}{dt} = k \times [\text{RBBR}]^{m} \qquad \text{Equation 3}$$

Where;

$\frac{dC}{dt}$: Concentration change over time
k : Reaction rate constant
[RBBR]: Concentration of RBBR
m: order of the reaction

Equation 3 is solved in literature for zero, first and second order conditions are the mathematical expression for these are given in Equation 4, 5 and 6.

$$C_t = C_0 + kt \text{(m=0)} \qquad \text{Equation 4}$$

$$\ln C_t = \ln C_o + kt \text{ (m=1)} \qquad \text{Equation 5}$$

$$\frac{1}{C_t} = \frac{1}{C_0} - kt \text{(m=2)} \qquad \text{Equation 6}$$

Where;
C_t: Concentration of RBBR at time t
C_0: Concentration of RBBR at the beginning
k: Reaction rate constant
t: Time

All of the three equations are linear line equations. In order to reveal which one shows the order of the ozonation of RBBR, samples were collected during the ozonation under three different pH conditions at different time intervals. Data were plotted in Microsoft Excel where x-axis represented the time intervals and y-axis represented the concentration values (C_t for zero order, ln C_t for first order and C_t^{-1} is for second order). The coefficient of determination was used to reveal the best fitted data.

OZONATION OF RBBR

This study was conducted under pH 3, 7 and 10 were used to test the performance of Ozonation for the removal of RBBR. The data are represented in Table 4.1, 4.2 and 4.3.

The concentration values were converted to ln C and C^{-1} in order to reveal the order of the reaction under each pH conditions (Table 4.4, 4.5 and 4.6). After 10 minutes the data were not involved in kinetic modelling because there wasn't considerable concentration change after this time.

Linear lines were plotted for zero, first and second order conditions and the coefficient of determination were calculated by Microsoft Excel. According to the results, the obtained data were best fitted to first-order model where the highest value of the coefficient of determination was observed (Table 4.7).

The first-order degradation curves for pH 3, 7 and 10 are given in Figure 4.1 and the observed first-order reaction rate constants are represented in Table 4.8.

Table 4.1 Data for Ozonation of RBBR under pH 3

Time (min)	Average RBBR concentration (mg.L^{-1})
0	95 ± 2.4
1	71 ± 1.9
3	44 ± 2.6
5	27 ± 2.2
7	19 ± 2.1
10	11 ± 1.5
30	2.6 ± 0.2
60	1.1 ± 0.3
90	0.4 ± 0.3

Table 4.2 Data for Ozonation of RBBR under pH 7

Time (min)	Average RBBR concentration (mg.L^{-1})
0	97 ± 0.8
1	76 ± 2.8
3	61 ± 2.4
5	42 ± 2.0
7	31 ± 2.0
10	22 ± 4.5
30	2.6 ± 0.7
60	1.5 ± 0.4
90	0.3 ± 0.3

Table 4.3 Data for Ozonation of RBBR under pH 10

Time (min)	Average RBBR concentration ($mg.L^{-1}$)
0	96 ± 2.3
1	58 ± 6.5
3	29 ± 5.0
5	18 ± 6.7
7	9.6 ± 4.4
10	4.5 ± 1.0
30	2.5 ± 0.6
60	1.3 ± 0.4
90	0.6 ± 0.6

Table 4.4 Investigation of reaction order under pH 3 conditions

Time (min)	C ($mg.L^{-1}$)	ln C	C^{-1}
0	95	4.6	0.01
1	71	4.3	0.01
3	44	4.0	0.02
5	27	3.5	0.03
7	19	3.0	0.05
10	11	2.7	0.07

Table 4.5 Investigation of reaction order under pH 7 conditions

Time (min)	C ($mg.L^{-1}$)	ln C	C^{-1}
0	97	4.6	0.01
1	76	4.3	0.01
3	61	4.1	0.02
5	42	3.7	0.02
7	31	3.4	0.03
10	22	3.09	0.05

Table 4.6 Investigation of reaction order under pH 10 conditions

Time (min)	C ($mg.L^{-1}$)	ln C	C^{-1}
0	96	4.6	0.01
1	58	4.1	0.02
3	29	3.4	0.03
5	18	2.6	0.07
7	9.6	2.3	0.10
10	4.5	1.9	0.15

Table 4.7 Values for estimated orders under three different pH conditions for the Ozonation of RBBR

pH	Order	r^2
3	Zero	0.872
	1st	0.992
	2nd	0.951
7	Zero	0.889
	1st	0.992
	2nd	0.961
10	Zero	0.752
	1st	0.991
	2nd	0.888

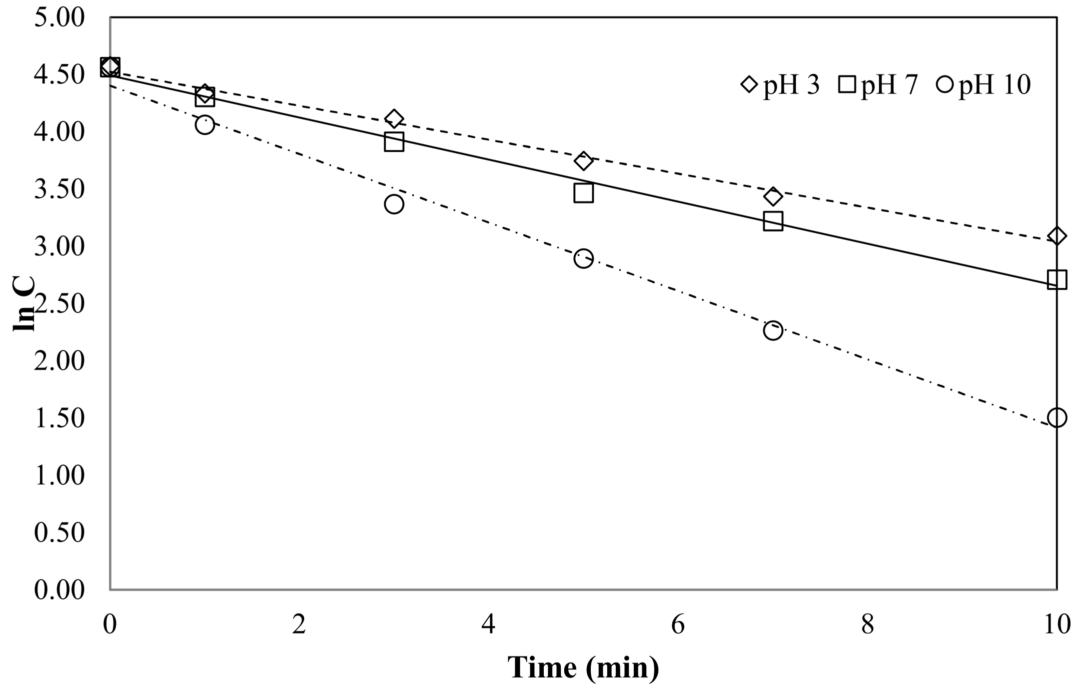


Figure 4.1

First-order degradation curves for RBBR under Ozonation treatment at pH 3, 7and 10

Table 4.8 The observed first-order reaction rate constants for Ozonation of RBBR at pH 3, 7 and 10

pH	Reaction rate constant (min^{-1})
3	0.148
7	0.183
10	0.298

Ozone is a strong oxidant which oxidizes pollutants by two different oxidative ways: direct or indirect oxidation. Direct way of Ozonation is done by the ozone molecule under acidic conditions whereas; indirect oxidation occurs as a result of decomposition of ozone into hydroxyl radicals that are the responsible species for the oxidation under neutral to alkaline conditions (Dong, et al 2008).

Ozone decomposition under alkaline conditions are represented by the following reaction pathways:

$O_3 + OH^- \rightarrow O_2^* + HO_2^*$ (Alkaline pH)

$O_3 + HO_2^* \leftrightarrow 2O_2 + HO^*$

$2HO_2^* \rightarrow O_2 + H_2O_2$

$O_3 + OH^* \rightarrow O_2 + HO_2^* \leftrightarrow O_2^* + H^+$

The above Ozonation mechanism reaction clearly shows that, increasing pH value will yield increased hydroxyl radical generation. It is known that hydroxyl radicals have higher oxidation potential than the ozone molecule. In this study, alkaline pH conditions resulted with faster RBBR removal (the highest reaction rate constant) which indicates the hydroxyl radicals were dominant.

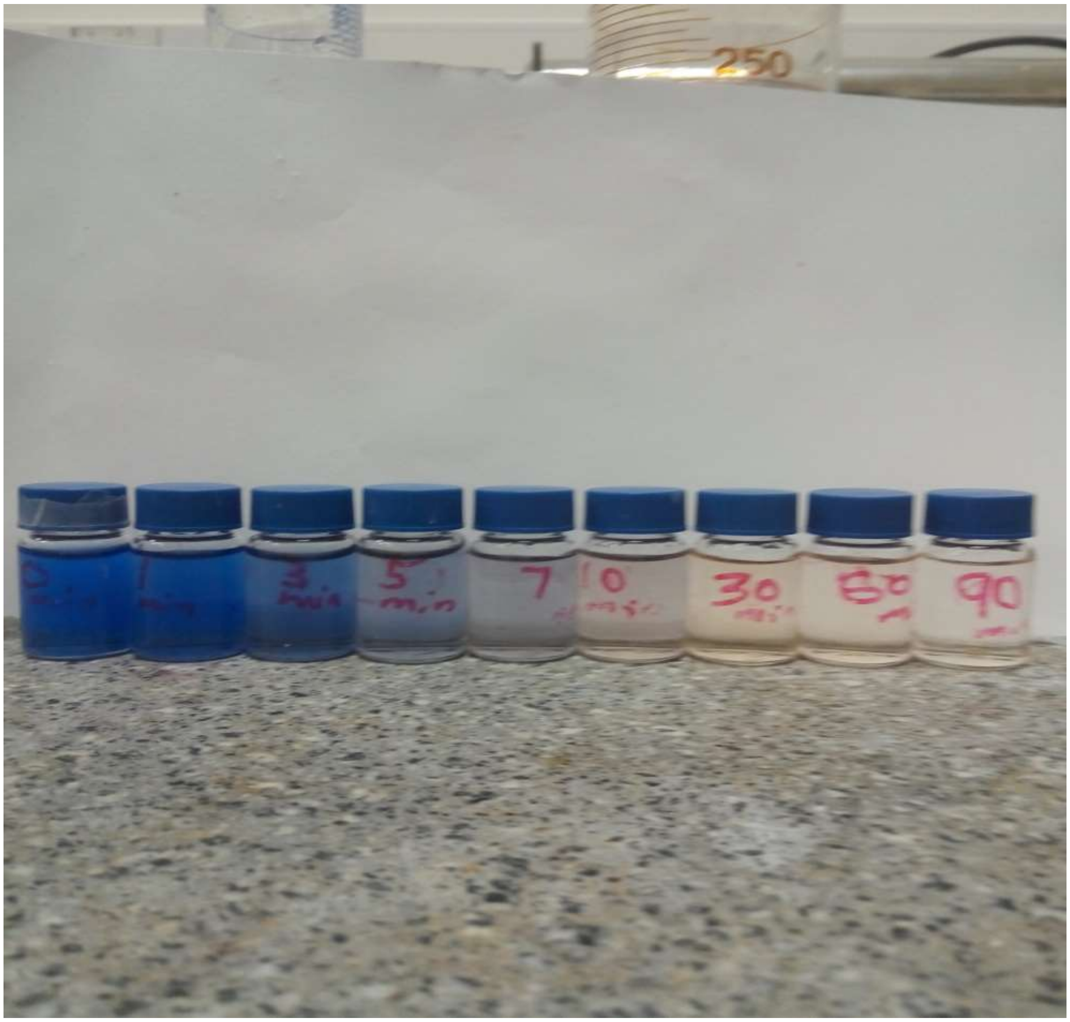


Figure 4.2 Experimental sample for the Ozonation of RBBR under pH 3

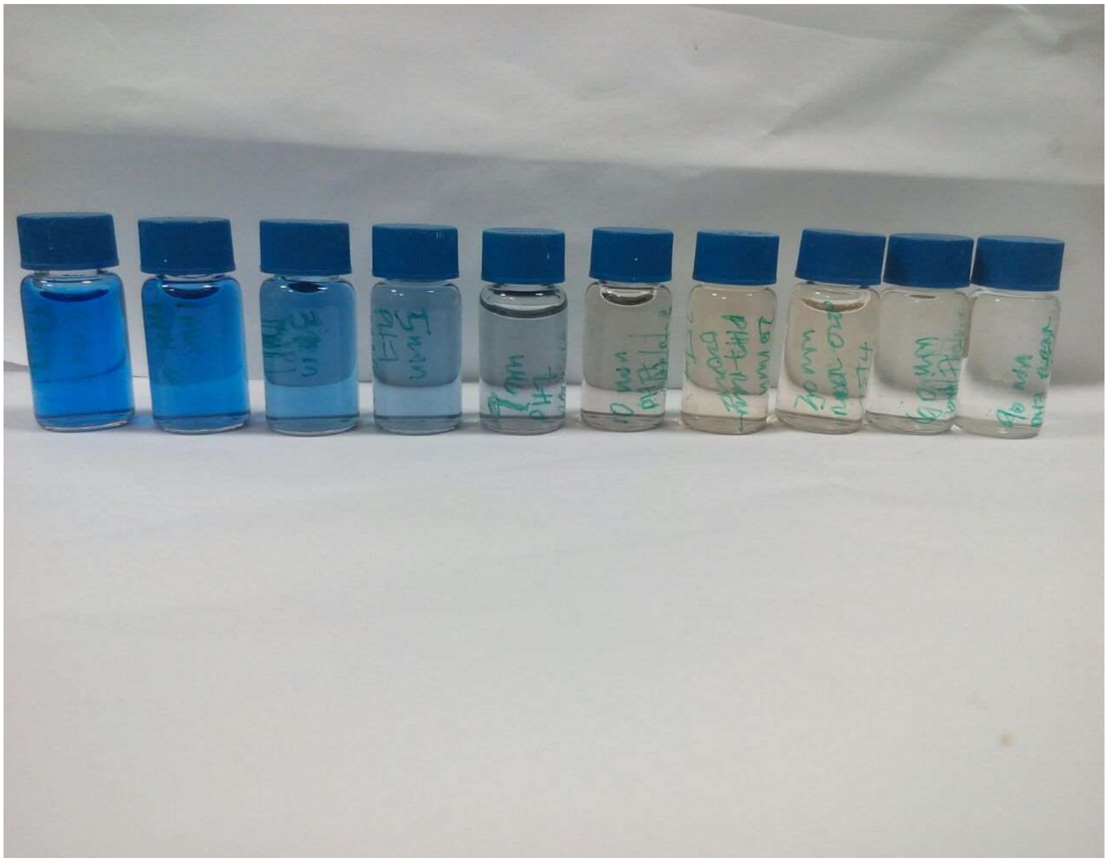


Figure 4.3 Experimental sample for the Ozonation of RBBR under pH 7

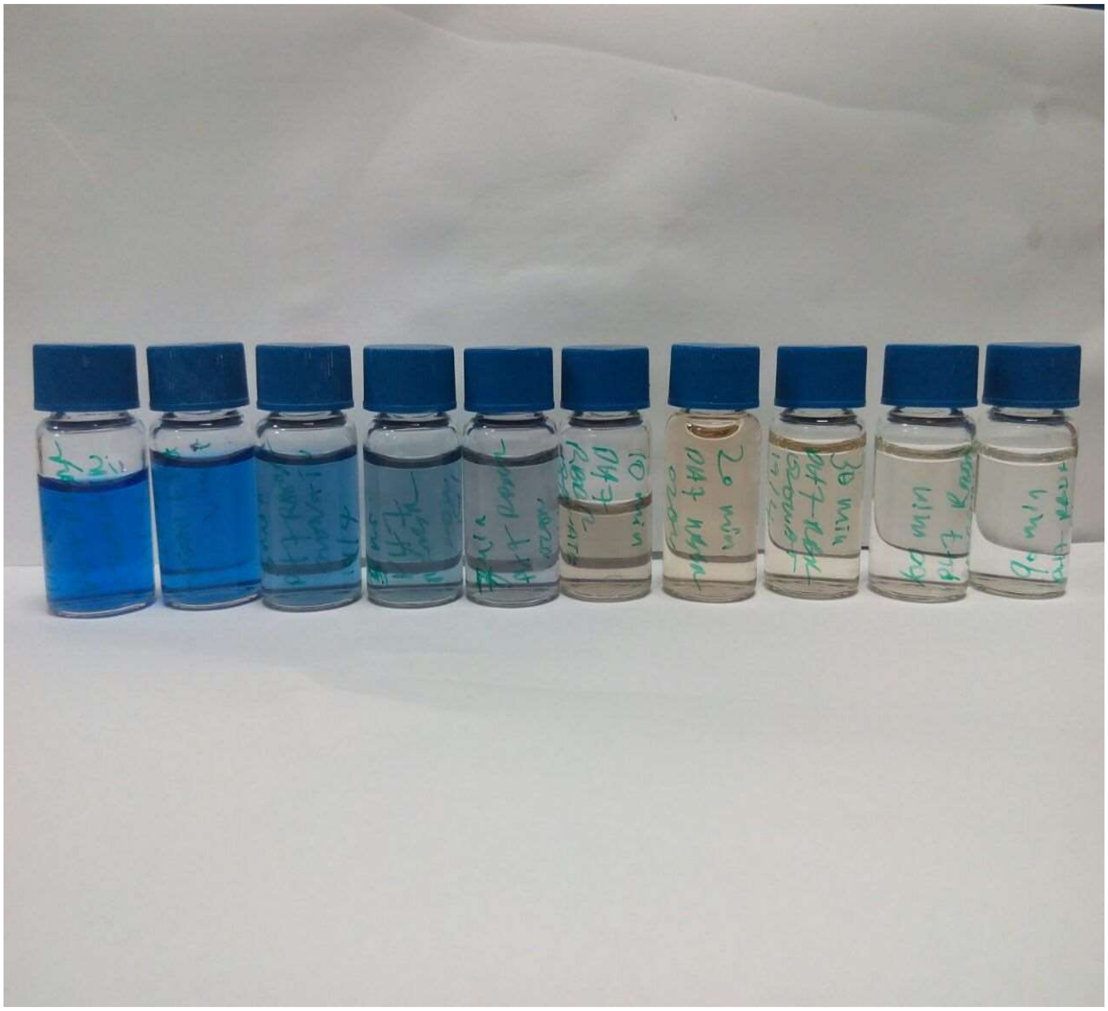


Figure 4.4 Experimental sample for the Ozonation of RBBR under pH 10

CATALYTIC OZONATION OF RBBR

Metals were found to increase the efficiency of pollutant removal during the ozonation. In this study, a solid catalyst CuO was used in order to reveal its effect on ozonation of the RBBR.

Adsorption Test

Adsorption tests were carried out in order to observe interaction between the solid catalyst and RBBR molecule. First, the 100 mg.L^{-1} aqueous solution of RBBR was continuously mixed with 0.75 g solid catalyst (Dose: 1g.L^{-1}) and kept for 24 hours (Figure 4.5).

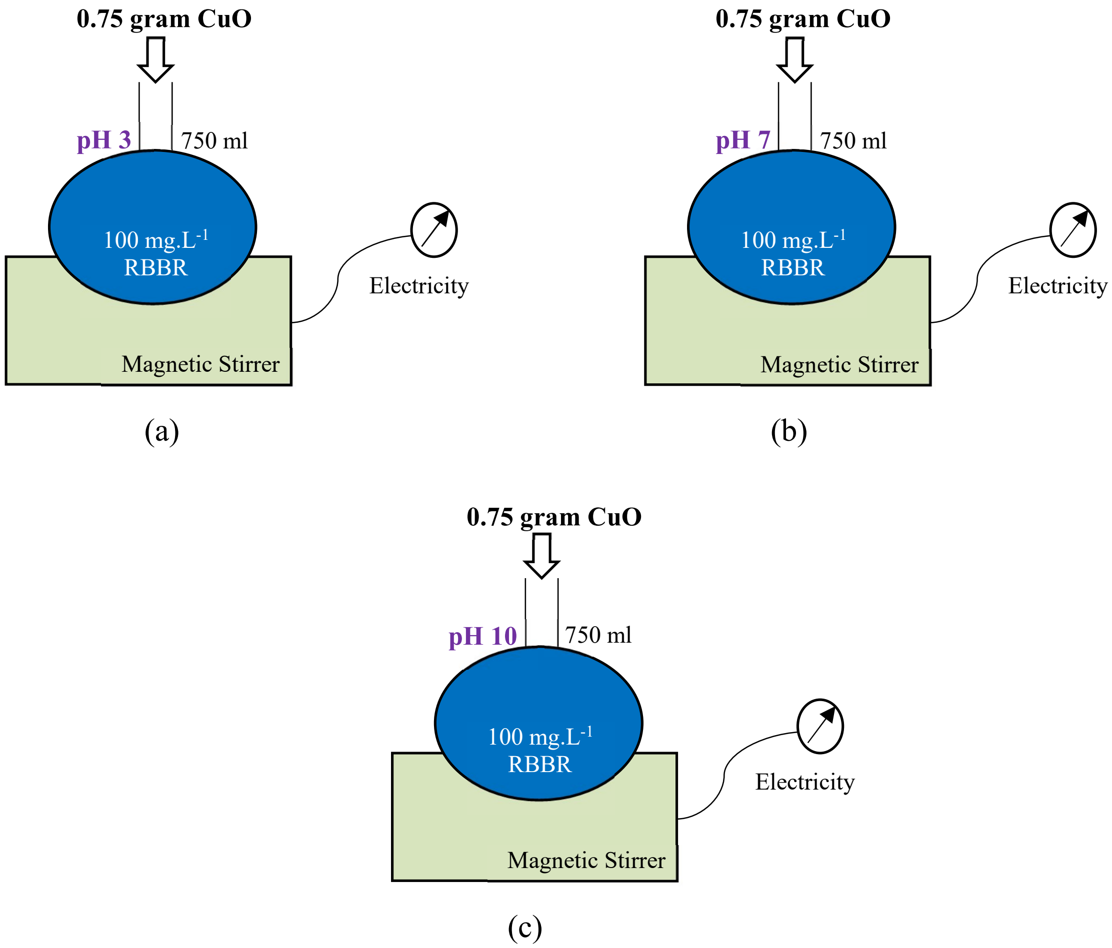


Figure 4.5 Adsorption test for solid catalyst (a) at pH 3, (b) at pH 7, (c) pH 10.

According to the results no reasonable adsorption were occurred (Table 9).

Table 4.9 Adsorption test results in the presence of 0.75 g/L solid catalyst

pH	Initial Absorbance of RBBR at 590 nm	Absorbance after 24 h
3	0.502	0.673
7	0.740	0.685
10	0.615	0.671

Results for Catalytic Ozonation of RBBR

Application of $1 g.L^{-1}$ dose of solid CuO catalyst increased the first-order reaction rate constant to $0.35 min^{-1}$ at pH 10 conditions (Figure 3). However for pH 3 and 7 applications no change was observed.

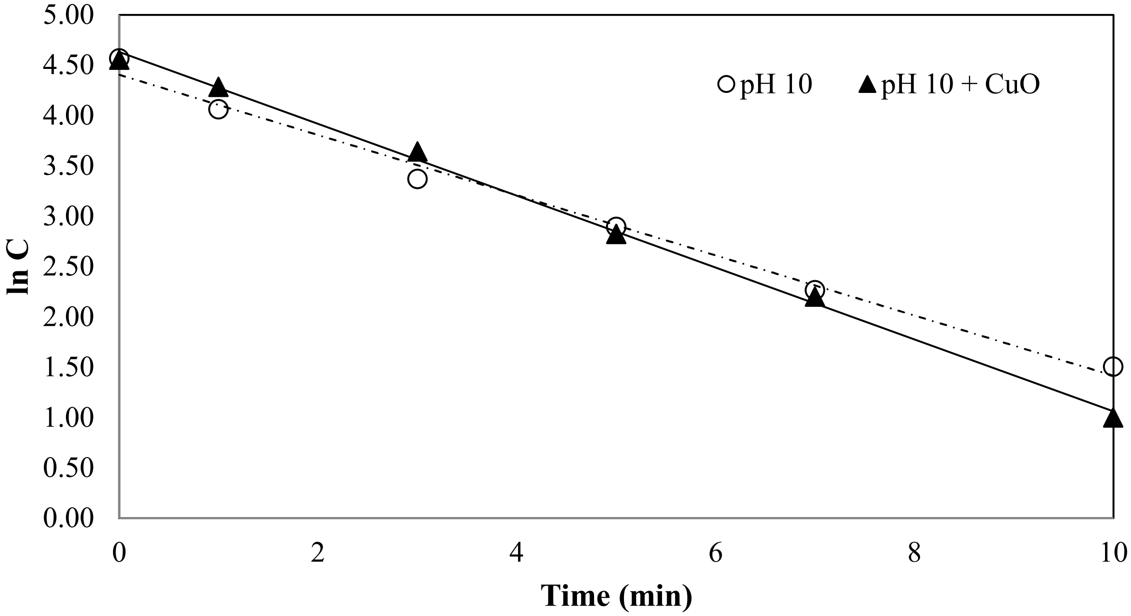


Figure 4.6 Ozonation in the presence of CuO under alkaline conditions for the removal of RBBR

MINERALIZATION OF RBBR

Mineralization measurement were done in order to reveal the remaining organic molecules in the solution. The RBBR molecules were decolorized during the ozonation however, it is important to search for either they have transformed into some other products (by-products) or they have turned into simple inorganic molecules such as CO_2 and H_2O. The results showed that only 6-8 % TOC was removed from the system during the ozonation (Table 4.10).

Table 4.10 TOC data for the Ozonation of RBBR under three different pH conditions

% TOC Removal	pH 3	pH 7	pH 10
	6.05	5.80	8.27

As reported as elsewhere (J.-M. Fanchiang & D.-H. Tseng, 2009) initially $100 mg.L^{-1}$ RBBR solution has $9.1 mg.L^{-1}$ SO_4^{2-} concentration. 10 minutes ozonation resulted with the sulfate concentration of 30 mg.L^{-1} and nitrate was found as 10 mg.L^{-1}. However, nitrate concentration has increased enormously which can be related to ionic by-product's interference.

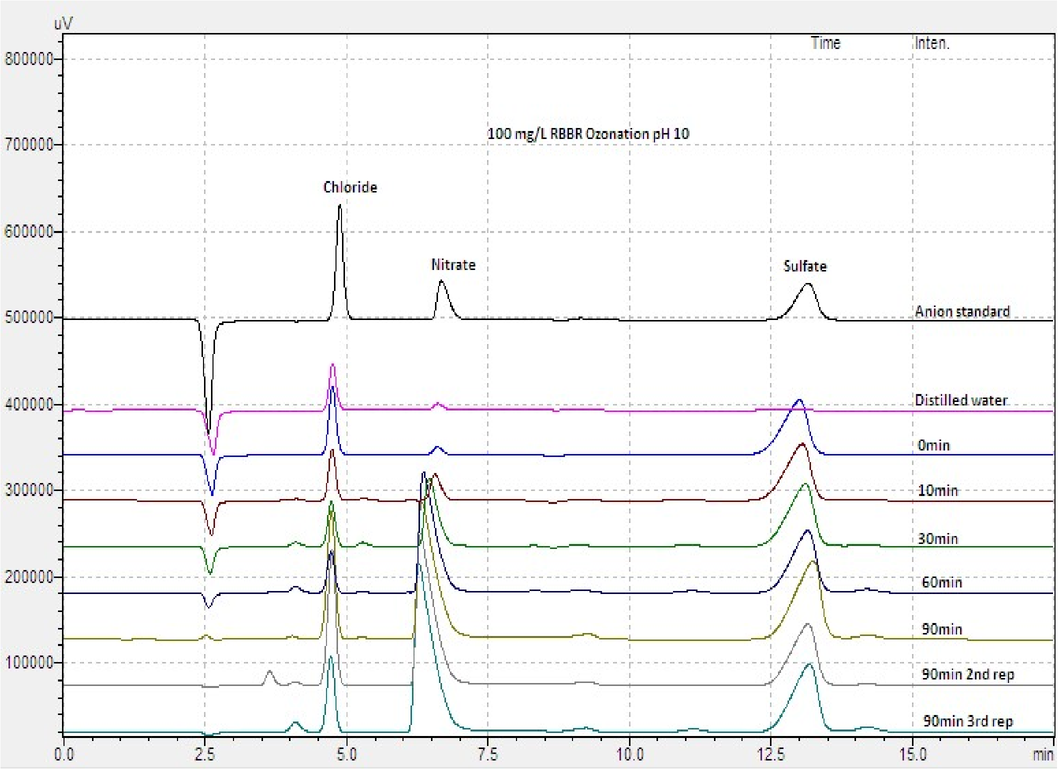


Figure 4.7 NO_3^- and SO_4^{2-} concentration after Ozonation

Table 4.11 Results for N-mineralization and S-mineralization

Time (min)	Concentration of NO_3^- (mg.L^{-1})	Concentration of SO_4^{2-} (mg.L^{-1})
10	10	30

CONCLUSION AND RECOMMENDATION

A study on the removal of RBBR by ozonation in a semi-batch reactor was conducted in the laboratory. Modelling of the reaction kinetics of the system was carrried out by observing changes in the RBBR concentration by time. Ozonation of RBBR was conducted under pH of 3, 7 and 10 to check the performance of ozonation for the removal of RBBR. According to the result of the kinetics modelling, the data obtained were best fitted to first-order model where the highest value was observed. In this study, alkaline pH conditions resulted to faster RBBR removal and which indicates that hydroxyl radicals were dorminant in the system. Catalytic ozonation of RBBR was also conducted where metals were found to increase the efficiency of pollutant removal during the ozonation of RBBR, in which solid catalyst CuO was used to reveal its effect on ozonation. Adsorption test were aslo carried out in order to observe interaction between the solid catalyst and RBBR molucules. From the adsorption test, result indicates that application of 1g/L dose of solid CuO catalyst increased the first-order reaction rate constant to 0.35 min^{-1} at a condition of pH 10. Mineralization measurement of RBBR were carried out in order to reveal the remaining organic molecules in the solution. From the observation, results showed that only 6-8% of TOC was removed from the system during the ozonation.

Based on the results and findings in this research work so far, the mineralization was very poor and following recommendations were suggested for future investigations:

- More ozone dose should be added to the system so as to make the removal of RBBR faster and effective.
- The time for the reaction between ozone and RBBR should be increased for the effective removal of RBBR from the system.
- The catalyst dose should also be adjusted so as to yield a better result for the removal of RBBR using Ozonation.
- Other catalyst which might have higher reaction rate than CuO can be applied to yield a better result.
- Mineralization is an important for the efficiency of Ozonation treatment, however, the results of this study has not shown any positive or significant influence of pH range on mineralization. Therefore this study will recommend that other catalyst should be tested to study the efficiency of mineralization on RBBR removal.
- Furthermore, leaching studies is also recommended as further studies; where a heterogonous and homogenous catalyst should tried at the same conditions in order to evaluate the processes efficiency.
- It should be noted that for industrial scale application, these findings should be modified for larger volumes.
- Other matrix parameters such as presence of other organic materials and heavy metals should be tested for their effect on RBBR removal.

- Toxicity evaluation of treated effluents is important. Microtox toxicity test using luminescent bacteria such as Vibrio Fischeri might give an idea about EC_{50} of the treated solutions.

- In this study, there was no significant mineralization of RBBR molecule. This means that, color causing functional group of RBBR has been broken and smaller products are formed. These smaller products are named as "byproducts". Byproducts are important monitoring parameter in oxidation studies especially when there is no complete mineralization. Byproducts might be more toxic than the main molecule of RBBR. Therefore, byproducts should be monitored during and after treatment of oxidation experiments.

- AOPs ultimate aim is to convert organic molecules to smallest harmless minerals such as CO_2, NO_3^- and H_2O. Complete mineralization is hard to achieve therefore, increasing the BOD of the treated effluents might help these effluents to be degraded biologically. Therefore; BOD monitoring is important in oxidation studies

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