Analysis of Dye Degradation by Ozonation and Fenton Oxidation

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***Abstract*— The widespread occurrence of organic micro pollutants such as pesticides, pharmaceuticals and personal care products, flame retardants, and endocrine disrupting compounds (EDCs) in receiving bodies and drinking water influents has been a global issue of concern for academia and environmental agencies for over two decades. With looming water scarcity in many parts of the world, providing clean drinking water and sustainable development will require the use of water recycling in the future and it will be imperative that recycled water will not impact both environmental and human health. Consequently, extensive research and development in both upstream processing and downstream monitoring are needed. Advanced Oxidation Processes (AOPs) refer to a set of oxidative water treatments that can be used to treat toxic effluents at industrial level, hospitals and wastewater treatment plants. AOPs are successful to transform toxic organic compounds (e.g. drugs, pesticides, endocrine disruptors etc.) into biodegradable substances. AOPs in general are cheap to install but involve high operating costs due to the input of chemicals and energy required. To limit the costs, AOPs are often used as pre-treatment combined with biologic treatment. Wastewaters from the various dyeing, paint and colour industries have been found to contain high amounts of harmful dyes such as RB-5 (Reactive Black T), Congo Red etc. The consumption of such wastewater is responsible for various type of diseases, cancers etc. The present study aims at the removal of these dyes from various effluents from a variety of methods including Ozonation, Catalytic Ozonation, Fenton and Photo Fenton. A series of experiments containing same concentration of dye were conducted and the effects of each were observed. Operating parameters such as effect of catalyst, rpm in the Ozonation experiments and the effect of different dosages of H_2O_2 ferrous ions and intensity of sunlight in Fenton and Photo-Fenton experiments were carefully observed. Finally the analysis is done by UV- spectrophotometer to calculate the concentration of the dye in the wastewater.**

***Keywords*— Ozonation, Catalytic Ozonation, Photo-Fenton, Fenton, RB-5**

I. INTRODUCTION

Advanced Oxidation Processes (AOPs) refer to a set of oxidative water treatments that can be used to treat toxic effluents at industrial level, hospitals and wastewater treatment plants. AOPs are successful to transform toxic organic compounds (e.g. drugs, pesticides, endocrine disruptors etc.) into biodegradable substances. AOPs in general are cheap to install but involve high operating costs due to the input of chemicals and energy required. [1]

Advanced Oxidation Process (AOP) is being studied extensively for waste-water treatment. This process makes use of hydroxyl radicals and oxidative radicals for removal of the organic compounds from streams of various waste water. But, high scale application of these effective technology in wastewater treatment are at present very limited due to high cost and incomplete information about the resultant water quality. The study is focusing on evaluating the upstream processing and downstream after treating analysis of the selective AOPs. Advanced oxidation process, which produces reactive species for example hydroxyl radical in-situ, is identified with one of the potential technology for the removing the trace concentrations of organics from different water streams. Traditional water disinfection treatment process like ozonation and UV disinfection can easily be modified to achieve advance oxidation in both water and wastewater treatment plants. There has been over three decades of intense research into many different types of AOPs as well as wide adoption of some of these processes. Of the many AOPs tested, ozonation, UV/ozone, UV/hydrogen peroxide, and UV/photocatalysis are most commonly studied and used for many applications. Unfortunately, the common disadvantage shared between all AOPs is the high operating cost, which has somewhat limited large-scale application of this otherwise very powerful technology. However, with the advent of higher efficiency UV lamps, visible light catalysts, and improved reactor design, with the help of computational fluid dynamics and energy modeling, both UV and solar-based photocatalysis have great potential for large-scale application. However, further research is still needed in developing new immobilized photocatalysis reactors and to improve the performance, the immobilization, and illumination in the reactor of the photocatalyst. [2]

Although AOPs are found to be expensive for complete mineralization of the organic compounds, partial oxidation of the initial compounds to less stable intermediates is a viable option, if the intermediates readily degrade in the environment and are harmless to the aquatic environment and human health. However, partial oxidation of organic contaminants can in some cases result in the formation of intermediates more toxic than the parent compound, and the nature and number of the degradation products will depend on the employed oxidation process, reaction time, and water quality metrics. Quantifying the accumulated effects of the resulting mixture of compounds on living systems rather than on the precise quantification of their chemical compositions, which is costly and time consuming, and can be futile without the prior knowledge of dose and effect relationship of an

intermediate, can be beneficial to assess the performance of a specific AOP. [2]

For the treatment of drinking water and tertiary wastewater advanced oxidation processes (AOPs) has garnered a significant level of interest academically and industrially over the last three decades. All AOPs are characterized by the production of highly reactive and non-selective hydroxyl radicals, which are the strongest oxidants in an aqueous medium. Hydroxyl radicals are capable of oxidizing nearly all organic compounds to water, carbon dioxide, and mineral salts through a process termed mineralization. [2] By far the most common method in AOP used for wastewater treatment is Ozonation. The main reason is the wide application of this process in disinfection, odor control and colour removal. The degradation of pollutants in water using ozonation follows two mechanisms. (1) Direct oxidation by ozone, which is a highly selective process with low reaction rates. (2) Indirect mechanism to produce hydroxyl radicals.

The first step in the second process is the decomposition of ozone by hydroxide ions.

$O_3 + OH^- \rightarrow O_2 + HO_2$

The formed hydroperoxyl radical is in an equilibrium state

$HO_2\bullet \leftrightarrow O_2\bullet^- + H^+$

The superoxide anion radical and ozone then react to form ozonide anion radical

$O_3 + O_2\bullet^- \rightarrow O_3\bullet^- + O_2$

It then immediately decomposes into oxygen and a hydroxyl radical

$O_3\bullet^- + H^+ \leftrightarrow HO_3\bullet$

$HO_3\bullet \rightarrow \bullet OH + O_2$

Overall:

$3O_3 + OH^- + H^+ \rightarrow 2OH^- + 4O_2$

Textile dyeing uses large amount of freshwater and synthetic dyes. Its effluents have to be subjected to certain treatments to remove the contaminants, especially for residue dyestuffs, before discharging to water bodies for elimination of adverse impacts to the environment. The objective of this study is to check catalyst, Lanthanum oxide, and study its catalytic performance in ozonation of simulated dyeing wastewater for dye degradation.

Synthetic dyes are frequently used in the textile dyeing plant for aesthetic consideration of the products. In the dyeing process considerable amount of colour effluents of high polluting degree are generated which will adversely influence not only the environment but also human health if it is discharged without adequate treatment .In particular, some dyes have toxic, carcinogenic and even genotoxic effects on the humans. Thus it is important to remove dyes in the textile wastewater before discharging to receiving water bodies. However the removal of different dyes is always a remarkable challenge.

The conventional biological method, which is effective for contaminants removal from municipal sewage, is however not particularly useful for treating textile dyeing wastewater due to low biodegradability of textile dyes. Although many studies show that the removal of textile dyes in effluent by specific natural clays via adsorption is effective and cost-competitive, the replacement burden of the adsorbent, which is saturated to dyes after certain service time, has to be carefully evaluated in real wastewater treatment.

Chemical oxidation is an effective method to treat textile wastewater by using several active oxidants including chlorine/chlorine dioxide, hydrogen peroxide and ozone. Particularly, ozone has outstanding oxidizing ability and can decompose to O_2 without byproducts in the whole oxidation process, which therefore has aroused the interests in water/wastewater treatment.

The heterogeneous catalytic ozonation, in which the catalyst is of solid form, has 80 received widely attention in removal of organic pollutants from aqueous solution because of its high efficiency and ambient operational conditions, which has potential practical applications in real water/wastewater treatment without any additional means such as thermal and light energy or second pollution involving ironic catalyst separation in homogeneous ozonation. In the past decades, various materials based on transition oxides such as manganese oxide, titanium oxide, zinc oxide, nickel oxide, copper oxide, cerium oxide and iron oxide were frequently used as ozonation catalysts. The ozone/catalyst process is more efficient than the ozone process alone because these catalysts act as a radical promoter and support.

The advantages of Ozonation are as follows: the rate of ozonation is rapid, it leaves small footprint to reduce the toxicity, it does not concentrate waste for further treatment with methods such as membranes, it does not produce materials that require further treatment such as “spent carbon” from activated carbon absorption, it does not create sludge like biological processes or any chemical process, the ozone also an effective bacteria killer, it oxidized substances like iron and sulfur such that they can be filtered out of the solution, there are no nasty odors or residues produced from the treatment, also ozone converts back into oxygen quickly, and leaves no trace once it has been used.

However the disadvantages of Ozonation are such that enhances the need for finding out other AOP’s. The disadvantages are as follows: It leads to formation of potentially harmful by-products which react with the different pollutants present at source like bromate (extremely harmful carcinogen, it is then important to optimize both the disinfection and oxidation processes of ozonation to minimize toxic by-product formation. The biggest disadvantage of using the Ozonation process as an AOP is that it isn’t cost friendly. The process involves the use of ozone gas which itself is

expensive.

The Fenton and photo-fenton reactions have a very long history in the field of water treatment, having been extensively studied for the removal of pollutants, dyes, chemicals, carcinogens etc. Treatment is achieved via the generation of reactive oxygen species when H_2O_2 reacts with iron ions, as per the following reactions:

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

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2\bullet$$

In water, Fe^{3+} is subjected to hydrolysis, forming different Fe^{3+} aqua complexes depending on pH. At around 3 $[Fe(H_20)_5(OH)]^{2+}$ is the predominant speices, which exhibits significantly photoactivity in the UV and visible regions of solar radiation. Under light, Fe^{3+} is regenerated in a variant called the photo Fenton reaction.

$$[Fe(H_2O)_5(OH)]^{2+} + h\nu \rightarrow Fe^{2+} + H^+ + HO\bullet$$

As the pH increases, amorphous iron hydroxides are formed which tend to precipitate. In the presence of ligands other than H_2O the reduction kinetics of Fe^{3+} to Fe^{2+} can be significantly different, while the operational pH is wider.

Homogenous photo fenton is a very well-known advanced oxidation process which uses Fe-II as a catalyst. Generally, catalysts are also used in the photo fenton which increases the rate at which the colour is removed. The most commonly used catalysts are Fe/Clay, Fe/TiO2, and Fe_3O_4/ Al_2O_3. A considerable pH has to be maintained during the reaction. The advantages of this process is: almost zero energy consumption, less experimental time. It has only one disadvantage that the process produces sludge which needs to be discarded also if any catalyst is present, it cannot be regenerated.

The present study aims at the removal of RB-5 (Reactive Black T) which belong to the class of double azo dye. It is predominantly used for cotton, viscose, wool and polyamide fiber disseminated, roll the dye, knot dyeing piled up and dyeing of continuous. Can also be used for cotton or viscose fabric printing and dyeing directly the printing and discharge printing. The structure of the dye is as follows;

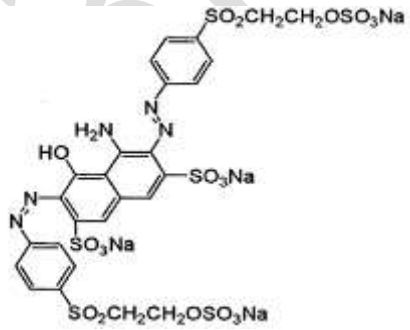

Figure 1 RB-5 (Reactive Black T) Structure

II. MATERIALS AND METHODS

The dye RB-5 was obtained from the respected faculty. The chemical that is Hydrogen peroxide (H_2O_2) was taken having 35% w/w. 10 grams of Ferric Oxide powder (Fe_2O_3) was used as a source of iron provided by _____was obtained from the laboratory.

The initial dye solution of 1000 ppm was produced as a stock solution by dissolving 1 gm of dye in a 1000 ml water.

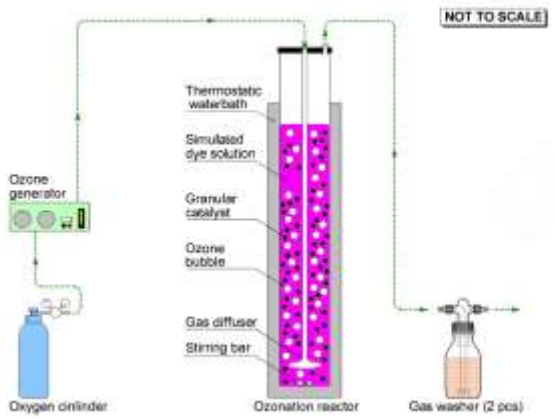

Figure 2 Ozonation Setup[6]

III.EXPERIMENT

A. Ozonation

Setup:-

The experiments were performed in a large cylindrical thermostatic bath which is connected with a constant oxygen supply and 2 gas washer containing potassium iodide solution. The oxygen is passed in an ozone generator. 2 experiments were performed; one without catalyst; and one with a catalyst-lanthanum oxide.

Procedure:-

Catalytic ozonation was performed in a glass reactor filled with 1L of 100 ppm dye solution, of which the temperature and stirring speed were controlled. Ozone was generated by a high precision ozone generator fed with oxygen. The mixture gas stream, comprising of ozone and oxygen, was continuously fed into the reaction system through a porous diffuser, which laid at the bottom of the glass reactor for generation of fine bubbles. Off-gas containing residual ozone was adsorbed by potassium iodide solution in two gas washing bottles. At each predetermined time interval of 5 minutes during ozonation, some amount of water sample was carefully pipetted.

B. Fenton

Setup:-

The experiments were performed in a Borosil beaker having 1 ltr capacity. Solution of 100 ppm of 500 ml was prepared and

taken in the beaker

Procedure:-

Dye solution of 100 ppm with 10 grams of ferric oxide powder and varying volumes of hydrogen peroxide of 50, 70, 80 and 100 ml was introduced and the beaker was covered with aluminium foil to prevent penetration of sunlight and samples of definite volume was taken for every 5 minutes and it was continued for 30 minutes.

IV. RESULTS

The samples taken after every 5 minutes for simple Ozonation and 10 minutes for catalytic ozonatiom is then analysed in a UV spectrometer. The results of the ozonation and catalytic ozonation are compared as below

Table 1 Ozonation-Colour removal

Time (Min)	Simple ozonation		Catalytic ozonation	
	Absorbance	%colour removal	Absorbance	%colour removal
0	3.102	0	3.193	0
5	1.420	45.44	-	-
10	0.655	74.83	0.014	99.588
15	0.306	88.24	-	-
20	0.154	94.08	0.007	99.794
25	0.085	96.73	-	-
30	0.036	98.61	0.005	99.853
35	0.016	99.38	-	-

Similarly, the samples obtained from fenton and photo-fenton experiments were analysed in the similar manner. The results obtained is tabulated as below.

Table 2 Fenton-Colour removal

Time (min)	% Colour Removal			
	Photo Fenton: 10 g of Fe2O3 and 50 ml of H2O2	Photo Fenton: 10 g of Fe2O3 and 100 ml of H2O2	Fenton: 10 g of Fe2O3 and 50 ml of H2O2	Fenton: 10 g of Fe2O3 and 100 ml of H2O2
0	0	0	0	0
5	99.882	99.538	38.600	97.056
10	99.870	99.846	41.962	97.600
15	99.870	99.907	42.665	99.360
20	99.870	99.907	43.215	99.840
25	99.870	99.907	45.293	99.840
30	99.870	99.938	46.913	99.840

V. CONCLUSIONS

After performing the experiments by 3 different methods i.e. Simple Ozonation, Catalytic Ozonation and Photo Fenton 100 % colour removal was observed at the end of the required time. On comparing simple ozonation and catalytic ozonation with lanthanum oxide it was observed that the later process took nearly 20 minutes for almost 100 % colour removal as compared to 35 minutes obtained in the simple ozonation process. Amongst all the process though photo fenton gave the best results as 100 % colour removal was observed in 10 minutes by using the ratio of 90:10.

The most efficient process was the photo fenton process however, the drawback of this process was the production of sludge. So, this is a disadvantage of the process that it also generates waste.

Considering the efficiency of all the above processes, both the ozonation process are costly as it requires ozone generator and electrical energy to work. But on the other end, Photo-Fenton utilizes zero energy so, is the most cost effective process. On comparing the two fenton process, simple fenton and photo fenton process it was found that it took more than 2 hours for the dye to completely degrade in the absence of direct sunlight for a simple fenton process while for a photo fenton process it took less than 2 hours.

On comparing with afore mentioned Photo-Fenton process, it was found that the sludge produced was much less in the 2nd photo fenton experiment conducted. On comparing the Fenton processes, the most favorable results are obtained in the 3rd Fenton process (10 g of Fe_2O_3 and 100 ml of H_2O_2). On comparing the Photo Fenton results, the 2nd experiment produces the most favorable result

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