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Review: Catalytic Ozonation of Textile Dyes

Pooja Shetty[1], Pooja Bugade[2], Indrajit N. Yadav[3] ,Manoj B. Mandake[4]

[1,2,3,4,5] *Department of Chemical Engineering, Bharati Vidyapeeth College of Engineering, Navi Mumbai*

Abstract — *The textile industry consumes large quantities of water and chemicals for textile processing units. The effluents have high concentrations of organic and inorganic compounds. Wastewater from spent dye baths and dye rinsing operations in the textile industry contains unfixed dyes that may be highly colored. Considering volume discharge and wastewater composition, textile wastewater is considered as the most polluting among all industrial sectors. Through new environmental concerns and regulations, pressure is being placed on textile companies to reduce pollutants and reuse process water and chemicals. The presences catalysts significantly improve the degradation efficiency of the dye, the utilization efficiency of ozone and the production of oxidative intermediate species compared to the results from non-catalytic ozonation, and the improvement of them is even more pronounced in the presence catalyst. Some of the main operating variables like amount of catalyst, ozone dose and pH exert a positive influence on the degradation efficiency of dye. Ozonation process along with catalyst was found to be effective.*

Keywords- *degradation, decolorization, catalyst*

I. INTRODUCTION

With urbanization in the world of textile, there has been a spike in textile industries due to it there has been an increase in textile effluents. The common textile processes include the most common textile-processing consists of de-sizing, scouring, bleaching, mercerizing and dyeing processes. These processes involves the release of toxic compounds into the water bodies like-polyvinyl alcohol, carboxyl methyl cellulose, sodium hypo-chlorite, hydrogen peroxide and the organic pollutants in terms of dyes.[1] The dyeing and rinsing process employs large amount of water and the 1-15% of the dye used for colorization is lost. They hence find its place in this water bodies affecting the ecosystem irreversibly. These dyes are the major contributors and hence becoming a major source of pollution worldwide. Textile mills effluents are known to contain various effects on the pH (acidic or alkaline), temperature, high biochemical oxygen demand and respective high chemical oxidation demand. Not only do they have an impact on chemical aspect but also on the physical attributes. [2, 3] In particular release of colored effluents is known to have undesirable effect; it affects the light penetrating property of the water. Thus, the inhibiting photosynthesis and hence making irrational changes into the aquatic food web. These residual dyes from the textile processes are known to carry toxicity which is supported by its stable nature. Hence treatment of the dye inflicted water by our conventional water treatment processes like- filtration, coagulation, biological treatment has proved inert. [3]

II. VARIOUS METHODS

Ozonation

In recent years water treatment involving degradation of these stable organic pollutants using chemical oxidation has been drawing attention. Amongst these advanced oxidation process, ozonation has been greatly popular. Its popularity lies in the fact that it is versatile and its environmental friendly. Having an oxidation potential of 2.07 volts it can degrade almost any organic molecule. But even in the high dosage it is incapable of degrading certain surfactant molecules. Ozone is said to oxidize organic dye by two mechanism direct oxidation and indirect oxidation. Direct oxidation being direct oxidation of dye by ozone molecule which is a selective oxidation.[2,3] Other pathway being oxidation by OH radical that is an intermediate formed by decomposition of ozone in water. This pathway is rather powerful and non-selective oxidation. Both the pathway contributes equally towards its efficiency.

It has been confirmed that mostly the ozonation is mass controlled process. The degradation of the dye is from the mass transfer of the ozone molecules/hydroxyl molecule form the gas phase to the liquid phase of the water effluent. The dependence of the driving force on the waste-water system results from the fact that the concentration of the dissolved ozone varies considerably with the rate of the self-decomposition of ozone, which depends on the waste-water's characteristics. [4] At low pH, ozone only reacts with compounds with specific functional groups through selective reactions such as electrophilic, nucleophilic or bipolar addition reaction (direct pathway).

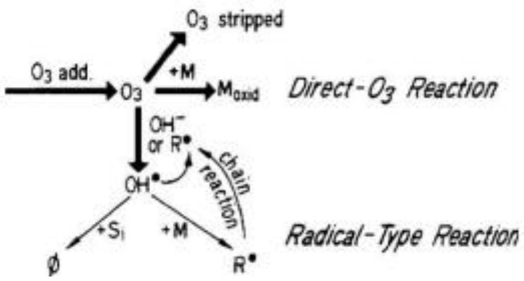

Fig. no. 1. Direct and indirect pathways for ozonation. [2]

The chemical properties of the ozone depend on the structure of the molecule.

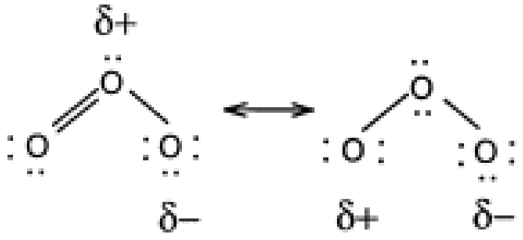

Fig no.2 Resonance of ozone molecule [2]

The molecule structure expressed above is that of ozone molecules in its two extreme forms of resonance. Due to its extreme forms, it has the ability to interact with another molecule as a dipole, an electrophilic or nucleophilic agent. Its highly reactive and hence is invariably unstable. Having the half-life time of only few seconds or minutes, it depends on the pH, water temperature and concentration of organic as well as the inorganic molecules in the effluent.
The decomposition of the ozone molecule

$$-\left(\frac{d[O_3]}{dt}\right)_{pH} = k'[O_3]$$

Follows a pseudo first-order kinetic law [3]:
where *k'* is a pseudo first-order constant for a given pH value.
Decomposition of ozone follows five steps mechanism:

$O_3 + H_2O \rightarrow 2HO^{\bullet} + O_2$
$k_2=1.1\times10^{-4}M^{-1}s^{-1}$

$O_3 + OH- \rightarrow O_2^{\bullet-} + HO_2^{\bullet}$
$k_2=70M^{-1}s^{-1}$

$O_3 + HO^{\bullet} \rightarrow O_2 + HO_2^{\bullet} \leftrightarrow O_2^{\bullet-} + H^+$

$O_3 + HO_2^{\bullet} \leftrightarrow 2O_2 + HO^{\bullet}$
$k_2=1.6\times10^{9}M^{-1}s^{-1}$

$2HO_2^{\bullet} \rightarrow O_2 + H_2O_2$

The step chain reaction mentioned below redirects the indirect ozonation reaction. Here, the decomposition of ozone can be significantly lowered in the presence of hydroxyl radical.

$HO^{\bullet} + O_3 \rightarrow O_2 + HO_2^{\bullet}$
$k_2=3.0\times10^{9}M^{-1}s^{-1}$

$HO^{\bullet} + HCO_3^{-} \rightarrow OH^{-} + HCO^{\bullet}$
$k_2=1.5\times10^{7}M^{-1}s^{-1}$

$HO^{\bullet} + CO_3^{2-} \rightarrow OH^{-} + CO_3^{\bullet-}$

$k_2=4.2\times10^8 M^{-1}s^{-1}$

$HO^{\bullet} + H_2PO^{4-} \rightarrow OH^- + H^2PO^{4\bullet}$
$k_2<10^5 M^{-1}s^{-1}$

$HO^{\bullet} + HPO_4^{2-} \rightarrow OH^- + H_2PO_4-$
$k^2<10^7 M^{-1}s^{-1}$

In water there are several initiators, promoters and inhibitors which greatly influence the mechanism of the ozonation reaction. The initiators are mostly formate, humic substances which are capable of forming peroxide ions O^{2-} from an ozone molecule. The promoter's aryl groups, long chain alcohol groups, formate etc. are influential for the regeneration of peroxide ions from hydroxyl radicals. The inhibitors are responsible for consuming these ions without further regeneration. [5]

Amongst all the oxidation processes, ozonation is considered the most effective and most promising in removing the color from the textile waste-water. [5,7] Owing to its mechanism mentioned above, it has the ability to rapidly and selectively attack unsaturated bonds of the chromophores and hence achieving its objective of decolorizing.

Mehmet et al [2] suggested that overall degradation of the dissolved organic matter contained in the waste water by ozone is the complex process with many step chain reactions. Hence approximate evaluation can be done by the test directly related to COD, TOC and color using them as they are global parameters for any waste water treatment performance.

Catalytic Ozonation

The by-products yielded by the ozonation of these dyes are organic acids, ketones and aldehydes. These products cannot be easily oxidized further by the ozone alone. The inability of the ozone molecule to further oxidise these organic molecule because of its low solubility and low stability in water counts as one of its major disadvantage. These limit its application for textile water treatment. Hence various advanced oxidation processes are investigated based on the generation of powerful radicals than ozone alone i.e. hydroxyl radical having oxidation potential 2.66 eV. Some important AOPs can be listed as the combinations of some chemicals and ozone or combinations of UV radiation and some chemicals such as O_3/H_2O_2, H_2O_2/Fe^{2+} (Fen ton's reagent), O_3/UV, H_2O_2/UV, O_3/H_2O_2/UV and catalytic ozonation.

Catalytic ozonation based on the activation of ozone molecule by metal ions then it is called as the homogeneous catalytic ozonation and secondly as heterogeneous catalytic ozonation in the presence of metal oxides or metals/metal oxides on supports. Catalytic ozonation has been proved efficient for removal of various organic compounds from drinking water and waste-water.

Homogeneous catalytic ozonation

The catalyst used for this ozonation is mostly transition metals as Fe(II), Mn(II), Ni(II), Co(II), Cd(II), Cu(II), Ag(I), Cr(III), Zn(II). The nature of the transition metals enhances the selectivity and also ozone consumption. It was observed that the TOC removal is more as compared to ozone alone when metal ion Fe(II), Mn(II), Ni(II) and Co(II) sulphate. The ozone molecule quickly reacts with the humic matter to produce easily biodegradable molecules. However, they do not benefit the COD and TOC removal. Ozonation in the presence of the other transition metals Fe(II), Cd(II), Fe(III), Cu(II), Zn(II), Co (II), Cr(II) was slightly less efficient. In summary, ozone dosages, which are usually applied in water treatment plants, do not cause the mineralization of humic substances. Higher TOC removal is observed in the case of very high ozone dosages; however, here again, total mineralization is not obtained. The application of catalytic ozonation, however, is a possible means of obtaining a significant increase of humic substances removal.

The Fe^{2+}/O^3 system involves the direct reaction of Fe^{2+} with ozone resulting in the production of $HO^{\bullet}$:

$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2$

$FeO^{2+} + H_2O \rightarrow Fe^{3+} + HO^{\bullet} + OH^-$

FeO^{2+} is also able to oxidize Fe^{2+} to Fe^{3+} (at a slower rate) with the termination of the chain reaction:

$FeO^{2+} + Fe^{2+} + 2H^+ \rightarrow 2Fe^{3+} + H_2O$

Heterogeneous Catalytic Ozonation

Many theories have been suggested for the proper mechanism of this type of ozonation but it has been difficult to report because of the lack of the experimental data in the published reports. There are generally two observed mechanism of catalytic ozonation in heterogeneous system:
The formation of the active sites on the catalyst surface due to the absorption of ozone molecule which interacts with the non-chemisorbed organic molecules

1. Chemisorptions of organic molecule on the catalyst surface and its further reaction with the liquid or gaseous phase.
2. Chemisorptions of the ozone as well as the organic molecule and they further interact with each other.

Effect of initial dye concentration:

A. R. Tehrani-Bagha et al. [8] studied the ozonation process at different concentrations of dye. Their experiments were carried out at neutral pH. The initial concentration of dye reactive dye was ranged from 100 to 800 mg/L. It was observed that with the increase in initial dye concentration, the decolorizing efficiency of the process decreases. Hence, the decolorization is achieved. This could be explained by the fact the ratio of ozone molecules required for the molecules of dye molecule decreases when the concentration is increased. Since, increasing the dye concentration would increase the consumption of ozone molecule, the rate is thus decreasing. Various intermediates formed when the concentration is high also interfere with the oxidation. Hence the time required for the complete decolorization would be longer as the initial dye concentration is higher.

Mehmet et al. [2] studied the effect of initial dye concentration with constant ozone dose 22.6 mgdm^{-3} min^{-1} at pH 7.0. There was an apparent decrease in the pseudo-first order rate, when the dye concentration increased. The dyes AR-183 and AB-158 dye solutions with 50 mgdm^{-3} were found to consume 0.32 and 0.63mg of ozone per decomposing dye respectively. When the initial dye concentration was increased to 500 mgdm^{-3}, the ozone consumptions of these dye solution rose to 0.12 and 0.82 mg ozone per decomposing dye. Hence, it can be concluded that with increasing the dye concentration not only rate decreases but also ozone consumption rate increases.

Effect of pH:

Mehmet et al. studied the ozonation of waste-water at various pH values ranging from 2.4-11.0. They suggested that direct oxidation was more favored under acidic conditions. The amount of ozone consumed was more when at alkaline conditions than at lower pH levels. Removal rates of color, COD and TOC were higher at higher pH levels.

Li Xin et al. [5] suggested that increasing pH could increase the decolorizing efficiency of catalytic ozonation process. Wei Chu et al. observed that decay rate of azo dyes were increasing with increase in the pH. And pH of solution decreased during ozonation.

Saltuk et al [7] studied the effect of single dye solution of RB-5. The rate of dye removal showed an increasing trend when pH level was increased. On the other hand, higher dye removal rates were observed at acidic and basic level, while at neutral level (pH 7.0) lower decolourization was observed for AR-151.

Selene Maria et al [9] observed that high pH leads to more percentage transfer of ozone also hydroxyl radicals are formed from decomposition of ozone at high pH values which results into the more decolourization of dye. At low pH, the degree of decolorization is depending on the direct attack of ozone. Hydroxyl radicals have greater oxidative power than that of ozone molecule which leads to a decrease in decolorization and increase in mineralization at higher pH.

Effect of ozone dose

Mehmet et al. [2] investigated the effect of ozone dose on COD removal by increasing the applied ozone dose. Ozone percentage in gas is adjusted the percentage of ozone in stream. It was observed that as the applied ozone dose increased, overall rate constants of color, COD, and DOC increase. The relationship between rate constant and applied ozone dose was suggested as logarithmic. This relationship was explained by two film theory. Ozone dose and ozone time increases then there will be a decrease in utilization of ozone. The decolourization of both samples from dye bath effluent and equalization tank reaches 75% in few minutes at high ozone dose. The limited COD & TOC removal was backed by incomplete oxidation of organic matter. Amount of ozone consumed was found to be remaining same even though applied ozone dose was different.

Wei Chu et al. [10] studied the effect of ozone concentration or oxidants. It was observed that, dissolving of ozone into water was kinetically controlled. Also fast zero order dissolution was observed. The concentration of ozone in stream was determined by spectrometric method. The over saturation of ozone was not suitable for the reaction also it was suggested that the pH of solution will alter the chemical composition of ozone.

Selene Maria et al. [9] observed that there was decrease in COD tendency as time of ozonation increased. Especially for 100 and 105 min. In some cases there is increase in COD in this reaction was due to formation of acetic acid, acetaldehyde and ketone from dye solution. These organic matters are not completely mineralized under oxidative condition which further contributes to an increase in COD as ozonation time increases.

K. Pacchade et al [11] suggested that there was decrease in absorbance peaks region of dye with time and disappeared at 10 min during ozonation of MXB dye. Removal of color, COD and TOC during ozonation was studied but there was increase in removal of COD and TOC as ozonation time increases. COD removal was 58% and 80% for ozonation time 5 and 30 min respectively. And for 5min 60.4% TOC removal was obtained. There was increase in TOC removal as time increased up-to 30 min. It gave TOC removal as 75%. Also, studied that color removal is faster than COD and TOC removal in ozonation process.

Effect of catalyst

Haiyan et al [12] studied the degradation of alachlor using Cu/Al_2O_3 powder as catalysts applied were found to be similar. But, the TOC removal rate was raised by 20%. More OH radicals were produced in the catalyzed ozonation than the uncatalyzed ozonation. Cu/Al_2O_3-honeycomb catalyzed ozonation led to 75.3% of TOC removal after 180 min into the process. It was also concluded that Cu/Al_2O_3-honeycomb was found to be more effective than the powdered catalyst.

Chung-Hsin Wu et al. [13] conducted the catalytic ozonation experiments in bubble column reactor on dye RR2 and AO6. The dosage of TiO_2 given was 0.5, 1, 2, and 3 g/L and of Mn (II) kept was 0.05, 0.1 and 0.15 g/L and that of MnO_2 was maintained at 0.05 and 0.8 g/L. Using heterogeneous catalytic MnO_2 or dissolved Mn ions helped the reaction at pH 2.0 and 4.0. After 120 min, decolourization efficiency observed for RR2 in O_3, O_3/MnO_2 (1g), O_3/MnO_2 (2g) and O_3/MnO_2 (3g) was 83%, 92%, 95% and 95% respectively while for the other dye AO6 was 67%, 91%, 90% and 93% respectively.

CONCLUSION

The water pollution caused by introducing textile waste water into the water bodies has been immense in the recent years. Thus, effluents are known to create imbalance pH level, temperature, high biological oxygen demand(BOD), high chemical oxygen demand (COD), and high concentration of suspended particles. Amongst various water treatment process condition is one of the most widely used process for the dye removal from textile effluent. However ozonation is one of the most widely used process for the dye removal from textile effluents. However, Ozonation alone has proof to be insufficient for complete degradation. Hence, catalytic ozonation has been favored. These type of ozonation has always been aimed to increase the degradation of dye and to cause intensive mineralization of these organic molecule. Various parameters have known to influence these process where pH, initial dye concentration, ozone dose and catalyst loading. Solution having greater pH is said to decolorize faster. While the initial dye concentration have inverse relation with decolorization. And both ozone dose and catalyst loading have known to influence the decolorization to some extent. By increasing these two parameters, decolorization is achieved extensively.

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