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# Treatment of textile dyes for color and COD removal by pretreatment with Ozonation followed by Granular Activated Carbon

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**Abstract-**The study consisted of Decolorization of textile dyes Direct yellow 12, Reactive Orange 16 and Acid Blue 7 using ozonation as Advanced Oxidation Process (AOP) in a Ozone batch reactor. In which Acid blue 7 was also subjected to Granular activated carbon (GAC) adsorption after its pretreatment with Ozonation to examine the reduction in color concentration and COD of the dye solution. The effect of Ozone contact time, initial concentration of dyes and effect of pH on the efficiency of decolorization was investigated. It was observed that increase in the initial concentration of dye, decreased decolorization. Whereas increase in the ozone contact time gave better efficiencies. Effect of pH was different for each dye, Ozonation of the textile dye solutions resulted in considerable amount of color removal in some cases nearly 100% decolorization and above 90% of COD removal was observed when ozone pretreatment was followed by Granular Activated Carbon adsorption.

**Keywords-** Textile dye decolorization, Ozonation, Activated Carbon adsorption, Advance Oxidation Processes

## I. INTRODUCTION

Textile industry which is considered as one of the complicated industries among many other industries due to its complex manufacturing processes, face a lot of difficulty in treating its waste. Different fibers used in the textile production, use different chemical processes in its production which most of the cases are very complicated chemicals. And huge amount of water is wasted in production of textile. The characteristics of waste water coming out of textile industry can vary in short period of time. And hence it becomes difficult to establish a specific treatment method. Wastes generated at various stages of production of textile like dying, sizing, wetting etc contribute huge amount of chemical pollutants which impart very high chemical oxygen demand (COD), biochemical oxygen demand (BOD), along with color and high suspended solids [1].

Textile wastewater can cause environmental problems due to their high color intensity, and huge amount of suspended solids with high chemical oxygen demands. It is said that about 7 $x10^5$ tons of dyestuff is produced every year [2]. The aquatic life and ecosystem is adversely affected by the presence of color in the water bodies. The textiles dyes which are present in the waste water absorb light from sun and affect the aquatic plants and fishes which are directly or indirectly dependant on the intensity of sunlight reaching to them[2]. Particularly few of the reactive azo dyes due to their products of degradation like aromatic amines are highly carcinogenic [3]; also that the dissolved oxygen gets affected and its depletion in the water bodies can be fatal for aquatic organisms.

Advance Oxidation Processes (AOP's) such are ozonation can effectively decolorize most of the dyes. But does not remove large amount of COD alone. Hence no such treatment can be capable of removing the complex nature of these effluents. Use of combined processes has been suggested for the purpose of overcoming the disadvantage. Most of the present processes which include an initial step like activated sludge treatment to remove the organic matter which is then followed by oxidation, UV radiation or RO treatment adsorption. Adsorption is another effective method of lowering the concentration of dissolved dyes.

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## II MATERIALS AND METHOD

Ozone is a tri-atomic state of oxygen comprising of three atoms of oxygen in its molecule. This has molecular formula $O_3$. It is a colourless and distinctly pungent in smell and which is one of the strongest disinfectant and a very strong oxidant used in recent days. Ozonation is the process in which Ozone is used as the oxidizing agent. Due to its very high oxidation potential even in its very low concentration makes it advantageous in treatment processes [4]. Also its high efficiency in decomposing specially the organic matter with low sensitivity towards temperature changes makes it powerful oxidant

The present study consists of ozonation of the textile dyes Direct yellow 12, Reactive orange 16 and Acid blue 7. Batch reactor of capacity 5 liters is fabricated with glass material with arrangement for dosing the ozone gas through venturi injector. Three liters of dye solution is used in each iteration. 200 mg /hr of ozone produced by laboratory scale ozone generator of capacity 200 mg/hr is injected to recirculating dye solution in reactor through a venturi injector to produce very fine bubbles of ozone to increase the contact surface area. A monoblock water pump is used to recirculate the water in the reactor. Dye solution with the concentrations 50, 100,150 mg/l are subjected to ozonation for different contact times of 10, 20,30,40,50,60 min and the iterations are repeated for three different values of pH to examine the effect of pH on oxidation of dye solution

### 2.1 Textile Dyes

Textile dyes namely Direct yellow 12 (Chrysophynine G), Reactive Orange -16 and Acid Blue 7 were used in the study. Dyes were procured from a locally available textile dyeing small scale industry in Belgaum, Karnataka, India. Following are the characteristics of textile dyes used.

#### 2.1.1 General Characteristics of Direct yellow 12 (Chrysophynine G)

Chemical formula $C_{30}H_{26}N_4Na_2O_8S_2$

Molar mass 680.66

Color index number 24895 $\lambda_{max}$ (nm) 403 nm

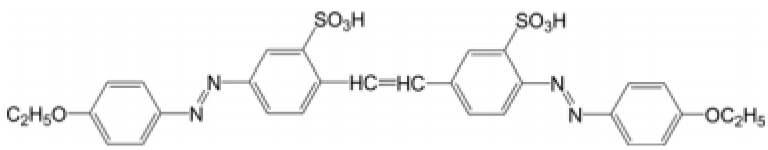


*Figure 1 Molecular structure of Direct yellow 12[7]*

#### 2.1.2 General Characteristics of Reactive Orange 16

Chemical formula $C_{20}H_{17}N_3Na_2O_{11}S_3$

Molar mass 617.54

Color index number 17757 $\lambda_{max}$ (nm) 494 nm

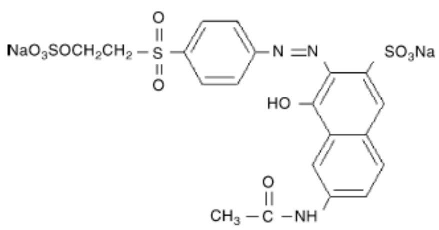


*Figure 2 Molecular structure of Reactive Orange 16[8]*

#### 2.1.3 General Characteristics of Acid Blue 7

Chemical formula $C_{37}H_{35}N_2NaO_6S_2$

Molar mass 690.81

Color index number 42080 $\lambda_{max}$ (nm) 640 nm

 

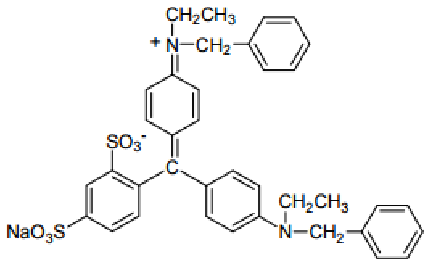


*Figure 3 Molecular structure of Acid Blue 7[9]*

**2.2 Ozone Reactor**

In this study, an attempt was made to make a batch reactor which had special arrangement to introduce ozone gas to the dye solution with a venturi injector to simulate in-line ozone dosing. To increase the mass transfer efficiency of ozone gas to dye solution as compared with conventional bubble column reactors which use a bubble diffuser at the bottom of column. Batch reactor was constructed with Glass material with separate compartments of 5 liters in volume for convenience, though only one reactor compartment was used during each iteration. Ozone generator of capacity 200 mg/hr ozone was used.

Reactor compartment was sized to hold 3 liters of dye solution. Hence the glass chambers of 6” x 4”x 24” was fabricated. A monoblock pump of discharge 500 lph was selected for the circulation of dye solution. To which in-line venturi manifold arrangement was made. The venturi injector for ozone was selected to match the discharge of 500 lph of the pump and 0.15 Kg/ $cm^2$ output pressure of Ozonator.

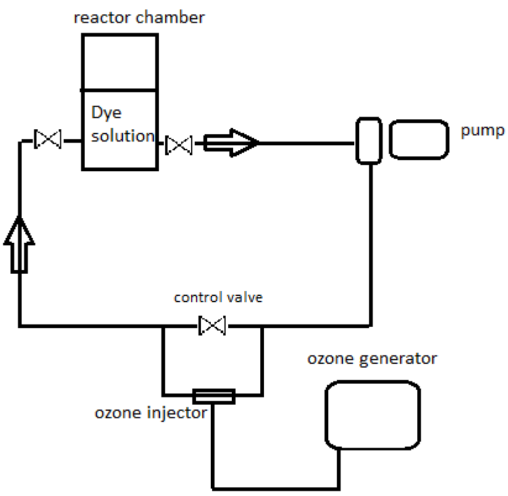


*Figure 4 Schematic Diagram For The Ozone Batch Reactor*

**2.3 Granular Activated Carbon (GAC) contactor**

Acid Blue 7 was subjected to activated carbon adsorption in an activated carbon contactor to have a comparative study on effect of pretreatment of textile dye solution with ozone prior to the activated carbon adsorption and its effect on colour and COD removal efficiency

**Specifications for activated carbon:**

*Table 1 Specifications of Granular Activated Carbon*

| | |
|---|---|
| Source material | Coconut shell |
| Grade | AG-900 |
| Iodine Value mg/gm | 900 |
| Total surface area $m^2$/gm | 900-1000 |

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| | |
|---|---|
| Bulk density gm/cc | 0.5 |
| % Ash content | 3-5 |
| Mean particle diameter mm | 1 |

Acid Blue 7 dye solution after pretreatment with ozone for different contact times was subjected to GAC with varying flow rates with the help of Chemical dosing pump with flow regulation. Hence the contactor was sized to give contact time of 15 min, having 60 mm diameter. Studies were carried out for three different contact times 5 min, 10 min, 15min for the dye solution, depth of GAC bed was adjusted to be 300mm, and the flow rates needed to achieve the required contact times were calculated. The GAC bed was supported with the glass beads at both sides in the contactor and intermediate layers of glass wool were at both sides [5] . Figure 5 shows schematic arrangement of GAC contactor.

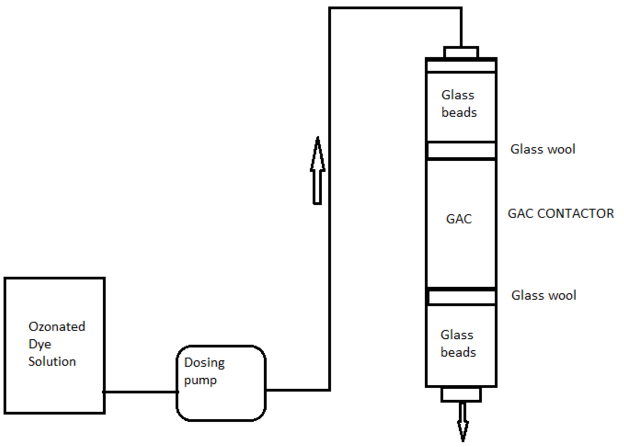


*Figure 5 Schematic Diagram For GAC Contactor.*

**2.4 Preparation of stock solution**

Stock solution for each dye was prepared by adding 1gram of dye to 1000ml of double distilled water[6] the same solution in different in required volumes is used to produce the dye solution of required concentrations for preparing calibration charts and in the preparation of dye solutions for ozonation

**2.5 Preparation of calibration chart**

Calibration charts were prepared for all the dyes. Dye solutions with concentrations 25-250 mg/l were prepared, and checked for absorbance values for the maximum absorbance values for each dye with the use of spectrophotometer of make ELICO. And graphs were plotted for concentrations against absorbance.

**2.6 Ozonation of dye solutions**

Ozonation of textile dyes Direct Yellow 12, Reactive Orange 16, Acid blue 7 was carried out. Effect of variation of Dye concentration on the efficiency of ozoation in decolorization of dye solution along with the effect of variation of pH was studied. Dye solutions in concentrations 50 mg/l, 100mg/l, 150 mg/l were prepared using stalk solution. 3 liters Solution was used in each iteration which was subjected to ozonation in the ozone reactor for contact times from 10 min-60 min, sampling was done at each interval of 10 min,5 ml of sample was collected from the reactor and absorbance values were checked, and hence the reduction in the concentration was calculated using the calibration charts.

**2.7 Granular Activated Carbon treatment**

One of the textile dyes, Acid Blue 7 was selected for the GAC treatment. Dye solution of 200 mg/l concentration was prepared using the stalk solution, and initial COD was checked. Solution was given pretreatment of ozonation with contact times 15 min, 30 min, 45 min and reduction in colour and effect of ozonation in reducing the COD was checked by testing the sample for COD with titration method and Colour by spectrophotometer. Finally, ozonated solution from each iteration was subjected to GAC adsorption with varying flow rate using chemical dosing pump. Further, reduction in the COD and colour after the GAC treatment was checked.

## III RESULTS AND DISCUSSION

### 3.1 Ozonation of Direct Yellow 12:

It was observed that efficiency of ozone in color removal decreased for both very low and high pH values. Further, increase in the concentration of dye reduced the efficiency of color removal. Maximum color removal for the selected ozone dose was observed for 100mg/l concentration in the pH range 6-7, also that large amount of color is removed during first 10 min of ozonation. Table no. 2 gives the percentage reduction of color for different pH and contact times.

***Table 2 Ozonation of Direct Yellow 12***

| Contact time in min | Direct yellow 12 | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Dye concentration 50 mg/l | | | Dye concentration 100 mg/l | | | Dye concentration 150 mg/l | | |
| | pH | | | pH | | | pH | | |
| | 3.42 | 7.42 | 9.22 | 3.57 | 6.67 | 9.02 | 3.42 | 6.35 | 10.3 |
| | % reduction in color | | | % reduction in color | | | % reduction in color | | |
| 10 | 34.53 | 58.24 | 44.32 | 33.77 | 40.2 | 24.47 | 28.3 | 34.53 | 18.04 |
| 20 | 39.17 | 65.97 | 53.09 | 42.3 | 58.5 | 23.67 | 36.6 | 58.59 | 26.4 |
| 30 | 39.69 | 66.49 | 60.82 | 42.3 | 67.8 | 24.19 | 38.65 | 63.74 | 28.4 |
| 40 | 39.69 | 70.01 | 66.49 | 43 | 70.9 | 27.01 | 38.83 | 66.15 | 32.64 |
| 50 | 39.69 | 74.22 | 67 | 43 | 82 | 31.22 | 38.83 | 66.75 | 41.23 |

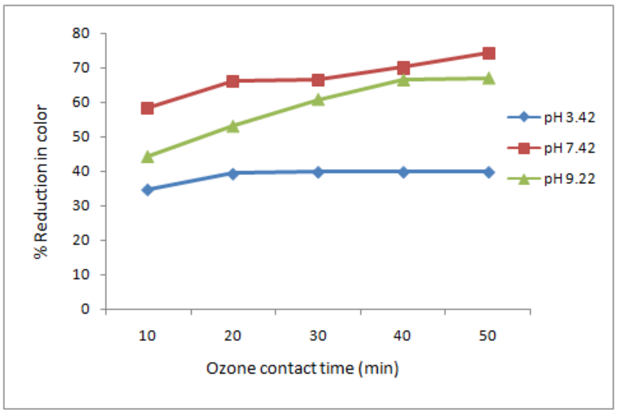


***Figure 6: Percentage color removal Direct yellow 12, concentration 50 mg/l***

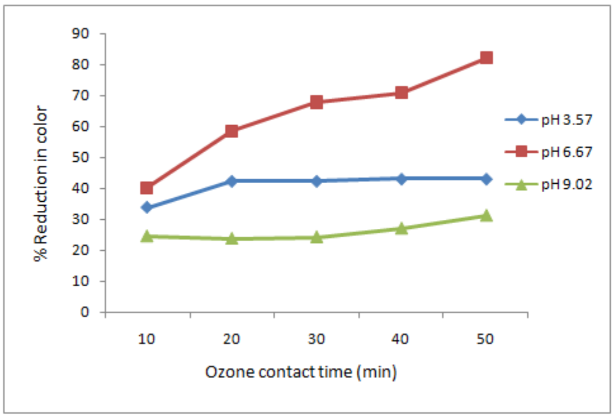


***Figure 7: Percentage color removal Direct yellow 12, concentration 100 mg/l***

 

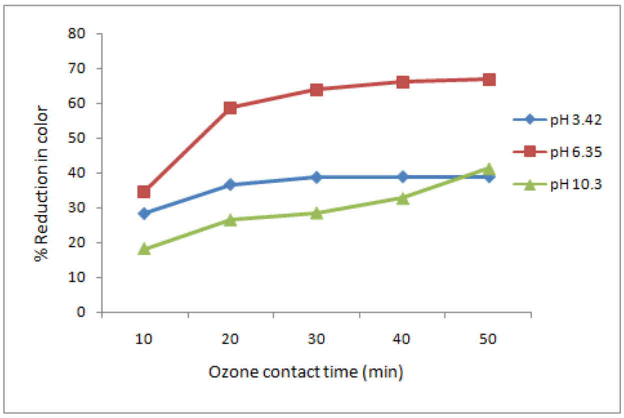


*Figure 8: Percentage color removal Direct yellow 12, concentration 150 mg/l*

### 3.2 Ozonation of Reactive Orange 16:

Color removal efficiency of ozone increased with decrease in the pH for the reactive orange 12 dye for all the three concentrations. Whereas higher pH solutions decreased the efficiency. Nearly 80% of color removal was observed in the pH range 3-3.5. Table no.3 gives the results for ozonation.

*Table 3 Ozonation of Reactive Orange 16*

| Contact time in min | Reactive Orange 16 | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Dye concentration 50 mg/l | | | Dye concentration 100 mg/l | | | Dye concentration 150 mg/l | | |
| | pH | | | pH | | | pH | | |
| | 3.36 | 7.17 | 10.52 | 3.26 | 7.36 | 10.56 | 3.2 | 7.06 | 10.5 |
| | % reduction in color | | | % reduction in color | | | % reduction in color | | |
| 10 | 39.34 | 37.08 | 16.3 | 33.15 | 25.36 | 29.5 | 40 | 32 | 18.6 |
| 20 | 62.94 | 59 | 33.72 | 46.63 | 36.8 | 41.5 | 55.8 | 40.08 | 26.78 |
| 30 | 72.48 | 68.36 | 46.64 | 60.68 | 51.13 | 53.9 | 65.5 | 49.06 | 38.58 |
| 40 | 76.98 | 74.16 | 55.62 | 69.95 | 57.31 | 57.59 | 73.4 | 58.8 | 44.38 |
| 50 | 79.22 | 78.1 | 59.56 | 75.29 | 63.77 | 59.8 | 77.16 | 64.8 | 49 |
| 60 | 80.34 | 79.78 | 67.42 | 77.25 | 69.7 | 60.68 | 80.9 | 68.54 | 52.9 |

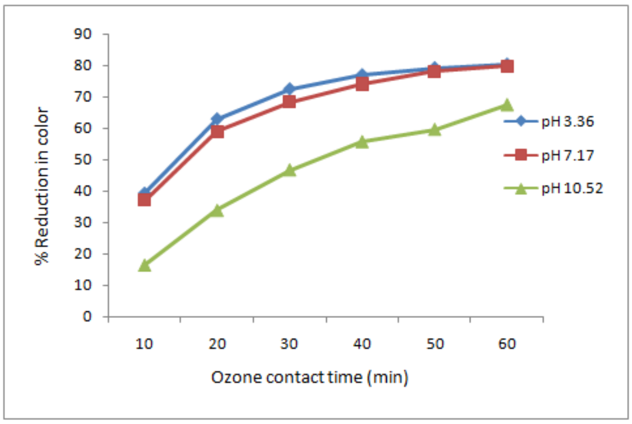


*Figure 9: Percentage color removal Reactive orange 16, concentration 50 mg/l*

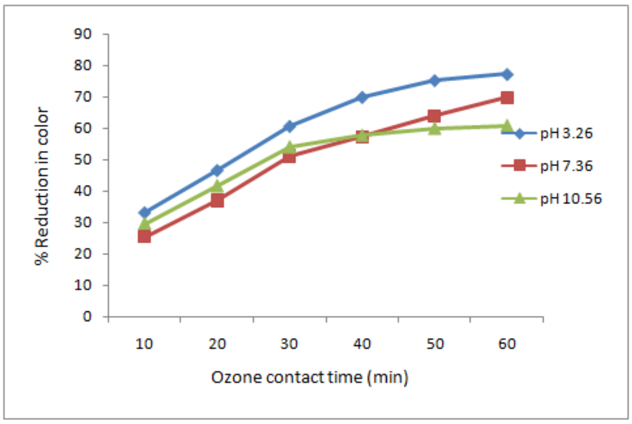


*Figure 10: Percentage color removal Reactive orange 16, concentration 100 mg/l*

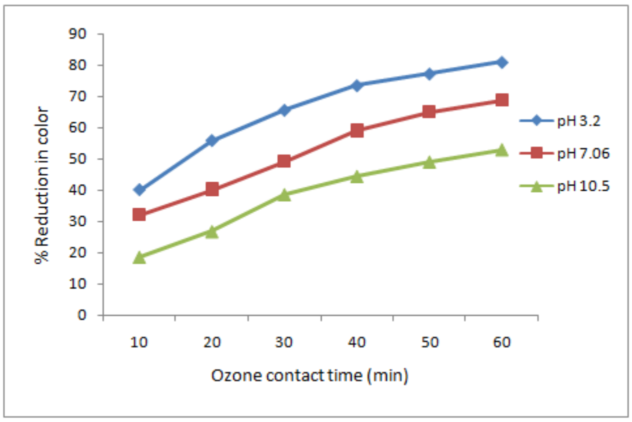


*Figure 11: Percentage color removal Reactive orange 16, concentration 150 mg/l*

### 3.3 Ozonation of Acid blue 7:

Acid blue 7 was most efficiently removed as compared with the direct and reactive dyes. The color removal was almost 100% for all the concentrations and pH ranges for 60 min contact time. It was observed that the efficiency is slightly higher for low pH. And also, over 97% of color was removed in first 10 min for low concentration. Same was observed to be in nearly 80% for higher concentration with low pH. Table no.4 gives results for ozonation.

*Table 4 Ozonation of Acid Blue 7*

| Contact time in min | Acid Blue 7 | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Dye concentration 50 mg/l | | | Dye concentration 100 mg/l | | | Dye concentration 150 mg/l | | |
| | pH | | | pH | | | pH | | |
| | 3.13 | 6.45 | 10.04 | 3.17 | 6.67 | 10.02 | 3.35 | 6.58 | 10.04 |
| | % reduction in color | | | % reduction in color | | | % reduction in color | | |
| 10 | 97 | 86.94 | 81.54 | 91.67 | 84.12 | 60.15 | 82.56 | 54.12 | 45.49 |
| 20 | 98.72 | 95.66 | 95.9 | 93.21 | 92.57 | 80.77 | 89.32 | 82.84 | 66.57 |
| 30 | 100 | 98.2 | 97.96 | 98.21 | 96.54 | 92.44 | 96.24 | 89.49 | 85.78 |
| 40 | 100 | 98.8 | 99.24 | 99.11 | 98.5 | 96.3 | 97.61 | 94.36 | 89.66 |
| 50 | 100 | 100 | 100 | 100 | 98.8 | 98.08 | 99.4 | 97.18 | 93.93 |
| 60 | 100 | 100 | 100 | 100 | 99 | 99 | 99.4 | 97.78 | 96.58 |

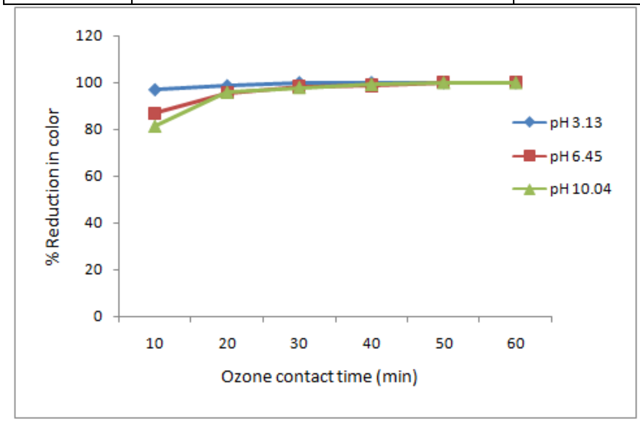


*Figure 12: Percentage color removal Acid blue 7, concentration 50 mg/l.*

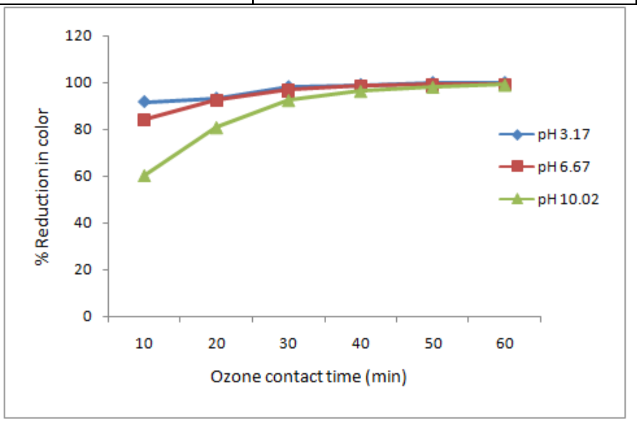


*Figure 13: Percentage color removal Acid blue 7, concentration 100 mg/l.*

 

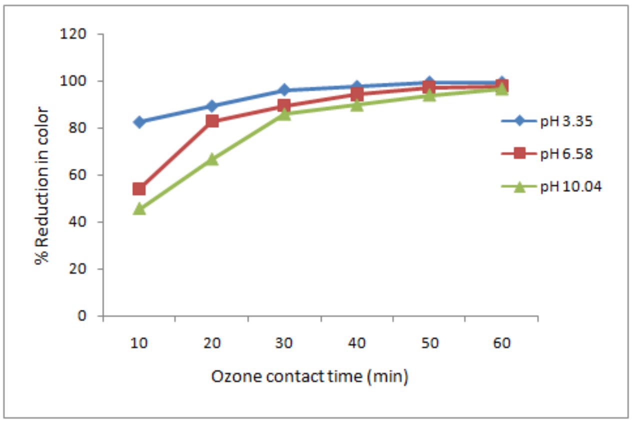


*Figure 14: Percentage color removal Acid blue 7, concentration 150 mg/l*

### 3.3 Combined Ozonation followed by Granular Activated Carbon treatment for Acid Blue7:

Treatment of acid blue 7 dye with concentration 200 mg/l, pH 5.0 and initial COD of 320 mg/l was carried out for different ozone contact times and varying contact time in GAC contactor. Results obtained show that even 15 min of ozone contact time gives more than 92% of color and 90% of reduction in the COD of solution. And the efficiency of treatment increases with the increase in contact time of ozone and GAC contact time. Table no.5 gives results for ozonation followed by GAC treatment.

*Table 5 Results for Ozonation followed with GAC treatment*

| Sl.no | ozone contact time | GAC contact time | absorbance | concentration mg/l | Final COD mg/l | % reduction in Dye | % reduction in COD |
|---|---|---|---|---|---|---|---|
| 1 | 15 min | 5 min | 0.11 | 14.4 | 32 | 92.8 | 90 |
| | | 10 min | 0.064 | 8.5 | 16 | 95.75 | 95 |
| | | 15 min | 0.009 | 1.4 | Negligible | 99.3 | Above 95 |

| Sl.no | ozone contact time | GAC contact time | absorbance | concentration mg/l | Final COD mg/l | % reduction in Dye | % reduction in COD |
|---|---|---|---|---|---|---|---|
| 2 | 30 min | 5 min | 0.036 | 4.8 | Negligible | 97.6 | Above 95 |
| | | 10 min | 0.02 | 2.8 | Negligible | 98.6 | Above 95 |
| | | 15 min | 0.005 | 0.2 | Negligible | 99.9 | Above 95 |

| Sl.no | ozone contact time | GAC contact time | absorbance | concentration mg/l | Final COD mg/l | % reduction in Dye | % reduction in COD |
|---|---|---|---|---|---|---|---|
| 3 | 45 min | 5 min | 0.012 | 1.7 | Negligible | 99 | Above 95 |
| | | 10 min | 0.007 | 1.15 | Negligible | 99.5 | Above 95 |
| | | 15 min | 0.002 | 0.5 | Negligible | 99.8 | Above 95 |

## IV CONCLUSION

Use of Ozone in treating textile dyes is found to be an effective method of pretreatment and which can increase the efficiencies of the conventional adsorption based treatments if used as a pretreatment. Ozone possessing high oxidation potential and require no consumables other than air for its generation it can be helpful in treatment of textile dyes.

According to the experiments carried out, following conclusions can be drawn.

1. pH of solution affects the color removal efficiency of the ozonation to a great extent
2. The efficiency increases with the contact time of ozone and decreases with increase in the dye concentration.
3. Color reduction occurs at higher rate for first 20 min in most of the cases.
4. Textile dye Direct yellow 12 has gives optimum results for color removal in the
Ranges of over 74 % at pH ranges 6-7
5. Reactive orange16, the color removal at 60$^{th}$ minute was observed to be nearly 67-70% at pH 7, at lower pH values, the efficiently was found to be increased to nearly 80%.
6. For Acid blue 7 dye, the efficiency of colour removal was as high as 100% for lower pH in the ranges of 3-4, whereas most of the dye degradation took place in first 10 min of ozonation reducing about 80% of dye concentration at high and low pH.
7.For the trials which involved the treatment of Acid blue 7 with GAC, the contactor could reduce the concentration of dye by 72, 89, 99 % for 5,10,15 min of contact time. And COD removed was 30, 50, and 80% for respective contact times. And the pretreatment of same dye solution in reactor gave 59, 84, 93% colour removal and 25, 55, 90 % of COD removal for 15, 30, 45 min of ozonation respectively.
8. The pretreatment of dye solution with ozonation and followed by GAC gave 90-95 % of reduction in dye for 15 min ozonation and 5, 10, 15 min of GAC contact time. And the % removal of dye and COD crossed 98% in all other cases of 30, 45 min of ozonation and 5, 10, 15 min of GAC contact time.

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