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Ozonation of Direct Red-23 dye in a fixed bed batch bubble column reactor

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Abstract: This study reports the decolourization of direct Red-23 dye by ozonation in a fixed bed batch bubble column reactor. The conversion percentage for bubble column with media is reported high. This research enhances our concept that fixed bed batch bubble column reactor is effective in degradation of dyes. The large utilization of synthetic dyes is a matter of environmental concern since some of them are potentially toxic, mutagenic and carcinogenic.

Keywords: Dyes, Red-23, ozone, bubble column, degradation, textile effluent.

Introduction

Textile industry generates highly polluting waste water. Various textile chemicals such as wetting agents, dyes, surfactants, fixing agents, softeners, and many other additives are used in wet processes such as bleaching, dyeing and finishing processes. Strong colour of the textile wastewater is the most serious problem of the textile waste effluent. Textile dyeing effluents are known to present extreme variations of pH, high temperature, high COD and high concentration of dissolved salts. Treatment of wastewater containing reactive dyes is a severe problem for the cotton textile industry. Ozonation is perhaps the most advanced method ever attempted for decolorization of the textile effluents.

The oxidation potential of ozone (2.07 V) is 1.52 times higher than that of chlorine which allows degrading most organic compounds. The oxidizing ability of ozone is derived from the third, or nascent, oxygen atom. Ozone and hydroxyl radicals (OH^{-1}) generated in the aqueous solution are able to open the aromatic rings. The use of ozone in textile effluent treatment appears as a very attractive alternative within considerable application potential. Ozone is a powerful oxidising agent (E^0=2.08V) and can react with several classes of compounds through direct or indirect reaction.

The chromophore groups generally are organic compounds with conjugated double bonds that can be broken by ozone (directly or indirectly) forming smaller molecules, which decrease the effluent colour. Table 1 provides the composite textile industry wastewater characteristics.

Table 1. Composite textile industry wastewater characteristics

Parameters	Values
pH	7.0-9.0
Biochemical oxygen demand(mg/L)	80-6000
Chemical oxygen demand(mg/L)	150-12000
Total suspended solids(mg/L)	15-8000
Total dissolved solids(mg/L)	2900-3100
Chloride(mg/L)	1000-1600
Total Kjeldahl nitrogen(mg/L)	70-80

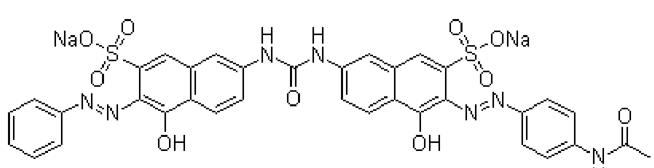

Fig.1. Structure of Direct Red 23 dye

Methods and literature survey

Konsowa *et al*. (2003) investigated the decolorization of wastewater containing direct dye by ozonation in a batch bubble column reactor. Their experimental set up included an air dryer, compressor, ozone generator, glass bubble column reactor and four washing bottles. The air dryer consisted of a column which was filled with a high adsorptive molecular sieve. Ozone was generated using a laboratory ozonizer Model 301-7 (Erwin Sander); water was used as the cooling medium. The reactor has a glass column of 5 cm diameter and 35 cm height with sintered glass at the bottom through which O_3 was introduced to the solution. The reactor was followed by four washing bottles each of them containing 250ml of acidified 2% KI solution for determining unreacted ozone. Before each run, the bubble column reactor was filled with 500 cm^3 of the dye solution. Compressed dry air was allowed to pass through the ozonizer where ozone formation takes place. The outlet stream from the ozonizer containing O_3,O_2 and a N_2 mixture was allowed to pass through tygon tubing connected to the bottom of the bubble column. The gas flow rate was controlled by a needle valve and was measured by air flowmeters. The temperature was fixed at 20^0C during all the experiments. The dye concentration time data during decolorization was detected using spectrophotometry.

The unreacted ozone was taken out of the bubble column reactor through the tygon tubing and bubbled into the 25 KI solution contained in the washing bottles where the potassium iodide reacted with the excess ozone according to the following equation:

O_3+KI+H_2O-------->$I_2+2KOH+O_2$

The resulting iodide was titrated using standard sodium thiosulphate in the presence of starch as the indicator. The values of unreacted and reacted ozone were determined accordingly.

Another landmark work was done by Turhan *et al*. (2009) in the area of decolorization of direct dye in textile waste water by ozonization in a semi-batch bubble column reactor. They have taken direct dye (Sirius Blue SBRR) and the

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experimental methodology applied by these researchers is as follows:

Ozone was generated from oxygen (99.9% purity) by a lab-scale ozone generator, Fischer 502 Model. The reactor had a glass column of 5 cm in diameter and 110cm height with sintered glass at the bottom through which ozone was introduced to the solution. Oxygen gas was allowed to pass through the ozonizer where ozone formation took place. The outlet stream from the ozonizer containing O_3 and O_2mixture was allowed to pass through tygon tubing connected to the bottom of the bubble column. The gas flow rate was controlled by a needle valve and measured by air flow meters. The temperature was fixed at 20+(-) 1^0C during all the experiments. The pH of wastewater was adjusted to the desired level with Merck quality analytical grade 0.1 N NaOH and H_2SO_4.The unused ozone was analysed in the same procedure as Konsowa *et al.* (2003).The concentrations of dye solutions were determined by Agilent 8453 model spectrophotometer at its maximum absorption wavelength of 594nm for Sirius Blue SBRR. The dye concentration time data during decolorization were analysed spectrophotometrically.

Table 2. provides the final degradation (with gravels)-a fixed bed system

Initial dye concentration (mg/l)	De-colorization (%)-D	Time (min)
60	96	30
70	91	25
80	75	30
100	70	30

Fig.2. Dye concentration vs time without media

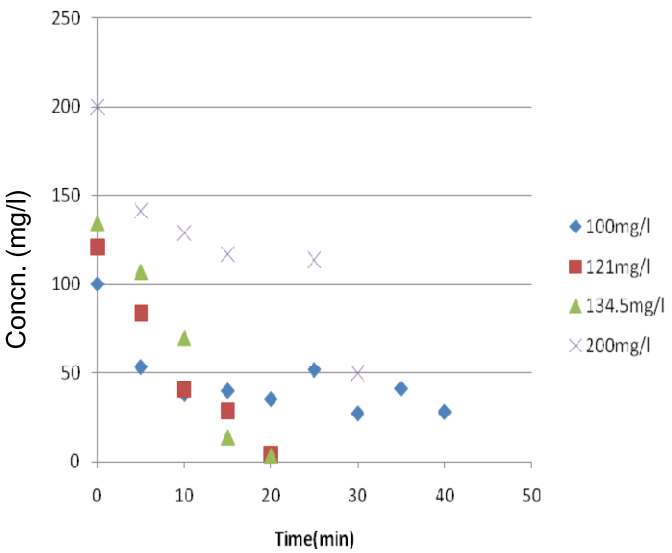


Fig.3. Dye concentration vs time with media

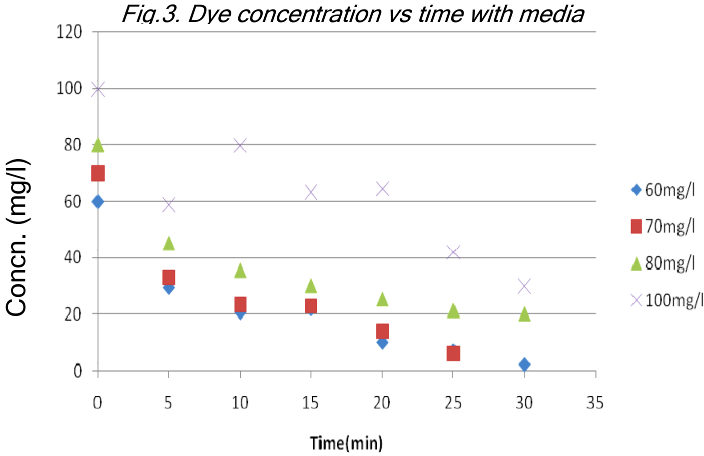
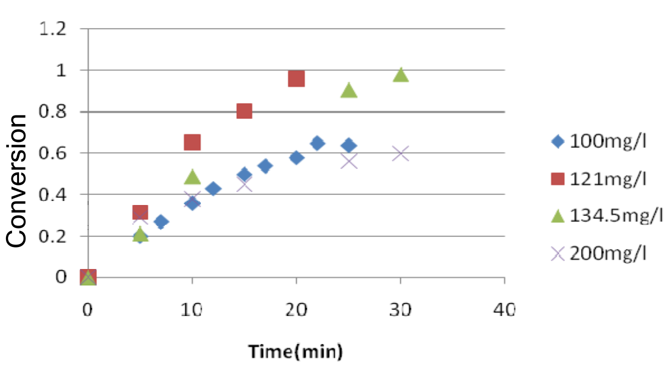


Fig.4. Conversion vs time without media



The present study is attempted to investigate the reaction (conversion) or decolorization efficiency of ozonation of Direct Red 23 dye (commonly used in textile industries) (Fig.1) at different concentrations by employing simple bubble column and a fixed bed bubble column. Initial dye concentrations of 100mg/l, 121mg/l,134.5mg/l,200mg/l are taken out for measuring the absorbance (or concentrations) at different time intervals of 5,10,15,20,25,30 and 35 minutes. The ozonation is done in an Ozonizer (ENALY-CHINA make) whose output is 200-300mg/hr. Also experiments are done with initial concentrations of 60mg/l,70mg/l,80mg/l and 100mg/l with gravels like fixed bed. Absorbances are measured with the help of UV spectrophotometer (UNICAM).

The relation between absorbance and concentration is

$y=0.0302 x +0.4135$

[y=Absorbance, x= concentration (mg/l)]

R^2=0.9655,R=Regression coefficient.

Then we investigated ozonation kinetics of Direct Red 23. The conversion/ decolorization efficiency is found out by $D=[(C_{A0}-C_A)/C_{A0}]100$

[C_{A0}=Initial dye concentration in mg/l, C_A=Dye concentration at any time t in mg/l]

Results and discussion

a) About 80% degradation obtained for 60mg/ l,70mg/l,80mg/l and 100mg/l of dye in presence of gravels.

b) Within 30 minutes of the initiation of ozonation, the degradation reaches 80% for all concentrations studied.

c) Table 2 provides the final degradation (with gravels)-a fixed bed system. Fig.2-6 reflects various factors considered in the study on the degradation of Red-23 dye.

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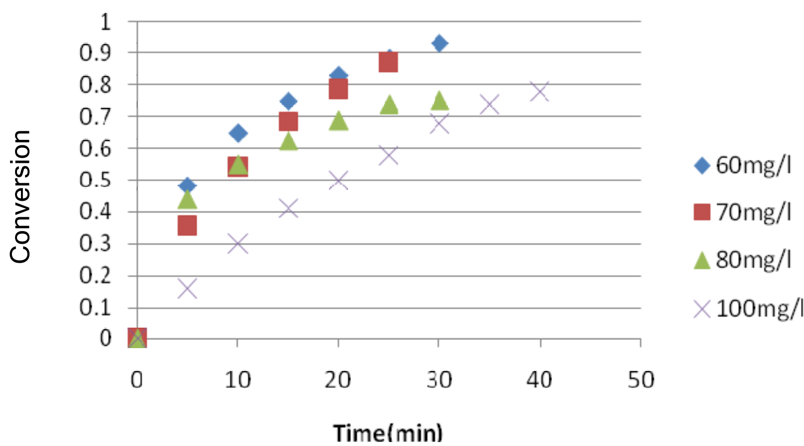
d) Some other trends (without media or gravels) are provided in Table 3.

The degradation rate is higher for bubble column reactor with gravels or media. It shows that the fixed bed bubble column reactor is effective. High mass transfer rate and high contact surface area are the probable helpful factors in dye degradation.

Fig.5. Conversion vs time with media



Conclusion

Dye ozonation can be a promising approach in textile-dye effluent treatment as approach is environmentally friendly, and produces non-hazardous products. Dye ozonation in a fixed bed batch bubble column reactor is a new and innovative approach. Presence of media enhances the reaction. Our research validates this concept.

Table 3. Final degradation without media or gravel

Initial dye concen. (mg/l)	De-colorization (%)-D	Time(min)
100	72	40
121	97	20
134.5	98	30
200	75	30

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Fig.6. Structure of a bubble column reactor