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Wastewater treatment of reactive dyestuffs by ozonation in a semi-batch reactor

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ABSTRACT

Water is quickly becoming both scarce and very expensive. Thus, it has become necessary for every industry to examine proposals for the purification and re-use of their wastewater and effluent streams. The Textile industry is one of the largest industrial consumers of water. Predominantly, wastewater from textile industry contains large amounts of dye and dyeing agents, as well as mordant and sizing agents. Current advanced oxidation processes (AOPs) which include ozone, photochemical and photo catalytic oxidation are techniques used for the treatment of such wastewater. Although AOPs are relatively expensive, they appear to be the most likely candidates for full-scale dye house effluent decolouration.

The ozonation of wastewater containing four different textile reactive dyestuffs in a semi-batch reactor have been studied. Various ozonation conditions – ozone dose, ozone consumption efficiency, etc. – were explored and studied for these various types of dyestuffs. The mass transfer coefficient of ozone in water and its relationship to the ozone efficiency was studied. Pseudo-first order decolouration rate constants for all dyestuffs were determined experimentally.

1. Introduction

Water is considered as the most constructive and in terms of volume, the leading solvent in textile manufacturing. During the wet processing steps, large amounts of water has to be used in the textile manufacturing for methods such as sizing and desizing, bleaching, mercerising, dyeing, printing and finishing of fabrics and dyed yarns. The major industrial consumers of water are textile mills. To create 1 kg of finished goods in textile industry, normally 0.2–0.5 m^3 of water is required. The chemical and mechanical action during processing is used to treat most impurities that are in the form of dirt, salts, oil, greases, and colours of natural fibres, used and dead dyestuffs, chemicals, polymers and fibres. Textile manufacturing as well as many other industries including pharmaceutical, food, paper and ink manufacturing use over 30 000 industrial dyes with 8000 varying chemical structures and more often than not they are released in waste water [1]. Approximately 10–20% of the dyes used in textile manufacturing do not adhere to the fibres during the dyeing process and are therefore discharged into the aquatic atmosphere [2]. These potentially toxic organic and mineral compounds form wastewater which is returned to the environment [3–5].

Due to water resources being very limited, costly and with many governments initiating more stringent governmental regulations, it is necessary for every industry to formulate and study suggestions for purification of their wastewater treatment and effluent streams [6]. The advanced oxidation process (AOPs) is presently the most applicable technology for full-scale dye house sewage decolourisation [7]. Hydroxyl radicals are believed to be the most important oxidants for the degradation of these biological wastes in the AOPs [8]. Ozonation one of the advanced oxidation processes (AOPs) is considered by many as the most competent treatment application for effluent decolourisation [9–16].

It is also possible for dye formulas to include auxiliary ingredients for desizing, scouring, mercerising and so on. Colour and salts may remain virtually unaltered when typical organic treatment techniques are employed and these substances, along with heavy metals, can be lethal to aquatic life [17,18]. Therefore, it must be recognised that manufacturing textile wastewater is an intricate combination of compounds and non-living salts which must be cleansed using cutting edge purification techniques [19].

In the present work, four representative reactive dyestuffs groupings were hydrolyzed and ozonated to the point of complete colour removal. The mass transfer coefficient for the dissolution of the ozone in the water was also measured as was the stoichiometry for one dye.

2. Materials and methods

2.1. Reactive dye and synthetic dye effluent

Four reactive dyestuffs (Table 1) were provided as samples by Dye Star (Durban, South Africa).

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Table 1
Physicochemical prosperities of the reactive dyes used in the present study.

Dye number	Dye brand name	Colour index reactive	Anchor group	Chromophore group	λ_{max} (nm)	Dye or metal content (%)
1	Remazol Red RB	Red 198	Vinylsulphone + monochlorotriazinyl	Azo	500	–
2	Remazol Turquoise	Blue 21	Vinylsulphone	Phthalocyanine copper complex	665	2.5% copper
3	Remazol Black RL	Black 31	Vinylsulphone	Azo cooper complex	570	43–45% dye
4	Remazol golden Yellow RNL	Orange107	Vinylsulphone	Azo	410	70–80% dye

Abbreviation: Red dye: Remazol Red RB, Blue Dye: Remazol Turquoise Blue G133, Black Dye: Remazol Black RL, Yellow Dye: Remazol golden Yellow RNL.

According to the procedure followed by Gregory Knitting Mills PTY Limited, a domestic textile dye house in Johannesburg, the synthetic wastewater was arranged by dissolving each dye in various concentrations to replicate un-rinsed dye bathes and in the form of diluted factory wastewaters [20].

Table 1 lists the physicochemical properties of the reactive dyes selected for the present study.

In order to achieve complete hydrolyzation of the reactive dye solution, 1000 mg/l water soluble stock emulsion of each dye was prepared by breaking up the dye in distilled de-ionized water. Following this, a 4.5 g/l from 48Bé NaOH solution was added under thermostatically controlled (60 °C) conditions and continuously stirred for a minimum of 4 h. For the next 24 h, the prepared "waste" dye solution was retained for an additional 24 h at room temperature. This final step ensures complete hydrolysis and corresponds to processes utilised in other exhausted dye batch studies [21].

According to the reference information, synthetic reactive dye bath effluent was prepared in the manner given in Table 2. Typically 20% of the dye-stuffs, in their unchanged structure and 100% of all applied dye-assisting chemicals remain in the exhausted reactive dye-bath solution [22].

For each dye, the UV–Vis absorption spectrum was measured and a place in the spectrum identified where the absorbance could be measured without interference from other species. The values of these wavelengths are given as λ_{max} in Table 1 and correspond to those recommended in the literature [6].

2.2. Ozone reactor and ozonation procedure

The reactive dye samples were ozonated in a 1 L semi batch reactor as shown in Fig. 1. Ozone was produced in an ozone generator (Model 502 Fisher Labor and Verfahernstechnik) with a maximum capacity of 8.5 g/h ozone.

Table 2
Elements of replicated textile wastewater.

Elements	The reactive dye recipe concentration (g/l)	Exhausted dye bath concentration (g/l)
Reactive dye	1.25–5	0.25–1
Na_2CO_3	5	5
NaOH	4.5–5	4.5–5
NaCl	40–50	40–50
Acetic acid	0.85	
Anti-creasing agent	0.9	
Sequestering agent	0.9	
Detergent	0.45	

Ozone transfer efficiency was determined by measuring the input and off-gas concentration of each pre-ozonation experiment iodometrically. For mass transfer experiments the concentration of ozone in the semi-batch reactor was determined in pure water acidified with Phosphoric acid with a pH level of 3.2 as recommended by the IOA Standardisation Committee. This was achieved by employing a spectrophotometer (Model, Unico, 4802 UV/Vis Double Beam), using an indigo based analysis [23,24].

Pure oxygen gas from a pressure cylinder was fed into the laboratory ozone generator, producing an ozone–oxygen mixture. A constant flow rate of oxygen generated approximately 5.8 g O_3/h. The concentration of ozone used was 52.5 mg/l. The decolouration experiments were conducted as a batch process in a 1000 ml flat bottomed flask. The ozone/oxygen mixture was bubbled through a frit (with ISO 4793 designation of P160) as shown in Fig. 1. Teflon tubing was used for all connections from the ozone generator to the reaction flask. Synthetic dye solution similar to textile wastewater was ozonated in the flask. Samples were taken at various times from the sampling tap and analysed using the spectrophotometer. Temperature was monitored with a thermometer. The magnetic stirrer was set at 500 rpm unless otherwise stated and the pH of

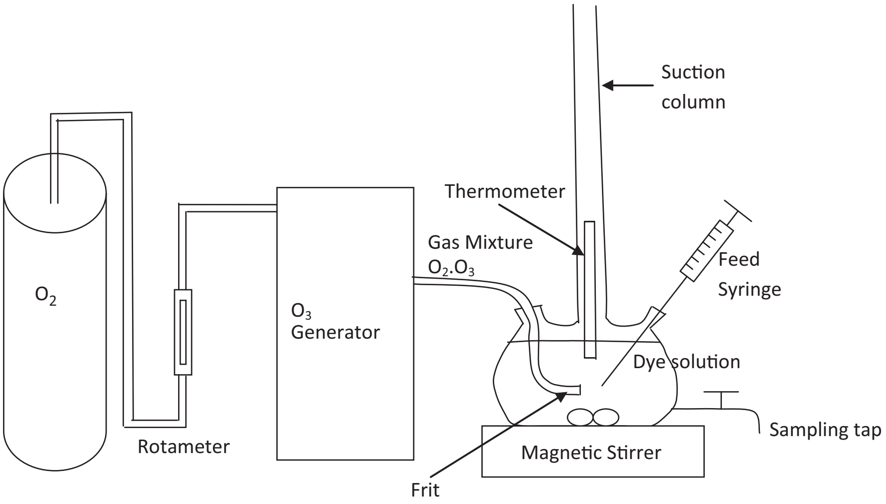


Fig. 1. Diagram of ozonation system for decolouration of wastewater.

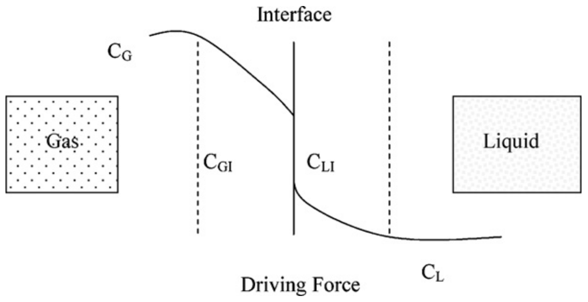


Fig. 2. Model of ozone mass transfer.

the synthetic dye solution containing the alkali and acid as given in Table 2 was measured at 8.7.

In some cases, the synthetic dye solution was added to the flask and then the ozone flow was started. These are referred as normal experiments and are not labelled. When the ozone was allowed to bubble through the liquid for 30 min, and then the dye added, these are referred to as pre-ozonated experiments.

3. Theory

To oxidize and disinfect wastewater with ozone, ozone must be dissolved in the water and this can be accomplished in various ways. To bring about a proper disinfection and oxidation, the ozone concentration should be as high as possible. Prediction of ozone solubility is more complicated than for many others gases, because ozone solubility is influenced by several factors including temperature, pH and dissolved matter. This is a direct consequence of the instability of ozone in water. When matter is transferred from one phase to another across a gas–liquid interface, a concentration gradient will occur in each phase as a consequence of resistance. Phase transfer from gas to liquid is called mass-transfer and is often represented by Fig. 2 (double-layer model) [25]. During the transfer of ozone from a gas to a liquid state, the following three stages are observed: diffusion of ozone across the gas/liquid interface, dissolving into the liquid, diffusion into the liquid. The transfer rate is dependent upon the physical properties of the gas and the liquid and the difference in concentration across the interface and turbulence [26].

where

C_G = concentration of ozone in the gas phase
C_L = concentration of ozone in the liquid phase
C_{GI} = concentration of ozone in the gas phase at the interface
C_{LI} = concentration of ozone in the liquid phase at the interface

The existing assumptions on mass transfer such as penetration, surface renewal and film assume that the confrontation in the mass fluid is insignificant and the main conflict takes place in the laminar films on whichever part of the interface. Mass transfer coefficient in the film is comparative to some of the power of the molecular transfusion coefficient D^n, while n differs from 0.5 to 1. The range of the amount of n to foresee the mass transfer coefficient depends on the scale of turbulence in the system:

K = mass transfer coefficient of film
D = molecular diffusion coefficient
n = 0.5–1; varying on system turbulence

Flux N in the mass transfer out of one of the segments is the creation of the film coefficient, multiplied by the concentration slope in the film, this is identical to the flux into the second phase:

$$N = K_G(C_G - C_{Gi}) = K_L(C_{Li} - C_L)$$

The diffusing material concentration in the two stages placed instantly next to the interface C_{Li}, C_{Gi} are usually not equivalent however frequently believed to be associated by the rules of thermodynamic equilibrium. In order to give an estimate of the precise mass rate into the liquid, mass per unit t unit volume, the specific surface area, a, known as transfer surface area per volume is required in addition to K_L.

m = precise mass transfer rate
$m = K_L a(C_{Li} - C_L)$
V_L = liquid volume
$a = A/V_L$ = volumetric interfacial area

The transfer boundary created by the mass transfer apparatus presented in this paper is in the shape of bubbles. Calculating the surface area of swarms of irregular bubbles is extremely complicated. This complication in forming the interfacial area is defeated by swelling it together along with the masstransfer coefficient calculating $K_L a$ as one limitation [27].

3.1. Model for prediction of mass transfer coefficient of ozone

In this situation, due to the fact that the ozone first has to be dissolved in the liquid before the decolouration takes place, it is important to establish whether mass-transfer is a rate limiting step.

In order to determine this, a mass transfer experiment was carried out. The experimental procedure was exactly the same as that used for the decolouration experiments but no dye was added to the liquid and the sample analysis was carried out as outlined in Section 2.1.

As previously shown, to model the mass transfer coefficient of a gas dissolving in a liquid, a first order model is frequently used in the literature [28–30].

The mass balance for ozone dissolution in a well mixed batch container can be shown to be:

$$V\frac{dC}{dt} = K_L a(C* - C) \qquad (1)$$

where

V = volume of the liquid contents of the vessel
C = concentration of dissolved ozone
C^* = the equilibrium ozone concentration in the liquid
$K_L a$ = the volumetric liquid controlled mass transfer coefficient for ozone [31].

In the above experiments, the decomposition rate of ozone can be disregarded because the ozone was absorbed into pure water. This was checked by stopping the ozone when saturation was achieved by isolating the reactor and analysing for ozone again an hour later.

When combining Eq. (1) with the boundary condition of $C = 0$ at $t = 0$ one can solve Eq. (1) to get

$$\mathrm{Ln}\frac{(C* - C)}{C*} = -\frac{K_L at}{V} \qquad (2)$$

The value of $K_L a/V$ is given by the slope of the straight line obtained by plotting the left hand side of Eq. (2) against the ozone water contact time.

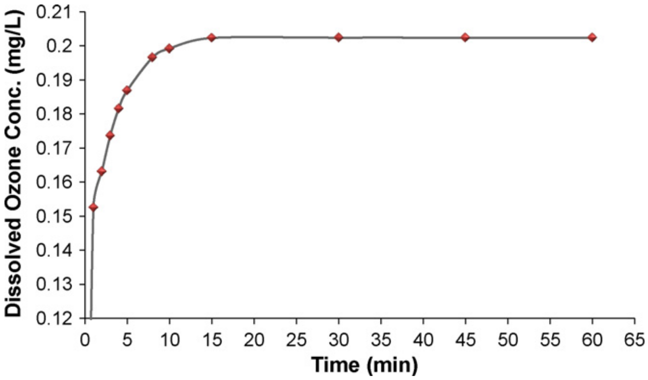


Fig. 3. Concentration of dissolved ozone in water with time.

3.2. *Experimental determination of mass transfer coefficient*

The value of C^*, is a function of the experimental conditions (pH = 8.7 and temperature 21 °C in our experiments). In view of the fact that ozone is only slightly soluble in water, it is likely that the process is controlled by the liquid phase resistance [32].

As the ozonation was achieved by vigorous bubbling of the ozonated oxygen through a glass sinter (frit) and the results were not significantly different using various frit sizes, K_La was used in the model above. The value of C^* was measured as the concentration of dissolved ozone at large gas–liquid contact times.

Fig. 3 illustrates how the dissolved ozone concentration varied with time. It is clear from Fig. 3 that saturation is reached (within about 15 min). Fig. 3 also allows one to determine the saturated ozone concentration.

The results are then plotted in Fig. 4 in line with Eq. (2) and a reasonably good straight line is obtained suggesting the model assumed in Eq. (1) is a good assumption. The value of K_La obtained from this plot is 0.21 min^{-1}. The value determined is close to that reported in literature [6].

We note the time for nearly complete dissolution of the ozone is of the order of about 15 min while we will later see that for complete reaction it is about 30 min. This suggests the reaction rate is not solely controlled by mass transfer but still, it might be affected by mass transfer to some extent.

4. Preliminary results and discussion

Some preliminary experiments were done to determine the best conditions to do the more definitive final experiments. The first of these related to whether to add the dye and start the ozone flow at the same time or to pre-ozonated the liquid before adding the dye. The second was to determine whether the bubbling of the ozone into the liquid caused sufficient stirring on its own or whether a liquid stirrer was required.

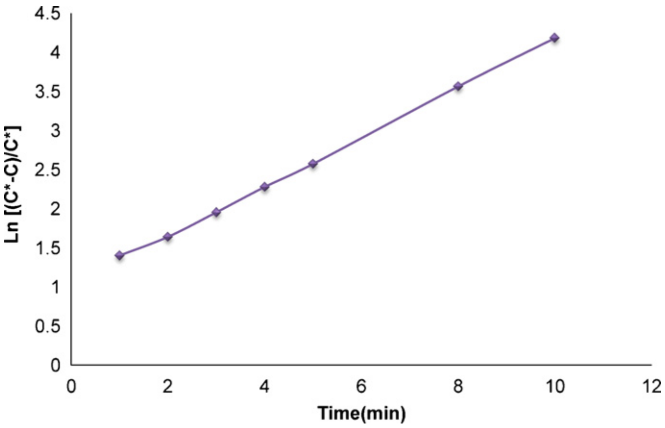


Fig. 4. Log-linear plot of data from Fig. 3 to estimate the mass transfer coefficient.

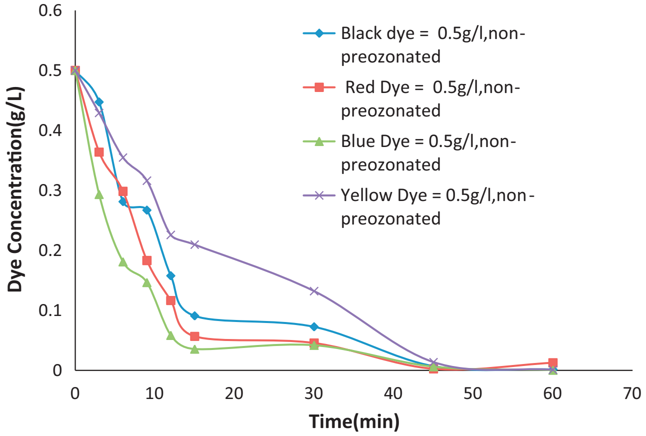


Fig. 5. Decolouration of different dyestuffs without pre-saturation of ozone in the liquid. Experimental conditions: initial concentrations of synthetic dyes solution 0.5 g/l, average O_3 input rate: 52.5 mg/l, duration of ozonation: 60 min, stirring speed: 500 rpm.

4.1. *Ozonation of reactive dyestuffs with 500 mg/l concentration of dye*

Originally dye was added to the water and then the ozone bubbling was begun. In this case, the initial ozone concentration in the liquid was zero. The results of these experiments are shown in Fig. 5. Once it was determined that the rate of dissolution of the ozone was of nearly the same order as the dye oxidation rate, the experimental procedure was changed to first saturate the liquid with ozone and then the dyestuffs were added. These results are shown in Fig. 6.

One can see from the results for the liquid being pre-saturated with ozone, that there is not a slow initial period of decolouration, the decolouration goes to completion more rapidly and the results appear to be more consistent. As a result, it was decided to do all future experiments using liquid pre-saturated with ozone. Note also, as might be expected, that the time for complete decolouration varies with the different dyes with the order being Blue, Red, Black and Yellow taking the longest. All the curves however seem

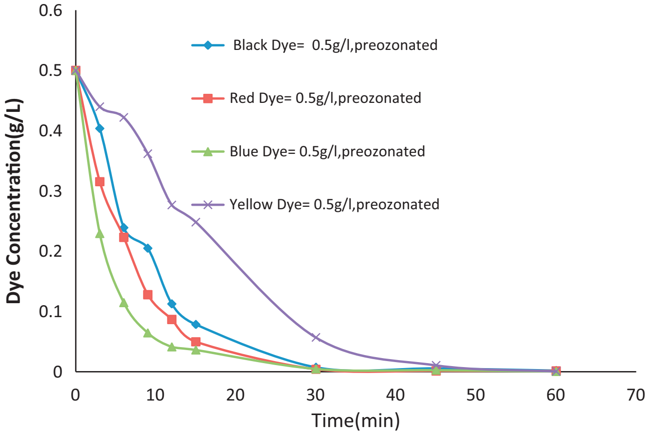


Fig. 6. Decolouration of different dyestuffs with pre-saturation of ozone in the liquid. Experimental conditions: initial concentrations of synthetic dyes solution 0.5 g/l, average O_3 input rate: 52.5 mg/l, duration of ozonation: 60 min, stirring speed: 500 rpm.

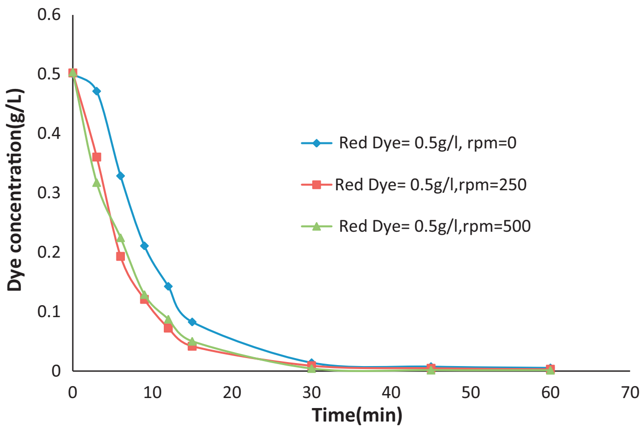


Fig. 7. Decolouration of a reactive Red dye solution of 500 mg/l at different stirrer speeds. Experimental conditions: initial concentrations of synthetic Red dye solution 0.5 g/l, average O_3 input rate: 52.5 mg/l, duration of ozonation: 60 min, stirring speed varying from 0 to 500 rpm, pre-ozonated.

to have the same shape and so for all the remaining experiments the Red dye was used as representative.

4.2. *The effect of stirrer speed on the decolouration of the dye*

To test whether mixing was effective and important decolouration experiments were done on the Red dye with various stirrer speeds. This was done at three different stirrer speeds of 0 rpm, 250 rpm and 500 rpm, respectively. The results are shown in Fig. 7. It can be seen that the dye effectively decolourises within the first 30 min. The results for “no stirring” are a bit different, particularly at short times, from those at 250 rpm and 500 rpm, with the latter two readings being virtually identical. This suggests that mixing only due to the gas being bubbled through the liquid was not sufficient enough to cause good mixing. It was thus decided to do all future experiments with a stirrer speed of 500 rpm.

5. Results

5.1. *Dye concentration versus time*

It was shown in Fig. 7 that ozone is effective in decolourising the Red dye and it is obvious the dye colour is considerably reduced within 15 min and after 30 min, almost full decolouration is achieved. We now want to investigate the effect of different initial dye concentrations. The results of these experiments are shown in Fig. 8.

5.2. *Different initial ozone concentrations*

Experiments were also done to see the effect of the ozone concentration in the gas. Unfortunately the ozonation apparatus did not easily allow one to easily change the concentration without changing the flow-rate. Three initial ozone concentrations 52.5 mg/l, 68.7 mg/l and 80 mg/l at flow-rates 160 l/h, 80 l/h and 40 l/h, respectively were used to decolourise 0.25 g/l of Red dye and the results are shown in Fig. 9.

A higher concentration of ozone decreases the rate of decolouration. This is a somewhat counter-intuitive result as one might expect higher ozone feed concentrations to lead to higher rates. However it should be noted that the higher concentrations occurred at lower flow rates. In any event the effects were not large and so it was decided it was not necessary to do any further experiments at different ozone conditions.

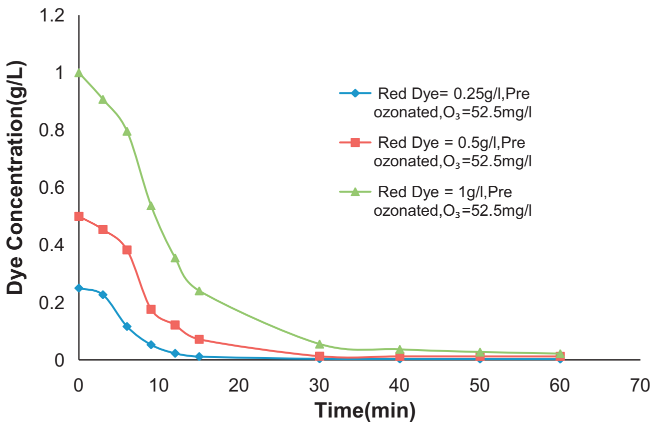


Fig. 8. Red dye concentration versus time for different initial concentrations. Experimental conditions: initial concentrations of synthetic Red dye solution varying from 0.25 g/l to 1 g/l, average O_3 input rate: 52.5 mg/l, duration of ozonation: 60 min, stirring speed: 500 rpm, pre-ozonated.

5.3. *Calculation of stoichiometric amount of ozone required to decolour dye*

As the stoichiometry of the reaction of ozone with the Red dye was not known, it was decided we would measure this. This was to be accomplished by pre-saturating the liquid with ozone and then effectively titrating it with a solution of a dye. Because the ozone’s reaction rate with the dye has been shown to be slow, this is a difficult experiment to perform accurately. However, it was regarded as important enough to attempt even if the results were not very accurate.

0.5 gram of Reactive Red 198 structure as shown in Fig. 10, with a molecule weight of 608.5 g was dissolved in 15 ml of water. This was gradually added to the liquid pre-saturated with ozone over a period of 45 min until the first sign of colour was seen. This occurred after 2.1 ml of the dye solution had been added.

Using these results, it was found that each ozone molecule de-colourises 28.1 molecules of dye. Such a large amount of dye decolouration by such a small quantity of ozone strongly suggests a radical-based chain reaction is taking place. Because of the potential of dye fragments to further decompose or react with ozone and the extended time the experiment took to perform, the probability is that if there is an error in

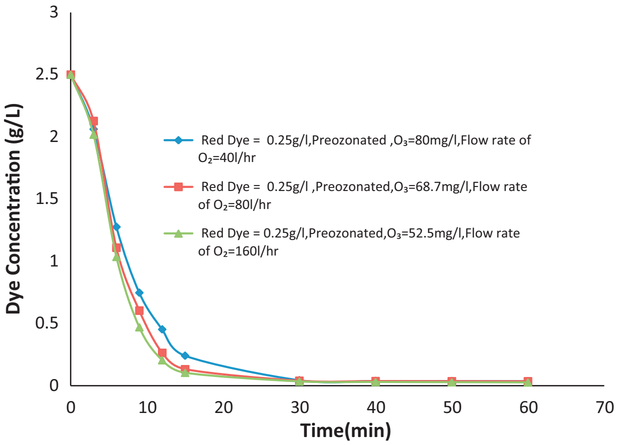
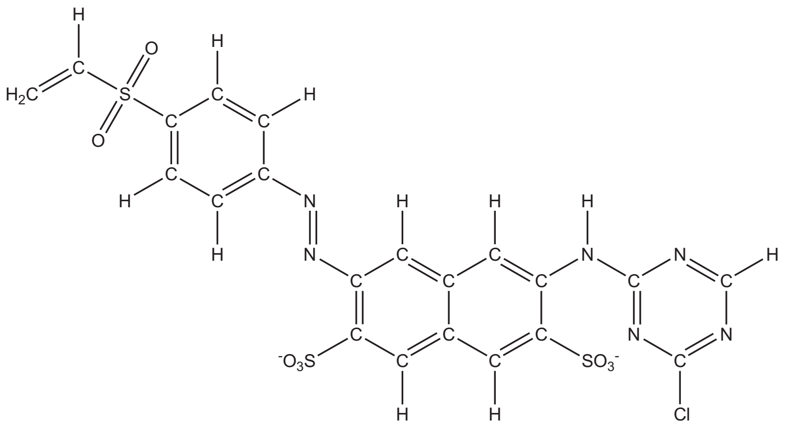


Fig. 9. Red dye concentration versus time for different feed ozone concentrations and flowrates. Experimental conditions: initial concentrations of synthetic Red dye solution 0.25 g/l, O_3 input rate varying from 52.5 mg/l to 80 mg/l, flow rate of O_2 varying from 40 l/h to 160 l/h, duration of ozonation: 60 min, stirring speed: 500 rpm, pre-ozonated.



(*E*)-3-(4-chloro-1,3,5-triazin-2-ylamino)-6-((4-(vinylsulfonyl)phenyl)diazenyl)naphthalene-2,7-disulfonate

Remazal Red RB

Fig. 10. Structural formula of C.I. Reactive Red 198 [33].

these results, the true stoichiometric coefficient would be even greater.

6. Discussion

6.1. Reaction kinetics during ozonation

Given that the rate at which ozone is fed to the reactor is constant and mass transfer is faster than reaction it might be the ozone concentration in the solution remains constant at its saturation level. In this case, the simplest model for the dyestuffs decolouration might be that the rate is first order with respect to the dye concentration. This has been suggested previously in the literature [34].

Fig. 11 shows a plot of $\ln((c - c_\infty)/(c_0 - c_\infty))$ versus time. This shows the latter part of each curve yields an approximate straight line. It can also be seen that the initial rates (slopes) are lower but generally all about the same. The other result to be clearly seen is the most surprising – the rates are lower for the higher initial concentrations (1 g/l) of dye after about 5 min.

6.2. Rate versus concentration

In order to better understand factors affecting the rate, it is convenient to plot the rate of reaction versus the concentration of dye. The rate is estimated by taking two successive points from the dye versus the concentration curve, subtracting them and dividing by the time interval.

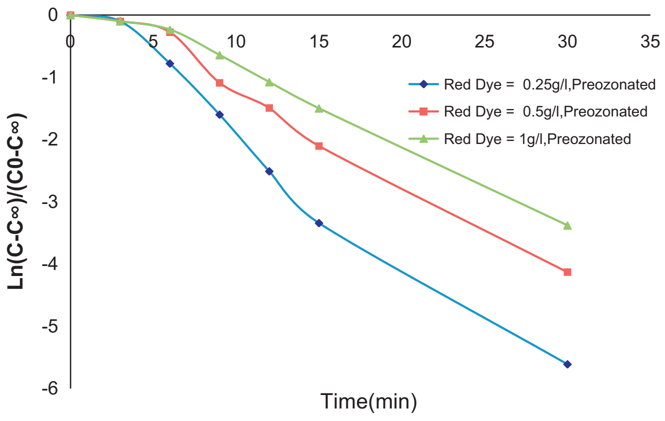


Fig. 11. Log of dye concentration versus time (first order test) for Red dye decolouration for different initial dye concentrations (pre-ozonated) using the results from Fig. 8.

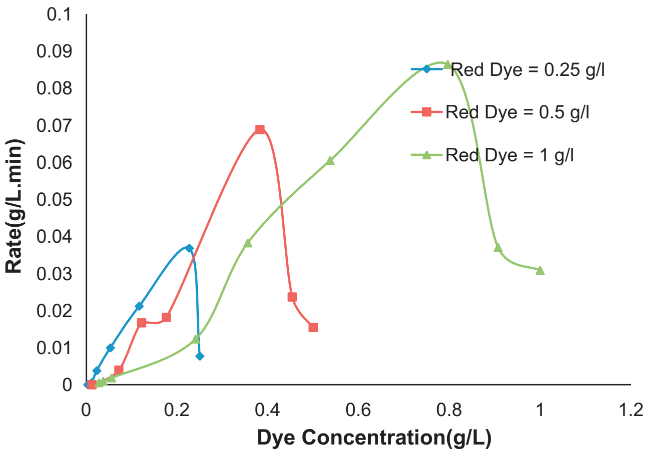


Fig. 12. The rate of dye decolouration versus dye concentration (pre-ozonated) for different initial dye concentrations. Results from Fig. 8.

Fig. 12 shows how the rate of dye decolouration varies with dye concentration at different initial dye concentrations. The results found do not follow what one might at first expect. The rate for each initial concentration starts low and builds up to a maximum. Then, it follows roughly a straight line through to the origin. This latter part of the curve one might attribute to a first order reaction for each of the curves as shown in Fig. 11. We note that on this plot, taking the logarithm of the dye concentration emphasises the latter part of the curve (low concentrations), while the plot in Fig. 12 emphasises the high concentrations.

The other very important point we discovered is: while for each of the separate initial concentration experiments, we get something approaching linear kinetics for the latter parts of the curves, the higher initial concentration curves give lower rates. Whatever models one produces to explain the results would need to address this apparently anomalous behaviour.

7. Summary and conclusions

The ozonation at alkaline pH of reactive dye hydrolysates was observed to be effective in partially oxidizing and completely decolourising textile dyes at relatively high concentrations. In order to better understand the process of decolouration, further experiments were conducted. This was done with the view to eventually model the process. It is clear from the results found that the process is complex. A summary of the important points is listed below in bullet form. A successful model would need to incorporate the phenomena listed here.

- Stoichiometry shows many dye molecules are expended per ozone molecule. This suggests a radical chain reaction.
- There was a difference between the results of experiments where the solution was pre-ozonated and those where it was not. The former gave more consistent results and showed slightly higher initial rates.
- Different coloured dyes had different rates of decolouration. This suggests the rates are not totally mass transfer controlled.
- The rate of ozone dissolution is relatively slow but faster than the reaction rate. This suggests that in doing the modelling, both phenomena may need to be taken into account.
- Mass transfer rate could be modelled using a standard mass transfer model.
- It was found with faster stirrer speeds the results were independent of stirrer speed, thus one could regard the vessel as well mixed.
- Different ozone concentrations in the gas phase gave rise to different rates of decolouration. However, in order to achieve the higher concentration, lower flow rates of gas were used. The effects were however quite small
- The latter part of each decolouration experiment could be described by first order kinetics in the remaining dye concentration.
- The higher the initial dye concentration, the lower this first order rate. Again, this is a very surprising result needing to be explained by the model.

It is clear from the above that the system's model will need to be quite complex. In order to design an industrial decolouration plant such understanding is necessary. In order to gain more information about the system, the same apparatus was used for experiments where the dye was flowed continuously through the apparatus. These results are described in a subsequent paper. If we can then produce such a model, then we will be in a position to effectively design systems for use in decolourising dye waste utilising ozone.

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