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Determination of fast ozone oxidation rate for textile dyes by using a continuous quench-flow system

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ABSTRACT

To study the fast kinetic decolourisation of textile dyes by ozone a continuous quench-flow system was used. This system has not been used before for these purposes. Reaction times in the range of 7–3000 ms were explored. The reaction was quenched with potassium iodide, which proved to be very effective, and the indigo method was used to follow the ozone concentration. Dyes from the most representative chemical classes currently used in the textile industry, i.e. azo and anthraquinone, were selected. Using the initial slope method, the effect of dye and ozone concentrations was researched and the kinetic equations thus established. Using *tert*-butyl alcohol, as radical scavenger, and pH close to 2.5, the second-order rate constant of the reactant dyes at 280 K varies in the range of 1.20×10^4–7.09×10^5 M^{-1} s^{-1}; the Acid Orange 7 exhibiting thus its lowest value, the Acid Blue 45 its highest value and the Acid Green 25 and 27 and Direct Yellow 4 intermediate values ($\approx 1.6 \times 10^5$ M^{-1} s^{-1}). Without radical scavenger and the pH close to 4, the reaction rate increases one order of magnitude, but, on the reverse, the efficiency of ozone to decolourisation decreases.

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1. Introduction

The environmental concern resulting from the increasing contamination of natural water supplies by refractory pollutants makes the use of less conventional depuration technologies highly pertinent, as it is the case of chemical oxidation. Thus, the powerful oxidizing capabilities of ozone alone or in combination with UV radiation and hydrogen peroxide are being increasingly applied to the treatment of wastewater effluents containing hazardous organic and inorganic compounds, namely pharmaceuticals, pesticides, aromatic compounds, absorbable organic halogens, textile dyes and many other chemicals, which are difficult or expensive to remove through biodegradation or through other physicochemical processes [1–3]. Ozonation can be applied to achieve pollutants complete oxidation (*i.e.* mineralization) or for biodegradability enhancement through chemical breakdown of refractory compounds into smaller and less recalcitrant molecules by partial oxidation [2,4].

Textile effluents are characterized by their strong colour due to incomplete dye fixation on fibres, which varies from 5% to 80% of the initial amount of dye used [5]. Besides, the direct impact on receiving waters coming from coloured wastewaters discharge, the recalcitrant nature of dye molecules to biological treatment processes and the possibility of toxicity and carcinogenicity of some dyes causes the use of physicochemical treatment processes, including chemical oxidation [1,5]. Dyes present in textile wastewaters are highly structured molecules comprising two key components: the chromophore that constitutes the colour, and the functional group, which bonds the dye to fibre. According to the Colour Index (C.I.) dyes are usually classified by their chemical structure as azo, anthraquinone, triarylmethine, phtalocyanine, etc.; or with regard to the method and domain of usage as direct, acid, basic, reactive, disperse, etc. The annual consumption of the 10,000 dyes currently available used in the textile industry is estimated to over 7105 tons [6]. Among these dyes, azo dyes are the largest and the most important of the chemical classes, accounting for over 50% of all commercial dyes [7]. These organic compounds are characterized by their chemical stability due to the presence of one or several azo groups (N=N), mainly bonded to substituted benzenes or naphthalene rings. Some azo dyes and their precursors are potentially hazardous compounds that have been shown to be or are suspected to be human carcinogens [1]. The pollution problem is aggravated for more than 53% of these chemicals are non-biodegradable, so the dyes release cannot be avoided, even though the most widespread treatment methods based on biological processes are used [8]. Anthraquinone dyes constitute the

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second most important class of textile dyes and are characterized by their wide range of colours, good fastness and durability due to the very stable anthraquinone structure, which is also responsible for their recalcitrant nature, the decolourisation being thus very difficult to achieve through conventional treatment processes [9]. Removing dyes from textile wastewaters by oxidation has proved to be a difficult and expensive process. However, from a practical point of view, decolourisation through ozonation requires a lower oxidant load than mineralization once only the chromophore group needs to be target, thus becoming a pre-treatment step for the conventional biochemical processes to be taken into account [1,10]. Besides the increasing interest on ozone oxidation in water and wastewater processing, the amount of information required for better knowledge of both the products and the rate of reaction of pollutants to be degraded by ozone on the aqueous phase is scarce [2,11,12]. Several methodologies have been used to study the oxidation of inorganic and organic compounds by ozone, including textile dyes. One of the most widespread methodologies utilizes a heterogeneous system where mass transfer from the gas phase to the liquid phase is concomitant with the chemical reaction [10,13–16]. In this approach the kinetic rate constant is estimated according to the film theory, after identifying the kinetic regime valid for those particular conditions [13]. A different approach has been used by Hoigné et al. [17–19] since 1983: the aqueous solutions of ozone and the substrate under research (organic and inorganic compounds) were mixed and the ozone concentration in the liquid phase followed through absorbance readings at 258 nm or by using the indigo method, exploring the 1–100 s time scale. The stopped-flow spectrophotometer systems have also been used to follow fast reactions in aqueous solution. Kuo and Huang [20] have used a stopped-flow spectrophotometer system, which enables the reagent concentration in milliseconds time scale in ozonation experiments with chlorophenols follow up. Recently, a continuous quench-flow system (CQFS) has been used to study the oxidation of pharmaceuticals by ozone [3].

As far as dyes concerned, the available kinetic data are relatively scarce and the majority was obtained in gas–liquid systems, where ozone mass transfer is certainly the limitation step, but from which it is possible to extract the accurate chemical reaction rate [13]. However, the published data revealed some contradictions. For example, López-López et al. [10] have reported that experiments with monoazo and diazo dyes present a decline in the overall rate constant with the increase in the initial dye concentration, which is *a priori* an unexpected conclusion. In addition, several authors have reported reaction rate constants lower than expected for aromatic compounds attained through the gas–liquid systems. On the contrary, Benitez et al. [13], using the same gas–liquid system, have reported values a few orders of magnitude higher, in the range of 10^5–10^6 M^{-1} s^{-1} for the ozonation of *p*-hydroxybenzoic acid. Several authors, using a homogeneous reaction medium [17–19], competitive kinetics [11] and rapid-scan stopped-flow systems [20,21] have reported second-order rate constants of the same magnitude of those reported by Benitez et al. [13]. Therefore, the development of an experimental methodology liable to enable the study of textile dyes ozonation in homogeneous medium clearly represents an advantage, particularly if the determination of substrate and ozone concentration is possible for very short reaction times.

The objective of this study was to analyse the very fast oxidation rate of representative classes of dyes by ozone in a homogeneous aqueous medium (without mass transfer limitations), using a micro-plug-flow reactor followed by a quenching system. Commercial and reactant dyes, namely azo and anthraquinone, were selected and *tert*-butyl alcohol (TBA) added as radical scavenger in order to minimize the impact of hydroxyl radicals on the oxidation rate. The effect of the dye and ozone concentrations on the reaction rate was analysed by using the initial rate method and therefore the kinetic established. The impact of radicals and pH of the reaction medium was also assessed.

2. Materials and methods

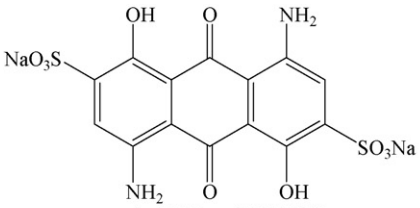
2.1. Reagents and dyes

All the chemicals used for these experiments, except the dyes, were of analytical grade and purchased from Merck (Darmstad, Germany) or Fulka (Buchs, Switzerland). The Acid Green 25 (AG25), Acid Green 27 (AG27) and Direct Yellow 4 (DY4) dyes were purchased from Aldrich (Buchs, Switzerland), and the Acid Orange 7 (AO7) and Acid Blue 45 (AB45) dyes from Acros Organics (Geel, Belgium), and will be referred as reactant dyes; the others were the commercially available dyes for current use in textile industry, and were directly used. The Acid Blue 62 (AB62) was the commercial product – Telon Lichtblau RR 182% and Acid Red 118 (AR118) the Supramin Red GW; were both provided by Dystar (Porto, Portugal). The dye contents of the reactant dyes are known (see Table 1) and the solutions were prepared accordingly. Regarding commercial dyes, no information is available, and they were considered as pure dyes. The chemical structure and main characteristics of the dyes are shown in Fig. 1 and Table 1. All solutions were prepared with distilled water (conductivity below 1 μS/cm).

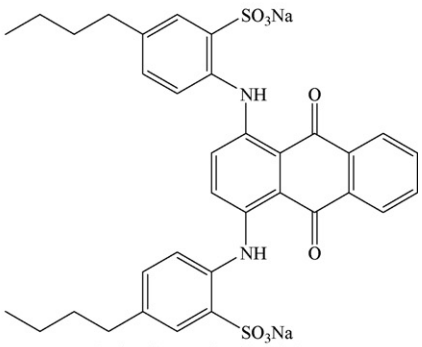
2.2. Experimental setup

A Fischer Model 502 (Bonn, Germany) ozone generator was employed to produce ozone gas from dry, pure oxygen. Aqueous solutions of dissolved ozone were prepared by bubbling the ozone/oxygen mixture into cooled (3–5 °C) distilled water, previously acidified to pH 2.5 with a sulfuric acid solution (2.5 M), during 15–30 min till saturation. The absorber is a closed vessel provided with a mechanical stirrer. Different ozone concentrations in the aqueous solution were obtained by changing the power of the ozone generator. The ozone concentration remains practically constant during each series of essays. Dye aqueous solutions were prepared by dissolving the appropriate amounts of reagent (dye), considering their purity (if available), in distilled water. Then, the pH was adjusted to 2.5 by means of a sulfuric acid solution 2.5 M. In short, if nothing further is mentioned, both the ozone solution and the dye solution have pH close to 2.5 in order to minimize the hydroxyl radicals generation by ozone decomposition in alkaline medium. A radical scavenger, *tert*-butyl alcohol (TBA), was added to the dye solutions in order to get a 94 mM concentration. TBA is practically inert towards ozone ($k_{O_3} \leq 3 \times 10^{-3}$ M^{-1} s^{-1}), but it is very effective as a radical scavenger ($k_{HO} = 6 \times 10^8$ M^{-1} s^{-1}) [22].

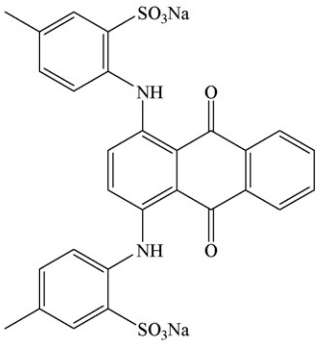
To carry out the kinetic studies, a micro-plug-flow reactor was setup (Fig. 2). The reactor (a Y connector) comprises a very small tube made of polyoxymethylene (internal diameter: 2.5 mm; tube length: 13 mm) filled with 1 mm glass beads with the aim to ensure good initial mixing of the two reactant streams, to reduce the volume and achieve a close to plug-flow pattern. A two channel peristaltic pump was used to drive both aqueous solutions (ozone and substrate solutions) into the reactor chamber and from it into the quenching solution: potassium iodide (KI) or indigo solution. Tubing made of Tygon ST, the Y connector and the peristaltic pump were produced by Ismatec (Glattbrugg, Switzerland). After reaching steady-state, the reactor exit flow is made to contact with a 1 g of finely dispersed KI introduced in a glass cup under magnetic agitation, where the reaction medium is progressively accumulated until almost 50 mL were collected (the reactor exit is placed below the liquid level). Parallel essays were carried out by using indigo reagent for the determination of the ozone concentration at the reactor exit in case of trials with dyes having absorbance bands



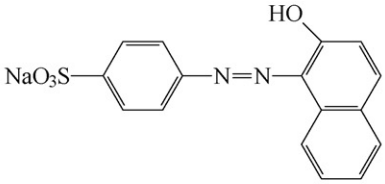
Acid Blue 45 (AB45)



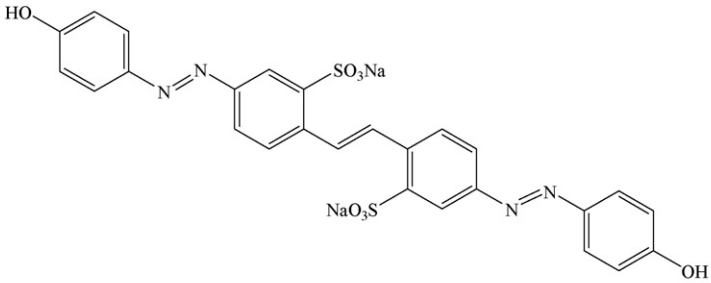
Acid Green 27 (AG27)



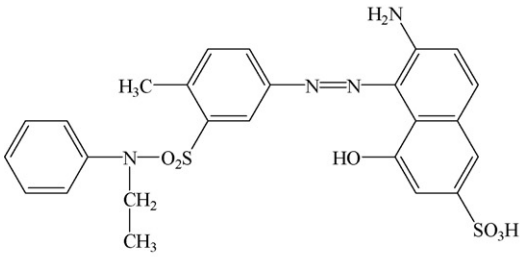
Acid Green 25 (AG25)



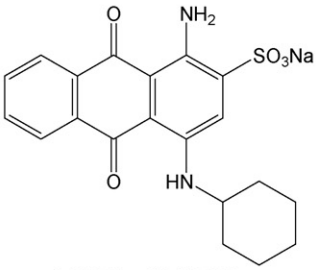
Acid Orange 7 (AO7)



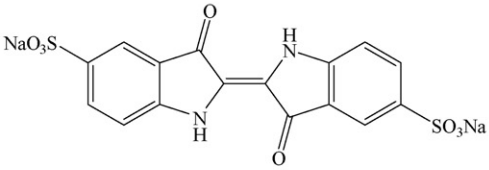
Direct Yellow 4 (DY4)



Acid Red 118 (AR118)



Acid Blue 62 (AB62)



Indigo

Fig. 1. Chemical structure of the selected dyes.

Table 1
Main characteristics of the selected dyes.

Name (code)	Dye class	Colour index	Purity (%)	λ_{max} (nm)	Molecular weight (g mol^{-1})
Acid Blue 45 (AB45)	Anthraquinone	63,010	100	596	474.3
Acid Green 27 (AG27)	Anthraquinone	61,580	65	604	706.7
Acid Green 25 (AG25)	Anthraquinone	61,570	75	607	622.6
Acid Orange 7 (AO7)	Azo (monoazo)	15,510	85	485	350.3
Direct Yellow 4 (DY4)	Azo (diazo)	24,890	70	404	624.6
Acid Blue 62 (AB62)[a,b]	Anthraquinone	62,045	–	596	431.0
Acid Red 118 (AR118)[a,c]	Azo (monoazo)	–	–	490	540.0
Sodium Indigo disulfonate	–	73,015	94	611	466.4

[a] Commercial dyes.
[b] Telon Lichtblau RR 182% (Dystar).
[c] Supramin Red GW (Dystar).

out of blue colour. The capacity of KI to stop the reaction between ozone and dye molecules, the remaining ozone being immediately consumed, will be demonstrated in Section 3.1.

The volumetric flow rate of each channel as well as the global one were measured at the beginning and end of each experimental series and less than 1% variation was reported. The free reactor volume is 50 μL and the global flow rate ranged from 50 to 420 mL/min, which made it possible to have space-times (equivalent to reaction times in batch reactor) between 7 and 60 ms. These very small reaction times proved to be essential to assess the very fast reaction rates between ozone and dye molecules. The attained values are 10 times lower than those previously reported by other authors who have also used the CQFS to study the oxidation of pharmaceuticals [3]. Higher reactor volumes were used to increase the reaction time, if or when necessary, for the study of slower reaction rates. The temperature of all experiments was measured at the reactor exit and a variation from 6 to 11 °C was verified. For each dye, several series of experiments were carried out with different initial dye and ozone concentrations. In turn, each series comprises four or more points corresponding to different reaction times. Each point represents the average of at least three determinations of the dye and ozone concentration, after the reactor has attained steady-state. In order to assess the contribution of the hydroxyl radicals to decolourisation, experiments were carried out without pH adjustment and/or scavenger addition.

2.3. Analytical methods

The decolourisation of the dyes was determined following the absorbance at the maximum visible absorbance wavelength of the dye (λ_{max}) in the KI quenching solution, after iodine reduction with sodium thiosulfate ($Na_2S_2O_3$). This procedure ensures practically no interference with the dye absorbance measurement, which is not the case with the indigo, even for the dyes whose absorbance bands do not match the blue colour. Several standard dye solutions were prepared with the KI titrated solutions used to measure the initial and final ozone concentration, and the correlation between concentration and absorbance was preserved (data not shown). The ozone concentration in the aqueous solutions was determined by the indigo method, using the procedure of Bader and Hoigné [23] where only minor modifications were introduced. Sodium indigo disulfonate (Table 1) was used, instead of potassium indigo trisulfonate. The 1 mM stock solution of indigo reagent was prepared by dissolving 0.496 g/L of sodium indigo disulfonate in 20 mM phosphoric acid. For the determination of the aqueous ozone concentration, series of 100 mL volumetric flasks were prepared. To each flask 10 mL of 0.5 M phosphate buffer reagent (for pH 2), 5 mL of 1 mM indigo stock solution and variable volumes of ozone aqueous solution were added; finally, distilled water was added to 100 mL mark and the absorbance at 611 nm measured by means of a spectrophotometer Thermo Scientific model Helios Omega (England). The absorbance was also measured in a blank solution, without ozone solution added. A stoichiometric factor of 1 was assumed for the reaction between ozone and indigo, as previously established by Bader and Hoigné [23]. For experiments with blue dyes, *i.e.* AB45 and AB62, the ozone concentration was measured by determining the iodine resulted from the reaction with potassium iodide by using the titration technique based on the standard method [24]. These analytical procedures and the experimental setup ensure a global repeatability close to 5%. Summing up, the experimental setup proved to be reliable and ensures a good global repeatability besides the very small reaction times necessary for decolourisation.

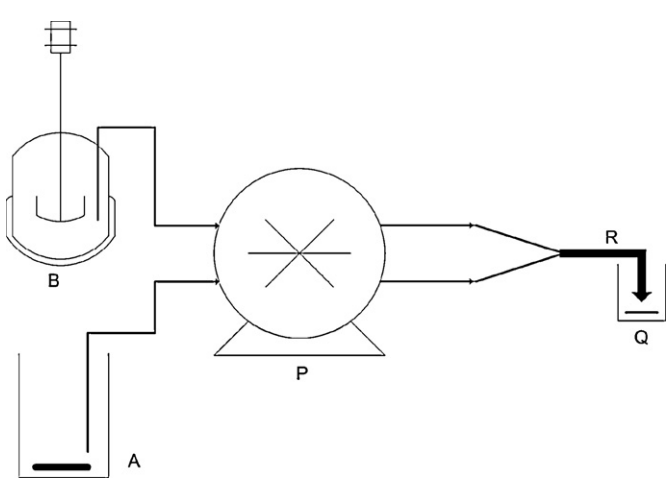


Fig. 2. Experimental setup (A, dye aqueous solution with magnetic stirring; B, ozone aqueous solution with mechanical stirring; P, peristaltic pump; R, micro-plug-flow reactor; Q, quenching solution with magnetic stirring).

3. Results and discussion

3.1. Methodology development

Preliminary decolourisation tests using a gas–liquid system have revealed the extremely low (close to zero) ozone concentration in the aqueous phase during the first minutes of reaction, which confirms the very high reaction rate expected and the gas–liquid mass transfer as the limiting resistance. According to these results, a new experimental setup was designed, including a micro-packed-bed reactor (of 50 μL volume), which enables the exploration of reaction times from 7 to 60 ms (for further details see Section 2.2).

In order to evaluate the suitability of the KI to immediately quench the reaction, competitive essays were carried out between KI and indigo. The rate constant for the reaction between indigo and ozone was reported to be 9.4×10^7 M^{-1} s^{-1} [11]. To carry out the competition study, a solution containing both indigo (5 mL of 1 mM

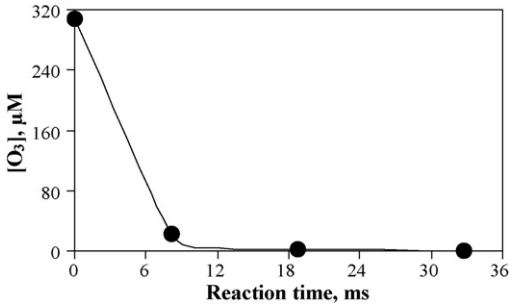


Fig. 3. Ozone concentration *vs.* reaction time, using Acid Red 118 in excess ($[AR118]_0$ = 2 mM).

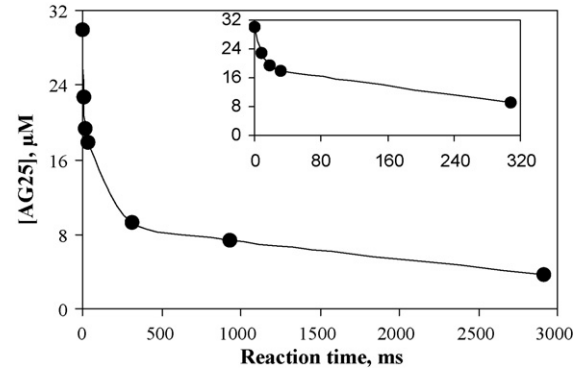


Fig. 4. Dye concentration *vs.* reaction time (inset figure: dye concentration for very short reaction times; the axes have the same units). *Experimental conditions*: $[AG25]_0$ = 30 μM, essays with scavenger [TBA] = 94 mM at pH close to 2.5.

indigo solution and 10 mL of 0.5 M phosphate buffer reagent) and 0.5 g of KI was prepared and used as quenching medium in essays with an ozone saturated solution. Parallel essays were carried out with the indigo alone, using in both cases 20 mL of ozone solution. Without KI, the indigo consumption was 4 μmol, corresponding to a 200 μM ozone solution. With 0.5 g of KI added, the indigo consumption was 0.14 μmol, which shows a higher reaction rate of ozone with KI than with indigo. Therefore, under the selected reaction conditions, KI proved to be even more effective to stop the reaction between ozone and dyes than indigo.

Using the experimental setup previously described, one series of preliminary tests were carried out with initial concentrations (after mixing the two streams) of 2 mM and 300 μM, respectively, for AR118 dye and ozone. This approach will ensure an excess of dye, regarding ozone, which enables the analysis of the ozone profile as a pseudo-first-order reaction with respect to ozone. However, the ozone concentration profile monitored by the indigo method presented in Fig. 3 reveals that after the first measurement the ozone concentration approaches zero. These data demonstrate the extremely high ozone reaction rate, but the sudden and complete consumption of ozone after 7–8 ms of reaction time makes the use of the integrated method unreliable to analyse the data in order to extract the pseudo-first-order reaction constant. Therefore, a different approach was decided for the kinetic studies. The initial reaction rate method (also referred in literature as initial slope method) was used to estimate the reaction rate and the initial concentrations ranged from 100 to 312 μM (or 4.8–15 mg/L) for ozone, and between 7.5 and 90 μM for the dyes (reactant and commercial mixtures). The ratio between ozone and dye ensures that ozone is available during the reaction period. For each set of initial ozone and dye concentrations one series of essays was carried out, corresponding to a reaction time which ranged from 7 to 3000 ms. The high range of reaction times was easily obtained using reactor volumes of 500, 1500 and 4500 μL. Fig. 4 illustrates the AG25 dye concentration profile up to 3 s reaction time, which resulted from the conversion of absorbance measurements at the λ_{max} for the dye using a calibration curve. It is important to notice that the oxidation rate for this anthraquinone dye is extremely high.

The complex nature of ozonation reactions with organic compounds is clearly pointed out in literature [17,25], and is mainly due to the presence of both molecular ozone and hydroxyl radicals in the reacting medium. Although decolourisation in most cases is fast to achieve because it only requires the cleavage of the chromophore group, parallel reactions with other electron rich groups will occur possibly at different rates. In addition, the partially oxidized sub-products, such as organic acids, aldehydes and ketones, undergo further transformations, consuming ozone. On the other hand, it is hard to keep one of the reactants (ozone or substrates) in large excess. In spite of the high initial ratio of ozone/dye, the ozone concentration can decrease 50% of its initial value, which not enable to consider it as practically constant in order to simplify the kinetic data analysis by the integral method. Therefore, the initial reaction rate method, which consists in the determination of the reaction rate for the initial reaction conditions, is the best suited, because the ozone and dye concentrations are unambiguously known and no sub-products are present.

In order to get the initial reaction rate, the experimental data of each series of essays should be fitted with an appropriate function and the derivative at zero time determined. The non-zero dye concentration for the time scale explored indicates that an irreversible reaction is not acceptable and instead an exponential decay function with a non-zero term of the type:

$$y = y_\infty + y_0 \exp(-kt) \quad (1)$$

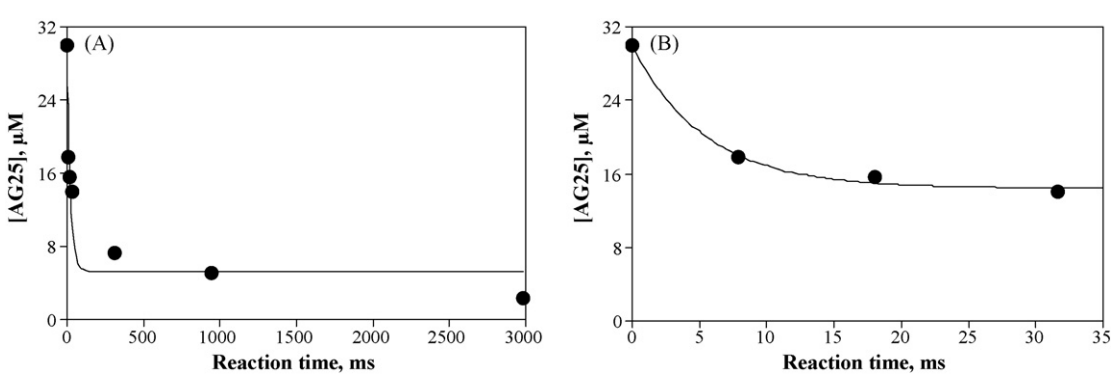


Fig. 5. (A) Model fitting considering all data points up to 3 s and (B) up to 40 ms of reaction time. *Experimental conditions*: $[AG25]_0$ = 30 μM, essays with scavenger [TBA] = 94 mM at pH close to 2.5.

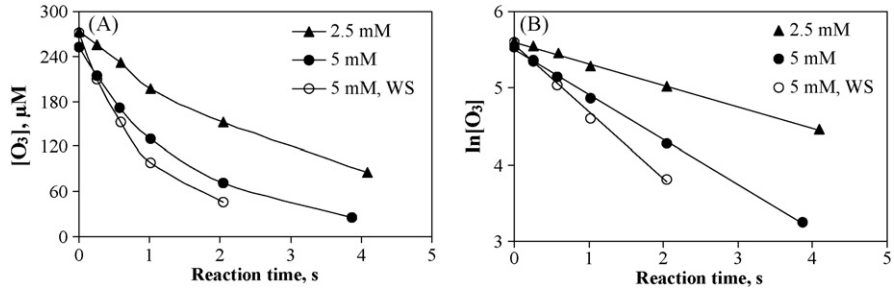


Fig. 6. (A) Ozone concentration profile and (B) logarithmic ozone concentration profile for experiments with anisole in large excess. *Experimental conditions*: $[\text{anisole}]_0$ = 2.5 and 5 mM with scavenger [TBA] = 94 mM and $[\text{anisole}]_0$ = 5 mM without scavenger – WS, the pH was set to 2.5 for all trials.

was used to fit the experimental data. If the results in the 7–3000 ms range were considered with the same weight the fit is unacceptable (Fig. 5(A)). On the reverse, the fit proves to be very good if only the first four experimental data points are considered, as shown in Fig. 5(B). The different quality of the fittings including all data or only the first four points (fast reaction period) suggests that the kinetic of the reaction under research changes according to the oxidation extent, which also reinforces the soundness of the previous choice of using the initial reaction rate method to analyse the dye oxidation kinetic by ozone. The choice of Eq. (1) for fitting the data of the fast reaction period is kinetically reliable because ozone can be considered in large excess in this short period of time, which leads to the pseudo-first-order reaction rate regarding the dye and thus to the exponential decay.

In order to confirm the robustness of the present experimental methodology, the oxidation of anisole by ozone was studied and the results compared with those already published by other authors. In this study the volume of the plug-flow reactor was 1.5 mL, once the reaction rate is lower than that for dyes decolourisation. In this case an excess of anisole in what ozone is related could be used. Fig. 6(A) shows the ozone concentration profile for three series of essays. Two of these essays were carried out with radical scavenger (TBA at 94 mM) and anisole initial concentrations of 2.5 and 5 mM, and one without radical scavenger (WS) and 5 mM anisole. Fig. 6(B) shows the same data by using logarithmic scale in the *Y*-axis, and the linear profile demonstrates the pseudo-first-order of the reaction with respect to ozone, as have previously been established by Hoigné and Bader [17]. All the data series represented in Fig. 6(B) had correlation coefficients over 0.99. A second-order rate constant of 113 and 117 $M^{-1}\,s^{-1}$ was obtained for the 2.5 and 5 mM anisole initial concentration, which makes it possible to point out a mean value of 115 $M^{-1}\,s^{-1}$ for the 7 °C reaction rate constant. Assuming an activation energy of 35 kJ/mol [17], at 23 °C the reaction rate constant would be 260 $M^{-1}\,s^{-1}$, which is in close agreement with the reported data of Hoigné and Bader [17]. Without radical scavenger, the rate constant increases to 175 $M^{-1}\,s^{-1}$, at 7 °C.

Table 2
Initial reaction rate for nine series of decolourisation experiments with AG27 and [TBA] = 94 mM at pH 2.5.

[AG27] (μM)	$[O_3]$ (μM)	Temperature (°C)	r_0 (mM s^{-1})
15.0	227.2	9.0	0.65
13.5	324.0	7.5	0.79
30.0	179.4	7.0	0.98
30.0	306.0	8.0	1.05
30.0	316.0	7.0	1.12
30.0	296.3	7.0	1.21
30.0	323.0	6.5	1.45
30.0	300.0	10.0	1.46
45.0	307.2	7.0	2.01

3.2. Oxidation rate of dyes

The oxidation kinetic of five textile dyes from the most representative chemical classes, *i.e.* anthraquinone (AG25, AG27 and AB45) and azo (AO7 monoazo and DY4 diazo) was researched in homogeneous medium using a quench-flow technique, enabling the exploration of reaction times in a very low range, from 7 to 60 ms. In order to assess the oxidation rate by ozone, acidic medium was selected (pH close to 2.5) and TBA was introduced as radical scavenger (94 mM). To evaluate the role of the hydroxyl radicals, experiments were also carried out neither with radical scavenger nor with pH adjustment. Besides these experiments with reactant dyes, two commercial mixtures with AB62 (anthraquinone) and AR118 (monoazo) were also studied.

Fig. 7 shows the profile concentration for essays with reactant dyes at pH close to 2.5 and TBA addition. In Fig. 7(A) and (B) the time frames were adjusted to decolourisation rate, which is clearly different for the AO7 and for the other dyes. As an example, Table 2 presents the initial reaction rates (r_0) for several sets of dye and ozone initial concentrations, for the AG27 dye. The decolourisation reaction rate increases significantly with ozone and dye concentration from 0.65 up to 2.01 mM s^{-1}, as expected. Results published by López-López et al. [10] using experimental conditions where

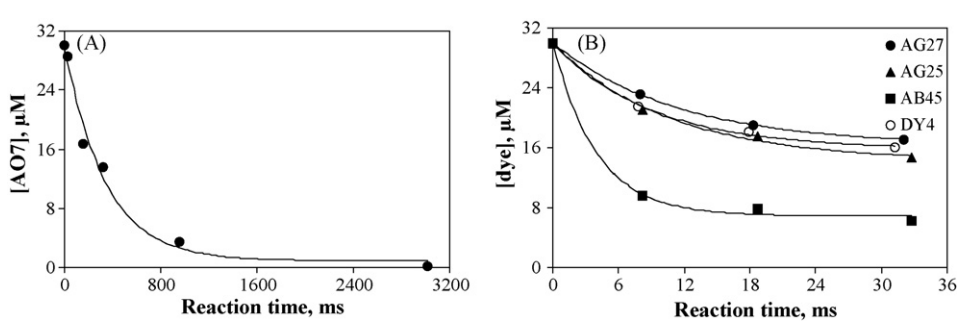


Fig. 7. Concentration profile of reactant dyes during ozonation: (A) for the monoazo dye and (B) for the other reactant dyes. *Experimental conditions*: $[\text{dye}]_0$ = 30 μM, scavenger [TBA] = 94 mM and pH close to 2.5, $[O_3]_0$ from 256 to 296 μM.

Table 3
Parameters of Eq. (2) estimated for the AG27 decolourisation by ozone.

Parameter	Estimate	Standard deviation	95% conf. interval
k_0[a]	5.74×10^3	1.10×10^4	-2.12×10^4 to 3.27×10^4
E_a[b]	35.0×10^3	Fixed	–
α	0.97	0.18	0.52 to 1.42
β	0.59	0.35	−0.26 to 1.44

[a] $\mu M^{-\alpha-\beta+1}\ ms^{-1}$.
[b] J/mol.

mass transfer and chemical reaction take place simultaneously have reported a decrease in the overall rate constant when initial dye concentration increases, but these results are probably a consequence of the lower ozone concentration in the aqueous phase, as the authors recognised.

The effect of the ozone and dye concentration on the decolourisation rate can be described according to the following equation:

$$-r_{dye} = k(T)[\text{dye}]^{\alpha}[O_3]^{\beta} \quad (2)$$

where $[O_3]$ and [dye] represent the concentration in the aqueous phase of ozone and dye, respectively. The equation parameters were estimated by using a weighted orthogonal distance regression software package (ODRPACK). The best estimates, the standard deviation and the parameter interval for 95% confidence, for the AG27 dye are summarized in Table 3. The activation energy was fixed at 35 kJ/mol, according to Hoigné and Bader results [17].

The model estimates *vs.* experimental data for AG27 and AB62 are represented in Fig. 8, showing a good fit quality. The best estimates are of the same magnitude as those reported by Hoigné and Bader [17] for several low molecular organic compounds, but significant differences in the reaction orders were revealed, however. The accepted mechanism describing the reaction of ozone with double bond in compounds is that proposed by Criegee, which comprises three elemental reaction steps [26]. If the first elemental step is bimolecular and the successive steps have a higher reaction rate, then the first one is the controlling step, and consequently the reaction rate should be of the first-order with respect to ozone and substrate concentration. Nonetheless, in complex molecules as it is the case of dyes, several double bonds of different electron densities are available for reaction, which probably contributes to a different extent to decolourisation. So, it is not totally unexpected that the reaction order with respect to ozone and dye concentration is not necessarily of first-order. Most frequently, the decolourisation rate results published were obtained considering the assumption of first-order with respect to ozone, and the values reported are those that best fit this model. As can be seen in Table 3, the 95% confidence interval for the ozone reaction order is relatively large and includes the first-order. Moreover, assuming that the reaction rate regarding ozone and dye concentrations is of first-order, the residuals only increase from 0.12 to 0.14. So, the experimental data do not enable us to state that the reaction orders are not unitary.

Similar series of experiments and data analysis were carried out for several other different dyes, including the commercial products. Table 4 resumes the best estimates and the overall second-order rate constants, assuming a first-order reaction with respect to both ozone and dye concentration. With reference to reaction orders, a significant variance was observed, as shown in the standard deviation, but the possibility of first-order reaction with respect to ozone and dyes is not completely excluded. Peng and Fan [27] have studied the kinetics of the reaction between Acid Blue 9 (monoazo) and ozone dissolved in aqueous phase, using a pulse-ejection microreactor, and concluded that pseudo-first-order with respect to ozone was only valid for ozone to dye molecular ratios from 5.57 to 9.31, and zero for lower ratios, which confirm the complexity of the reacting system.

Due to similar chemical structures both AG25 and AG27 anthraquinone dyes present close reaction rate values, as expected. DY4 (diazo) exhibits similar reaction rate, AO7 (monoazo) one order of magnitude lower and AB45 (anthraquinone) close to 5 times the reaction rate of AG25, AG27 and DY4. The reaction rate depends on the chemical structure of the dye, but it is difficult to establish a correlation as only five reactant dyes, from two chemical classes, were studied. It is important to notice that these results clearly show the sensitivity of the experimental setup and the analytical procedures followed in this paper. Secondly, the magnitude of the second-order rate constant achieved for the dyes is very high, as expected for aromatic compounds. If the rate constant is referred to ozone, the value will be 3–5 times higher due to ozone/dye stoichiometry, which is situated at least in the range of 3–5. The rate constants are in good agreement with other researches, where other aromatic compounds are used. For instance, Muñoz and Sonntag [11], using competitive kinetic studies in a homogeneous medium, have reported second-order rate constants of 1.3×10^5 and $9.4 \times 10^5\ M^{-1}\ s^{-1}$ for 1,4-dimethoxybenzene and 1,3,5-trimethoxybenzene, respectively. Kuo and Huang [20] reported values between 1.08×10^4 and $5.60 \times 10^4\ M^{-1}\ s^{-1}$, for *p*-chlorophenol as temperature increases from 10 to 35 °C. The rate constants obtained for the commercial dyes (Table 4) are probably overestimated, as their dye content is certainly lower than the 100% assumed.

In advanced oxidation processes, the overall performance is closely associated with the production of reactive hydroxyl radicals. This chemical species exhibits one of the highest oxidation potential, which may reach up to $E^0 = 3.06$ V enabling it to oxidize a broad class of organic and inorganic compounds [28]. To assess the contribution of hydroxyl radicals to decolourisation, experiments were carried out without radical scavenger or acidification of either solutions, so the pH of the solution resulted from the mixture of dyes and ozone aqueous solutions was close to pH 4. Fig. 9 shows the concentration profile of AG27 dye in three series of essays, with (WS) and without (WOS) TBA at pH 2.5 and without scavenger and pH 4.3 (WOS at pH 4.3). It is evident the enhancing decolourisation rate without radical scavenger in the series. The initial

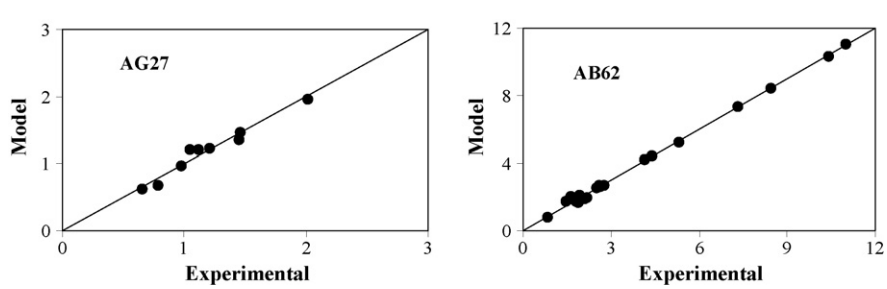


Fig. 8. Model *vs.* experimental reaction rate, for the anthraquinone reactant dye AG27 and commercial product with AB62.

Table 4
Kinetic parameters for the decolourisation of textile dyes.

Dye (number of series)	k_0 ($\mu M^{-\alpha-\beta+1}$ ms^{-1})	α	β	Residuals	k_{280K} (M^{-1} s^{-1})	Residuals
AG27 (9)	5.74×10^3	0.97 ± 0.18	0.59 ± 0.35	0.12	$1.56 \pm 0.07 \times 10^5$	0.14
AG25 (13)	4.99×10^4	0.67 ± 0.11	0.40 ± 0.23	0.37	$1.66 \pm 0.13 \times 10^5$	0.99
AB45 (8)	7.29×10^4	0.63 ± 0.28	0.61 ± 0.44	0.71	$7.09 \pm 1.04 \times 10^5$	2.13
DY4 (11)	1.49×10^2	0.70 ± 0.07	1.44 ± 0.19	0.07	$1.71 \pm 0.10 \times 10^5$	0.29
AO7 (6)	9.73×10^1	0.65 ± 0.12	1.06 ± 0.20	0.0002	$1.20 \pm 0.07 \times 10^4$	0.0010
AB62[a] (21)	3.35×10^2	0.96 ± 0.10	1.22 ± 0.20	2.83	$2.68 \pm 0.15 \times 10^5$	3.05
AR118[a] (9)	2.65×10^5	1.02 ± 0.11	0.21 ± 0.11	0.26	$1.20 \pm 0.12 \times 10^6$	2.58

[a] Commercial dye.

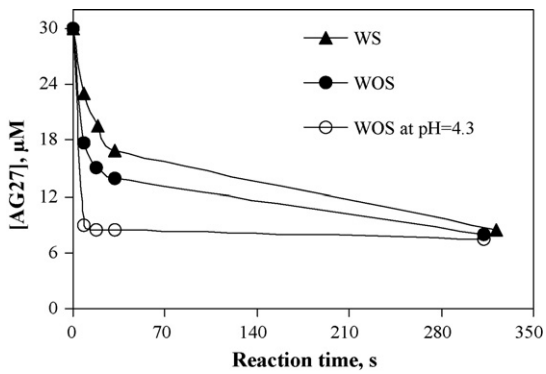


Fig. 9. AG27 concentration profile for experiments at pH 2.5 with radical scavenger TBA ([TBA] = 94 mM) (WS), without radical scavenger (WOS) and at pH 4.3 without radical scavenger (WOS at pH 4.3).

reaction rate increases from 1.12 to 2.86 mM s^{-1} and 11.3 mM s^{-1} respectively, which confirms the positive role of the hydroxyl radicals in the medium. Assuming second-order reaction, the reaction constant increases from 1.18×10^5 to 1.37×10^6 M^{-1} s^{-1}. Similar trends were observed for other dyes (data not shown).

Concerning stoichiometry, the experimental data have revealed a complex behaviour but only the general trend will be discussed here. The stoichiometric ratio (moles of ozone/moles of dye) may vary between 3 and 9. In general, there is an exponential increase of the stoichiometric ratio as the decolourisation increases with the reaction time. This is an expectable result considering ozone oxidation of sub-products and the increasing importance of other secondary reactions. The dyes of a higher molecular weight exhibit, in general, higher stoichiometric ratios, which is rational, considering the higher number of available points susceptible of being oxidized by ozone, not all of them contributing to decolourisation. In addition, the ozone efficiency decreases (the stoichiometric ratio increases) in absence of radical scavenger and particularly at pH 4, regarding pH 2.5, which is probably a consequence of ozone decomposition with hydroxyl radical generation and lower selectivity of these radicals towards the dye group.

4. Conclusions

The continuous quench-flow system was proved to be a good tool for determining fast reaction rates, as it is the case of the ozone decolourisation of the textile dyes under research. The kinetic rates of five reactant dyes and two commercial dyes, from the two most representative chemical groups of textile dyes (anthraquinone and azo dyes), were established, after having researched their decolourisation behaviour as far as reaction times in a range of 7–60 ms were concerned. The second-order rate constant for the reactant dyes at pH 2.5, temperature 7 °C and using a radical scavenger is situated in the range of 1.20×10^4–7.09×10^5 M^{-1} s^{-1}. Working without radical scavenger and at pH 4.3, the reaction rate increases one order of magnitude. In short, the reaction rate is very fast for all the dyes used in the experiments, thus meaning that the critical parameter in the design of decolourisation reactors at industrial scale is the gas–liquid mass transfer coefficient and the gas–liquid interfacial area. Another practical consequence of the very fast reaction rates of all the dyes is that the reactor performance will be practically insensitive to the dye to be dealt with.

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