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UV/H_2O_2 oxidation of azodyes in aqueous media: evidence of a structure—degradability relationship

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Abstract

Textile finishing wastewaters, discharged to rivers and public sewage treatment plants, are very often highly coloured. Faced with the resulting psychological impact on population and more rigorous standards for rejecting waste waters that has being established, textile industries have to find effective methods for discolouration. In the present paper, we demonstrate that the UV/H_2O_2 oxidation process is able to destroy totally the chromophore structure of azodyes. However the reaction rate strongly depends on the basic structure of the molecule and on the nature of auxiliary groups attached to the aromatic nuclei of the dyes. Indeed, whereas hydroxy monoazodyes are very reactive, aminoazobenzenes, chromium complex dyes and disazodyes are on the whole less sensitive to OH-induced oxidation in neutral or slightly acid media. Oxidation by hydroxyl radicals is slowed down by chloro groups or alkyl chains in the dye molecule. After a detailed analysis of the degradation rate of some specific dyes we can now propose a mechanism for the first step of the dye degradation. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Textile wastewaters; UV/H_2O_2 oxidation process; Azodyes; Chemical structure influence; Kinetics

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1. Introduction

In nearly all processes of textile finishing, problematic wastewaters occur with a high organic carbon content and strong colouration. At present, some coloured waters may be discharged into rivers and public sewage treatment plants without preliminary treatments. To remedy this problem, rigorous standards for discharging wastewaters are being established in many European countries. Thus there is an urgent need for textile industries to develop effective methods of water processing.

Recently, attention has been focused on chemical techniques that could be used to discolour textile wastewaters [1,2]. In particular, the UV/H_2O_2 oxidation process is of potential practical importance [3,4]. It is characterized by the generation of a very powerful oxidizing species, namely hydroxyl radicals [5,6]. The general pattern of the reactions of these radicals with saturated aliphatic products involves abstraction of an H atom in the rate-determining step [7,8]. On the other hand, when the organic molecule contains a double bond, the abstraction of the H atom is competed by an addition of $OH^{\bullet}$ radicals on this unsaturated bond [9]. With monosubstituted benzene rings, the main reaction is electrophilic addition

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[10,11]. However, the mechanism of the OH•-induced degradation of more complex molecules, for instance water soluble dyes, has not yet been extensively studied. In this paper, we try to formulate a structure–activity relationship to predict oxidation rate constants for a variety of azodyes. A choice of model molecules was made, based on availability and on chemical similarity with dyes of commercial importance.

2. Experimental

2.1. Reagents

The dyes were obtained from commercial suppliers (Aldrich, Fluka), from the collection of the Institut Textile de France, direction régionale de Mulhouse, or were received as a gift from Steiner Co. All products were salt free. The *O*-methyl-derivative of 4-(4-sulfophenylazo)-1-naphthol was prepared by the method advocated by Desai and Giles [12]. Hydrogen peroxide (30% w/w) and Tween 80, a commercial surfactant, are from Prolabo.

2.2. Photochemical degradation

The reactions were performed in a reversed-immersion photoreactor fitted with a low-pressure mercury lamp (15 watts, emission at 253.7 nm). The solution (5 liters) is projected at the top of the reactor, forming a thin film (about 3 mm thick) at the inner surface of the external tube. The solution is then collected in a 10-liter-reservoir, from which it is continuously pumped, as shown in Fig. 1. A sample was collected every 15 min and the remaining dye content was measured on a Perkin–Elmer 554 spectrophotometer. Rate constants and order of reaction were calculated. Where appropriate, chloride concentration was determined by the mercurimetric method [13].

2.3. Methodology

Dye concentrations were set at a value within the range of typical concentrations in textile wastewaters (5.7×10^{-5} mol liter^{-1}). The selected organic compound, at the required concentration level, was dissolved in distilled deionized water. A large excess of hydrogen peroxide with respect to the dye was added (859 mol: 1 mol), so that $[H_2O_2]$ could be considered as a constant during the whole experiment and that, comparing the extinction coefficients of H_2O_2 and of the dyes at 253.7 nm, more than 50% of the incident light was absorbed by the peroxide. The pH of the solution was measured with a TS 70/N-1 Tacussel pH-meter; it was adjusted to a value close to 5.6 by addition of sodium hydroxide or hydrochloric acid.

3. Results and discussion

The UV/H_2O_2 induced oxidation of 27 azodyes was studied. The degradation curves of some of them are shown, in Fig. 2, as the time dependent

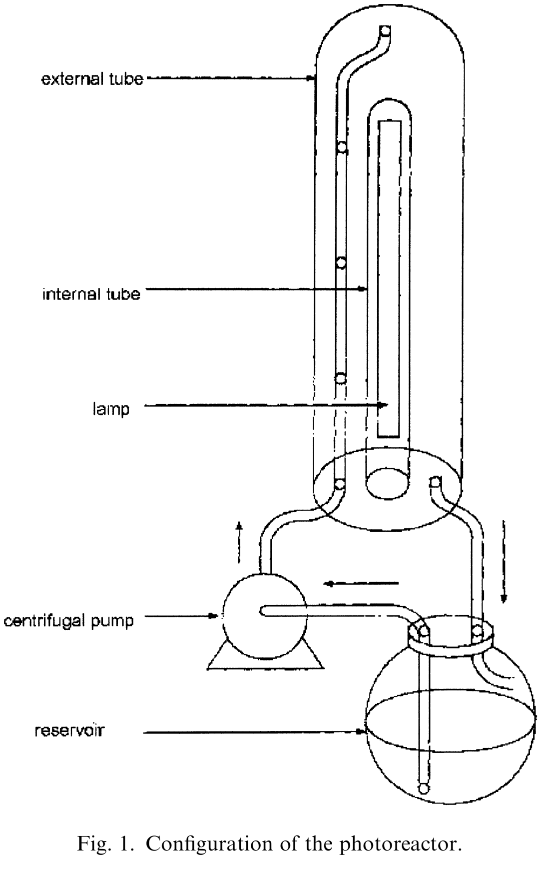


Fig. 1. Configuration of the photoreactor.

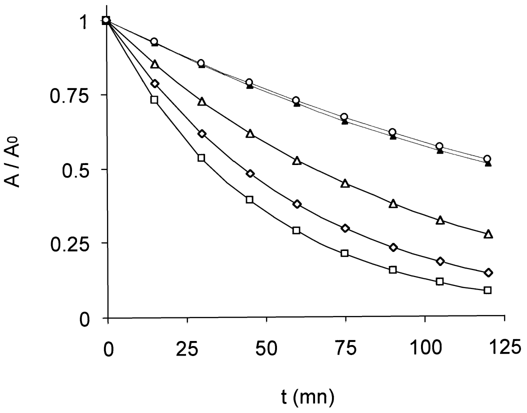


Fig. 2. Evolution of the absorbance of the solution as a function of irradiation time during the degradation of AO7 (◇), AO20 (□), AR1 (△), AO52 (▲) and AR151(o) dyes.

dye concentration. The pertinent kinetics can be described as first order with respect to the dye concentration, viz,

$$-\frac{dC}{dt} = k.C$$

where k is the first order rate constant and C is the dye concentration at time t.

The colour of an azo dye is the result of the interaction between an azo function (–N = N–) and two aromatic species: the dyes carry an acceptor group which is an aromatic nucleus frequently containing a chromophoric group, e.g. NO_2, and a donor group, e.g. an aromatic nucleus containing an auxochromic group such as NR_1R_2, or OH [14]. Decrease in intensity of the band at the maximum absorption wavelength during the irradiation also expresses the loss of conjugation, e.g. especially the cleavage near the azo bond of the organic molecule.

Fig. 2 demonstrates that, in fact, the degradation kinetics notably depend upon the basic molecular structure of the dyes. For instance, the rate for AO20, a hydroxy monoazodye, is more than three orders of magnitude higher than that of AO52, an aminoazobenzene derivative, AB161 (a chromium complex dye) and AR151 (a disazodye). Comparison of the A0 and $A0Cl_{2,4,6}$ rates permit us to postulate that the molecular structure of the auxiliary groups attached to the aromatic nucleus also plays an important part in the degradability of azodyes.

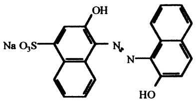
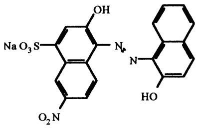
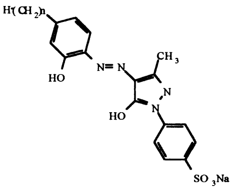
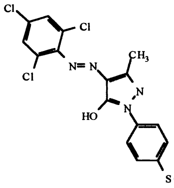
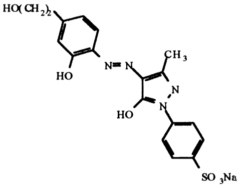
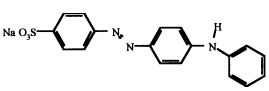
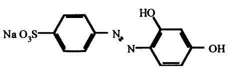
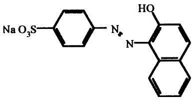
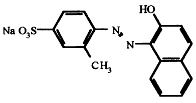
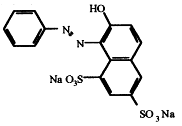
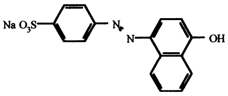
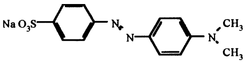
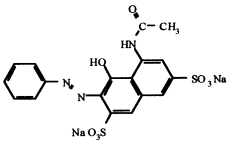
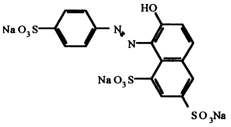
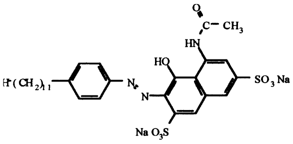
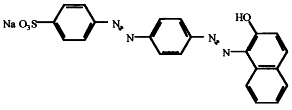
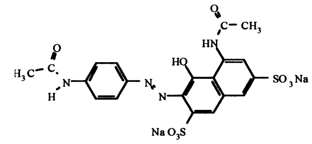
3.1. Study of the selectivity of the $OH^{\bullet}$-induced oxidation

Before assessing the effect of any substituents on the degradation rate, an analysis of the eventual selectivity and of the nature of the oxidation mechanism needs to be carried out. With this aim in view, the reactivity of some specific dyes was considered.

Only the azo tautomeric form of AO6 exists, while the hydrazone form of phenylazonaphthols (such as AO7 and AR1) and of pyrazolone derivatives (A0 for instance) predominates in aqueous solutions. However we did not observe (Table 1) any relationship between the nature of the predominant tautomeric structure and the value of the rate constant. This result is in agreement with the high reactivity of hydroxyl radicals. We can also conclude that $OH^{\bullet}$-induced oxidation is less selective than the degradation by other active forms of oxygen, for instance singlet oxygen. Indeed, in the latter case, only the hydrazone form of the dyes is destroyed at a significant rate [15].

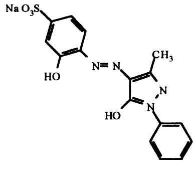
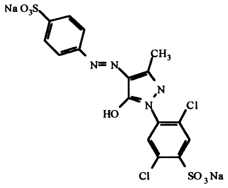
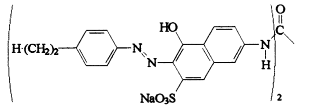
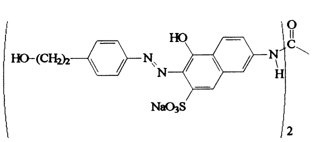
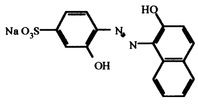
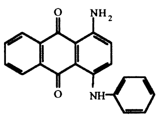
We also noticed that, in neutral media, aminoazobenzenes exhibit especially low reactivities. This particular behaviour can be explained by the absence of a labile hydrogen atom on the azo function. Indeed, in a previous paper [16], we demonstrated that the oxidation rate of AO52 can be increased by more than three orders of magnitude by protonation on the β nitrogen of the azo bond. We also noted both an important rise of the kinetic constant of the dye AO5 and an increase of the bulk acidity, as shown in Fig. 3. In the case of aminoazobenzenes, the reaction rate also drastically increases, and is of similar magnitude to that of phenylazonaphthols when the pH of the solution is close to the pKa of the organic molecule, i.e. when the percentage of the azonium protonated form of the molecule predominates in aqueous solution. An additional experiment was carried out with the *O*-methyl-derivative of AO20. In comparison to the mother dye, the latter exhibits a very marked increase in its resistance to

Table 1
Structure and reactivity of studied dyes: (1) $[\mathrm{dye}]_0 = 5.7 \times 10^{-5}$ mol liter^{-1}, (2) $[\mathrm{dye}]_0 = 1.4 \times 10^{-5}$ mol liter^{-1}

No.	Name	Structure	$1000\,k'$ (mn^{-1})
1	AB161	Chromium complex of: 	5.4
2	AB52	Chromium complex of: 	3.6
	An		
3	n=0		12.2
4	n=2		10.7
5	n=4		9.3
6	n=6		8.9
7	A0Cl$_{2,4,6}$		7.2
8	A$_2$OH		11.1
9	AO5		4.0
10	AO6		9.2
11	AO7		16.3
12	AO8		19.0
13	AO10		15.0
14	AO20		20.9
15	AO52		5.6
16	AR1		10.8
17	AR18		15.9
18	AR138		7.7
19	AR151		5.4
20	AVi7		12.7

(continued)

Table 1—*contd*

No.	Name	Structure	1000 k′ (mn^{-1})
21	AVi90	Chromium complex of: 	2.0
22	AY17		9.3
	Bn		
23	n=0		3.3 (1) 9.1 (2)
24	n=2		6.6 (2)
25	n=6		1.5 (2)
26	B2OH		2.9 (1)
27	MVi5		18.9
28	DB19		/

attack by hydroxyl radicals ($k \approx 4 \times 10^{-3} mn^{-1}$). This illustrates, once again, the far lower susceptibility to degradation of molecules which do not have a labile H atom. It is also important to notice that aminoazobenzenes and the *O*-methyl-derivative of AO20 have nearly the same reactivity. Their degradation pathway may also be similar. These observations can be explained as follows:

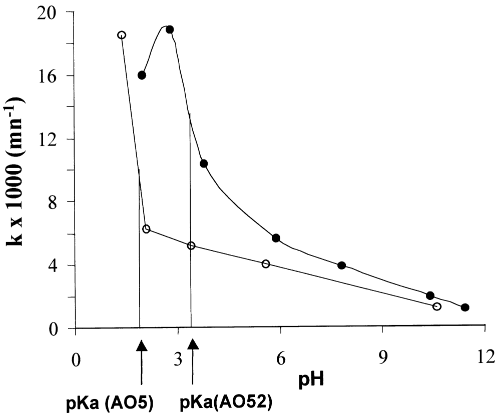


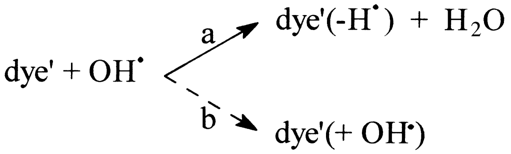
Fig. 3. Effect of pH on the photodegradation rate constant of AO52 (◇) and AO5 (□).

- According to the proposal of Spadaro [17], only an addition of an OH• radical on an aromatic ring of molecules which do not contain a labile H atom can occur.

$$\text{dye} + OH^{\bullet} \xrightarrow{b} \text{dye}(+OH^{\bullet})$$

This reaction rate is low ($k < 5.6 \times 10^{-3} mn^{-1}$).

- This mechanism is unsatisfactory for hydroxy azodyes. In that case, abstraction of a H atom (carried by an oxygen atom in the azo form and by a nitrogen atom in the hydrazone form) competes with the addition of OH• on a phenyl or naphthyl nucleus.



For dyes which are highly reactive (for instance AO20), we can postulate that (a) is the sole important pathway.

In view of these observations, we must consider whether there is any relationship between the very low reactivity of chromium complex dyes and the absence of any labile hydrogen atom on these molecules (Table 1).

On the other hand, all the dyes which contain a mobile H atom do not have the same reactivity.

For this reason, we decided to evaluate the influence on the reaction rate of the addition of specific substituents on hydroxy azodyes. The hydroxyl radical is a electrophilic entity, and whatever the main pathway may be, the electronic properties of auxiliary groups will affect the electronic density in the aromatic nucleus and on the β nitrogen atom of the azo bond. Moreover, we must bear in mind that a very large excess of hydrogen peroxide with respect to the dye was added to the solution. Thus, whereas few primary $OH^{\bullet}$ radicals generated by photolysis of H_2O_2 initiate the chain decomposition of dye molecules, most of them are scavenged by hydrogen peroxide, producing $HO_2^{\bullet}$ radicals. In fact, in the preceding mechanisms, the contribution of the reaction between these species and aromatic matter was neglected because the corresponding rate constants are very low; on the whole, they do not exceed $2\times10^{4}\,\text{liter}\,\text{mol}^{-1}\,\text{s}^{-1}$ [18]. Finally, whether we take this reaction into account or not, the relative kinetic constant values are unchanged and comparison of the reactivities of the dyes is still possible.

3.2. *Influence of acetamido and hydroxyl groups*

In order to evaluate the influence of an acetamide group, an analogous pair of dyes, AR1 and AVi7, was chosen, one of which contained an acetamido group in the para position with respect to the azo function. This substituent interacts with the phenyl ring and there is a consequent delocalization of the π electrons of the ring and of the unpaired electrons of the heteroatom. As a result, the phenyl ring is electron enriched, and the acetamido group thus favors attack of an electrophilic entity. The experiment confirms this hypothesis: the AVi7 reaction rate is slightly higher than the AR1 degradation rate.

The electronic properties of a hydroxyl group are similar to those of the acetamido substituent, i.e. −I and +M effects. That is the reason why the rate constant values increase by the same scale by replacing AO7 (an *o*-hydroxylated azodye) by MVi5 (an *o*,*o*′-dihydroxylated azodye).

Two other pairs of dyes were then selected: A2–A2OH and B2–B2OH. In both pairs, one molecule contains a hydroxyl group in a side chain. The resonance effect of a substituent operates only when the group is directly connected to the unsaturated system, so that to explain the effect of the hydroxyl group on the reactivity of the organic matter, only the field effect (−I) must be considered. Fig. 4 shows that there are no significant variations of the rate constant. In that case, the inductive effect has little influence, because of the large distance between the β nitrogen atom of the azo bond (which carries the labile H atom) and the substituent.

3.3. *Influence of alkyl side chains*

Hydroxyl radicals have a very short lifetime, so that they can only react where they are formed. Indeed, Land et al. [19] indicated that its lifetime is, for instance, approximately 70 ns in the presence of 1 mM phenol, which means that—using the Einstein–Smoluchowski equation: $\Delta x = (2Dt)^{1/2}$ with $D = 2.3\times10^{-5}\,\text{cm}^2\,\text{s}^{-1}$ for $OH^{\bullet}$ radicals—the inorganic radical can diffuse through an average distance of 180 Å. Thus oxidation reactions can only be successfully performed in homogeneous media. Consequently, every group that tends to decrease the solubility of molecules in water will disfavour degradation. This explains, at least partly, why the rate of decomposition clearly decreases with increasing length of the side chain, i.e. with increasing hydrophobicity of the substituent, as shown in Fig. 5.

Additional experiments were conducted with a disperse dye: DB19. Its basic structure (anthraquinone) is not important. The reason for selecting

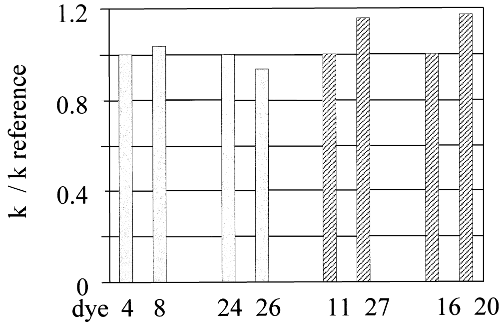


Fig. 4. Influence of hydroxyl (dyes **8**, **26** and **27**) and acetamide groups (dye **20**) on the rate constant.

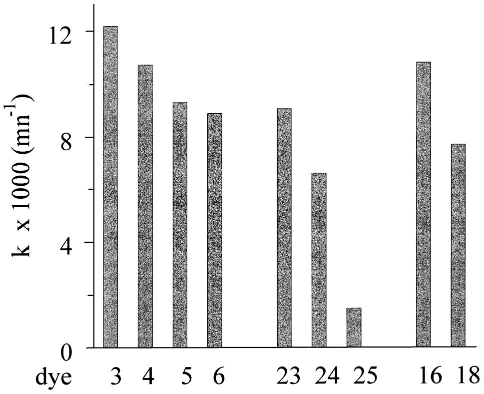


Fig. 5. Photodegradation of dyes containing a saturated side chain.

this compound is that it does not contain any sulfonate group, so that it is insoluble in water. In aqueous media, this dye also strongly aggregates. In order to decrease the size of the particules, a non-ionic surfactant (Tween 80) was added to the dispersion before irradiation. Fig. 6 shows that a very small quantity of surface-active-agent can only partly disperse the dye. As a result, the decrease of the absorbance stops after a few minutes. The size of the residual dye particules is too large and contact of hydroxyl radicals with dye molecules cannot occur any more. An increase of the surfactant concentration leads to a rise of the initial reaction rate and to an increase of the destroyed dye percentage. This is evidence of the great impact of the solubility in water of organic molecules and of their aggregation degree on the oxidation rate.

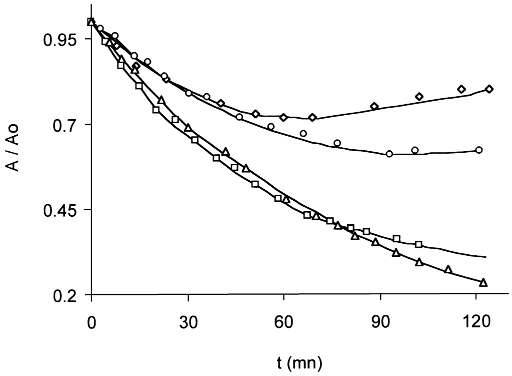


Fig. 6. Evolution of the absorbance of DB19 solutions as a function of a surfactant concentration: 0.1 g/liter (◇) –0.15 g/liter, (○) –0.3 g/liter, (△) –0.6 g/liter (□).

It is interesting to notice that, in the preceding dyes series, the rate constant depends almost linearly on the number of hydrogen atoms in the side chains (Fig. 7). This observation presupposes that the phenomenon is more complex than expected. A parallel reaction may take place between the OH$^\bullet$ radical and the hydrogen atoms of the side chains. This reaction competes with the destruction of the dye chromophore, without leading to a decrease in the absorbance of the solution.

3.4. *Influence of chloro groups*

A large decrease of the rate was observed when two or three chloro substituents were present on the phenyl ring of a pyrazolone dye. Indeed, comparison of the A0, AJ17 and A0Cl$_{2,4,6}$ rates suggests that the difficulty of the dye to be degraded directly depends on the number of electron with-

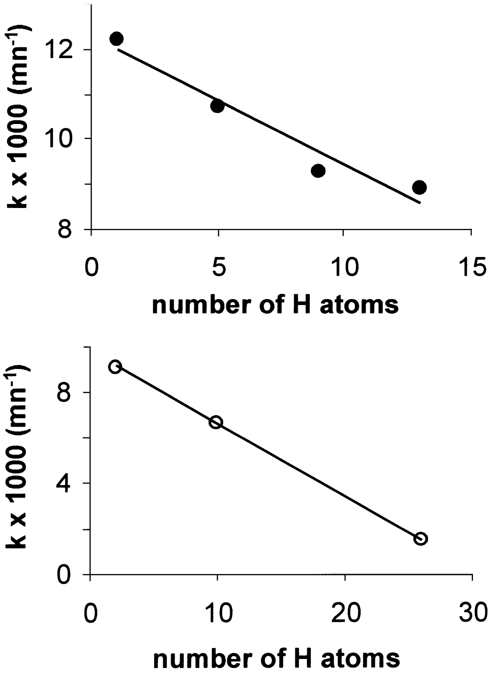


Fig. 7. Relation between the number of H atoms in side chain and the rate constant. (A series : (●), B series: (○).

drawing chloro groups in the molecule. The discolouration kinetics in decreasing order are: A0, AJ17, $A0Cl_{2,4,6}$. The −I effect of the chloro substituents largely surpasses the +M resonance effect, and consequently halogens deactivate the ring which carries them. Steric effects may also be involved when both ortho positions are occupied by chlorine, as reflected by the lower absorbance for the dye $A0Cl_{2,4,6}$ with respect to A0.

Substitution of chloro groups in dye molecules by hydroxyl radicals may occur, leading to the formation of chloride anions in the solution. To evaluate the importance of this reaction, chloride appearance was followed by the mercurimetric method during the degradation of $AOCl_{2,4,6}$. Fig. 8 shows that an organic chlorine mineralization occurs, which expresses the high mobility of chlorine atoms. However, the chlorine elimination is low during the first minutes of irradiation, and it only dramatically intensifies when most of the dye is already destroyed. For instance, when the absorbance of the solution is reduced by half, only about 3.8 10^{-5} mol of chloride (i.e. an organic chlorine mineralization rate of 22%) are formed. That means $AOCl_{2,4,6}$ degradation leads to colourless chlorinated compounds and removal of chlorine atoms in the organic matter preferentially takes place with these products. This reaction is, however, going to compete with the dye chromophore destruction, because it also consumes hydroxyl radicals.

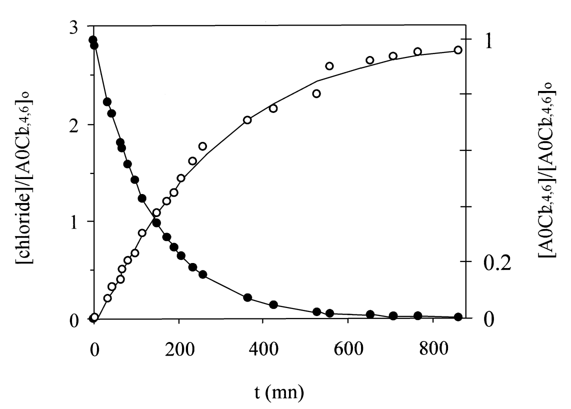


Fig. 8. Chloride formation as a function of irradiation time during $A0Cl_{2,4,6}$ degradation.

3.5. *Influence of the number of sulfonate substituents*

Surprisingly, the presence of the more powerful electron withdrawing sulfonate group on a molecule makes it only very slightly less sensitive to oxidation. Indeed, molecules with one, two or three sulfonic functions have almost the same reactivity with respect to oxidation by hydroxyl radicals. After a reaction time of 120 mn, 86% of AO7 was degraded while, respectively, 83 and 85% were removed for AO10 and AR18. In fact, study of the influence of the sulfonate group is very difficult, because this substituent operates in different fields: it decreases electron density in the aromatic rings and the β nitrogen atom of the azo bond by −I and −M effects, but on the other hand, it increases the hydrophilic–lipophilic balance of the dye molecules, and as a consequence slows down their aggregation degree.

4. Conclusion

The UV/H_2O_2 process is a useful method for discolouration of dilute aqueous azodye solutions. The photoreactor we used is not adequate for utilization on an industrial scale, because of its low light absorption efficiency. Irradiation times are also very long, so that the process is not profitable. Nevertheless, in our case, we used that weak efficiency to good effect; it afforded us the opportunity to determine the kinetics of the dye degradation over a long interval of time, thus limiting measurement uncertainties, while permitting us to compare reactivities of the dyes. We have demonstrated that the oxidation rate is strongly affected by the molecular structure of the organic matter. Aminoazobenzenes, metal complex dyes and disazodyes are not very sensitive to $OH^\bullet$-induced oxidation; chloro groups and saturated side chains have a large negative effect on the degradation kinetics. Moreover, when aminoazobenzenes behave like monosubstituted benzenes as far as oxidation by an electrophilic entity is concerned by $OH^\bullet$ adducts on the rings, abstraction of the labile H atom is the first step of the degradation for hydroxy azodyes. Additional mechanistic studies to examine further the relationship of the dye structure and degradability will be reported subsequently.

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