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Dyes and Pigments 62 (2004) 221–228
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Studies on the effect of inorganic salts on decolouration of acid dye effluents by ozonation

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Received 21 July 2003; received in revised form 12 October 2003; accepted 5 November 2003

Abstract

This paper deals with the effect of presence of inorganic salts namely, sodium chloride and sodium sulphate and their concentration on decolouration of acid dye effluents by ozonation. Studies have been conducted at various pH levels on synthetic dye effluents, having a concentration of 500 μmol, prepared using Acid Red 14, Acid Violet 12, Acid Brown 14 and Acid Blue 113. Salt concentration of 0, 5 and 15 g/l and pH of 3, 7 and 11 were used. It has been found that salt content in the effluent increases the decolouration time of the acid dye effluents and it is more at neutral pH than at acidic and alkaline pH. Higher the salt content more is the decolouration time and among the salts, sodium chloride requires more time than sodium sulphate. Diazo acid dyes are found to take more time for decolouration than monoazo dyes, irrespective of the nature and quantity of the salt and pH used.

Keywords: Acid dyes; Inorganic salts; Sodium chloride; Sodium sulphate; Ozonation and colour removal

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1. Introduction

Salts find major usage in the application of variety of dyes on textiles. They can act as exhausting as well as retarding agents. For example, they act as exhausting agents in the application of direct dyes on cellulosic fibres, acid milling dyes on wool and reactive dyes on cotton and as retarding agents in the application of leveling acid dyes on wool and basic dyes on acrylic. Sodium chloride and sodium sulphate are the very commonly used exhausting and retarding agents. The quantity of these agents required for dyeing varies with the chemical nature of the dye and the fibre used. In general, the quantity varies from 5 to 60 g/l. The addition of salt in the dye bath increases the pollution load on the effluent generated as well as has an effect on various effluent treatment processes.

The survey of literature revealed that there are number of studies on ozone treatment of effluent, which were carried out in presence of additives. The effect of additives such as silicone type antifoaming agents, salt, sodium silicate, surfactants, thickeners and urea in reactive dye bath, chelating agents such as ethylene diamine tetra acetic acid, diethylene triamine penta acetic acid in disperse dye bath and gar gum in acid dye bath on ozonation have been reported by different authors [1–4].

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doi:10.1016/j.dyepig.2003.11.002

Ghar et al. [2] were the only authors who have made a brief mention about the effect of salt during ozone decolouration of reactive dye effluent. But the authors have not discussed about the nature and quantity of the salt used in their study. It is reported that at higher pH levels, presence of salt lowers the decomposition of reactive dyes.

This paper describes the effect of presence of inorganic salts namely, sodium chloride and sodium sulphate at various pH levels on decolouration of acid dye effluents by ozonation. Synthetic effluents prepared using dyes namely, Acid Red 14, Acid Violet 12, Acid Brown 14 and Acid Blue 113 were used in the study.

2. Experimental

2.1. Apparatus and experimental procedure

The experimental set-up consisted of an oxygen generator (Sim O_2 plus, Italy), ozone generator (Ozonetek Ltd., India), ozonation chamber and an ozone destroyer (Ozonetek Ltd., India). Concentration of ozone produced by the ozone generator was determined using ozone analyser (BMT 201, Berlin), working on the principle of UV absorption method. The ozonation column consisted of a 35 cm glass tube with 5 cm inner diameter having a capacity to hold 750 ml of effluent. It was provided with a sample port, an inlet—connected to the ozone generator and an outlet—connected to the ozone destroyer. A diffuser was provided at the bottom of the column to ensure proper distribution of ozone–oxygen mixture produced. Unutilized ozone coming out of the ozonation chamber was destroyed in the ozone destroyer, maintained at 300 °C.

Acid dyes possessing monoazo and diazo groups were used in this study (Fig. 1). The particulars of the dyes used are given in Table 1. A quantity of 500 ml of synthetic effluent having a fixed concentration of 500 μmol of dye was taken in the ozonation column. Salt concentration of 5, 10 and 15 g/l and pH levels of 3, 7 and 11 were used in the effluents. The acidic and alkaline pH was adjusted with sulphuric acid and sodium hydroxide respectively. A controlled flow rate of 2 l/min oxygen from oxygen generator was passed through ozone generator. The ozone–oxygen mixture having ozone concentration of 2 g/h produced was bubbled through the dye effluent in the column.

Table 1
Properties of the dyes

C.I. Name	Mol wt.	λ_{max} (nm)	Chemical nature
Acid Red 14	502	530.4	Monoazo, disulphonic
Acid Violet 12	539	551.2	Monoazo, disulphonic
Acid Brown 14	622	463.6	Diazo, disulphonic
Acid Blue 113	681	567.0	Diazo, disulphonic

3. Analysis

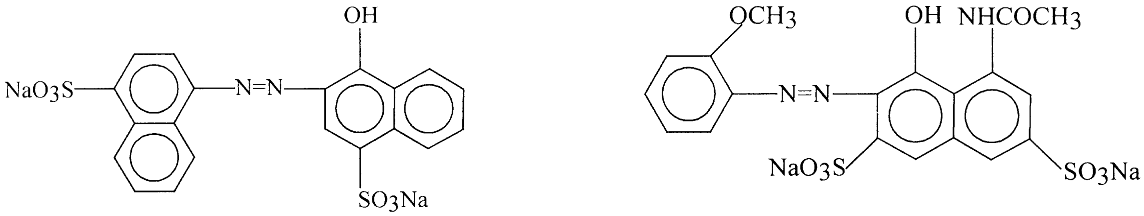
Decolouration of the effluent by ozone was determined through absorbance at maximum wavelength (λ_{max}) of the respective dyes (Table 1) using UV–visible spectrophotometer (model U-3210, Hitachi, Japan). The treatment was continued till the absorbance value reached zero and the time required for complete decolouration was finally noted down.

4. Results and discussion

4.1. Effect of presence of salts and various pH levels on complete decolouration time of effluents

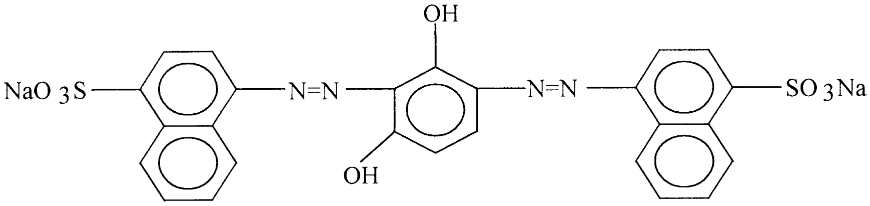
From the studies conducted on decolouration of popular classes of textile dyes by ozonation, it can be said that vat and disperse colours are more persistent towards decolouration. There are number of studies which supports decolouration of acid dyes by ozone [4–9]. All the acid dyes considered in this work undergo complete decolouration but the time of decolouration vary with the nature and quantity of the salts and pH.

Figs. 2 and 3 shows the time required to completely decolour the dyes when the effluent containing 0, 5 and 15 g/l of sodium sulphate/sodium chloride at different pH levels were subjected to ozonation. The plots clearly indicate that the complete decolouration time is the lowest when

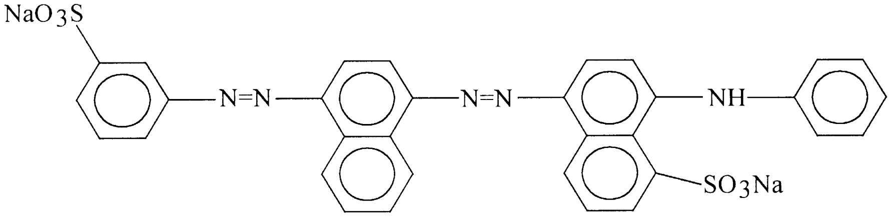


Acid Red 12

Acid Violet 12



Acid Brown 14



Acid Blue 113

Fig. 1. Chemical structure of the dyes used.

the effluents contain no salt content in it, irrespective of their pH levels.

4.2. *Effect of pH on complete decolouration time*

It can also be observed from the Figs. 2 and 3 that, irrespective of whether the salt is present in the effluent or not, the time required for complete decolouration is more at neutral pH than at acidic or alkaline pH, except in the case of Acid Blue 113 in presence of 5 g/l sodium sulphate at acidic pH. This can be explained as follows. Decomposition of ozone is pH dependent and its action depends on the decomposition products produced. In acidic pH ozone is available as molecular ozone and in alkaline pH it decomposes into secondary oxidants such as OH°, HO_2°, HO_3° and HO_4°. Among these, OH° is an important one and has the highest oxidation potential of 2.8 V. The oxidising potential of ozone decreases from 2.08 V at lower pH values to about 1.4 V in alkaline solutions [10]. This indicates that as the pH increases ozone stability decreases resulting in generation of secondary oxidants. Hoigne and Bader [10] reported that the hydroxyl free radical was the primary reactive species in ozonolysis at pH values in excess of 6. Rice [11] reported that the production of hydroxyl free radical starts when the pH exceeds 5 through the following mechanism.

$$O_3 + OH^- \rightarrow HO_2^{\cdot} + O_2^- \tag{1}$$

$$HO_2^{\cdot} \leftrightarrow O_2^- + H^+ \tag{2}$$

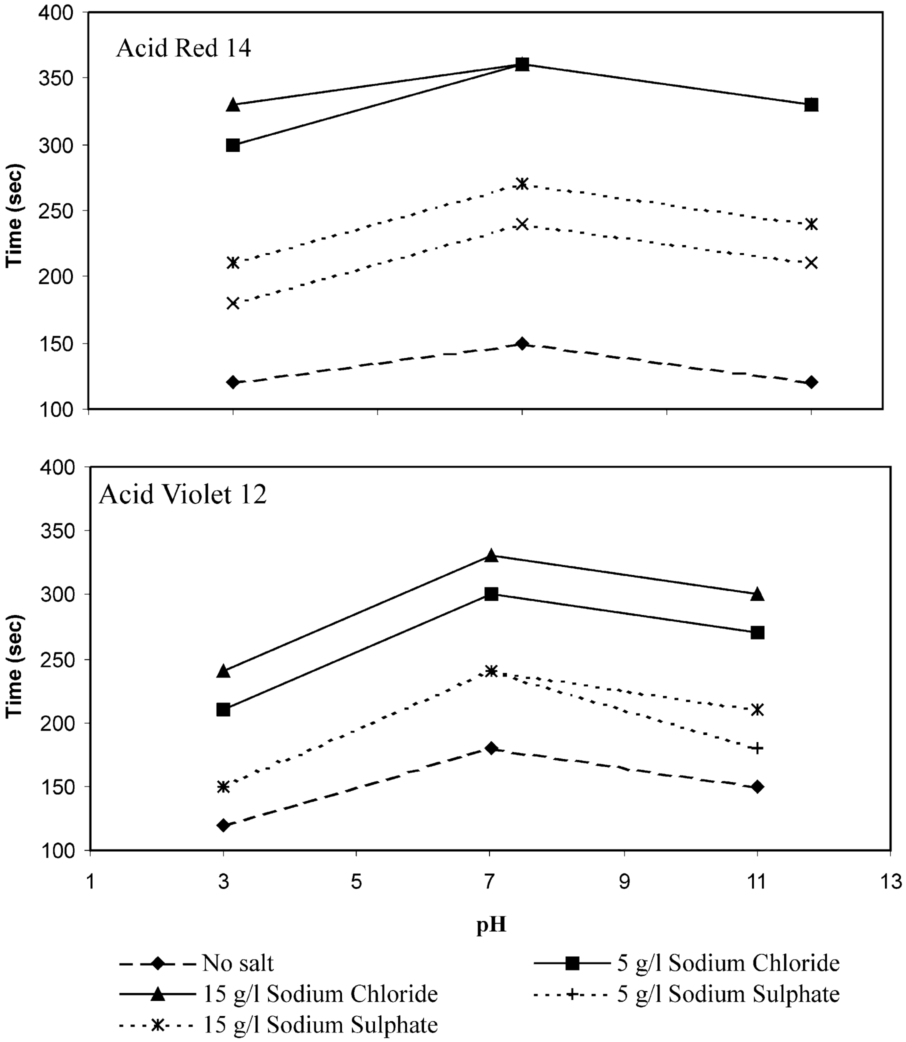


Fig. 2. Effect of salt and pH on complete decolouration time of monoazo acid dye effluents.

$$O_3 + O_2^- \rightarrow O_3^- + O_2 \quad (3)$$

$$O_3^- + H^+ \leftrightarrow HO_3^{\cdot} \quad (4)$$

$$HO_3^{\cdot} \rightarrow OH^{\cdot} + O_2 \quad (5)$$

This brings out clearly that the ozone decomposition and the production of hydroxyl free radicals commences at weakly acidic pH. Sotelo et al. [12] reported that the dissolved ozone concentration decreases when the pH increases and is about 4.3×10^{-4} mol/l at a pH of 4 and 1.5×10^{-4} mol/l at a pH of 10. Hence at neutral pH, efficiency of the ozone reaction is lesser than acidic pH because of the reduction in ozone dissolution and less amount of hydroxyl free radical produced. At alkaline pH, since more hydroxyl free radicals are generated, the efficiency is better than that at neutral pH, in spite of the reduction in ozone dissolution. Another observation that can be made is that, in general, for all the dyes,

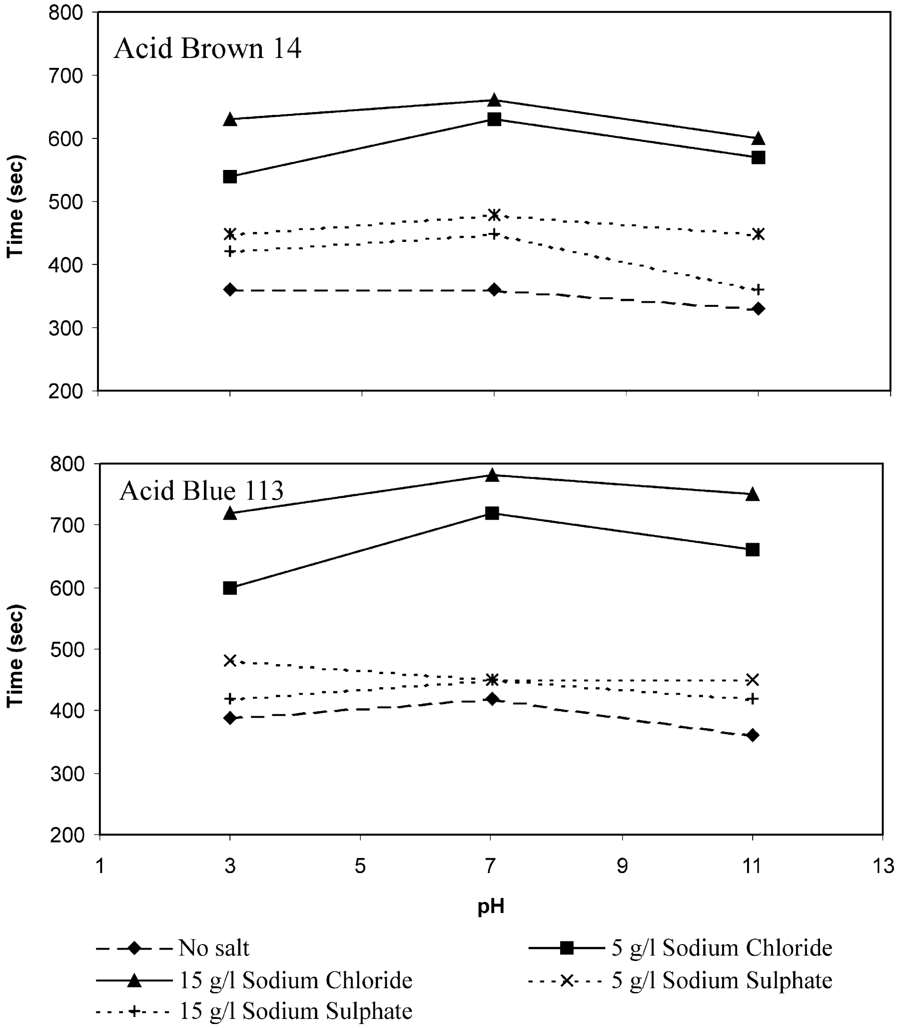


Fig. 3. Effect of salt and pH on complete decolouration time of diazo acid dye effluents.

decolouration at acidic pH requires lesser time than at alkaline pH.

4.3. *Effect of nature of salts on complete decolouration time*

It can be seen from the plots in Figs. 2 and 3 that, for all the dyes, the complete decolouration time required is lower when sodium sulphate is present in the effluent than that for sodium chloride at any given salt concentration and pH.

4.4. *Effect of sodium chloride*

It is reported that the following reaction can take place in acidic and alkaline pH in presence of sodium chloride [13,14]. In acidic pH,

$$\mathrm{NaCl} \leftrightarrow \mathrm{Na^+ + Cl^-} \tag{6}$$

$$\mathrm{Cl^- + H_2O} \leftrightarrow \mathrm{HOCl + H^+ + 2e^-} \tag{7}$$

$$HOCl \leftrightarrow H^+ + ClO^- \quad (8)$$

$$HOCl + H^+ + Cl^- \leftrightarrow Cl_2 + H_2O \quad (9)$$

$$Cl_2 + O_3 \rightarrow OCl^{\cdot} + Cl^{\cdot} + O_2 \quad \text{initiation} \quad (10)$$

$$\rightarrow OCl^{\cdot} + {}^{\cdot}ClO_2 \quad (11)$$

$$OCl^{\cdot} + O_3 \rightarrow Cl^{\cdot} + 2O_2 \quad \text{propagation} \quad (12)$$

$$Cl^{\cdot} + O_3 \rightarrow ClO^{\cdot} + O_2 \quad (13)$$

$$OCl + {}^{\cdot}OCl \rightarrow Cl_2 + O_2 \quad \text{termination} \quad (14)$$

$$Cl^{\cdot} + Cl^{\cdot} + M \rightarrow Cl_2 + M \quad (15)$$

where, M is an organic moiety.

The consideration of the above set of equations along with the fact of existence of ozone as molecular ozone in acidic pH reveals that the presence of sodium chloride results in consumption of ozone by it.

The reactions that can take place in alkaline pH are,

$$Cl^- + OH^{\cdot} \leftrightarrow Cl^{\cdot} + OH^- \quad (16)$$

$$Cl^- + Cl^{\cdot} \rightarrow Cl_2 + e^- \quad (17)$$

The chlorine formed would undergo reactions represented in Eqs. (10)–(15). This group of equations reveals that the presence of sodium chloride results in depletion of ozone also take place in alkaline pH through the consumption of OH° as well as by the direct consumption of dissolved ozone.

4.5. *Effect of sodium sulphate*

It is stated that sodium sulphate undergoes dissociation as follows [13]:

$$Na_2SO_4 \leftrightarrow 2Na^+ + SO_4^{2-} \quad (18)$$

In acidic pH, where ozone remains as molecular ozone, sulphate ions do not react with ozone. In alkaline pH, where the decomposition of ozone results in the production of OH°, the following reactions can take place [13].

$$SO_4^{2-} + OH^{\bullet} \rightarrow SO_4^{\bullet -} + OH^- \quad (19)$$

$$2SO_4^{\bullet -} \rightarrow S_2O_8^{2-} + 2e^- \quad (20)$$

The oxidation potential of sulphate radical and peroxydisulphate ions is 2.01 V [13]. It is higher than the oxidation potential of hypochlorous acid (1.5 V), hypochloric ion (0.89 V), chlorine dioxide (1.15 V) and chlorine (1.36 V) [15], which are produced in presence of sodium chloride depending on acidic or alkaline pH. Moreover, it has been stated that the $SO_4^{\circ -}$ has a unique nature of attacking the dye molecules at various positions resulting in rapid fragmentation of the molecules [16]. From the above discussion, it can be said that the presence of sodium chloride results in higher reduction in the efficiency of the decolouration process by ozone compared with that of sodium sulphate. It can also be observed from the above Figs. 2 and 3 that at all pH levels, dyes require more time for complete decolouration when the effluent contains higher salt content except in the case of Acid Blue 113 in presence of sodium sulphate.

4.6. *Effect of number of azo groups on complete decolouration time*

Fig. 4 shows the behaviour of monoazo and diazo dyes on decolouration time in presence of sodium chloride and sodium sulphate. It can be seen from the plots that the time taken by diazo dyes for complete decolouration is always more than that of monoazo dyes, irrespective of the nature and quantity of the salt and pH.

In neutral pH both mono and diazo dyes take more time for complete decolouration compared with acidic and alkaline pH. When sodium sulphate is present in the effluent, monoazo dyes take same or less time in acidic pH compared to

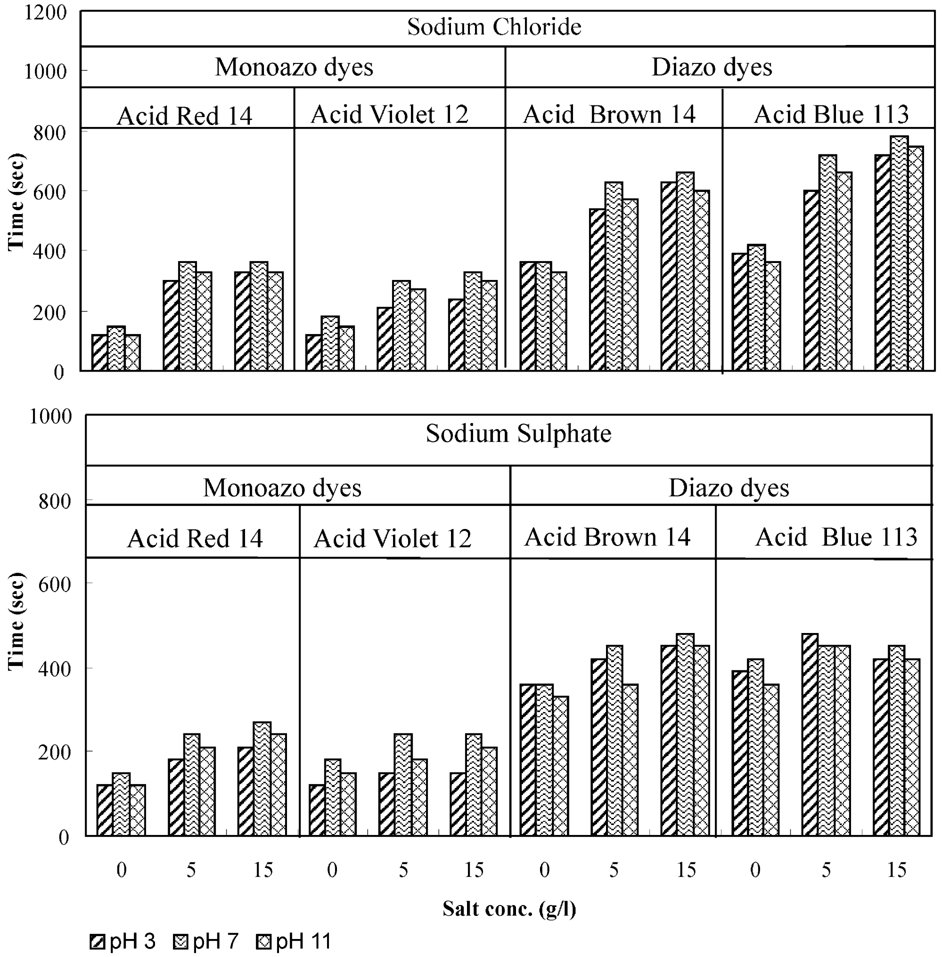


Fig. 4. Effect of number of azo groups on complete decolouration time.

alkaline pH whereas the diazo dyes take same or less time in alkaline pH compared with acidic pH. When sodium chloride is present in the effluent, the behaviour of monoazo dyes in acidic pH is similar to that of the presence of sodium sulphate whereas no trend is followed by the diazo dyes between acidic and alkaline pH.

5. Conclusions

Following conclusions can be drawn from the study conducted. Presence of salt content in the acid dye effluent increases the complete decolouration time and hence decreases the decolouration efficiency of ozone. Irrespective of whether the salt is present or not in the effluent, the complete decolouration time required is longer at neutral pH compared to acidic and alkaline pH.

In general, higher the salt content in the effluent more is the reduction in the decolouration efficiency of ozone. The presence of sodium chloride in the effluent reduces the decolouration efficiency of ozone more than that of sodium sulphate.

Time taken for complete decolouration of diazo acid dyes is more than that of monoazo acid dyes and in neutral pH, both mono and diazo dyes take more time compared to acidic and alkaline pH.

Acknowledgements

One of the authors, M. Muthukumar, thanks the Council of Scientific and Industrial Research, India for awarding Senior Research Fellowship to carry out this work.

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