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Homogenous photocatalytic degradation of a disperse dye and its dye bath analogue by silicadodecatungstic acid

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Abstract

A new method for disperse dye decolourization using the photochemically active silicadodecatungstic acid ($H_4SiW_{12}O_{40}$) + isopropanol (electron donor) redox system has been described. Results of a series of control experiments have indicated that the one-electron reduced form of the silicadodecatungstic acid, $SiW_{12}O_{40}^{5-}$, was responsible for reductive cleavage of disperse dye as evidenced by photochemical heteropoly blue generation upon $H_4SiW_{12}O_{40}$ + isopropanol UV-illumination. A threshold (0.09 mM) and an optimum (0.5 mM) heteropoly acid dose existed for minimum and maximum decolourization rates, respectively. It was also evident that decolourization kinetics were first-order with respect to dye concentration for concentrations up to 75 mg/l, and the photochemical degradation rate became UV-light penetration limited (zero order) above 100 mg/l dye concentration.

Keywords: Decolourization; Heteropoly acid; Heteropoly blue; $H_4SiW_{12}O_{40}$; Disperse dyes; Photochemical degradation

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1. Introduction

Waste waters generated at various stages of textile dyeing differ in composition, strength and volume. Their pollution load is high and they arise mostly from spent dye baths that are principally composed of dyes, dispersing agents, surfactants, electrolytes, acids and different organics, which have been washed from dyed material. These effluents are characterized by their intense colour, high chemical oxygen demand (COD), salinity and fluctuating pH [1]. Many dyeing facilities currently use conventional wastewater treatment technologies such as activated sludge, chemical coagulation and membrane filtration [1–3]. The major drawbacks of these processes, such as sludge formation and inefficient colour removal, have been recently overcome for water soluble (hydrophilic) dyes by employing lab- or pilot-scale advanced oxidation technologies such as O_3/OH^-, H_2O_2/UV, Fenton's reaction, Photo-Fenton processes, as well as TiO_2-mediated heterogeneous photocatalysis [4–8]. Investigations of the partial oxidation and decolourization of hydrophobic disperse dyes are limited to just a few studies and are rather controversial in terms of their reported efficiency [9,10].

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The dyeing of synthetic fabrics, such as polyester, cellulose acetate, acrylic and polyamide materials, is usually accomplished using disperse dyes. This class of dyes comprises organic nonionic compounds that are generally characterized by their low solubility in water. They can be structurally classified as mainly azo, anthraquinone, nitrophenylamino and triphenylmethane chromophoric systems [11]. The –N=N– groups in azo dyes are well known electron (hydrogen) acceptors and there exists extensive literature on the photoreduction of azo dyes to aromatic amines, which may be further degraded to environmentally acceptable products, such as carboxylic acid, if aerobic conditions are employed [12]. According to previous literature, the direct photodegradation of disperse dyes is difficult mainly due to their low aqueous solubility which can be enhanced by the introduction of organic solvents such as acetone, which not only increases dye solubility but also has an additional photosensitizing ability in the triplet state [13,14]. For dye photosensitization studies, acetone must be used in large quantities ($\geqslant 65\%$ v/v) which would seriously reduce its applicability, from a practical point of view [14].

A fundamental limitation of heterogeneous photocatalytic technologies has been the lack of acceptable liquid phase quantum yields. An extensive search of the photocatalysis literature reveals that the majority of publications have focused on TiO_2, which is well known to be the most robust and photocatalytically active semiconductor material. A considerable volume of literature, over the last three decades, has been devoted to the TiO_2-mediated heterogeneous photocatalytic treatment of recalcitrant organic pollutants [15]. A more complex class of photocatalytically active materials form the heteropoly acids and salts that are thermally and photochemically active metal–oxygen anion clusters. These have been used as efficient and selective redox catalysts in a variety of biochemical, chemical and environmental applications [16,17].

Fig. 1 shows the common photocatalytic cycle of Keggin type heteropoly acids (HPAs) being quite similar to the more well-known mechanism of semiconductor photocatalysis, along with two possible reaction scenarios (I and II) [18].

Irradiation of the ligand-to-metal charge transfer band at around 260 nm produces the excited state HPA*, with reduction potentials of 2.5 eV against NHE for most HPA's [17]. The electron reduction of HPA (usually one electron) by an electron donor (substrate S) to form HPA_{red} is followed by the facile re-oxidation to its original electron state by an electron acceptor such as dioxygen (Pathway I). Reaction pathway II involves pre-complexation between S and HPA prior to photoactivation and has been evidenced

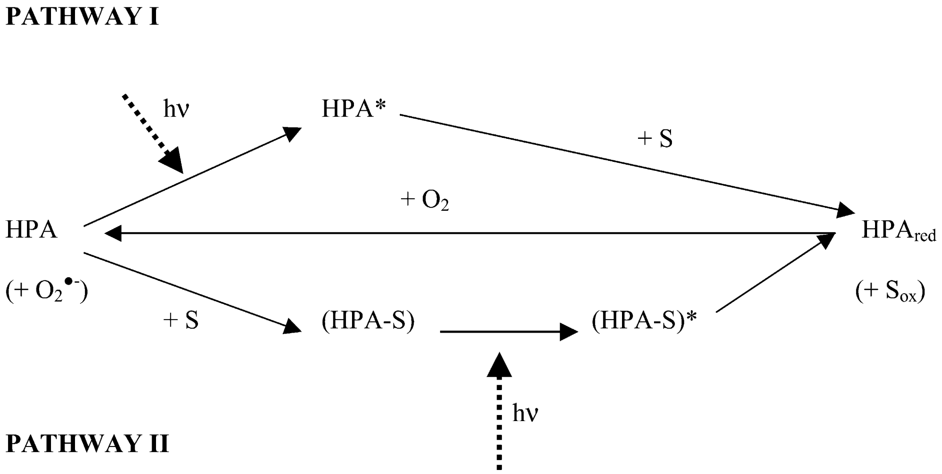

Fig. 1. Redox scheme for the HPA-mediated photodegradation mechanism.

for the oxidation of alcohols [18,19]. Photoexcitation of the (S-HPA) complex produces an excited state in which an electron or hydrogen atom transfers from S to HPA. The reverse-electron transfer and re-oxidation process is proposed to be the rate-limiting step of the HPA redox system [20].

In the present work, the degradation of a disperse dye and its dye bath analogue in aqueous solution and in the presence of the organic solvents isopropanol (IsOH) and acetone, (Ac) with the silica-based, Keggin-type HPA, $H_4SiW_{12}O_{40}$, was investigated under UV-C light at $\lambda \approx 254$ nm irradiation. $H_4SiW_{12}O_{40}$ was selected as the index HPA owing to its hydrolytic and chemical stability within the pH range typically encountered in disperse dye baths (≈3.0–3.5) as well as its prompt re-oxidation potential under aerobic conditions, which is critical for maintaining its photocatalytic property [21–23]. Decolourization kinetics of the disperse dye were used to explore the effect of catalyst dose and initial dye concentration on the process, as well as to optimize operating parameters. Separate experiments were conducted in the presence of different disperse dye auxiliaries (dispersing agent, levelling agent, acetic acid buffer), separately and in full combination, to predict how different dye assisting chemicals would influence colour removal efficiency and kinetics of disperse dyes in real exhausted dye baths.

2. Experimental

2.1. Reagents and supplies

$H_4SiW_{12}O_{40}$ hydrate (MW = 2878.29 g/mol) was obtained from Fluka and used as received. Analytical grade H_3PO_4, acetone and isopropanol (2-propanol, 99.99% in purity, abbreviated as IsOH) were all purchased from Riedel. The disperse dye preparation, i.e. a confidential blend of C.I. Disperse Blue and C. I. Disperse Orange (patent of SETAS Kimya Corp.), anionic levelling agent *Rucogal SBM* (Rudolf-Duraner), anionic dispersing agent *Breviol A-69* (Henkel), and also technical grade acetic acid were kindly supplied by SETAS Kimya Corp. and Pisa Tekstil Dyeing and Finishing company, respectively.

2.2. The UV-C photoreactor

A 2000-cm^3 capacity annular *plexiglas* reactor equipped with a 21 W low pressure mercury arc lamp emitting UV-C light at 253.7 nm and housed in a quartz sleeve was used throughout the experiments. Photocatalytic reactions were run for 30 min and 5 ml samples were taken from the reactor at regular time intervals for colour analysis. The light intensity of the UV-C lamp was 3.65 $W\ l^{-1}$ ($= 1.73 \times 10^{-4}$ Einstein $l^{-1}s^{-1}$). The reaction solutions were vigorously mixed from the reactor bottom by means of a magnetic stirrer to provide rapid re-oxidation of the HPA catalyst that is proposed to be the rate-limiting step of the HPA-mediated redox system.

2.3. Disperse dye bath analogues

The effect of dye assisting chemicals being typically employed during disperse dyeing was studied in separate experiments. Disperse dye bath analogues were made up comprising:

- 150 mg/l disperse dye (a mixture of C.I. Disperse Blue 79 and C.I. Disperse Orange 30, both 9 5% in purity);
- 2 g/l dispersing agent (a sulfonated naphthalene condensation product, anionic, prevents dye agglomeration, 68 ± 2% in purity);
- 2 g/l levelling agent (an aromatic carboxylic acid compound, a mixture of poliacrylate and ethoxylated fatty acid, anionic, enhances migration and controls exhaustion, 68 ± 2% in purity); and
- 2 g/l acetic acid solution (functions as a pH buffer).

The above concentrations of dye and dye auxiliaries were chosen on the basis of typical disperse dyeing formulations obtained from a local textile plant. Dye solutions were always buffered with concentrated H_3PO_4 to pH 2.90 ± 0.1 to keep $H_4SiW_{12}O_{40}$ stable.

2.4. Apparent colour analysis

The relationship between absorbance and dye concentration is governed by the Lambert–Beer law [24,25];

$$A = \log(I_o/I) = \varepsilon \cdot c \cdot L \qquad (1)$$

where

A: absorbance (measured in 1 cm quartz cells, cm^{-1});
I_o, I: intensity of light entering and leaving the optical cell length;
ε: extinction coefficient or absorptivity ($(\text{mg/l})^{-1}\ \text{cm}^{-1}$);
L: optical cell (path) length (cm); and
c: concentration of dye (mg/l or mol/l, if molecular weight is exactly known).

The apparent colour of the disperse dye preparation and its dye bath simulation were determined by absorbance measurements using a double beam UV–VIS spectrophotometer (Shimadzu Corp.). As the dyes were only partially soluble in water, this measurement gave the sum of both colour and turbidity. To ensure the validity of the Lambert–Beer law and to check if the method preferred for colour determination was suitable, three sets of aqueous calibration solutions were prepared in: (a) pure bi-distilled water; (b) 10% IsOH + 90% water (v/v); and (c) 10% Ac + 90% water (v/v) at five different disperse dye concentrations (25, 50, 75, 100 and 125 mg/l; note that the given dye concentration always refers to the technical mixture). These dye concentrations were chosen because the solution for testing the absorbance–intensity correlation are best kept in the range 0.2–1.5 absorbance units (per cm quartz cell path length, i.e. 1/cm). Fig. 2 illustrates the effect of solvents on the absorbance–concentration curves obtained for the aqueous dye solutions at $\lambda_{max} = 600$ nm. The figure insert presents the calculated absorptivity coefficients obtained for different organic solvents. It can be seen that upon acetone addition a steeper curve was obtained as a consequence of the improved intermolecular solute–solvent interaction force improving the dye solubility significantly. Although the extinction coefficient for the acetone/water solution was almost two times higher than that for dye solutions in IsOH/water or pure water, no shift was observed for the maximum absorption band of the

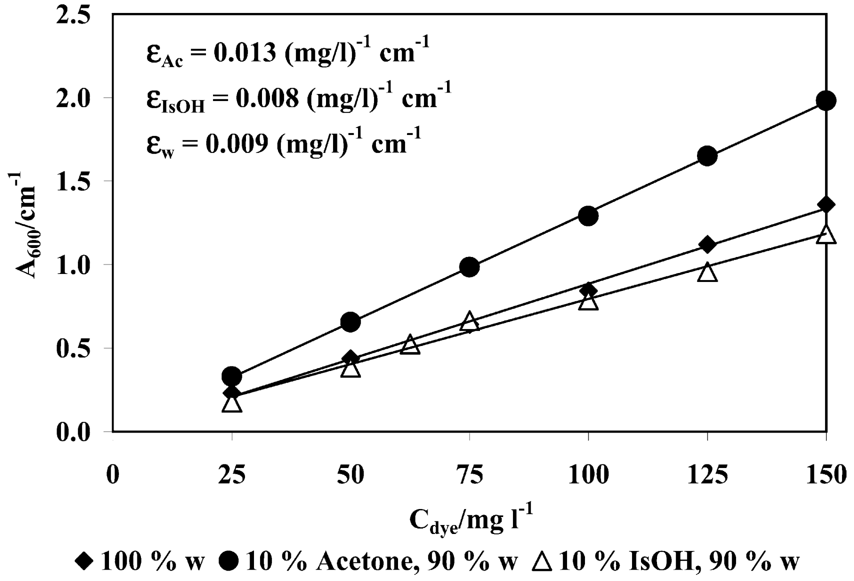

Fig. 2. Absorptivity of disperse dyestuff preparation at 600 nm in mixtures of water and organic solvent (selected dye concentration range = 25–150 mg/l).

disperse dye at all. Hence the apparent colour approach was chosen for the determination of colour. A similar procedure was used in the studies of Szpyrkowicz et al. [26] and Do and Chen [27].

3. Results and discussion

3.1. Colour removal mechanism and evidence of heteropolyblue formation

Several control experiments were conducted to establish a baseline for disperse dye degradation. For this purpose aqueous dye solutions ($C_{\text{dye}} = 75$ mg/l) were illuminated for 30 minutes in the presence of: (1) 10% v/v Ac; (2) 10% v/v IsOH; (3) 10% v/v Ac + HPA (0.5 mM); (4) 10% v/v IsOH + HPA (0.5 mM); and (5) HPA (0.5 mM) only; in addition, control, (6), i.e. direct UV-C photolysis of the dye solution was performed. Fig. 3 displays photodegradation experiments for the controls listed above. It is evident that only control experiments (1) and (4) exhibited a detectable loss in colour over the selected time scale that could be quantified by the abatement of absorbance at $\lambda_{\max}$. As expected, slow colour abatement was observed when Ac was introduced. Chu and Ma [13] and Chu and Tsui [14] have recently demonstrated that the dye solubility is the dominant parameter for its decomposition and that Ac not only functions as a photosensitizer but also as a solvent to increase overall disperse dye solubility. However, the presence of HPA appreciably retarded the Ac-mediated photolysis of the dye, control 3, due to competition of Ac and the HPA for UV light, and IsOH was necessary for effective dye decolourization in the presence of HPA. HPA-mediated, IsOH-assisted disperse dye degradation

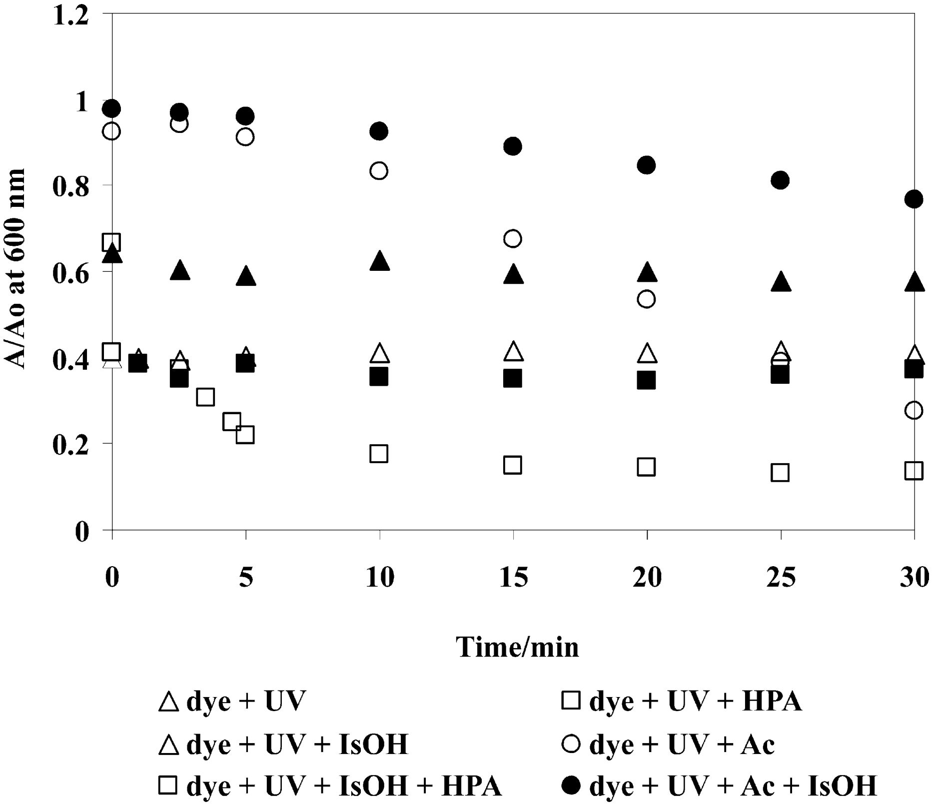

Fig. 3. Control experiments for the photodegradation of aqueous disperse dyestuff preparation. Experimental conditions: 10% v/v organic solvent; 75 mg/l disperse dye; 0.5 mM HPA; pH 2.9; UV-C exposure for 30 min at $I_o = 3.5$ W/l.

proceeded much faster than the other studied photochemical systems, with apparent first-order kinetics for the selected dyestuff concentration instead of apparent zero order kinetic behaviour which was observed for Ac + UV (0.0253 cm^{-1} min^{-1}) and Ac + HPA + UV (0.0072 cm^{-1} min^{-1}) treatment systems.

The electron storage of HPA, which gives a deep blue colour, has been evidenced in the presence of alcohols upon illumination with UV light [28] and the above findings suggest that IsOH was required to bring about the redox reaction between HPA and dyes. A separate experiment was carried out to track the formation of "heteropoly blue" (HPB; i.e. the one-electron reduced form of the HPA, $SiW_{12}O_{40}^{5-}$). Accumulation of HPB during UV-C photolysis of HPA in the presence of IsOH can be easily observed through monitoring the formation of the $SiW_{12}O_{40}^{5-}$ absorption band ($\lambda_{max} = 730$ nm; $\varepsilon = 1500$ M^{-1} cm^{-1}) [21,26]. Fig. 4 demonstrates HPB formation up to a steady-state amount during illumination of 10% v/v IsOH + HPA (initial concentration = 0.5 mM) and its subsequent abatement starting after UV-C light was turned off at $t = 45$ min. From the figure it is obvious that HPB formation is concentration limited and hence slows down when all available HPA is almost completely reduced, whereas subsequent HPB abatement proceeded quickly as a consequence of re-oxidation under the selected conditions. Kinetics in HPB decrease exhibited zero order behaviour once again confirming that re-oxidation of HPB is the rate-limiting step of the photochemical HPA + IsOH redox system. Accordingly, the following reaction scheme is proposed for HPA-catalyzed disperse dye degradation in the presence of IsOH in accordance with previous studies [19, 29];

3.1.1. Photoexcitation and pre-complexation of HPA and IsOH:

$$SiW_{12}O_{40}^{4-} + (CH_3)_2CHOH + h\nu \rightarrow \left(SiW_{12}O_{40}^{4-} + (CH_3)_2CHOH\right)^*. \quad (2)$$

3.1.2. Charge transfer reaction of the excited HPA + IsOH complex:

$$\left(SiW_{12}O_{40}^{4-} + (CH_3)_2CHOH\right)^* \rightarrow SiW_{12}O_{40}^{5-} + (CH_3)_2CHO^{\bullet} + H^+. \quad (3)$$

The oxidation potential of azo dyes is reported to be around 0.76 eV [30], and thus significantly

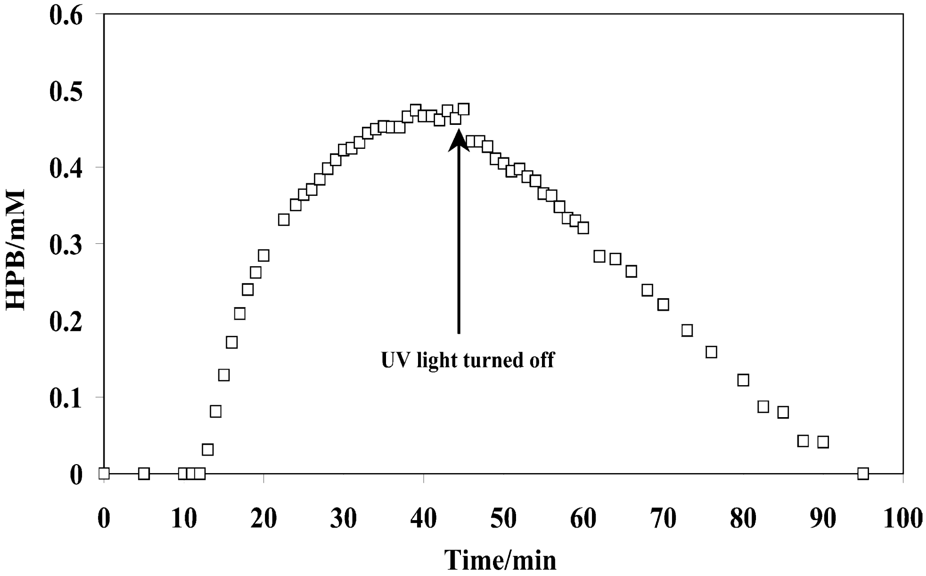

Fig. 4. Formation and disappearance of the one-electron-photo-reduced form of HPA, "Heteropoly blue" (HPB), during and after UV-C irradiation of aqueous HPA solution in the presence of IsOH, respectively. Experimental conditions: 0.5 mM HPA; 10% v/v IsOH; pH 2.9; UV-C exposure for 45 min at $I_o = 3.5$ W/l.

lower than the oxidation potential of photoexcited HPA and/or HPA–alcohol complexes. The disperse dye D (represented as D) is hence reduced by $SiW_{12}O_{40}^{5-}$ (HPB) as follows:

$$SiW_{12}O_{40}^{5-} + D \rightarrow SiW_{12}O_{40}^{4-} + D^{\bullet -} \tag{4}$$

$$D^{\bullet -} + H^{+} \rightarrow DH^{\bullet}. \tag{5}$$

Re-oxidation by dioxygen:

$$SiW_{12}O_{40}^{5-} + O_2 \rightarrow SiW_{12}O_{40}^{4-} + O_2^{\bullet -} \tag{6}$$

$$DH^{\bullet} + O_2^{\bullet -} \rightarrow DH^{-} + O_2 \tag{7}$$

$$DH^{-} \rightarrow \rightarrow DH_2 \quad \text{(reduced leuco form)} \tag{8}$$

$$D + O_2^{\bullet -} \rightarrow \text{oxidation products}. \tag{9}$$

3.2. Effect of $SiW_{12}O_{40}^{4-}$ dose

Typically, photocatalytic acitivity increases with catalyst dose up to a certain value beyond which its activity starts to decrease. The dependence of k_d (observed first-order decolourization rate constant, in min^{-1}) on HPA concentration in the range 0.026–1 mM is presented in Fig. 5. A significant decolourization rate was observed when the applied HPA dose was $\geqslant 0.087$ mM ($k_d = 0.18$ min^{-1}). The maximum k_d value for dye degradation occurred at 0.5 mM HPA and thereafter decreased considerably. The fall of the photodegradation rate at high HPA doses might be attributable to accelerated HPB accumulation that hinders effective UV light absorption of HPA or the HPA–IsOH complex. The optimum HPA dose was selected as a basis for the forthcoming experiments and fell within the range that has been typically applied during HPA-mediated photocatalysis [18,19,29].

3.3. Effect of initial dyestuff concentration

The effect of initial dye concentration (50, 62.5, 75, 100, 125 and 150 mg/l disperse dye solutions) on colour abatement kinetics is presented in Fig. 6. The decolourization rate enhancement observed for 50–75 mg/l disperse is a consequence of the

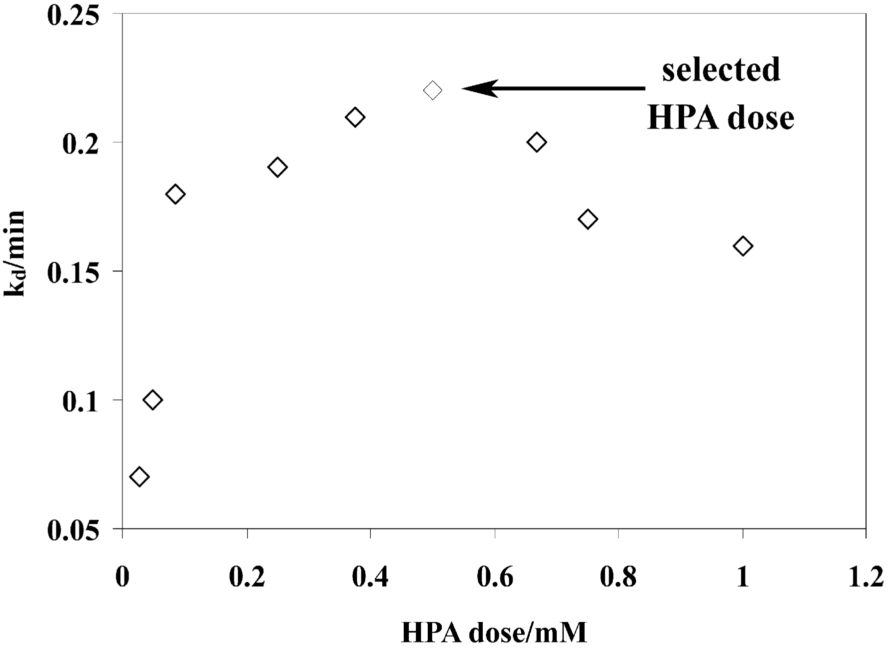

Fig. 5. Effect of HPA dose on apparent first order decolourization kinetics. Experimental conditions : 75 mg/l disperse dye; 10% v/v IsOH; pH 2.9; UV-C exposure for 30 min at $I_o = 3.5$ W/l.

apparent first-order kinetics being applicable for the above mentioned initial dye concentration range;

$$dC/dt = k_d \cdot C^d. \quad (10)$$

For dye concentrations at 100, 125 and 150 mg/l, decolourization rates decreased with increasing initial dye concentration suggesting that beyond a threshold, initial dye concentration effective light penetration is seriously hindered and competitive absorption plus light scattering caused by turbidity starts to inhibit the photochemical formation of HPA_{red}.

3.4. Effect of dye auxiliary chemicals

Dye auxiliaries can seriously affect dye degradation rates depending upon their type, nature and on the dye degradation mechanism. Degradation based on free radical reactions are usually dramatically inhibited in the presence of organic (acetic acid, tertiary alcohols) and inorganic (carbonate, bicarbonate, sulphate, chloride) free radical scavengers [4,31,32]. It should also be considered that the selected dye auxiliaries are anionic and hence more water soluble and amenable to homogenous photochemical reactions than the disperse dyestuff preparation itself. Investigation of the possible individual and combinative inhibiting effects of dye auxiliaries is expected to provide information about both the rate of process inhibition and the degradation mechanism during the investigated redox scheme. Fig. 7 shows the effects of acetic acid, dispersing agent, levelling agent and combinations thereof on colour abatement kinetics. Generally speaking, decolourization rates are particularly inhibited by the introduction of the levelling agent. The effects of the dispersing and levelling agents are rather consequences of enhanced dye solubility–dispersability and opacity, respectively, whereas acetic acid speculatively competes for charge (electron) transfer sites, i.e. HPA, that is, however, only of secondary significance. In the presence of the dispersing agent, total decolourization of the disperse dye bath recovers to 55% instead of only 41% when only

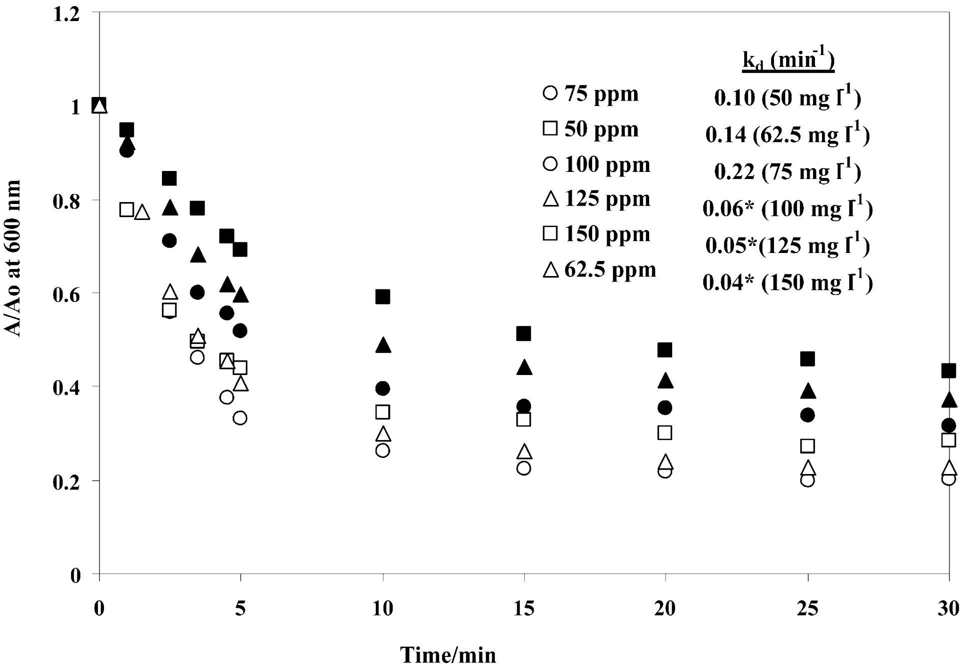

Fig. 6. Effect of initial dyestuff concentration on decoluorization kinetics and efficiency. Experimental conditions: 0.5 mM HPA; 10% v/v IsOH; pH 2.9; UV-C exposure for 30 min at $I_o = 3.5$ W/l; "*" indicates that apparent decolourization rate constants were calculated from the initial absorbance abatement rates for $C_{dye} = 100$, 125 and 150 mg/l (different unit).

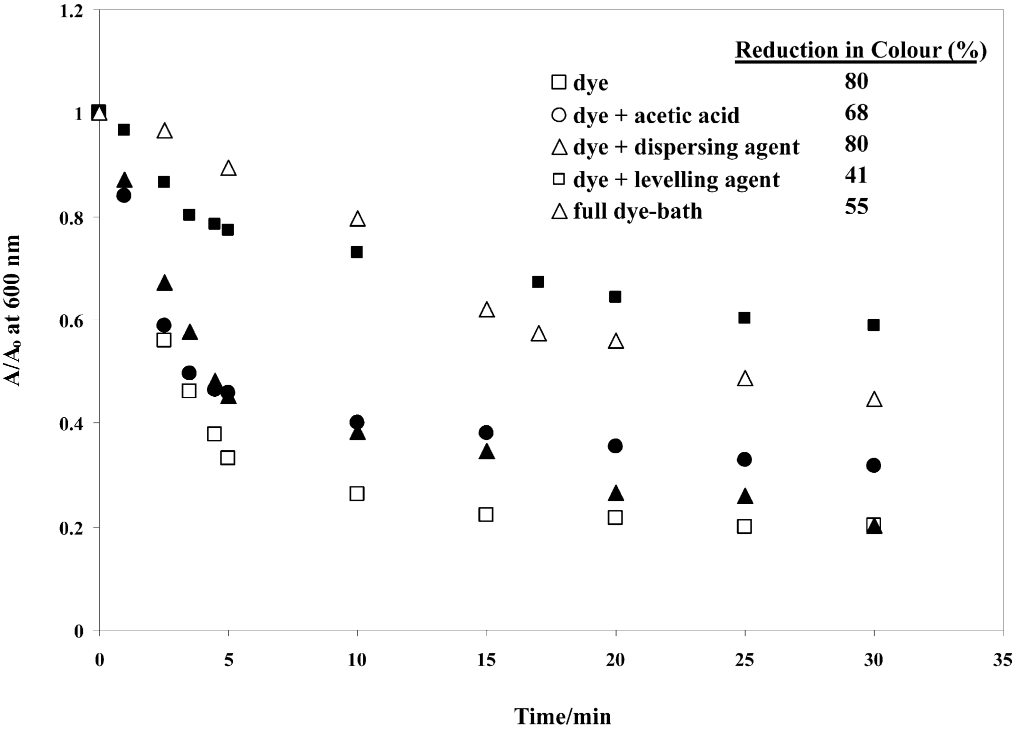

Fig. 7. Effect of disperse dye assisting chemicals on decolourization kinetics and colour removal efficiencies. Experimental conditions: 75 mg/l disperse dye; 0.5 mM HPA; pH 2.9; UV-C exposure for 30 min at $I_o = 3.5$ W/l.

the turbidity causing levelling agent is added to the aqueous dyestuff preparation.

4. Summary and conclusions

The results of the present study have demonstrated the feasibility of heteropoly acid-mediated and isopropanol induced photocatalytic degradation of dye baths bearing disperse dyestuffs. The efficiency of decolourization depended upon the amount of catalyst loading, initial dye concentration, nature of the organic solvent and the presence of dye assisting chemicals. From the above presented results it can be inferred that the encouraging first-order colour removal rate constants (0.22 min^{-1} for 75 mg/l disperse dye solution; 0.03 min^{-1} for the full disperse dye bath analogue) obtained at relatively low doses of heteropoly acid (0.5 mM) and isopropanol (10% v/v) at the natural acidic pH of disperse dye bath effluents present the possibility of applying photochemical degradation with heteropoly acids for pre-treatment purposes to overcome biorecalcitrance problems associated with hydrophobic and refractory disperse dyes.

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