

# Near-UV–VIS light induced acid orange 7 bleaching in the presence of $\text{SiW}_{12}\text{O}_{40}^{4-}$ catalyst

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## Abstract

The azo dye acid orange 7 (AO7) was decolourized by  $\text{SiW}_{12}\text{O}_{40}^{5-}$ , the one-electron photo-chemically reduced form of  $\text{SiW}_{12}\text{O}_{40}^{4-}$  catalyst, in aqueous solutions of aerated and de-aerated sacrificial electron donor isopropanol. Under our experimental conditions, the AO7 decay rate depended upon the competition between the azo dye and molecular oxygen for  $\text{SiW}_{12}\text{O}_{40}^{5-}$ . The colour removal rate constant was found as  $5.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  by applying AO7– $\text{O}_2$  competition kinetics based on a simple kinetic reaction scheme.

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**Keywords:** Acid orange 7; Textile azo dyes; Competition kinetics; Heteropolyblue; Polyoxometalates; Photochemical treatment;  $\text{SiW}_{12}\text{O}_{40}^{4-}$  catalyst

## 1. Introduction

Environmental issues associated with residual colour in waste streams of the dye-manufacturing and dye-consuming industries have gained more attention in the recent years due to the increasing public awareness in environmental issues and the introduction of stricter wastewater regulations worldwide. Dyes are required to exhibit a high degree of photolytic and microbial stability to fulfill the fastness requirements of textile consumers. As a consequence, commercial dyes are not readily degradable by conventional chemical and biochemical treatment processes [1,2]. Though fixation and biodegradability of new commercial dyes have been improved significantly, still significant losses occur during manufacturing and processing of dye products that end up in publicly owned treatment plants.

Within the overall category of dyestuffs, azo dyes constitute a significant portion and probably have the least desirable consequence in terms of environmental impact [3]. They are readily reduced under anoxic conditions to potentially hazardous aromatic amines and are carcinogenic in their own right [4].

Most methods practiced for dye removal include physical adsorption or coagulation–flocculation steps, biological

treatment as well as destructive chemical oxidation (i.e. ozonation and advanced oxidation processes) and reduction [2,5]. More recently, research has focused on alternative methods of degrading textile azo dyes via heterogeneous photocatalysis [6–12] as well as uncatalyzed and catalyzed [13–15] wet air oxidation processes. Both approaches involve the formation of active oxygen species, such as hydroxyl ( $\text{OH}^\bullet$ ) and hydroperoxyl ( $\text{HO}_2^\bullet$ ) radicals [16] that initiate fast catalytic reactions resulting in the complete colour removal. From the ecological point of view, destructive treatment processes are preferred to phase transfer methods to prevent a secondary contamination of the residual effluent by the treatment agents.

The ability of polyoxometalates (heteropolyacids and their salts; abbreviated herein as POM) and their transition-metal substituted derivatives to undergo reversible one or multi-electron transfer with retaining their original structure, has rendered these compounds attractive acid and redox catalysts in a variety of industrial catalytic applications [17,18]. For instance alternative  $\text{K}_5\text{SiW}_{11}\text{VO}_{40}$  and  $\alpha\text{-Na}_x\text{H}_{5-x}\text{PMO}_{10}\text{V}_2\text{O}_{40}$ -mediated catalytic processes have been developed that proceed at higher rates and consume significantly less chemicals than conventional technologies [18,19]. As such, they pose less threat to the environment.

Particularly the polyoxotungstates  $\text{PW}_{12}\text{O}_{40}^{3-}$ ,  $\text{SiW}_{12}\text{O}_{40}^{4-}$  and  $\text{W}_{10}\text{O}_{32}^{4-}$  undergo fast, step-wise and reversible redox reactions, acting as facile multi-electron and dioxygen relays [19,20]. Absorption of near-UV light

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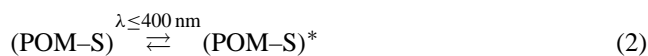
E-mail address: arslanid@itu.edu.tr (I. Arslan-Alaton).

( $280 \leq \lambda \leq 390$  nm) at the OMCT (oxygen-to-metal charge transfer) bands enhances their oxidizing ability rendering them powerful oxidizing agents able to degrade a variety of organic pollutants [21–25]. Photolysis of POM in the presence of an electron donor (substrate S) results in the formation of POM<sub>red</sub> (reduced form) and concomitant oxidation of S according to the following briefly summarized reaction scheme [26,27].

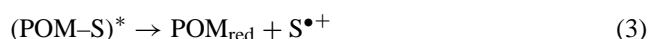
S–POM pre-complexation:



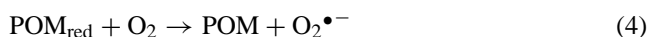
Photo-excitation of the POM–S complex:



Charge transfer and photoreduction of POM:



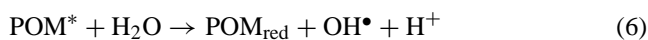
Re-oxidation (regeneration) of POM upon exposure to dioxygen:



Formation of hydroperoxyl radicals in acidic medium:



In the absence of an electron acceptor, the process leads to the accumulation of POM<sub>red</sub>, i.e. well-characterized blue complexes of POM [28]. No re-oxidation via H<sup>+</sup> takes place when the one e<sup>-</sup>-reduced form of POM is formed. It has also been proposed that the excited POM (POM\*) can also react indirectly with organic substrates via OH<sup>•</sup> according to [29]:



Possible involvement of OH<sup>•</sup> has been verified for some POMs by using spin-trapping reagents, a deuterium kinetic isotope effect in the production of acetone, detection of OH<sup>•</sup> adducts, reaction rates with different organic substrates, and the changes in absorbance profiles of de-aerated aqueous solutions of POM<sub>red</sub> photolyzed in the presence of organic and inorganic substrates at varying S:H<sub>2</sub>O ratios [25,29,30]. However, a disagreement still exists between the OH<sup>•</sup>-scenario and recent experimental results obtained for the light-induced photocatalytic oxidation of chlorinated aromatic compounds in the presence of phosphomolibdates and phosphotungstates [31]. Therein could be demonstrated that OH<sup>•</sup> do not play a major role during POM-mediated photocatalysis and that the process can be rather envisioned as a charge (electron)-transfer mechanism as will be speculated for azo dye degradation in the proceeding sections.

The scope of this investigation was to present an alternative approach to the well-examined photosensitized degradation of coloured compounds on semiconductor surfaces by applying SiW<sub>12</sub>O<sub>40</sub><sup>4-</sup>-mediated photobleaching of the well-studied textile azo dye acid orange 7 (AO7; also known as Orange II) in aqueous solutions. In the sensitizer-based

photocatalytic degradation, the coloured pollutant (D) gets oxidized on a semiconductor surface (i.e. TiO<sub>2</sub>), by injecting electron (e<sup>-</sup>) from its excited state (D\*) into the conduction band of the semiconductor and becomes a cation radical (D<sup>•+</sup>) [6]. By scavenging the injected electrons with a redox couple (O<sub>2</sub>/O<sub>2</sub><sup>•-</sup>), one can suppress the back electron transfer between D<sup>•+</sup> and e<sup>-</sup>. D<sup>•+</sup> quickly undergoes degradation to stable products by reacting with O<sub>2</sub><sup>•-</sup> provided that reaction conditions are appropriate [6]. Dye molecules can also be sensitized by UV light excited acetone, which results in the formation of D<sup>•+</sup> and its degradation products [32]. Similar responses might be expected when AO7 or AO7 + alcohol mixtures are exposed to near-UV–VIS light irradiation in the presence of POM catalyst. On the other hand, alcohols such as methyl alcohol or 2-propanol (IsOH) added to the reaction solution might compete for POM and act as effective oxidant/electron scavengers.

## 2. Experimental

### 2.1. Materials

AO7 (C.I. 15,510; 87% purity; molecular weight = 350.33 g mol<sup>-1</sup>) and dodecatungstic acid hydrate (H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>, molecular weight = 2878.29 g mol<sup>-1</sup>) were both purchased from Aldrich and used as received. Isopropanol (IsOH), methanol (MeOH), methyl-*tert*-butyl ether (MTBE), acetonitrile (AcN), and acetone (Ac), all GC<sup>2</sup> quality, were obtained from Fisher Scientific.

### 2.2. The photocatalytic reactor (solar simulator)

Thirty minutes photolysis experiments were performed with an Oriel 1000 W Xenon lamp (incident light flux  $I_0 = 2.60 \times 10^{-5}$  Einstein min<sup>-1</sup> as determined by ferrioxalate actinometry [33]), using a circulating water filter to avoid overheating of the reaction solution. The lamp was turned on at least 20 min before the start of photocatalytic reactions to obtain a constant light output. The reactor flask was made of pyrex glass so that only light with  $\lambda \geq 300$  nm was absorbed and could not pass through the reaction solution.

### 2.3. Analytical methods

Residual (unreacted) AO7 concentration was determined by monitoring the decrease in its peak absorption band (i.e.  $\lambda_{\text{max}} = 484$  nm;  $\epsilon_{\text{AO7}} = 20587 \text{ M}^{-1} \text{ cm}^{-1}$  at pH = 2.80 ± 0.05) in the samples on a Perkin-Elmer Lambda 14 double beam spectrophotometer with 10 mm quartz cells. When photolysis was performed in de-aerated (N<sub>2</sub>-sparged) solutions, the degree of POM reduction (extent of POM<sub>red</sub> formation) was calculated from the known extinction coefficient ( $\epsilon = 2000 \text{ M}^{-1} \text{ cm}^{-1}$  at  $\lambda = 730$  nm for SiW<sub>12</sub>O<sub>40</sub><sup>5-</sup> [34]) of the one-electron reduced blue product (SiW<sub>12</sub>O<sub>40</sub><sup>5-</sup>) using the same spectrophotometer.

The amount of  $\text{POM}_{\text{red}}$  formation was also verified by employing 2,2-diphenyl-1-picrylhydrazyl sulfonic acid (DPPH, purchased from Fluka), an extremely stable free radical scavenger and thus antioxidant, as the electron trap [35]. For that purpose, 1 ml photocatalytically treated sample aliquots were immediately added to 9 ml degassed DPPH solutions in 100% ethanol (prepared in 10 ml Erlenmeyer flasks at an equimolar dose with respect to  $[\text{POM}]_0$ ) and vigorously stirred for 1 min. Gentle  $\text{N}_2$ -purging of the sample flasks to avoid  $\text{POM}_{\text{red}}$  re-oxidation continued during the whole procedure. The instantaneous reaction between  $\text{POM}_{\text{red}}$  and DPPH in the prepared flasks caused bleaching of the initially deep purple coloured DPPH solution. The rate of purple colour fading was followed via UV–VIS spectrophotometry as the decrease in the optical density at the peak absorbance of DPPH ( $\lambda_{\text{max}} = 520 \text{ nm}$ ;  $\epsilon_{\text{DPPH}} = 10,200 \pm 100 \text{ M}^{-1} \text{ cm}^{-1}$  according to [35]) and was inversely proportional to the formation rate of one-electron reduced heteropolyblue ( $\text{POM}_{\text{red}}$ ). The above described experiments for the direct and indirect quantitation of  $\text{POM}_{\text{red}}$  were conducted at otherwise identical experimental conditions.

Identification of reaction products formed during POM-catalyzed photochemical treatment of AO7 solutions was accomplished by GC/ITMS (mass spectrometry with ion trap detection) analysis. For that purpose, 0.5 ml treated samples withdrawn from the photocatalytic reactor were promptly exposed to 1 min MTBE extraction. Thereafter, the organic phase was analyzed on a GC/ITMS system equipped with a Varian 8200 autoinjector and A Varian Saturn 200 ITMS. A high resolution DB-5 capillary column (30 m in length;  $0.25 \mu\text{m}$  in film thickness) was operated by the following temperature program: isothermal for 2 min at  $70^\circ\text{C}$ , heating up linearly to  $250^\circ\text{C}$  at a rate of  $10^\circ\text{C min}^{-1}$ ,

isothermal at  $250^\circ\text{C}$  for 10 min. The injection port was set at  $250^\circ\text{C}$ . The carrier gas was ultra-pure He and used at a flowrate of  $1 \text{ ml min}^{-1}$ . Intermediates were identified by comparing the mass spectrum of the 30 min treated samples with spectra of the compounds stored in the NBS library.

#### 2.4. Experimental procedures

For the experiments conducted in the presence of  $\text{O}_2$ , ASTM grade water acidified with phosphate buffer to the working pH (2.8) was first stirred vigorously for 60 min. The AO7 solution ( $30 \text{ mg l}^{-1}$ ; corresponding to  $75 \mu\text{M}$  dye) was prepared in an alcohol:water mixture of 10:90 (% v/v) to give a final reactant volume of 100 ml ( $V_r$ ), thus alcohol (i.e. the electron donor agent) was provided in large excess. The initial POM concentration,  $[\text{POM}]_0$  was selected as 0.75 mM.

For the experiments in the absence of  $\text{O}_2$ , the pH-adjusted water was first degassed for 20 min by gently bubbling  $\text{N}_2$  at a rate of  $50 \text{ ml min}^{-1}$ . Then the catalyst, dye, and finally alcohol were added, mixed and thereafter the reaction was started under continuous  $\text{N}_2$  sparging. During all experiments, 0.5 ml sample aliquots were periodically withdrawn from the reactor flask for immediate UV–VIS spectrophotometric analysis.

### 3. Results and discussion

#### 3.1. Evidence for reductive AO7 bleaching

Fig. 1 shows the changes in the UV–VIS absorption spectra during direct photolysis of AO7 for 30 min under air. AO7

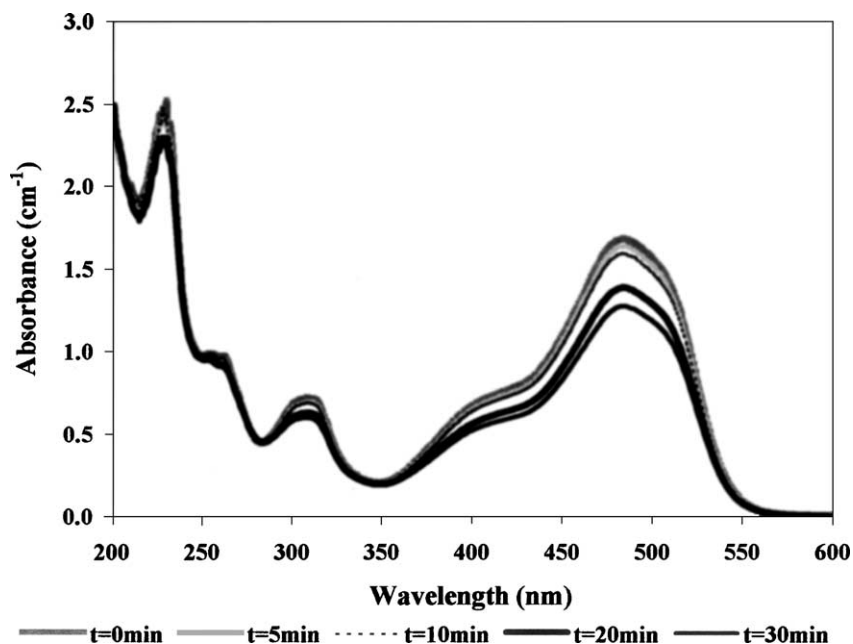


Fig. 1. AO7 bleaching during direct near-UV–VIS photolysis. Experimental conditions:  $[\text{AO7}]_0 = 75 \mu\text{M}$ ;  $I_0 = 2.6 \times 10^{-5}$  Einsteins per min; pH = 2.8.

experienced only a slight colour fading throughout the investigated reaction period. Aerated and de-aerated ( $N_2$ -gassed) solutions of  $74.5 \mu\text{M}$  AO7 were rapidly photo-decolourized in the presence of  $0.75 \text{ mM}$   $\text{SiW}_{12}\text{O}_{40}^{4-}$  in an aqueous IsOH (10%, v/v) solution. Almost concomitantly,  $\text{SiW}_{12}\text{O}_{40}^{5-}$ , the reduced form of  $\text{SiW}_{12}\text{O}_{40}^{4-}$ , was reproduced, as evidenced from the appearance of a dark blue colour in the reaction solution. The deep blue colour of the poly anion indicative for  $\text{POM}_{\text{red}}$  formation was not observable in the absence of light, POM, alcohol, and in the presence of AcCN or Ac. Moreover, the heteropolyblue did not appear during dye bleaching but directly followed the decolourization process. The blue colour was also observed when MeOH (also 10%, v/v) was used instead of IsOH, however, complete disappearance of AO7 colour was achieved in 8 min instead of 4 min in the presence of MeOH indicating that the type of alcohol might play an important role in the rate of  $\text{POM}_{\text{red}}$  production and hence, in the decolourization rate. Undoubtedly these will have larger values for alcohols, which possess readily abstractable  $\alpha\text{-H}$  atoms. The above described experimental findings strongly suggest that AO7 bleaching was an indirect, reductive process depending upon formation of a reductant (i.e. heteropolytungstate) via oxidation of IsOH. It has been evidenced in previous studies that the colour causing  $-\text{N}=\text{N}-$  bonds of azo dyes can be readily cleaved via reducing chemicals such as bisulfite-mediated borohydride [36] or zerovalent iron [37,38].

### 3.2. Photochemical reduction of $\text{SiW}_{12}\text{O}_{40}^{4-}$

The oxidation state of the reduced catalyst form was established via UV–VIS spectrophotometry as the one-electron

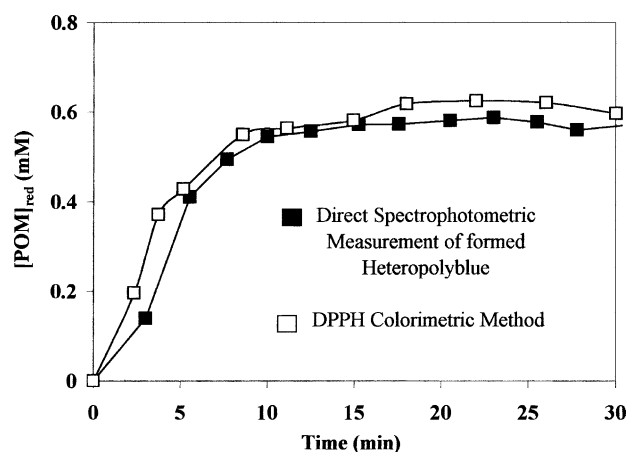


Fig. 2. Comparison of  $\text{POM}_{\text{red}}$  (i.e.  $\text{SiW}_{12}\text{O}_{40}^{5-}$ ) formation kinetics obtained by direct UV–VIS spectrophotometry of formed heteropolyblue and the DPPH method. Experimental conditions:  $[\text{AO7}]_0 = 75 \mu\text{M}$  in aerated (+air) and de-aerated (+ $N_2$ ) IsOH (10%, v/v) +  $\text{H}_2\text{O}$  reaction solution;  $[\text{POM}]_0 = 750 \mu\text{M}$ ;  $I_0 = 2.6 \times 10^{-5}$  Einsteins per min; pH = 2.8.

reduced form of the Keggin type heteropolytungstate  $\text{SiW}_{12}\text{O}_{40}^{5-}$  and also verified by the DPPH method (Fig. 2). According to Fig. 3, absorption spectra of the heteropolyblue anions obtained after 30 min irradiation in the presence and absence of AO7 and/or aeration implied that only the one-electron reduced POM at  $\lambda_{\text{max}} = 730 \text{ nm}$  was formed. Fig. 4 displays the rate of  $\text{SiW}_{12}\text{O}_{40}^{5-}$  generation throughout photocatalysis of AO7 for the same experimental conditions presented in Fig. 3. The most notable feature in the figure is that in de-aerated reaction solutions  $\text{SiW}_{12}\text{O}_{40}^{5-}$  reached its steady-state concentration

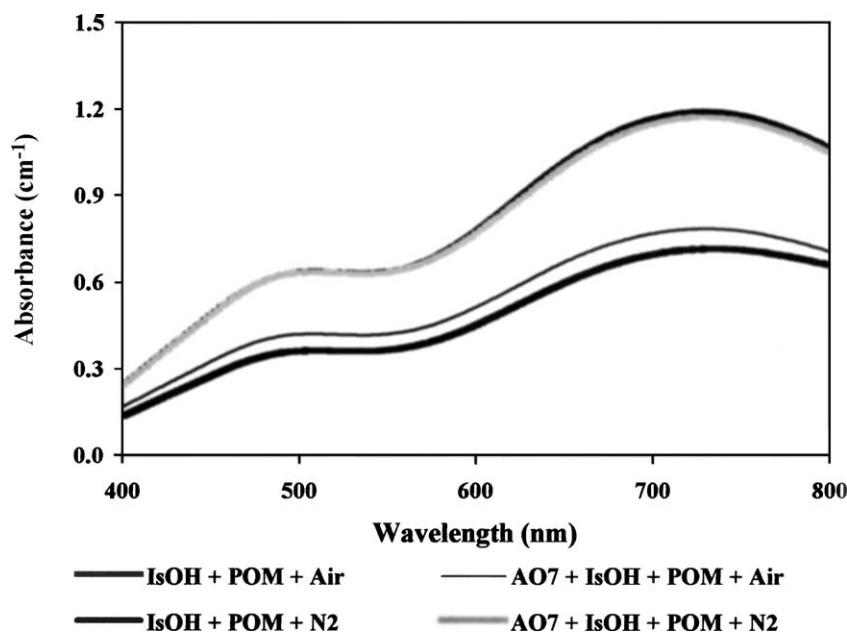


Fig. 3. UV–VIS absorption spectra of formed  $\text{POM}_{\text{red}}$  obtained upon 30 min photolysis of aerated (+air) and de-aerated (+ $N_2$ ) aqueous reaction solutions of AO7 + IsOH (10%, v/v) or MeOH (10% v/v) at pH = 2.8.  $[\text{AO7}]_0$  and  $[\text{POM}]_0$  as in Fig. 2.

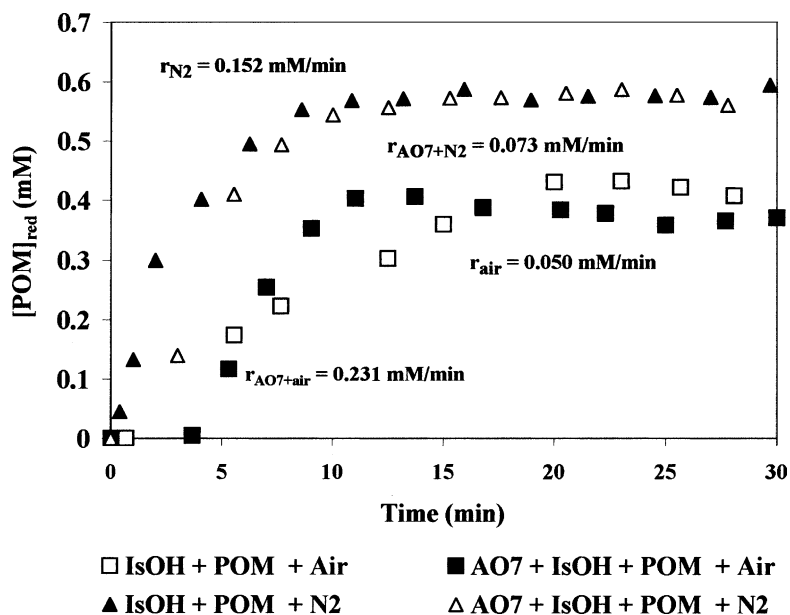


Fig. 4. Comparison of  $\text{POM}_{\text{red}}$  formation rates during photolysis of aerated (+air) and de-aerated (+ $\text{N}_2$ ) aqueous reaction solutions of AO7 + IsOH (10%, v/v) at pH = 2.8.  $[\text{AO7}]_0$  and  $[\text{POM}]_0$  as in Fig. 2.

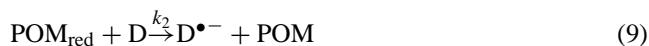
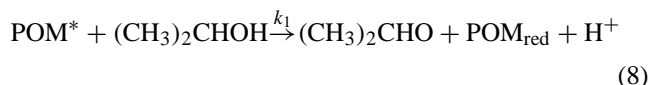
(0.59 mM) appreciably faster than under aeration (steady-state  $[\text{POM}] = 0.41 \text{ mM}$ ).  $\text{POM}_{\text{red}}$  formation rates (obtained from the initial slopes of  $[\text{POM}_{\text{red}}]$  versus irradiation time graphs) are also given in Fig. 4. Steady-state  $\text{POM}_{\text{red}}$  ( $[\text{POM}]_0 = 0.75 \text{ mM}$  in all experiments) concentrations were obtained in 15 and 11 min for de-aerated and aerated samples, respectively. In contrary, formation of  $\text{POM}_{\text{red}}$  was faster for the aerated samples than for de-aerated samples when AO7 was introduced. This might be attributable to additional  $\text{POM}_{\text{red}}$  formation via oxidation of the dye degradation products. In the presence of  $\text{O}_2$ , dye intermediates will also be oxidized and thus contribute to  $\text{POM}_{\text{red}}$  concentration, whereas  $\text{O}_2$  will simultaneously re-oxidize  $\text{POM}_{\text{red}}$ , so that a different steady-state concentration is established in aerated reaction solutions.

### 3.3. Kinetics of AO7 bleaching

A simple mechanism being probably consistent with our experimental findings involves the following reactions for de-aerated reaction solutions:



where  $I_A$  is the rate of photon absorption by POM ( $\text{M}^{-1} \text{s}^{-1}$ ) and  $\Phi$  the quantum yield for production of  $\text{POM}^*$ . Redox (charge transfer) reactions between isopropyl alcohol and dye molecule D are presented below:



In the presence of  $\text{O}_2$  the reaction shown below will compete with (9):



It is also expected that at the studied reaction pH,  $\text{O}_2^{\bullet-}$  will be fully protonated to  $\text{HO}_2^{\bullet}$  ( $\text{p}K_a = 4.69$ ). Assuming that  $\text{SiW}_{12}\text{O}_{40}^{5-}$  undergoes relatively rapid re-oxidation in the presence of excess  $\text{O}_2$  supply ( $k_{\text{obs}} = 1.3 \text{ s}^{-1}$ ;  $k = k_3 = 6500 \text{ M}^{-1} \text{ s}^{-1}$  for  $[\text{O}_2]_{\text{sat}} = 0.2 \text{ mM}$  [37]), AO7 decolorization rate simplifies to:

$$r_D = \frac{-dD}{dt} = k_1[\text{POM}^*][\text{IsOH}] \quad (11)$$

A stationary  $[\text{POM}_{\text{red}}]$  was established under aerated as well as de-aerated conditions. Approximation of steady-state conditions:

$$\frac{d[\text{POM}_{\text{red}}]}{dt} = \frac{[\text{POM}_{\text{ox}}]}{dt} \quad (12)$$

$$k_1[\text{POM}^*][\text{IsOH}] - k_2[\text{POM}_{\text{red}}][\text{D}] - k_3[\text{POM}_{\text{red}}][\text{O}_2] = k_2[\text{POM}_{\text{red}}][\text{D}] + k_3[\text{POM}_{\text{red}}][\text{O}_2] \quad (13)$$

Rearrangement of (13) gives:

$$[\text{POM}^*] = 2[\text{POM}_{\text{red}}] \frac{(k_2[\text{D}] + k_3[\text{O}_2])}{k_1[\text{IsOH}]} \quad (14)$$

Combining Eqs. (11) and (14) for aerated systems:

$$r_D = \frac{-dD}{dt} = 2[\text{POM}_{\text{red}}](k_2[\text{D}] + k_3[\text{O}_2]) \quad (15)$$

For de-aerated systems:

$$r_D = \frac{-dD}{dt} = 2k_2[\text{POM}_{\text{red}}][\text{D}] \quad (16)$$



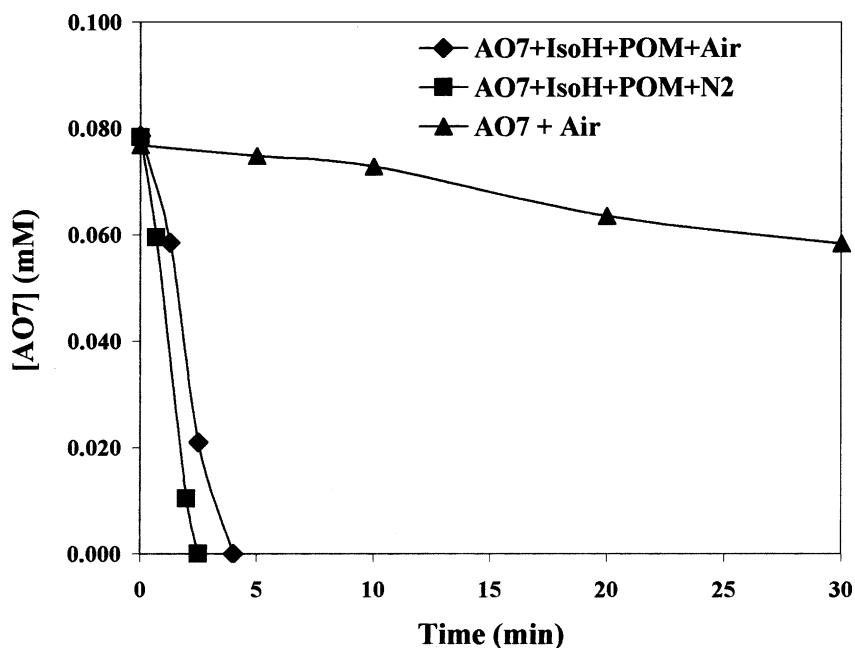


Fig. 5. AO7 abatement rates during photolysis of aerated (+air) and de-aerated (+N<sub>2</sub>) aqueous reaction solutions of AO7 + IsoH (10%, v/v) and POM at pH = 2.8. A control experiment for bleaching upon direct photolysis of aerated 75 μM aqueous AO7 solution without IsoH is also included. [AO7]<sub>0</sub> and [POM]<sub>0</sub> as in Fig. 2.

Eqs. (15) and (16) indicate that dye decolourization rate is first-order with respect to both POM<sub>red</sub> and dye concentration and  $k_2$  is a bimolecular rate constant. In the same manner, competitive reaction kinetics can be applied for photocatalytic re-oxidation of POM<sub>red</sub> with O<sub>2</sub> and AO7 by using Eqs. (15) and (16) derived from reactions (9) and (10):

$$\frac{k_{D+O_2}}{k_D} = \frac{k_2[D]}{k_2[D] + k_3[O_2]} \quad (17)$$

where  $k_{D+O_2}$  and  $k_D$  refer to the observed pseudo-first-order decolourization rate constants (IsoH was introduced in excess and hence, assumed to remain nearly constant under the experimental reaction conditions) in the presence and absence of POM<sub>red</sub> competitor O<sub>2</sub>, respectively, whereas  $k_2$ ,  $k_3$  are bimolecular rate constants for reactions of POM<sub>red</sub> with D and O<sub>2</sub>, respectively. Fig. 5 illustrates AO7 decolourization rates under varying reaction conditions. In all treatment cases decolourization follows first-order kinetics with respect to AO7, with the first-order colour removal rate constant found as  $k_{D+O_2} = 0.99 \text{ min}^{-1}$  (aerated, IsoH + POM) and  $k_D = 1.32 \text{ min}^{-1}$  (de-aerated, IsoH + POM). For comparative purposes, Fig. 5 also contains the direct AO7 photolysis experiment performed under air, that followed zero-order kinetics with  $k_{D+O_2}$  found as  $7 \times 10^{-4} \text{ M min}^{-1}$ . Inserting known values for [D] = [AO7]<sub>0</sub> = 0.0745 mM, [O<sub>2</sub>] = 0.2 mM, and  $k_3 = 6500 \text{ M}^{-1} \text{ s}^{-1}$ , gave  $k_2 = 52349 \text{ M}^{-1} \text{ s}^{-1}$ ,  $\approx 5.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  for AO7 reductive decolourization via photo-reduced SiW<sub>12</sub>O<sub>40</sub><sup>5-</sup>.

### 3.4. Identification of AO7 degradation products

Abiotic and biotic reduction products of azo dyes are expected as environmentally hazardous aromatic amines (*o*-toluidine, benzidine, chloroaniline, diaminotoluene, etc.) and thus the fate of azobenzene and related azo dyes during chemical and biochemical processes is of utmost environmental significance. As a consequence, to establish whether the extent and reaction pathway of dye degradation poses an ecological hazard, it is necessary to identify reaction products.

In previous studies, major oxidation products being identified during the early stages of AO7 oxidative degradation were benzenesulfonic acid, hydroxybenzenesulfonic acid, naphthol, and phenylazonaphthol, whereas at the end of the oxidation process low molecular weight carboxylic acids such as phthalic, formic, acetic, glycolic, glyoxylic, oxalic and malic acid [14] have been observed as the final oxidation products. Acetic acid is usually detected as the common end product of advanced oxidation processes. On the other hand, reductive cleavage of the –N=N– bond in AO7 typically produces sulfanilic acid and 1-amino-2-naphthol, or alternatively the stable SO<sub>3</sub><sup>-</sup>-adduct of the dye, whereas the photocatalytic reduction in the presence of TiO<sub>2</sub> semiconductor results in the formation of *p*-aminobenzenesulphonic acid and naphthaquinone [6].

Under our experimental reaction conditions, no AO7 degradation products were detectable under anoxic conditions, whereas for aerated reaction samples phthalic acid could be qualified on GC/ITMS (detention time on the GC

column was  $t_r = 22.625$  min). This observation implies that under aerobic conditions  $\text{POM}_{\text{red}}$  is readily re-oxidized by dioxygen, that is promptly reduced to  $\text{O}_2^{\bullet-}$ , and thus to  $\text{HO}_2^{\bullet}$ . These radicals as well as POM can further oxidize dye intermediates to carboxylic acids via multiple free radical/charge transfer processes.

#### 4. Summary and conclusions

In the present experimental investigation, it has been demonstrated that the dye AO7 could be rapidly decolourized via  $\text{SiW}_{12}\text{O}_{40}^{5-}$ -mediated photochemically induced reduction in the presence of a sacrificial electron donor, i.e. isopropanol that was simultaneously oxidized. Under the described reaction conditions reductive decolourization was complete in only few minutes. An additional advantage of this reduction–oxidation system is the repeated reuse of the catalyst, for decolourization purposes, provided that a reducing agent (an electron donor such as isopropanol) is available. Dye decolourization rate depended upon the type of alcohol used and the presence of dioxygen. Near-UV–VIS light induced dye bleaching was more rapid under  $\text{N}_2$  (de-aerated reaction conditions), since  $\text{O}_2$  (in air-equilibrated reaction solutions) competed with the azo dye for  $\text{SiW}_{12}\text{O}_{40}^{5-}$  (i.e. the one-electron reduced form of the catalyst). On the other hand,  $\text{O}_2^{\bullet-}$  that is formed from  $\text{O}_2$ , may further oxidize carcinogenic aromatic dye reduction products (i.e. aromatic amines and/or hydrazo intermediates) to potentially less toxic compounds (i.e. hydroxylated phenolic compounds and to organic acids) under aerobic conditions. Thus, AO7 degradation could be further extended to phthalic acid, the only detectable reaction product, provided that the system was aerated during the reaction. Though relatively less explored than  $\text{TiO}_2$ -mediated heterogeneous photocatalysis and the photosensitization approach, polyoxometalate-mediated photocatalysis could be an intriguing choice for the degradation of coloured pollutants using even natural (solar) light.

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