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# Application of polyoxotungstates as environmental catalysts: wet air oxidation of acid dye Orange II

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## Abstract

The catalytic effect of two Keggin-type polyoxotungstates, namely $H_4SiW_{12}O_{40}$ and $Na_2HPW_{12}O_{40}$, on the wet air oxidation of azo dye Acid Orange 7 (AO7; $C_{dye} = 248$ μM) at varying reaction temperatures ($T = 160$–$290$ °C at $P_{H_2O} = 0.6$–$3.0$ MPa, respectively) was examined. Arrhenius parameters for catalytic and non-catalytic wet air oxidation were obtained in terms of temperature dependent AO7 and TOC abatement kinetics. To get a further insight into the dominant reaction pathway of the catalytic and non-catalytic wet air oxidation processes, isopropyl alcohol and bromide (300 μM) were added as $OH^\bullet$ scavengers. Obtained results revealed an important homogenous contribution for WAO of AO7 (Arrhenius parameters $E_a = 84$ kJ mol$^{-1}$ and $A = 5.6 \times 10^7$ min$^{-1}$). However, mineralization (TOC removal) was noticeably influenced by the investigated polyoxotungstates ($C_{catalyst} = 140$ μM) and the activation energy decreased from 40 kJ mol$^{-1}$ in the absence of catalyst to only 28 kJ mol$^{-1}$ ($PW_{12}{}^{3-}$) and 22 kJ mol$^{-1}$ ($SiW_{12}{}^{4-}$). The catalytic processes were appreciably less sensitive to the presence of $OH^\bullet$ scavengers than uncatalyzed wet air oxidation implying that polyoxotungstate-catalyzed wet air oxidation did not solely depend upon a free radical type reaction mechanism. The obtained results tend to support the free radical chain mechanism to account for Orange dye degradation only for uncatalyzed wet air oxidation. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Acid Orange 7 (Orange II); Azo dyes; Catalytic wet air oxidation; Polyoxometalates; $PW_{12}O_{40}^{3-}$; $SiW_{12}O_{40}^{4-}$; $OH^\bullet$; Scavengers

## 1. Introduction

Colour removal has become a challenging aspect of textile wastewater treatment because of the growing concern about residual colour that is closely associated with toxicity and aesthetics of the discharged effluent [1,2]. In particular azo dyes, that constitute a major portion and probably have the least desirable consequences in terms of environmental legislation, are readily reduced to potentially hazardous aromatic amines under anoxic conditions [3,4]. Most commonly practiced physico-chemical (i.e. coagulation, activated carbon adsorption, membrane filtration) and biochemical (aerobic biological treatment) methods have already proven to be inefficient for decolourization [5] due to the fact that commercial textile dyes are intentionally designed to exhibit a high degree of chemical, photolytic, and microbial stability as to

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fulfil the fastness requirements of consumers [1,2]. The treatability of textile azo dyes and dyehouse effluent by employing different advanced chemical oxidation methods has already been extensively studied in the past [6–20]. The advantage of so-called advanced oxidation processes (AOPs) over conventional oxidation processes originates from the reactivity of the free radical species involved that is mainly the hydroxyl radical(s), $OH^{\cdot}$ [21,22]. The extremely short–lived free radical $OH^{\bullet}$ ($\leqslant 10^{-3}$ s) [23] is associated with reaction systems where its instantaneous concentration is very low [18] because of its high reaction rates with substrates ($10^6$–$10^9$ $M^{-1}$ $s^{-1}$) and hence non-selective nature [23]. In other words, $OH^{\cdot}$ will attack readily and almost equally fast all inorganic and organic species in the reaction medium thus resulting in enormous active oxidant wastage and inefficient destruction rates of the target pollutant.

Hydrothermal oxidation processes (HOP) have been extensively studied for their application to a variety of refractory model pollutants and actual wastewater [24,25]. Wet air oxidation (WAO) refers to the aqueous phase oxidation of organic and inorganic compounds under sub-critical conditions ($T = 175$–$320$ °C; $P = 0.5$–$20$ MPa) [26]. WAO is a well-established technology of major importance for wastewater treatment, especially when the waste effluent is too dilute for incineration and too concentrated for the effective application of AOPs [27]. However, the severe operating conditions associated with WAO result in high capital investments and high maintenance costs [28]. As a consequence, considerable attention has been paid to the use of homogenous and heterogeneous/supported oxidation catalysts that can potentially accelerate the oxidation rate and allow milder operating conditions [29,30].

The rapid oxidation of aromatic substrates and their transformation to lower molecular weight fractions and organic acids in sub-critical water has been explained as a free radical chain auto-oxidation process 31. It has been suggested that WAO oxidation might occur through the formation of alkyl, alkyl peroxyl radicals and hydroperoxides with the latter being responsible for the autocatalytic decomposition of the original substrate (S) described in the following manner [32];

$$RH + O_2 \longrightarrow R^{\bullet} + HO_2^{\bullet}\ \text{(initiation)} \tag{1}$$

$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet}\ \text{(propagation)} \tag{2}$$

$$RO_2^{\bullet} + RH \longrightarrow ROOH + R^{\bullet}\ \text{(propagation)} \tag{3}$$

$$ROOH \longrightarrow RO^{\bullet} + OH^{\bullet}\ \text{(autocatalytic decomposition)} \tag{4}$$

$$RO^{\bullet} + RH \longrightarrow ROH + R^{\bullet} \tag{5}$$

$$OH^{\bullet} + RH \longrightarrow R^{\bullet} + H_2O \tag{6}$$

$$2ROO^{\bullet} \longrightarrow ROOR + O_2\ \text{(termination)} \tag{7}$$

Transition metal ion catalysts such as Cu (II), Fe (III), Mn (IV) and Co (III) have been used to promote WAO [26,30,33]. It is thought that at high temperatures, these ions may facilitate the process, possibly by direct electron transfer between the substrate and metal (M) in a new initiating step;

$$RH + M^{n+} \longrightarrow R^{\bullet} + H + +M^{n-1}\ \text{(catalytic initiation)} \tag{8}$$

Particularly copper ion, but also other transition metal ions, has been reported as a promising catalyst applied for WAO in the homogenous state, but has to be removed after treatment to prevent contamination of the receiving water body by toxic copper ion [28,29]. In respect to post-treatment (i.e. easy separation/reuse of the catalyst after the oxidation process), heterogeneous catalysts that can be easily set-up for continuous operation have become preferable [30]. However, catalyst leaching and deactivation in the early stages of application have been recognized in investigations with heterogeneous catalysts, often accompanied with low treatment efficiencies as compared with those obtained for homogenous type transition metal catalysts speculatively due to the limited mass transfer rates in heterogeneous systems [34].

Polyoxometalates (POMs) and hetero-polyoxometalates are suitable materials for catalyst design in heterogeneous and homogenous media mainly because of their high acidity and oxidizing ability that can be systematically controlled by changing the constituent atoms and polyanion structures [35]. By far the most important application of POMs is the field of catalysis, particularly the selective oxidation of industrial materials and products [36,37]. Recently, they have also been applied as environmental catalysts for the photo-induced decomposition of several organic pollutants [38]. POM-catalyzed oxidation is envisioned as a mainly two-stage redox cycle, where first an interaction takes place between organic substrate (S) (an electron donor) and the oxidized form of the POM ($POM_{ox}$), leading to products (P) and reduced form of the catalyst ($POM_{red}$). The latter stage is also thought to be the rate-determining step throughout POM-catalyzed aerobic oxidation 37;

$$POM_{ox} + S \rightarrow P + POM_{red} + nH^+ \quad (9)$$

Thereafter, the catalytic cycle is completed by re-oxidation of the reduced catalyst, preferably by molecular oxygen 37;

$$POM_{red} + n_{/2}O_2 + nH^+ \rightarrow POM_{ox} + n_{/2}H_2O \quad (10)$$

In the present study, the polyoxotungstates $H_4SiW_{12}O_{40}$ ($SiW_{12}^{4-}$) and $Na_2HPW_{12}O_{40}$ ($PW_{12}^{3-}$), or abbreviated as POTs, have been employed as WAO catalysts owing to their relatively high thermal and hydrolytic stability as well as the fact that POTs are capable of undergoing facile re-oxidation under aerobic conditions and/or the presence of an acidic environment [37,38]. According to our knowledge, there is only one application of a water soluble POM ($\alpha$-$Na_5[PV_2Mo_{10}O_{40}]$) used as a potential WAO catalyst in the scientific literature. It refers to the combined anoxic delignification and oxidative degradation of pulp mill effluents [39,40].

In order to examine WAO and polyoxotungstate-catalyzed WAO rates, the azo dye Acid Orange 7 (AO7; also termed Orange II) was selected as a commercially important, readily available, well-examined and representative azo type textile dye. AO7 is a water-soluble dyestuff preparation used for wool and nylon dyeing in slightly acidic media. The ortho-substitution tends to stabilize this dye because of strong internal bond formation and tautorism that inhibits ionization, hydrogen abstraction and even cis-trans isomerization being common for many azo dyes and azobenzene [17]. Thus AO7 is resistant to visible, near-UV light irradiation (300 nm $< \lambda <$ 400 nm) and biodegradation, the action of $O_2$, $H_2O_2$, common acids and bases hence representing a typical refractory model pollutant [17,41]. Only ozonolysis at high doses as well as free radical based advanced oxidation processes, such as $H_2O_2$-induced photochemical treatment in the presence of UV-C light Fenton's and Photo-Fenton's reaction, has led to Orange II decomposition [6–20, 42]. Its uncatalyzed [9] and catalyzed [11,19] oxidation in subcritical water via transition metals and supported metal oxides has already been investigated in the past, hence this contribution will add some facts to this field.

## 2. Experimental

### 2.1. Materials

Acid Orange 7 dye (AO7, C.I. number 55510; 87% dye content; 350.33 g $mol^{-1}$ formula weight; 10 g $l^{-1}$ water solubility) was purchased from Aldrich and used as received. $H_4SiW_{12}O_{40}$ and $Na_2HPW_{12}O_{40}$ (both reagent grade) were obtained from Fluka.

### 2.2. WAO apparatus and procedure

WAO reactions were conducted in batch mode. For this purpose, 500-μl aliquots of $O_2$ saturated aqueous AO7 (80 mg $l^{-1}$; 248 μM) solutions were placed into 316 stainless steel (SS) unions (*Swagelok*©, Columbia Fluid Technologies, LLC). Thereafter, the filled SS unions (0.25″ outer diameter; 1200 μl total volume capacity) were submerged in a Techne SBS-4 model fluidized sand bath that was pre-heated to the desired reaction temperature ($T$ = 100–300 °C, corresponding to operating water vapor pressures of 0.1–8.6 MPa, respectively). Temperature control was monitored with a thermocouple (Fisher Scientific, Inc) inserted in the sand bath. Typically, the temperature in the sand bath varied between + 3 °C during the WAO reactions. The turbulence originating from air sparging of the sand bath kept the reaction solutions in the SS unions agitated. At designated time intervals throughout the oxidation reactions ($t = 0$–100 min) one SS union was removed from the sand bath, rapidly cooled under flushing tap water and then opened to obtain the treated sample.

The pH of the ASTM-grade water used to prepare AO7 and POT solutions was pre-adjusted to 2.60 (±0.01 at $T = 25$ °C) using 1.00 N phosphoric acid solution. Phosphate was chosen as the pH buffer because of its relatively slow reaction rate with $OH^\bullet$ ($k_{H_2PO_4^-} = 1.8\times10^4$ $M^{-1}s^{-1}$; $k_{H_3PO_4} = 2.1\times10^4$ $M^{-1}s^{-1}$). Measurements taken before and after the WAO experiments did not show a significant change in pH (±0.2 pH units).

### 2.3. Sample analysis

UV-Vis absorption spectra ($\lambda = 200$–800 nm) and the reduction in visible absorbance at $\lambda_{max} = 484$ nm were monitored by a Perkin-Elmer Lambda 14 model double beam spectrophotometer through a 1 cm path length. The molar extinction coefficients obtained for aqueous AO7 solutions at $\lambda_{max} = 484$ nm at varying dye concentrations (5 mg–100 mg $l^{-1}$) were used to determine the residual dye concentration in the untreated and oxidized dye samples. The extinction coefficients were found as $\varepsilon_{484} = 21857$ $M^{-1}$ $cm^{-1}$at pH 2.6 (i.e. reaction pH for $SiW_{12}^{4-}$–catalyzed WAO) and as $\varepsilon_{484} = 19836$ $M^{-1}$ $cm^{-1}$at pH 1.6 (the reaction pH for $PW_{12}^{3-}$–catalyzed WAO). Spectral analysis of the raw and oxidized reaction solution confirmed that both $SiW_{12}^{4-}$ ($\lambda_{max} = 262.4$ nm) and $PW_{12}^{3-}$ ($\lambda_{max} = 263.8$ nm) remained stable throughout the catalytic WAO reactions. The extent of mineralization was measured by a Shimadzu TC-5000A model organic carbon analyzer. Nitrate analysis was carried out with the cadmium reduction colorimetric method using a Hach DR2000-VIS spectrophotometer for absorbance measurement. The analysis range was 0.5–20 mg/l $NO_3$–N by employing Hach Method Number 355.

Identification of organic 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 μm in film thickness) was operated by the following temperature program: isothermal for 2 min at 70 °C, heating up linearly to 250 °C at a rate of 10 °C/min, isothermal at 250 °C for 10 min. The injection port was set at 250 °C. The carrier gas was ultra-pure He and used at a flowrate of 1 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.

## 3. Results and discussion

### 3.1. Wet air oxidation

AO7 removal as a function of uncatalyzed WAO time at varying reaction temperatures is presented in Fig. 1.

As apparent from the fig. dye degradation proceeded appreciably faster at elevated temperatures. For instance, at $T = 230$ °C complete colour removal was achieved in 40 min, whereas only 5 min were required at $T = 290$ °C. No induction period for AO7 degradation was observed at the investigated reaction conditions and the obtained data could be directly fitted to first order kinetics with respect to AO7 ($k_{AO7}$ stands for the first-order AO7 degradation rate constant, in $min^{-1}$). It has been already reported that AO7 breaks thermally into fragments that are most probably nitrogen (gas), naphtol and benzene sulphonic acid via electrophilic cleavage of the labile azo bond (–N=N–), provided that a pollutant-specific threshold temperature and/or a steady state free radical concentration has been achieved [11,43]. The reductions in TOC values for the same experiments are shown in Fig. 2.

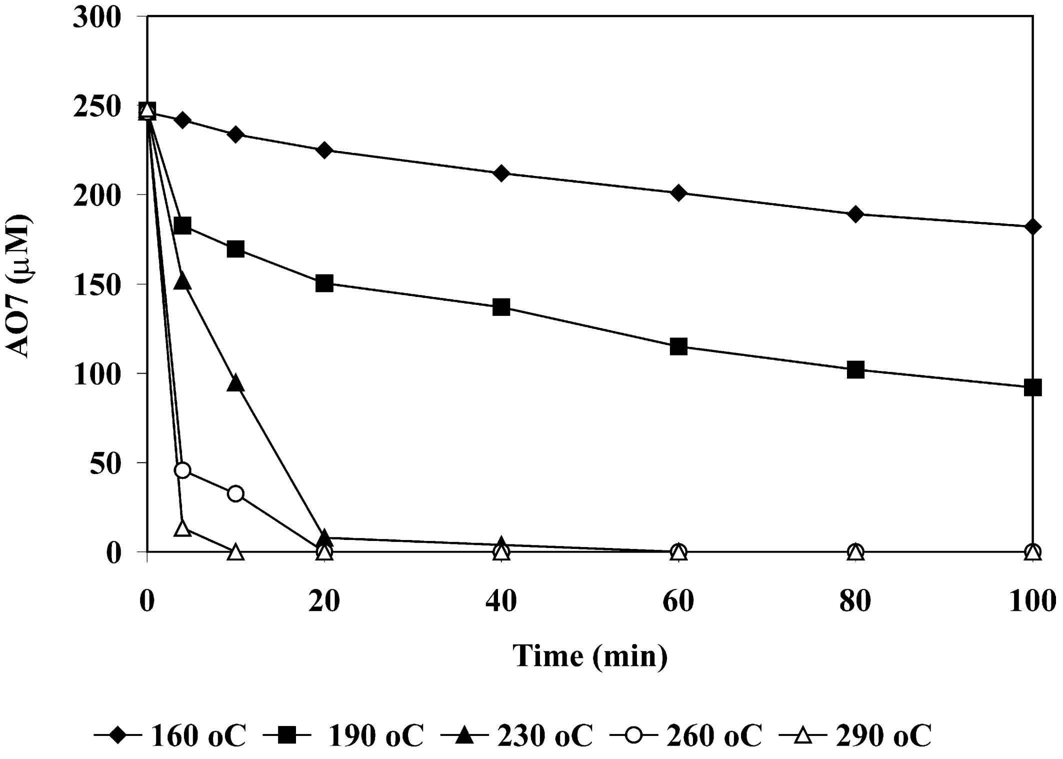

Fig. 1. Effect of WAO temperature on AO7 abatement rates.

The positive effect of increasing the reaction temperature was also evident for TOC removal. No TOC reduction was observed at $T = 160$ °C at all. For the highest studied reaction temperature ($T = 290$ °C), 92% mineralization was obtained after 100 min WAO. TOC abatement rates were also found to be first order with respect to organic carbon content ($k_{TOC}$ = first order TOC removal rate constants). Based on the experimental data obtained for AO7 and TOC removal kinetics at different oxidation temperatures, Arrhenius parameters could be established by using the following empirical kinetic equation;

$$k = A \times \exp(-E_a/R \times T) \qquad (11)$$

where $k$ is the first order reaction rate constant (in $\text{min}^{-1}$), $E_a$ is the activation energy (in kJ $\text{mol}^{-1}$) and $A$ refers to the frequency factor (in $\text{min}^{-1}$). $E_a$ (= 84.3 kJ $\text{mol}^{-1}$) and $A$ (= $5.6 \times 10^7$ $\text{min}^{-1}$) values found for uncatalyzed WAO of parent compound AO7 (Fig. 3) were completely in accordance with activation energies obtained for thermal degradation of Orange II and related aromatic azo compounds [9,19,43,44].

The Arrhenius constants obtained for WAO TOC abatement rates ($E_a = 40.4$ kJ $\text{mol}^{-1}$; $A = 174.2$ $\text{min}^{-1}$) are significantly lower than those established for the parent compound, AO7, due to the fact that the activation energy for ultimate oxidation (mineralization) not only accounts for the oxidation of aromatic dye intermediates and several ring opening products (such as carboxylic acids), but also for the direct oxidation of the initial reactant to $CO_2$.

### 3.2. $SiW_{12}^{4-}$ and $PW_{12}^{3-}$- catalyzed wet air oxidation

Temperature dependence of 140 µM $SiW_{12}^{4-}$ and $PW_{12}^{4-}$-catalyzed WAO together with the Arrhenius parameters obtained for catalytic WAO of 248 µM AO7 are depicted in Fig. 4. The Arrhenius constants found for AO7 degradation were similar for both catalyzed and uncatalyzed WAO (Fig. 3)

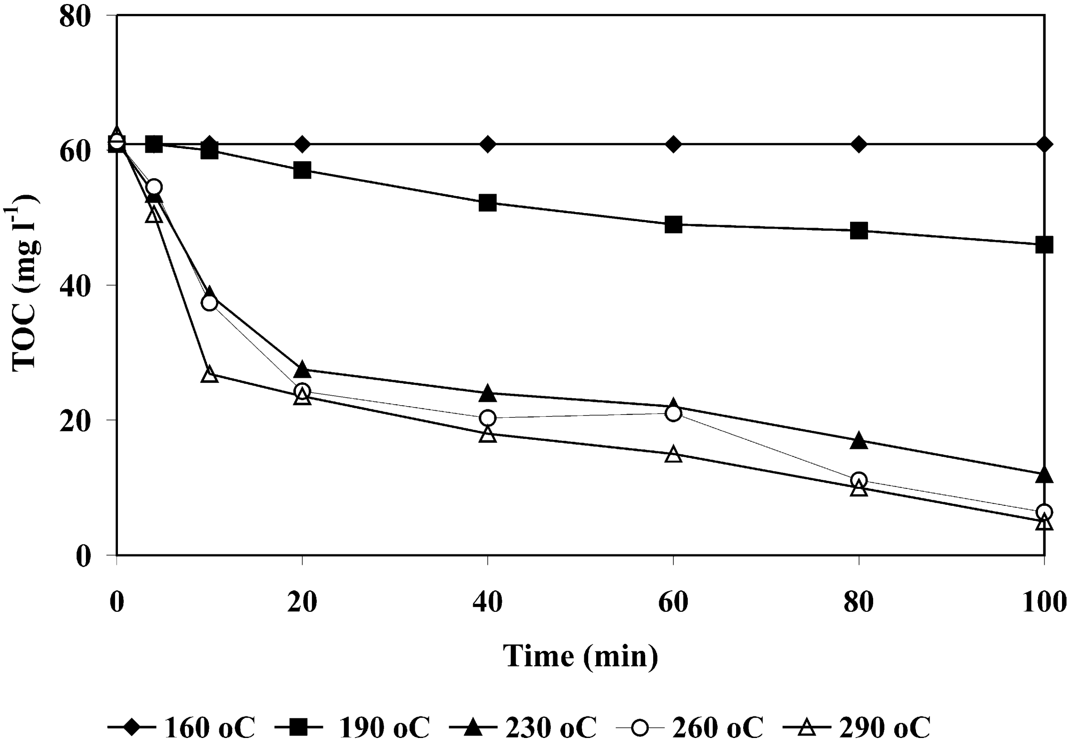

Fig. 2. Effect of WAO temperature on TOC abatement rates.

since azo dyes are known to thermally decompose rapidly under WAO conditions and even under anoxic conditions as has been mentioned previously. Consequently, if only colour removal is required, the introduction of a catalyst to WAO might not be necessary.

However, in terms of ultimate oxidation of the parent compound and oxidation byproducts (expressed as the values obtained for TOC removal), $E_a$ values decreased by a relative rate of 45 and 31% for SiW$_{12}^{4-}$ and PW$_{12}^{4-}$-catalyzed WAO, respectively (Fig. 4). It has been suggested in former related studies that a promoted carbon dioxide yield or higher selectivity (i.e. the per cent ratio of $CO_2$ gas formation per parent compound oxidation) of catalytic WAO might be responsible for the noticeable reduction in TOC- based activation energies [45].

It has been demonstrated in previous publications that particularly acid strength is an important factor in bringing about the unique catalytic activity of heteropolyacids [38] and other catalytic compounds. The indifference in catalytic activity of the selected POTs can be explained by the fact that acid strength, that is in the order SiW$_{12}^{4-}$ $<$PW$_{12}^{3-}$ becomes insignificant for aqueous phase reactions, where acidities differ only slightly since most heteropolyacids are completely protonated. Besides, it should be kept in mind that PW$_{12}^{3-}$ was employed as its disodium salt, which reduces its acid strength appreciably [37,38].

Fig. 5 displays the normalized changes in TOC values for WAO and POT-catalyzed WAO obtained at $T = 260$ °C in the presence of 140 μM POT. From the figs. it is apparent that TOC abatement rates were not significantly affected by the introduction of POT. The shapes of the normalized curves as a function of WAO time are typical of a "consecutive reaction scheme" were the parent compound rapidly disappears at the beginning of the reaction and is simultaneously converted to several intermediate oxidation products [29].

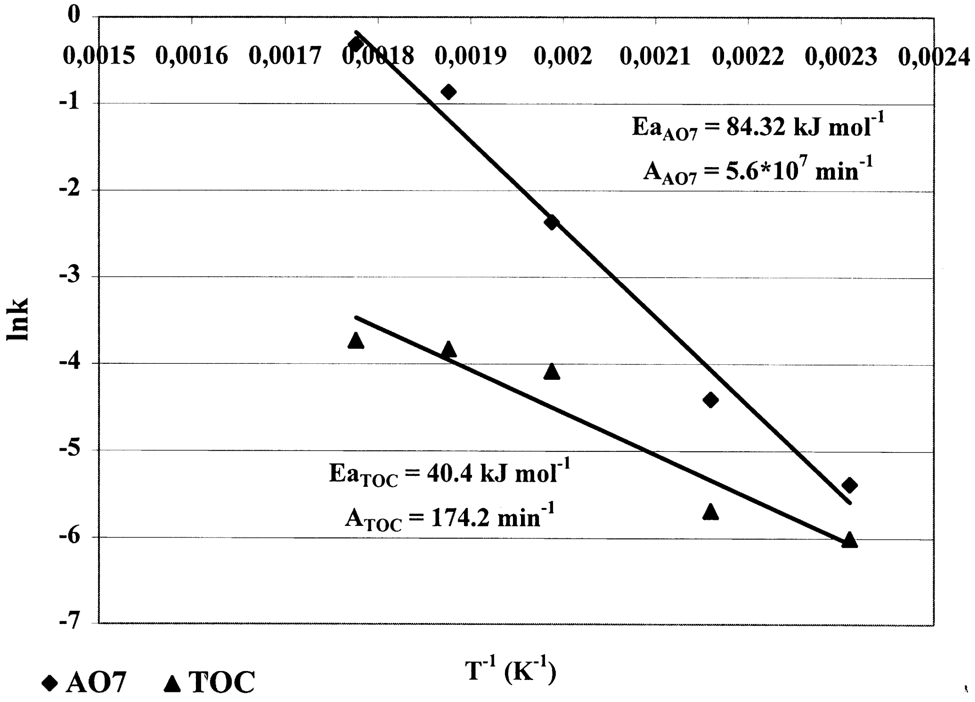

Fig. 3. Temperature dependence of AO7 WAO. Arrhenius parameters for AO7 and TOC removal.

### *3.3. Oxidation products*

Abiotic and biotic reduction products of azo dyes are expected as environmentally hazardous aromatic amines (*o*-toluidine, benzidine, chloroaniline, diaminotolune etc.) and thus the fate of azobenzene and related azo dyes during chemical and biochemical processes is of utmost environmental significance [2,4]. 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.

Former investigators have concluded from the appearance of hydroxylated aromatic intermediates during catalytic and non-catalytic WAO that both processes involve free radical type chain reactions and possibly the same reaction pathway [29,31] though quantitatively less oxidation products were detected for seemingly more selective catalyzed WAO 29. Accordingly, the proposed reaction scheme for the conversion of thermally formed radicals into corresponding hydroperoxyl radicals could be directly applied to WAO. In related experimental work, benzenesulfonic acid, hydroxybenzenesulfonic acid, naphtol, and phenylazonaphtol were identified as the major oxidation products during the early stages of AO7 oxidative degradation, whereas at the end of the oxidation process low molecular weight carboxylic acids such as phythalic, formic, acetic, glycolic, glycoxylic, oxalic and malic acid [11,36] have been detected as the stable end products of advanced oxidation.

Only phythalic acid could be qualitatively identified on GC/ITMS (GC column detention time = 22.675 min) for catalyzed and uncatalyzed WAO under our experimental conditions, from which finding it might be speculated that for both oxidation systems reaction pathways similar to each other and to those observed for photocatalytic oxidation of Orange II are possibly involved. Samples were also analyzed for inorganic oxidation products (i.e. $NH_4^+$, $NO_3^-$, and $NO_2^-$). Since neither ammonium, nitrite, nor nitrate could be detected throughout the course of catalyzed and uncatalyzed WAO (the method detection limit was 0.1

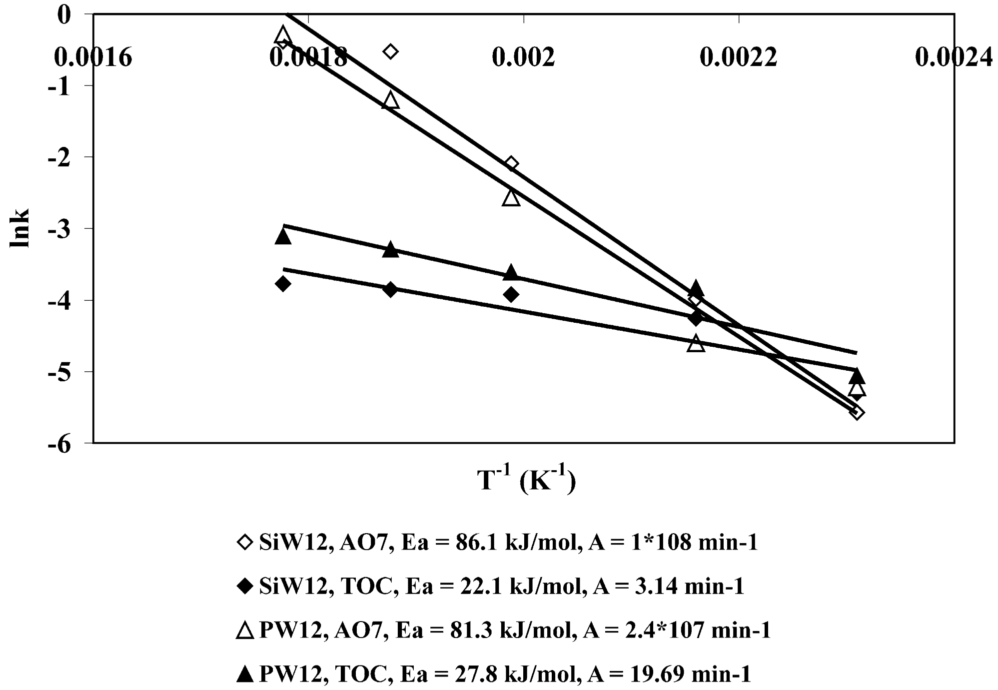

Fig. 4. Temperature dependence for POT ($SiW_{12}^{4-}$ and $PW_{12}^{3-}$)-catalyzed WAO of AO7. Arrhenius parameters for AO7 and TOC removal.

mg $l^{-1}$ $NO_3^-$- N) under our experimental conditions, it might be argued that most probably nitrogen was released as gaseous nitrogen formed during the thermal cleavage of the –N=N– bond [46].

### 3.4. *Effect of $OH^{\bullet}$ scavengers*

The reaction mechanism by which polioxometalates oxidize organic compounds is very critical to their potential application. It has been reported that the polyoxometalate-mediated photocatalytic degradation of organic compounds in aqueous solution resulted in the formation of hydroxylated byproducts, a result that is consistent with an $OH^{\bullet}$-induced reaction mechanism on the first sight [47]. However, it should be considered that other mechanisms can also account for the formation of $OH^{\cdot}$-adducts. Hence qualitative byproduct identification may not sufficient to explain differences between catalytic and non-catalytic WAO reaction mechanisms or pathways. The probability that besides the electron-transfer reaction mechanism, as has been suggested for the heterogeneous photocatalytic oxidation of propan-2-ol and 2,3,4,-trichlorophenol in a recent study, $OH^{\cdot}$ might be involved in POM-catalyzed oxidation, was not only deduced from the detection of $OH^{\cdot -}$ adducts, but also EPR-trapping during UV-photolysis experiments with aromatic HC's, and a deuterium isotope effect of $k_H/k_D$ $\approx$3.7 in the production of ketone from tertiary alcohol [47]. However, these studies have all been conducted for ambient temperature advanced oxidation systems. Thus an alternative experimental approach has to be applied for the present case.

The addition of radical reaction inhibitors (radical scavengers) often proves or confirms a radical chain mechanism. The chain reaction inhibitor reacts rapidly with $OH^{\cdot}$, leading to other, more stable and less reactive radicals that do not function as radical chain carriers [23]. The reaction has to be considerably reduced to conclude that a free radical chain reaction is involved.

Considering the above-mentioned facts, the possible role of $OH^{\bullet}$ in WAO of AO7 was tested by observing how $k_{AO7}$ and $k_{TOC}$ were affected by

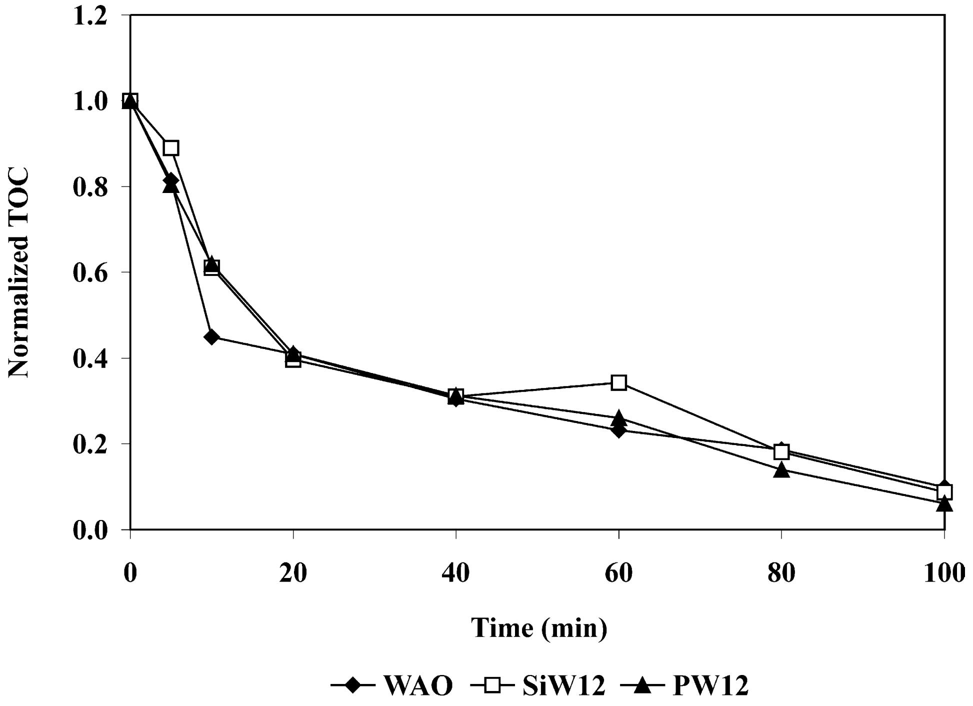

Fig. 5. Normalized TOC abatement rates for WAO and POT-catalyzed WAO.

the presence of OH• scavengers. For this purpose, WAO of AO7 at $T = 260$ °C was conducted in the presence of an organic (isopropanol; IsOH) and an inorganic (bromide in the form of KBr) OH• scavengers at a concentration of 300 μM. Table 1 lists the $k_d$ and $k_{TOC}$ values found for WAO and POT-catalyzed WAO in the absence and presence of the selected OH• probes [48].

From the table it is apparent that WAO based on AO7 and TOC removal rates are seriously retarded in the presence of both scavengers. In fact, the appreciably stronger decrease in $k_d$ and $k_{TOC}$ values in the Br$^-$– added WAO as compared to the less effective OH· scavenger IsOH clearly suggests (as theoretically expected from a mainly OH•- governed reaction mechanism) that free radicals play a major role in case of uncatalyzed WAO as has been demonstrated before by using several OH· traps [49,50]. In the presence of POTs, on the other hand, no significant decrease

Table 1

Effect of OH• scavengers on the first order AO7 and TOC removal rate constants ($k_d$ and $k_{TOC}$, respectively) during WAO, $SiW_{12}{}^{4-}$ and $PW_{12}{}^{3-}$- catalyzed WAO ($C_{AO7} = 248 \pm 4$ μM; $T = 260$ °C; $C_{POT} = 140 \pm 3$ μM)

| Process type | WAO | | WAO + $SiW_{12}^{4-}$ | | WAO + $PW_{12}^{3-}$ | |
|---|---|---|---|---|---|---|
| | $k_d$(min$^{-1}$) | $k_{TOC}$ (min$^{-1}$) | $k_d$(min$^{-1}$) | $k_{TOC}$ (min$^{-1}$) | $k_d$(min$^{-1}$) | $k_{TOC}$(min$^{-1}$) |
| No scavenger (control) | 0.828 | 0.022 | 0.786 | 0.012 | 0.889 | 0.024 |
| IsOH[a] | 0.361 | 0.011 | 0.731 | 0.019 | 0.780 | 0.019 |
| Br$^-$[a] | 0.286 | 0.008 | 0.691 | 0.019 | 0.811 | 0.022 |
| $I_{r,IsOH}$[b] | 0.564 | 0.500 | 0.071 | 0.030 | 0.123 | 0.203 |
| $I_{r,KBr}$[b] | 0.654 | 0.628 | 0.121 | 0.056 | 0.088 | 0.091 |

[a] $C_{IsOH} = C_{KBr} = 300 \pm 9$ μM.

[b] $I_r$ = inhibition of the first order reaction rate constants relative to the controls.

in $k_d$ and $k_{TOC}$ values was observed that provides evidence that another type of reaction mechanism, probably electron-transfer [51] and/or hydrogen abstraction [52], dominates the POT-catalyzed WAO. Most commercial textile dyes are in fact formulations of several components, and the content (purity) of the actual dye lies in the range of 10–98%. The rest is a mixture of impurities (ash, salt residue etc.) and several dye assisting chemicals added to improve dyeing and solubility properties. Thus in practice it has to be considered that the dye is usually present in a "competing" environment, even in the absence of additional dye auxiliary chemicals (acetic acid buffer, leveling agents, chelating agents etc.). From the practical point of view the obviously higher selectivity of POT-mediated WAO would result in more energy efficient and hence economically attractive remediation processes, where the target pollutant (azo dye) could be preferably oxidized in the complex background matrix of textile industry wastewater.

## 4. Conclusions

The Keggin-type polyoxotungstates $SiW_{12}O_{40}^{4-}$ and $PW_{12}O_{40}^{3-}$ have been applied as environmental catalysts for Acid Orange 7 (Orange II) degradation in sub-critical water. While the parent compound was oxidized rapidly, TOC removal seemed to be the rate-controlling step. The experimental results have shown that the addition of polyoxotungstates had no dramatic effect on decolourization and mineralization rates. However, the activation energy in terms of TOC decreased significantly in the presence of polyoxotungstate catalysts. It could also be demonstrated that upon the use of polyoxotungstates, the oxidation mechanism shifts from a mainly free radical (mainly $OH^{\cdot}$) involved chain reaction to a charge (an electron) transfer controlled, more selective and hence preferable process in the presence of $SiW_{12}{}^{4-}$and $PW_{12}{}^{3-}$ as evidenced via $OH^{\cdot}$ scavenger addition experiments. In conclusion, the free radical theory seemed to significantly account only for uncatalyzed wet air oxidation of Orange II and catalytic WAO should be preferred for a more selective and hence efficient decolourization of dyehouse effluents.

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