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Photocatalytic reductive destruction of azo dyes by polyoxometallates: Naphthol blue black

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Abstract

Various polyoxometallates (POM) $PW_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$, $P_2W_{18}O_{62}^{6-}$ and $P_2Mo_{18}O_{62}^{6-}$ have been used as photocatalysts for the reductive destruction of the azo dye naphthol blue black (NB). In the process POM absorb light and mediate the electron transfer from a sacrificial donor, propan-2-ol, to the azo dye. NB is rapidly destructed in the presence of POM, while toxic intermediate products, such as aromatic amine derivatives (aniline, *p*-nitro-aniline and *p*-phenylene-diamine) are observed in a multi-electron process. Increase of catalyst and/or propan-2-ol concentration accelerates the photodegradation of dye till a saturation value, while an optimum concentration of the added dye is required. The nature of the POM catalyst dictates the efficiency of the reductive decoloration of NB, following the order $PW_{12}O_{40}^{3-} > SiW_{12}O_{40}^{4-} > P_2W_{18}O_{62}^{6-}$ according to their photooxidizing ability. No reaction is noticed with the 2-e-reduced molybdate, $P_2Mo_{18}O_{62}^{8-}$, which exhibits a more positive redox potential.

Keywords: Photocatalysis; Polyoxometallates; Azo dyes; Naphthol blue black; Reductive decomposition

1. Introduction

Azo dyes are synthetic organic pigments of great environmental risk due to their toxicity and the potential carcinogenic risk of their degradation products, combined with their wide usage in textiles, papers, leathers, gasoline, additives, food and cosmetics [1]. Thus, it is essential to develop methods to destruct such compounds. Beyond the conventional methods suitable for azo dyes decoloration, such as adsorption on activated carbon, biological, chemical or photocatalytic oxidation, an interesting alternative involves the implementation of reduction. Efforts in this direction lead to facile reductive decoloration of the dye under anaerobic conditions via cleavage of the azo bond by electrolytic [2] or chemical reduction, i.e., with sulfide [3], metal iron, trivalent iron [4], etc. Since the reduction products are used to be more amenant to oxidations compared to the recalcitrant azo dyes, this reductive process might facilitate the action of a subsequent biological or chemical oxidation in an integrated, first reductive and then oxidative treatment [5].

1.1. Dye sensitised TiO_2 or POM assisted degradation of azo dyes

Generally speaking, the redox potential of the visible light excited states of azo dyes is negative enough to inject an electron to the conduction band (CD) of TiO_2 or the LUMO of POM. This has been observed by various workers for TiO_2 [6,7], but not for POM including this work. This process with TiO_2 leads to effective decomposition of dyes in the presence of oxidants such as O_2, H_2O_2, etc., that further assist the degradation via formation of superoxy, O_2^-, hydroperoxy, HO_2, hydroxy, OH, etc. radicals.

This case has not been observed with POM as mentioned earlier. However, dye sensitised-POM assisted degradation of dyes has been observed: (a) with positively charged dyes that are electrostatically attracted to negatively charged POM [8] and (b) with POM immobilized in various supports in which the microenvironment favors preassociation of POM with the dyes [9].

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Reductive decomposition of dyes by both TiO_2 and POM via UV–near visible excitation of catalysts, in the presence of a sacrificial reagent, has been observed as shown below.

1.2. Advanced oxidation processes in reductive destruction of azo dyes

Among the modern techniques for treatment of organics, Advanced Oxidation Processes (AOP) are very promising, well known for their oxidizing efficiency even in traces of the target compounds. Especially, TiO_2 and POM photocatalysis are more elegant and practical since they can combine oxidations and reductions in one pot system and in a catalytic mode. In this frame, TiO_2 has been used as photocatalyst to mediate electron transfer from an organic donor, such as alcohol, to azo dyes, which are degraded [10–12].

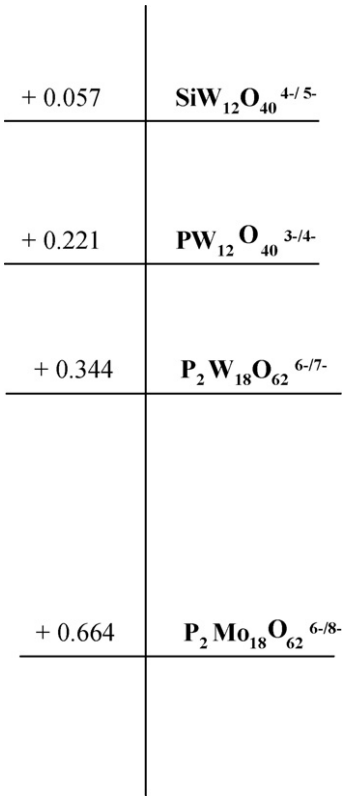
Polyoxometallates (POM) is a class of molecular metal oxide anions that exhibit rich photocatalytic action [13,14], analogous to this of semiconductors [15]. POM are, relatively, not toxic and inexpensive. Absorption of UV–near vis light by POM leads to the formation of strong oxidant excited state, able to mineralise plethora of organic species, including organic pollutants [16–20]. The photoreduced POM species can in turn reduce a great variety of chemical species [21], i.e. O_2 [22], H^+ [23], nitroaromatics [24] or metal ions [25–28]. Arslan-Alaton and Ferry have shown that the photochemically reduced POM $SiW_{12}O_{40}^{5-}$ can efficiently reduce and decompose the acid orange-7 dye in the presence of propan-2-ol as electron donor [29,30]. Herein we examine the photocatalytic reductive degradation of another typical azo dye, NB and show that: (i) By taking advantage of the ability of POM to exhibit widely, yet precisely varied redox potentials (Scheme 1), redox-control is imposed in the process. (ii) Although the process is highly efficient in decolorizing aqueous solutions of the dye, great caution is needed concerning the mineralization of the solution, since toxic amines (aniline, *p*-nitro-aniline and *p*-phenylene-diamine) are liberated upon NB reduction. (iii) The effect of operational parameters such as the concentration of catalyst, propan-2-ol, dye or oxygen, on the photocatalytic cycle and the efficiency of decoloration of the dye is also investigated.

2. Experimental

2.1. Materials and reagents

$H_4SiW_{12}O_{40}$ and $H_3PW_{12}O_{40}$ were purchased from Aldrich and PanReac, respectively, while $K_6P_2W_{18}O_{62}$ and $(NH_4)_6P_2Mo_{18}O_{62}$ were prepared according to literature methods [31,32]. $SiW_{12}O_{40}^{4-}$ and $P_2W_{18}O_{62}^{6-}$ are stable up to pH ca. 5.5, whereas $PW_{12}O_{40}^{3-}$ is stable at pH ca. 1 and $P_2Mo_{18}O_{62}^{6-}$ up to 2.5. Since $PW_{12}O_{40}^{3-}$ is the most efficient in the degradation of the dyes, it was studied in more details in our experiments.

NB was obtained from Aldrich and $HClO_4$ was from Riedel de Haen. Ultra pure water was obtained from a compact apparatus from Barnstead. Extra pure argon (99.999%) and dioxygen (>99.95%) were used for deaeration or oxygenation of solutions.



Scheme 1. Reduction potentials of the POM photocatalysts (volts vs. NHE).

2.2. Irradiation procedures

The photolysis lamp was an Oriel 1000 W Xe arc lamp equipped with a cool water circulating filter to absorb the near IR radiation and a 320 nm cut-off filter in order to avoid direct photolysis of propan-2-ol. A slit diaphragm was used to reduce the incident radiation to about 40%. The total photonic flux (320–345 nm) determined by ferrioxalate actinometry was 7.9×10^{-6} Einstein min^{-1}.

In a typical experiment, 4 ml of aqueous dye solution containing propan-2-ol and POM catalyst were added to a spectrophotometer cell (1 cm path length), deaerated (or non-deaerated) and covered with a serum cap. The cell was mounted on a thermostated cell holder, under constant stirring, and the lamp focused with a lens on the contents. The temperature was $18 \pm 1\,^{\circ}C$. The pH was adjusted at 1 with $HClO_4$. Analysis was performed using all 4 ml of the photolyzed solution every time.

2.3. Analytical procedures

Reduced POM were monitored in the photolyzed solutions by the known extinction coefficients of the one-equivalent reduced 12-tungstophosphate, $PW_{12}O_{40}^{4-}$ ($\varepsilon_{752} = 2000\,M^{-1}\,cm^{-1}$), one-equivalent reduced 12-tungstosilicate, $SiW_{12}O_{40}^{5-}$ ($\varepsilon_{730} = 2100\,M^{-1}\,cm^{-1}$), one-equivalent reduced 18-tungstodiphosphate, $P_2W_{18}O_{62}^{7-}$ ($\varepsilon_{909} = 4400\,M^{-1}\,cm^{-1}$) and the two-equivalent reduced 18-molybdodiphosphate, $P_2Mo_{18}O_{62}^{8-}$ ($\varepsilon_{758} = 11{,}000\,M^{-1}\,cm^{-1}$) [33], using a Perkin-Elmer Lambda 19 Spectrometer. The concentration of the dye molecules

was measured from the known extinction coefficient of NB ($\varepsilon_{618} = 23200\ M^{-1}\ cm^{-1}$).

The initial rate of dye degradation was measured from the slope of the curve obtained by monitoring the concentration of the dye in the photolysed solutions versus time, for the first ca. 30% of dye decoloration using a least squares treatment.

The products of dyes degradation were determined by HPLC, using an HPLC apparatus consisted of a Waters (Milford, MA, USA) Model 600E pump associated with a Waters Model 600 gradient controller, a Rheodyne (Cotati, CA, USA) Model 7725i sample injector equipped with 20 μl sample loop, a reversed phase (RP) C_{18} analytical column by Phase sep (25 cm × 4.6 mm ID, 5 μm) and a Water Model 486 tunable absorbance detector controlled by the Millenium (Waters) software. The products of NB degradation, aniline, *p*-nitro-aniline and *p*-phenylene-diamine were monitored at 236 nm with a gradient mobile phase of flow rate 1 ml/min starting from 15% methanol and 85% phosphate buffer solution (potassium dihydrogen phosphate 5 mM) and increasing methanol up to 50% for the first 16 min, then 55% methanol till 20 min run and finally return at 15% methanol at 21 min.

3. Results

3.1. Photocatalytic reductive decoloration of NB

A deaerated solution (NB 0.05 mM, propan-2-ol 0.5 M and $PW_{12}O_{40}^{3-}$ 0.25 mM) was irradiated with UV–near vis light, λ > 320 nm, to examine the mechanism of the photocatalytic reduction and decoloration of the dye. A gradual lowering of the absorbance peak at 618 nm and fading of the deep blue color was observed for NB upon photolysis, within a few minutes (Fig. 1) in parallel to the formation of pink color. Less than 5×10^{-7} M of the dye was left in the treated solution after 2 min of illumination, beyond which a blue color is gradually formed.

The formation of degradation products is depicted in Fig. 2, based on HPLC measurements (conditions to facilitate the analysis are selected: lower concentration of POM, 2.5×10^{-5} M, and higher concentration of dye, 1.0×10^{-4} M). Aniline, *p*-nitro-aniline and *p*-phenylene-diamine were detected upon photolysis of the NB solutions.

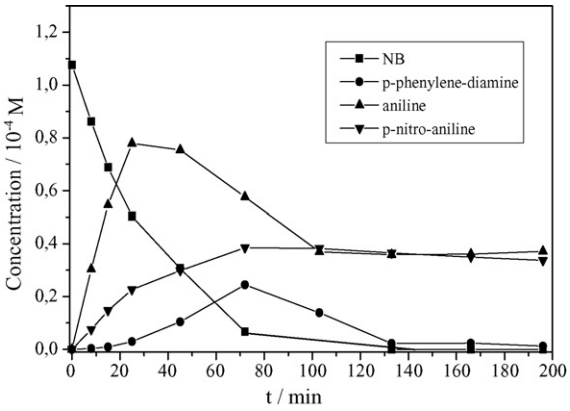


Fig. 2. Destruction of NB and concomitant formation of aniline, *p*-nitro-aniline and *p*-phenylene-diamine upon photolysis of a deaerated aqueous solution containing propan-2-ol 0.5 M, $H_4SiW_{12}O_{40}$ 2.5×10^{-5} M, NB 1.0×10^{-4} M (pH 4).

3.2. Effect of POM

The effect of the kind of POM on the initial rate of dye decoloration was investigated, keeping all the other experimental conditions constant. Illumination of a deaerated solution (propan-2-ol/POM/NB) led to gradual decoloration, with a rate depending on the POM catalyst. The efficiency of the process, increased in the order $PW_{12}O_{40}^{3-} > SiW_{12}O_{40}^{4-} > P_2W_{18}O_{62}^{6-} >$ no POM = 0 (see Fig. 3).

The same order was noticed in another set of experiments where the rate of formation of the one-equivalent reduced POM in the absence of dye was followed. Deaerated (POM 0.25 mM/propan-2-ol 0.5 M (pH 1)) solutions were illuminated and the photochemical production of the one-electron reduced POM was monitored by its characteristic

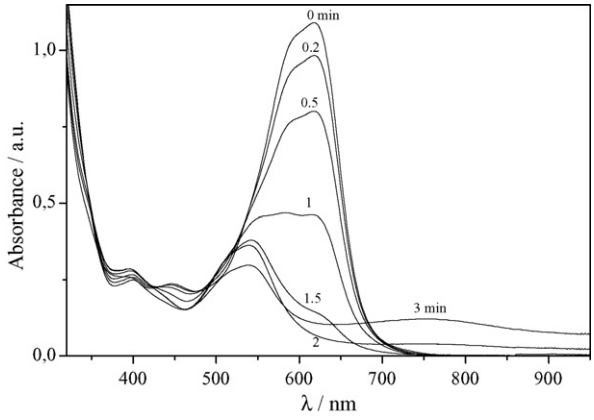


Fig. 1. UV–vis spectra of photolysed deaerated aqueous solutions containing propan-2-ol 0.5 M, $H_3PW_{12}O_{40}$ 2.5×10^{-4} M, NB 0.5×10^{-4} M at pH 1, for various irradiation times, showing the decoloration of NB as well the formation of the one-equivalent reduced tungstate, $PW_{12}O_{40}^{4-}$ after 3 min of photolysis.

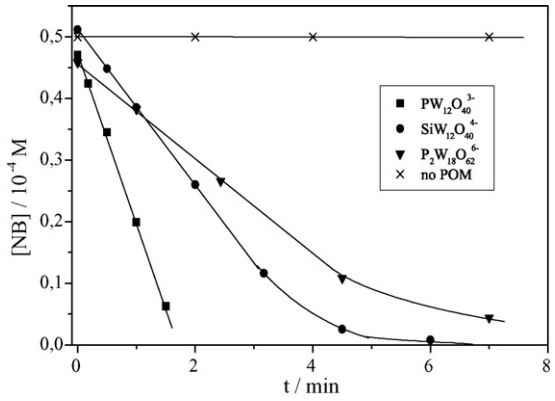


Fig. 3. Influence of POM photocatalyst, $PW_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$ and $P_2W_{18}O_{62}^{6-}$, on the rate of NB degradation upon photolysis of deaerated aqueous solutions containing propan-2-ol 0.5 M, POM 2.5×10^{-4} M, NB 0.5×10^{-4} M (pH 1).

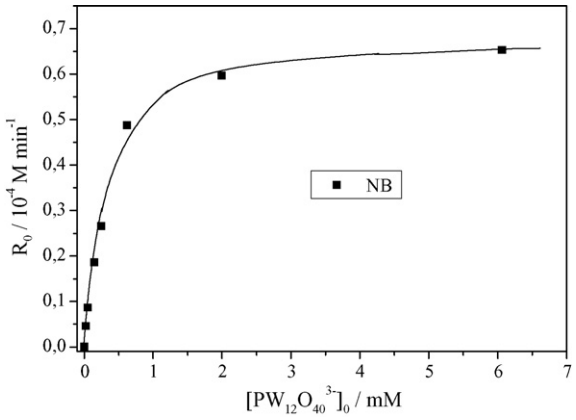


Fig. 4. Influence of $PW_{12}O_{40}^{3-}$ concentration on the initial rate, R_0, of NB decoloration. Non-deaerated solutions propan-2-ol 0.5 M, NB 0.5×10^{-4} M (pH 1).

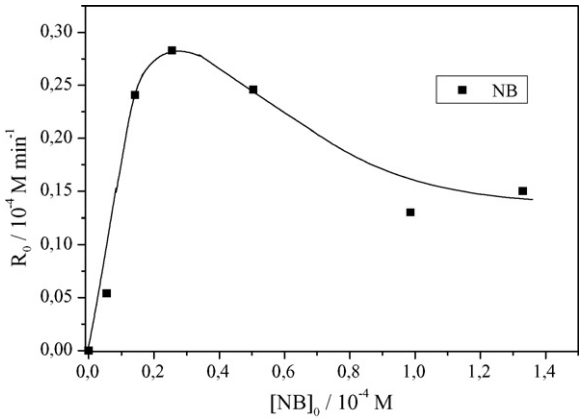


Fig. 6. Effect of NB concentration on the initial rate, R_0, of NB decoloration. Non-deaerated solutions of $PW_{12}O_{40}^{3-}$ 2.5×10^{-4} M, propan-2-ol 0.5 M (pH 1).

absorbance at ca. 750 nm at the initial stage of the photolysis. The corresponding values for the photochemical formation of $PW_{12}O_{40}^{4-}$, $SiW_{12}O_{40}^{5-}$ and $P_2W_{18}O_{62}^{7-}$ were 1.2, 0.27 and 0.22×10^{-4} M min^{-1}.

Illumination of a solution (propan-2-ol/POM/NB) led to fading of the deep blue NB and formation of a pink color, while in turn a blue color appeared. In the case of $PW_{12}O_{40}^{3-}$ or $P_2W_{18}O_{62}^{6-}$ as photocatalysts, the pink color co-existed with the gradually formed blue one and in turn disappeared. On the contrary, in the case of $SiW_{12}O_{40}^{4-}$, the blue one appeared only after the pink color had disappeared.

3.3. Effect of POM concentration

The influence of catalyst ($PW_{12}O_{40}^{3-}$) concentration on the initial rate of dye decoloration in non-deaerated solutions is depicted in Fig. 4. For concentrations of $PW_{12}O_{40}^{3-}$ below ca 0.25 mM a linear dependence is observed, while for concentrations of $PW_{12}O_{40}^{3-}$ greater than 1.5 mM the system reaches, practically, saturation in photon absorption and the rate becomes zero order with respect to the catalyst.

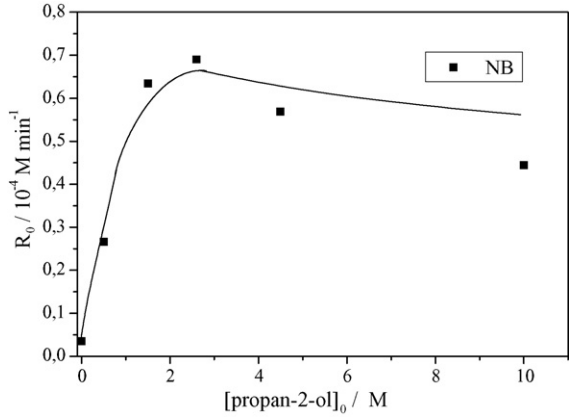


Fig. 5. Influence of propan-2-ol concentration on the initial rate, R_0, of NB decoloration. Non-deaerated solutions of $PW_{12}O_{40}^{3-}$ 2.5×10^{-4} M, NB 0.5×10^{-4} M (pH 1).

3.4. Effect of propan-2-ol concentration

Fig. 5 illustrates the variation of the initial rate of photocatalytic decoloration of the dye with the concentration of the propan-2-ol, in non-deaerated solutions. A linear dependence on [propan-2-ol] for concentration below ca 1.5 M and roughly zero order dependence for concentration over ca. 2 M is noticed.

3.5. Effect of NB concentration

The initial concentration of dye affects the initial rate of dye destruction, Fig. 6. This rate exhibits an optimum concentration of the dye (0.025 mM) above which further increase in the concentration value, decelerates the destruction of the dye.

3.6. Effect of oxygen

A non-deaerated solution of (propan-2-ol 0.5 M, $PW_{12}O_{40}^{4-}$ 0.25 mM, NB 0.05 mM (at pH 1)) was compared with a deaerated one, the other conditions left identical. As depicted in Fig. 7, the presence of O_2 does not influence the rate of NB decoloration.

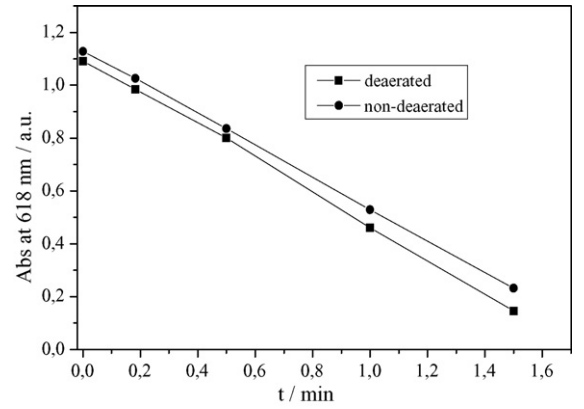


Fig. 7. Decrease of NB concentration in deaerated (a) or non-deaerated (b) photolysed solutions. Propan-2-ol 0.5 M, $PW_{12}O_{40}^{3-}$ 2.5×10^{-4} M, NB 0.5×10^{-4} M (pH 1).

3.7. Thermal reduction of NB by reduced POM

Solutions of blue colored, one-equivalent reduced tungstates, $PW_{12}O_{40}^{4-}$, $SiW_{12}O_{40}^{5-}$ or $P_2W_{18}O_{62}^{7-}$ or two-equivalent reduced molybdate, $P_2Mo_{18}O_{62}^{8-}$, were produced after photolysis of deaerated aqueous solutions of propan-2-ol 0.5 M, POM 0.25 mM, $HClO_4$ 0.1 M. Photolysis time was adjusted in order to produce the same quantity of reduced POM (ca. 1.5×10^{-4} M) in each POM experiment. After cutting off the light, the photolyzed solutions were mixed with a deaerated solution of NB (ca. 0.5×10^{-4} M). The process was monitored at the characteristic absorbance of the reduced POM, around 750 nm. Upon mixing any of the reduced tungstates with NB, a sudden decrease of the absorbance at ca. 750 nm and the concomitant formation of a pink product was observed, indicating that the one electron reduced tungstates are efficiently reoxidised by dye molecules in the absence of light. On the contrary, no reaction took place with $P_2Mo_{18}O_{62}^{8-}$ even after 2.5 h.

4. Discussion

The proposed mechanistic scheme involving the photocatalytic reductive decoloration of NB in the presence of polyoxotungstates, can be summarized as follows:

$$POM + h\nu \leftrightarrow POM^* \quad (1)$$

$$POM^* + \text{propan-2-ol} \rightarrow POM(e) + \text{oxidized products (i.e. } Me_2COH) \quad (2)$$

$$POM(e) + NB \rightarrow POM + \text{reduction products} \quad (3)$$

Reactions (1) and (2) describe the overall photocatalytic oxidation of propan-2-ol, avoiding details concerning the involvement of radicals, etc. [15,34,35]. In the presence of NB, the blue reduced catalyst, POM(e), is reoxidized according to reaction (3). This has been verified by independent thermal (dark) experiments, (see Section 3.7). Thus, no blue color is produced upon illumination of a solution (propan-2-ol/POM/NB). The blue color of the one-equivalent reduced tungstate is freely developed only after the solution is depleted of the dye.

The decomposition of the dye could also be triggered reductively by the Me_2COH radicals, from reaction (2), via reaction (4) below, in accordance with pulse radiolysis studies that indicate fast reduction of several azo dyes by 2-hydroxy-2-propyl radical with a rate constant of the order of ca. 10^9 ($M^{-1}\,s^{-1}$) [36]:

$$Me_2COH + NB \rightarrow Me_2CO + \text{reduction products} \quad (4)$$

However, since the evolution of the blue reduced POM prevails only after the entire dye is consumed, such a scenario is minimized. Moreover thermal experiments suggest the ability of reduced POM to reduce efficiently the dye molecules [independent verification of reaction (3)].

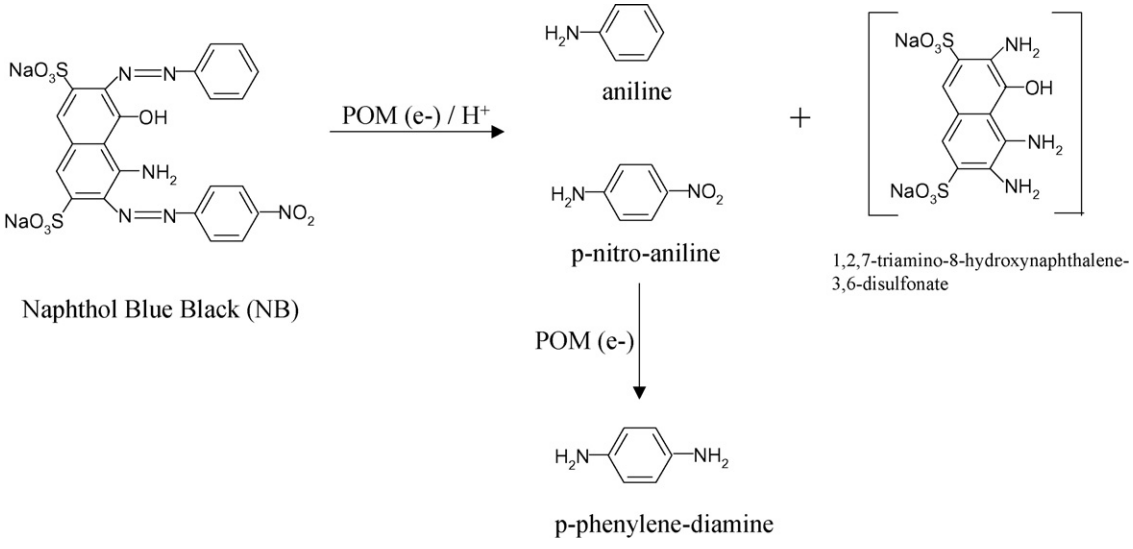
The lowering of the absorption peaks at 618 for NB, characteristic of the –N=N– bond, suggests break of the azo-bond. This reductive cleavage of the azo-bond in NB molecule results in the formation of the aromatic amines aniline and *p*-nitro-aniline according to the mechanistic Scheme 2. 1,2,7-Triamino-8-hydroxynaphthalene-3,6-disulfonate, the third fraction, could not be detected due to its rapid autoxidation [37]. *p*-Phenylenediamine could be the product of further reduction of *p*-nitro-aniline by reduced POM, a reaction known to occur (Scheme 2) [24].

Reduction of NB does not lead to prompt decoloration, due to the formation of (pink) colored intermediates, as has also been noticed in other cases [37,38]. However, finally, colorless products are obtained.

We present below how various operational parameters influence the efficiency of the reductive decoloration of NB.

4.1. Propan-2-ol effect

An enhancement in the degradation rate is noticed upon increasing propan-2-ol concentration (Fig. 5). As propan-2-ol



Scheme 2. Mechanism of the photocatalytic reductive degradation of NB in the presence of POM.

is a reducing reagent it favors reaction (2), that is the formation of POM(e), enhancing finally reaction (3). In this way, the whole process is driven to a reductive pathway, which results in the selective break of the azo-bond. In the absence of propan-2-ol the process is still effective (Fig. 5, rate at zero concentration of propan-2-ol), although much slower. In this case photooxidation of the dye takes place by the excited POM and/or OH radicals, thereby suggesting that the reductive degradation of NB is much faster than the oxidative process.

4.2. Dye effect

Blank experiments, where visible light $\lambda > 395$ nm was impinged in order to minimize POM absorption, were completely fruitless to suggest a dye-sensitized process as a parallel mechanism.

For the POM sensitized process, increase in dye concentration till an optimum value leads to an increase in the degradation rate, through favoring of reaction (3). However, further increase in dye concentration performs a detrimental effect in the degradation rate, possibly due to an inner filter effect, where dye molecules start absorbing light from the POM absorption region (Fig. 6).

4.3. Effect of catalyst redox properties. Thermodynamic and kinetic effect

Isolated thermal reaction (3) follows thermodynamics, i.e., the greater the redox potential difference between reduced POM and NB, the faster the decoloration rate, following the order $SiW_{12}O_{40}^{5-} > PW_{12}O_{40}^{4-} > P_2W_{18}O_{62}^{7-} > P_2Mo_{18}O_{62}^{8-} = 0$, in accordance with the redox potentials (Scheme 1).

Thus, $SiW_{12}O_{40}^{5-}$ causes rapid and complete decoloration of NB, whereas, the decoloration caused by $PW_{12}O_{40}^{4-}$ and $P_2W_{18}O_{62}^{7-}$ leads to a pink colored intermediate. This suggests that intermediates are also reductively degraded by $SiW_{12}O_{40}^{5-}$ but not by $PW_{12}O_{40}^{4-}$ and $P_2W_{18}O_{62}^{7-}$.

The overall rate of photodegradation of NB follows the order $PW_{12}O_{40}^{3-} > SiW_{12}O_{40}^{4-} > P_2W_{18}O_{62}^{6}$ which parallels the rate of photoformation of the one-equivalent reduced POM. Thus, the overall rate of photodecomposition of NB is kinetically rather than thermodynamically controlled.

The quantum yields (q.y.) of formation of the one-equivalent reduced POM at 254 nm are ca. 12% for $PW_{12}O_{40}^{4-}$, independent of wavelength below ca. 350 nm [13]. Since independent thermal experiments in Section 3.7 have shown that the stoichiometry for reaction (3) is (3 mol POM/(1 mol NB), the quantum yield of NB degradation would be more than three times less, i.e. somewhat less than 4% in the case of $PW_{12}O_{40}^{3-}$. This value is close to the one for the TiO_2-photocatalyzed decoloration of another azo dye, acid orange-7 (4.7%) [10], confirming once again the similar efficiency of the two processes [15]. The degradation rate increases upon increasing POM concentration (Fig. 4), while it reaches a plateau above 0.7 mM due to photon saturation [reaction (1)].

4.4. Effect of oxygen

Fig. 7 shows that introduction of oxygen does not influence the photodegradation of NB. Although O_2 molecules are efficient oxidants for reduced POM, reaction (5) [22], they seem not to compete effectively with NB, reaction (3) in abstracting electrons from reduced POM, thus leaving the rate of NB decoloration intact:

$$2\text{POM(e)} + O_2 \rightarrow 2\text{POM} + O_2^{2-} \quad (5)$$

This is of practical importance since a pre-dearation step is not necessary.

4.5. Environmental aspects of the process

The photocatalytic process presented herein might be of environmental interest since it is effective for the complete removal of dyes up to non-detected traces (less than 5.0×10^{-7} M) and for a wide range of dye concentration, varying from 5×10^{-7} to more than 10^{-4} M. This is a great practical advantage compared with heterogeneous processes such as the iron-based treatment, which cannot be quantitative, leaving ca. 4% of the target azo dyes unaffected [39].

However, caution is needed concerning the aspect of mineralization of the dyes, since toxic amines are released as initially formed intermediates, which could pose even more threats to the public health. This phenomenon, which is a general halt of the reductive treatment of azo dyes, has made European Union to proceed to regulations concerning marketing of dyes that are capable of reductively splitting carcinogenic amines [40]. However, although the reduction products are not environmental friendlier, they are more amenable to oxidation than the initial azo compounds. Thus, a sequential reductive/oxidative treatment might be the case for these oxidatively recalcitrant azo dyes. Work is in progress in the concept of combining first reduction and then oxidation of azo dyes by POM in an integrated system.

4.6. Conclusions

Rapid (life time 1–4 min.) photocatalytic reduction decoloration of NB is obtained by a series of polyoxotungstates in the presence of a sacrificial reagent propan-2-ol. Polyoxomolybdates have no effect. In the process, polyoxotungstates mediate electron transfer from the sacrificial reagent to the azo dye releasing, however, various toxic amines. These are, though, more amenable to oxidation so that a sequential reduction/oxidation treatment might be the case for this oxidatively recalcinant azo dyes.

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