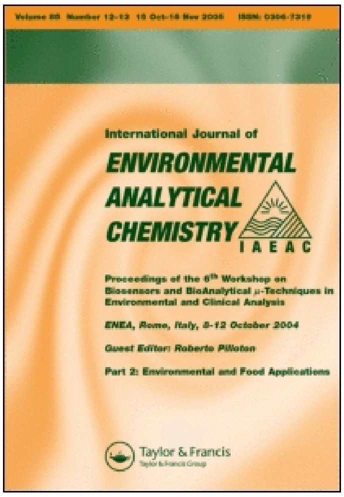

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Polyoxometallate photocatalysis for decontaminating the aquatic environment from organic and inorganic pollutants

Anastasia Hiskia[a]; Aristidis Troupis[a]; Stamatia Antonaraki[a]; Eleni Gkika[a]; Pigi Kormali[a]; Elias Papaconstantinou[a]
[a] NCSR 'Demokritos', Institute of Physical Chemistry, 153-10 Athens, Greece

To cite this Article Hiskia, Anastasia , Troupis, Aristidis , Antonaraki, Stamatia , Gkika, Eleni , Kormali, Pigi and Papaconstantinou, Elias(2006) 'Polyoxometallate photocatalysis for decontaminating the aquatic environment from organic and inorganic pollutants', International Journal of Environmental Analytical Chemistry, 86: 3, 233 — 242
To link to this Article: DOI: 10.1080/03067310500247520
URL: http://dx.doi.org/10.1080/03067310500247520

Intern. J. Environ. Anal. Chem.
Vol. 86, Nos. 3–4, 15 March–10 April 2006, 233–242

Polyoxometallate photocatalysis for decontaminating the aquatic environment from organic and inorganic pollutants

ANASTASIA HISKIA*, ARISTIDIS TROUPIS,
STAMATIA ANTONARAKI, ELENI GKIKA,
PIGI KORMALI and ELIAS PAPACONSTANTINOU

NCSR ‘Demokritos’, Institute of Physical Chemistry, 153-10 Athens, Greece

(*Received 12 October 2004; in final form 20 March 2005*)

Polyoxometallates (POMs), i.e. metal oxide clusters of mainly tungsten, are effective homogeneous photocatalysts for the mineralization of organic pollutants. $^{\bullet}OH$ radicals formed by the reaction of the photo-excited POMs with H_2O appear to play a key role in the process. POMs are similar to TiO_2. In this article, the photocatalytic activity of POMs has been presented on several diversified organic pollutants of interest such as phenol, chlorophenols, chloroacetic acids, and pesticides to determine the feasibility of decontamination of aqueous solutions from these pollutants. The results show that aqueous solutions containing the target pollutants, upon photolysis in the presence of POMs, undergo effective degradation to CO_2, H_2O, and the corresponding inorganic anions. The intermediates identified give rise to complicated degradation mechanisms prior to mineralization. In addition, photolysis of an aqueous solution of metal ions in the presence of POMs and organic substrate leads to the oxidative degradation of the organic and the simultaneous reduction–precipitation of metals in elemental state. This process has been successful in the removal–recovery of a great variety of metal ions including either toxic metallic compounds (chromium and mercury) or valuable metals (such as copper, silver, gold, palladium, and platinum). Finally, the two pathways were combined into a simple one-pot process for the decontamination of aquatic environment from both organic pollutants and metal cations.

Keywords: Polyoxometallates; Photocatalysis; Pollutants; Metals; Reduction

1. Introduction

POM compounds are well-characterized metal–oxygen clusters mainly of molybdenum and tungsten [1–3]. The best-known, typical categories of POMs are (a) isopoly-compounds with the general molecular structure $[M_mO_\psi]^{p-}$, for example $(W_{10}O_{32})^{4-}$

---

*Corresponding author. Fax: +30-210-6503633. Email: hiskia@chem.demokritos.gr

International Journal of Environmental Analytical Chemistry
ISSN 0306-7319 print: ISSN 1029-0397 online
DOI: 10.1080/03067310500247520

and (b) hetopoly compounds with the general molecular structure $[X_\chi M_m O_\psi]^{q-}$, where X can be one of about 60 elements of various groups of the periodic table except the noble gases and $\chi < m < \psi$, e.g. $(PW_{12}O_{40})^{3-}$. The $\chi : m$ ratio can take various values, for example 1 : 12 or 2 : 18 for the Keggin and Dawson structure, respectively.

POMs are generally prepared by the condensation reaction occurring upon acidification of solutions of MoO_4^{2-} or WO_4^{2-}. Whereas chromium, of the same group, undergoes only dimerization upon acidification ($Cr_2O_7^{2-}$ from CrO_4^{2-}), MoO_4^{2-} and WO_4^{2-} form a series of POMs (isopoly compounds) in equilibria with each other, typical representatives of which are $Mo_7O_{24}^{6-}$, $Mo_8O_{26}^{4-}$, $W_{10}O_{32}^{4-}$, and $H_2W_{12}O_{40}^{6-}$. If the condensation takes place in the presence of a so-called heteroatom X, i.e. P^{5+}, As^{5+}, Si^{4+}, Fe^{3+} etc., as mentioned earlier, the heteroatom becomes incorporated into the POMs, and heteropoly compounds are formed ([1] and references therein).

POMs have characteristic properties that render them interesting substances for catalysis and photocatalysis. These properties can be summarized into the following: (a) solubility in water and organic solvents, (b) thermal stability, (c) low toxicity, (d) ability to serve as electron and oxygen relays, (e) strong absorption in UV–near VIS light (<400 nm), (f) reduction in POMs leaving their structure intact, and (g) the reduced form can be re-oxidized by various oxidizing reagents (i.e. O_2, H^+, M^{n+}, etc.).

It is well documented that irradiating with visible and near-UV light makes POMs powerful oxidizing reagents [4] capable of destroying a great variety of organic compounds. In this context, the photocatalytic oxidation of many organic pollutants has been demonstrated using POMs [5–10]. The reduced form of POMs was re-oxidized by O_2.

Recently, the re-oxidation of POM reduced forms by metal cations—which are precipitated as metal particles of zero valence—has been reported [11–14]. In this way, metal ions are removed from the solution, and purification of wastewaters from both organic and inorganic pollutants can be achieved in principle. Until now, the decontamination process has been studied separately in terms of organic and inorganic pollutants accordingly. In this review, we summarize and comment on both decontamination processes, focusing on the photocatalytic degradation of organics in the presence of POMs, using metal cations (inorganic pollutants) for the regeneration of the photocatalyst and, at the same time, for their reduction and removal from aquatic solutions.

2. Photocatalytic degradation of organic pollutants with POMs: mechanistic aspects

POMs, upon excitation with near-visible and UV light, become powerful oxidizing reagents capable of destroying a great variety of pollutants in the aquatic environment. During the process, the reduced form of POMs is formed. Dioxygen is important in that it oxidizes (regenerates) the reduced POMs and, through reductive activation, may or may not participate further in the process, depending on the substrate [15]. The reactions that take place in the photocatalytic circle (see figure 1) that occurs

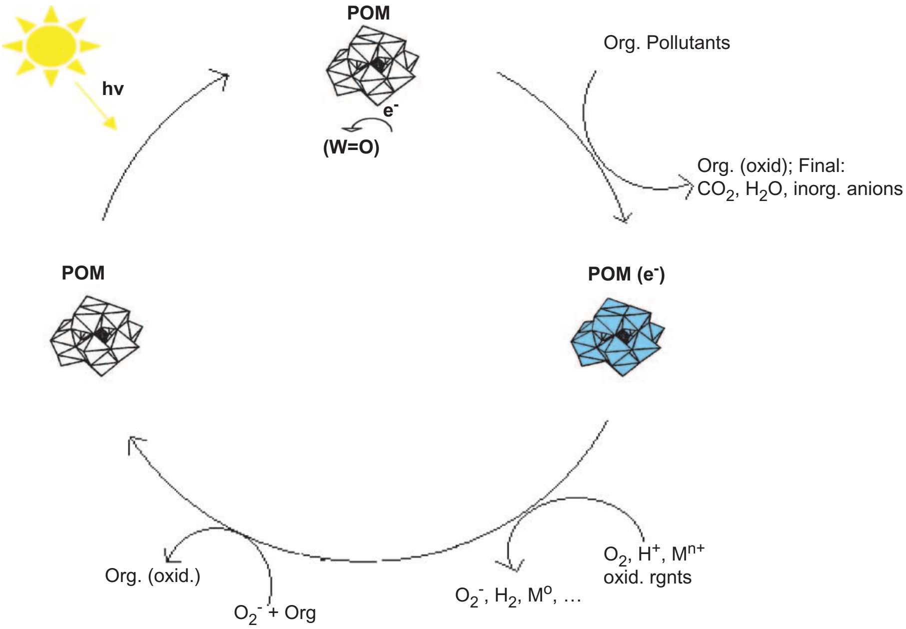

Figure 1. Photocatalytic circle of degradation of organic pollutants in the presence of POM.

upon illumination of POMs in the presence of oxygen are given below:

$$\mathrm{POM} \xrightarrow{hv} \mathrm{POM}^* \tag{1}$$

$$\mathrm{POM}^* + \mathrm{H_2O} \rightarrow \mathrm{POM}^- + {}^{\bullet}\mathrm{OH} + \mathrm{H}^+ \tag{2}$$

$$\mathrm{POM}^* + \mathrm{org.} \rightarrow \mathrm{POM}^- + \mathrm{org}^+ \tag{3}$$

$${}^{\bullet}\mathrm{OH} + \mathrm{org.} \rightarrow \text{oxidation products} \rightarrow\rightarrow\rightarrow \mathrm{CO_2},\ \mathrm{H_2O} \text{ and inorganic anions} \tag{4}$$

$$\mathrm{POM}^- + \mathrm{O_2} \rightarrow \mathrm{POM} + \mathrm{O_2^-} \tag{5}$$

$$\mathrm{O_2^-} + \mathrm{org.} \rightarrow \text{oxidation products.} \tag{6}$$

Moreover, it is documented that upon mixing POMs with the organic substrate, a pre-association complex or pre-association equilibrium is established. Evidence of this is that even traces of organic pollutant (at the ppb level) undergo effective photodecomposition in homogeneous aqueous solutions containing POMs [16]. Further evidence includes NMR, kinetic, X-ray, electronic spectra data, and the Langmuirian behaviour of the system [17]. For simplicity reasons, the pre-association complex of POMs with the organic substrate into the solution has not been referred individually into the reactions.

Irradiation of the POMs with $\lambda < 400\,\mathrm{nm}$ results in the formation of the excited state (see equation (1)). This excited state of the associated complex that POMs and organic substrates form results from the O → M CT band of POMs. The excited state of POMs is a strong oxidant able to oxidize and, most often, mineralize organic substrates, including organic pollutants. Progressively, POMs are reduced to coloured, generally blue species (see equations (2) and (3)). The reduced POMs can be easily monitored owing to their characteristic spectra in the visible. At the same time, organics, after oxidation to intermediate products, are generally mineralized to CO_2, H_2O, and inorganic anions (see equations (3) and (4)).

Concerning the mechanism of the photo-oxidation reactions, it seems that there are two general pathways through which the excited POMs reacts with organic substrates in aqueous solution: (a) direct reaction (see equation (3)) and (b) indirect reaction (see reaction 4) through formation of $^{\bullet}OH$ radicals from the reaction of the excited POMs with H_2O (equation (2)). There is evidence for the generation of $^{\bullet}OH$ radicals that can be summarized as follows: (a) determination of hydroxylation products prior to mineralization; (b) ESR experimental data; and (c) high excited-state potentials for the oxidation of H_2O to $^{\bullet}OH$ radicals. Recently, more experimental data have been reported, in agreement with the formation of $^{\bullet}OH$ radicals, based on the comparison of photo-degradation of all chlorophenols with POMs and H_2O_2 [18]. However, the formation of $^{\bullet}OH$ radicals by POMs cannot be generalized. Few studies tend to exclude the possibility of these reactions occurring via $^{\bullet}OH$ radicals, giving rise to a mechanism of direct reaction [19].

The reduced POMs can be re-oxidized by dioxygen, which undergoes reductive activation through the formation of O_2^- species (see equation (5)). These species are also strong oxidants capable of initiating further oxidation (see equation (6)).

3. Specific pathways of photodegradation. Examples

The above method has been applied to many organic pollutants, such as phenol, chlorophenols and chloroacetic acids [5–7]. Recently, the photocatalytic degradation of some diversified pesticides has been performed. Among the target pesticides was lindane [20], a typical organochlorine insecticide with a very high stability in the environment, the organophosphorous insecticide fenitrothion [21], the herbicide atrazine [22], and the acid herbicide, bentazone [23]. In all cases, the final degradation products were CO_2, H_2O, and inorganic anions, with the exception of atrazine, which is degraded into the non-toxic but persistent cyanuric acid.

The photodegradation of fenitrothion is a typical example of POM photocatalysis [21]. Fenitrothion was fully degraded in the presence of POMs ($H_3PW_{12}O_{40}$) within 60 min, while in the absence of POMs, less than 12% was degraded in 120 min. The mineralization of the substrate to CO_2, H_2O, and inorganic ions (PO_4^{3-}, SO_4^{2}, NO_2^-, NO_3^-) is demonstrated in figure 2.

A detailed study of the process reveals the formation and decay of several intermediates (i.e. fenitrooxon, 3-methyl-4-nitrophenol, 3-methyl-4-nitroanisole, 2-methylhydroquinone, 2-methyl-1,4-benzoquinone, formylfenitrothion and O,O,S-trimethyl phosphorothioate), prior to the final decomposition to CO_2 and inorganic ions [21]. The intermediates identified by HPLC-DAD and GC-MS give rise to complicated degradation mechanisms prior to mineralization. The proposed mechanism for the formation of 3-methyl-4-nitrophenol, fenitrooxon, formylfenitrothion, and 2-methylhydroquinone was based on $^{\bullet}OH$ radical attack [21]. The characteristic reactions that

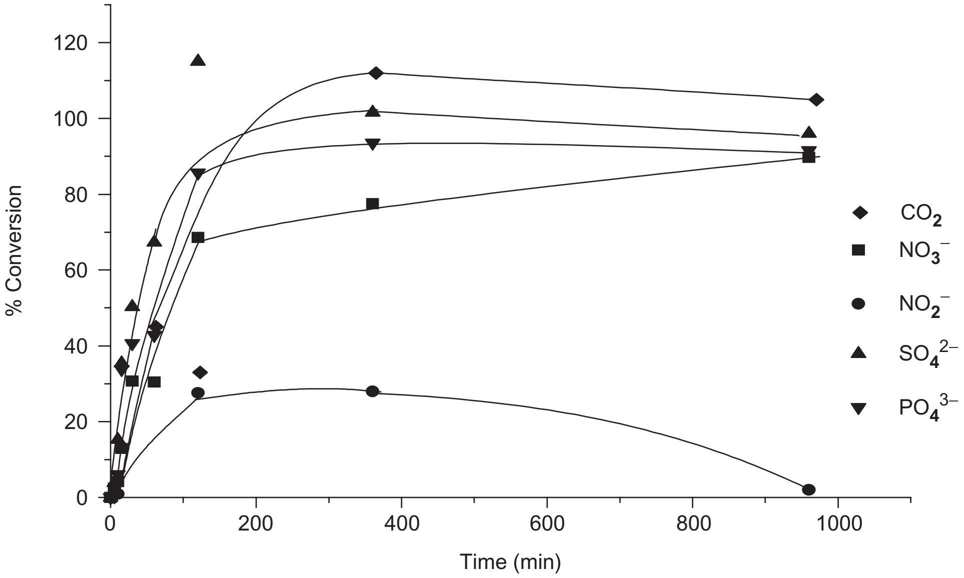

Figure 2. Formation of CO_2 and inorganic ions during photocatalytic degradation of fenitrothion in the presence of POM (reprinted from [21]).

take place consist of hydroxylation, H-abstraction, denitration, desulphurization, breakage of the C–C bond, etc.

Another example of the reactions taking place in the photodecomposition process by POMs is based on the degradation study of atrazine [22]. When POMs were added to an oxygenated aqueous solution of atrazine, irradiation by means of a cutoff filter (320 nm) resulted in efficient photodecomposition of the substrate. Several intermediates form and decay, namely deisopropylatrazine (CEAT), deethylatrazine (CIAT), hydroxyatrazine (OIET), chlorodiaminoatrazine (CAAT), ammeline (OAAT), ammelide (OOAT), prior to the formation of cyanuric acid (OOOT). No decomposition of the non-toxic OOOT was observed, which was one of the final products, together with CO_2, H_2O, chloride ions, and nitrates. According to the degradation pathway proposed [22], the first sites of attack of $^{\bullet}OH$ radicals on atrazine units are the aminoalkyl groups of the side chains, as well as chlorine. During this process, the gradual replacement of the side chains by amino and finally by $^{\bullet}OH$ groups continues, yielding OOOT as the final degradation product.

From various comparative studies, it turns out that POMs, as far as the photo-oxidation of organic compounds (organic pollutants) is concerned, are similar to the widely studied TiO_2 [24]. Upon photolysis with visible and near-UV light, both systems mineralize a great variety of organic pollutants to CO_2, H_2O, and inorganic anions, via similar intermediates. This similar behaviour occurs, mainly, due to the fact that the excited states of both systems are able to oxidize H_2O to $^{\bullet}OH$ radicals, which play an important role in the photo-oxidation process. In fact, this mechanism means that POMs in combination with visible and near-UV light render a new advanced oxidation process among H_2O_2/UV, fenton reagent, TiO_2 photocatalysis, etc. The advantages of photodegradation of organic pollutants in the presence of POMs found to date are summarized below. The oxidation of pollutants leads to a final degradation product, CO_2. The $^{\bullet}OH$ radicals produced during the process are powerful oxidants, capable of attacking the target substrate in a non-selective way. This mechanism makes the process applicable in almost all organic substrates, without the need for any other additional remediation method. This technology is environmentally friendly and can be performed under ambient temperature and pressure, using atmospheric O_2 as oxidant.

4. Photocatalytic purification of aqueous systems from metal ions using POMs

Recovery of metals is a topic of great concern from an environmental and economic aspect. Since many metals are either toxic or valuable, the development of methods to recover metals could help solve many environmental problems and save finite resources also.

It has been shown recently that photocatalysis with POMs could help in the recovery of metals: photolysis of an aqueous solution of metal ions in the presence of POMs and organic substrate leads to the oxidative degradation of the organic and the simultaneous reduction–precipitation of metals in the elemental state [11–14, 25]. In particular, the mechanistic scenario comprises the photochemical oxidation of a sacrificial organic donor, i.e. propan-2-ol, by excited POMs and the concomitant formation of reduced POMs. In turn, reduced POMs are reoxidized by metal ions, via

$$\mathrm{POM}^- + \mathrm{M}^{n+} \rightarrow \mathrm{POM} + \mathrm{M}^0 \downarrow,$$

thus closing the photocatalytic cycle (see figure 1).

Figure 3 depicts the reductive precipitation–removal of mercury ions upon photolysis of a deaerated aqueous solution ($Hg_2^+/PW_{12}O_{40}^{3-}$/propan-2-ol). After ca. 40 min of photolysis, less than 50 ppb (detection limit) of mercury has been found to remain in the filtered photolysed solution [25].

The process has been successful in the removal–recovery of a great variety of metal ions including both toxic metallic compounds (such as chromium and mercury) and valuable metals (such as copper, silver, gold, palladium, and platinum). It is effective even in traces of metal ions (ppm to ppb) that are completely removed from the treated solution (final concentration of ppb range), exhibiting a quantum yield of ca. 5–10%. What is more, compared with the widely reported TiO_2 photocatalyst [26–29], which is suspended in aqueous solution, the POM-based process exhibits further advantages attributed to the solubility of POMs: (a) the final metal product is obtained in pure form, and (b) no poisoning of the catalyst is noticed, keeping the process catalytic throughout photolysis.

Moreover, using various POMs with suitable redox potentials, selective recovery of certain metal ions—in a mixture of metal ions—can be achieved. Reduced POMs are able to reduce metal ions efficiently with more positive redox potentials, while they leave intact metal ions with more negative redox potential values, thus serving as 'soluble cathodes'. Figure 4 depicts the selective precipitation of palladium from a mixture that also contains copper and nickel ions at 10-fold higher concentrations, using the POM $SiW_{12}O_{40}^{4-}$ as photocatalyst [14]. Similarly, illumination of a $PW_{12}O_{40}^{3-}$/2,4 dichlorophenol aqueous solution that also contains Ag^+, Pd^{2+}, Cu^{2+}, or Ni^{2+} leads to complete precipitation of elemental palladium within 1 h of photolysis

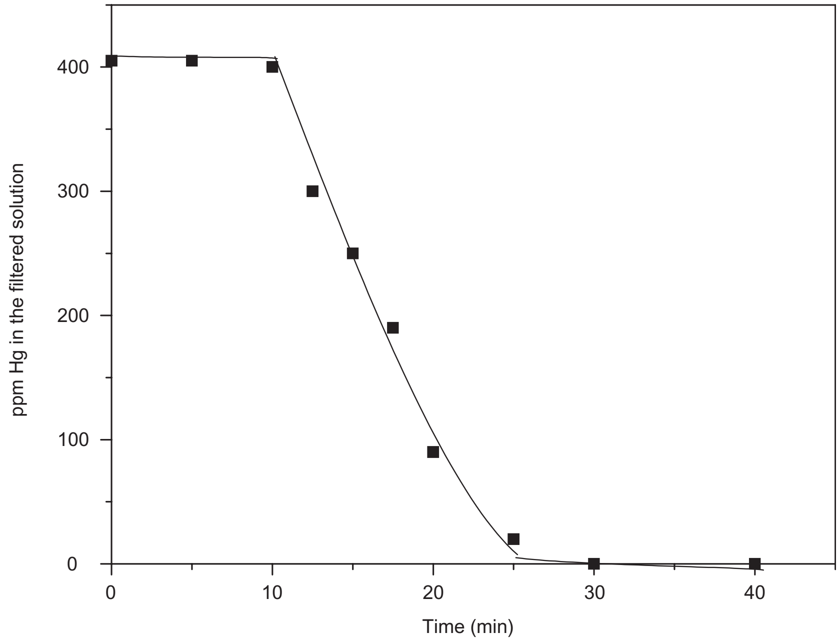

Figure 3. Variation of Hg^{2+} concentration upon irradiation of deaerated aqueous solutions containing 0.5 M propan-2-ol, 7×10^{-4} M $H_3PW_{12}O_{40}$, 2×10^{-3} M Hg^{2+} at pH 1 ($\lambda > 320$ nm, $T = 18°C$), with illumination time.

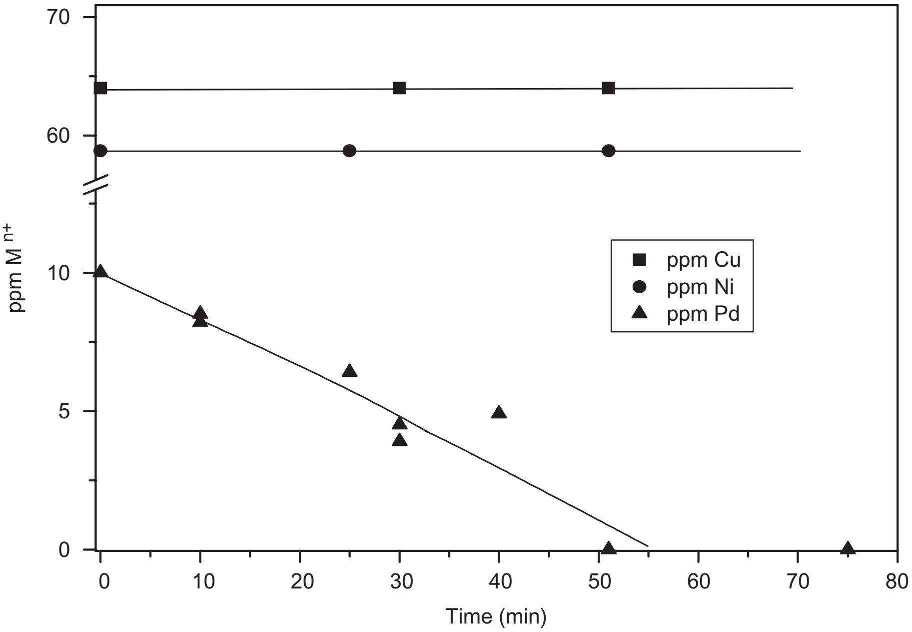

Figure 4. Selective recovery of palladium from a mixture of Pd^{2+}, Cu^{2+}, Ni^{2+}. Photolysis of a deaerated solution of $SiW_{12}O_{40}^{4-}$ (7×10^{-4} M), propan-2-ol (10^{-3} M), Pd^{2+} (10^{-4} M), Cu^{2+} (10^{-3} M), Ni^{2+} (10^{-3} M). pH 3, $NaClO_4$ 0.1 M, $\lambda > 320$ nm, $T = 18°C$ (reprinted from [14]).

and silver after 2 h of photolysis, while leaving copper and nickel intact even after 3 h [11].

Other parameters that must be taken into account are as follows:

- The kind of POM which controls the rate of metal recovery. POM with more positive redox potentials, i.e. according to the order $PW_{12}O_{40}^{3-}$ > $SiW_{12}O_{40}^{4-}$ > $H_2W_{12}O_{40}^{6-}$, are more efficient in reducing and precipitating metal ions (since greater quantities of reduced POM are formed photochemically, amenable in turn to reducing metal ions) [14].
- The concentration of the reactants, i.e. organic and metal ions, as well as the POM photocatalyst concentration. Increases in concentration values accelerate the recovery of metals up to a saturation value [12, 13].
- Anions that complex strongly metal ions may alter their reduction potential drastically and greatly affect the efficiency of the process. For instance, the presence of $S_2O_3^{2-}$ in Ag^+ solutions or Cl^- in Cu^{2+} solutions hinders the reduction because of the formation of the stable $Ag(S_2O_3^{2-})_2^{3-}$ [13] and $CuCl^-$ [12] compounds, respectively. On the contrary, the presence of NO_3^- or ClO_4^- (which do not complex the metal ions) leaves the process unaffected.
- The ionic strength, which plays a crucial role in the recovery of metals, affecting not only the rate but also the nature of the metal product obtained. At high ionic strength values ($>3 \times 10^{-2}$ M), elemental metals precipitate. However, at low values ($<10^{-2}$ M) a slower reduction of metal ions takes place, resulting in the formation of colloidal metal particles [30]. These nanoparticles are desirable from the aspect of materials chemistry, but not when recovery of metals is the goal, since they pass through the conventional filters rendering the process non-quantitative.

Interestingly, the presence of oxygen has a minimal, if any, detrimental effect. Thus, the process is efficient under open-to-air conditions, and a deaeration step is not necessary.

Moreover, although experiments with $PW_{12}O_{40}^{3-}$ are limited at pH 1 because of its hydrolytic degradation at higher pH, other POMs, i.e. $SiW_{12}O_{40}^{4-}$ or $P_2W_{18}O_{40}^{6-}$ among others, are efficient in neutral solutions. Varying the pH from 0.5 to 6 did not seem to alter the rate of copper recovery [12].

5. Purification of aqueous systems from both organic and inorganic pollutants

Of great practical importance in POM photocatalysis is (a) the ability to generate both oxidizing (POM*) and reducing equivalents (reduced POMs) in one stage and (b) the efficiency of the process in almost any oxidizable organic, even when it is present in trace amounts (ppm or ppb). Thus, instead of using high amounts of sacrificial organic donors, i.e. propan-2-ol, in order to reduce–recover metals, one could make use of harmful organics that are to be disposed of. In this sense, the oxidative degradation of toxic organics can be combined with the simultaneous reduction of metal ions. Figure 5 illustrates the degradation of 2,4-dichlorophenol (2,4-dcp) and the simultaneous quantitative recovery of silver (>99.9%) in the presence of $H_3PW_{12}O_{40}$ photocatalyst in aqueous solution.

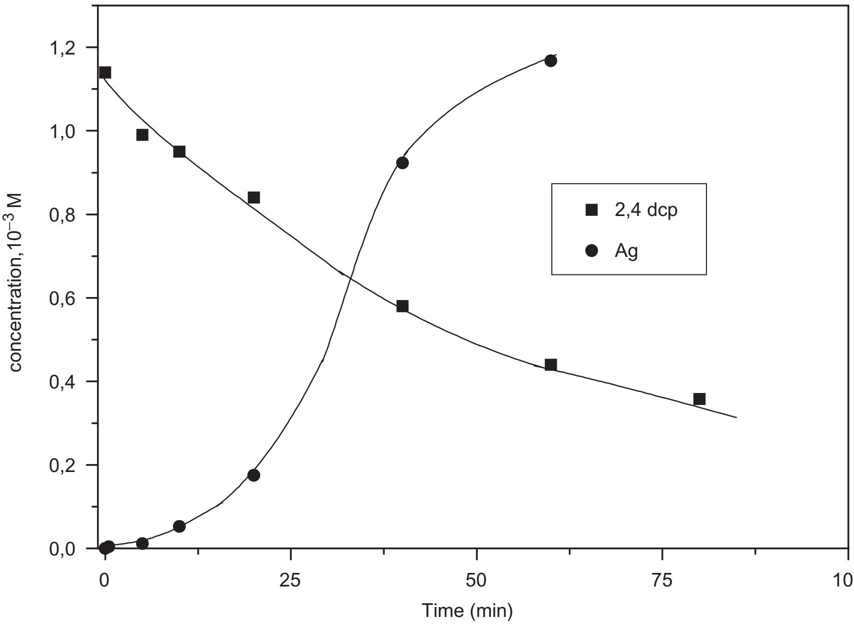

Figure 5. Degradation of 2,4-dcp and simultaneous recovery of silver upon photolysis of a deaerated solution 2,4 dcp (10^{-3} M), $H_3PW_{12}O_{40}$ (7×10^{-4} M), Ag^+ (1.2×10^{-3} M). pH 1, 4 mL, $T = 20°C$, $\lambda > 345$ nm.

This process combines an 'uncontrolled' photochemical oxidation reaction, which is desirable since it leads to complete degradation of a great variety of organic pollutants, with a 'mild', selective, thermal reduction of metal ions. In this way, complete destruction of organic pollutants can be combined with the simultaneous controlled removal of inorganic (metal) pollutants under ambient conditions in a simple one-pot process.

References

[1] M.T. Pope. Heteropoly and isopoly oxometallates. In *Inorganic Chemistry Concepts 8*, C.K. Jorgensen, M.F. Lappert, S.J. Lippard, J.L. Margrave, K. Niedenzu, H. Noth, R.W. Parry, H. Yamatera (Eds), Springer, Berlin (1983).
[2] M.T. Pope, A. Muller. *Angew. Chem. Int. Ed., Engl.*, **30**, 34 (1991).
[3] V.W. Day, W.G. Klemperer. *Science*, **228**, 533 (1985).
[4] E. Papaconstantinou. *Chem. Soc. Rev.*, **16**, 1 (1989).
[5] E. Androulaki, A. Hiskia, D. Dimoticali, C. Minero, P. Calza, E. Pelizzetti, E. Papaconstantinou. *Environ. Sci. Technol.*, **34**, 2024 (2000).
[6] A. Mylonas, A. Hiskia, E. Papaconstantinou. *J. Mol. Catal. A: Chem.*, **114**, 191 (1996).
[7] A. Mylonas, E. Papaconstantinou. *J. Photochem. Photobiol. A: Chem.*, **94**, 77 (1996).
[8] H. Einaga, M. Misono. *Bull. Chem. Soc. Jpn*, **70**, 1551 (1997).
[9] R. Ozer, J. Ferry. *J. Phys. Chem. B*, **104**, 9444 (2000).
[10] S. Kim, H. Park, W. Choi. *J. Phys. Chem. B*, **108**, 6402 (2004).
[11] A. Troupis, A. Hiskia, E. Papaconstantinou. *New J. Chem.*, **25**, 361 (2001).
[12] A. Troupis, A. Hiskia, E. Papaconstantinou. *Environ. Sci. Technol.*, **36**, 5355 (2002).
[13] A. Troupis, A. Hiskia, E. Papaconstantinou. *Appl. Catal. B: Environ.*, **42**, 305 (2003).
[14] A. Troupis, A. Hiskia, E. Papaconstantinou. *Appl. Catal. B: Environ.*, **52**, 41–48 (2004).
[15] A. Hiskia, E. Papaconstantinou. *Inorg. Chem.*, **31**, 163 (1992).
[16] A. Hiskia, E. Androulaki, A. Mylonas, S. Boyatzis, D. Dimotikali, C. Minero, E. Pelizzetti, E. Papaconstantinou. *Res. Chem. Intermed.*, **26**, 3, 23 (2000).

[17] E. Papaconstantinou, A. Hiskia. In *Polyoxometalate Molecular Science, NATO ACS Series*, J.J. Borras, E. Coronado, A. Muller, M. T. Pope (Eds), pp. 379–414, Kluwer Academic, Dordrecht (2003).

[18] S. Antonaraki, E. Androulaki, D. Dimotikali, A. Hiskia, E. Papaconstantinou. *J. Photochem. Photoiol. A: Chem.*, **148**, 191 **(**2002).

[19] I. Texier, J.A. Delaire, C. Giannotti. *Phys. Chem. Phys.*, **2**, 1205 (2000).

[20] A. Hiskia, A. Mylonas, D. Tsipi, E. Papaconstantinou. *Pestic. Sci.*, **50**, 171 (1997).

[21] P. Kormali, D. Dimoticali, D. Tsipi, A. Hiskia, E. Papaconstantinou. *Appl. Catal. B: Environ.*, **48**, 175 (2004).

[22] A. Hiskia, M. Ecke, A. Troupis, A. Kokorakis, H. Hennig, E. Papaconstantinou. *Environ. Sci. Technol.*, 35, **11**, 2358 (2001).

[23] E. Gkika, P. Kormali, S. Antonaraki, D. Dimoticali, E. Papaconstantinou, A. Hiskia. *Int. J. Photoenergy*, **6**, 227 (2004).

[24] A. Hiskia, A. Mylonas, E. Papaconstantinou. *Chem. Soc. Rev.*, **30**, 62 (2001).

[25] E. Gkika, A. Troupis, A. Hiskia, E. Papaconstantinou. *Environ. Sci. Technol.*, **39**, 4242 (2005).

[26] M. Litter. *Appl. Catal. B: Environ.*, **23**, 89 (1999).

[27] C. Maillard-Dupuy, C. Guillard, P. Pichat. *New J. Chem.*, **18**, 941 (1994).

[28] T. Madden, A. Datye, M. Fulton, M. Prairie, S. Majubdar, B. Stange. *Environ. Sci. Technol.*, **31**, 3475 (1997).

[29] K. Tennakone, K. Wijayantha. *J. Photochem. Photobiol. A: Chem.*, **113**, 89 (1998).

[30] A. Troupis, A. Hiskia, E. Papaconstantinou. *Angew. Chem. Int. Ed.*, **41**, 1911 (2001).