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Effect of Scavengers on the Photocatalytic Digestion of Organic Matter in Water Samples Assisted by TiO_2 in Suspension for the Voltammetric Determination of Heavy Metals

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A influência de *scavengers* de elétrons e de lacunas positivas na digestão fotocatalítica de matéria orgânica na presença de partículas de TiO_2 em suspensão, foi investigada. O processo, que visa a determinação eletroquímica de traços de metais pesados em amostras de água, foi acompanhado mediante observação da recuperação da onda voltamétrica de Cd(II) em presença de EDTA, escolhido como ligante-modelo na simulação do efeito complexante da matéria orgânica natural. Confirmou-se o poder acelerador de O_2, que atua como removedor de elétrons. Na ausência de O_2, função análoga é exercida pelo íon nitrato, mas não, ao menos aparentemente, pelo analito Cd(II). Já a adição de CH_3OH apresenta efeito antagônico de *scavenger* de lacunas positivas, o que pode explicar porque a operação na presença de acetato (usado como tampão de pH), ao mesmo tempo em que proporciona um eficaz controle da acidez do meio, provoca uma certa redução do rendimento da fotodegradação.

The influence of electron and hole scavengers in the photocatalytic digestion of organic matter in the presence of suspended particles of TiO_2 was investigated. The process, aiming at the electrochemical determination of traces of heavy metals in water samples, was followed through the recovery of the voltammetric wave of Cd(II) in the presence of EDTA, chosen as model ligand that mimics the complexing effect of natural dissolved organic matter. The accelerating power of O_2, acting as electron scavenger, was confirmed. In the absence of O_2, a similar function is played by nitrate ions but not, as it seems, by the analyte, Cd(II). On the other hand, CH_3OH exhibits an antagonist effect as hole scavenger. This observation may explain why the acetate (from the pH buffer), used to control the medium acidity, leads to a certain reduction in the photocatalytic yield.

Keywords: photodigestion, TiO_2, scavengers, voltammetry

Introduction

In recent years, intense investigation has been undertaken on the TiO_2-assisted photochemical mineralisation of organic substances by UV radiation, either with the semiconductor catalyst in suspension or immobilized on a solid support.[1-26] The method was originally contemplated as a possibility to employ solar radiation as an energy source in water decontamination processes in connection with the treatment of industrial effluents and with water potabilisation.[5,11,18,21] At a certain stage, however, studies and trials have markedly shifted towards the use of artificial UV source, mainly mercury vapour lamps, because of the scarce efficacy obtained with the solar radiation, the practical inconvenient of having to rely on the unpredictable availability of a natural light source and, not least, the poor overlapping of the solar spectrum with the TiO_2 absorption range.[7] Nonetheless, to date, such photocatalytic degradation has been successfully tested on a wide variety of organic substrates,[7,16] both at laboratory and industrial – or at least semi-industrial – scale.[15,21]

This decomposition method has also set foot in the area of analytical chemistry. Initially, in the post-treatment of toxic reagents and products used in or generated by analytical procedures,[22] looking at developing clean analytical routines, but still as an effluent treatment process, though at a small-scale. Then, in an attempt to upgrade the conventional UV photolysis in TOC determination devices.[24]

More notably, the authors of this article have recently proposed and evaluated the use of TiO_2 suspensions in the

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photocatalytic pre-treatment of water samples aiming at the determination of heavy metals by voltammetric detection on mercury drop electrodes (MDE).[26] It is well known that the presence of dissolved organic matter, present in natural waters, e.g. as humic substances, impairs the determination of total metal due to formation of stable and inert adducts between organic species and metal ions.[27-28] For this reason, to access the total metal concentration, sample digestion is generally required and the UV photodegradation seems to represent a very suitable option when the organic load is not to high.[29] This technique is, as a rule, carried out under temperature and pressure conditions closer to ambient, hence it is more easily manageable than the irradiation in microwave ovens. Therefore, the implementation of in-line (*e.g.* FIA) and in-situ procedures with UV digestion[30] is favoured and there is also strictly no need for the addition of concentrated acids and reagents, potential sources of sample contamination. The experiments hitherto conducted with model samples containing Cd(II) (down to concentrations of 30 ppb) and dissodium ethylenediaminotetracetate (at concentrations of 10 to 500 fold in excess the Cd(II) content) have proven the efficacy of the photocatalytic destruction of the ligand and the complete recovery of the voltammetric metal signal, without prior filtration of the TiO_2 suspension.

Beside displaying the already mentioned benefits of the conventional UV digestion, the photocatalytic variant yields to the enhancement of the decomposition reaction speed and to widening the effective radiation range towards less short wavelengths, what enables the use of PTFE tubing in the irradiation chamber (instead of the customary quartz ones, more expensive and unpractical) and a likely wider range of light sources.[26]

Nevertheless, in order to extend the results obtained with a somewhat well-behaved model solution to real samples, it is of primary importance to assess the influence of other species present in the sample in the photocatalytic mechanism. This is centred on the formation of an electron-hole pair on the TiO_2 (anatase) surface upon the incidence of a photon with energy equal to or higher than the gap between the valence and the conduction band within the semiconductor crystal (3.23 eV):[1-8]

$$TiO_2 \xrightarrow{h\nu} e^-_{CB} + h^+_{VB} \qquad (1)$$

An electron is promoted to the conduction band (CB) while a positive hole is formed in the valence band (VB). In order for this process to have a net chemical effect, the recombination of the electron-hole pair has to be precluded so that the energy stored in chemical form is not dissipated as heat.[7,8] The natural fate for h^+_{VB} and e^-_{CB} is the extraction of the electron to an external electric circuit,[21,25] as it happens solar cells based on this principle, or the removal of either of them by means of redox reactions involving species present at the semiconductor surface, i.e. in the solid-liquid interface in the case of aqueous suspensions of TiO_2.[7]

As far as the degradation of organic substances is concerned, the process is triggered by the h^+_{VB}, either by direct oxidation of the organic substrate or, more likely, via attack of $OH^\bullet$ radicals formed, for instance, through the following route:[6-8]

$$OH^- + h^+_{VB} \xrightarrow{h\nu} OH^\bullet \qquad (2)$$

Nonetheless, it is clear that the rate of the oxidative half reaction involving h^+_{VB} is closely related to the effective removal of the partner species, *i.e.* e^-_{CB}, by suitable electron scavengers, that must be present in the solution and available at the semiconductor interface.[6] On the other hand, in processes aiming at the oxidative destruction of a target organic substrate, any hole scavengers present in the same environment are potential competitors for the consumption of h^+_{VB}.[7,8]

As far as electron scavenging is concerned, the most common electron scavenger, in aerated aqueous solution, is O_2 and its role has been emphasised,[1,7] including in the formation of "so-called selective oxygen species, which take part in the process of oxo functionalization of hydrocarbons".[31]

Upon reacting with photogenerated electrons on the surface of TiO_2, O_2 molecules form extremely reacting species such as the superoxide radical $O_2^{-\bullet}$ and the singlet oxygen $^1O_2$, which, in turn, trigger radical chain reactions, involving the generation of strong oxidants like H_2O_2 and O_3.[29]

A number of potential inorganic electron receptors have been pointed out in literature: Cl^-, SO_4^{2-}, NO_3^-, HCO_3^- and PO_4^{3-},[7] peroxides like $S_2O_8^{2-}$, IO_4^- and ClO_3^-,[32] $C(NO_2)_4$.[31] However, what perhaps has not yet been pointed out with clarity is the importance of O_2 in the concomitant presence of other electron scavengers.

Metal ions are also involved in the photocatalytic mechanism and their role in photodegradation processes was widely reviewed in a recent paper by Litter.[8] In most cases, they tend to enhance the destruction of organic substances, either through heterogeneous or homogeneous (mainly photo-Fenton type reactions) pathways,[9] but only when present at low quantities and in the absence of dissolved O_2. Among them, the behaviour of Fe, Cu and Ag ions has been thoroughly studied in connection with operating conditions such as pH, counter-ion type, solution composition and O_2 content. The same source lists a number of common effective hole scavengers. The more commonly used are: methanol and ethanol,[14,20] 2-propanol,[20] but also acetic acid,[14,12] salicylic acid and EDTA.[14]

The goal of the work accounted in the present article was to show the influence, in the photocatalytic digestion, of species possibly present in solution and capable to trap and consume electrons or positive holes and, thus, to interfere favourably or unfavourably in the oxidation mechanism of organic substrates. Such an investigation, in the first place, intended to incorporate into the previous model system, elements able to turn it a more realistic system, with the possibility of a more reliable prediction of the behaviour of real samples submitted to the analytical treatment. Secondly, it aimed to explore the possibility of using effective electron scavengers in order to optimise the mineralisation process. This study was conducted with O_2 and NO_3^- (at different concentrations) as representative electron scavengers. Some experiments were also carried out with different concentrations of Cd(II), used as target analyte, in order to bring to light any possible effect of this species as an electron scavenger. Methanol was chosen as a hole scavenger. The likely effect of the acetate buffer as a hole scavenger was also checked out in a run carried out in unbuffered medium. In this case the pH was constantly monitored and adjusted by H^+ addition (more details in the Results and Discussions section).

Experimental

The photocatalytic process was tested in the absence and in the presence of (different amount of) electron or hole scavengers, on a model system[26,34] comprising $1x10^{-4}$ mol L^{-1} Cd(II) (unless otherwise stated) and $1x10^{-3}$ mol L^{-1} sodium ethylenediaminetetraacetate (NaEDTA, present as H_2Y^{2-} at pH near 4, hereafter designated as EDTA for brevity), dissolved (unless otherwise stated) in an AcNa/AcH buffer pH 4.0.

The photodigestion of EDTA was followed, at regular interval, through the recovery of the suppressed Cd(II) signal, upon sample exposure to the radiation of a medium pressure mercury lamp. In all results presented, the metal signal was normalised, considering the signal value measured before EDTA addition as 100%.

Chemicals

All solutions were prepared using deionised water (18MΩ) purified by a Barnstead Nanopure system. All chemicals were of analytical grade: $CdSO_4$, Na_2EDTA, glacial acetic acid, sodium acetate, CH_3OH. O_2 was of standard medical type (Air Liquide). Vacuum-bidistilled mercury was used in polarography.

All samples were prepared daily by dilution of stock $1x10^{-2}$ mol L^{-1} Cd(II) and EDTA solutions. The supporting electrolyte was (unless otherwise stated) an acetate buffer of $1x10^{-2}$ mol L^{-1} NaAc brought to pH 4.0 ± 0.05 by glacial AcH.

Titanium dioxide suspensions (0.1% w/w) were obtained by homogenising, in a mortar, solid TiO_2 (Degussa P25 without further purification) with 5 mL of the buffer solution, bringing to the final volume (15 or 20 mL) and sonicating for 30 min in an ultrasound bath. Other reagents (notably Cd(II) and EDTA) were added at this stage to desired portions of this suspension.

Photochemical digestor

The photochemical device used in the experiments of this work was designed and constructed in the authors' laboratory and it was described in detail elsewhere.[26] It consists of a mercury vapour lamp (Osram 400 W) and a coiled PTFE reactor tube both placed within a tubular chimney that blocks the radiation and guides a cooling air flux from an electric fan situated at the lower end of the chimney. With the fan constantly turned on, the temperature settles around 30 °C.

The system can be operated in the batch mode, with sample re-circulation from and to an external reservoir, or in FIA mode with the introduction of a single sample plug with a volume equal to or smaller than the coiled tube that functions as irradiation cell.

All experiments were conducted with 15 and 20 mL of sample in the batch/re-circulation mode at a flow rate of 16 mL min^{-1}. Since the internal volume of the tube reactor was 6.1 mL, under these operation conditions, during the treatment only about one third of the sample was being irradiated. This does not change the relative results that will be presented, however, under continuous irradiation conditions, all recovery times would be considerably shortened. For O_2 trials, the pure gas was bubbled continuously in the external reservoir. Complete O_2 saturation of the solution was assumed but not demonstrated, although in a preliminary test it was confirmed, voltammetrically, that the O_2 content in the solution reached a plateau after only 10 s of purging by pure O_2.

At regular time intervals, the solution was transferred to the electrochemical cell for Cd(II) determination and then returned to the photochemical system for further treatment. A diagram of the experimental set-up is illustrated in Figure 1.

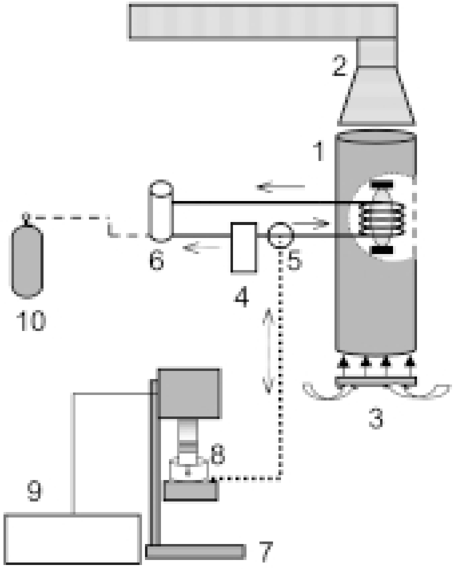

Figure 1. Experimental set-up. 1: photochemical reactor (with insight of the internal UV lamp and the PTFE coiled tube reactor); 2: exhaust; 3: cooling fan; 4: peristaltic pump; 5: commutation valve; 6: sample reservoir; 7: electrochemical stand; 8: electrochemical cell; 9: potenciostat; 10: O_2/N_2 supply.

Electrochemical apparatus

Cd(II) determination was carried out either by normal pulse polarography (NPP) or by differential normal pulse polarography (DNP) (as indicated in the figure captions). In the former case, a EG&G PAR 384B Polarographic analyser coupled with a PARC 303A Stand was used, whereas in the latter, a 646 VA Processor (Metrohm) coupled with a 647 VA Stand (Metrohm) was employed. The operating parameters were: working electrode = SMDE; drop size = “medium” (PAR 303) or “5” (VA-Stand); reference electrode = Ag/AgCl (3 mol L^{-1} KCl); auxiliary electrode = Pt; onset potential = -0.300 V; final potential = -0.900V; pulse amplitude = 50 mV; step time = 1 s; potential increment = 5 mV; purge time (N_2) = 400 s.

Results and Discussion

The effect of O_2 as an electron scavenger in the photocatalytic degradation of EDTA is shown in Figure 2. The rate of recovery of the Cd(II) signal was compared with two other runs conducted either bubbling N_2 – for complete O_2 removal – or exposing the solution to open air. The advantage of O_2-enriched solutions over the other two modes is evident. In particular, the decomposition performed on the air-exposed solution, although more effective than the degradation in a O_2-deprived sample and more convenient in practical and economical terms, it is not as profitable as when pure O_2 is injected.

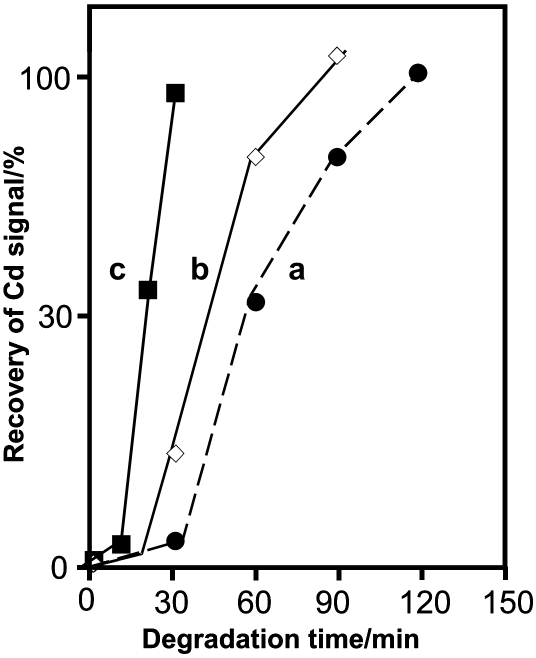

Figure 2. Recovery of Cd(II) signal upon photocatalytic degradation: (a) with N_2 purging; (b) with no N_2 nor O_2 purging; (c) with O_2 purging. 10^{-4} mol L^{-1} Cd(II); 10^{-3} mol L^{-1} $EDTA_i$ in acetate buffer pH 4.0. Cd(II) determination by NPP with 400 s of N_2 purging prior to the metal determination. Sample volume = 20 mL.

The scavenger role of NO_3^-, at concentrations of $1x10^{-3}$ and $1x10^{-2}$ mol L^{-1}, is shown in Figures 3A and 3B, in the absence and in the presence of O_2, respectively. In the latter case, assuming complete saturation of the solution and considering 760 mmHg atmospheric pressure and 30 °C sample temperature, the dissolved-O_2 concentration is approximately 0.2 mmol L^{-1},[35] that is, a value at least 5-fold lower than the NO_3^- concentration, but still twice larger than the EDTA concentration.

Without O_2, the increase in the amounts of NO_3^- results in a patent enhancement of the degradation process, with a marked reduction of the time required to achieve almost complete recovery. The outcome is in agreement with some earlier literature data showing that the photocatalytic degradation of methyl orange in deareated conditions is faster in the presence of Ag and Cu nitrates, than with the sulphate salts of the same metals. Other researchers have also detected some photocatalytic formation of ammonium ions upon irradiating a $Hg(NO_3)_2$ solution at pH 8, likely to be ascribed to the nitrate photochemical reduction.[8] On the other hand, in the presence of O_2 there seems to be no influence from the nitrate.

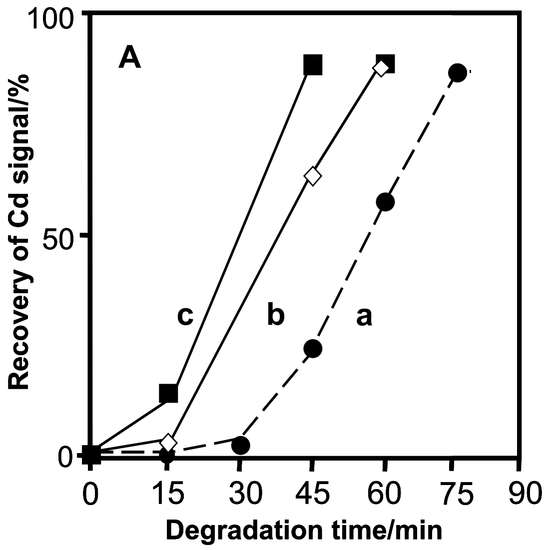

Figure 3A. Recovery of Cd(II) upon photocatalytic degradation with N_2 purging: (a) without NO_3^-; (b) with 10^{-3} mol L^{-1} NO_3^-; (c) with 10^{-2} mol L^{-1} NO_3^-; 10^{-4} mol L^{-1} Cd(II); 10^{-3} mol L^{-1} $EDTA_i$ in acetate buffer pH 4.0. Cd(II) determination by DNP with 400 s of N_2 purging prior to the metal determination. Sample volume = 15 mL.

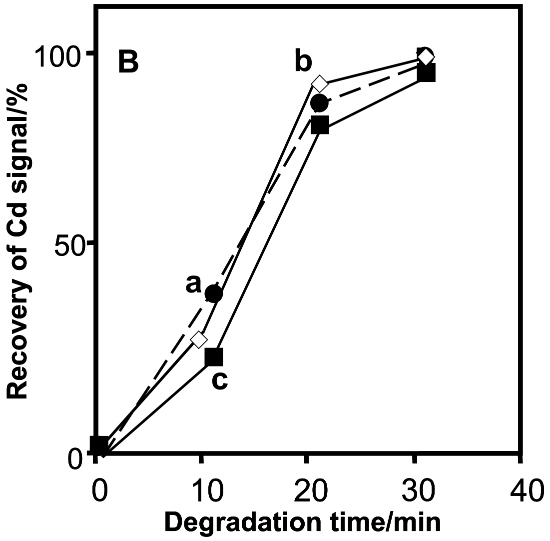

Figure 3B. Recovery of Cd(II) upon photocatalytic degradation with O_2 purging: (a) without NO_3^-; (b) with 10^{-3} mol L^{-1} NO_3^-; (c) with 10^{-2} mol L^{-1} NO_3^-; 10^{-4} mol L^{-1} Cd(II); 10^{-3} mol L^{-1} $EDTA_i$ in acetate buffer pH 4.0. Cd(II) determination by DNP with 400 s of N_2 purging prior to the metal determination. Sample volume = 15 mL.

It can be speculated that the role of electrons scavenger is entirely fulfilled, at least at this level of TiO_2 content, by the molecular oxygen and that, therefore, the presence of nitrate becomes ineffectual. This means, apparently, that O_2 is already exerting the whole scavenging activity required by the number of photogenerated electron-hole pairs produced on the semiconductor surface under the present experimental conditions, *i.e.* with mere O_2 sparging the system is operating in optimised conditions of electron scavenging.

As a rule of thumb, it may be noted that the concentration of required electron scavengers is, firstly, related to concentration of species that can undergo oxidation through h^+_{VB} via the companion half reaction. Secondly, it is associated with the actual amount of electron-hole pairs generated by the incident photon flux, *i.e.* to factors such as the content of TiO_2, the reactor geometry, light scattering and screening effects. Kinetic aspects, not dealt here, can be also relevant when comparing the efficiency of scavengers (O_2, in all probability, has better chances to undergo faster reduction than NO_3^- on account of the direct uptake of electrons without the necessity of molecular rearrangements).

The effect of the presence Cd(II) is displayed in Figure 4A. This experiment was conducted with and without the metal ions during the photoirradiation. In one of the experiments (curve a), the same mother sample was divided in different portions that were treated for increasing lengths of irradiation time (with O_2 purging). Here, Cd(II) was added only before the voltammetric analysis and after that the sample was disposed (the only exception in the general procedure of returning the same solution for further irradiation).

The process is clearly favoured by the absence of Cd(II). Electron scavenging by Cd ions is thermodynamically unviable since the metal redox potential does not match the position of the energy levels of the electron-hole pair on the photocatalyst, a fact that is well documented in literature.[8] In contrast, there is a retarding effect of Cd(II) ions on the EDTA degradation, or better, a slower decomposition of the complex CdH_2Y. This fact was already reported in literature under similar experimental conditions[19] and may be associated with a lower propensity of the adduct to approach the TiO_2 surface vicinity where the photochemical reaction takes place, or simply with a lesser degree of interaction of the ligand with the semiconductor which may be required for an effective photocatalytic effect. In support to this deduction, the effect of Cd(II) in the conventional UV photolysis of EDTA, *i.e.* without TiO_2, was tested and reported in Figure 4B. This process does not, of course, involve heterogeneous phase transfer and is not significantly affected by the presence or absence of cadmium ions.

Finally, the question of hole scavenging was approached. The effect of methanol, a recognised hole scavenger, is shown in Figure 5, in which the lines a and c refer to photodegradations carried out without CH_3OH (in the presence and absence of O_2), while lines b and d correspond to processes conducted with 1% (v/v, *i.e.* approx. 0.25 mol L^{-1}) of methanol.

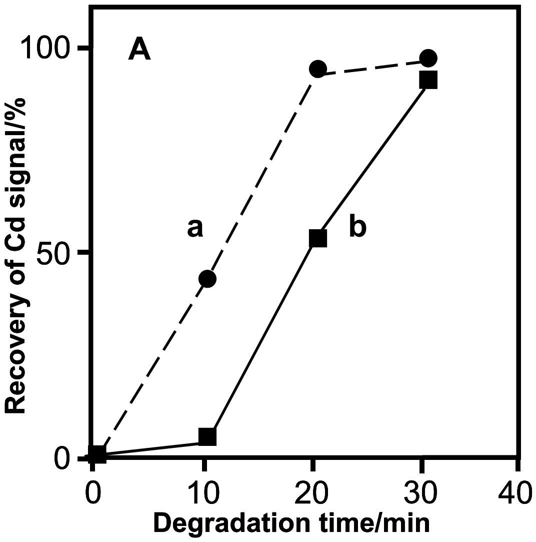

Figure 4A. Recovery of Cd(II) upon photocatalytic degradation with O_2 purging: (a) without Cd(II) during the photodegreadation; (b) with Cd(II) during the photodegradation. 10^{-4} mol L^{-1} Cd(II) (added after each irradiation step in (b)); 10^{-3} mol L^{-1} $EDTA_i$ in acetate buffer pH 4.0. Cd(II) determination by NPP with 400 s of N_2 purging prior to the metal determination. Sample volume = 20 mL.

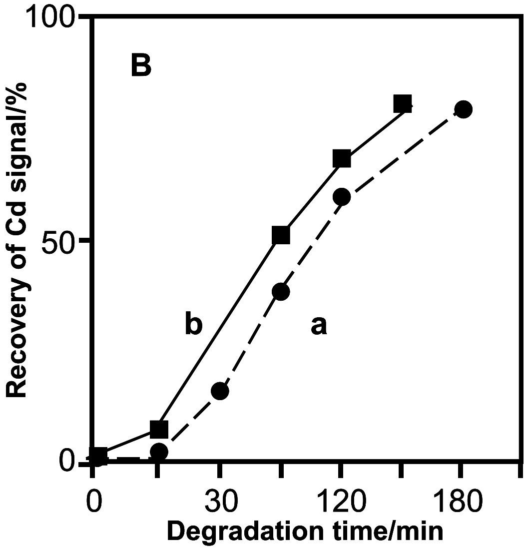

Figure 4B. Recovery of Cd(II) upon photodegradation in the absence of TiO_2: (a) without Cd(II) during the photodegreadation; (b) with Cd(II) during the photodegradation. 10^{-4} mol L^{-1} Cd(II) (added after each irradiation step in (b)); 10^{-3} mol L^{-1} $EDTA_i$ in acetate buffer pH 4.0. Cd(II) determination by NPP with 400 s of N_2 purging prior to the metal determination. Sample volume = 20 mL.

Once again, a shift to shorter degradation times for processes carried out in the presence of O_2 is observed. In addition to that, it is possible to distinguish two phases: an initial one, in which the presence of methanol seems to delay the process and a second one where the effect is deadened, with no substantial difference in the overall degradation time. It must borne in mind that not only does methanol act as an hole scavenger, as it plays a role in the propagation of the radical chain mechanism with the formation of highly reactive species such as $\bullet CH_2OH$.[23] It could be argued that, at an early phase when the direct hole oxidation is predominant, CH_3OH competes with EDTA in the consumption of h^+_{VB} causing a setback in the degradation of the targeted organic substrate, though with a positive curvature of the recovery curve. Later on, this effect is dampened perhaps because of the lesser importance of this step and the formation of beneficial reactive radicals.

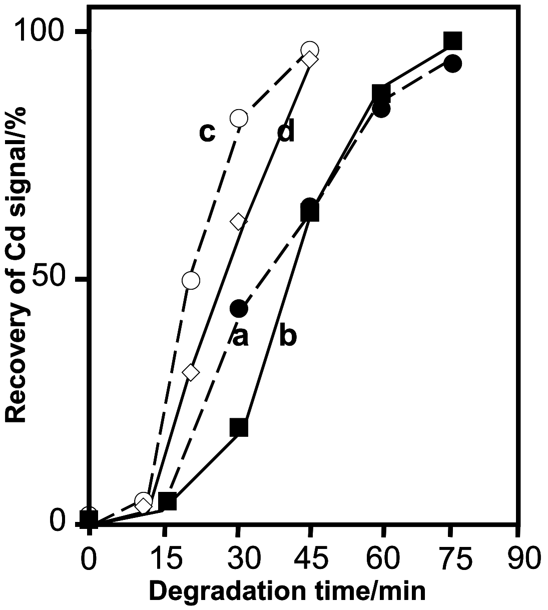

Figure 5. Recovery of Cd(II) upon photocatalytic degradation: (a) without CH_3OH and N_2 purging; (b) with CH_3OH (1% vol.) and N_2 purging; (c) with no CH_3OH and O_2 purging; (d) with CH_3OH (1% vol.) and O_2 purging. 10^{-4} mol L^{-1} Cd(II); 10^{-3} mol L^{-1} $EDTA_i$ in acetate buffer pH 4.0. Cd(II) determination by DNP with 400 s of N_2 purging prior to the metal determination. Sample volume = 15 mL.

In the light of this outcome, it was expected a similar effect in connection with the acetate buffer used to prevent pH increase associated with the degradation of EDTA and described elsewhere.[26] In the experiment whose results are illustrated in Figure 6, two degradation runs were performed and compared: one with the usual buffering system and another without buffer, both with O_2 purging. In the latter, HNO_3 was used to initially set the acidity of the medium to pH 4.0 and thereafter to correct it in the course of the photodegradation. The pH was read with a portable pH-metre (Corning pH-30) in the external sample reservoir. In accordance with the results observed in the electron scavengers investigation, in this case – with O_2 purging – the NO_3^- effect ought to be negligible.

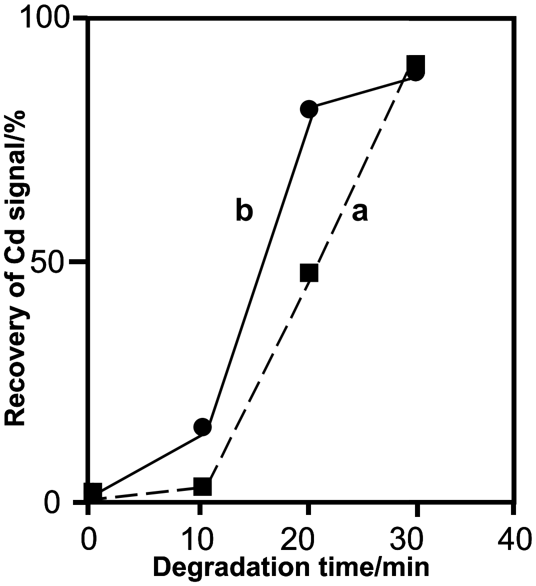

Figure 6. Recovery of Cd(II) upon photocatalytic degradation with O_2 purging: (a) in acetate buffer pH 4.0; (b) without acetate buffer, at pH 4.0 by HNO_3 (with pH adjustment by HNO_3 during photodegradation). 10^{-4} mol L^{-1} Cd(II); 10^{-3} mol L^{-1} $EDTA_i$. Cd(II) determination by DNP with 400 s of N_2 purging prior to the metal determination. Sample volume = 15 mL.

The presence of acetate hampers the photodegradation process, in agreement with literature data that report the chance of the acetate substrate to behave as a hole scavenger effect via the so-called photo-Kolbe reaction.[12] The effect is similar to the case of methanol, although the concentration of the alcohol was about an order of magnitude higher.

Still, a distinct tendency of the solution to shift towards less a acidic status was observed in the absence of buffer, at least in the presence of EDTA as model ligand, and this has to be avoided to prevent analyte losses by hydrolytic precipitation.[26]

Conclusions

This article is the second part of a series of papers concerning the exploration of the use of photocatalytic processes for analytical purposes, notably in the pre-treatment of water samples aiming at the destruction of natural dissolved organic matter for total metal determination. It has been previously highlighted the effectiveness of this technique for model and real samples, the possibility of integration in a FIA system comprising injection, in-line digestion, degassing and voltammetric detection, and, finally, the advantages of the use of TiO_2 in terms of better/faster photochemical yields. Now, the results described in the above section bring a better insight on the factors that can affect the performance of the semiconductor-assisted photomineralisation. In particular, a further confirmation of the accelerating power of O_2, acting as electron scavenger, in the photocatalytic degradation of EDTA was shown. A similar function is exercised by nitrate ions but, interestingly enough, this is completely overshadowed by the presence of O_2, which makes believe that the electron scavenging role is entirely satisfied by oxygen, at least under the investigated experimental conditions. The analyte so far used, Cd(II), does not have any scavenging effect and therefore is not lost by reduction.

Experiments with model hole scavengers like CH_3OH and acetate/acetic acid buffer (convenient to control the medium acidity) presented a visible effect as antagonists of the desired photocatalytic decomposition, more visible at the early stage of the process of Cd(II) release. At relatively high concentrations (above expected ones in most natural matrixes), the effect of such scavengers can somewhat delay the proposed photocatalytic sample treatment method, but does not impair its application.

In short, on the one hand, the increase of O_2 concentrations above air saturation is a simple and convenient way to accelerate the TiO_2-assisted photodecomposition of molecules like EDTA since it dispenses with the addition of other reagents acting as electron scavengers, a fact that also reduces the risk of contamination. On the other hand, the presence of moderate amounts of hole scavengers like low molecular weight alcohols or carboxylic acids in the samples or the addition of carboxylate buffers is admissible because their effect is very limited.

These results bring more confidence to the use of the novel in-line TiO_2-assisted photodegradation system described in the first paper, widen its potential electroanalytical application[26] and it is likely to trigger new studies regarding, for example: metal type and concentration, type and concentration of dissolved organic matter, simultaneous determinations and immobilization of the photocatalyst for use with suspension-incompatible detectors.

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