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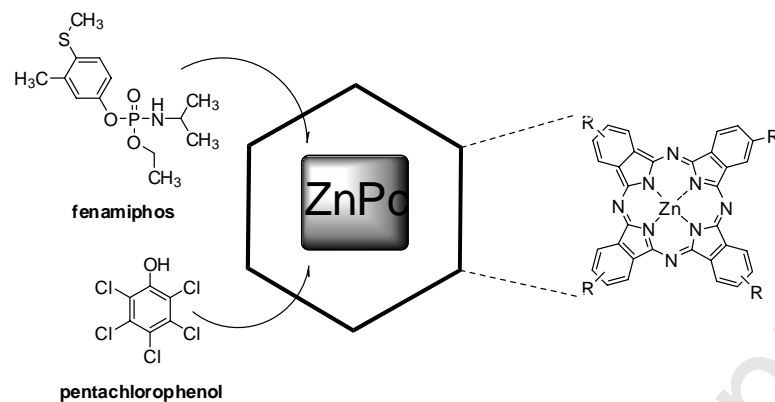
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Zinc(II) phthalocyanines immobilized in mesoporous silica Al-MCM-41 and their applications in photocatalytic degradation of pesticides

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- Complete immobilization of zinc(II) phthalocyanines accomplished in AlMCM-41.
- Efficient photodegradation of model pesticides achieved using 365 nm irradiation.
- Sodium azide experiments showed the involvement of singlet oxygen ($^1\text{O}_2$).

Zinc(II) phthalocyanines immobilized in mesoporous silica Al-MCM-41 and their applications in photocatalytic degradation of pesticides[†]

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ABSTRACT

In the present study the authors investigated a set of three new zinc(II) phthalocyanines (zinc(II) tetranitrophthalocyanine (ZnTNPc), zinc(II) tetra(phenyloxy)phthalocyanine (ZnTPhOPc) and the tetraiodide salt of zinc(II)tetra(*N,N,N*-trimethylaminoethyloxy)phthalocyaninate (ZnTTMAEOPcI)) immobilized into Al-MCM-41 prepared via ship-in-a-bottle methodology. The samples were fully characterized by diffuse reflectance-UV-Vis spectroscopy (DRS-UV-Vis), luminescence, thermogravimetric analysis (TG/DSC), N₂

adsorption techniques and elemental analysis. A comparative study was made of the photocatalytic performance upon irradiation within the wavelength range 320-460 nm of these three systems in the degradation of pesticides fenamiphos and pentachlorophenol. ZnTNPc@Al-MCM-41 and ZnTTMAEOPcI@Al-MCM-41 were found to be the most active systems, with the best performance observed with the immobilized cationic phthalocyanine, ZnTTMAEOPcI@Al-MCM-41. This system showed high activity even after three photocatalytic cycles. LC-MS product characterization and mechanistic studies indicate that singlet oxygen ($^1\text{O}_2$), produced by excitation of these immobilized photosensitizers, is a key intermediate in the photocatalytic degradation of both pesticides.

Keywords: Zinc(II) Phthalocyanines, Al-MCM-41, photocatalysis, pesticide, singlet oxygen

[†] The authors dedicate this paper to the memory of Fernando Ramôa Ribeiro, Full Professor of the Instituto Superior Técnico and Rector of the Technical University of Lisbon, who contributed greatly to the development of heterogeneous catalysis, but sadly passed away on 29th August 2011.

1. Introduction

The search for new methodologies to promote the photodecomposition of organic pesticides is of major relevance for the elimination of pollutants under a variety of environmental situations. Although many of these molecules can undergo direct photochemical decomposition with the UV component of natural solar light, this can be markedly enhanced

through advanced oxidation processes (AOPs), like $\text{H}_2\text{O}_2/\text{UV}$, O_3/UV and $\text{H}_2\text{O}_2/\text{O}_3/\text{UV}$, heterogeneous photocatalysis, homogeneous photo Fenton, etc., have been proposed for treatment of polluted water by pesticides [1,2].

In particular, heterogeneous photocatalysis is an efficient technique to eliminate organic pollutants in water [3,4]. Semiconductors (TiO_2 , ZnO , Fe_2O_3 , ZnS , etc.) can act as sensitizers for light induced redox processes and the photocatalytic experiments showed that the addition of semiconductors in tandem with the oxidant ($\text{Na}_2\text{S}_2\text{O}_8$) strongly enhances the degradation rate [5].

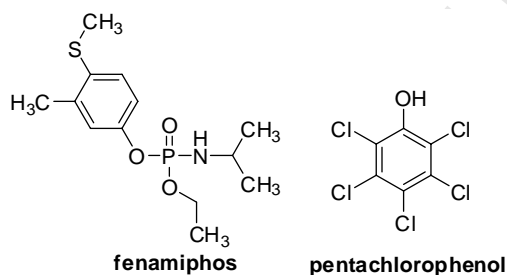
In the last decade, increased interest has developed on the immobilization/adsorption of tetrapyrrole macrocyclic sensitizers into solid supports. These organic-inorganic hybrid materials combine stability under a variety of reaction conditions with intense absorption in both the blue and red regions of the visible spectrum, such that they can collect up to 50% of solar energy and act as potentially viable photocatalysts [6-20].

Exploitation of supported, photoactive metallophthalocyanines as catalysts to treat organic pollutants has emerged as an active research topic due to both good stability and ease of recovery, resulting from their incorporation into an inert matrix [6,8-10,14,18,20,21].

The confinement of metal complexes within the constrained environment of ordered mesoporous oxides is particularly important, and has been actively developed since the discovery of M41S family [16-18,20,22-29]. Although there are reports on the use of metallophthalocyanines anchored onto the surface of Al-MCM-41 as catalysts in the oxidation of aromatic compounds [17,23-29], their employment as photocatalysts has not received much attention [16,18,20,21].

In this study, we describe the immobilization of three phthalocyanines, ZnTNPc , ZnTPhOPc and ZnTTMAEOPcI into Al-MCM-41 by post-synthesis method (*ship-in-a-bottle*). The resulting solid products were characterized by various techniques (DRS–UV-Vis,

luminescence, TG/DSC, N₂ adsorption and elemental analysis). The materials were evaluated for the photocatalytic decomposition of the important, and representative, pollutants fenamiphos and pentachlorophenol. To obtain mechanistic information, the influence of the oxygen concentration in solution, the amount of the catalyst, pH and the presence of singlet oxygen quencher on the degradation rate have been investigated. Photoproducts have been identified by LC-MS. To test for potential practical applications, studies on the continued photocatalytic efficiency of recovered immobilized sensitizers are also presented.



2. Experimental

2.1. Materials

All solvents were purchased from Aldrich and used as received. Al-MCM-41 (Si/Al~40) was from Aldrich and pre-treated in an oven at 500 °C during 18 h under self-generated atmosphere. It was subsequently allowed to equilibrate at room temperature in air. The zinc(II) acetate dihydrate (>97%), anhydrous potassium carbonate (pure reagent) and anhydrous sodium sulfate (>98%) were obtained from Fluka, fenamiphos (99.9% purity) from Riedel-de Hën and pentachlorophenol (97% purity) from Carlo Erba. They were used

without further purification. Sodium azide was from Sigma-Aldrich ($\geq 99.5\%$). All aqueous solutions were prepared with water from a Millipore Milli-Q ultrapure water system having a resistivity $>18 \text{ M}\Omega \text{ cm}^{-1}$.

2.2. Catalyst preparation: "Ship-in-a-bottle" synthesis of zinc phthalocyanines

The immobilization of phthalocyanine complexes in the mesoporous aluminosilicate MCM-41, Fig. 1, was carried out by mixing the corresponding substituted phthalonitrile (4 mmol), zinc (II) acetate dihydrate (1.3 mmol), Al-MCM-41 (1 g) and DMF (10 mL) under vigorous stirring, at $130 \text{ }^\circ\text{C}$, during 12 h. After cooling to room temperature, the prepared materials, ZnTNPc@Al-MCM-41 (**2a**), ZnTPhOPc@Al-MCM-41 (**2b**) and ZnTDMAEOPc@Al-MCM-41 (**2c**) were filtered off, sequentially Soxhlet extracted with acetone, CH_2Cl_2 , THF, $\text{H}_2\text{O}:\text{CH}_3\text{OH}$ (1:5) and finally with acetone until no phthalocyanine or precursor molecules were detected, in the solution, by UV-Vis spectroscopy. The resulting immobilized sensitizers were dried in an oven at $70 \text{ }^\circ\text{C}$ during 24 h.

The transformation of ZnTDMAEOPc@Al-MCM-41 (**2c**) into its corresponding tetraalkylammonium cationic species was carried out by reacting **2c** with methyl iodide (5.96 g, 40 mmol) in dichloromethane under reflux for 8 h. Finally, the resulting solid ZnTTMAEOPcI@Al-MCM-41 (**3**) was washed and dried as described above. The full characterization of the catalysts is described in the next section.

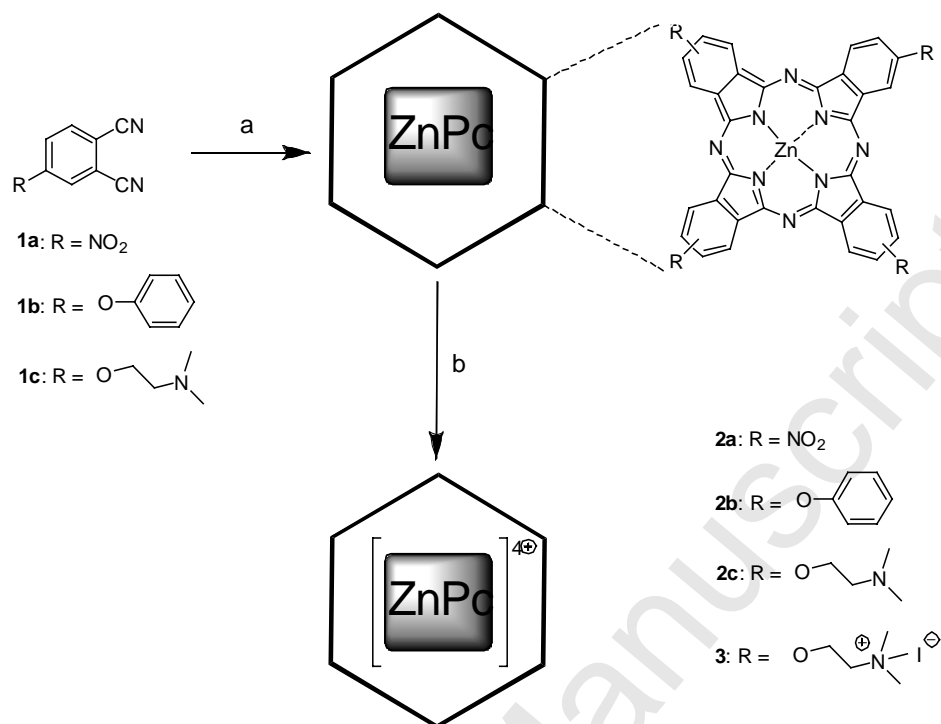


Fig. 1. Synthesis of immobilized phthalocyanines **2a-2c** and **3**. Reagents and conditions: a) Zn(OAc)₂·2H₂O, Al-MCM-41, DMF, 130 °C, 12 h (for **2a**, **2b** and **2c**), and b) CH₃I, CH₂Cl₂, 40 °C, 8 h (for **3**).

For comparison, the free metallophthalocyanines were also prepared and characterized using the same spectroscopic techniques. ZnTNPc, ZnTPhOPc and ZnTTMAEOPcI were synthesized with slight modifications of literature procedures, and characterization data are in agreement with reported values [30-32].

2.3. Instrumentation

UV-Vis absorption spectra in solution were measured over the range 200–800 nm on a Shimadzu UV-2010 double-beam spectrometer.

Luminescence spectra were obtained on a SPEX Fluorolog 3-22 spectrophotometer, using a 300 W xenon arc lamp as excitation source. The luminescence spectra were measured on solid samples using a specially designed metal support with a quartz window.

DRS-UV-Vis spectra of solid samples were recorded over the range 300–800 nm on a Shimadzu UV-2450 double-beam spectrometer with an integrating sphere (with barium sulphate as reference material).

Thermogravimetric analyses were made in air using Setaram TG/DSC 92 with a heating rate of 10 °C min⁻¹ to a maximum temperature of 800 °C. All the samples were saturated in a humid atmosphere (90%) before measurements.

Nitrogen adsorption measurements were carried out with a Micromeritics ASAP 2010 apparatus. Prior to analysis, all samples were pre-treated for 6 h at 110 °C under vacuum.

The zinc and aluminium contents were evaluated by inductively coupled plasma-optical emission spectrometry (ICP-OES) measured on a Perkin Elmer Optima 2000 DV instrument; the silicon content was obtained by Atomic Absorption Spectrometry (AAS) on a Perkin Elmer Analyst 300; other elements were determined by Elemental Analysis (EA) using a Fisons Instruments EA 1108 (CHNS-O).

HPLC analysis was performed using a Millennium system equipped with a photodiode array detector (DAD). The detection wavelength was set at 220 nm (pentachlorophenol) or at 250 nm (fenamiphos). The elution for pentachlorophenol was accomplished using a reverse phase C8, Agilent XDB column (250 mm×4.5 mm i.d., 5 µm) with water (0.1% formic acid) and methanol (20:80 by volume) as eluents. The flow rate was 1.0 mL min⁻¹ and an injection volume of 25 µL was used. For fenamiphos, the elution was made using a reverse phase C18, Agilent XDB column (250 mm×4.5 mm i.d., 5 µm) with water (0.1% formic acid) and

methanol (30:70 by volume) as eluents. The flow rate was 1.0 mL min⁻¹ and an injection volume of 50 µL was used.

Liquid chromatography-mass spectrometry (LC-MS) studies were carried out with Q-TOF-Micro/waters 2699 equipped with an electro spray ionization source (ESI) and a Waters photodiode array detector. Each experiment permitted the simultaneous recording of both UV chromatograms at a pre-selected wavelength and a full ESI-MS scan. Data acquisition and processing were performed by Mass Lynx NT 3.5 system. A Nucleosil 100-5 C18 ec (250 mm×4.6 mm, 5 µm) column was used. Samples (5–10 µL) were injected either directly or after evaporation of the solvent for better detection. A gradient program (Table 1) was employed, using water with 0.4 vol% acetic acid (A) and acetonitrile (B) as eluents, and a flow of 1 mL min⁻¹.

Table 1

Gradient program for LC-MS.

Time, min	Eluent A (%)	Eluent B (%)
0	95	5
15	5	95
25	5	95
35	95	5

2.4. Irradiation set-up

Photocatalytic experiments were carried out at room temperature using a laboratory-built photoreactor consisting of three Philips HPW125 mercury discharge blacklight lamps (I=125

W and $\eta=50 \text{ lm W}^{-1}$). The reactions were carried out in a 50 mL glass flask, with the top open to allow entrance of air. For these experiments, 25 mL of substrate solution and 25 mg of the desired sensitizer immobilized into Al-MCM-41 were mixed. The pH values of the freshly prepared solutions of fenamiphos and pentachlorophenol were 7 and 5, respectively. The initial concentration in all experiments was $1 \times 10^{-4} \text{ mol L}^{-1}$ for fenamiphos and $1 \times 10^{-5} \text{ mol L}^{-1}$ for pentachlorophenol. Before irradiation, a catalyst suspension containing the pesticide was allowed to equilibrate for 90 min in the dark. The adsorption of pesticide onto the catalyst surface was negligible (<1% adsorption, as confirmed by HPLC experiments). The solutions were irradiated with polychromatic light within the wavelength range 320-460 nm ($\lambda_{\text{max}}=365 \text{ nm}$) for 180-300 min. Aliquots were taken at regular time intervals (0, 30, 60, 90, 120, 180, 240 and 300 min) from the irradiated solution.

The solution was centrifuged twice to remove the catalyst particles before analysis. Both, the disappearance of the pesticide and formation of the photoproducts were monitored using HPLC. Product identification was performed by LC-MS without any extraction or pre-concentration procedures. In the experiment with fenamiphos, the participation of $^1\text{O}_2$ in the photolysis was evaluated by the effect of NaN_3 ($^1\text{O}_2$ quencher) on the photolysis using **2a** as sensitizer.

2.5. Recycling of the catalyst

After the first cycle, the selected catalysts (**2a** and **3**) were collected by centrifugation as described above. The catalyst was washed with acetonitrile and stirred for 10 min. The mixture was centrifuged, and the solvent removed. This procedure was repeated three times. Finally, the catalyst was dried in an oven at $70 \text{ }^\circ\text{C}$.

The second and third cycles were carried out with 1.0 g L⁻¹ recycled catalyst added to a fenamiphos solution (1×10⁻⁴ mol L⁻¹) under the same irradiation conditions.

Leaching of the sensitizers was checked by UV-Vis spectrometry and the presence of the sensitizers within the Al-MCM-41 was monitored by DRS-UV-Vis spectra.

3. Results and discussion

3.1. *Ship-in-a-bottle synthesis of zinc phthalocyanines*

Our recent experience on the immobilization of porphyrins into Al-MCM-41 has shown that the “*ship-in-a-bottle*” method is more efficient than simple adsorption to incorporate polypyrrole macrocycles into these porous matrices [16,18]. In this paper we extend this synthetic methodology to the immobilization of zinc phthalocyanines (ZnPcs). The special properties of mesoporous materials as hosts in terms of site isolation, space compartmentalization, polarity and the presence of acidic and other sites are very interesting and contribute to the operation and design of these hybrid solids.

3.2. *Characterization of the immobilized zinc phthalocyanines*

3.2.1. *Electronic absorption spectra and luminescence spectroscopy*

The absorption spectra of ZnTNPc, ZnTPhOPc and ZnTTMAEOPcI, in DMF, were recorded and the extinction coefficients determined for comparison with the corresponding immobilized sensitizers. The tetrasubstituted ZnPcs have a typical dark green color and show two characteristic Q bands between 600 and 750 nm in their UV-Vis spectra, Table 2, with the main absorption maximum around 700 nm, in agreement with previous reports [30,31].

Table 2

Electronic Absorption Spectral Data of Tetra substituted ZnPcs Complexes

Catalyst	Q band in solution ^a , nm ($\epsilon/\text{mol}^{-1} \text{ L cm}^{-1}$)	Q band in Al-MCM-41 ^b , nm
ZnTNPc	647 (<i>n.d.</i>), 688 (<i>n.d.</i>)	650 (<i>sh</i>), 690
ZnTPhOPc	608 (27799), 677 (149531)	650 (<i>sh</i>), 690
ZnTTMAEOPcI	611 (60500), 678 (304000)	640, 680

^a Electronic absorption spectra in DMF.^b Diffuse reflectance spectra.*n.d.* not determined.

Fig. 2 shows the DRS–UV-Vis absorption spectra of the solids Al-MCM-41, ZnTNPc@Al-MCM-41 (**2a**), ZnTPhOPc@Al-MCM-41 (**2b**) and ZnTTMAEOPcI@Al-MCM-41 (**3**). The spectrum of **2a** presents a broad band at 690 nm and a shoulder at 650 nm, close to the values in the absorption spectrum in DMF solution (Table 2).

In contrast, the DRS-UV-Vis spectra of **2b** and **3** are red shifted compared with the corresponding UV-Vis spectra of ZnTPhOPc and ZnTTMAEOPcI, in DMF solution, from 608 to 620 nm and from 611 to 640 nm, respectively. These spectral changes may result from structural distortions of the phthalocyanines due to interactions with the pore walls of Al-MCM-41. Similar effects have been reported for immobilized Cu and Ru phthalocyanines [14,24].

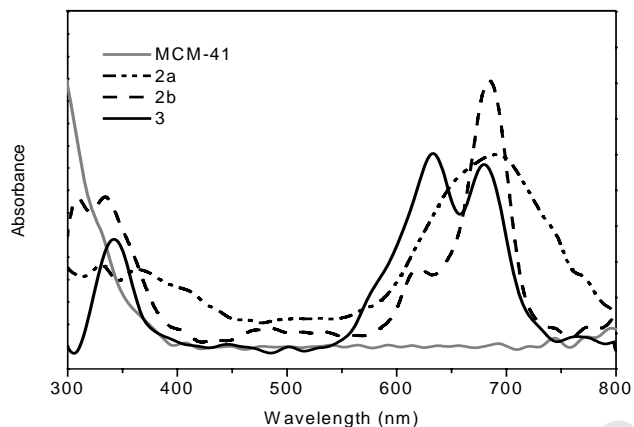


Fig. 2. DRS–UV-Vis absorption spectra of the Al-MCM-41, ZnTNPc@Al-MCM-41 (**2a**), ZnTPhOPc@Al-MCM-41 (**2b**) and ZnTTMAEOPcI@Al-MCM-41 (**3**) (BaSO₄ as reference).

The fluorescence emission and excitation spectra of ZnTNPc@Al-MCM-41 (**2a**), ZnTPhOPc@Al-MCM-41 (**2b**) and ZnTTMAEOPcI@Al-MCM-41 (**3**) are shown in Fig. 3. With **2a** and **3**, the diffuse reflectance and fluorescence excitation spectra are very similar, and there is a negligible Stokes shift between absorption and emission band maxima, which indicates no structural change between the ground and excited states of the immobilized phthalocyanines. In contrast, with the nitro-substituted compound **2b**, a Stokes shift of about 13 nm is seen and, concomitantly, with a shoulder at 680 nm, which may be attributed to the existence of aggregation.

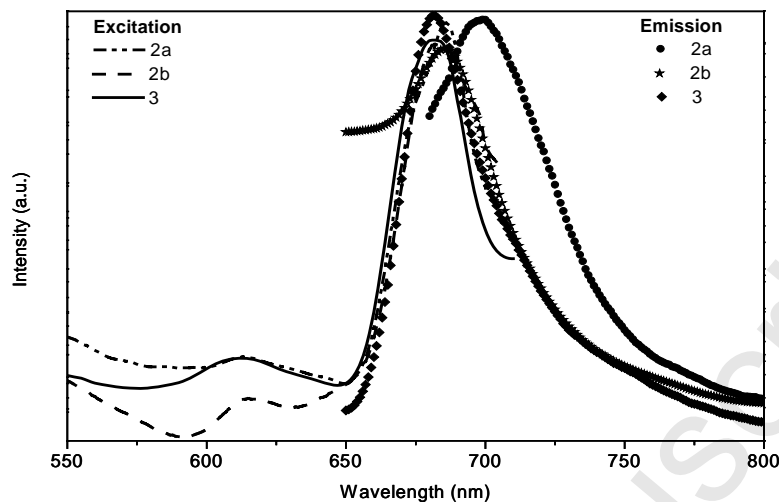


Fig. 3. Emission ($\lambda_{\text{exc}}=610$ nm) and excitation ($\lambda_{\text{em}}=710$ nm) spectra of ZnTNPc@AlMCM-41 (**2a**), ZnTPhOPc@Al-MCM-41 (**2b**) and ZnTTMAEOPcI@Al-MCM-41 (**3**).

3.2.2. Thermogravimetric analysis

TG/DSC analysis of the solids ZnTNPc@Al-MCM-41 (**2a**), ZnTPhOPc@Al-MCM-41 (**2b**), and ZnTTMAEOPcI@Al-MCM-41 (**3**) are presented in Fig. 4. For comparison, results for the Al-MCM-41 sample are also presented. With all the phthalocyanine containing samples, a broad endothermic peak was observed in the range of 25-200 °C, corresponding to a weight loss of about 10%. This is attributed to the removal of physically adsorbed water molecules. However, these water losses are much lower when compared with pure mesoporous Al-MCM-41, even though samples have been saturated with H₂O vapor. This observation is in line with the phthalocyanine complexes being incorporated within the interior of the mesopores, giving a more hydrophobic surface with less space for water to adsorb. The mass loss in the range 200-700 °C corresponds to approximately 10%, and

matches an exothermic peak observed, which is indicative of the phthalocyanine molecule decomposition.

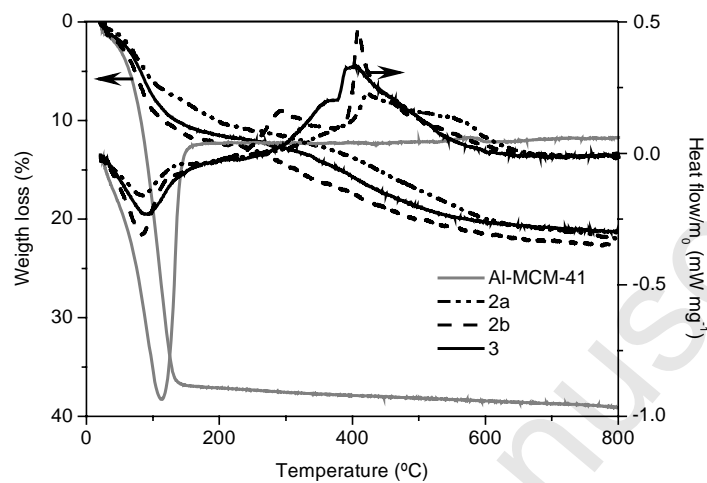


Fig. 4. Thermoanalysis of ZnTNPc@Al-MCM-41 (**2a**), ZnTPhOPc@Al-MCM-41 (**2b**) and ZnTTMAEOPcI@Al-MCM-41 (**3**).

Results of thermoanalysis of the pure phthalocyanines is presented in Fig. 5. An increase in the decomposition temperature was observed on going from the non-immobilized to the immobilized phthalocyanines, providing support for immobilization and indicating that incorporation of ZnPcs into Al-MCM-41 increases their thermal stability.

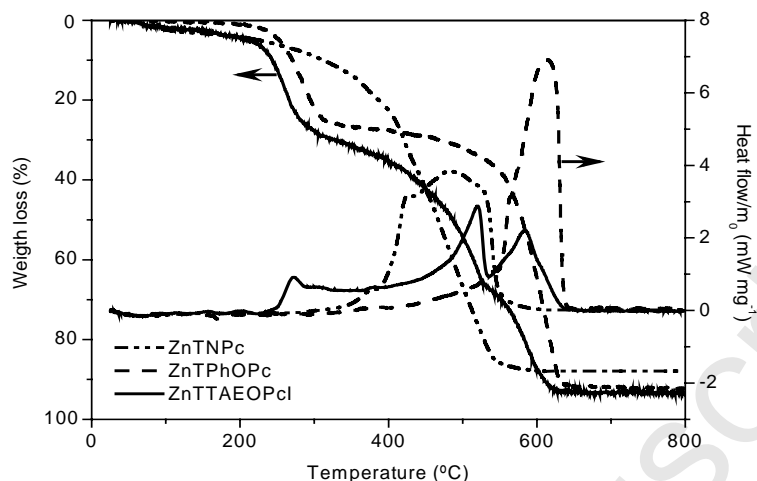


Fig. 5. Thermoanalysis of ZnTNPc, ZnTPhOPc and ZnTTMAEOPcI.

3.2.3. Nitrogen adsorption analysis

Nitrogen adsorption isotherms of Al-MCM-41, **2a**, **2b** and **3** are presented in Fig. 6. All the systems display the typical type IV adsorption isotherm characteristic of mesoporous solids. The Al-MCM-41 support presents an isotherm with a sharp inflection (capillary condensation step) at about 0.4 relative pressure (P/P_0), indicating a narrow pore size distribution. In contrast, with the isotherms of the mesoporous materials loaded with zinc phthalocyanines, the condensation step is shifted to lower P/P_0 values (0.3-0.35) while the total amount of N_2 adsorbed, calculated from the top of the adsorption step, decreases significantly. The textural parameters, S_{BET} and V_{meso} , obtained from the adsorption isotherms, decrease compared with pure Al-MCM-41 (Table 3). These observations are in complete agreement with successful immobilization of zinc phthalocyanines within the pores of the MCM-41 [24]. As expected, the maxima of the pore size distribution obtained from the BJH method also decreases with the incorporation of the ZnPcs (Table 3).

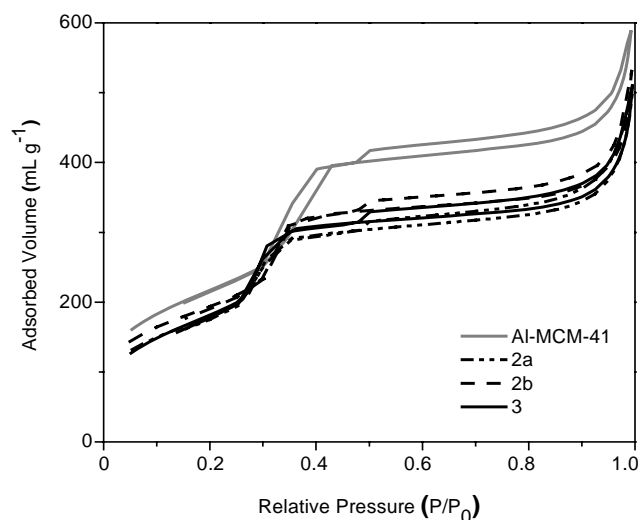


Fig. 6. Nitrogen adsorption isotherms of Al-MCM-41, ZnTNPc@Al-MCM-41 (**2a**), ZnTPhOPc@Al-MCM-41 (**2b**) and ZnTTMAEOPcI@Al-MCM-41 (**3**).

Table 3

Textural parameters of the catalysts samples

Catalyst	S_{BET} ($\text{m}^2 \text{g}^{-1}$) ^a	V_{meso} (mL g^{-1}) ^b	D_{BJH} (nm) ^c
Al-MCM-41	785	0.65	3.1
ZnTNPc@Al-MCM-41 (2a)	700	0.53	2.7
ZnTPhOPc@Al-MCM-41 (2b)	680	0.50	2.6
ZnTTMAEOPcI@Al-MCM-41 (3)	655	0.48	2.5

^a S_{BET} is the surface area derived from BET equation.

^b V_{meso} is the mesopore volume calculated from the adsorption step.

^c D_{BJH} is the maxima of the pore size distribution obtained from BJH method.

3.2.4. Elemental analysis

Elemental analysis was also used, in conjunction with the TG/DSC and nitrogen adsorption measurements, to characterize the catalysts. In Table 4 are the atomic ratios on the ZnPcs@Al-MCM-41. The weight percentage of Zn on Al-MCM-41 is variable. The lower C/Zn atomic ratio obtained (when compared with pure phthalocyanine complexes) can be attributed to the presence of extra Zn(II) species probably compensating the negative charges generated by the presence of Al in the mesoporous silica framework.

The theoretical carbon/nitrogen atomic ratio (C/N), based on the structures of the non-immobilized phthalocyanines is 2.7 for ZnTNPc, 7.0 for ZnTPhOPc and 4.3 for ZnTTMAEOPcI. The values for the corresponding immobilized systems are 5.8 (**2a**), 5.5 (**2b**) and 4.7 (**3**) (Table 4). Although the other techniques provide good evidence for immobilized phthalocyanines, the observed ratios for **2a** and **2b** are different from those expected. This may be due to the presence of trace impurities.

From elemental analysis results, the amount of zinc(II) phthalocyanines immobilized depends on the structure of the photosensitizer, but is within the range 0.13-0.23 mmol g⁻¹. This is in good agreement with values obtained by thermogravimetry.

Table 4

Elemental analysis data (% wt) and amount of ZnPcs immobilized in Al-MCM-41.

Catalyst	Si	Al	C	N	Zn	[ZnPcs]/ mmol g ⁻¹
Al-MCM-41	41.0	1.1	0	0	0	-
ZnTNPc@Al-MCM-41 (2a)	32.0	1.0	6.0	1.2	3.7	0.23
ZnTPhOPc@Al-MCM-41 (2b)	33.0	0.9	6.1	1.3	2.1	0.13

ZnTTMAEOPcI@Al-MCM-41 (**3**) 29.0 0.8 7.7 1.9 3.9 0.20

3.2.5. Photocatalytic studies

The absorption spectra of the two selected pesticides, fenamiphos and pentachlorophenol, in aqueous solution, at pH 7 and 5, respectively, are given in Fig. 7. The former presents an absorption maximum at 249 nm and a shoulder at 280 nm while the latter shows two well defined absorption bands at 249 nm and 315 nm.

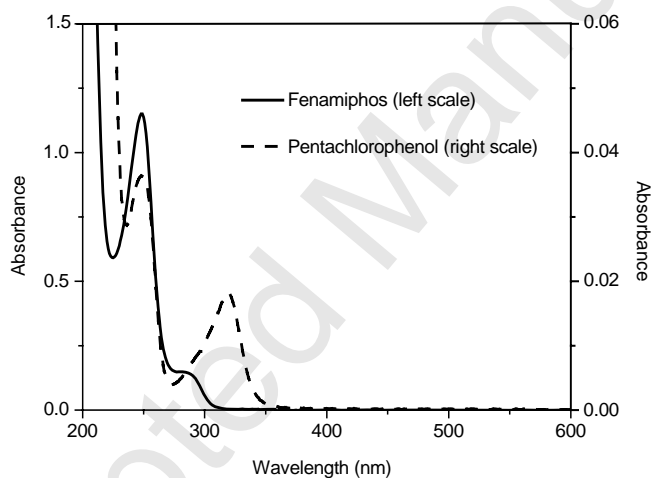


Fig. 7. UV-vis spectra of fenamiphos (1.0×10^{-4} mol L⁻¹, pH=7) and pentachlorophenol (1.0×10^{-5} mol L⁻¹, pH=5), in aqueous solution.

The effect of the immobilized phthalocyanines **2a**, **2b** and **3** on the kinetics of photodegradation of fenamiphos and pentachlorophenol was studied. Initially, a suspension of photocatalyst in solution of the desired pesticide was allowed to equilibrate in the dark during 90 min. The UV-Vis spectra revealed that no significant adsorption of pesticide occurs onto the catalyst surface. After this equilibration period, the suspensions were irradiated with UV

light ($\lambda_{\max}=365$ nm). Aliquots were taken at regular time intervals, and the reaction followed by HPLC/DAD. Kinetic data for the photodegradation of fenamiphos and pentachlorophenol are presented in Figs. 8a and 8b, respectively.

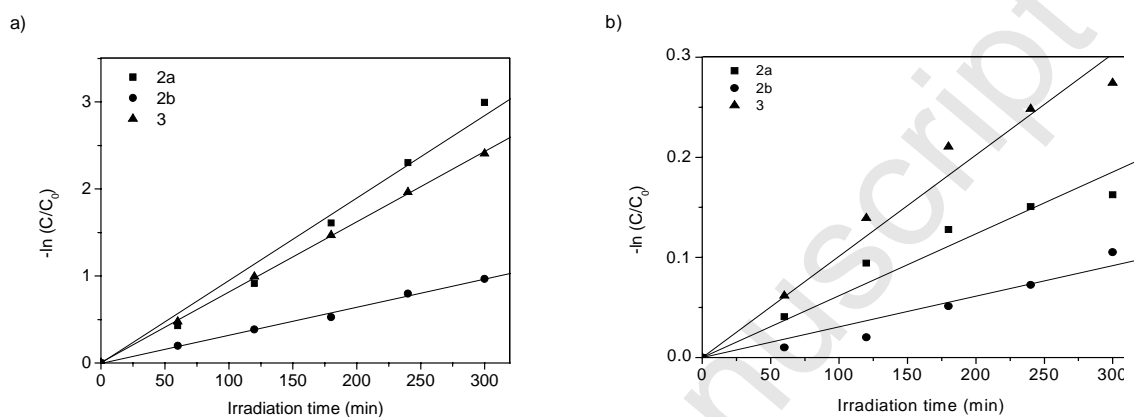


Fig. 8. a) Kinetics of fenamiphos photodegradation ($C_0=1.0 \times 10^{-4}$ mol L $^{-1}$) using **2a**, **2b** and **3** as catalysts, and **b)** Kinetics of pentachlorophenol photodegradation ($C_0=1.0 \times 10^{-5}$ mol L $^{-1}$) using **2a**, **2b** and **3** as catalysts ($C_0=1.0 \times 10^{-5}$ mol L $^{-1}$).

Irradiation of aqueous solutions of fenamiphos (1.0×10^{-4} mol L $^{-1}$, pH=7) or pentachlorophenol (1.0×10^{-5} mol L $^{-1}$, pH=5) in the presence of ZnPcs immobilized onto Al-MCM-41 led to a decrease of pesticide concentration, which depends on the structure of the immobilized phthalocyanine. In the case of fenamiphos, almost complete degradation was observed within 300 min irradiation. With all catalysts (**2a**, **2b** and **3**) photodegradation follows pseudo first-order kinetics in fenamiphos, with rate constants 8.5×10^{-3} min $^{-1}$, 3.0×10^{-3} min $^{-1}$ and 8.1×10^{-3} min $^{-1}$, respectively (Fig. 8a). It should be noted that under the above experimental conditions, no significant degradation of either pesticide was observed when the reaction was performed in the dark or just with Al-MCM-41. Similarly, no photodegradation of the pesticides occurred upon 365 nm irradiation in the absence of catalyst, even for longer irradiation times (12 h).

Irradiation of pentachlorophenol in the presence of the same catalysts (**2a**, **2b** and **3**) for 300 min, led to significantly less photodegradation than with fenamiphos. Pseudo first-order kinetics in pentachlorophenol were followed, with rate constants $7.3 \times 10^{-4} \text{ min}^{-1}$, $2.7 \times 10^{-4} \text{ min}^{-1}$ and $1.1 \times 10^{-3} \text{ min}^{-1}$, respectively (Fig. 8b).

Concerning the oxygen dependence, within experimental error the kinetics are independent of $[\text{O}_2]$ in the fenamiphos' experiments, but shows an oxygen dependence, with order less than one in the pentachlorophenol case.

With both pesticides, the observed rate constants follow the order $k_{\text{ZnTTMAEOPcI@Al-MCM-41 (3)}} \geq k_{\text{ZnTNPc@Al-MCM-41 (2a)}} > k_{\text{ZnTPOpc@Al-MCM-41 (2b)}}$, with **2a** and **3** being the most efficient catalysts to promote their photodegradation.

The effect of the amount of catalyst **2a**, within the range 0.25–2.0 g L^{-1} , on the photodegradation rate of both pesticides was also investigated and the results are presented in Fig. 9.

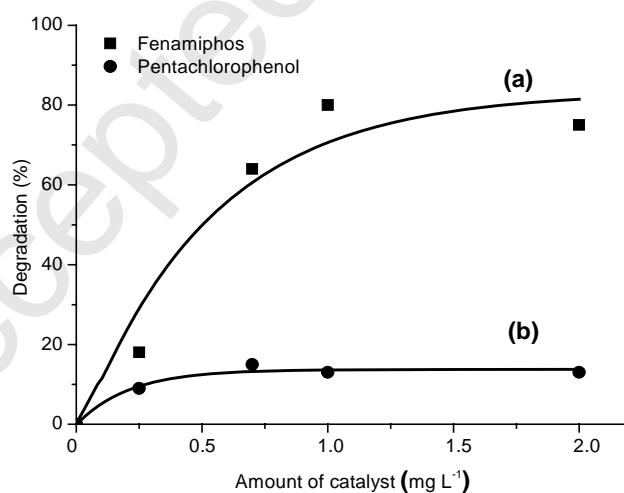


Fig. 9. Degradation analysed by HPLC/DAD of fenamiphos (a), $C_0=1.0 \times 10^{-4} \text{ mol L}^{-1}$, and pentachlorophenol (b), $C_0=1.0 \times 10^{-5} \text{ mol L}^{-1}$, as a function of **2a** concentration ($t=300 \text{ min}$).

The observed non-linear plots, as well as the limiting value of the percentage of conversion (plateau), are most likely to result from decreased light transmission due to scattering at high catalyst concentrations due to an inner filter effect, as had already been reported with porphyrins immobilized into Al-MCM-41 [18]. This was observed when the concentration of ZnTNPc@Al-MCM-41 was greater than 1.0 g L^{-1} .

3.2.6. Mechanistic studies and photoproduct characterization

Mechanisms of sensitized photodegradation of pesticides in the presence of oxygen and porphyrin or phthalocyanines, either immobilized [18,20,33] or in solution [34-37], may involve both type I (electron or atom transfer) [18,20,34,36] and/or type II (singlet oxygen) [33,35,37-39] processes. To test whether the mechanism of reactions of the systems in these studies involves electron transfer and/or singlet oxygen, photodegradation reactions were carried out in the presence and absence of oxygen and in the presence of sodium azide, used as a singlet oxygen quencher. Since ZnTNPc@Al-MCM-41 (**2a**) showed good catalytic activity for photodegradation of both pesticides, the mechanistic studies and photoproduct characterization were performed exclusively with this catalyst.

The photodegradation of both pesticides catalyzed by ZnTNPc@Al-MCM-41 (**2a**) was performed in air, oxygen saturated solutions and in a solution degassed with nitrogen, Figs. 10a and 10b. Within experimental error, the photodegradation of fenamiphos was virtually complete after 300 min irradiation when experiments were carried out in air or oxygen-saturated solutions, while under oxygen-free conditions less than 3% conversion was achieved (Fig. 10a). It is worth noting that during these experiments no substantial change of pH was observed during the reaction period. Similar behaviour was observed for the photodegradation of pentachlorophenol with the same catalyst (**2a**), (Fig. 10b).

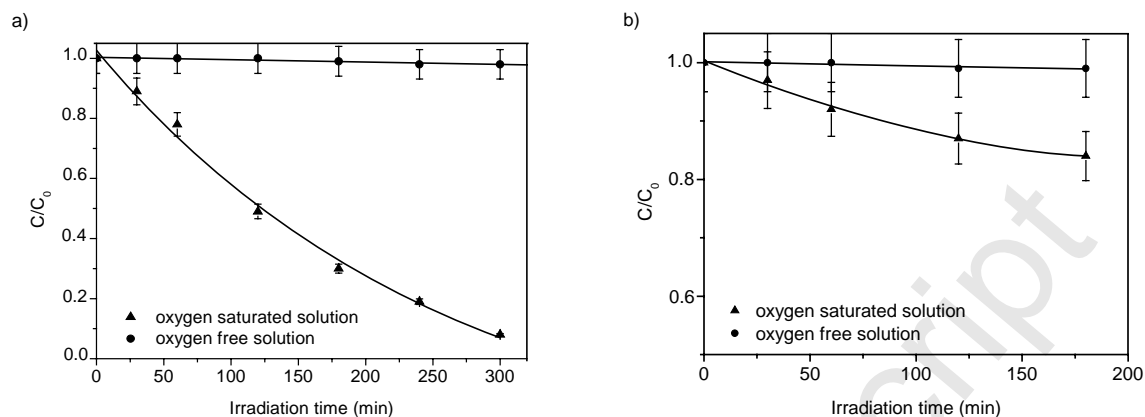


Fig. 10. a) Effect of oxygen on the kinetics of fenamiphos photodegradation ($C_0 = 1.0 \times 10^{-4} \text{ mol L}^{-1}$), and **b)** Effect of oxygen on the kinetics of pentachlorophenol photodegradation ($C_0 = 1.0 \times 10^{-5} \text{ mol L}^{-1}$).

To test the possible involvement of singlet oxygen in the photodegradation of fenamiphos in the presence of catalyst **2a**, some experiments were performed in the presence of sodium azide (Fig. 11). An aerated solution of **2a** (1.0 g L^{-1}) and fenamiphos ($1.0 \times 10^{-4} \text{ mol L}^{-1}$) was irradiated with UV light at $\lambda_{\text{max}} = 365$ with sodium azide ($1.0 \times 10^{-2} \text{ mol L}^{-1}$). A rate constant of $3.1 \times 10^{-3} \text{ min}^{-1}$ was obtained, which is significantly smaller than that in the absence of sodium azide ($1.0 \times 10^{-2} \text{ min}^{-1}$), strongly suggesting that singlet oxygen is involved in the mechanism of photodegradation (type II mechanism).

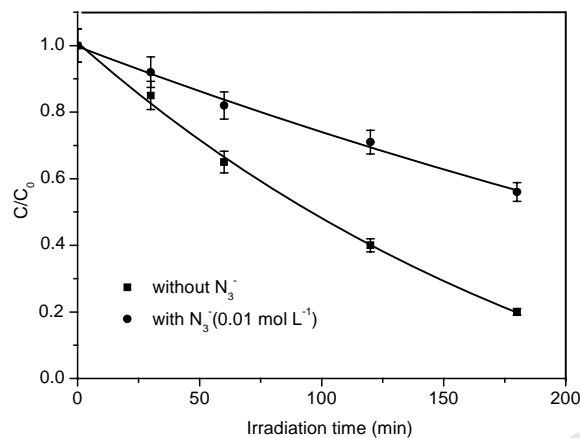
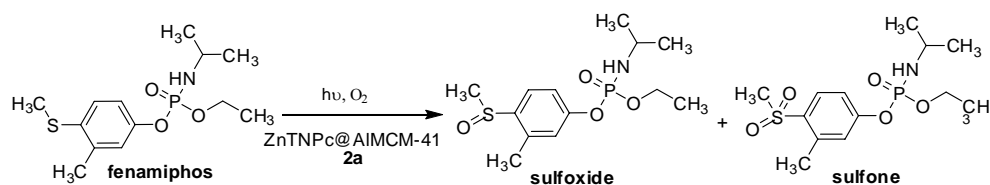


Fig. 11. Kinetics of fenamiphos degradation in aerated solution in the presence of **2a** ($C_0=1.0 \times 10^{-4}$ mol L $^{-1}$).

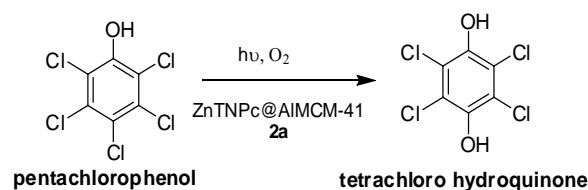
From these studies (Figs. 10a, 10b and 11) it is possible to conclude that the presence of oxygen is essential for the photodegradation of both pesticides. However, since complete inhibition was not observed when the reaction was carried out in the presence of sodium azide, the contribution to the overall photodegradation by radical species (type I mechanism) should not be excluded. This is similar to what was observed using porphyrins immobilized into Al-MCM-41 as sensitizers [18].

The transformation of fenamiphos in aerated solutions by excitation of **2a** at 365 nm led to 98% conversion after 300 min irradiation. The main photoproducts, characterized by LC-MS in the positive mode, were the corresponding fenamiphos-sulfoxide, $[M+1]=320$ (retention time of 11.1 min), and fenamiphos-sulfone, with $[M+1]=336$ (retention time of 12.2 min), Scheme 1.



Scheme 1. Fenamiphos photodegradation products

The characterized fenamiphos photoproducts, sulfoxide and sulfone, are well documented and in agreement with the involvement of both singlet oxygen [40,41] (type II) and electron transfer process [42-44]. Fenamiphos photoproducts (sulfone and sulfoxide) are less toxic than the source compound, as determined by Cáceres *et al.* [45], where the oxidation products of fenamiphos (FSO and FSO₂) did not show any toxicity to both algal species tested up to a concentration of 100 mg L⁻¹. The photoproducts obtained from the pentachlorophenol photodegradation, in aerated solutions in the presence of **2a**, after 300 min of irradiation, were also characterized by LC-MS in negative mode. The main photoproduct has been identified as 2,3,5,6-tetrachloro-hydroquinone [M-1]=245, retention time 13.6 min, Scheme 2. The formation of this photoproduct has previously been described in photocatalytic reactions of this compound involving a radical mechanism [46-48]. However, the pentachlorophenol photoproducts can be more toxic than the corresponding source material as determined by Jardim *et al.* [49], where acute toxicity tests of samples at different time intervals of light exposure, were carried out by measuring the respiratory inhibition in the bacteria *Escherichia coli*. Implications of such findings are discussed, considering the fact that, under certain circumstances, the photocatalytic degradation of chlorinated organics can yield compounds that are more toxic than the original pollutant to be destroyed.”



Scheme 2. Pentachlorophenol photodegradation products.

3.2.7. *Recycling of the ZnTNPc@AlMCM-41 and ZnTTAEOPcI@AlMCM-41 after photodecomposition of fenamiphos*

Recycling experiments were carried out to evaluate the stability and reusability of the catalysts **2a** and **3**, and the results are presented in Fig. 12.

For each new cycle, the catalysts were separated from the reaction mixture, washed extensively with methanol and water, dried and re-used under the same experimental conditions. Fig. 12 shows the conversion (%) of fenamiphos as a function of number of cycles performed with ZnTNPc@Al-MCM-41 (**2a**) and ZnTTAEOPcI@Al-MCM-41 (**3**), for a constant irradiation time (180 minutes).

The conversion of fenamiphos achieved was 80%, 37% and 19%, respectively, for the 1st, 2nd and 3rd reuse for **2a** catalyst, and 80%, 70% and 65%, respectively, for the 1st, 2nd and 3rd reuse using **3** as catalyst, under the above conditions.

The UV-Vis spectra of the washes did not reveal the presence of catalyst in solution, within the detection limits. Therefore, the deactivation of catalyst **2a** cannot be explained by a leaching process, but must come, essentially, from its degradation under the irradiation conditions. The high activity retained by the cationic catalyst (**3**) after three cycles (65%) should be noted. This may result from the high affinity of the cationic sensitizer for the support walls, which, consequently, inhibits photodegradation of this catalyst.

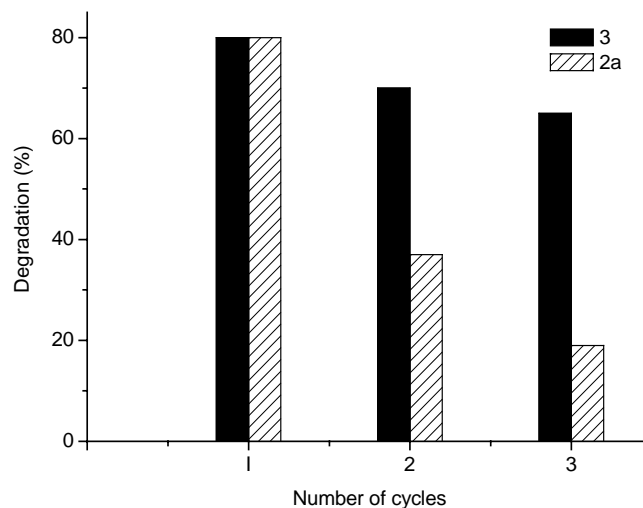


Fig. 12. Photodegradation(%) of fenamiphos with catalysts **2a** and **3**, after three cycles (180 min of irradiation).

Our long-term goal is the mineralization of the pesticides. However, because of the synthetic problems of preparing sizeable quantities of immobilized photocatalysts, in the present work we have concentrated on identifying the best immobilized systems on the laboratory scale level for continuous use in appropriate (probably flat-bed) photoreactors and have not looked at prolonged irradiation.

4. Conclusions

Efficient *ship-in-a-bottle* synthesis of ZnPcs within the Al-MCM-41 mesoporous channels was achieved, and three new immobilized phthalocyanines were successfully characterized by various techniques. The amount of immobilized phthalocyanines are within 0.13-0.23 mmol g⁻¹, depending on the photosensitizer.

These systems are photoactive and a comparative study of the effect of the substituted group in the immobilized phthalocyanines on the photodegradation of the pesticides, fenamiphos and pentachlorophenol, in aerated solutions, shows that ZnTNPc@Al-MCM-41 and ZnTTMAEOPcI@Al-MCM-41 are the catalysts with the best performances for both pesticides.

The photodegradation in aqueous solutions of the herbicide fenamiphos in the presence of ZnTNPc@Al-MCM-41 leads to the sulfoxide and sulfone as the main photoproducts. This follows pseudo-first order kinetics with respect to pesticide, in an oxygen dependent process, without photodegradation in deaerated solution, with around 70-80% of conversion in the presence of air and in oxygen saturated solution after 180 min of irradiation.

Product analysis following pentachlorophenol photodegradation with ZnTNPc@Al-MCM-41 shows that 2,3,5,6-tetrachloro-hydroquinone is the main photoproduct. Pseudo-first order kinetics are followed in an oxygen dependent process (order lower than one), with no photodegradation in deaerated solution after 180 min of irradiation.

The presence of oxygen is revealed to be essential for photodegradation, and the decreased reactivity observed in the presence of sodium azide indicates that $^1\text{O}_2$ is involved in the mechanism, although involvement of radical species is also relevant.

Finally, the best in recycling is the cationic ZnTTAEOPcI@Al-MCM-41 (3), which presents high photocatalytic activity even after three cycles. This immobilized phthalocyanine is an excellent candidate for future studies on the photocatalysed degradation of other organic pollutants. These photocatalysts will be used in similar reactors to those currently being applied in the photocatalytic degradation of pollutants using titanium dioxide and other inorganic catalysts. But because of their enhanced spectral response, these photocatalysts will have the advantage of more efficient use of the irradiating light source.

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