



Hexagonal mesoporous silica modified with copper phthalocyanine as a photocatalyst for pesticide 2,4-dichlorophenoxyacetic acid degradation

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ARTICLE INFO

Article history:

Received 28 January 2008

Accepted 6 April 2008

Available online 16 April 2008

Keywords:

Silica

Copper phthalocyanine

2,4-Dichlorophenoxyacetic acid (2,4-D)

Photodegradation

ABSTRACT

A new mesoporous catalyst was prepared by the reaction between 3-aminopropyltrimethoxysilane and Cu(II)-hexadecafluorophthalocyanine, followed by co-condensation of tetraethylorthosilicate around a micelle formed by *n*-dodecylamine. The surfactant was removed from the pores by continuous extraction with ethanol, giving the Si–CuF₁₆Pc catalyst. This catalyst was characterized by SEM, FTIR, TGA, ²⁹Si NMR, N₂ adsorption and X-ray diffraction. SEM images confirmed that the catalyst material is formed by nanoaggregates with a diameter of 100 nm. N₂ adsorption isotherms showed that Si–CuF₁₆Pc has a surface area of approximately 200 m² g⁻¹ and a porous diameter of 7.7 nm, characterizing the mesoporosity of this product. This novel material shows an excellent photocatalytic activity, degrading almost 90% of 2,4-dichlorophenoxyacetic acid (2,4-D) up to 30 min, while only approximately 40% of photodegradation was obtained in its absence.

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1. Introduction

The amounts of several pesticides present in the surface and underground waters have increased in the last years. The consequent effects on environment and mankind are leading to efforts for the development of efficient technologies for water treatment in order to remove and/or degrade organic contaminants from water [1–4]. In this sense, photodegradation processes based on heterogeneous semiconductor catalysts have been extensively studied in recent years [3–6]. However, these methods are based on high energetic UV light excitation, which contains only 4–5% of the sunlight. Environmentally friendly processes move toward energy economy and, therefore, the use of hydrogen peroxide or molecular oxygen as the oxidant and water as the solvent are well accepted [7,8].

As a result, removal of recalcitrant and toxic chlorinated phenols in water by green chemical method has been investigated lately [7,8]. Green chemistry means the quest for environmentally friendly processes such as the activation of H₂O₂ by supported metallophthalocyanine (MPc), which allows visible light irradiation to degrade contaminants. In this direction, metallophthalocyanines are efficient photocatalysts for the degradation of organic contaminants. One of the most accepted reaction mechanisms for the

photodegradation of organic compounds depends on the interaction of the excited triplet MPc sensitizer with ground state oxygen to generate the singlet oxygen by a triplet–triplet energy transfer process, as shown in Eqs. (1)–(3) [4,9].



On the other hand, phthalocyanines have a good solubility in water, which difficulties their separation from solution and catalyst recycling. In order to solve this problem, the immobilization of this catalyst must allow its simple recuperation as well as facilitate its reutilization [10–15].

Nowadays, an excessive diversity of man-made pesticides is associated to current agricultural practices. The use of pesticides, mainly herbicides, is common procedure in the extensive modern agriculture [16,17]. These kinds of xenobiotics are used to eliminate different undesirable forms of life in agriculture and in urban areas. The pesticide 2,4-dichlorophenoxyacetic acid (2,4-D) is normally used to control a wide range of broad-leaved weeds and grasses in plantation crops and along highways [16,17]. The pesticide is commonly used in Brazilian agriculture, mainly in sugar cane plantations [16,17]. Thus, the development of degradation methods of this agrochemical is of paramount importance to environment and to mankind.

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In this sense, the current investigation reports a methodology for the attachment of Cu(II)-hexadecafluorophthalocyanine to mesoporous silica by a co-condensation process and applies this material in the photodegradation of pesticide 2,4-dichlorophenoxyacetic acid (2,4-D).

2. Experimental

2.1. Chemicals

The silica source for the inorganic framework formation was derived from tetraethylorthosilicate (TEOS) (Acros). The silylant agent, 3-aminopropyltrimethoxysilane (APTS) (Aldrich), Cu(II)-hexadecafluorophthalocyanine (CuF₁₆Pc) (Aldrich), 2,4-dichlorophenoxyacetic acid (2,4-D) (Aldrich), H₂O₂ (Vetec), the surfactant *n*-dodecylamine (Sigma), *N,N*-dimethylethanolamine (DMEA) (Acros) and ethanol (Aldrich) were all of reagent grade.

2.2. Catalyst preparation

CuF₁₆Pc (21.5 mg; 0.025 mmol) was dissolved in DMEA (10 mL) at 80 °C for 4 h, resulting in a blue solution.

The catalyst was prepared by stirring *n*-dodecylamine (1.25 g; 6.75 mmol) in water/ethanol (100 mL; 3:1, v/v) for 30 min until an opalescent solution was obtained as a consequence of micelle formation. To this micellar suspension were added in sequence: TEOS (0.556 mL; 2.5 mmol), APTS (0.07 mL; 0.3 mmol) and the CuF₁₆Pc blue solution. This suspension was stirred for 48 h at room temperature, resulting in a precipitate that was then filtered. The *n*-dodecylamine inside the pores of the synthesized compound was extracted with ethanol in a Soxhlet apparatus for 72 h producing the final bluish material Si-CuF₁₆Pc.

Hexagonal mesoporous silica (HMS) without CuF₁₆Pc was synthesized in order to carry out the blank of the photocatalytic studies. The parent mesostructure of HMS was prepared by stirring *n*-dodecylamine (4.3 g; 23.2 mmol) in water/ethanol (100 mL; 3:1, v/v) for 30 min until an opalescent solution was obtained. TEOS (23.65 mL; 106 mmol) was then added and the mixture was stirred for 24 h. The resultant solid was filtered and dried in air for 24 h. Dodecylamine was extracted with ethanol in a Soxhlet apparatus for 72 h producing the material named HMS.

2.3. Characterization

Thermal gravimetric analysis (TGA) curves of the samples were acquired in a TA Instruments mod. SDT 2960 equipment in air flux from 25 to 1200 °C with a heating rate of 10 °C/min.

The amount of Cu present in the catalyst was measured by Atomic absorption spectrometry (AAS) using an atomic absorption spectrometer (Buck mod. A-200) after treating 5.0 mg of the catalyst with 10 mL of HF/HNO₃ (1:2, w/w) at 70 °C for 3 h. All experiments were realized in triplicate.

Fourier transform infrared (FTIR) spectra of all samples were taken in KBr pellets in the 4000–400 cm⁻¹ region with 4 cm⁻¹ resolution, using a Perkin-Elmer FTIR 502 spectrophotometer.

Nuclear magnetic resonance (²⁹Si NMR) spectrum of the solid sample was obtained on a Varian Mercury Plus 300 spectrometer at room temperature. For each run, approximately one gram of catalyst was compacted into a 7 mm silicon nitride rotor. The measurements were obtained at frequencies of 59.61 MHz for silicon, with a magic-angle spinning speed of 3 kHz. In order to increase the signal-to-noise ratio of the solid-state spectra, the coupled plasma/mass atomic spectrometry (CP/MAS) technique was used with pulse repetitions of 1 s and contact times of 1 ms.

Nitrogen adsorption-desorption data were acquired on a Quantachrome Nova 2200 analyzer, at 77 K. The surface area was calculated by the Brunauer-Emmett-Teller (BET) method, and the pore

size distribution was derived from the adsorption branches of the isotherms using the Barrett-Joyner-Halenda (BJH) method.

Scanning electron microscopy (SEM) images were carried out on a Zeiss EVO 50 equipment. The samples were coated with a gold film in a controlled deposition by using a Bal-Tec SCD 050 sputtering system.

Powder X-ray diffraction (XRD) patterns were measured on a D 5005 X-Siemens diffractometer using CuK_α radiation.

2.4. Photodegradation of pesticide 2,4-dichlorophenoxyacetic acid (2,4-D)

The photolysis of the pesticide 2,4-D was carried out in a home-made photo-reactor with 50.0 mL of aqueous solution have H₂O₂ (1.2 wt%) and containing 10 mgL⁻¹ of 2,4-D solution. This photolysis was followed in the presence of Si-CuF₁₆Pc (0.5 gL⁻¹), in the presence of HMS and in the absence of these materials. The reaction solutions were illuminated with a 125 W mercury vapor lamp and the temperature of the reactor was kept at 30 °C [18]. The solution irradiation was followed by an Instrutherm MRU-201 radiometer, which was maintained at 970 μW/cm² during the reaction.

2.5. Degradation analysis of 2,4-dichlorophenoxyacetic acid (2,4-D)

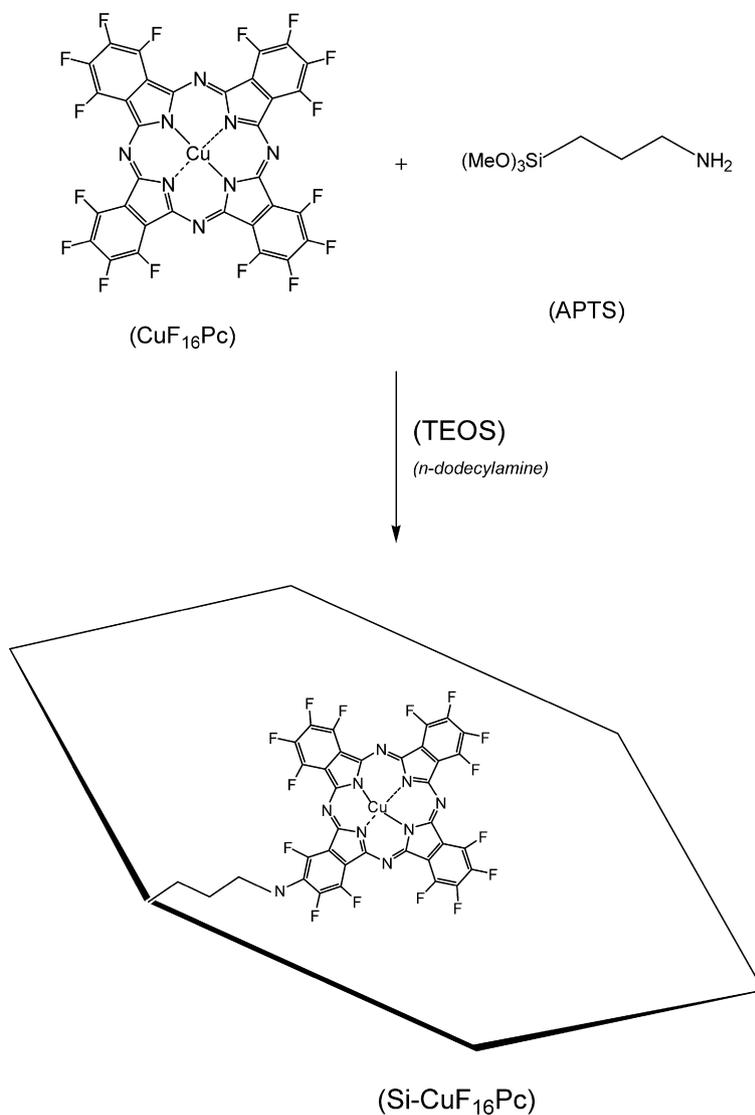
The amount of 2,4-D degraded by the reaction catalyzed by Si-CuF₁₆Pc was determined on a high performance liquid chromatography (HPLC) system from Perkin-Elmer, Series 200, equipped with an LC Series 200 pump, a Series 200 UV-vis detector with wavelength set at 280 nm, and a Spheri-5 RP-18 column with partial size of 5 mm. Manual injection was carried out with a 20 mL loop, using water with 2% of acetic acid/acetonitrile (60:40, v/v) as the mobile phase [7]. After the end of the reaction, the solution was filtered to recover the catalyst, which was subsequently washed with water and used again. The amount of leached Cu(II)-hexadecafluorophthalocyanine was determined after each photodegradation cycle by Cu amount in reaction solution after each cycle. This solution was analyzed by atomic absorption spectrometry using a Buck A-200 atomic absorption spectrometer after treatment of the solution with 15 mL of HNO₃ at 70 °C for 3 h.

3. Results and discussion

The synthetic route to produce the catalyst was based on a modification of CuF₁₆Pc by aromatic substitution reaction with APTS, followed by the co-condensation with TEOS in the presence of *n*-dodecylamine as the micellar template. The template was removed from the catalyst pores by hot solvent extraction [19,20], forming an hexagonally ordered mesoporous catalyst named Si-CuF₁₆Pc, as shown in Scheme 1.

The organic phthalocyanine pendent group content was determined with confidence by TGA through use of residual data as reported previously [20–22]. The TGA curve of HMS (Fig. 1) presented a mass loss of 6.47% up to 100 °C, related to adsorbed water, and presented a mass loss of 7.11% above 200 °C, assigned to lost water from condensation of silanol groups that formed siloxane groups. The TGA curve of the Si-CuF₁₆Pc catalyst (Fig. 1) presented a mass loss of 8.35%, assigned to adsorbed water up to 100 °C. Above this temperature, a mass loss of 18.57% was observed, characterizing 0.67 mmol of CuF₁₆Pc per gram of silica. The atomic absorption data showed that the Si-CuF₁₆Pc catalyst gave 0.65 ± 0.03 mmol of Cu per gram of catalyst, a value that is in agreement with the pendant group amount determined by TGA.

The FTIR spectra of Cu(II)-hexadecafluorophthalocyanine, HMS and modified silica (Si-CuF₁₆Pc) present some characteristic peaks



Scheme 1. Co-condensation of TEOS, APTS and CuF₁₆Pc to produce the hexagonal mesoporous Si-CuF₁₆Pc catalyst.

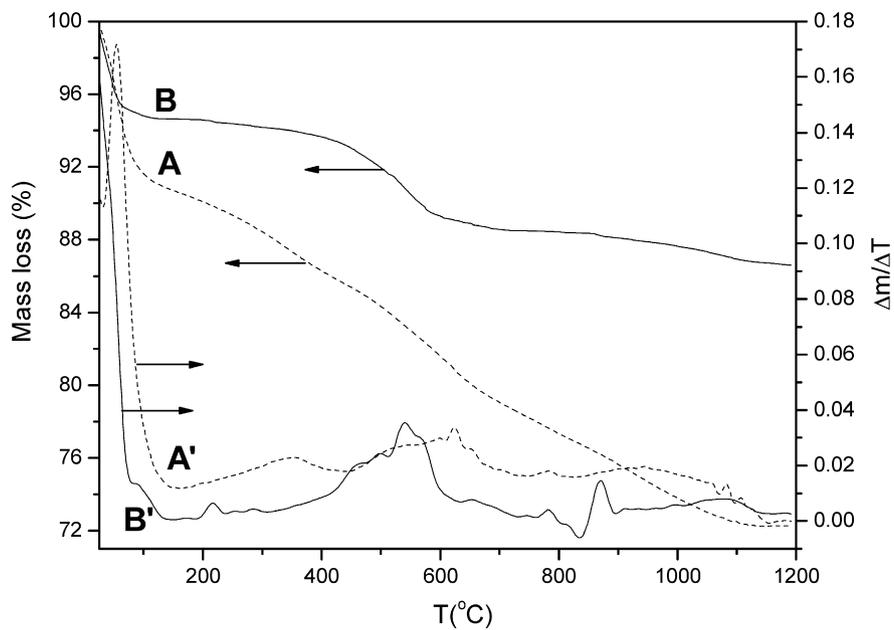


Fig. 1. Thermogravimetric curves of Si-CuF₁₆Pc (A) and HMS (B) and DTG curves of Si-CuF₁₆Pc (A') and HMS (B').

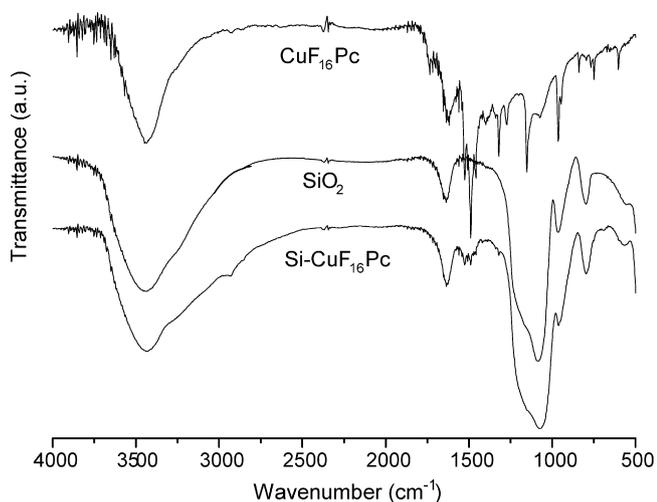


Fig. 2. Infrared spectra of HMS, CuF₁₆Pc and Si-CuF₁₆Pc.

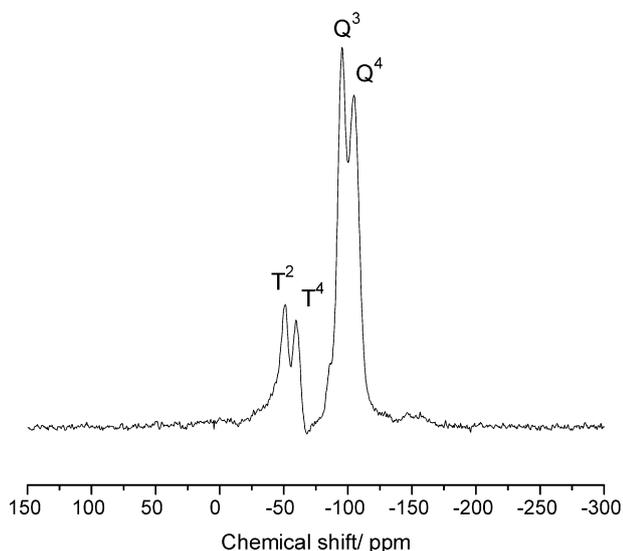


Fig. 3. Solid state ²⁹Si NMR spectrum of Si-CuF₁₆Pc.

(Fig. 2), such as: (1) a broad band due to the OH stretching of silanol groups bonded to the inorganic structure, and also hydrogen bonds between adsorbed water at 3449 cm⁻¹; (2) an angular vibration peak from adsorbed water molecules at 1635 cm⁻¹; (3) an intense band related to the ν_{as} (Si-O-Si) asymmetric stretching at 1068 cm⁻¹; (4) a shoulder band assigned to the Si-OH bending frequency at 964 cm⁻¹; (5) the ν (N=C=N) stretching was confirmed by a band at 1618 cm⁻¹; (6) a weak peak at 1500 cm⁻¹ assigned to the ν (-N=) stretching, (7) the ν (-C=C-N=) stretching at 1320 cm⁻¹, (8) a peak at 798 cm⁻¹ assigned to the bending of a secondary amine (-NH) [23,24]. These peaks confirm that the CuF₁₆Pc molecule is attached on the silica surface by covalent bonds.

The solid-state ²⁹Si NMR spectrum of Si-CuF₁₆Pc presents four peaks (Fig. 3): -54 ppm assigned to Si-OH of RSi(OSi)(OH)₂ group (T²) and -62 ppm assigned to RSi(OSi)₃ group (T⁴), which should be related to the presence of the organic part chemically bonded to the inorganic backbone silica structure. Two other typical peaks correspond to the inorganic polymeric structure of silica: -104 ppm assigned to Si(OSi)₄ group (Q⁴) and -96 ppm assigned to the free silanol group of Si(OSi)₃OH (Q³) [25,26].

Fig. 4 presents the nitrogen adsorption isotherms of the Si-CuF₁₆Pc and HMS materials. The isotherms reveal that the adsorption-

desorption process is not reversible and, in addition, is caused by the moment where the capillary tension in the pores exceeds the intermolecular forces between nitrogen molecules [27–29]. The isotherm is reversible up to a relative pressure of about 0.65. Irreversibility is observed between 0.65 and 0.95, whereas the pores of the material abruptly lose their adsorbate, which is a characteristic of the condensation in primary mesopores [27–29]. From the nitrogen adsorption isotherms it was calculated the BET surface area of the materials, which gave 820 and 198 m²g⁻¹ for HMS and Si-CuF₁₆Pc, respectively. The BJH pore diameters calculated from the adsorption branch of the isotherm were 6.4 and 7.7 nm for HMS and Si-CuF₁₆Pc, respectively, thus confirming the mesoporosity of these materials.

SEM images showed that Si-CuF₁₆Pc presents mostly agglomerates consisting of hollow spheres with mean size of 2 μm (Fig. 5A). A more accurate investigation of the surface showed some fragmented spheres (Fig. 5B). SEM images of HMS (Figs. 5C and 5D) present polydisperse spheres with high level of aggregation, which is caused by supramolecular formation of the hydrogen bonds among the silanol groups of the silica particles. SEM images of HMS also showed that most of the HMS particles present a radius lower than 100 nm. In the concave surface of these agglomerates it is possible to observe very well-defined, narrowly-distributed nanoparticles with an average diameter of 100 nm.

The X-ray diffraction powder patterns of HMS and the synthesized catalyst are depicted in Fig. 6. Single diffraction peaks appear at the low values of $2\theta = 2.14^\circ$ and 2.31° for HMS and Si-CuF₁₆Pc, which are characteristic of the hexagonal structure with interplanar distances of 4.03 and 3.82 nm for HMS and Si-CuF₁₆Pc, respectively. The characteristic [30] peak of CuF₁₆Pc at $2\theta = 6.1^\circ$ was not observed, meaning that the macrocycle is completely bonded to the silica matrix. Both diffractions exhibit a single diffraction line consistent with the expected hexagonal framework structure, which can be considered as an indication of the ordered mesoporous channels [31–36].

Fig. 7 shows the 2,4-dichlorophenoxyacetic acid (2,4-D) degradation in the presence and absence of Si-CuF₁₆Pc and in the presence of HMS. These experiments were also followed with and without UV irradiation. In the experiments under UV irradiation, it can be observed that 2,4-D degraded abruptly up to 30 min in the presence of the Si-CuF₁₆Pc catalyst. However, the degradation of 2,4-D in the absence of Si-CuF₁₆Pc or in the presence of HMS was much lower than in the presence of the catalyst, as observed in Fig. 7. These plots show that 90% of this pesticide was degraded up to 30 min of reaction by using Si-CuF₁₆Pc as catalyst, while the same reaction without catalyst or in the presence of HMS degraded only 40% of 2,4-D up to 60 min.

In the experiments without application of UV irradiation, the degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) was much lower than that seen for the irradiated experiments. Almost 24.9% of 2,4-D was degraded in the presence of the catalyst after 1 h, while only 8 and 6% of 2,4-D was degraded in the absence of the catalyst and in the presence of HMS, respectively. These results suggest that Si-CuF₁₆Pc can be explored as a photocatalyst to degrade contaminants from water. The development of new materials with these properties moves toward a sustainable science, which is fundamental for life in Earth.

Langmuir-Hinshelwood kinetic model should be applied in order to understand such a heterogeneous degradation catalysis [37, 38]:

$$r_{LH} = -\frac{dC}{dt} = \frac{kKC}{1 + KC} \quad (4)$$

where r_{LH} is the reaction rate, k the kinetic constant, K the Langmuir adsorption constant and C is the concentration of the degraded product.

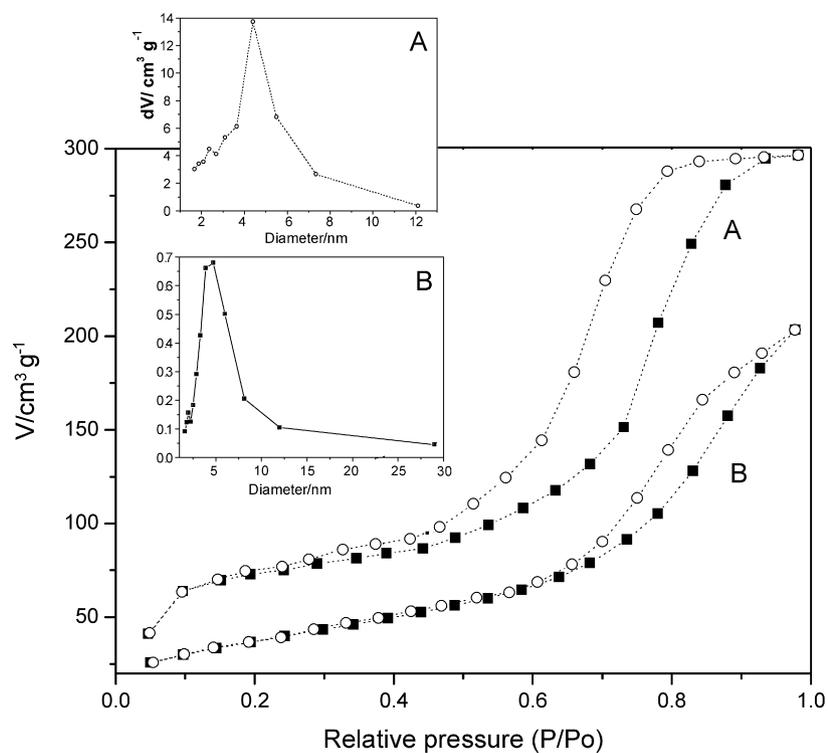


Fig. 4. Nitrogen adsorption-desorption isotherms of HMS (A) and Si-CuF₁₆Pc (B). The inserts show the corresponding BJH pore size distribution curves.

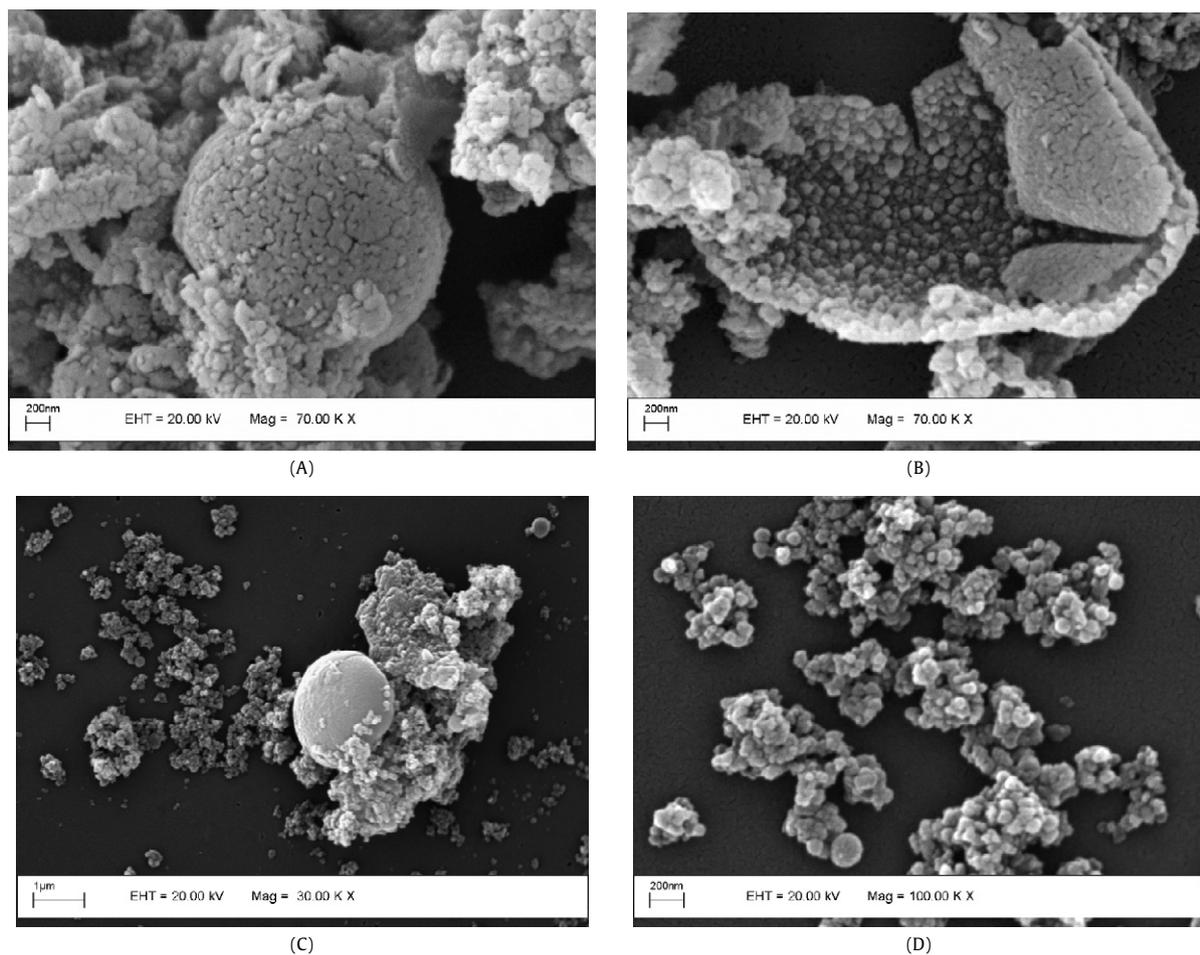


Fig. 5. SEM images of Si-CuF₁₆Pc (A, B) and HMS (C, D).

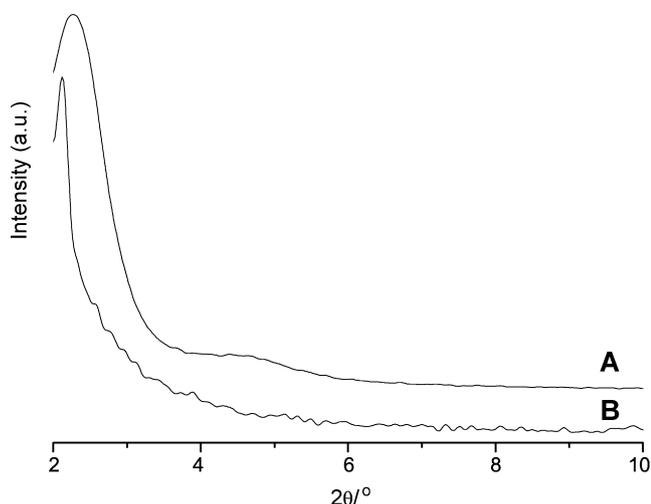


Fig. 6. X-ray diffraction patterns of Si-CuF₁₆Pc (A) and HMS (B).

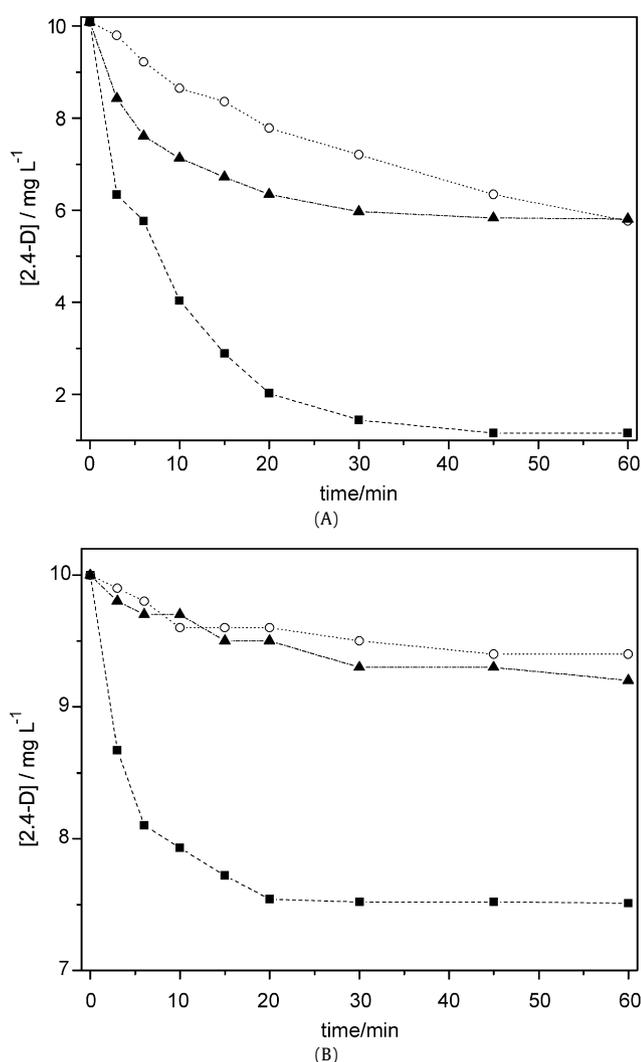


Fig. 7. 2,4-Dichlorophenoxyacetic acid (2,4-D) pesticide degradation by Si-CuF₁₆Pc (■), HMS (▲) and in the absence of any material (○) under UV irradiation (A) and without UV irradiation (B).

2,4-D degradation catalyzed by Si-CuF₁₆Pc was adjusted for Langmuir–Hinshelwood model, and presented an excellent square

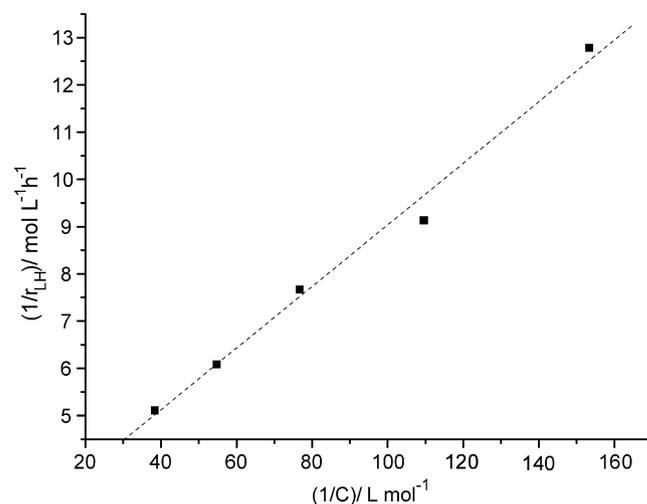


Fig. 8. Linear curve obtained using the Langmuir–Hinshelwood kinetic model of the 2,4-dichlorophenoxyacetic acid (2,4-D) degradation catalyzed by Si-CuF₁₆Pc.

correlation coefficient ($R^2 = 0.9947$), showing that this catalysis can be explained by this model. From Fig. 8, it was obtained $k = 0.3969 \pm 0.0552 \text{ mol L}^{-1} \text{ h}^{-1}$ and $K = 38.54 \pm 2.39 \text{ L mol}^{-1}$.

According to the Langmuir–Hinshelwood model, the number of surface adsorption sites at the equilibrium is constant, and only one substrate can bind to each surface active site. Thus, the substrate adsorption rate is the same for all sites, does not depend on the surface coverage, and there is no interaction between the adjacently adsorbed molecules. Therefore, the 2,4-dichlorophenoxyacetic acid (2,4-D) degradation depends on its adsorption on the Si-CuF₁₆Pc surface, as well as on the reaction rate. K and k data showed that this degradation is based on a fast adsorption followed by a lower reaction rate. Indeed, this model suggests that its kinetic reaction is dependent on the degradation reaction.

Fig. 9 shows the recycling experiments of the catalyst and the quantification of CuF₁₆Pc leached. Recycling experiments showed a photocatalytic activity reduction from 90% to 60% of 2,4-D degradation after six catalytic cycles, after which the activity maintained constant up to the tenth cycle. The activity reduction observed during the recyclings might have occurred by leaching of part of CuF₁₆Pc attached on the silica according to Fig. 9, which shows that 3.1 mmol g⁻¹ of CuF₁₆Pc was leached after ten cycles. However, the CuF₁₆Pc practically does not leach after the sixth application of the Si-CuF₁₆Pc, which makes this catalyst proper for degradation of water contaminants.

4. Summary

The phthalocyanine CuF₁₆Pc covalently bonded to silica gel by the co-condensation reaction directed with *n*-dodecylamine shows a favorable process to obtain the functionalized hexagonal mesoporous silica Si-CuF₁₆Pc. The characterization methods by TGA, FTIR, SEM, ²⁹Si NMR, N₂ adsorption and XRD confirm that the phthalocyanine was incorporated on the hexagonal mesoporous inorganic surface. The novel material demonstrates to have an excellent catalytic activity (90%) for the 2,4-dichlorophenoxyacetic acid (2,4-D) photodegradation in approximately 30 min, while in its absence the photodegradation was lower than 40%. This catalyst demonstrates its efficacy for photodegradation of organochloride compounds, industrial dyes and pesticides with unproblematic recuperation from the reaction medium.

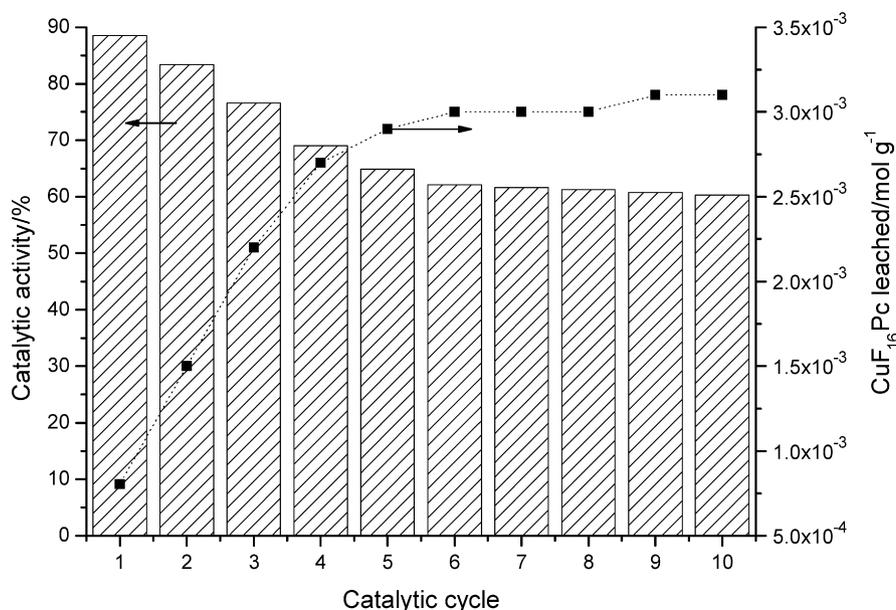


Fig. 9. Conversion rate for recycling experiments of the Si-CuF₁₆Pc catalyst at 25 °C after 1 h reaction and amount of CuF₁₆Pc leached after each recycling.

Acknowledgments

The authors acknowledge FAPESP, CNPq and CAPES for the fellowships and financial support.

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