Coupling process between solid–liquid extraction of amino acids by calixarenes and photocatalytic degradation

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ABSTRACT

The removal of biological or pharmaceutical compounds through the wastewater treatment becomes relevant. These compounds are present as traces in sewage. In this work, we propose a coupling process which combines the pre-concentration of the pollutant by selective extraction and then degradation of these pollutants by photocatalysis in presence of TiO_2. This process is efficient at room temperature by activation of a photocatalyst (TiO_2) under UV light. Aromatic amino acids were chosen as model of pharmaceutical pollutants. Their extraction from water, ensured by calixarene derivatives, and their photocatalytic degradation were investigated. It was shown that photodegradation follows a first-order kinetic and that the rate constant enhances with amino acid concentration. The effect of the pH on the rate constant will be discussed.

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1. Introduction

Data of the EU research projects [1–3] have confirmed that antibiotics and other pharmaceuticals are present in sewage and in natural water. In some cases, metabolites were also found in drinking water sources. The removal rates of individual compounds through the wastewater treatment are variable, and some standard removal techniques cannot eliminate all of the compounds.

The development of new water treatment processes is still relevant. The conventional water disinfection technologies, such as chlorination and ozonation, can lead to the formation of harmful by-products (e.g. trihalomethanes) [4]. Photocatalysis has emerged as a promising technology and is considered as one of the most important advanced oxidation technology (AOT), for water and air purification [5,6]. Among all semiconductor catalysts tested until nowadays, the most widely used is TiO_2 because of its very important photoactivity, its lack of toxicity and its high stability [7].

Photocatalytic process begins when the TiO_2 particles absorb light at a wavelength smaller than 384 nm. Consequently, valence band electrons are promoted through the band gap into the conduction band, generating an electron–hole (e^-/h^+) pair. These pairs are able to initiate oxidation and reduction reactions at the TiO_2 surface. The positive holes can oxidize the organic molecules adsorbed at the surface, through the formation of $^\bullet OH$ radicals. On the other hand, the photogenerated electron can produce radical species such as superoxide $O_2^{\bullet-}$ and hydroperoxide $HO_2^\bullet$ as described in the following equations:

- Absorption of efficient photons by titania ($h\upsilon \geq E_G = 3.2\,eV$)

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

- Oxygen ionosorption

$$(O_2)_{ads} + e^-_{CB} \rightarrow O_2^{\bullet-} \qquad (2)$$

- Neutralization of HO^- groups into $HO^\bullet$ by photoholes

$$(H_2O)_{ads} + h^+_{VB} \rightarrow H^+ + HO^\bullet \qquad (3)$$

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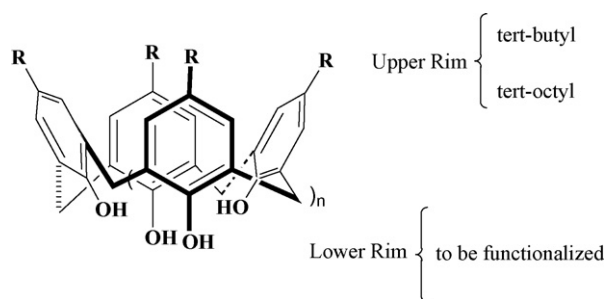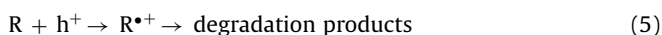E-mail address: francis.vocanson@univ-st-etienne.fr (F. Vocanson).

Fig. 1. Schematic representation of calix[*n*]arene.

- Oxidation of the organic reactant via successive attacks by HO• radicals

$$R + HO^{\bullet} \rightarrow R'^{\bullet} + H_2O \tag{4}$$

- Or by direct reaction with holes

$$R + h^{+} \rightarrow R^{\bullet +} \rightarrow \text{degradation products} \tag{5}$$

All these radicals initially oxidize the substrate intermediates which subsequently undergo complete mineralization.

One of the limitations of the photocatalytic system is the insufficiently large intrinsic quantum yield for the reaction (it can be translated to the cost of electric power for the UV lamps). This means that the concentration of the substrate can increase the efficiency of photocatalysis by decreasing the recombination of (e^-, h^+) pairs. The combination of the photocatalytic process with an adsorbent would improve the water treatment.

Calixarenes are macrocyclic molecules built from phenolic units linked via methylene bridges. In the field of supramolecular chemistry, calixarenes are extremely popular building blocks for molecular recognition, forming host–guest complexes [8–10]. During the past 10 years, much attention has been focused on the recognition of amino acid and derivatives in aqueous media [11–14]. The design of the calixarene receptor can be modulated by the number of the phenolic units and by the nature of the functionalised pendant groups (Fig. 1). It is known that carboxylic acid substituted calixarenes exhibit host–guest properties towards amino acids [15]. Hydrogen bonds between host and guest are responsible for the

good recognition properties observed. The binding ability was also related to the presence of a *tert*-octyl group instead of a *tert*-butyl group on the upper rim of the calixarene [16–18]. This group improved the recognition of organic compounds.

There are few examples in the literature of solid–liquid extraction experiments involving calixarene derivatives. Works on the extraction properties of calixarenes incorporated into materials by grafting were described [19–21]. During the course of our studies, our group developed an original method implying unsupported calixarene derivatives as solid extractant in solid–liquid extraction of metal cations [22]. In the present work, we describe that this method can be generalised to organic molecules, and we used functionalised calixarenes as solid extractant for amino acids in aqueous solution. Then the pre-concentrated amino acids were released and degraded by photocatalysis using TiO_2.

2. Experimental

2.1. Synthesis of calixarene derivatives

Fig. 2 shows the structure of extractants used in this study. The calixarene derivatives were abbreviated as depicted in Table 1. All calixarene derivatives were synthesized according to the literature [16,23,24] and their spectroscopic data matched that of previous works.

Analytical grade of (dl)-amino acids were purchased from Sigma–Aldrich and employed without further purification as guest molecules.

2.2. Extraction protocol

The solid–liquid experiments were conducted at a temperature above 15 °C to avoid the dissolution of the calixarene derivatives in water (Fig. 3). The evolution of the absorbance, showing the dissolution of the macrocycles, is the same for the different calixarenes; from 25 °C it is growing with the enhancement of the temperature of the suspension. All the experiments were conducted as followed (Fig. 4): an aqueous suspension of the calixarene derivative in water (10^{-5} mol) was prepared, and then the amino acid (Fig. 5) was added in a 1:1 molar ratio. The pH of the aqueous
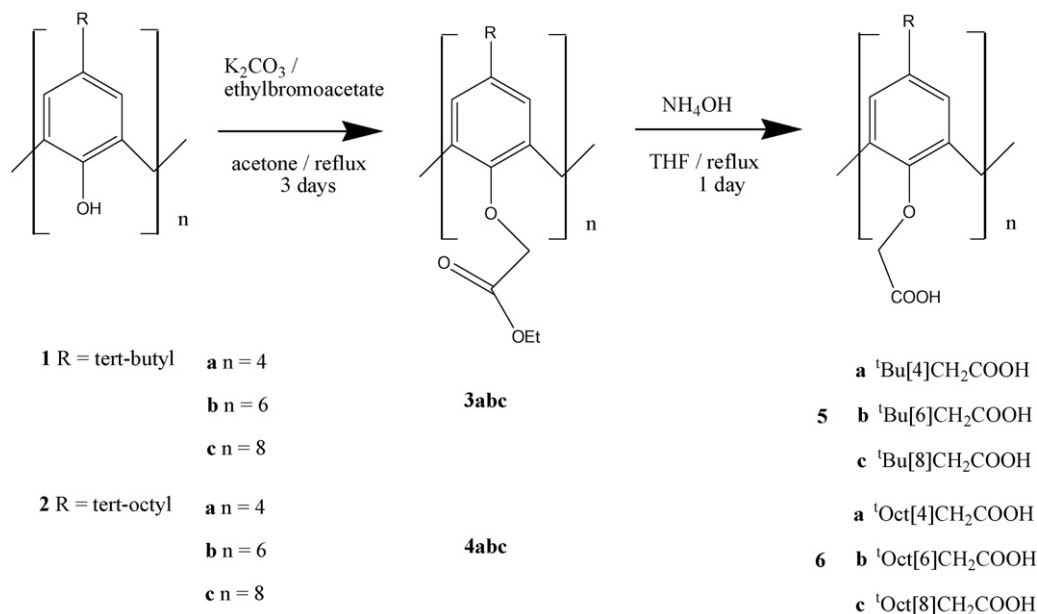

Fig. 2. Synthesis and abbreviations of the calixarene derivatives.

Table 1
Abbreviations of calixarene derivatives.

|		
5a	25,26,27,28-Tetrakis(carboxymethoxy)-5,11,17,23-tetrakis(1,1-dimethylethyl) calix[4]arene	**$^tBu[4]CH_2COOH$**
5b	37,38,39,40,41,42-Hexakis(carboxymethoxy)-5,11,17,23,29,35-hexakis(1,1-dimethylethyl) calix[6]arene	**$^tBu[6]CH_2COOH$**
5c	43,44,45,46,47,48,49,50-Octakis(carboxymethoxy)-5,11,17,23,29,35,41,47-octakis(1,1-dimethylethyl) calix[8]arene	**$^tBu[8]CH_2COOH$**
6a	25,26,27,28-Tetrakis(carboxymethoxy)-5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl) calix[4]arene	**$^tOct[4]CH_2COOH$**
6b	37,38,39,40,41,42-Hexakis-(carboxymethoxy)-5,11,17,23,29,35-hexakis(1,1,3,3-tetramethylbutyl) calix[6]arene	**$^tOct[6]CH_2COOH$**
6c	43,44,45,46,47,48,49,50-Octakis(carboxymethoxy)-5,11,17,23,29,35,41,47-octakis(1,1,3,3-tetramethylbutyl) calix[8]arene	**$^tOct[8]CH_2COOH$**
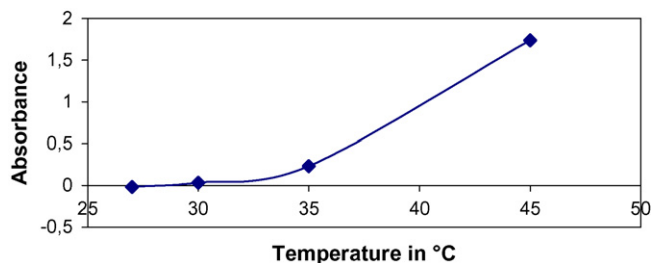
Fig. 3. Evolution of absorbance of suspension of macrocycle **6b** in water at pH 6.5 in function of the temperature.
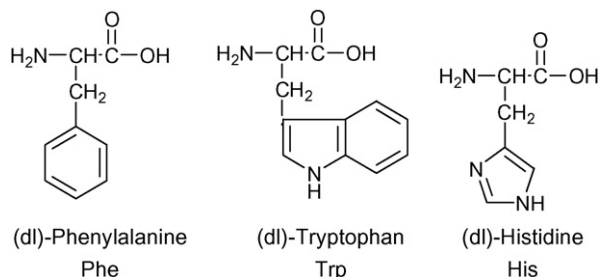

Fig. 5. Structure of the amino acids used as guests.

phase was still remained to 6.5 or lowered to 4 by addition of an aqueous HCl solution. The suspension was vigorously stirred to avoid the formation of aggregates. After a variable time the complexes were formed and the suspension was filtered using a 0.20 μm Teflon filter. The concentration of amino acid remaining in the aqueous phase was monitored by a UV–vis spectrometer (Shimadzu UV-2401 PC spectrophotometer) and compared to the calibration curve corresponding. The detailed experimental conditions are listed in Table 2. After forward extraction was performed from the aqueous to the solid phase, the solid calixarene–amino acid complexes were suspended in an HCl aqueous phase (pH 1) to promote the guest released. This solution containing the released amino acid was filtered and the concentration of residual amino acid was monitored by UV–vis spectroscopy. Blank experiments showed that no amino acid extraction occurred in the absence of calixarene derivative. By UV–vis spectroscopy, it was verified that no calixarene remained in the aqueous phase after filtration. Moreover the solid phase constituted by the calixarenic receptors was studied by NMR ^{1}H in solution (Bruker AM 300 with CDCl$_3$

as solvent and TMS as internal standard). The results showed the pureness of the macrocycles and the absence of amino acids. Then calixarenes were reused for the recovery of amino acids. The BET surface areas were determined on a Tristar 3000 apparatus. They were ca. 2.456 m^2/g ± 0.026 for macrocycle **5a**, 4.169 m^2/g ± 0.04 for **5b**, 3.971 m^2/g ± 0.02 for **5c** and 6.437 m^2/g ± 0.03 for macrocycle **6b**.

2.3. Photodegradation of tryptophan

Commercially available Degussa P-25 was used in this study. This sample contains ca. 80% anatase and 20% rutile. Its BET surface area is ca. 55 m^2/g. The batch reactor was a cylindrical flask made of Pyrex with a bottom optical window of 11 cm^2 of surface which was open to the air. UV irradiation was provided by a high pressure mercury lamp and was filtered by a circulating-water cell equipped with a 340 nm cut-off filter (Corning 0-52). The water cell was used to remove IR radiation, thus preventing any heating of the suspension. Water was purified with a Milli-Q water ion exchange system (Millipore Co.). The photocatalytic test was performed at room temperature (293 K); 25 mg of Degussa P-25 TiO$_2$ was added under stirring to a solution of tryptophan in water. The initial pH of the suspension was adjusted by addition of either NaOH 1 M or HNO$_3$ 1 M solutions. The suspension was maintained in the dark for 1 h to reach the adsorption equilibrium. At time $t = 0$, the photoreactor was irradiated. Samples of the suspension were taken at regular time intervals, filtered through 0.45 μm millipores discs to remove TiO$_2$ powder. The HPLC analysis was determined using a column Hypersil BDS-C18 (4 mm × 125 mm). The eluent was a solution of CH$_3$COONH$_4$ (95%, 3.8 g/L) in acetonitrile (5%, flow rate of 0.3 mL/min). It was adjusted to pH 5 with acetic acid.

Table 2
Experimental conditions for amino acids extraction.

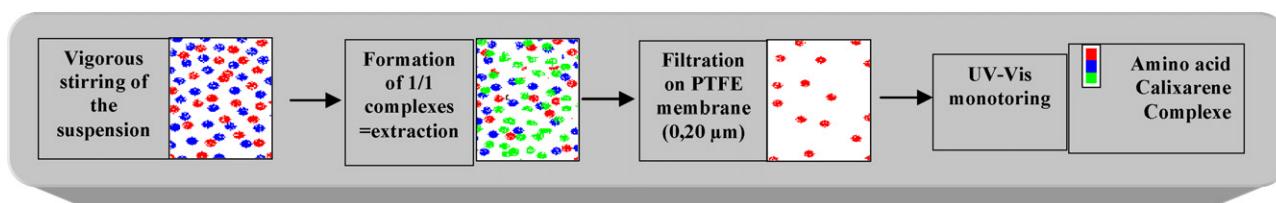| Aqueous phase	
Volume	10 mL
Amino acids	(dl)-Trp, (dl)-Phe, (dl)-His (10^{-3} M)
pH	6.5 (pH of tap water) 4 (hydrochloric acid medium)
Calixarene derivative	Powder (10^{-5} mol)
Temperature	$273 \le T \ge 288$ K
Contact time	Variable time (from 1 h to 8 h)
Absorbance analysis	
Wavelength (λ)	Trp (279.5 nm); Phe (257 nm); His (202.5 nm)

Fig. 4. Schematic representation of extraction experiments.
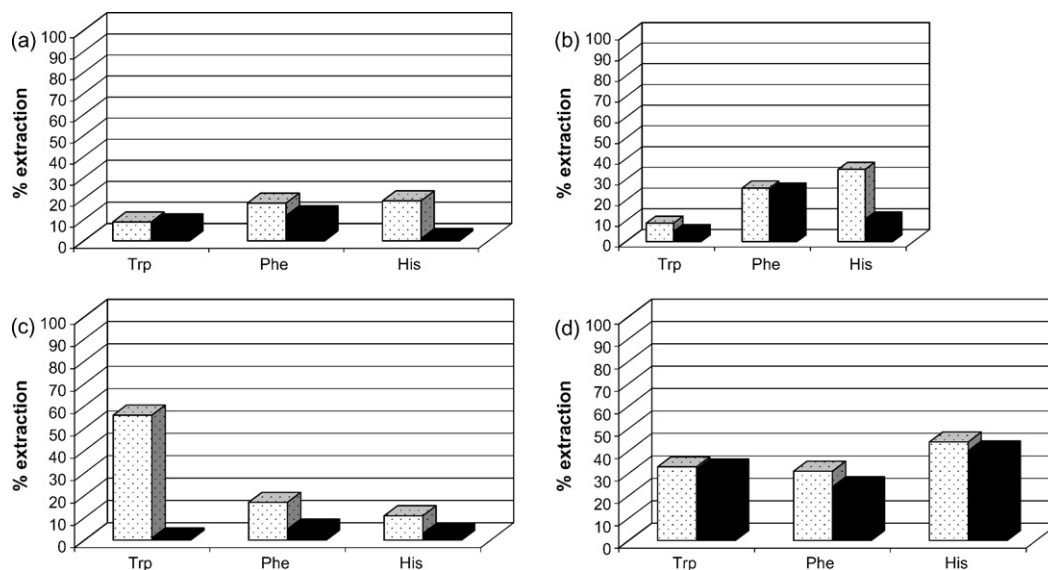
Fig. 6. Extraction profiles of Trp, Phe and His with (a) ^{t}Bu[4]CH$_2$COOH, (b) ^{t}Bu[6]CH$_2$COOH, (c) ^{t}Oct[6]CH$_2$COOH and (d) ^{t}Bu[8]CH$_2$COOH. pH 4 (■) or 6.5 (□) (host/guest in 1:1 molar ratio).

3. Results and discussion

3.1. Functionalisation of calix[n]arenes

Regarding all the above-mentioned observations, we have synthesized a series of calix[n]arene derivatives bearing carboxylic acid functions at the lower rim, and *tert*-butyl or *tert*-octyl groups at the upper rim. A two step reaction led to desired receptors from the parent calixarene (Fig. 2).

In a typical experiment, the first step involved a nucleophilic attack on the lower rim, with K$_2$CO$_3$ as base and ethyl bromoacetate as electrophile [23]. The second step consisted to the saponification reaction of the ester functions with tetramethylammonium hydroxide in THF [24]. All compounds were obtained in quantitative yields. Before beginning the study of solid-liquid extraction, the insolubility of the calixarenic macrocycles was tested by mixing calixarenes with aqueous solutions at pH 4 or 6.5, and was monitored by UV spectrometry (Fig. 3). No basic aqueous solutions were employed because the carboxylate function would enhance the solubility of the ligand in water. The dissolution of macrocycles began from temperature more than 25 °C also the experiments of extraction were realised at 15 °C nearly of the temperature of the water in environment.

3.2. Solid–liquid extraction investigations

Tryptophan, histidine and phenylalanine in racemic (dl) mixture were chosen for the extraction study because of their aromatic ring which allows the experiments to be monitored by UV spectrometry (Fig. 5). The binding ability of calixarene derivatives towards amino acids in liquid–liquid extraction process has been previously described and showed the formation of 1:1 complexes [16]. From these results, we used functionalised calixarenes as solid extractant for amino acids in aqueous solution. The percent extraction (*E*%) has been calculated as

$$E\% = \frac{A_0 - A}{A_0} \times 100 \tag{6}$$

where A_0 and A are the initial and final concentrations of the amino acids before and after the extraction, respectively. Extraction profiles of amino acid by different calixarene derivatives (in neutral or acidic media) are displayed in Fig. 6. As shown in the figure, the
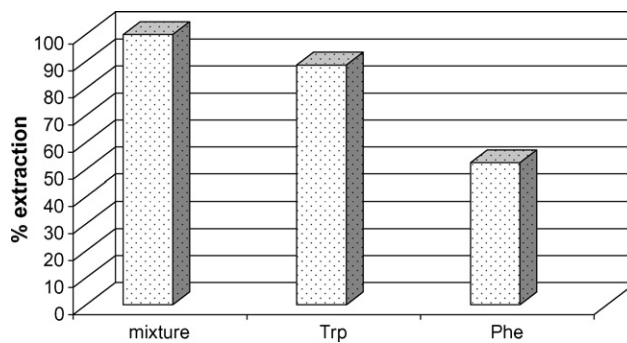

Fig. 7. Extraction profile of Trp, Phe and a mixture of Trp/Phe/His (1:1:1 molar ratio) with ^{t}Bu[8]CH$_2$COOH in a 5/1 (host/guest) molar ratio at natural pH of water after 6 h of stirring.

extraction efficiency was not dependant on the pH. It allows working at the pH of drinking water. Amino acids were extracted with the calix[6] and [8]arene derivatives, which have larger cavities to include the guest molecule. On the other hand, the alkyl group at the upper rim plays an important role. Neither the ^{t}Bu[6]CH$_2$COOH nor ^{t}Bu[8]CH$_2$COOH calixarene derivative show any selectivity towards the amino acid extracted. Extraction with the ^{t}Oct[6]CH$_2$COOH derivative seems to be more dependant on the pH. Moreover the ^{t}Oct[6]CH$_2$COOH derivative displays a preference for the extraction of tryptophan. The hydrophobic interactions favour the insertion of the amino acid aromatic moiety into the calixarene cavity. It can be related to the ability to form π–CH$_3$ interaction and π–π stacking between host and guest.

Attempts has been conducted with the ^{t}Bu[8]CH$_2$COOH derivative using a molar ratio of 5:1 (host–guest) (Fig. 7). Better extraction efficiency was observed for the extraction of the mixture of the three amino acids (1:1:1 molar ratio). The extraction of the mixture of amino acids was monitored by UV–vis at each amino acid specific wavelength (Table 2) and compared to each calibration curve. In these conditions, no amino acid was recovered after 6 h of stirring.

3.3. Regeneration test

The macrocycles were recovered by acidification of the suspension at pH 1, using hydrogen chloride. A solution containing the
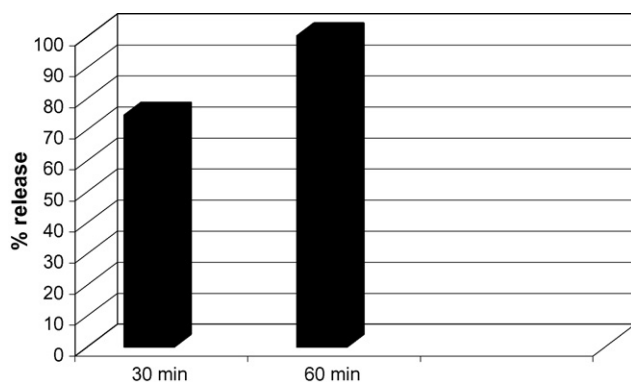
Fig. 8. Release profiles of the mixture of amino acids from $^tBu[8]CH_2COOH$ at 30 min and 60 min at pH 1.

amino acid was separated and monitored by UV–vis spectrometry to determine the degree of release. The percent release has been calculated as

$$R\% = \frac{A_c - A_r}{A_c} \times 100 \tag{7}$$

where A_c is the concentration of the amino acid–calixarene complex and A_r is the concentration of amino acid after release. Fig. 8 presents the result of the release of the mixture of amino acids. After 30 min, 70% of guests were released and the totality was removed after 1 h. The calixarene derivatives were then ready to be used again in a new extraction experiment.

3.4. Photocatalytic degradation of amino acids

Some characteristics of Degussa P-25 TiO$_2$ are given in Table 3. The particle size is 23 ($\pm$2) nm. The crystallite size is a crystallographic consideration and has been determined by X-ray diffraction (XRD) using the Debye–Scherrer equation [25]. The result for P-25 is 21 ($\pm$2) nm. It means that a P-25 particle corresponds to one crystallite; this is confirmed by the study of Hadj-Salah et al. [26]. Considering isoelectric point (IEP) value, below pH 7, there are many positive charges (TiOH^{2+}) on P-25. As reported in the literature, an important number of studies showed that these characteristics (particle size, aggregate size in suspension solution, BET specific surface area, crystalline phase and IEP) can influence the rate of formation of the oxidative surface species and play a role in photocatalytic degradation of organic pollutants [27].

In this preliminary study, a photocatalytic process in presence of TiO$_2$ was used to degrade tryptophan at tap water pH and acidic pH. Tryptophan was shown to photodegrade rapidly. In 50 min, we could observe a total disappearance of the amino acid at pH 2. The study of the degradation rate as a function of the initial concentration of tryptophan is presented in Fig. 9.

The photocatalytic degradation of tryptophan follows the Langmuir–Hishelwood equation:

$$V_0 = \frac{kKC_0}{1 + KC_0} \tag{8}$$

Table 3
Characteristics of Degussa P-25 TiO$_2$ photocatalyst.

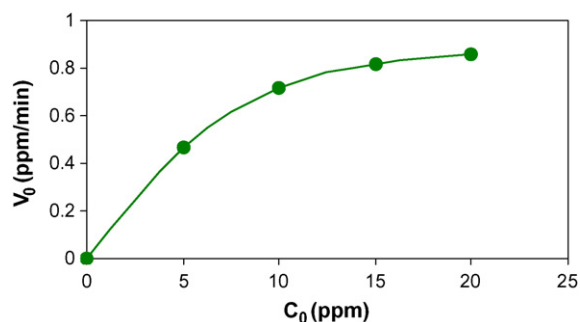|	
BET (m^2/g)	50
Particle size (nm)	23 ($\pm$2)
Crystallite size (nm)	21 ($\pm$2)
Crystalline phase	80% anatase, 20% rutile
Aggregate phase (nm)	1400
IEP	7

Fig. 9. Influence of the initial concentration of Trp on the degradation rate. pH 2.
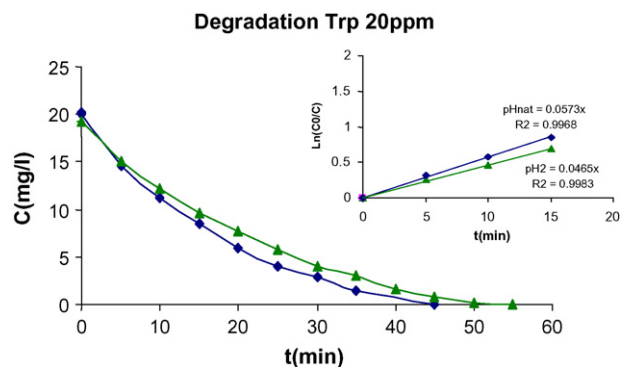

Fig. 10. Photocatalytic degradation of Trp. Influence of the pH value. In insert, first-order linear transforms $\ln(C_0/C) = f(t)$. Conditions: $C_0 = 20$ mg L^{-1}, TiO$_2 = 2.5$ g L^{-1}, $V = 20$ mL, $T = 20\,^\circ$C ($\blacklozenge$: pH 6.5, $\blacktriangle$: pH 2).

where V_0 is the initial rate, C_0 the initial concentration of tryptophan, k the rate constant and K the adsorption constant.

This result clearly pointed out that the degradation occurred more rapidly for a concentrated solution. The pre-concentration of amino acid plays a major role to enhance the efficiency of the photocatalytic process.

The study of the effect of pH on the degradation of tryptophan (Fig. 10) shows that only a small decrease of efficiency was observed at acidic pH. This indicates that it is possible to degrade amino acids after their extraction by calixarene derivatives. The first-order rate constant k was found equal to 0.05 min^{-1} at pH 2 and 0.06 min^{-1} at natural pH.

4. Conclusion

Calix[n]arene carboxylic acid derivatives are good receptors for the solid–liquid extraction of amino acids in water. The extraction experiments display a relationship between the size and feature of the calixarene and they show the whole extraction of amino acids by these receptors. Then amino acids can be released by washing the solid phase by acidic solution, giving a concentrated solution of guest. The photocatalytic degradation is presented, its rate is dependent on the initial concentration of amino acid. This emphasizes the advantage of the pre-concentration of pollutants. This work exhibits that solid–liquid extraction is a method of choice for its simple usefulness. Moreover it is a recyclable process. These preliminary results suggest further possibilities for optimal extraction of amino acids and other pharmaceuticals.

Acknowledgments

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