Marine sponge skeleton photosensitized by copper phthalocyanine: A catalyst for Rhodamine B degradation

1 Introduction

Phthalocyanines are macrocyclic, aromatic compounds based on the porphyrin structure, in which four indole rings are connected by azomethine bridges. Because of their specific chemical structure, they exhibit unique properties, which make them suitable for a wide range of applications. Metalphthalocyanines possess high chemical and thermal stability, high reactivity, redox properties and high molar absorption coefficients [1-4]. Moreover, the type, position, and number of substituents and the central atom can change the physical and chemical properties of a phthalocyanine molecule [5].

Metalphthalocyanines are used as sensors [2,5], photosensitizers in photodynamic therapy and solar cells (DSSC) [3] and dyes (photochromic substances, fluorescent probes in sensing or in vitro imaging applications). They are semiconductive and light-absorbing electron donor compounds, and can serve in electronic and optoelectronic devices [6], photovoltaic cells, electrode modifications [7,8], liquid crystals [9] and data storage systems [10,11]. Phthalocyanines are also commonly used as catalysts, in organic synthesis [12], degradation of organic pollutants (e.g. 2,4-D acid [13], synthetic dyes [14,15]), and oxidation of harmful and undesirable compounds (e.g. bisphenol A [16], phenols [17], thiols [18,19]).

Metalphthalocyanines exhibit high catalytic activity (in a so-called biomimetic catalytic system) even in ambient conditions [20]; in addition they are relatively easy to synthesize and commercially available [21]. However, one limitation of these compounds is that they are inconvenient to use, since they are generally available only as powder, in solution (which hinders their separation from the solution and catalyst recycling) or in the form of thin film [22-24]. Moreover, some molecules are prone to aggregation, which greatly decreases the number of active sites for catalysis [25]. A better strategy for their practical use might be to attach them to a suitable support.
material. Adsorption of metalphthalocyanines on a solid support is an effective way to remedy the drawbacks of the homogeneous catalyst and enable the creation of a heterogeneous system (possibility of reutilization, increase in the surface area of the catalyst). Adsorbents used to date include zeolites [26], silica [13], TiO$_2$ [27], carbon materials [19,28], polymers [29] and fabrics [1].

In the present work we decided to use 3-dimensional fibrous proteinaceous skeletons (built from a specific protein – spongin) of marine demosponge origin. In comparison with traditional supports, this material does not have to be synthesized, and the process of adsorption is fast, facile and takes place in mild conditions. Mediterranean *Hippospongia communis* sponge possess a fibrous, anastomosing, spatial, reticular structure. The structure of spongin is multileveled - single fibers, composed of microfibers, combine into a complex hierarchical network. Spongin fibers may range in thickness from a few mm to about 10-15 mm. The combination of this renewable material with a relative large internal surface area (between 25 and 34 m$^2$ for a 3- to 4-gram skeleton [31]) with copper phthalocyanine enable the production of the heterocatalyst.

Sponges (phylum *Porifera*) are one of the phylogenetically oldest multicellular organisms, which evolution dates back to 600 million years ago. They are aquatic animals, currently described in four classes: *Demospongiae*, *Calcarea*, *Hexactinellida* and *Homoscleromorpha* [30]. Demosponges skeletons are fibrous and contain species dependent chitin, or spongin as main organic constituents. Spongin contains both collagen- and keratin-like structural proteins that are responsible for the rigidity of the sponge skeleton [31,32]. Because of their unique spatial structure and properties (e.g. high thermal stability) spongin-based skeletons of diverse demosponges are currently the subjects of numerous studies related to tissue engineering [33,34], as well as to Extreme Biomimetics [35,36]. Due to diverse marine ranching techniques used for the cultivation of spongin-based demosomes, spongin is the renewable source (which affect their relatively low price) of proteinaceous scaffolds with good perspective for practical applications.

In the present work, for the first time, copper phthalocyanine tetrasulfonic salt (CuPC) was successfully adsorbed onto purified marine bath sponge skeleton from the species *Hippospongia communis*. In addition, we investigated the photocatalytic properties of the resulting systems for organic pollution degradation, using the synthetic dye Rhodamine B as the target compound. Although UV light-assisted photocatalytic degradation of RB has been reported in the literature, adsorption using marine sponge skeleton has not previously been studied.

### 2 Experimental

#### 2.1 Materials

Specimens of *Hippospongia communis* demosponge were collected on the Mediterranean coast in Tunisia and supplied by INTIB GmbH (Germany). Pieces of selected sponges were prepared by washing with sea water, followed by drying and rinsing again with fresh water five times. To remove contaminants (such as CaCO$_3$) the pieces were immersed in a 3M HCl solution for 72 h at room temperature and finally washed with distillated water up to a neutral level of pH. Copper phthalocyanine-3,4′,4″,4″′-tetrasulfonic acid tetrasodium salt (CuPC) and Rhodamine B (RB) were purchased from Sigma Aldrich (Germany). Other chemicals were of reagent grade and used as supplied.

#### 2.2 Adsorption and desorption process

To evaluate the adsorption properties of the purified marine sponge skeleton with respect to CuPC, a series of adsorption experiments were performed. Typically, sponge pieces of 0.1 g were shaken with 25 mL of experimental solutions of desired concentrations (for kinetic studies 50, 100 and 200 mg/L) at pH=2. After predetermined time intervals, the adsorbed quantity (mg/g) of CuPC at time $t$, $q_t$, was calculated from the following equations:

\[
q_t = \frac{(C_0 - C_t)V}{m}
\]

\[
E(\%) = \frac{C_0 - C_t}{C_0} \times 100\%
\]

where $C_0$ and $C_t$ are the concentrations of the dye in the solution before and after sorption (mg/L), $V$ is the volume of the solution (L), and $m$ is the mass of sorbent (g). Initial dye concentrations for kinetic studies ranged from 50 to 200 mg/L (pH=2).

In order to study the adsorption isotherm, 0.1 g of marine sponge skeleton was kept in contact with 25 mL of dye solution at different concentrations (50, 100, 200, 300, 400 and 500 mg/L) at pH=2 for 240 min with constant shaking at ambient temperature.

To define the most suitable condition for adsorption the effect of several parameters on this process was checked.
For studying the effect of solution pH on dye adsorption, experiments at different pH values (ranging from 2 to 11) were performed for an initial dye concentration of 100 mg/L. To observe the effect of NaCl on dye adsorption, different amounts of salt (in concentrations from 0.01 to 1.0 M) were used with 100 mg/L of CuPC solution at initial pH. An adsorbent dose of 0.1 g, contact time 60 min, initial pH and no NaCl were used for all of the above experiments.

The desorption efficiencies of CuPC from the sorbent were measured after the adsorption experiments were completed (100 mg/L, pH=2, contact time 120 min). These studies were carried out in water at ambient temperature and in water with ultrasound at 40, 50 and 60 °C, for 300 min. A standard technique was used to determine the dye concentration using a UV-Vis spectrophotometer (Jasco V750, Japan).

2.3 Analysis

Cross polarization solid state magic angle spinning nuclear magnetic resonance (13C CP MAS NMR) spectra were obtained at a 13C frequency of 100.63 MHz on a DSX spectrometer (Bruker, Germany). Samples were packed in a 4-mm-diameter cylindrical zirconia rotor and spun at 8 kHz.

To confirm the effectiveness of the adsorption process, Fourier transform infrared spectroscopy (FTIR) was performed, using a Vertex 70 spectrometer (Bruker, Germany). The samples were analyzed in the form of tablets, produced by pressing a mixture of anhydrous KBr (ca. 0.25 g) and 1 mg of the tested substance in a special steel ring under a pressure of 10 MPa. The investigation was performed over a wavenumber range of 4000–400 cm⁻¹ at a resolution of 0.5 cm⁻¹.

Energy dispersive spectroscopy (EDS) measurements were carried out using a PTG Prism Si(Li) (Princeton Gamma Tech., USA) energy-dispersive X-ray spectrometer. Before the analysis, samples were placed on the ground with a carbon paste or tape. The presence of carbon materials is needed to create a conductive layer which provides the delivery of electric charge from the sample.

Thermogravimetric (TG) analysis of samples of products was carried out with a Jupiter STA 449F3 analyzer (Netzsch, Germany) with an Al2O3 crucible. The measurements were performed in a nitrogen atmosphere at a heating rate of 10 °C·min⁻¹, over a temperature range of 25–1000 °C, with an initial sample weight of approximately 5 mg.

Samples of H. communis sponge skeleton before and after the adsorption process were observed using a Keyence BZ-9000 (Japan) microscope in light as well as in fluorescent microscopy mode.

Photographs were also taken using an EVO40 scanning electron microscope (Zeiss, Germany) to obtain data on surface morphology and structure.

2.4 Photocatalytic activity

The catalytic reactions were carried out by adding 20 mg of a photocatalyst (sponge skeleton with CuPC, obtained after adsorption from 400 mg/L solution at pH=2 for 4 h) to a glass tube reactor containing 30 mL of 10 mg/L RB solution. The reaction mixture was continuously shaken by a magnetic stirrer. Photochemical degradation was carried out in a UV-reactor system (UV-RS-2, Heareus, Germany), equipped with a 150 W medium-pressure mercury lamp, surrounded by a water-cooling quartz jacket to cool the lamp. At given intervals of illumination, 1 mL of the RB solution was taken and decreases in the concentration of dye were analyzed by a Jasco V750 UV-Vis spectrophotometer (halogen lamp) at λ=554 nm. The efficiency of degradation catalyzed by marine sponge skeleton–CuPC hybrid material (CuPC-HcS) was evaluated by means of the RB degradation ratio, given by the following formula:

\[
\frac{(C_0 - C)}{C_0} \times 100\%
\]

where \(C_0\) and \(C\) represent the time-dependent concentration and the initial concentration (determined from the calibration curve), respectively. All the experiments were performed three times.

3 Results and discussion

3.1 Adsorption and desorption process

3.1.1 Influence of time and initial dye concentration

The influence of time and initial dye concentration was investigated in optimal experimental conditions, with controlled pH, ionic strength and temperature.

The changes in the quantity of dye adsorbed (\(q\)) are significant in the first minutes of the process; then with time they become smaller until equilibrium is reached (Fig. 1). Equilibrium is reached faster for a CuPC
solution with lower initial concentration (60 min for dye concentrations of 50 and 100 mg/L and 300 min for 200 mg/L). The adsorption efficiency reaches 100% for CuPC (independently of initial dye concentration). The quantity of dye adsorbed on the support increases when the initial dye concentration increases, which is a typical situation explained by the influence of mass gradient and the action of mass transfer driving forces [37].

3.1.2 Influence of pH and ionic strength

The next stage of the study involved examination of different adsorption conditions (pH and ionic strength) and their influence on process efficiency. In each case only one parameter was changed, while all other variables (time, initial concentration) were kept constant.

In the case of CuPC the greatest effect on the quantity of dye adsorbed ($q_t$) resulted from the pH of the dye solution. Under basic and weak acidic conditions, the values obtained for the efficiency of the process are similar, at around 60%, but a considerable change is noted at pH=2, where the efficiency increases to 98%. In these conditions ionization of functional groups of the amino acids building spongin (NH$_2$→NH$_3^+$) takes place, which results in their mutual attraction (in contrast to the repulsive forces in an alkaline environment). These results suggest that the driving force of the adsorption may be electrostatic interactions [38]. The dye molecules can reach the surface of the $H. communis$ sponge skeleton, where they can interact via hydrogen bonding. The pH=2 was chosen as the best condition for all further adsorption process.

The adsorption of dye on the marine sponge skeleton was positively affected by the presence of NaCl. The best results were obtained in the presence of 1M NaCl in the dye solution. The addition of salt ions affects the interaction between adsorbent and adsorbate, due to the increase in ionic strength, a decrease in the thickness of the electrical double layer surrounding particles in solution is observed. Both repulsive and attractive interactions will be weaker, which increases or decreases the efficiency of the process, depending on which of these interactions occur between the particles in solution [39]. Furthermore, the addition of NaCl increases the value of van der Waals forces, ion-ion and ion-dipole forces, which positively influences the effectiveness of the adsorption process [40].

Desorption tests were performed to evaluate the strength of the connection between $H. communis$ skeleton and dye. It was observed that shaking with water at room temperature and ultrasound-assisted washing at 30, 50 and 60 °C, causes only slight elution of the previously adsorbed CuPC (5%).

3.2 Kinetics and isotherms of adsorption

To determine the rate and mechanism of the process of adsorption, pseudo-first-order and pseudo-second-order kinetic models were fitted to the experimental data. These models present the correlations between changes in the concentration of adsorbate as a function of the time for which the adsorption process is continued, until equilibrium is reached.

The linear forms of the kinetic models of pseudo-first and pseudo-second order are given and described in detail in [41] and [42].

As can be seen from Fig. 2a and Table 1, the pseudo-second-order model better describes the experimental data. In spite of the relatively high values of the correlation coefficients for the pseudo-first-order model, it cannot be considered useful because of the large differences between the experimental and calculated sorption capacities.

The adsorption isotherm parameters were calculated according to the Freundlich (4) [43] and Langmuir (5) [44] models:

$$q_e = K_f \cdot \frac{1}{C_e^n}$$

where $C_e$ denotes the equilibrium concentration of the dye solution (mg/L), $q_e$ is the quantity of dye adsorbed at equilibrium (mg/g), $K_f$ (mg/g) and $n$ are the Freundlich constants. The values of $K_f$ and $n$ can be determined from the intercept and gradient of the plot of log($q_e$) against log($C_e$).
where Ce is the equilibrium concentration of the dye solution (mg/L), qm is the maximum adsorption capacity (mg/g), and b is the Langmuir constant (L/mg), which is calculated from the intercept and downward linear slope of the graphs of Ce/qe and Ce.

A graph of qe against Ce for the adsorption isotherms of CuPC on marine sponge skeletons is shown in Fig. 2b.

Analysis of the isotherm parameters obtained for the Freundlich and Langmuir models indicates that the adsorption of CuPC on marine sponge skeleton is a complex process. The calculated correlation coefficients (r) are similar, 0.917 for Langmuir and 0.957 for Freundlich model. H. communis sponge skeleton has a relatively high maximum adsorption capacity (qm) for copper phthalocyanine (83.36 mg/g). The parameter n in the Freundlich isotherm model is equal to 3.46 (n>1). A value of 1/n below one indicates normal adsorption, while if 1/n is above one it indicates cooperative adsorption; additionally, the smaller the value of 1/n, the greater the heterogeneity of the adsorbate.

### 3.3 13C CP/MAS NMR

Figure 3 shows the results of 13C MAS NMR analysis.

Marine sponge spongin has an inexact chemical structure, but tentative assignments of some of the unknown components can be made. Signals in the range 17.7–69.6 ppm suggest the presence of alkyl carbons (R CH2, RCH3), carbons bonded to oxygen (R CH2O–) (above 50 ppm), nitrogen (RCH2NH2), as well as halogen atoms (C–Cl, C–Br, C–I, C–SR) (below 50 ppm). The peaks above 115 ppm can be assigned to RHC=CH and aromatic carbons, and those at 170.0 and 172.1 to C=O in acids and esters respectively. As stated in [45,46] the signals observed in the CuPC spectrum can be ascribed to C1 (141.3 ppm), C2 (128.4 ppm), C3 (126.2 ppm) and C4 (138.4 ppm) incorporated in the carbon structure. Comparing the carbon NMR spectra of marine sponge skeleton with copper phthalocyanine (Fig. 3b and 3c) with the spectra of a sample of H. communis (Fig. 3d) and CuPC (Fig. 3a), it is evident that the CuPC macrocycle carbons appear as a series of lines.
in the range 120–130 ppm in the spectra of samples 1 and 2. Furthermore a slight downfield shift movement of the alkyl carbons of the marine sponge skeleton provides additional characterization of the new materials.

### 3.4 FTIR

The results of FTIR analysis of marine sponge skeleton prior to and after the adsorption process, and of CuPC, are presented in Fig. 4. The detailed characterization of the *H. communis* skeleton can be found in our previous work [47]. Many differences appear in the spectrum after dye adsorption, especially below 1200 cm⁻¹, compared with the *H. communis* spectrum. The most important changes related to the stretching asymmetric vibrations of sulfonic acid salts (–SO₃⁻M⁺) occurring in the wavenumber range 1250–1140 cm⁻¹ in the form of a broad band divided into a few smaller peaks. The position of these signals is strongly dependent on the nature of the metal ion which is incorporated in the –SO₃⁻ group, as reported earlier in [48]. The effect of the type of carbon atom (alkyl or aryl) connected to the sulfur atom on the position and shape of these bands is much less significant. Additionally, it should be noted that an additional signal is present in the spectrum of the CuPC-HcS material at 1026 cm⁻¹. This peak is shifted in comparison with the spectrum of the crude dye (maximum at 1032 cm⁻¹), which proves the effective adsorption of the CuPC [13]. Furthermore, a signal confirming deposition of the dye, absent from the spectrum of *H. communis*, is present at 1339 cm⁻¹, generated by stretching vibrations of the –C=C–N– bonds in indole rings. In the CuPC-HcS spectrum a series of specific bands are observed at wavenumbers 746, 699, 649 and 599 cm⁻¹, which come from the interactions between Cu and its ligands. Additionally, the broad and strong signal in the range 3500–3200 cm⁻¹ in this spectrum can be attributed to stretching vibrations of –OH and –NH groups. This signal has a different shape than in the spectra of the materials before the adsorption process. A slight shift in the maximum of this band suggests the formation of chemical bonds (hydrogen bonds) between the sponge and the phthalocyanine dye.

### 3.5 EDS

Table 2 shows the results of energy dispersive spectroscopy (EDS) analysis for *H. communis* skeleton, copper phthalocyanine and selected samples obtained after the adsorption process (sample 1: pH=2, 120 min, 500 mg/L; sample 2: pH=2, 120 min, 400 mg/L; sample 3: pH=2, 120 min, 300 mg/L).

The *H. communis* skeleton, as well as CuPC, consists mainly of carbon and nitrogen, but these elements are not shown in the table. The data given in Table 2 indicate the presence of oxygen, sodium, aluminum, silica, sulfur, chlorine, iodine and calcium. These elements are naturally occurring in the *H. communis* skeleton. The occurrence of elements at low concentration (I, Cl, S, Ca, Al) is in accordance with previously published reports [49,50] and implies that some of the spongin-built amino acids may contain heteroatoms. However, the chemical composition of spongins has not yet been precisely determined. In the measured region of the samples after the adsorption...
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...process we observe the presence of Cu atoms, which provides direct confirmation of the effectiveness of the adsorption process.

### 3.6 TG

Figure 5 shows TG curves for the *H. communis* skeleton (*HcS*), copper phthalocyanine tetrasulfonic acid (CuPC), and the obtained hybrid material (CuPC-*HcS*).

Thermal decomposition of sulfonated phthalocyanine proceeds in a few steps. The first slight mass loss (about 10%) is probably connected with loss of moisture (up to 200 °C). Between 430 and 530 °C, the material had lost another 10% of its mass, the loss and fragmentation of substituent units of the environment of the phthalocyanine molecule occurs [51]. Studies [52] have found that in the range

![Figure 5: TG curves of thermal decomposition of the *H. communis* skeleton, copper phthalocyanine and selected sample obtained after the adsorption process (pH=2, 120 min, 400 mg/L).](image)

| Element content (wt.%) | *H. communis* | CuPC | SAMPLE 1 | SAMPLE 2 | SAMPLE 3 |
|------------------------|---------------|------|----------|----------|----------|
| O                      | 68.42         | 22.06| 74.77    | 73.48    | 68.48    |
| Na                     | 0.99          | 26.18| 1.70     | 1.06     | 1.07     |
| Al                     | 6.12          | 0.59 | 3.65     | 3.99     | 4.97     |
| Si                     | 6.98          | 1.03 | 1.41     | 5.11     | 2.28     |
| S                      | 5.91          | 31.45| 8.63     | 9.50     | 11.97    |
| Cl                     | 0.96          | 6.81 | 5.63     | 5.07     | 7.09     |
| Cu                     | -             | 11.88| 0.31     | 0.28     | 0.19     |
| K                      | -             | -    | 2.31     | 1.45     | 3.41     |
| I                      | 9.20          | -    | 1.51     | 0.04     | 0.28     |
| Ca                     | 1.42          | -    | 0.09     | 0.03     | 0.27     |
| Total                  | 100.00        | 100.00| 100.00   | 100.00   | 100.00   |

Table 2: Quantification of elements in the analyzed marine sponge skeleton, copper phthalocyanine and selected samples.

![Figure 4: FTIR spectra of the purified *H. communis* skeleton, CuPC and dye adsorbed onto sponge skeleton (pH=2, 120 min, 400 mg/L), in different wavenumber ranges.](image)
530–730 °C rupture of macroheterocycles takes place. The residues remaining after thermal decomposition correspond to the metal (in this case copper) oxides [53].

The rate of degradation of marine sponge skeleton is higher than that of CuPC. This is a result of the thermal decomposition of spongin. As observed on the TG curve, the obtained hybrid material undergoes two stages of mass loss: the first below 120 °C, and the second starting at 230 °C to reach a plateau near 560 °C. These can be attributed respectively to water loss and degradation of the protein-like support. The total mass loss in the case of HcS alone (73%) is higher than in the case of CuPC-HcS (67%).

### 3.7 Microscopy observations

The images from light, fluorescent and SEM microscopes of samples before and after the adsorption process are presented below. The adsorption process conditions were as follows: pH=2, 120 min, 400 mg/L.

It is reported in the literature [54] that autofluorescence is usually a superposition of fluorescence from a mixture of individual fluorescent molecules (fluorophores). Fluorophores such as amino acids (e.g. tyrosine) emit fluorescent light due to heterocyclic aromatic rings (such structures are also present in spongin) or conjugated double bonds within their molecular structures. *H. communis* fibers exhibit photoluminescence, in blue, green as well as red light. A decrease in fluorescent intensity is clearly visible especially in the case of red light, which provides indirect confirmation that the adsorption is a chemical process (Fig. 6).

Fluorescence of some other Demospongiae species have been reported, but the measurements were made *in situ* and fluorescence was caused by symbiotic or commensal algae or cyanobacteria on the sponge skeletons [55].

Although the photographs from the light microscope imply that the spongin fibers are entirely covered, the SEM images reveal that there is not a homogenous layer of CuPC on the fibers. The bundle of fibrils forming the spongin fibers is still visible (Fig. 7).

### 3.8 Catalysis

Electro- and sonochemical reactions or oxidation by ozone are sometimes used to remove Rhodamine B, but the most frequently used methods are adsorption and photodegradation. Very often porphyrin or phthalocyanines are used as catalysts in these processes. The photodegradation process is very often enhanced by using an external oxidant, e.g. hydrogen peroxide [56-58].

To investigate the catalytic performance of the prepared heterogeneous catalysts and the influence of various factors on RB elimination, a number of experiments were carried out. We monitored the photodegradation of RB molecules under UV irradiation (190–300 nm) by measuring the UV-
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Vis spectra of filtrate solutions. *H. communis* skeleton is capable of adsorbing dyes, as was demonstrated above, thus it is possible that RB will also be adsorbed on this support. According to the results presented in Fig. 8 (curve b), the adsorption of Rhodamine B on the sponge skeleton does indeed take place, and the efficiency of the process reaches 32%. This parameter is even higher (65%) when CuPC-HcS (obtained from dye solution at concentration of 400 mg/L at pH=2 for 4 h) is used as the adsorbent (Fig. 8, curve d). A possible explanation of this effect (that sponge with previously adsorbed dye adsorbs better than the pure spongin) may be that functional groups of CuPC interact with the cationic dye RB by electrostatic interaction.

UV irradiation itself does not have any influence on RB degradation (Fig. 8, curve a). The effect is observed in the presence of H$_2$O$_2$ (62%; Fig. 8, curve c) and CuPC-HcS (75%; Fig. 8, curve e). As expected, the addition of H$_2$O$_2$ improves the efficiency of decolorization, but is not effective enough to oxidize RB if used alone. Up to 95% of the RB was photodegraded when both CuPC-HcS as catalyst and H$_2$O$_2$ as oxidant were present, and the concentration of RB decreased quickly within 1 h (Fig. 8, curve f).

A possible mechanism of dye degradation under irradiation is proposed based on the reported mechanism involving both H$_2$O$_2$ and CuPC. The action of metalphthalocyanine causes several successive reactions with the excited singlet and triplet form of metalphthalocyanine and oxygen, which finally decompose the dye [13,59]:

\[
\text{MPc} + \text{hv} \rightarrow \text{°MPc}^* \rightarrow \text{°MPc} \quad (I)
\]

\[
\text{°MPc}^* + \text{O}_2 \rightarrow \text{°O}_2^* + \text{MPc} \quad (II)
\]

\[
\text{°O}_2^* + \text{dye} \rightarrow \text{degradation product} \quad (III)
\]

According to [60,61], simultaneously the photolysis of H$_2$O$_2$ generates the hydroxyl radical (equation IV) and other reactive oxygen species via the corresponding propagation reactions (V–VII):

\[
\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2\text{OH}^* \quad (IV)
\]

\[
\text{H}_2\text{O}_2 + \text{OH}^* \rightarrow \text{HO}_2^* + \text{H}_2\text{O} \quad (V)
\]

\[
\text{H}_2\text{O}_2 + \text{HO}_2^* \rightarrow \text{OH}^* + \text{O}_2 + \text{H}_2\text{O} \quad (VI)
\]

\[
2 \text{OH}^* \rightarrow \text{HO}_2^* + \text{O}_2 \quad (VII)
\]

Moreover CuPC can act as a catalyst and activate the H$_2$O$_2$ molecules:

\[
\text{Cu}^{II}\text{Pc} + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^{II}\text{Pc} + \text{OH}^* + \text{OH}^* \quad (VIII)
\]

As stated in [62] there is a possibility for copper to exist as Cu(III) in a complex with porphyrin. The produced hydroxyl radical oxidizes RB:
RB + OH• → [RB(OH•)] (IX)
[RB(OH•)] → degradation product (X)
RB + hv → RB* (XI)
RB* + O₂ → RB+• + O₂• (XII)
RB+• + O₂ → degradation product (XIII)

The hydroxyl radical generated from hydrogen peroxide reacts with RB (equation IX) and gives an intermediate product, which decomposes into the final oxidation product (X). Furthermore, irradiation with UV light causes the excitation of rhodamine (XI). The produced RB* reacts with oxygen, and as a result the cationic radical form of the dye (RB+•) and superoxide (O₂•) are formed (XII). Subsequently, via further reaction with oxygen, the dye is degraded [14,63]. The oxidation products of RB are thoroughly investigated and described in [64,65].

Zhang et al. investigated the photocatalytic activities of 2,9,16,23-tetra-nitrophthalocyanine copper(II) (TNCuPc)/TiO₂ composites with respect to Rhodamine B degradation. The TiO₂ nanofibers function as an electron trap for the excited surface-adsorbed TNCuPc dye. The trapped electron subsequently induces the generation of active oxygen species, which degrade Rhodamine B with high efficiency, up to almost 90% [57]. Shang et al. also showed the effect of copper phthalocyanine tetrasulfonic acid-sensitized TiO₂ on Rhodamine B degradation [58]. The authors achieved total degradation efficiency, although the process required the hydrothermal synthesis of the catalyst, which increases operational costs in comparison with the fast and facile adsorption technique described in the present work. The authors confirmed that the presence of copper phthalocyanine considerably enhanced the photocatalytic activity of titanium dioxide. Another study on the synthesis of a titanium dioxide–copper phthalocyanine hybrid composite and its use in decomposition of Rhodamine B under UV irradiation was published by Mekprasart et al. The system obtained cause decomposition of over 80% of the dye. The significant improvement in photocatalytic activity in the case of the hybrid composite may be linked to the enhancement of optical absorption and the inhibition of electron–hole recombination caused by the presence of CuPC in the TiO₂ matrix [66].

In the cited works, copper phthalocyanines were immobilized on TiO₂, which itself is photocatalytically active. Thus the results obtained represent a combination of the photocatalytic properties of both materials. By contrast, in our study we used a biopolymer matrix which is inert under UV irradiation. Hence the presented results relate only to the activity of the phthalocyanine in the dye decomposition process.

4 Conclusions

In this study a copper phthalocyanine–H. communis marine sponge skeleton hybrid material (CuPC-HcS) was produced with high efficiency by an adsorption process. Adsorption is a fast and simple way to obtain such systems, and does not require sophisticated equipment. The highest efficiencies were obtained from an acidic solution, which suggests that electrostatic interactions occur between the dyes and support. Furthermore, results from spectroscopic analysis indicate the formation of hydrogen bonds. The product was used in the photobleaching of Rhodamine B solution. In these reactions CuPC-HcS serves as a photosensitizer and H₂O₂ as an external oxidant. Adsorption and simultaneous catalytic oxidation are responsible for RB removal, and all of the analyses performed suggest that it is highly desirable to integrate the advantages of both high adsorption capacity and photocatalytic activity into a single compound.

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