

Microwave-assisted valorization of pig bristles: towards visible light photocatalytic chalcocite composites

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Waste valorization for the production of valuable materials is of great importance for a sustainable development. Herein, a new green methodology for the synthesis of photocatalytically active copper sulfide (Cu₂S) carbon composites using pig bristles is reported. The catalyst was prepared via microwave-assisted methodology using ethylene glycol as solvent, pig bristles as sulfur and carbon source, and copper chloride as metal precursor. Cu₂S carbon composites (denoted as *pb*-Cu₂S, where “*pb*” states for “pig bristle”) were characterized by XRD, N₂ physisorption, EDX and UV-Vis spectroscopy. In order to validate the practical utilization of pig bristles-derived chemicals, the photocatalytic degradation of methyl red using *pb*-Cu₂S was investigated under white, blue, green and red visible light irradiation.

1. Introduction

Moving our society dependence away from petroleum to renewable biomass resources is one of the most important challenges for a future development of sustainable industries.¹ An extremely captivating challenge is the valorization of bio-wastes for the production of valuable chemicals.² Considering EUROSTAT data (EU 28 countries), ca. 250 million pigs were slaughtered in the European Union in 2017.³ Since each slaughtered pig delivers ~0.9 kg of pig bristles, approximately 225 k tons of wasted pig bristles are produced annually.⁴ Despite such large quantities of waste products, research on new ways of valorization of pig bristles has not received the pulse to upsurge to date. Boiled (sanitized) pig bristles are exclusive commercial products currently employed in brushes factories. Therefore, as every commercially available product, boiled pig bristles could be easily collected and studied in laboratory scale aiming to provide potential roadmaps for the valorization of wasted pig bristles at industrial scale.

Only counted reports about the reutilization of wasted pig bristles are available in literature. Importantly, they are limited to the reutilization of pig bristles as sources of fodder food supplements (*e.g.* for the high content of keratin).⁴⁻⁷

Herein we report an unprecedented simple route for the valorization of pig bristles for the production of a high performance material as photocatalyst. Specifically, the synthesis of Cu₂S carbon nanocomposite (denoted as *pb*-Cu₂S,

where “*pb*” states for “pig bristle derived”) was accomplished using pig bristles as sulphur and carbon source.

Since biorefineries should be based on new, highly efficient and sustainable strategies for biomass conversion,^{1,8-10} we have also employed a microwave approach for the synthesis of *pb*-Cu₂S. Microwave-assisted reactions offer several advantages that include fast reaction time, the possibility to obtain higher yields, different selectivity as well as the potential to accomplish reactions/chemistries that generally do not take place under conventional heating conditions.¹¹⁻¹⁵ In addition, the unique characteristics of microwave assisted reactions are attracting lot of attentions for the valorization of biomass.¹⁶⁻²⁰

Based on our experience in microwave chemistry, we have developed an environmentally friendly, simple and straightforward method for the valorization of pig bristles under microwave-assisted conditions.^{17, 18, 21-24} A low-toxicity mixture of ethylene glycol, copper chloride and pig bristles, was treated in a microwave oven to directly obtain *pb*-Cu₂S avoiding any calcination steps. Where appropriate, a small amount of sodium hydroxide was used to optimize the synthesis and favour the formation of copper sulphide in the form of the more photocatalytically active Chalcocite crystals. The material was characterized by XRD, N₂ physisorption, EDX and UV-Vis spectroscopy, demonstrating the formation of Cu₂S carbon composites.

In order to validate the practical utilization of pig bristles-derived chemicals, *pb*-Cu₂S was tested as photocatalyst.

Indeed, photochemistry is widely studied for harvesting the sunlight radiation with clean and green conversion to chemical power through different materials.²⁵⁻²⁷ In detail, semiconductors with a specific band gap can resonate if irradiated with a light of a specific wavelength producing electrons and holes, consequently generating active hydroxyl radicals in solution.²⁸ These hydroxyl radicals can degrade organics by advanced oxidation processes (APOs).²⁹

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Considering that Cu_2S is a p-type semiconductor with a narrow bulk band gap of 1.2 eV, the synthesized material could be a suitable photocatalyst under visible light irradiation.³⁰ The photocatalytic activity of *pb*- Cu_2S was tested in the photodegradation of a toxic and contaminant colorant. Truly the environmental impact caused by dye used in the textile industries is one of the most sensible: because of their toxicity and ability to reduce the uptake of light; dyes interfere with the photosynthesis of aquatic plants hence having a direct impact in the oxygen content of water sources. Therefore, the degradation of contaminant dyes is of remarkable importance. The photodegradation of methyl red dye (CI 13020) catalysed by *pb*- Cu_2S , was investigated under visible light and, in order to deeply understand the activity of the catalyst in function of specific wavelength, under red, green, and blue light. Lighting emitting diodes (LEDs) were employed pointing to the design of an efficient photoreactor.³¹

2. Experimental sections

Copper (I) chloride (CuCl , 98.8%) was purchased from Panreac Quimica SLU, Barcelona, Spain. Ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$, 99.9%), methyl red (4-Dimethylaminoazobenzene-2'-carboxylic acid), TiO_2 (Titanium (IV) oxide nanopowder, Aeroxide® P25), sodium hydroxide (NaOH) and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, 99.5%) were purchased from Sigma-Aldrich Inc., St. Louis, MO, USA. All reagents were used without any further purification.

2.1 Synthesis of *pb*- Cu_2S with microwave assisted method

In a typical synthesis, pig bristle (1.5 g, cut in pieces of ~ 0.5 cm) and the metallic precursor CuCl (480 mg, 4.85 mmol) were added to ethylene glycol (20 mL) in a 50 mL Teflon microwave tube equipped with a stirrer. Eventually, different amount of NaOH (up to 100 mg, 2.5 mmol) were added to the mixture to favour the formation of the more photocatalytically active Chalcocite crystals. The mixture was sequentially stirred for 10 minutes at 700 rpm at room temperature. Successively, the tube was introduced into a Milestone Ethos D (Milestone Srl, Italy) microwave reactor. The tube was irradiated with microwaves at 500 W using a temperature ramp of 3 minutes and maintained at maximum 200°C for one additional minute. After the reaction, the mixture was cooled to room temperature naturally. The precipitate was filtrated and washed with 10 mL ethanol and 10 mL acetone and oven-dried (100°C) for 24 h.

2.2 Synthesis of *pb*- Cu_2S with conventional heating

To avoid any safety issue (please see below paragraph 2.3 for details) the synthesis of optimized *pb*- Cu_2S under conventional heating was carried out in an oil bath. Pig bristle (1.5 g, cut in pieces of ~ 0.5 cm), sodium hydroxide and the metallic precursor CuCl (480 mg, 4.85 mmol) were added to ethylene glycol (20 mL) in a 250 mL round flask equipped with a stirring bar and a reflux. The mixture was heated in an oil bath for 6 h at 200°C. The precipitate was filtrated and washed with 10 mL ethanol and 10 mL acetone and oven-dried (100°C) for 24 h.

2.3 IMPORTANT Warning notes about mixing ethylene glycol and NaOH

Despite no significant pressure increases nor safety issues (overtemperature, pressure, explosions, *et.*) were never detected during all the experiments, an important note on the utilization of ethylene glycol mixed with NaOH should be stated. Indeed, during late 60s, a few incidents occurred in some industrial plants while operating with ethylene glycol and sodium hydroxide.³² Even though the toxically problems were related to other components in the reactors (e.g. dioxins) and not to the mixture of EG and NaOH , some important safety procedures must be mentioned. As demonstrated by Milnes, an exothermic decomposition of ethylene glycol mixed with NaOH could start in the 230°C range and rapidly increases to 400°C, realising white vapour.³³ The exothermal reaction is related to the decomposition of sodium 2-hydroxyethoxide ($\text{NaOCH}_2\text{CH}_2\text{OH}$), which rapidly forms the vapour. It should be notice that the amount of sodium hydroxide should be quite high to form enough quantity of the sodium 2-hydroxyethoxide and cause a rapid vapour release. For example, in the cases of industrial incidents, the amount of ethylene glycol and NaOH was 3:1 in weight.³² In order to operate in safe conditions and avoid any uncontrollable issue, all the reactions were made operating at maximum 200°C for maximum four minutes. In addition, the maximum weight ratio of ethylene glycol and NaOH was set to 180:1. In order to avoid any explosions, all the operation were made using a Teflon tube equipped with a safe vale (48 bar max pressure). All the reactions were carefully monitored, controlling both internal and external temperature, and setting safe temperature limits of 200°C as internal temperature limit and 60°C as external temperature limit. Due to the impossible control of the online internal temperature of an autoclave and the absence of any safe vale, no reactions under conventional heating were carried out in closed containers.

2.4 Characterization

Powder X-ray diffraction (XRD) pattern of *pb*- Cu_2S was recorded using a Bruker D8 DISCOVER A25 diffractometer (PanAnalytic/Philips, Lelyweg, Almelo, The Netherlands) using $\text{CuK}\alpha$ ($\lambda=1.5418\text{\AA}$) radiation. Wide angle scanning patterns were collected over a 2θ range from 10° to 80° with a step size of 0.018° and counting time of 5 s per step.

Textural properties of the samples were determined by N_2 physisorption using a Micromeritics ASAP 2020 automated system (Micromeritics Instrument Corporation, Norcross, GA, USA) with the Brunauer-Emmet-Teller (BET) and the Barret-Joyner-Halenda (BJH) methods. The samples were outgassed for 24 h at 100 °C under vacuum ($P_0 = 10^{-2}$ Pa) and subsequently analysed.

Scanning electron microscopy images were recorded with a JEOL JSM-6300 scanning microscope (JEOL Ltd., Peabody, MA, USA) equipped with Energy-dispersive X-ray spectroscopy (EDX) at 15 kV at the Research Support Service Center (SCAI) from University of Cordoba.

2.5 Photocatalytic activity measurements

The photocatalytic activity of *pb*-Cu₂S was evaluated in the degradation rate of methyl red (C.I. 13020) under visible-light irradiation. The experimental set up consisted in a 50 mL Pyrex glass tube irradiated by a commercially available LED lamp 6A. The distance between the lamp and the tube was set up to 2 cm. (see S.1 for a schematic illustration of the reactor). The mixture was irradiated with blue (peak centred at 465 nm), green (peak centred at 515 nm), red (peak centred at 630 nm) and white (as simultaneous irradiation of the three light) visible lights. Fig. 1 shows the emission spectrum of LED lamp: the three different colour components and the white light.

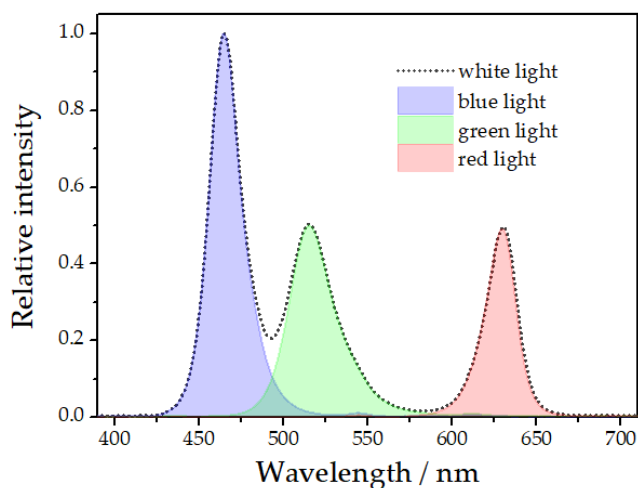


Fig. 1 Emission spectra of the LED lamp and the three major light components used in the photocatalytic degradation of methyl red

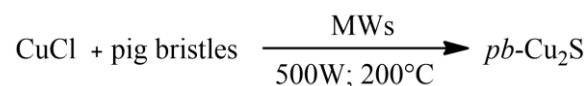
In a typical experiment, 10 mL ethanol solution of methyl red (50 ppm) was mixed with 5.0 mg of *pb*-Cu₂S in a 50 mL Pyrex glass tube equipped with a stirrer. Before irradiation, the mixture was sonicated for 30'' in an US bath in order to achieve a good homogenization of the solution. After the photoreaction runs, samples of 0.35 mL were withdrawn from the solution at regular time intervals and diluted in 2 mL ethanol. Before UV-Vis absorption measurements, the solutions were filtrated to remove the catalyst. The quantitative determination of residue methyl red was conducted by measuring the maximum absorption at the maximum wavelength of 405 nm. For comparison, the methyl red degradation was conducted under the same condition without any catalysts and employing commercially available Aeroxil®P25 TiO₂. UV-visible (UV-vis) absorption spectra were recorded using a Lambda 365 UV-Vis Spectrophotometer (PerkinElmer, Waltham, MA, USA).

3. Results and discussion

3.1 Formation of *pb*-Cu₂S

A facile, fast and low toxicity one-pot route is herein reported for the synthesis of Cu₂S carbon composites from wasted pig bristles. As illustrated in Scheme 1, the preparation involved a simple microwave assisted heating step of a mixture of pig

bristles, copper (I) chloride, ethylene glycol and, where appropriate, sodium hydroxide.



Scheme 1 Reaction scheme for the synthesis of *pb*-Cu₂S

The formation of *pb*-Cu₂S could be explained in terms of thermo-degradation of pig bristles, which served as source of sulphur and carbon. As reported by Gonzalo et al., pig bristles are mainly composed of keratin, an insoluble protein packed with cross-linked fibres by disulfide bonds.⁴ The disulfide bonds are found in cysteine, while other amino acids containing sulfur are methionine and cysteic acid. In general, the total amount of sulphur contained in pig bristles could be quantified as ca. 5% wt.^{5, 34, 35} Pig bristles started to decompose upon microwave irradiation at high temperature and sulphur, mainly in the form of ions, was released. Copper sulfide was then formed by combining S²⁻ with Cu⁺ and particles were self-aggregated to minimize the surface energy. During the aggregation step, the particles bind together with pig bristles residual carbon, as observed in SEM images.

Sodium hydroxide was employed in order to optimize the synthesis and accelerate the degradation of pig bristles and the formation of Chalcocite, which was found to be the most photocatalytically active crystalline form of copper sulfide. However, as shown in Fig.2, NaOH was not essential for the formation of Cu₂S. The optimized sample was synthesized using 100 mg of NaOH (2.5 mmol). Based on previous experience, ethylene glycol was chosen for its ideal stabilising behaviour, low toxicity, high boiling point (198°C) and high viscosity under MW heating.²⁴ Aiming to make Cu₂S, the molar amount of sulphur, therefore the amount of pig bristles (1.5 g equals to 2.34 mmol of S), and copper (4.85 mmol) was set up to an ideal 2:1. XRPD and SEM-EDX analysis confirmed the formation of copper sulfide carbon composites.

The synthesis of *pb*-Cu₂S under conventional heating was carried out aiming to investigate the effect of MWs in the formation of the material. Due to safe issues described in paragraph 2.3, conventional heating experiments were ran in an oil bath open vessel at 200°C. The formation of the first crystals of Cu₂S was detected after 6 h of reaction by XRPD analysis. The pattern of the obtained material was compared with the material obtained in the microwave, confirming the efficiency of microwave heating for the crystallization of Cu₂S. (for the XRD patterns comparison, please see S.2).

3.2 Morphology and Properties of *pb*-Cu₂S

Fig.2 shows the XRPD pattern of the prepared *pb*-Cu₂S. Cu₂S was found in all the samples, while the crystalline form of Chalcocite was facilitated by the addition of different amount of NaOH (from 10mg/0.25 mmol to 100mg/2.5 mmol). Considering the pattern of the optimized sample, produced with 2.5 mmol of

NaOH, the most intense diffraction peaks observed at 2θ values of 23.85° , 26.90° , 28.15° , 30.25° , 32.85° , 37.45° , 45.95° , 47.45° , 53.75° and 73.82° could be index to (2 4 2), (1 8 0), (2 6 2), (0 9 1), (0 4 4), (1 11 1), (2 13 1), (6 6 2), (4 0 6) and (0 20 3) planes of Chalcocite Cu_2S with orthorhombic structure (JCPDS 00-023-0961).³⁶ (For a complete list of the peaks and the assigned planes please see Table S.2)

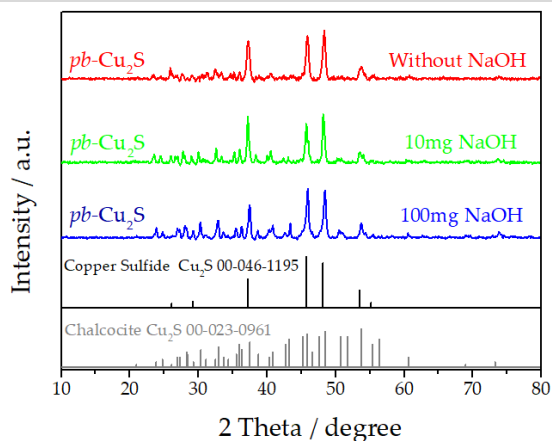


Fig. 2 XRD pattern of $pb\text{-Cu}_2\text{S}$ produced with different amount of sodium hydroxide. All the samples showed copper sulfide, while the increasing of the content of NaOH facilitated the formation of Chalcocite, more photocatalytically active.

The morphology of optimized $pb\text{-Cu}_2\text{S}$ was investigated by SEM and EDX spectrum. Fig.3 shows SEM images of the material. The material exhibited a structure that can be defined as coral-like homogeneous structure where fine granular particles were aggregated together. The structure rose from the fast degradation of the pig bristles, which left fine homogeneous carbon particles residues. The agglomeration of the carbon particles with the Chalcocite built the coral-like structure.

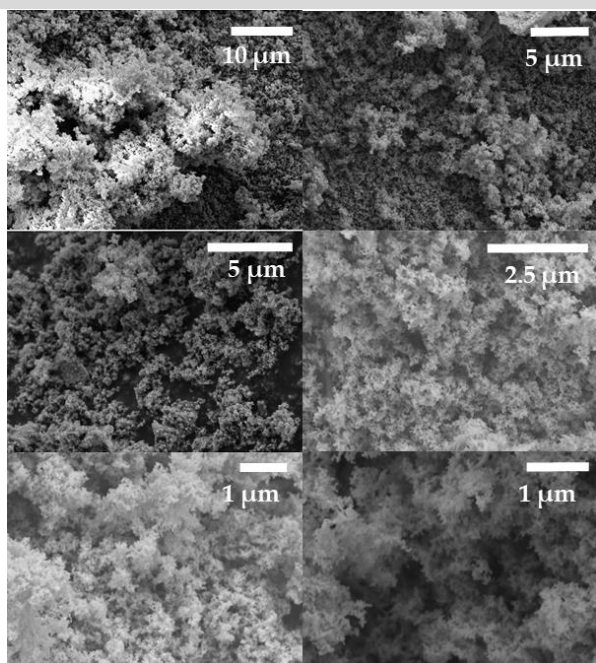


Fig. 3 SEM images of $pb\text{-Cu}_2\text{S}$

SEM-EDX mapping results are summarized in Fig.4. Sulfur atomic content average was measured as $\sim 13\%$, while copper content was determined to be $\sim 31\%$. The atomic ratio about 2:1 between Copper and Sulfur was in line with XRPD analysis, which demonstrated the formation of Chalcocite Cu_2S . The atomic content of carbon was determined to be $\sim 50\%$, or $\sim 20\%$ weight. Except for oxygen, most likely absorbed as CO_2 , no other elements were detected in EDX analysis, pointing to a high purity of the material. The closeness of EDX mapping results in different area demonstrated a good homogeneity of the sample. (For the complete results of EDX mapping, please see S.4)

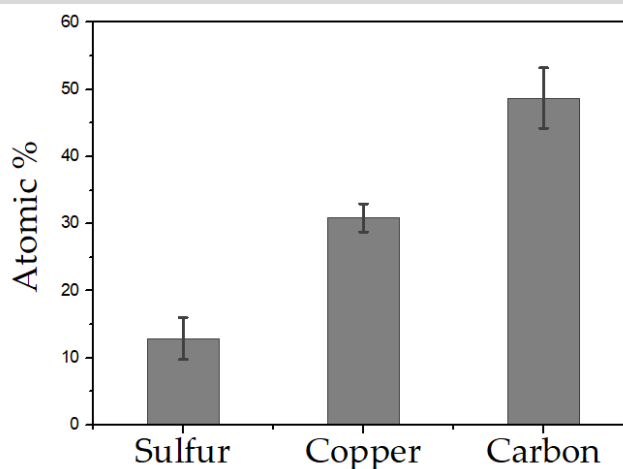


Fig. 4 SEM-EDX mapping results of $pb\text{-Cu}_2\text{S}$

Brunauer–Emmett–Teller (BET) physisorption was conducted to determine the specific surface area of $pb\text{-Cu}_2\text{S}$ carbon composite by nitrogen adsorption–desorption measurements. The BET surface area was found to be $17\text{--}20\text{ m}^2/\text{g}$, with isotherms clearly indicating a non-porous material, in good agreement with SEM analysis. (ESI, Figure S.5)

To investigate the optical behaviour of $pb\text{-Cu}_2\text{S}$, UV-Vis absorption spectrum was recorded, and reported in the form of Kubelka-Munk, as shown in Fig.4 A. The spectrum exhibited an adsorption edge at ca. 1050 nm , remarkably higher as compared to reported Chalcocite phases.^{30, 37} This can be explained by the presence of carbon. The spectrum clearly showed that the $pb\text{-Cu}_2\text{S}$ could absorb visible light and hence $pb\text{-Cu}_2\text{S}$ can be a promising photocatalytic material. The optical band gap was obtained by the equation:³⁸

$$(\alpha h\nu)^n = A(h\nu - E_g)$$

To determine the energy bad gap, $(\alpha h\nu)^2$ vs $(h\nu)$ was plotted, as shown in Fig.4 B (" α " was the absorption coefficient, " $h\nu$ " was the photon energy and " A " was a constant, " E_g " was the band cap and " n " was either $\frac{1}{2}$ for an indirect transition or 2 for a direct transition). The plot gave a straight line whose intercept on the energy axis resulted in the direct energy gap. Fig. 4 C

shows the plot of $(\alpha h\nu)^{1/2}$ vs $(h\nu)$ used to calculate the indirect band gap. The band gap obtained for *pb*-Cu₂S were 1.17 eV (direct) and 0.85 eV (indirect), remarkably reduced as compared to reported values for Chalcocite.³⁹

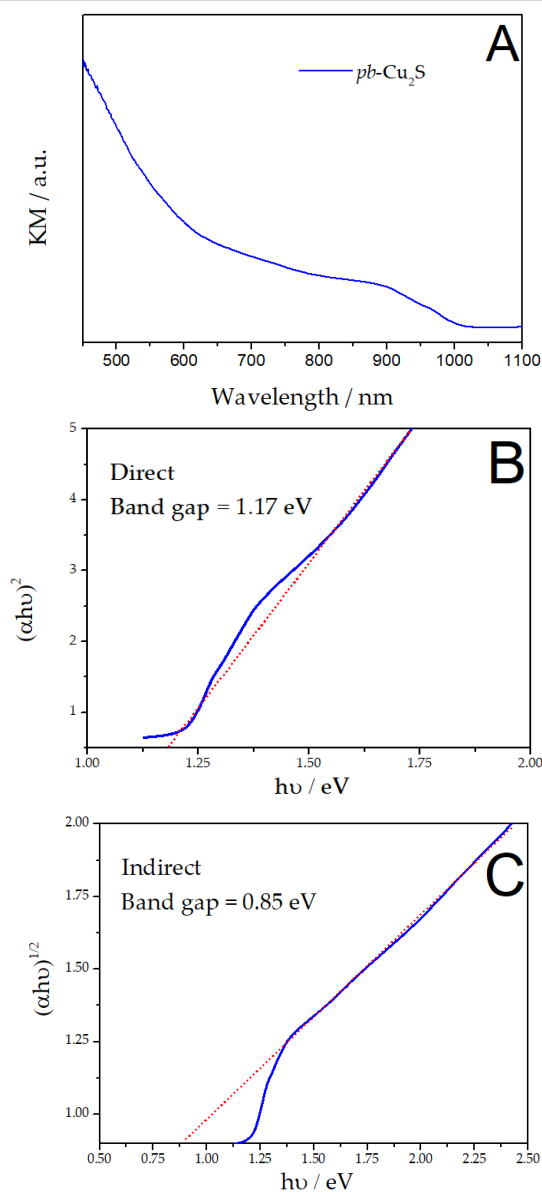


Fig. 4 Optical measurements of as-synthesized *pb*-Cu₂S. (A) Kubelka Munk spectra. (B) Plot of $(\alpha h\nu)^2$ vs photon energy $h\nu$ for determination of direct band gap (C) Plot of $(\alpha h\nu)^{1/2}$ vs photon energy $h\nu$ for determination of indirect band

3.3 Photocatalytic activity measurements

The photocatalytic activity of *pb*-Cu₂S was demonstrated in the photodegradation of a model organic dye. Methyl red (CI 13020), a commercially available dye used in industry, was chosen as model compound for pollutants removal. In fact, methyl red is an environmentally recalcitrant, possible carcinogen and toxic agent, and its degradation has important impact.

Despite all the materials showed photocatalytic properties, most active *pb*-Cu₂S was in the form of Chalcocite (please see S.6 for a comparison of the photocatalytic activity of *pb*-copper sulfide and *pb*-Chalcocite).

Two different sets of blank experiments for the dye solution were performed. The activity of optimized *pb*-Cu₂S was compared with the activity of commercial Aeroxil®P25 TiO₂ and with a blank run (to ascertain potential photobleaching of the dye) in the same reaction conditions. Results are shown in Fig.5 and clearly point out a remarkable dye degradation performance of *pb*-Cu₂S under white LEDs irradiation (black line), particularly with a negligible degradation observed for P25 (dotted black line). *pb*-Cu₂S could also provide certain photodegradation activity at different wavelengths (465, 515 and 630 nm).

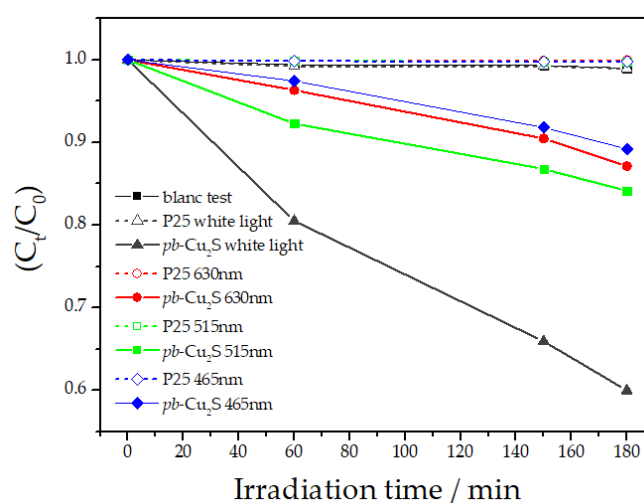


Fig. 5 Photodegradation of methyl red catalysed by *pb*-Cu₂S in function of time at different wavelength irradiation

To better understand the activity of the catalyst, the kinetic parameters were evaluated by pseudo first-order model: $\ln(C_0/C_t) = kt$.³⁰ Results are illustrated in Fig.6 while k and R^2 data are given in table 1. The closeness of R^2 to 1 indicated a good fitting of the data to pseudo-first order reaction.

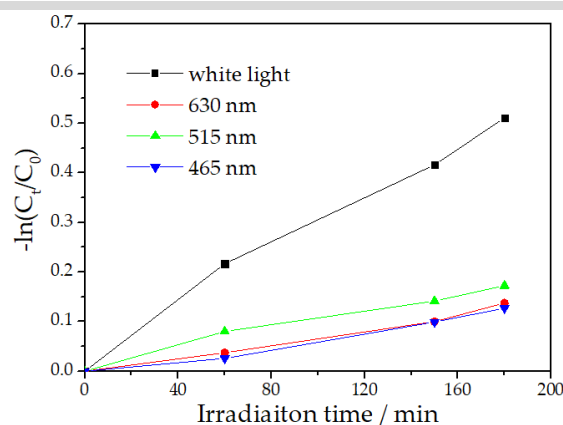


Fig. 6 Plot of $-\ln(C_t/C_0)$ versus irradiation time

Table 1 k and R² data

Irradiation light	k / min ⁻¹	R ²
White	0.00273	0.98924
630 nm	7.42643E-4	0.98748
515 nm	9.11448E-4	0.98115
465 nm	6.31303E-4	0.98513

4. Conclusions

An unprecedented approach for the valorization of pig bristles to valuable photoactive materials has been developed. The use of environmentally friendly reagents and the utilization of microwaves provide an environmentally sound, facile, efficient and fast synthetic route. Pig bristles were used as sulphur and carbon source for the synthesis of copper sulfide carbon composite. The material was used as photocatalyst for the degradation of methyl red, with promising results that may pave the way to the utilisation of *pb*-Cu₂S in a wide range of applications not limited to the field of photochemistry.

The new method successfully demonstrated, for the first time, the possibility to valorize wasted pig bristles. We believe the proposed eco-friendly approach could act as springboard for the development of additional applications for wasted pig bristles that will be reported in due course.

Conflicts of interest

The authors declare no conflicts of interest.

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