



# Heterojunction CuO thin coated CaO derived from eggshell waste for fast removal of organic pollutants from water under visible light

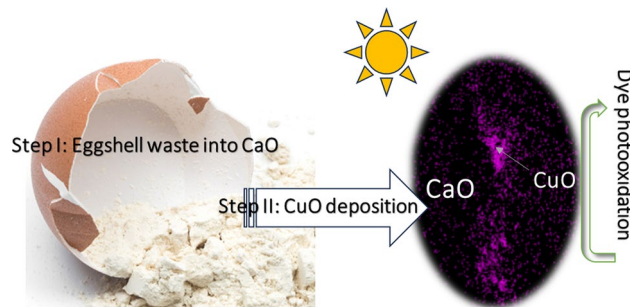
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## Abstract

The conversion of food and agro-industrial wastes to produce useful products is one of the goals of economic and sustainable development, as also evidenced in the 2030 Agenda for Sustainable Development, adopted by all United Nations Member States in 2015. This work aims to study the transformation of  $\text{CaCO}_3$  based eggshell waste (ES) into a face centered cubic oxide form (namely, CaO), followed by CuO coating to be used as photocatalytic material (ES@CuO) for fast removal of basic fuchsin (BF) dye from water under visible light. Different ES@CuO samples with different CuO amounts (2.5, 5 and 10%, respectively) and calcined at different temperatures (600, 800, and 1000 °C) were prepared by hydrothermal method. Samples with CuO from medium to high amounts (5 and 10%) demonstrated excellent photocatalytic activity, as compared to low CuO amount (2.5%). In addition, the samples calcined at higher temperature (800 and 1000 °C) exhibited superior degradation rates, reaching 88.11% and 88.33%, respectively. The effect of operating parameters was investigated to understand the behavior of ES@CuO under different conditions. ES@CuO shows rapid removal of BF which combines adsorption and photooxidation, wherein the removal rate reaches up 99% for a BF dye concentration of 100 ppm within 30 min using 75 mg/L of ES@CuO<sub>5%</sub>. ES@CuO exhibits superior adsorption ability and excellent photoproducted charges transfer which provide synergistic effects to boost the quick removal of dye from water. The finding of this investigation encourages valorizing food wastes into sustainable materials for water remediation.

## Graphical abstract



**Keywords** Food waste valorization · Solar photocatalysis · CuO coated eggshell · Water treatment · Adsorb and shuttle process · Sustainable development

## Introduction

Over the recent decades, punctual environmental, energy and economic restrictions have been launched to reach the goals of sustainable development (Djellabi et al. 2022). The valorization of wastes into high value production and

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useful materials is one of the promising strategies which has received a lot of attention from both scientific and industrial communities (Ambaye et al. 2023; Galloni et al. 2024). The conversion of wastes into useful products reduces the content of solid wastes in our environment and meanwhile it opens alternative clean and economic produce sources (Aboagye et al. 2023; Andhalkar et al. 2023). Food biowastes are widely available with huge quantities especially in large population cities. Its valorization into different useful materials is very highly recommended from environmental and economic points of view (Nayak and Bhushan 2019). Eggs are an essential and globally consumed food for household and industrial applications. It offers several health benefits, including supporting the healing of body tissues and maintaining a healthy immune system. About 8 million tons of eggshell wastes are globally produced each year, and thrown away as garbage in landfills, becoming a source of a serious environmental issue (De Angelis et al. 2017). Eggshells (ES) represent an abundant source of calcium carbonate and exhibits large number of high value products such as bioactive elements and minerals with high commercial interest (Zaman et al. 2018). Several research studies have been reported to extract natural calcium from eggshells to fortify foods and manufacture vitamins and dietary supplements (Waheed et al. 2019; Singh et al. 2021).

Within the context of biomass valorization, many studies have examined the possible use of eggshell biowaste as a catalyst or/and material in different applications, such as metal matrix composites (Vickers 2017; Ononiwu and Akinlabi 2020), bioactive compounds in anaerobic fermentation (Luo et al. 2020), and even in water treatment (Carvalho et al. 2011; Laca et al. 2017). Li et al. (Mandado et al. 2006) previously demonstrated the effective adsorption of reactive dyes on eggshell based adsorbents. In another study reported by Zhai et al. (2022),  $\text{CaCO}_3$ -containing material generated from eggshell exhibits excellent adsorption ability for dye removal from water. Modified eggshell composites have been widely reported for adsorption or/and (photo)-catalytic applications. Dickon et al. created an eggshell/ $\text{MgFe}_2\text{O}_4$  matrix structure allowing the removal of the antibiotic doxycycline from polluted waters (Li et al. 2017). Other researchers have used eggshells to develop membranes for wastewater treatment, serving as both auxiliary and primary material for photocatalytic degradation (Cao et al. 2020; George et al. 2020; Zou et al. 2020). Eggshell has been coated with many photocatalytic materials for enhanced water treatment such as with  $\text{TiO}_2$  (Dzinun et al. 2022),  $\text{BiOBr}$  (Deng and Guan 2013),  $\text{ZnO}$  (Elsayed et al. 2021),  $\text{Cu/Fe}_3\text{O}_4$  (Nasrollahzadeh et al. 2016),  $\text{Bi}_2\text{O}_3$  (Li et al. 2018) and so on. Several studies proved that  $\text{CaO}$  can be obtained from eggshell to be used as a photocatalytic material (Sree et al. 2020; Eskikaya et al. 2022).

The aim of this work is to prepare  $\text{CuO}$ -coated  $\text{CaO}$  material ( $\text{ES@CuO}$ , obtained from eggshell waste) for the photocatalytic removal of basic fuchsin (BF) under visible light irradiation. The optimization of the synthetic parameters, including  $\text{CuO}$  ratio and calcination temperature, was carried out to maximize the photocatalytic performance. The effect of operational factors such as pH solution, photocatalyst dosage, contact time, initial dye concentration, and temperature was investigated to determine the optimal conditions. The performance of  $\text{ES@CuO}$  in dark and under light irradiation was compared and discussed. The regeneration and recycling of the various  $\text{ES@CuO}$  were studied to determine the long-term stability of the material.

## Materials and methods

Basic fuchsin (BF) and copper (II) chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) used in this study were obtained from Sigma-Aldrich-Fluka (Saint-Quentin, Fallavier, France). Chicken eggshell waste was collected from a local restaurant in Souk Ahras province, Eastern Algeria. The pH adjustment of the solution was controlled by a pH Meter (HANNA HI98125). The dye used in this study is basic fuchsin (BF), also known as triaminotriphenylmethane ( $\text{C}_{20}\text{H}_{20}\text{ClN}_3$ ).

### Preparation of ES biomaterial

The collected eggshells were thoroughly washed with tap water to remove any surface contaminants. The clean shells were then boiled in distilled water for 15 min to remove all remaining bacteria and the inner membranes were manually separated. The membraneless biomaterial was then dried in an oven at  $105^\circ\text{C}$  for 24 h. The recovered amount was crushed and sieved to obtain a fine and uniform powder, of which only particles with a size in the 100–250 nm range were used.

### Preparation of $\text{ES@CuO}$ photocatalyst

The  $\text{ES@CuO}$  photocatalysts were prepared at different percentages of  $\text{CuO}$  by the hydrothermal method, which consists in mixing a determinant quantity of ES with a 100 mL solution of copper (II) chloride dihydrate at different concentrations (1, 2, and 4 g/L). The mixtures were then placed under mechanical stirring for 24 h at room temperature, followed by filtration, and transferred to a muffle furnace, where calcination took place at different temperatures (600, 800 and  $1000^\circ\text{C}$ ) for 3 h at a rate of  $12^\circ\text{C}/\text{min}$ . This step was carried out to obtain  $\text{ES@CuO}$  photocatalysts with different  $\text{CuO}$  final percentages (2.5%, 5%, and 10%).



## Characterization

FTIR-ATR spectra were obtained on solid samples with a Bruker Vertex 70 spectrophotometer equipped with Harrick MVP2 ATR cell and DTGS detector (64 scan,  $4\text{ cm}^{-1}$  resolution). FT-Raman spectra were obtained with the same instrument, equipped with the RAMII accessory and Ge detector, by exciting samples with Nd:YAG laser source (1064 nm), with resolution of  $4\text{ cm}^{-1}$ . The morphology of both eggshells (ES) and the photocatalyst morphology and elemental analyses were evaluated by means of a scanning electron microscope operating with a field emission source (FESEM), model TESCAN S9000G (Overcoated, Germany) equipped with a Schottky type FEG source; resolution: 0.7 nm at 15 keV (in In-Beam SE mode) and equipped with EDS Oxford Ultim Max (operated with Aztec software 6.0). The sample was supported on metallic stabs with C tape and then coated with Cr by means of ion-sputtering technique to improve the conductivity of the materials. X-ray diffraction (XRD) data in the 10–90 range was collected with Cu K $\alpha$  radiation using a Philips X'Pert X-ray diffractometer to determine the possible crystalline phase(s) present in the materials.

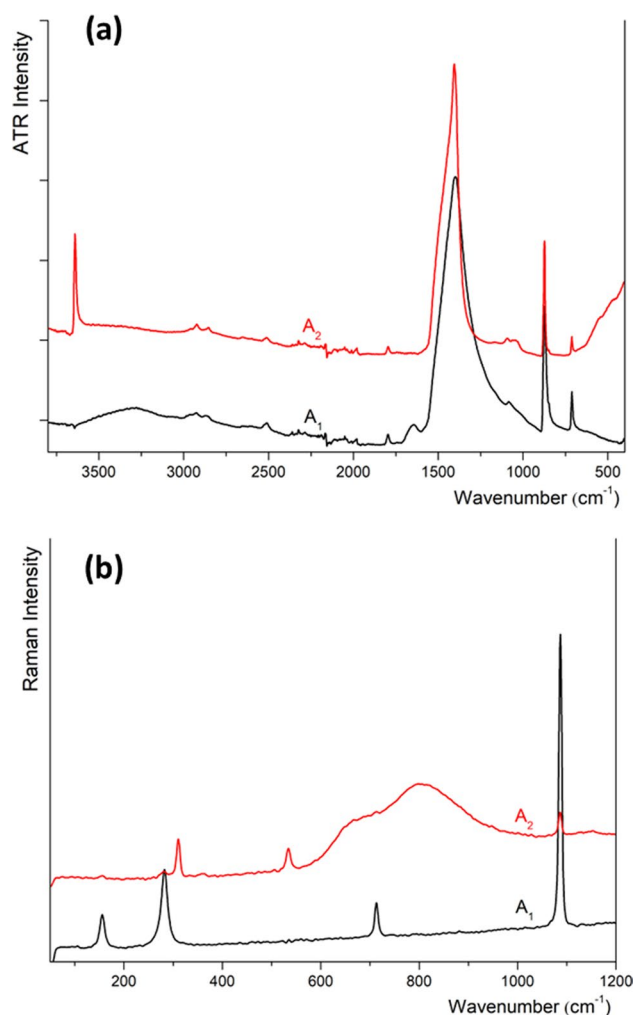
## Photocatalytic experiments and kinetic models

The photocatalytic tests to evaluate the performance of ES@CuO materials were tested for the oxidation of basic fuchsin (BF) in a 250 mL beaker under visible light irradiation (LED bulb, 10 W). The pH of the solution was adjusted with 0.1 M HCl and 0.1 M NaOH. At fixed time intervals, 4 mL of the solution was taken, centrifuged, and measured using a UV–Vis spectrophotometer (JENWAY 7315) at 550 nm.

## Results and discussion

### Characterization

Figure 1 reports both FTIR-ATR and FT-Raman spectra of raw ES and ES@CuO<sub>5%</sub> photocatalyst. The occurrence of several characteristic peaks of calcite was observed in the case of the raw ES sample, in particular typical carbonate modes at 1400 ( $\nu_3$ ), 1085 ( $\nu_1$ ), 875 ( $\nu_2$ ), 715 ( $\nu_4$ )  $\text{cm}^{-1}$  (see section a in Fig. 1). In the Raman spectrum (see section b in Fig. 1), other diagnostic peak of calcite are evident, namely at 284 and 157  $\text{cm}^{-1}$ , arising from external vibrations of the CO<sub>3</sub><sup>2-</sup> groups (Gunasekaran et al. 2006). The broad peak observed in the 3600–3400  $\text{cm}^{-1}$  region is related to the stretching vibration of the OH group of the adsorbed water molecules, whose bending mode is observed at ca. 1650  $\text{cm}^{-1}$ . Calcium oxide does not possess any Raman-active modes and IR-active modes are expected in far IR

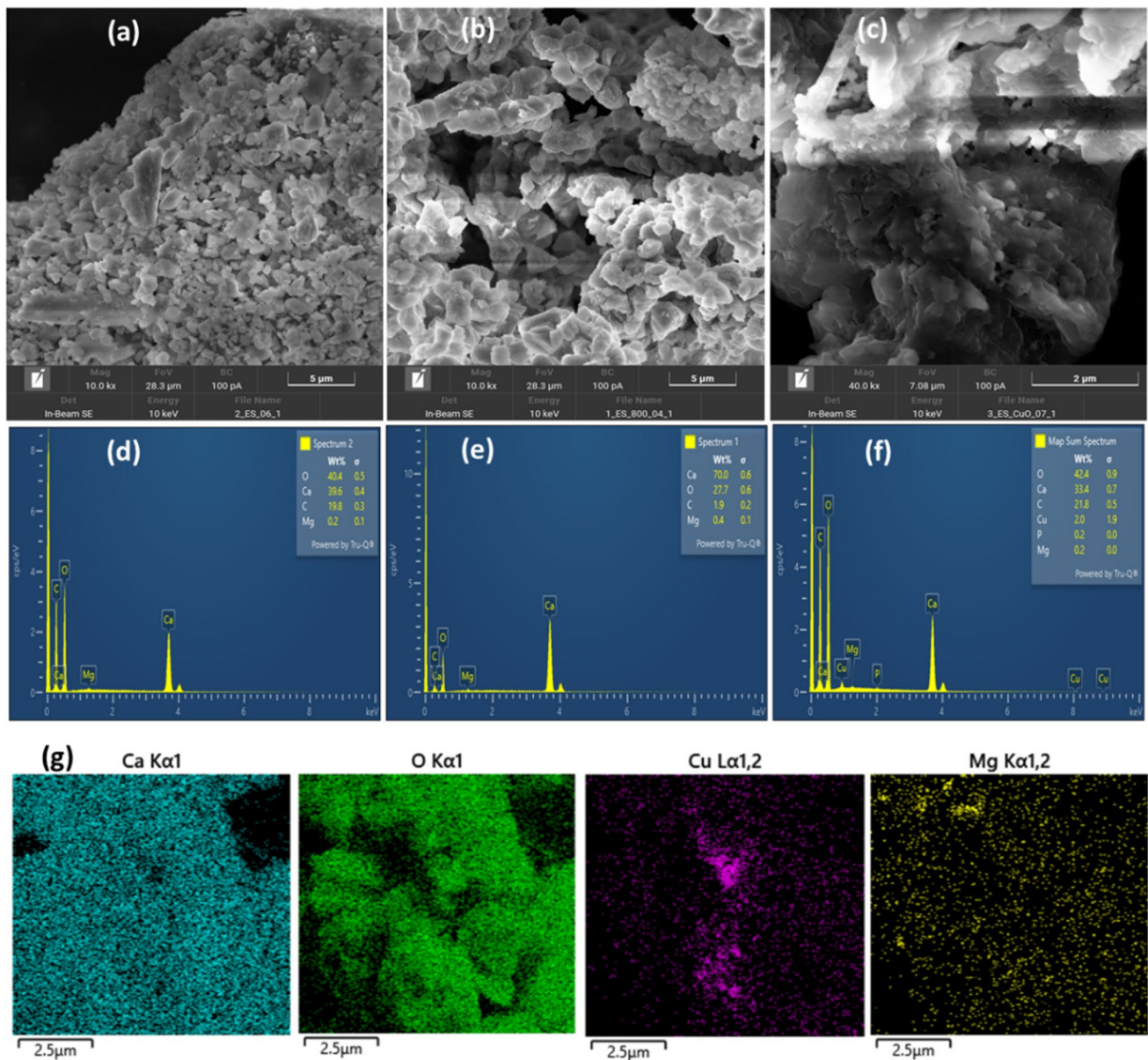


**Fig. 1** a: FTIR-ATR and b FT-Raman spectra of (A<sub>1</sub>) Raw ES and (A<sub>2</sub>): ES@CuO<sub>5%</sub>

region (not observed) (Schmid and Dariz 2015), but some signals are observed in both Raman and ATR spectra of ES@CuO<sub>5%</sub> photocatalyst, due to inevitable traces of Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> formed in this highly reactive material. In fact, in the FTIR-ATR spectrum (see section a in Fig. 1) we observe a sharp peak at 3640  $\text{cm}^{-1}$ , ascribable to the stretching mode of OH groups belonging to surface water, and some characteristic bands of carbonate groups (in the form of a broad and intense absorption in the 1600–1200  $\text{cm}^{-1}$  spectral range and as tiny band(s) in the 1150–1000  $\text{cm}^{-1}$  range). In the Raman spectrum of ES@CuO<sub>5%</sub> the occurrence of a signal at 310  $\text{cm}^{-1}$  confirms the formation of CuO (Hagemann et al. 1990).

Figure 2a refers to the morphological characterization carried out by FESEM. It is evident that the raw ES exhibits a hard and sharp surface structure, with no protrusions or noticeable pores, which reduces their adsorption ability. However, calcined ES (Fig. 2b) and calcined





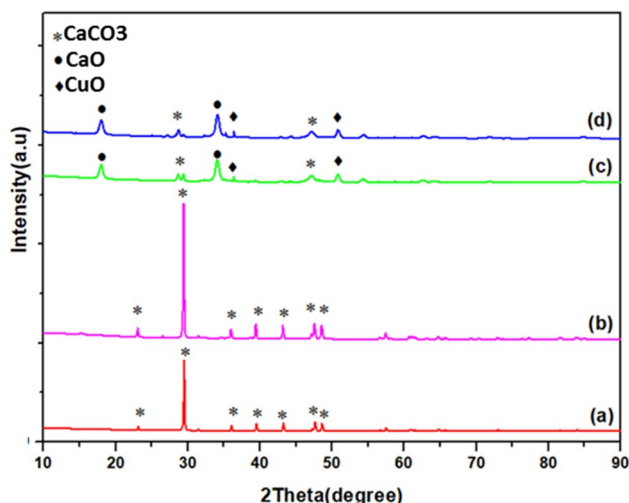
**Fig. 2** SEM images of **a** raw ES, **b** ES<sub>800</sub> and **c** ES@CuO<sub>5%</sub><sub>800</sub>. EDS spectra of **d** ES, **e** ES<sub>800</sub> and **f** ES@CuO<sub>5%</sub><sub>800</sub>. **g** EDS elemental mapping of ES@CuO<sub>5%</sub><sub>800</sub>

ES coated with CuO particles (Fig. 2c), a new layer with heterogeneous morphology and irregular distribution was formed on their surface. Due to the well-integrated CuO particles, the photocatalyst exhibits a high porosity. It is further aggravated through voids and holes ranging from 0.1 to 5 μm in size.

EDS spectra show the presence of Ca, C, O and Mg (Fig. 2d, e, f). The content of Ca increases from 40 to 70% after calcination at 800 °C which attributed to conversion of CaCO<sub>3</sub> (40% Ca) to CaO (70%). In the case of ES@CuO<sub>5%</sub>, Cu element appeared with ratio of 2%. The distribution of elements including Ca, Cu, O and Mg is shown the EDS

elemental mapping images (Fig. 2g). CuO is well dispersed on the surface of CaO, allowing good efficiency.

Figure 3 shows the XRD pattern of the raw ES and ES@CuO<sub>5%</sub> photocatalysts calcined at 600, 800, and 1000 °C. The XRD pattern indicates the presence of a CaCO<sub>3</sub> rhombohedral phase in raw ES and ES@CuO<sub>5%</sub> catalyst calcined at 600 °C as well, with the highest diffraction peak at  $2\theta = 29^\circ$ , which is in good agreement with the reported standards values. The intensity of this peak is higher in ES@CuO<sub>5%</sub> calcined at 600 °C and might be due to the removal of grain boundary, leading to an enhanced crystal size. At higher calcination temperatures (800 and 1000 °C, respectively),



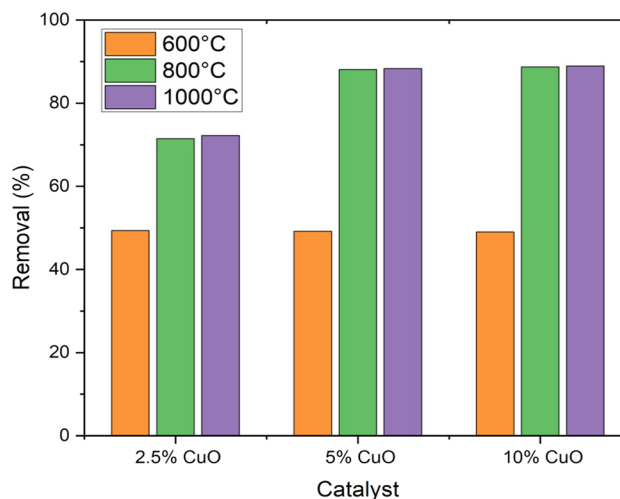
**Fig. 3** XRD analysis of **a** raw ES, **b** ES@CuO<sub>5%</sub> 600, **c** ES@CuO<sub>5%</sub> 800, and **d** ES@CuO<sub>5%</sub> 1000

both CuO and CaO diffraction peaks are evident. The transformation of the rhombohedral form (CaCO<sub>3</sub>) into a face centered cubic form (CaO) requires higher calcination temperature to allow the decomposition of CaCO<sub>3</sub> and the crystallization processes to form CaO (Risso et al. 2018). It was reported in the literature that the transformation of CaCO<sub>3</sub> into CaO is optimal at calcination temperature of ca. 900 °C (Tangboriboon et al. 2012). At a calcination temperature of 600 °C, characteristic peaks of CuO are absent and this feature could be due to the low crystallite size. It is important to mention that the ratio of CuO in CaO is only 5%, and if the crystallinity is very low, peaks can be hardly detected. The increase of temperature pushes the crystallite size due to the boosted atom diffusion which enhances the generation of crystal nucleation phases. The raising of temperature leads to remove grain boundary, resulting in better crystallinity.

## Photocatalytic tests

### Effect of CuO ratio and calcination temperature

To evaluate the performance of different samples, photocatalytic experiments for the oxidation of Basic Fuchsin (BF) were performed with composites at various CuO percentages (2.5%, 5%, and 10%), previously calcined at 600 °C, 800 °C, and 1000 °C and the results are reported in Fig. 4. It can be seen that ES@CuO<sub>5%</sub> and ES@CuO<sub>10%</sub> exhibit higher photocatalytic oxidation as compared to ES@CuO<sub>2.5%</sub>. Meanwhile, ES@CuO<sub>5%</sub> and ES@CuO<sub>10%</sub> exhibit similar performance. In addition, samples calcined at 800 and 1000 °C are more efficient for the oxidation of BF dye and this might be due to the formation of CaO and CuO oxides at these temperature values, in opposition to lower



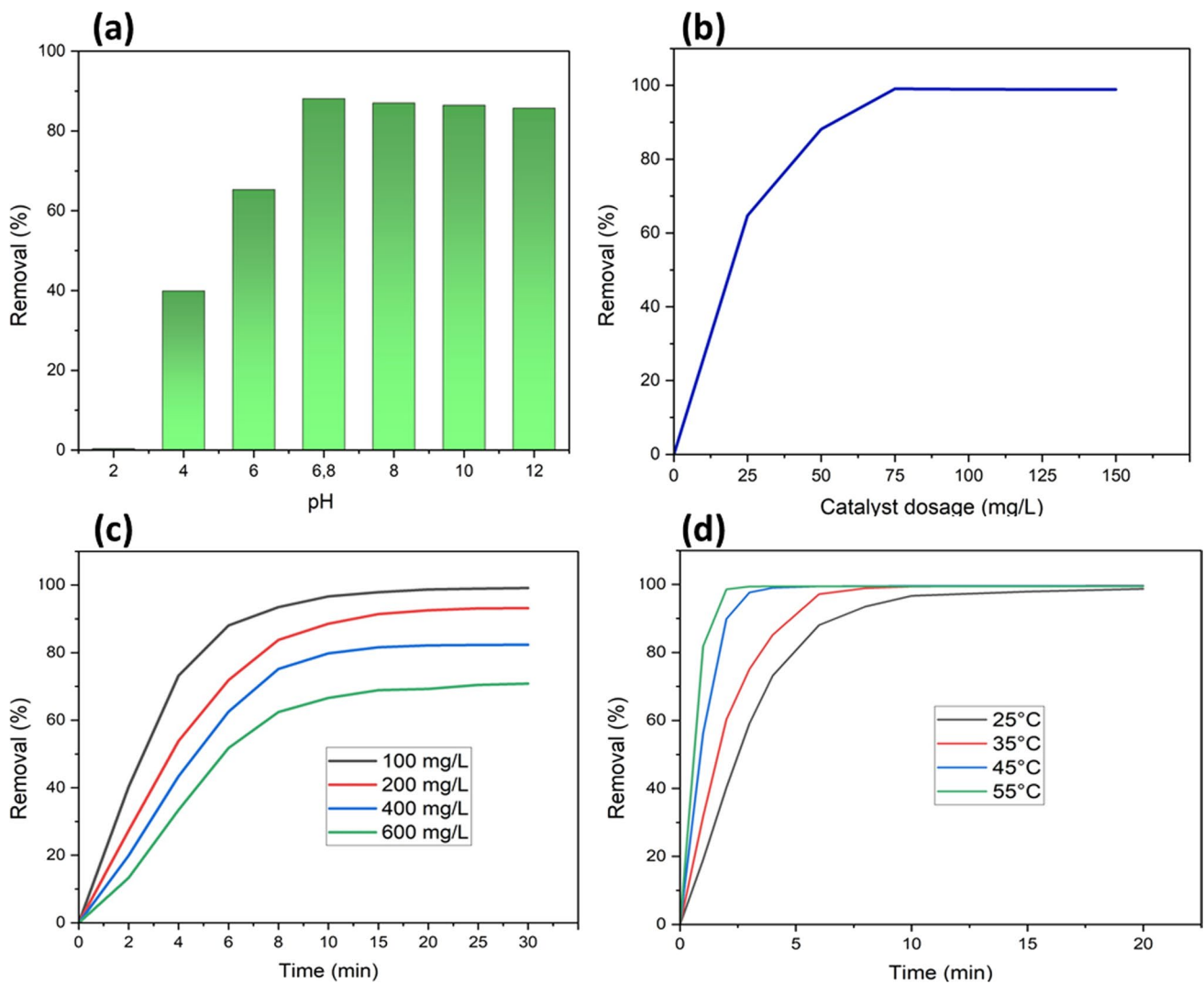
**Fig. 4** The effect of CuO percentage and calcination temperature on the efficiency of BF degradation ([ES@CuO] = 50 mg/L; C<sub>0</sub> = 100 mg/L; t = 30 min; T = 25 °C; pH = 6.8)

calcination temperature 600 °C. The oxidation rates were found to be 88.11% and 88.33% using ES@CuO<sub>5%</sub> 800 °C and ES@CuO<sub>5%</sub> 1000 °C, respectively. Due to the efficiency and less energy and chemical consumption, ES@CuO<sub>5%</sub> sample was selected as optimal photocatalyst to carry on the next experiments.

### Effect of operating parameters on photocatalytic oxidation

Studying the effect of pH solution on the photocatalytic process is an important step in understanding the impact of degradation experiments in a complex environment. Photocatalytic tests were conducted under different pH values ranging from 2 to 12 under visible light irradiation for 30 min, and the obtained results are shown in Fig. 5a. Overall, the performance of dye removal was better at pH 6.8, and similar BF removal are observed at basic pH values, while at acidic pH values the removal decreases by more than the half. During the photocatalytic activity, the adsorption or surface interaction is a crucial factor to get effective radical oxidation due to the short half time of photogenerated reactive oxygen species (ROS) (Nouacer and Djellabi 2023; Radji et al. 2024). The pH can affect the charge of the photocatalyst surface by protonation at acidic medium and deprotonation at basic pH, which make the surface positively or negatively charged, respectively. Since BF is a cationic dye, absorption is favored on negatively charged surface.

The effect of ES@CuO<sub>5%</sub> photocatalyst mass on BF degradation was studied in the range of 25–150 mg/L (Fig. 5b). As the catalyst mass increases, the oxidation rate increases, and total removal of the dye is observed for mass values greater than 75 mg/L. The increase in the performance with the increase of photocatalyst mass is related to the higher



**Fig. 5** **a** Effect of solution pH on the degradation rate of BF dye ( $[ES@CuO_{5\%}] = 50$  mg/L;  $C_0 = 100$  mg/L;  $t = 30$  min;  $T = 25$  °C). **b**: Effect of photocatalyst dosage on the degradation rate of BF dye ( $C_0 = 100$  mg/L;  $t = 30$  min;  $T = 25$  °C;  $pH = 6.8$ ). **c**: Effect of initial

dye concentration on BF degradation efficiency ( $[ES@CuO_{5\%}] = 75$  mg/L;  $t = 30$  min;  $T = 25$  °C;  $pH = 6.8$ ). **d** Effect of temperature on the degradation rate of BF dye ( $[ES@CuO_{5\%}] = 75$  mg/L;  $C_0 = 100$  mg/L;  $t = 20$  min;  $pH = 6.8$ )

number of available active sites and so an high yield of photogenerated oxidative ROS. In a normal scenario, an optimum mass of photocatalyst could be the maximum amount when the surface is well irradiated to generate ROS before reaching the phenomenon of screen effect (Ernawati et al. 2021). The optimization of the photocatalyst mass depends on several factors including the size and density of the photocatalyst, irradiation intensity, photoreactor configuration and stirring conditions.

The effect of BF concentration on the oxidation rate was carried out at various values including 100, 200, 400, and 600 mg/L, at neutral pH and room temperature. The obtained results are presented in Fig. 5c.  $ES@CuO_{5\%}$  proved to be effective material for the removal of BF under light irradiation, even at concentrations relatively high compared to real

conditions.. The increase of BF concentration from 100 to 600 mg/L reduced the oxidation rate only with 30%, suggesting a superior performance of  $ES@CuO_{5\%}$ . The higher concentration might delay the oxidation by photogenerated ROS due to the accumulation of surface blockage and screen effect (Yang et al. 2021).

The effect of temperature on the photocatalytic oxidation of BF using  $ES@CuO_{5\%}$  was studied within the range 25–55 °C and the results are shown in Fig. 5d. It was found that the removal rates are the same within 20 min, while the kinetics is faster whit increasing temperature. At 55 °C, a total removal of BF dye was observed within only 2 min. In photocatalytic reaction, the effect of temperature is basically related to the enhanced mass transfer, rather than the photocatalytic action itself. The physical adsorption of dye



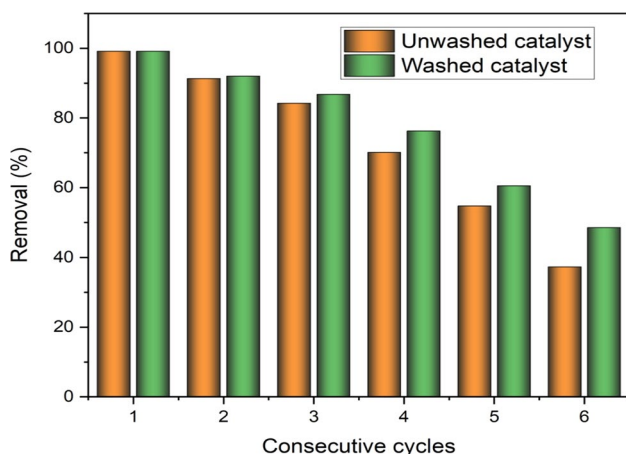
species on the surface of the photocatalyst is promoted by heat, allowing quick radical interaction and so oxidation.

### Photocatalyst reuse

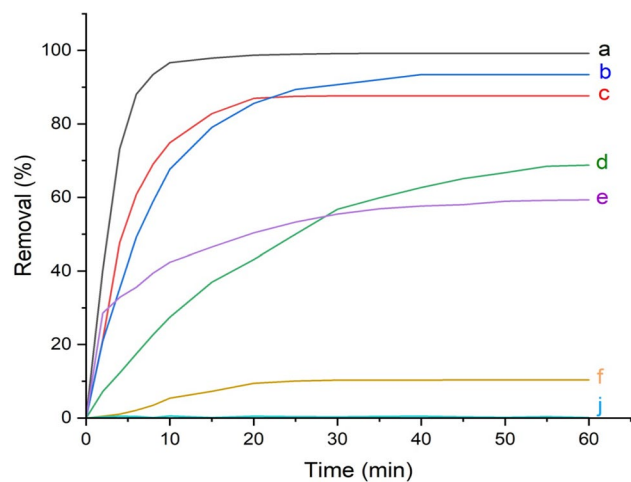
The recyclability of catalysts is a crucial factor at large scale from the economic and sustainability points of view (Djellabi et al. 2021). The deactivation can take place through two main processes: chemical degradation of the catalyst itself or deposition of chemical species on the surface. After each treatment, the photocatalyst was filtered and separated from the treated water, washed three times with distilled water, and then dried in an oven at 60 °C. Figure 6 shows that in the case of the unwashed catalyst, the BF removal efficiency dropped from 99.17% to about 54.72% after five cycles and 37.34% after six cycles of use. On the other hand, the efficiency of the washed catalyst decreased from 99.17 to 60.53% after five cycles and down to 48.53% after the sixth cycle. It can be deduced that the treatment of the catalyst after each use might increase the long time of the photocatalyst as the by-products can be removed. Even though, there was a reduction in the efficiency which could be due to leaching of CuO particles leading to a partial change in the characteristic of the photocatalyst.

### Comparison between photocatalysis and adsorption

To evaluate the contribution of CaO and CuO in ES@CuO<sub>5%</sub> composite photocatalyst, adsorption and photocatalytic studies using bare CaO (obtained from ES), bare CuO and ES@CuO<sub>5%</sub> were carried out under the same conditions. The obtained results are shown in Fig. 7. Firstly, it can be noticed that bare CaO showed excellent adsorption and photocatalytic activity. Under light irradiation, the removal of



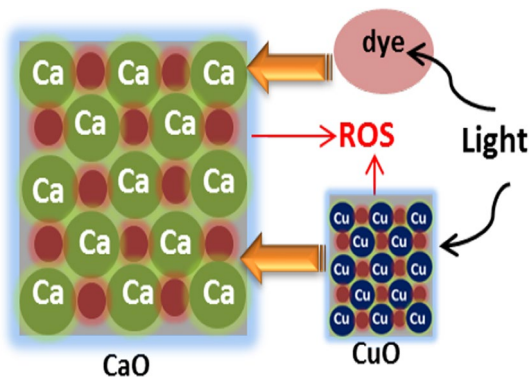
**Fig. 6** Consecutive cycles of ES@CuO<sub>5%</sub> catalyst for BF degradation with and without washing ([ES@CuO<sub>5%</sub>]=75 mg/L; C<sub>0</sub>=100 mg/L; t=30 min; T=25 °C; pH=6,8)



**Fig. 7** BF removal efficiency as a function of time using **a** ES@CuO<sub>5%</sub> in light conditions, **b** Calcined ES in light conditions, **c** ES@CuO<sub>5%</sub> photocatalyst in dark conditions, **d** Calcined ES in dark conditions, **e** CuO in light conditions, **f** CuO in dark conditions, and **j** light, ([material]: 75 mg/L; C<sub>0</sub>=100 mg/L; T=25 °C; pH=6,8)

the dye was found to be around 90% within the first 30 min, against 57% without light irradiation. This proves the high efficiency of this low cost material even without modification. ES is rich of calcium carbonate, around 94% (Sree et al. 2020), which can be converted by thermal heating into photoactive CaO. As above discussed, the heat treatment is very important to obtain a highly adsorptive and photoactive material. Solid CaO is made of an array of Ca<sup>2+</sup>, and O<sup>2-</sup>, and it exhibits a wide band gap which is not able to produce ROS under visible light via the photoexcitation process (Bolrizadeh et al. 2004). The oxidation of dye by CaO under visible light could be driven by photosensitizing effect, wherein dye molecules absorb visible light and transfer the obtained energy to CaO (Peralta et al. 2018). In this study, the adsorption capacity of ES@CuO<sub>5%</sub> photocatalyst was studied in dark conditions and compared to the photodegradation capacity of ES@CuO<sub>5%</sub> and light photolysis capacity, as shown in Fig. 7. It can be observed that the light has no effect on the degradation of the dye. The adsorption capacity of ES@CuO<sub>5%</sub> in dark is around 87%, but under light condition the removal efficiency is 96.63% in 10 min and 99% in 30 min. These results demonstrate the role of CuO in dye degradation. The synergistic effects of adsorption and photocatalytic action can be behind the fast removal of BF dye. This synergism is known as Adsorb and Shuttle process (Djellabi et al. 2020; Mergbi et al. 2023). In this process, the adsorbing area concentrates the amount of dye pollutant nearby the photoactive area, favoring the oxidation process. In general, the use plain photocatalysts suffers from the mass transfer, and in addition, a high adsorption of pollutant on the surface of plain photocatalysts might limit the photocatalytic generation of ROS due to the screen effect (Nouacer





**Fig. 8** Plausible mechanistic pathways for the removal of dye by ES@CuO composite under visible light

and Djellabi 2023). Therefore, the combination of adsorptive materials and photoactive nanoparticles is regarded as one of the best options to enhance the photocatalytic kinetics for the removal of pollutants from water (Djellabi et al. 2021). On top of the Adsorb and Shuttle process, the combination of CaO and CuO, followed by calcination, led to the formation of optimized heterojunction system which allows the absorption of visible light and boosts the separation of photogenerated charges. CaO is known for its wide band gap and low photocatalytic activity (Ikram et al. 2022), which requires structural and surface modification to enhance its performance. This study shows that bare CaO exhibits excellent photocatalytic activity under visible light which could be explained by the dye photosensitizing effect (Djellabi et al. 2017). In this process, the dye absorbs the light, then after excitation, it transfers energy to CaO, leading to photogenerate ROS (Koh et al. 2017). In addition, CuO is recognized as effective photocatalyst under visible light itself and also it can catalyze the photosensitizing effect (Raizada et al. 2020) which in turn enhances the photogeneration of ROS by the ES@CuO composite. The possible mechanisms of dye degradation by ES@CuO are simplified in Fig. 8.

It should be noted that ES@CuO composite proves to be an effective photocatalyst for the removal of BF under visible light irradiation. The total removal of 100 mg/L of BF can be achieved within less than 30 min under irradiation using 0.075 g/L of the photocatalyst. This is considered as relatively fast compared to most reported photocatalysts. For example, Zhang et al. (2021) reported that the removal of 30 mg/L using 0.2 g/L of 5%-Eu-doped ZIF-8(Eu)/Mc-TiO<sub>2</sub> requires 1 h under UV light irradiation. In another study, 0.6 g/L of Ce(MoO<sub>4</sub>)<sub>2</sub> was used to remove BF at 3.10<sup>4</sup> M (~97 mg/L) under solar light with 100 min. Most of other reported materials showed lower performance compared to ES@CuO composite. On top of that, ES@CuO is very cheap which could be obtained from available food waste including the incorporation of 5% of CuO and thermal treatment.

## Conclusion

The finding of this investigation proves the excellent performance of CuO coated ES-based CaO for the photocatalytic oxidation of BF dye under visible light. The transformation of ES-based CaCO<sub>3</sub> into CaO takes place at calcination temperature  $\geq 800$  °C. The results of photocatalytic oxidation of BF under visible light was found to be superior using samples with CuO ratios of 5 or 10%, while it was weaker at lower CuO ratio (2.5%). To summarize, ES@CuO<sub>5%</sub> calcined at 800 °C was considered as the most effective catalyst that requires the lowest chemicals and energy consumption. ES@CuO<sub>5%</sub> proves superior removal of BF under visible light irradiation at concentration ranging from 100 to 600 mg/L using 0.75 mg/L of photocatalyst. It was found that the removal is relatively fast compared to other common systems. ES@CuO<sub>5%</sub> combines both physical adsorption and radical oxidation by photogenerated ROS. ES@CuO<sub>5%</sub> showed excellent recycling ability which suggests its chemical and physical stability. Overall, the design of photocatalysts from wastes is regarded as sustainable and green technology that fits well with the aspects of circular economy and sustainable development. This study shows significant pros in terms of low-cost valuable products and valorization of food wastes for environmental remediation.

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**Author contributions** Atef Ali Ahmed: Methodology, Investigation, Formal analysis and Writing—original draft; Yamina Berredjem & Zhou Hattab: Supervision, Project administration, Conceptualization, writing and review, Alessia Giordana & Giuseppina Cerrato: Investigation, review and validation; Ridha Djellabi: Supervision, Writing—review & editing.

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## Declarations

**Conflict of interest** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Ethical approval** Not applicable.

**Consent to participate** The study does not involve any human participants, human data, or human tissues.

**Consent for publication** All authors have read and approved the final manuscript to be published.

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