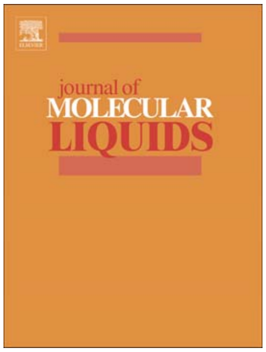

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Catalytic degradation of methyl violet without light irradiation using nanostructured CuS

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Abstract

Nanostructured CuS catalyst with two different morphologies was prepared for degradation of methyl violet without light irradiation. The prepared catalysts were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and Uv-visible spectroscopy. The effect of different conditions including: temperature, solution pH, H_2O_2 volume, catalyst dosage, dye concentration and presence of a salt on catalytic reaction rate and efficiency were investigated, as well. It was found that these catalysts can operate in mild conditions (room temperature and neutral pH) without light irradiation very well and also can be regenerated effectively by simple washing using water or ethanol.

Keywords: Degradation, Catalytic, Nanostructured CuS, Methyl violet, Aqueous solution

1. Introduction

In recent decades, one of the main sources of water pollution is dye molecules as a result of different industrial activities. Presence of dye compounds in water not only is harmful for human health but also has negative effects on the ecosystem. One of the hazardous dye molecules, using for production of paper, cloth, wool and so on, is methyl violet [1], known as carcinogenic and mutagenic compound [2]. So, its removal from aqueous systems is really vital.

Different methods can be used in order to remove of dye compounds from water containing: catalytic degradation [3-6], photocatalytic destruction [7], adsorption [8-10], coagulation and biological treatment [11]. Catalytic destruction is one of the most useful methods, because of operation in mild conditions and also transformation of very poisonous compounds to the less poisonous one.

CuS is a p-type semi-conductor having been used as a photocatalyst [12]. Although, recently, Kundu et al reported that this compound can be used as a catalyst (in absence of light) for destruction of methylene blue in aqueous phase [13]. There are different methods for the synthesis of nanostructured CuS, such as: hydrothermal [14], reflux [15] and chemical vapor deposition (CVD) [16].

The purpose of the present work is synthesis of nanostructured CuS having different morphologies, and then study of their performances as a catalyst for degradation of methyl violet in aqueous media. The effect of different parameters for instance: dye concentrations, H_2O_2 volume, mass of catalyst, time, temperature, pH and presence of salt on catalytic performance of CuS has been investigated too.

2. Material and methods

$CuCl_2.2H_2O$ (> 99.0 %), thioacetamide (TAA) (> 99.0 %), ethylene glycol (> 99.0 %) and methyl violet were purchased from Merck Co. and used without any further purification. Distilled water was used in all experiments. Chemical structure of methyl violet is shown in Fig. S1.

The catalyst (CuS) was prepared with two different methods [17,18] and consequently different morphologies. In the first one, 0.85 g of $CuCl_2.2H_2O$ and 0.32 g of TAA were dissolved in 40 ml of ethylene glycol. The prepared solution was irradiated in a microwave oven (Mulinex, 2450 Hz) at 230 W for 20 cycles (each cycle includes “on” for 10 s and “off” for 40 s). The obtained black suspension was centrifuged and washed several times using water and ethanol, followed by drying in an oven at 80 ˚C for 12 h. In the second procedure, 0.17 g of $CuCl_2.2H_2O$ and 0.09 g of TAA were dissolved in 50 ml of distilled water. The prepared solution was irradiated in a microwave oven at 700 W for 150 s. The black suspension was centrifuged and then the obtained precipitate was washed by water and dried at room temperature.

In order to study of catalytic destruction of dye molecule, specified amount of catalyst (CuS) and H_2O_2 were added to a 50 ml of the methyl violet solution. Afterwards the system was agitated in a dark condition. At specific time intervals, sampling was performed and the residual concentration of methyl violet was determined by Uv-visible spectroscopy (PG Instrument LTD T80) at λ=585 nm.

The morphologies of the prepared catalysts were determined by scanning electron microscopy (SEM) (TSCA- Czech Republic) and transmission electron microscopy

(TEM) (LEO 912 OMEGA Zeiss). X-ray diffraction (XRD) patterns were obtained by ADD2000 LTALSTRUCTYR italia at 2θ ranging from 20 to 70 °.

3. Results and discussion

3.1. Characterization of catalysts

Fig.1a, shows the SEM image of the first sample of CuS. It is obviously seen that the prepared CuS is an assembly of nanosheets having thickness about 15-30 nm. For further confirmation, the TEM image of this sample was taken and shown in Fig.1.b. The TEM image clearly shows the presence of nanosheets. The XRD pattern of this nanostructured sample is shown in Fig.S2.a. The observed peaks at 2θ= 28°, 32° and 47° correspond to the (110), (103) and (102) planes of CuS, respectively [17]. The Uv-visible spectra of dispersed sample in water is illustrated in Fig.S2b. From this spectrum the band gap of this sample was estimated (inset of Fig.S2.b) approximately 1.9 eV.

Fig.S3, shows the TEM image of the prepared CuS (second sample).It can be concluded that second sample is nanoparticles having prolate spheroid structure. The thickness and length of each particle are estimated about 5 and 11 nm, respectively. The XRD pattern of this sample is shown in Fig.S4a. Presence of small peaks including: 24.3°, 24.7°, 31.8°, 35,8° and 39.4° is in agreement with reported peaks of CuS [18,19], but low intensity peaks indicate that sample crystallinity is poor. Fig.S4b is the Uv-visible spectra of dispersed nanoparticles in water. The band gap of this sample is estimated (inset of Fig.S4.b) about 2.1eV. The wider band gap of the prepared nanoparticles (2.1 eV) in comparison to the band gap of the prepared nanostructured one (1.9 eV) confirms the fact that the smaller particles have wider band gap.

3.2. Comparison of catalysts performance

The catalytic performances of both prepared CuS samples for degradation of methyl violet were compared to select the best catalyst. Fig.S5 shows the time dependency of degradation of methyl violet (100 ppm) by both nanostructured CuS and CuS nanoparticles. Based on this figure, it is clear that both the rate of degradation and the final degradation efficiency for nanostructured CuS are higher than CuS nanoparticles. For example, the required time for 50% degradation by nanostructured CuS is about 3 minutes while by CuS nanoparticles, it is about 10 minutes. Therefore nanostructured CuS was selected for further investigations.

The higher performance of nanostructured CuS in comparison to the CuS nanoparticles can be explained based on volcano plot [20,21] indicating the optimum catalytic activity obtained when adsorption energy is intermediate. As the particles become smaller, the number of edge and corner atoms increases leading to higher adsorption energy [20,21]. Sometimes, this increase in adsorption energy by decrease in the particle size causes to shift the catalytic activity toward the maximum of volcano plot (i.e. increase catalytic activity) and sometime shifts from maximum to the lower activity values because of increasing of adsorption energy and blocking of catalyst active surface sites [21]. In the present system, catalytic activity reduced by decrease in particle size meaning the catalytic activity shifted from maximum to the lower one due to higher bonding energy of reactants to the catalyst surface, and therefore lower tendency for reaction.

3.3. Reaction mechanism

In order to investigate whether the removal of methyl violet from water is adsorption or oxidative degradation just by H_2O_2 or catalytic degradation in presence of H_2O_2, four sets of experiments have been performed. In the first one, just H_2O_2 was added to the dye solution. The result (Fig. 2a) indicates after one hour just 6% of dye was destructed. In another experiment, nanostructured CuS was added to the dye solution (in the absence of H_2O_2). The result (Fig. 2a) shows that after one hour just 9% of dye was removed from solution indicating adsorption is not the main process of dye removal. In the third experiment, CuS and H_2O_2 were added simultaneously to the dye solution. The result (Fig.2a) indicates that dye removal starts rapidly, and within 5 min about 60% of dye was destructed. In the last experiment, firstly CuS was added to the dye solution and waited for 15 min until adsorption is completed and then H_2O_2 was added to this system. The result (Fig 2b) indicates by addition of H_2O_2, the dye degradation starts rapidly. These results indicate for effective degradation of methyl violet, presence of H_2O_2 and CuS catalyst are necessary and the mechanism of reaction is catalytic oxidative degradation. Simplified suggested mechanism is:

$H_2O_2 \xrightarrow{CuS} 2\ OH^{\circ}$ (1)
$OH^{\circ} + H_2O_2 \rightarrow HO_2^{\circ} + H_2O$ (2)
$OH^{\circ} + RH \rightarrow R^{\circ} + H_2O$ (3)
$RH + HO_2^{\circ} \rightarrow R^{\circ} + H_2O_2$ (4)
$R^{\circ} + OH^{\circ}$ or HO_2° or $O_2 \rightarrow$ mineralized products

3.4. The *effect of H_2O_2 and dye concentrations*

In order to study the effect of dye concentration on the degradation efficiency, 0.02 g of nanostructured CuS and 2 ml of H_2O_2 were added to 50 ml of the methyl violet solution having different concentrations including: 60, 100 and 160 ppm. The plot of time dependency of dye concentration is shown in Fig S6.a. It is clear that the dye molecules can efficiently destructed by CuS and H_2O_2 at different concentrations. At all concentrations, most of the dye molecules were destructed within 10 min.

The effect of H_2O_2 content is illustrated in Fig.S6.b. It is obvious that by addition of H_2O_2 volume from 0.25 ml to 1 ml, the rate of dye degradation increases, but further addition of H_2O_2 (2 or 3 ml) has the small effect on the rate of degradation.

3.5. *The effect of catalyst dosage*

The effect of catalyst mass on degradation of methyl violet was investigated and the results are shown in Fig.S7. By increase in catalyst mass form 0.01 to 0.03 g, the rate of degradation increases as it is expected [22]. But the efficiency of degradation rises slightly by increasing of catalyst mass.

3.6. *The effect of temperature*

Catalytic degradation of methyl violet by nanostructured CuS was studied at different temperatures. Fig.S8 shows that by increasing of temperature from 25 to 40 °C the rate of reaction increases slightly. Therefore one of the important advantages of this system is its high efficiency at room temperature.

3.7. *The effect of solution pH*

The effect of solution pH on the catalytic rate of methyl violet degradation was investigated. The results are shown in Fig.S9. This figure shows that at pH=3 both rate and total efficiency are low. But at higher pH values (4-9), no significant difference in catalytic activity was observed. Probably, at pH=3, the surface charge of catalyst is positive and therefore the cationic dye cannot be adsorbed due to repulsive forces [23]. The interesting point of this study is that the reaction can be proceed at neutral medium and does not need sever conditions such as: high acidic or alkaline medium.

3.8. *The effect of presence of salt*

In order to study the performance of the prepared catalyst in more real systems, catalytic destruction of methyl violet was investigated in the presence of a salt (NaCl). The results were presented in Fig.S10. It is concluded that presence of salt has no effect on the catalytic reaction efficiency and reaction rate. Hence this catalyst can be used for effective dye destruction also in the presence of salts.

3.9. *Regeneration of catalyst*

Fig.3a, shows the reusability of the prepared catalyst (without any treatment) for degradation of methyl violet after three cycles and at different solution pH values. It is clear that the catalytic activity decreases by using in further cycles. So, the catalyst needs to be regenerated before using in other cycles.

The results of catalytic performances of the regenerated catalyst (washed using distilled water or ethanol) were presented in Fig.3b. As can be seen, the catalyst activity remains constant by simple regeneration using water or ethanol. So, simple regeneration, by washing with water or ethanol, can be accounted as one of the rewarding advantages of this catalyst.

3.10. Reaction products

The Uv-visible spectra of methyl violet at different times is demonstrated in Fig.4a. A rapid decrease in methyl violet absorbance indicates a rapid catalytic degradation of this compound. The corresponding concentrations at different times are illustrated in Fig.4b.

Also the photographs of methyl violet solution (corresponding to Fig.4) after different times of catalytic degradation by CuS is shown in Fig.5. This figure clearly indicates decolorization of the solution was done successfully using H_2O_2 and nanostructured CuS. In order to investigate, what is the product of this degradation (decolorization) process, the CO and CO_2 concentrations (using CO and CO_2 sensors) have been measured within 1 min, where most of methyl violet was degradated. No CO was detected during this time. But, as shown in Fig.S11, a rapid increase in CO_2 concentration was observed. These data clearly show that H_2O_2 in presence of nanostructured CuS catalyst can effectively destructs methyl violet into CO_2, and therefore can be used for water treatment.

3.11. Kinetic modeling

The kinetic data of the methyl violet degradation by nanostructured CuS were fitted to the following equation, which is fractal like first order model:

$$Ln(1-f) = -kt^{\alpha} \qquad (5)$$

$$f=(C_0-C)/(C_0-C_e) \qquad (6)$$

where C_0 , C_e and C are the initial, equilibrium and at any time concentrations of methyl violet. k is the rate coefficient, t is time and α is a coefficient obtaining from fractal like concept of reaction dynamic, and it corresponds to the heterogeneity in distribution of reactants in solution [24] or heterogeneity of active sites on the surface of the catalyst [25,26]. The results of fitting of kinetic data at different conditions are listed in Table S1. Typically, the results of modeling with eq. (5) are illustrated in Fig.4 as dashed line. As can be observed, this kinetic model can be used for prediction of concentration profile very well.

Conclusion

The obtained results in the present study indicate that the nanostructured CuS, including assembly of nanosheets, is an effective catalyst for degradation of methyl violet, as one of the environmental pollutants. It is observed that this catalyst can destruct methyl violet in aqueous media rapidly and efficiently. The advantages of this catalyst for degradation of methyl violet can be listed as: no need to light energy, working at mild solution conditions (no need to very strong acidic or alkaline conditions), working at room temperature efficiency, activity without any change by presence of salt, rapid degradation rate of methyl violet, simple preparation procedure, only need low volume of H_2O_2, oxidation of methyl violet to CO_2, regeneration easily.

Formatting of funding sources

Acknowledgment

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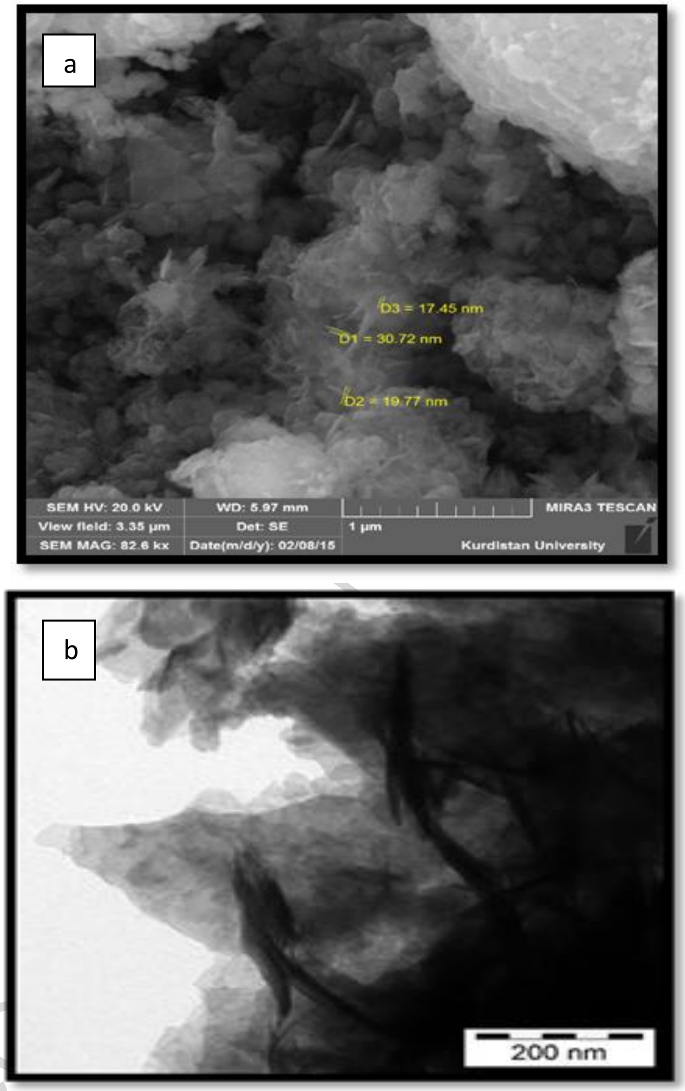


Fig.1. (a) SEM and (b) TEM micrographs of the prepared CuS (first sample).

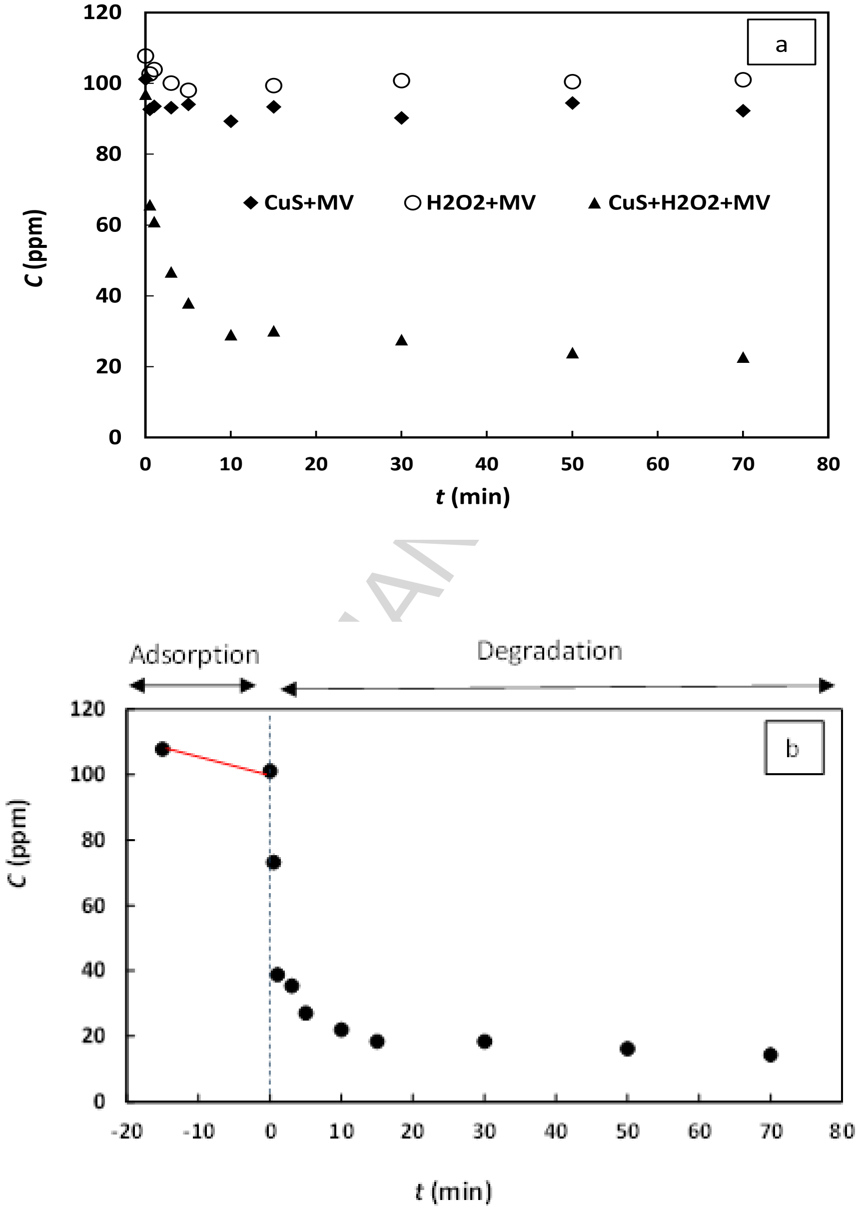


Fig.2. (a) Effect of CuS, H_2O_2 and CuS+H_2O_2 on the methyl violet removal, (b) degradation of methyl violet by H_2O_2+CuS proceeded by adsorption on CuS.

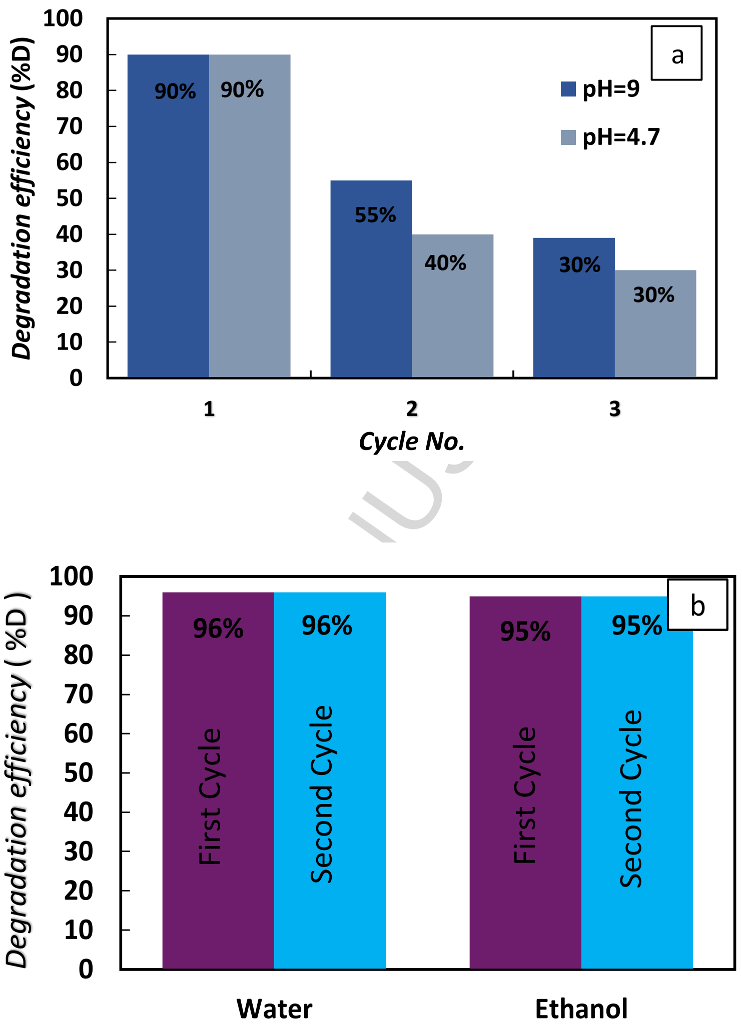
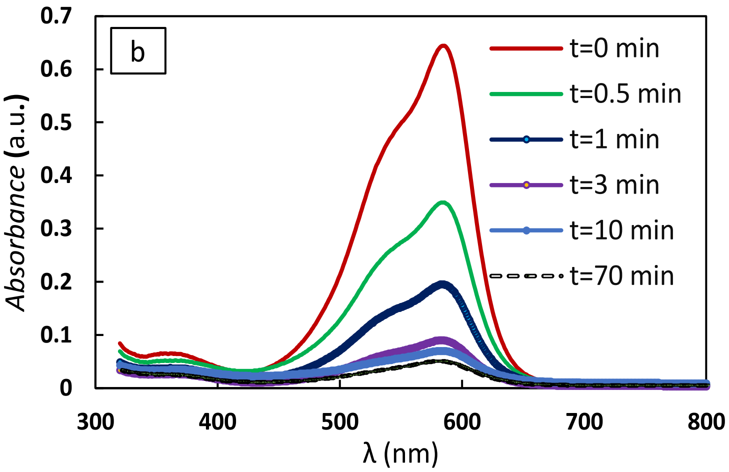


Fig.3. Degradation efficiency (a) of used catalyst (without any treatment) and (b) regenerated catalyst, at different reaction cycles.



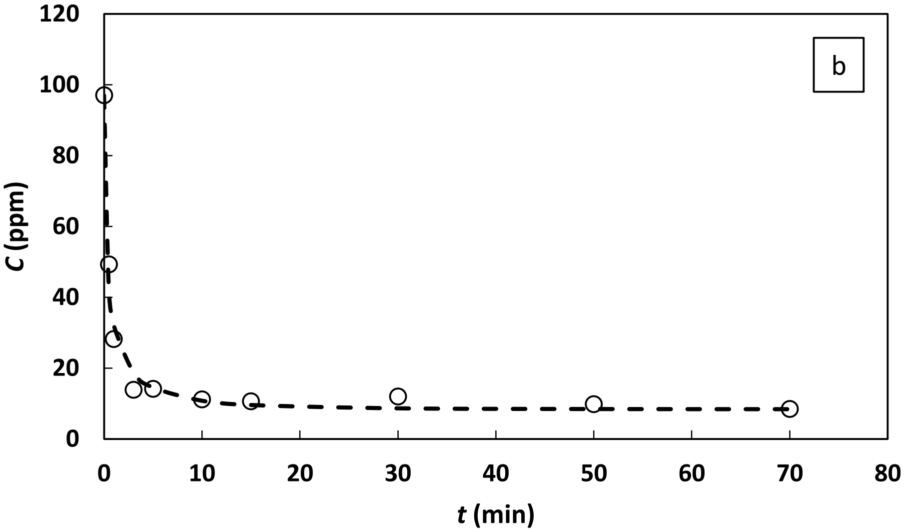


Fig.4. (a) Uv-visible spectra of methyl violet at different time intervals, (b) corresponding concentration as a function of time, symbols are experimental data and dashed line is the predicted values by eq. (5). (C= 100 ppm, T= 40˚C, pH= 9, catalyst mass= 0.03 g, V_{H2O2}= 3ml).

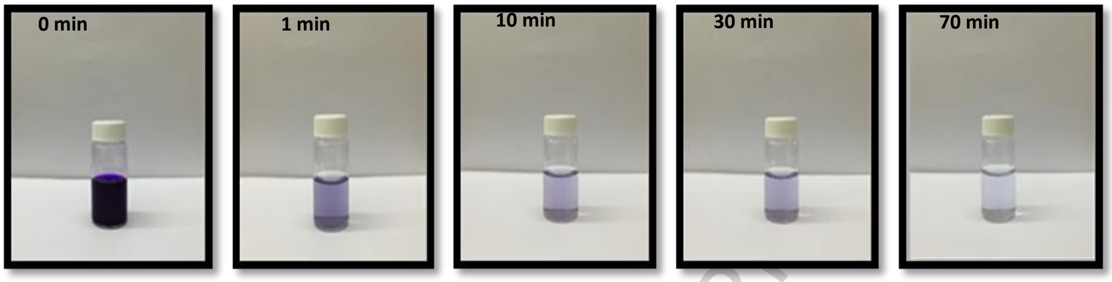
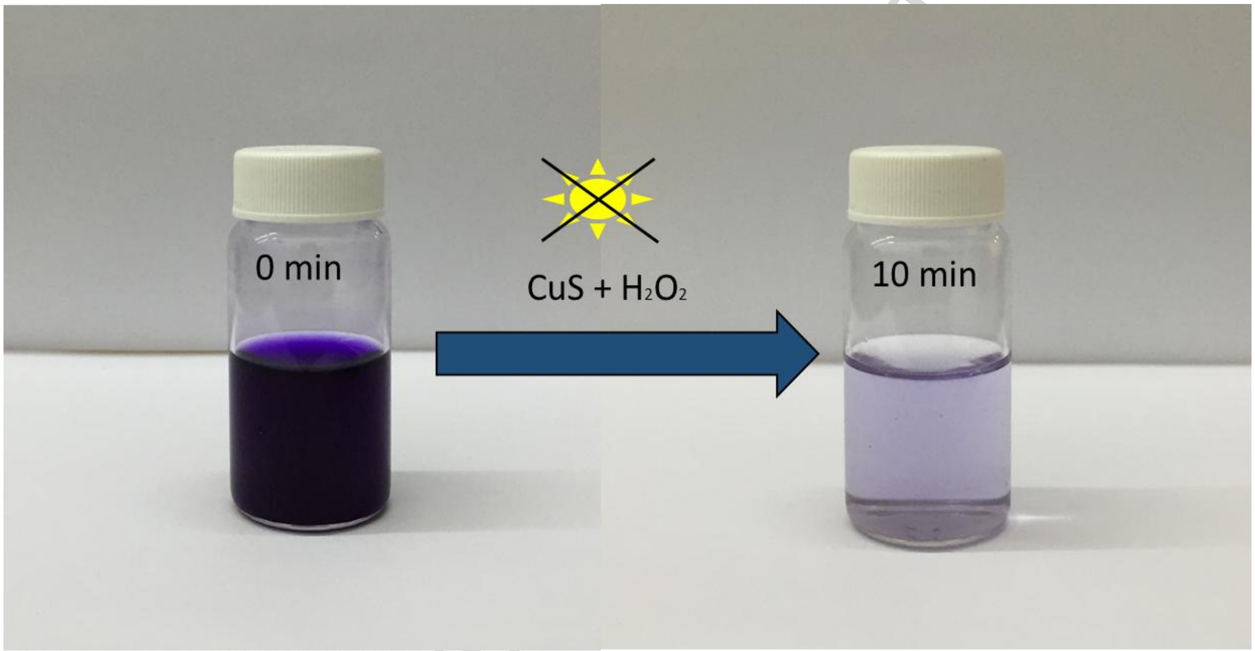


Fig.5. Photographs of methyl violet solution at different times (degradation by H_2O_2 and CuS).

Graphical Abstract



Highlights

- Nanostructured CuS is an efficient catalyst for methyl violet degradation.
- This catalyst works at mild conditions for pollutant degradation.
- The catalyst can be regenerated easily by washing with water.