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Photocatalytic Degradation of Malachite Green by Copper Sulfide Photocatalyst

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Abstract: Copper sulfide (CuS) photocatalyst using different surfactant agents such as pluronic 123 (Plu.), Polyvinylpyrrolidone (PVP) and poly Polyethylene glycol (PEG) via precipitation method. The produced samples were analyzed using XRD powder diffraction. The photocatalytic degradation of malachite green dye (MG) was studied for CuS photocatalysts samples under direct sunlight. The results indicate that the CuS-Plu. sample shows a higher photocatalytic activity compared to others samples. Moreover, the kinetic study of MG degradation was also investigated and the result showed that there is a pseudo-first order reaction. The reducibility of CuS-Plu. photocatalyst was performed 5 times for degradation of malachite green dye under direct sunlight and the data revealed a high stability and good efficiency.

keywords: Photocatalysis, Copper Sulfide, Malachite Green, Direct Sunlight

1.Introduction

Photocatalysis is the Advanced Oxidation Process (AOP), which is considered an effective process in photodegradation dyes that can be used instead of conventional methods [1, 2]. Heterogeneous photocatalysis has proved to be of real interest as an efficient tool for degrading both aquatic and atmospheric organic contaminants. Recently many researches were focused on the growth of hierarchical structures for use in catalytic processes. This technology had been positively applied to water splitting [3, 4], hydrogen formation [5] and dye-sensitized cells production [6]. It has achieved great success in treatment of toxic and non-biodegradable organic and inorganic dyes from wastewater by their total conversion into species that are non-toxic. Semiconductors act as a photocatalyst for the light-induced photochemical reactions owing to their unique electronic band structure including filled valence band (VB) and empty conduction band (CB) such as TiO_2, ZnO, CuS, ZnS, Fe_2O_3, Nb_2O_5, $BiTiO_3$, $SrTiO_3$, $ZnWO_4$. α – Sulfur crystals are used in pollutants degradation in both the liquid and gaseous system [7–9].

A p-type semiconductor metal chalcogenide, copper sulfides (CuS) have drawn abundant attention owing to their interesting optical and electrical properties. CuS with narrow bandgap exhibits the potential in absorbing solar light from ultraviolet (UV) to visible light, even near-infrared (NIR) have shown capacity as highly efficient, econimec materials for the processing of environmental pollutants [10–12]. CuS nanoparticles have been used as photocatalysts for the degradation of organic dyes such as Methyl Red, Methyl Orange, Methylene Blue, Rhodamine B, and 2,4-Dichlorophenol. Copper sulfide [13–15] can be prepared with different morphologies such as nanoflowers, nanoplates, nanotubes, nanorods, nanoflakes, nanospheres, nanocubes, and complex hierarchical micro/nanostructures [15–18].

In the present article, we are reporting photocatalytic activity of Copper sulfide synthesized by precipitation method for treatment of wastewater pumped from textile dying. Using photocatalytic process for

degradation textile dying such as Malachite green.

2. Materials and Methods

2.1. Materials

The chemical materials used for preparation of CuS photocatalysts are copper acetate (LOBAChemie, 98%), thiourea (Sigma Aldrich), DMF (HPLC, 99.7%), pluronic123 (Sigma Aldrich), polyethylene glycol 2000 (Fluka analytical, 99.99%), polyvinylpyrrolidone k15 (Fluka analytical, 99.99%), Ammonia (25%, Honeywell), malachite green (Alpha CHEMIKA, 99%).

2.2. Synthesis of CuS

CuS nanoparticles were synthesized by a precipitation method using different surfactant agents. A certain amount of the surfactant was dissolved in 90 ml DMF with stirring, followed by the addition of copper acetate at room temperature. Then the temperature was slowly increased to 80° C. The corresponding weight of thiourea dissolved in 10 ml DMF was added dropwise to the solution under stirring for 2 h. Then the pH was maintained around 10 by using NH_4OH (25%) to prepare CuS nanoparticles. The product was filtered and washed with absolute ethanol and hot deionized water. Finally, The product was dried at 100° C over night [19].

2.3. Characterization of CuS nanocatalyst

The crystal structure of the as-prepared CuS was characterized by using X-ray diffraction patterns (XRD) (Bruker, D8Advance, Germany) with Cu-Kὰ radiation (λ = 1.5406 Å) (40 Kv, 40 mA). The optical and photocatalytic activity of CuS nanoparticles were recorded at room temperature using UV-VIS-NIR spectrophotometer (Jasco-V-570 spectrophotometer, Japan).

2.4. Photocatalytic experiments

The produce particles of CuS was test as a photocatalyst to degrade the MG, which derived from the wastewater out of the textile industries under the direct sunlight using a homemade reactor. A certain amount of CuS was dispersed in aqueous solution of 10 ppm of MG. To establish adsorption/desorption equilibrium state, the dispersion solution was kept in dark for 1 h under magnetic stirring. Then the dispersion solution was exposed to direct sunlight 2 ml of solution was taken at certain time intervals. To analyze the MG concentration, UV-Vis. Spectrophotometer at wavelength 618 nm was used. The CuS prepared by different surfactants were reused for five times to check its efficiency and the stability. Moreover, the kinetics studies for degradation of MG under direct sunlight. To calculate the degradation percentage (***D***%) was calculated by using the following equation

$$D\% = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

Where $\boldsymbol{C_o}$ is the initial concentration of MG (ppm) and $\boldsymbol{C_t}$ is the concentration of MG at various time intervals (ppm) [20, 21].

3. Results and Discussion

3.1. X-ray diffraction of CuS prepared by different surfactants

The different surfactants have been used to eliminate the optimum surfactant agent for prepare of CuS with high homogeneity in the nanoscale. Fig. 1 shows the diffraction peaks of XRD diffraction patterns for CuS prepared using different surfactants. The observed diffraction peaks (Fig. 1a, b) at (2Ɵ) values of 27.95°, 29.418°, 31.93°, 48.133°, 52.859°, and 59.281° are corresponding to (101), (102), (103), (110), (108) and (116) reflections of pure hexagonal phase of CuS according to (JCPDS card no. 97-2321), respectively [20–22]. Pure hexagonal CuS prepared using Plu.123 have higher intensity than PVP. Whereas, the diffraction peaks of CuS prepared by using PEG showed two intermediates $Cu_4(OH)_6SO_4$ and $Cu_4SO_4(OH)_6H_2O$ are observed at an angles (2Ɵ) values of 35.6° at d = 2.51 Å for $Cu_4(OH)_6SO_4$ and 12.7° and 25.7° at d = 6.91 Å and 3.46 Å for $Cu_4SO_4(OH)_6H_2O$ according to (JCPDS card no. 85-1316, 83-1410), respectively. From these results, it can confirmed that the Plu.123 is a convenient surfactant to synthesize a pure hexagonal CuS. The particle size of the produce CuS in the presence of different surfactants as shown in table 1 indicate that the particle size of CuS depends on the type of the surfactant.

Table (1) Crystallite size of prepared CuS by different surfactants.

Surfactants	Crystallite size (nm)
Plu.123	3 – 27.5
PVP	3
PEG	3 – 69.9

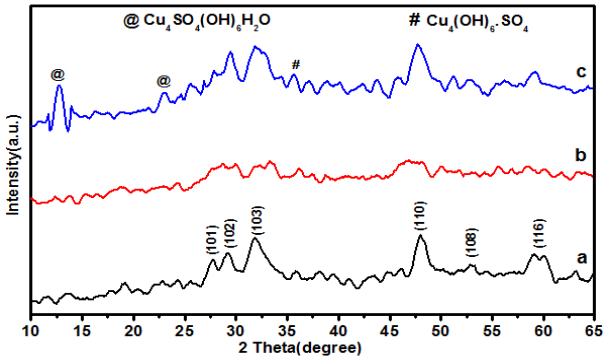

Fig. (1) XRD patterns of CuS prepared by using different surfactants (a) Plu.123, (b) PVP and (c) PEG.

3.2. The photocatalytic activity of the CuS prepared by different surfactant agents

The photocatalytic activity of the as-prepared CuS nanoparticles synthesized by different surfactants (Plu.123 and PVP) was evaluated for MG degradation under direct sunlight in acid media. The photodegradation efficiency of the CuS-Plu. and CuS-PVP photocatalysts were 93.3% and 89.2%, respectively after 120 min in direct sunlight as shown in Fig. 2. It is known that the photodegradation efficiency depends on the number of active sites of CuS nanoparticles. So, the highest photodegradation efficiency of CuS-Plu. is attributed to the highest number of active sites on the surface of CuS-plu. compared to CuS-PVP catalyst [11, 23, 24]. As shown in absorbance spectra in Fig. 3, the MG adsorption properties were tested in the dark for 60 min to reach the adsorption-desorption equilibrium.

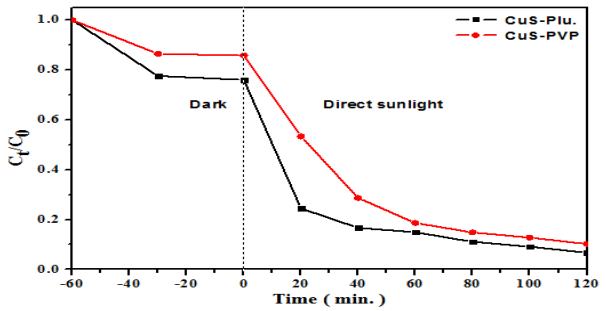

Fig. (2) Variation of MG concentration at different time intervals in the presence of CuS prepared different surfactant agents.

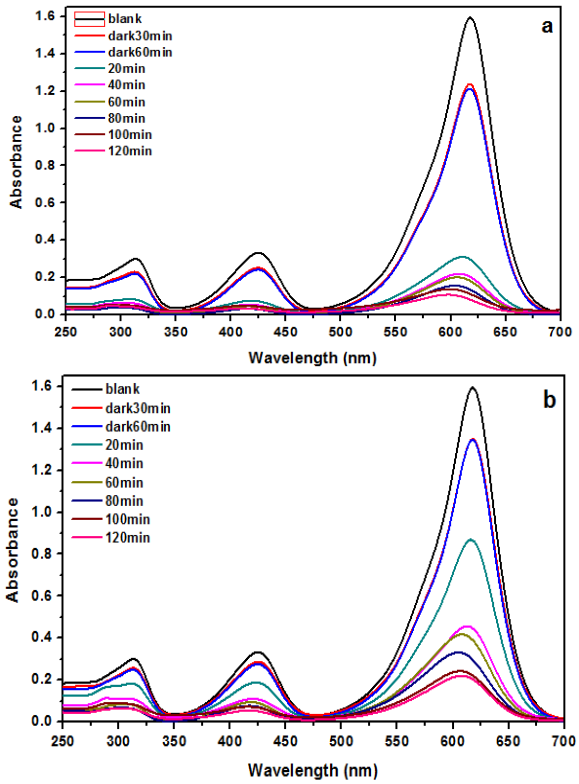

Fig. (3) Absorbance spectra of MG with CuS photocatalyst by different surfactant agents **(a)** Plu. and **(b)** PVP.

3.3. Kinetics studies

The kinetic studies of the MG photodegradation of the CuS photocatalysts prepared by different surfactants is shown in Table 2. The results showed that there is a pseudo-first order reaction, as given in Eq. 2. The data have been fitted well and gave a correlation coefficient (R^2) of 0.9883 and 0.9918 for the CuS-Plu. and CuS-PVP, respectively as shown in Fig. 4.

$$-\ln\left(\frac{C_t}{C_o}\right) = K.t \qquad (2)$$

$$r_o = K.C_o^n \qquad (3)$$

Where $\boldsymbol{C_t}$ is the concentration of MG at various time intervals (mg/L), $\boldsymbol{C_o}$ is the initial concentration (mg/L) in Eq. (2) but in Eq. (3) $\boldsymbol{C_o}$ (mol/L), $\boldsymbol{K}$ is the first-order rate constant (min^{-1}), t is the irradiation time (min), $\boldsymbol{n}$ is the reaction order (n = 1) and $\boldsymbol{r_o}$ is the initial reaction rates.

The rate constant of the reaction (k) calculated from Eq. 2 was found to be 0.0262 and 0.02186 min^{-1} for the CuS-Plu. and CuS-PVP, respectively. The initial photocatalytic degradation rates (r_o) of the MG using CuS photocatalyst were calculated from Eq. (3)

which illustrative in Table 2 [10, 25]. The high value of K with a high value of degradation rate (54.77 * 10^{-8} M min^{-1}) proved that CuS-Plu. is effective photocatalyst under direct sunlight irradiation with the higher degradation efficiency of 93.31 % at 10 ppm of MG.

Table (2) Langmuir-Hinshelwood kinetic-pseudo 1st. order reaction rate constant (k, min^{-1}), 1st. order reaction rates (r_o, $Mmin^{-1}$), R^2 and degradation efficiency (D %) of MG by CuS.

Photocatalyst	K(min^{-1})	r_o*10^{-8} (M min^{-1})	R^2	D % of MG
CuSPlu	0.0262	54.77	0.9883	93.31
CuSPP	0.0218	51.57	0.9918	89.20

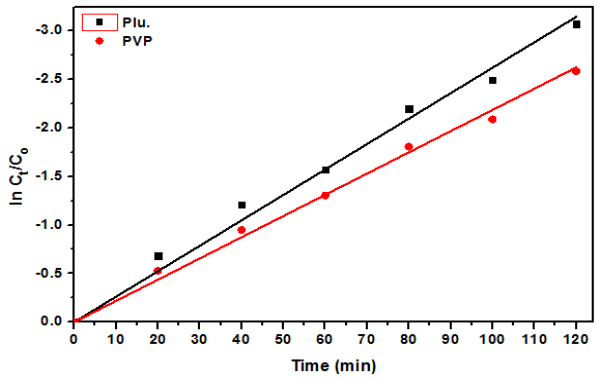

Fig. (4) Kinetic study for photodegradation of MG with CuS photocatalyst prepared using different surfactants.

3.4. Recycling of CuS-Plu. photocatalyst

The stability of the CuS-Plu. photocatalyst was investigated by studying the recyclability of the catalyst for the photodegradation of 10 ppm MG dye concentration under direct sunlight for 120 min as shown in Fig. 5. The CuS-Plu. photocatalyst was effectively reused for five times. After each run, the CuS photocatalyst was filtered by using filter paper, washed two times by deionized water then dried and activated at 100° C and transfer to the experiment. The results showed that there is no significant loss in activity after five cycles of MG degradation. The degradation efficiency were recorded after 1st, 2nd, 3rd,4th and 5th runs yielding 93.3 %, 92.9 %, 92.7 %, 92.6 % and 92.2%, respectively as shown in Fig. 5. Thus, the CuS-Plu. photocatalyst is very stable under sunlight irradiation and effective for degradation of the textile dyes [20, 26].

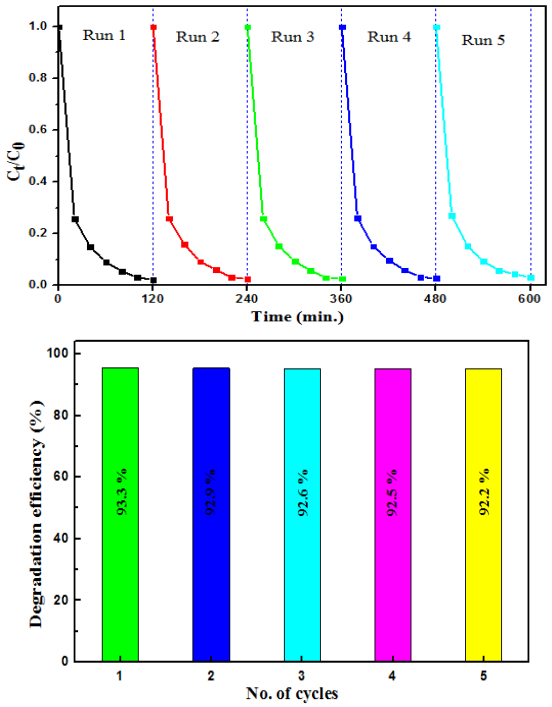

Fig. (5) Recycling of CuS-Plu. photocatalyst for degradation of 10 ppm MG dye solution.

4. Conclusions

CuS photocatalyst was synthesized by precipitation method using different surfactants. The XRD patterns confirmed that Plu. 123 as surfactant enhance the formation of pure hexagonal phase with high crystallinity of CuS. The CuS-Plu. photocatalyst achieved 93.31% degradation effeciency of MG dye and showed good recyclability under direct sunlight.

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