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Synthesis of Copper Sulfide and Copper-Iron Sulfide Nanoparticles and Their Utility for Photocatalytic Degradation Of Dyes

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ABSTRACT

Copper sulfide and copper-iron sulfide nanoparticles were prepared from bis(N-(pyrrol-2-ylmethyl)-N-butyldithiocarbamato-S, S′) copper(II) (1) and bis(N-methylferrocenyl-N-(2-phenylethyl) dithiocarbamato-S, S′)-copper(II) (2), respectively. Photocatalyticactivities of as-prepared nanoparticles were studied by decolourization of methylene blue and rhodamine-B under ultraviolet light. It was found that the copper-iron sulfide degrades methylene blue and rhodamine-B much better than copper sulfide

Keywords:
Copper(II) Dithiocarbamates; Copper Sulfide; Copper-Iron Sulfide; Photodegradation

1. Introduction

Dithiocarbamate ligands, have found ample use in coordination chemistry [1,2]. Their wide range of applications e.g. industry, agriculture and medicine has generated a large collection of crystallographic data for their metal complexes [3].Dithiocarbamates are versatile ligands capable of stabilizing transition metals in both high and low oxidation states [4] and complexes of Cu(I), Cu(II) and Cu(III) are all known, being inter conversable via reversible one-electron redox process [5]. Metal sulfides can also serve as an important semiconductor photocatalysts which offer the potential for complete elimination of toxic chemicals [8]. Here in we report synthesis, characterization and anion sensing properties of copper(II) dithiocarbamate complexes containing pyrrole and ferrocene moieties. In addition, synthesis, characterization and photocatalytic activities of copper sulfide and copper-iron sulfide nanoparticles, which are synthesized from as-prepared from **2-4**, are also presented.

2. Experimental

2.1. Materials and techniques

Reagent grade chemicals were purchased from commercial sources and used as such. IR spectra were recorded on a Thermo Nicolet Avatar 330 FT-IR spectrophotometer (range: 4000–400 cm^{-1}) as KBr pellets. A Shimadzu UV-1650 PC double-beam UV-vis spectrophotometer was used for recording the electronic spectra.

2.2. Photocatalytic experiments

The photocatalytic activity of copper sulfide and copper-iron sulfide was evaluated by degradation of aqueous solution of methylene blue and rhodamine-B. All the solutions were prepared using double distilled water. A typical photocatalytic experiments, 0.1 g of catalyst was added to 50 ml of an aqueous solution of rhodamine-B in the concentration of 1.0 X 10^{-4} M. The solution was maintained under darkness for 30 min to reach dye solution adsorption–desorption equilibrium. The solution with the suspended nano-photocatalyst was irradiated by UV light from mercury vapour lamp. At given time intervals, 3ml of aliquots was withdrawn and centrifuged to

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remove catalyst, concentration of both dye solution was determined with the help of UV-vis spectrophotometer.

2.3.Preparation of Copper sulfide and Copper-iron sulfide

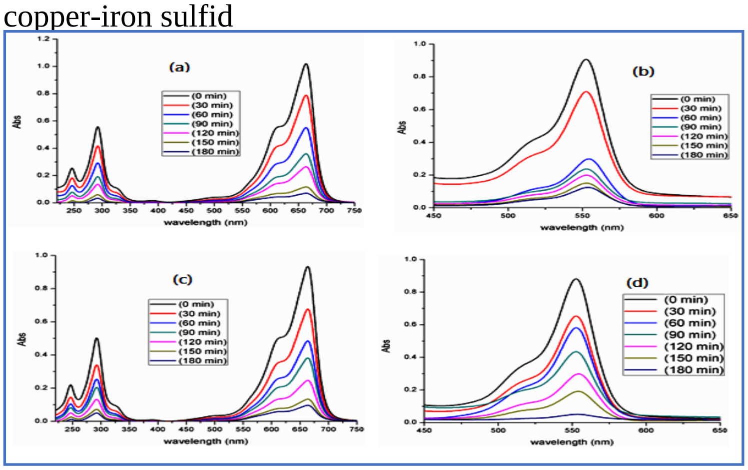
0.5 g of **1**was mixed in 15 ml triethylenetetraamine in a round bottom flask and then the content of the flask was refluxed for 15 minutes. The black precipitate obtained was filtered off and washed with methanol.
Similar procedure was adopted for the preparation of copper-iron sulfide from **2**.

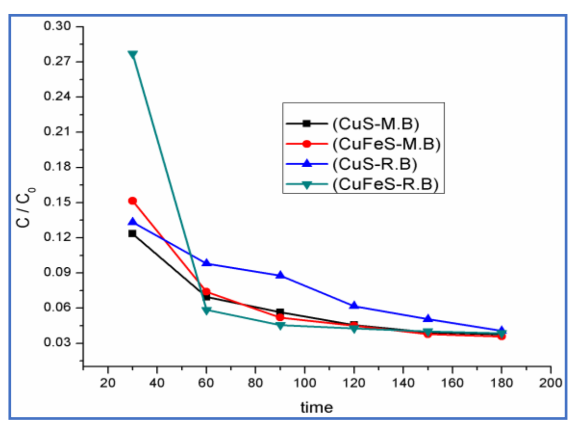
3. Characterization of copper sulfide and copper-iron sulfide nanoparticles

3.1. Photocatalytic activity of copper sulfide and copper-iron sulfide

The photocatalytic activity performance of as-prepared copper sulfide and copper-iron sulfide-**1** were evaluated by photocatalytic degradation of methylene blue and rhodamine-B aqueous solutions. The degradation of methylene blue and rhodamine-B was carried out subjecting into ultraviolet light irradiation as followed spectrophotometric monitoring. **Figure 8**shows the temporal evaluation of the absorption spectra during the photocatalytic degradation of methylene blue and rhodamine-B in the presence of copper sulfide and copper-iron sulfide. As the irradiation time extended the absorption peaks decreased. **Figure 9**shows the photodegradation efficiency of methylene blue and rhodamine-B as a function of irradiation time. C is the absorption of methylene blue and rhodamine-B at 662 and 554 nm, respectively at time (t) and C_0 is the absorption of methylene blue and rhodamine-B before irradiation.
The experiments showed the good photocatalytic activity of copper sulfide and copper-iron sulfide-**1** for the degradation of methylene blue and rhodamine-B under ultraviolet irradiation. It was observed that copper sulfide degraded 89% of methylene blue in 180 min while copper-iron sulfide-1 degraded 93 % of methylene blue in 180 min under UV light. It was also observed that copper sulfide and copper-iron sulfide degraded 82 and 86 % of rhodamine-B, respectively under UV light irradiation in 180 min. The degradation efficiency of copper-iron sulfide is greater than copper sulfide for the investigated dyes. The presence of iron in copper-iron sulfide-**1** can also enhance the photocatalytic degradation activity due to lower crystal size, higher efficiency for the electron-hole regeneration and charge trapping.

Figure 8. Absorbance spectral changes of methylene blue and rhodamine-B using copper sulfide (a) and (b) and copper-iron sulfide (c) and (d) under ultraviolet light.
Figure 9. Photocatalytic degradation of methylene blue and rhodamine-B using copper sulfide and copper-iron sulfid





4. Conclusion

Copper(II) dithiocarbamate complexes (**1** and **2**) containing pyrrole and ferrocene moieties were prepared and characterized. This study demonstrates spherical shape copper sulfide and copper-iron sulfide and oval shape copper-iron sulfide can be prepared from copper dithiocarbamate complexes.Copper-iron sulfide (bimetallic) nanoparticles revealed better photocatalytic activity for the photo degradation of methylene blue and rhodamine-B under UV light compared to copper sulfide (monometallic). This study indicates that preparation of new copper(II) dithiocarbamate complexes containing various N-bound organic moiety is useful for sensing anions and preparing effective photocatalysts (copper sulfide and copper-iron sulfide nanoparticles with various shape).

Conflict Of Interest

The authors declare no conflict of interest.

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