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Synthesis of Cobalt Sulfide and Cobalt-Iron Sulfide from Cobalt (III) Dithiocarbamate Complexes and Their Utility for Photocatalytic Degradation of Dyes

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ABSTRACT

Tris(N-(pyrrol-2-ylmethyl)-N-butyldithiocarbamato-S, S′) cobalt(III) (1), bis(N-methylferrocenyl-N-(2-phenylethyl) dithiocarbamato-S, S′) nickel(II) (2) complexes were used as single source precursors for the preparation of cobalt sulfide and cobalt-iron sulfide nanoparticles. IR spectral studies on nanoparticles confirm the presence of capping agent (triethylenetetramine). The nanoparticles are explored as photocatalysts to study the degradation of dyes using methylene blue and rhodamine-B in aqueous solution under UV irradiation. The cobalt-iron sulfide works as an efficient photocatalyst for degradation of rhodamine-B..

Keywords:
Cobalt (III) dithiocarbamate; cobalt sulfide; cobalt-iron sulfide; nanoparticles; single source precursors

1. Introduction

A wide range of metal-dithiocarbamate complexes is known with examples finding use in applications as diverse as industry, agriculture, medicine and material science [1-7]. Metal sulfide nanoparticles have shown vital applications in many fields as an advanced material such as IR detectors [6], photocapacitors for energy conversion and storage [7], sensors [8], photonic materials [9] and advanced optoelectronic devices [10]. In recent years, transition metal dithiocarbamate complexes have received a great deal of attention because of their importance as single source precursors for the preparation of metal sulfide nanoparticles [11,12].

2. Experimental

2.1 Materials and instrumentation

Reagent grade chemicals were procured from commercial sources and used as such. The synthesis of the compounds was carried out under an inert-gas atmosphere of nitrogen. Solvents were purified according to standard procedures and dried before use whenever required. IR spectra were recorded on a thermo NICOLET AVATAR 330 FT-IR spectrophotometer. The $^{1}H/^{13}C$ NMR spectra were recorded on BRUKER 400/100 MHz NMR spectrometer at room temperature in $CDCl_3$ solvent. SHIMADZU UV-1650 PC double beam UV-visible spectrophotometer was used for recording the electronic spectra of the complexes.

2.2. Photocatalytic experiments

The photocatalytic activity of cobalt sulfide and cobalt-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 1.0×10^{-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

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vapour lamp. At given time intervals, 3ml of aliquots was withdrawn and centrifuged to remove catalyst, concentration of both dye solution was determined with the help of UV-Vis spectrophotometer.

2.3. Preparation of Cobalt sulfide and Cobalt-iron sulfide

0.5 g of **2** 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 cobalt-iron sulfide from **2**.

3. Results and Discussion

3.1 Photocatalytic activity

The photocatalytic activity performance of as-prepared cobalt sulfide and cobalt-iron sulfide were evaluated by photocatalytic degration of methylene blue and rhodamine-B aqueous solutions. It should be noted that the experiment in the absence of catalysts exhibited very small methylene blue and rhodamine-B photodegradation, indicating that self-photolysis of methylene

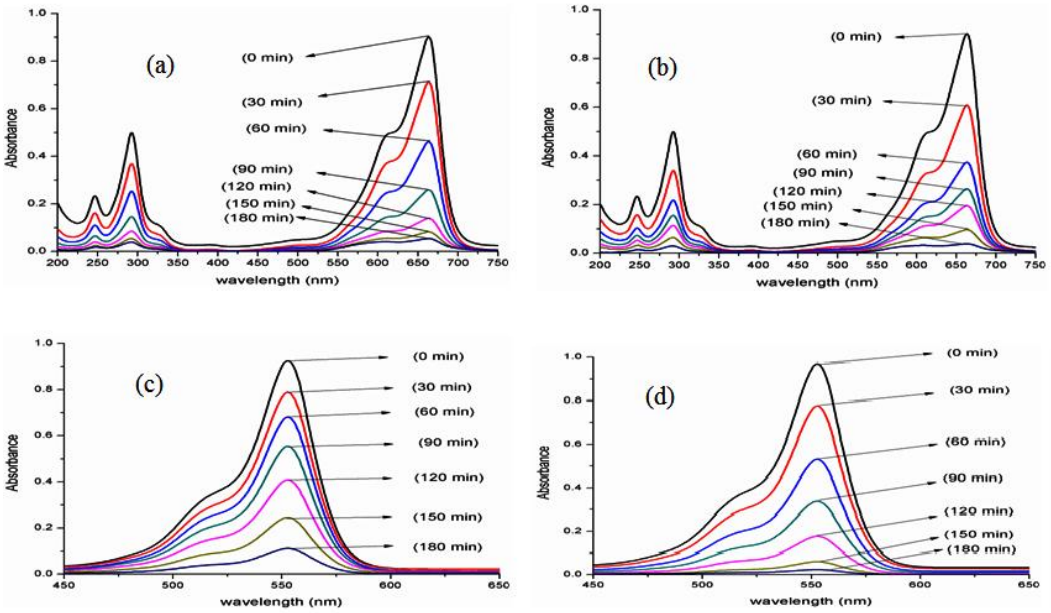

Figure 1. Absorbance spectral changes of methylene blue and rhodamine-B using cobalt sulfide (a) and (b) and cobalt-iron sulfide (c) and (d) under ultraviolet light.

blue and rhodamine-B is negligible under ultraviolet irradiation. We have carried out the degradation of methylene blue and rhodamine-B subjecting into ultraviolet light irradiation as followed by spectrophotometric monitoring. The experimental results are expressed by the change in relative concentration of dyes with irradiation time and are shown in **fig.1.**

This **shows** the continuous decrease in concentration of aqueous solution of dyes in presence of both catalysts with UV light irradiation. After irradiation of 180 min, the spectra suggest the 94 % and 95 % of decolourization/ degradation of methylene blue in presence of cobalt sulfide and cobalt-iron sulfide, respectively. In the case of rhodamine-B, 81 % and 97 % degradation

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were observed in the presence of cobalt sulfide and cobalt-iron sulfide, respectively. This study indicates that cobalt-iron sulfide exhibit better catalytic activity than cobalt sulfide [14].

4. Conclusion

These complexes have been exploited as single source precursors for the preparation of cobalt sulfide and cobalt-iron sulfide nanoparticles. Photocatalytic activities of both nanoparticles are evaluated by decolourization of methylene blue and rhodamine-B in aqueous solution under UV light irradiation. Cobalt-iron sulfide is found in enhancing the rate of photodegradation of toxic dyes as compared to cobalt sulfide. We expect this simple approach can be used for the synthesis of monometallic and bimetallic sulfide semiconductor nanoparticles with different morphologies, compositions and properties from single source precursors.

Conflict Of Interest
The authors declare no conflict of interest.

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