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Synthesis and characterization of Cu(II), Co(II) and Ni(II) complexes of a number of sulfadrug azodyes and their application for wastewater treatment

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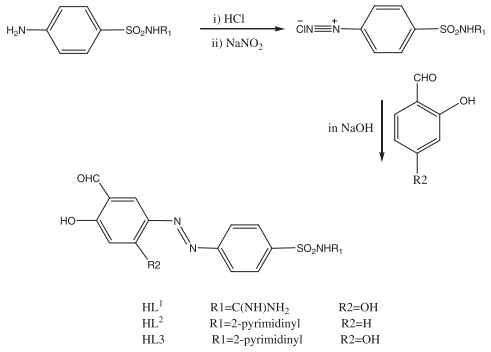
HIGHLIGHTS

- A number of sulfa drug azodyes were synthesized.
- The synthesized azodyes were characterized by ^{1}H NMR, mass and IR spectral analysis.
- Cu(II), Co(II) and Ni(II) complexes the azodye ligands were synthesized and characterized.
- The prepared complexes have been found to have octahedral structures.
- Applications of the prepared complexes in the oxidative degradation of indigo carmine dyes were evaluated.

GRAPHICAL ABSTRACT



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ABSTRACT

The azodye ligand (HL^1) was synthesized from the coupling of sulfaguanidine diazonium salt with 2,4-dihydroxy-benzaldehyde while the two ligands, HL^2 and HL^3, were prepared by the coupling of sulfadiazine diazonium salt with salicylaldehyde (HL^2) and 2,4-dihydroxy-benzaldehyde (HL^3). The prepared ligands were characterized by elemental analysis, IR, ^{1}H NMR and mass spectra. Cu(II), Co(II) and Ni(II) complexes of the prepared ligands have been synthesized and characterized by various spectroscopic techniques like IR, UV–Visible as well as magnetic and thermal (TG and DTA) measurements. It was found that all the ligands behave as a monobasic bidentate which coordinated to the metal center through the azo nitrogen and α-hydroxy oxygen atoms in the case of HL^1 and HL^3. HL^2 coordinated to the metal center through sulfonamide oxygen and pyrimidine nitrogen. The applications of the prepared complexes in the oxidative degradation of indigo carmine dye exhibited good catalytic activity in the presence of H_2O_2 as an oxidant. The reactions followed first-order kinetics and the rate constants were determined. The degradation reaction involved the catalytic action of the azo-dye complexes toward H_2O_2 decomposition, which can lead to the generation of HO. radicals as a highly efficient oxidant attacking the target dye. The detailed kinetic studies and the mechanism of these catalytic reactions are under consideration in our group.

Introduction

Recently, several studies have been published on the synthesis and spectral properties of azo dyes [1–3]. This reflects their widely important applications in different fields, such as polyester fiber [4], disperse dyes [5] as well as their involvement in many biological reactions and in analytical chemistry [6]. Heterocyclic azo dyes have played an important role in the development of coordination chemistry. The importance of these compounds may steam from their biological activity and analytical investigations [7]. Also, it is well known that heterocyclic azo compounds

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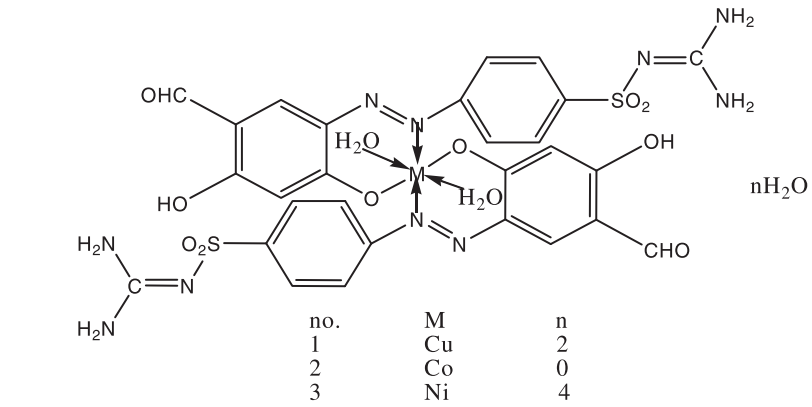
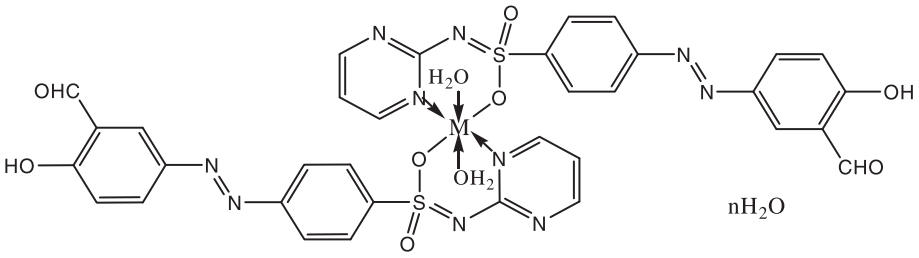
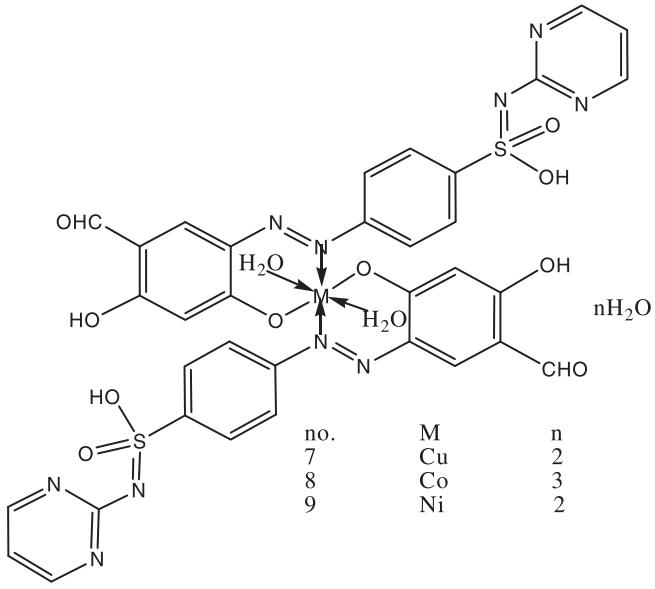


no.	M	n
1	Cu	2
2	Co	0
3	Ni	4



no.	M	n
4	Cu	1
5	Co	4.5
6	Ni	1.5



no.	M	n
7	Cu	2
8	Co	3
9	Ni	2

Fig. 1. Structure of metal complexes.

have been used to stabilize the low oxidation states of different metal ions [8–10].

Sulfonamides have been long used as drugs for treating cancer, tuberculosis, malaria, diabetes and leprosy [11]. What appears more important, for this study, is that sulfonamide and azo-sulfonamide derivatives have applicability as potential ligands for a large number of metal ions [12–16] due to presence of several potential donor atoms and their flexibility and ability to coordinate in either neutral or deprotonated form. They also contain C—N—NH structure unit, which form a strong chelate ring giving possible electron delocalization associated with extended conjugation that may affect the nature of the complex formed [13].

Complexes of transition metals are widely used in catalytic oxidations of hydrocarbons with molecular oxygen and peroxides [17]. The transition metal–ligand complexes can perform hydrogen peroxide decomposition with the resulting production of reactive oxygen species such as hydroxyl radicals [18]. Various methods have been employed for the generation of hydroxyl radicals such as O_3/UV, H_2O_2/UV, TiO_2 photo-catalysis, photo assisted Fe (III)/H_2O_2 reaction [19–21]. Recently, there has been increasing interest in the application of advanced oxidation process (AOPs) as attractive alternative treatments for the degradation of dyes in wastewater.

Textile dyeing is a significant consumer of water and producer of contaminated aqueous waste streams [22]. Indigo carmine (IC)