



Novel metal–organic photocatalysts: Synthesis, characterization and decomposition of organic dyes



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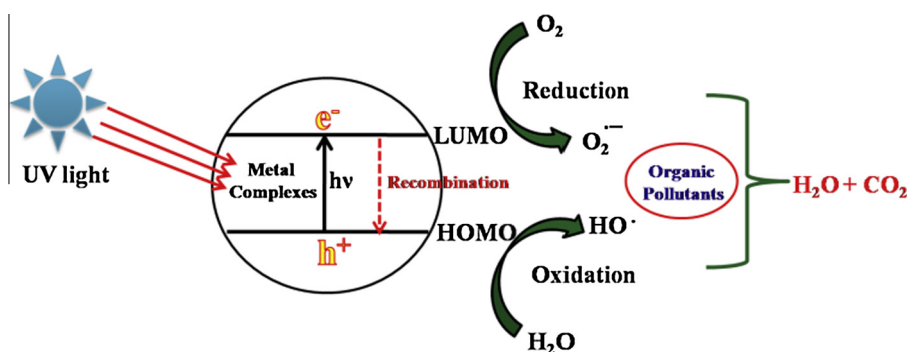
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HIGHLIGHTS

- The chemical and structural environments of the metal complexes were specified.
- The interaction of the hydrazone with $MCl_2 \cdot nH_2O$ afforded square planar complexes.
- Transition metal complexes are used as photocatalysts for the degradation of methylene blue dye under UV-light.
- Ni(II) complex shows higher photodegradation of MB than Co(II) complex at alkaline pH.
- Tentative mechanism of the photodegradation of dye in the presence of metal complex is described.

GRAPHICAL ABSTRACT

Tentative mechanism of the photodegradation of dye in the presence of metal complex is.



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ABSTRACT

An efficient method for the photocatalytic degradation of methylene blue in an aqueous medium was developed using metal–organic complexes. Two novel complexes were synthesized using, Schiff base ligand, *N*'-[(*E*)-(4-ethylphenyl)methylidene]-4-hydroxybenzohydrazide (HL) and Ni(II) (Complex 1)/Co(II) (Complex 2) chloride respectively. These complexes were characterized using microanalysis, various spectral techniques. Spectral studies reveal that the complexes exhibit square planar geometry with ligand coordination through azomethine nitrogen and enolic oxygen. The effects of catalyst dosage, irradiation time and aqueous pH on the photocatalytic activity were studied systematically. The photocatalytic activity was found to be more efficient in the presence of Ni(II) complexes than the Co(II) complex. Possible mechanistic aspects were discussed.

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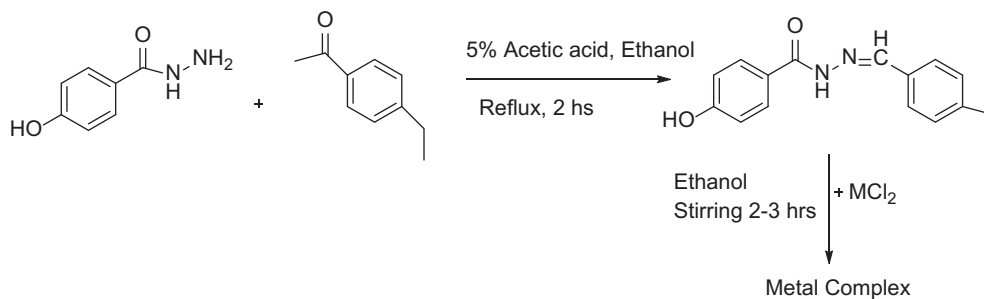
Introduction

Dyes are applied in textile manufacturing, leather tanning, and paper production and food technology industries as dyeing agents

[1]. The release of those colored waste waters in the ecosystem is a dramatic source of esthetical pollution, of eutrophication and of perturbations in the aquatic life. Hence effluents from industries contain a high level of environmentally hazard dyeing agents. Therefore, the effluent water has to be treated before disposal. There are many physicochemical techniques that can remove dyes from its aqueous solution which includes biological techniques-aerobic and anaerobic process, physical techniques-membrane

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Scheme 1. Synthesis of ligand and its complexes.

filtration, coagulation/flocculation, precipitation, flotation, adsorption, and chemical techniques chemical oxidation process of chlorination, bleaching, ozonation, Fenton oxidation and photocatalytic oxidation [2]. However, low removal efficiency or high cost of operation often limits their application [3].

In this concern, extensive work has been done recently on the photocatalytic degradation of environmentally hazardous pollutants using metal oxides due to their superior photocatalytic performance, non-toxicity, low production cost and high persistence to photocorrosion [4–7]. The process is based on the generation of the hydroxyl radicals ($\cdot\text{OH}$) that can oxidize a broad range of organic contaminants non-selectively in a short period of time. Interestingly, “advanced oxidation processes” (AOPs) also offer different routes to $\cdot\text{OH}$ production, allowing easier tailoring of the process for specific treatment requirements [8–12]. Since, structurally, dyes are double bonded such as $-\text{C}=\text{C}-$, $-\text{N}=\text{N}-$ and heterocyclic compounds, therefore transition metal ions are able to coordinate with most of the organic substances containing this type of bonds. This is because of their lenience in change of the oxidation state and presence of unpaired electrons the metal ions react readily with molecular oxygen, thereby mediating oxygenation of other compounds easily [13]. These properties have made use of transition metal complexes for the chemical, biological, photochemical and photo-biological degradation of the organic ligands. So far a number of metal complexes involving degradation of dyes and other pollutants has been reported from time to time [14].

From the previous reports it is evident that in all the cases hydrogen peroxide plays an important role in generating reactive species such as hydroxyl free radical and is used in the destruction of dispersed dyes. However, higher concentration of H_2O_2 is hazardous and it is harmful to eyes, lungs and skin. Recently reported degradation of MB in the absence of H_2O_2 using Co(II) , Ni(II) and Cu(II) complexes of $(2E)$ -2-[($2E$)-3-phenylprop-2-en-1-ylidene]hydrazinecarbothioamide [15]. In the continuation of our research on MB degradation using metal complexes, herein reporting with Ni(II) and Co(II) complexes of N -[(E)-(4-ethylphenyl)methylidene]-4-hydroxybenzhydrazide as a catalysts and also investigated the influence of various parameters such as

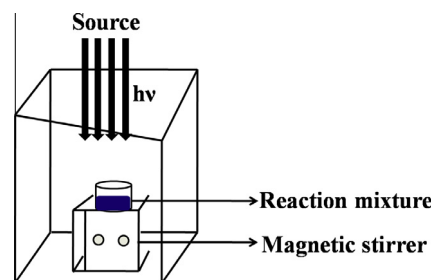


Fig. 1. Experimental setup for the photocatalytic degradation.

catalyst dosage, irradiation time and aqueous pH on the photocatalytic activity.

Experimental

Materials

Methylene Blue ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$) was used in this work which was purchased from s.d fine-chem limited, Bombay [99.0% pure]. 4-Hydroxybenzhydrazide [98% pure] and 4-Ethylbenzaldehyde [98% pure] were purchased from Sigma–Aldrich, Bangalore. Nickel chloride hexahydrate and Cobalt chloride hexahydrate [99% pure] were purchased from HiMedia laboratory Pvt. Ltd. Bombay and were used as received to prepare the precursor for the synthesis of photocatalytic complexes. Double-distilled water was used throughout the experiments.

Instruments used

C, H and N estimated on a Perkin Elmer CHN 2400 analyzer. Melting points of the compounds were determined by using capillaries in Sigma melting point apparatus, Sigma instruments, Chennai, India. Magnetic susceptibility measurements were carried at room temperature on a magnetic susceptibility balance (Sherwood Scientific, Cambridge, England) using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as standard. Electronic spectra were recorded on Elico-150 in DMSO solvent.

Table 1
The analytical and physical data of the ligand and its complexes.

Compound	Mol. Wt (g/mol)	Color	Melting point ($^{\circ}\text{C}$)	Elemental analysis data (%calculated/%observed)				μ_{eff} BM
				C	H	N	O	
HL	268.37	Color less	200–202	71.62 (71.56)	6.01 (5.89)	10.44 (10.39)	11.92 (11.78)	–
Complex I	593.30	Light blue	>300	64.78 (64.73)	5.10 (4.98)	9.44 (9.23)	10.79 (10.59)	0.77
Complex II	593.54	Rose	>300	64.75 (64.71)	5.09 (5.01)	9.44 (9.31)	10.78 (10.61)	0.99

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