



Photocatalytic Decomposition of Thiazole Yellow G Dye Using Cobalt Oxide and Cobalt Sulphide Nanoparticles

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ABSTRACT

Cobalt oxide and Cobalt sulphide nanoparticles were synthesized by using a series of new chiral mixed ligand (CML) ternary Cobalt(II) complexes [Co(MINAP)(aa)-2H₂O], where MINAP is p-methylisoinitrosoacetophenone as primary ligand and aa is various chiral amino acids such as L-alanine (Ala), L-valine (Val), L-leucine (Leu), L-methionine (Met) and L-phenylalanine (Phe) as secondary ligand. The CML-Metal complex precursors were heated at 700°C for three hours to obtain Cobalt oxide and Cobalt sulphide nanoparticles. The properties such as size, morphology and crystallinity of as-synthesized nanoparticles were studied by powder XRD, FTIR and SEM images. The XRD patterns confirm the presence of Co₃O₄ and CoS₄ nanoparticles. The SEM analyses of Cobalt oxide and Cobalt sulphide particles showed the formation of particles in nanosizes.

KEYWORDS

Cobalt oxide, Cobalt sulphide, Nanoparticles, CML-Metal complex

INTRODUCTION

The advancements in nano chemistry has given scope to synthesize wide range of nanostructured materials having unprecedented properties and usage¹⁻³. Sub-micron to nano-phased metal powders having variety of shapes find wide applications as catalysts, optical and magnetic recording media, superconductors, high performance engineering materials, dyes, pigments, adhesives, photographic suspensions, drug delivery media and so on⁴⁻⁸. Nano particle oxides of transition metals have exceptional properties which stimulate many advanced applications⁹⁻¹¹. Cobalt oxide is a very important material extensively used in catalysis, gas sensors, electrochromic films, battery cathodes, heterogeneous catalytic materials, rechargeable batteries, catalyst for abatement of carbon monoxide, gas sensors and as magnetic materials¹²⁻¹⁶. Several methods have been employed for synthesis of nanocrystalline materials such as bottom-up approach, top-down approach i.e. physical vapor deposition, inert gas condensation, molecular beam epitaxy, chemical vapor deposition (CVD), laser ablation, sol-gel process, cathode sputtering etc¹⁷⁻²¹. In the present study the CML-Cobalt complexes were sintered at 700°C for three hours to achieve Cobalt oxide and Cobalt sulphide nanoparticles.

EXPERIMENTAL MATERIALS

Highly pure Analytical Grade chemicals and reagents were used throughout. The chiral amino acids were used as procured from THOMAS BAKER. The previously reported methods²² were used to prepare sodium salt of p-methylisoinitrosoacetophenone. All the solvents were distilled and purified according to standard procedures²³ prior to their use.

The FTIR spectra of Cobalt oxide and Cobalt sulphide nano sized particles were recorded in KBr on Perkin-Elmer *Precisely* Spectrum 100 FT-IR Spectrometer between 4000-400 cm⁻¹ region. The X-ray diffraction measurements of the Cobalt oxide and Cobalt sulphide nanoparticles were recorded on Rigaku Miniflex X-ray diffractometer CuK radiation (λ = 1.542Å) with Nickel filter in the range of 20° to 80° at a scan speed of 5°/min. The SEM images of the particles prepared were captured on SEM instrument.

METHODS

(a) Preparation of Complexes

An aqueous solution (1mmol) of sodium salt of p-methylisoinitrosoacetophenone was added slowly with constant stirring to the aqueous solution (1mmol) of Cobalt sulphate heptahydrate. This mixture was then kept in a boiling water bath for 30 minutes. Further it was cooled and added an aqueous solution (1mmol) of the sodium salt of chiral amino acid to it. The resultant mixture of 1:1:1 stoichiometry was then refluxed for three hours in a hot water bath. The brown coloured complexes thus obtained were filtered, washed with ice-cold water followed by 1:1:ethanol:water. Complexes were dried under vacuum. Synthesis of present complexes may be given by following equation.



Where Na-MINAP: Na salt of p-methylisoinitrosoacetophenone, Na-aa: Na salt of L-amino acid.

The CML complexes were characterised by elemental analysis and different physicochemical techniques²⁴.

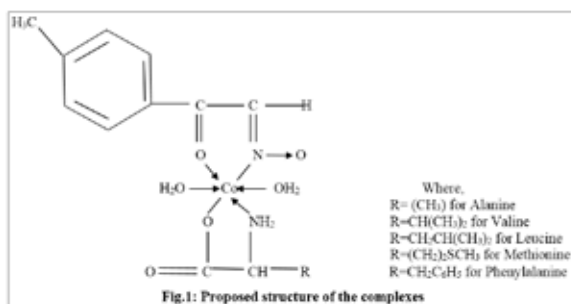


Fig.1: Proposed structure of the complexes

(b) Preparation of Cobalt oxide and Cobalt sulphide nanoparticles

The synthesized CML-Cobalt complexes were used as precursors for

the preparation of Cobalt oxide and Cobalt sulphide nanoparticles. These precursor complexes were sintered in a muffle furnace at temperature of 700°C for three hours. The particles thus obtained were cooled to room temperature and stored in desiccator. The morphological characterisation and structural study of these nanoparticles was done by using FTIR, SEM and powder-XRD instruments. The elemental analyses of the Cobalt oxide and sulphide materials were done on EDAX in-built in Jeol SEM instrument.

RESULTS AND DISCUSSIONS

The XRD pattern of all the Cobalt oxide and Cobalt sulphide nanoparticles obtained from sintering of the chiral mixed ligand complexes have shown that, all the materials obtained were crystalline in nature. The peak positions found at 2 scattering angles of about 31, 37, 45, 59 and 65 degrees with corresponding hkl planes of (111), (311), (400), (511) and (533) respectively are assigned to diffraction for Cobalt oxide (JCPDS 73-1701) and Cobalt sulphide (JCPDS 75-1561) cubic nanoparticles crystal lattice, which confirms the absence of characteristic peaks for any impurities. The powder X-Ray diffraction patterns of the present Cobalt oxide and Cobalt sulphide nanoparticles as obtained from the Rigaku Mini-flex X-ray Diffractometer are shown in the following figures 2a-2e.

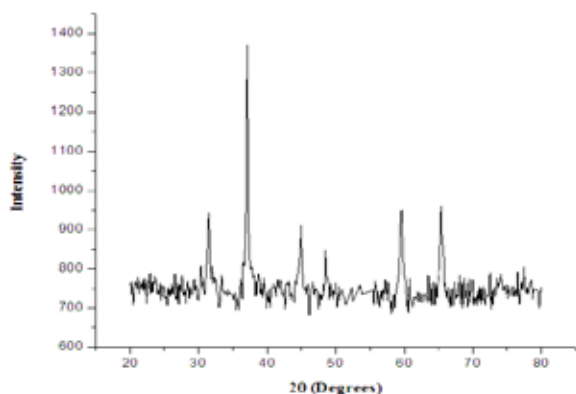


Fig.2a: XRD pattern of Cobalt oxide, nanoparticles of [Co(MINAP)(Ala).2H2O]

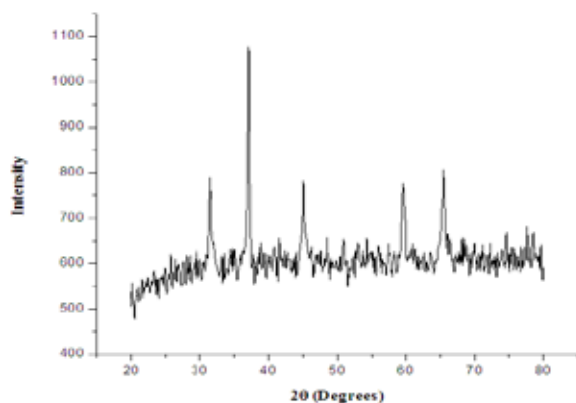


Fig.2b: XRD pattern of Cobalt oxide nanoparticles of [Co(MINAP)(Val).2H2O]

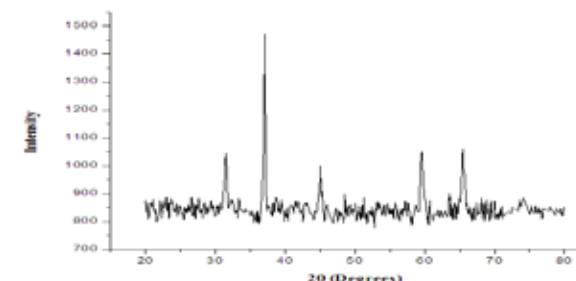


Fig.2c: XRD pattern of Cobalt oxide nanoparticles of [Co(MINAP)(Leu).2H2O]

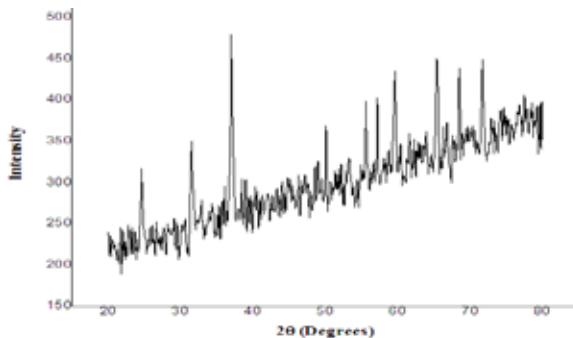


Fig.2d: XRD pattern of Cobalt sulphide nanoparticles of [Co(MINAP)(Met).2H2O]

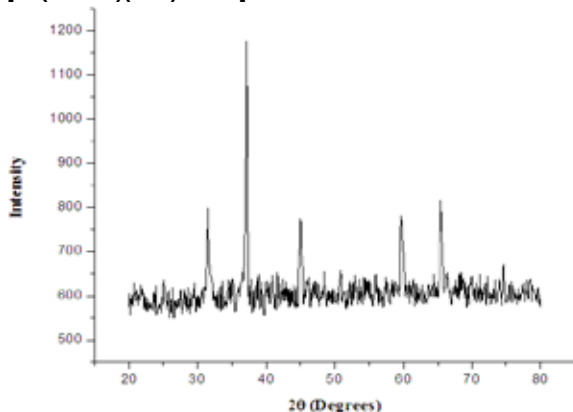


Fig.2e: XRD pattern of Cobalt oxide nanoparticles of [Co(MINAP)(Phe).2H2O]

The FTIR spectra of present Cobalt oxide and Cobalt sulphide nanoparticles show the significant absorption bands at 580cm⁻¹ were assigned to Co-O stretching vibration mode⁸ and 670cm⁻¹ was assigned to the bridging vibration of O-Co-O bond²⁵⁻²⁷. Fig. 3a and 3b shows the representative FTIR spectra for the Cobalt oxide and Cobalt sulphide nanoparticles.

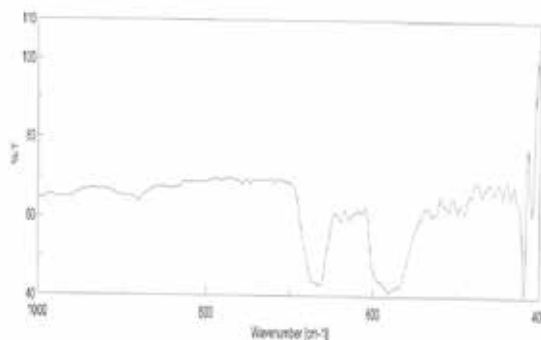


Fig.3a: FTIR Spectrum of Cobalt oxide nanoparticles of [Co(MINAP)(Val).2H2O]

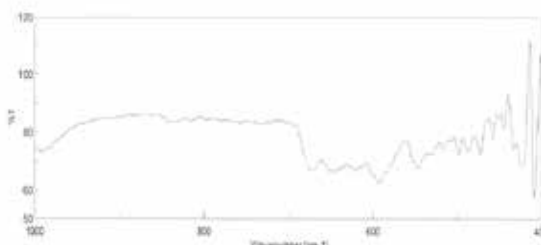


Fig.3b: FTIR Spectrum of Cobalt sulphide nanoparticles of [Co(MINAP)(Met).2H2O]

The SEM micrograph of the Cobalt oxide and Cobalt sulphide nanoparticles are presented in Fig.4a-4e with an image magnification. The characterisation data of all the nanoparticles is tabulated in Table-1.

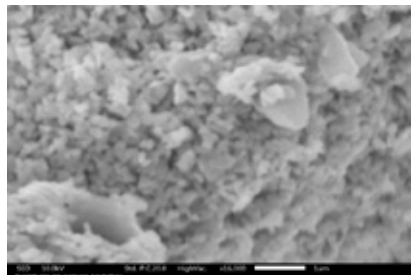


Fig.4a: SEM image of Cobalt oxide nanoparticles of [Co(MINAP)(Ala).2H2O]

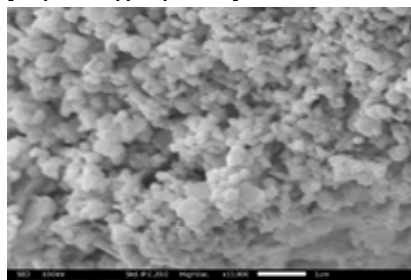


Fig.4b: SEM image of Cobalt oxide nanoparticles of [Co(MINAP)(Val).2H2O]

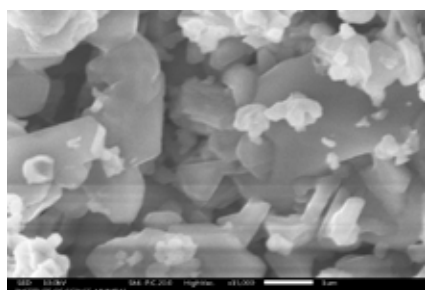


Fig.4c: SEM image of Cobalt oxidenanoparticles of [Co(MINAP)(Leu).2H2O]

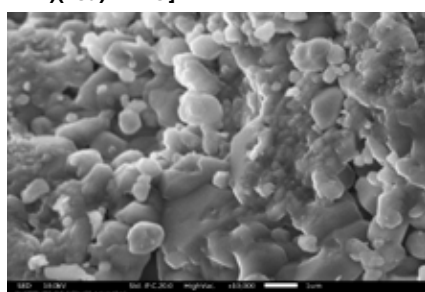


Fig.4d: SEM image of Cobalt sulphide nanoparticles of [Co(MINAP)(Met).2H2O]

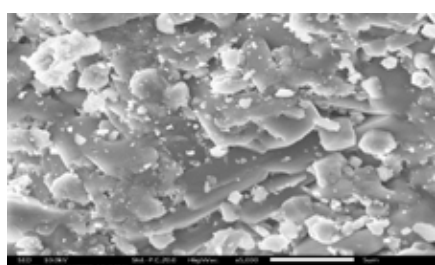


Fig.4e: SEM image of Cobalt oxidenanoparticles of [Co(MINAP)(Phe).2H2O]

Table-1: Characterisation Data of Nanoparticles obtained from CML Cobalt Complexes

Sr. No.	Precursor complex	Nanoparticles obtained	FTIR (cm ⁻¹)		SEM Particle size (nm)
1	[Co(MINAP)(Ala).2H ₂ O]	Cobalt oxide	586	664	80
2	[Co(MINAP)(Val).2H ₂ O]	Cobalt oxide	582	665	60
3	[Co(MINAP)(Leu).2H ₂ O]	Cobalt oxide	588	670	75
4	[Co(MINAP)(Met).2H ₂ O]	Cobalt sulphide	593	673	95
5	[Co(MINAP)(Phe).2H ₂ O]	Cobalt oxide	571	675	67

DECOMPOSITION OF TOXIC DYE:

The azo dyes are most extensively used class of synthetic dyes in various large scale and small scale industries, laboratories etc due to their variety of applications. But during dyeing process about 20% of total dyes production is lost worldwide causing environmental pollution and health hazards to living organisms including human. Some azo dyes are found to be mutagenic, highly toxic and highly stable. Thus, it is necessary to degrade these dyes and alter their toxic effects towards lower toxicity before disposing them as effluents into sewage.

The present nanomaterials were applied for the photocatalytic degradation of potentially hazardous Thiazole Yellow G dye in a homemade photocatalysis reactor and various parameters such as contact time, amount of nanomaterial, type/origin of nanomaterial were optimized. The nanomaterials were found to be effective for TYG degradation under optimized reaction conditions.

PART-I: COBALT OXIDE NANOPARTICLES

EFFECT OF TIME:

The time required for optimum degradation of the TYG dye using Cobalt oxide nanoparticles was studied, which is tabulated (Table-2) and represented in the curve (Fig.5) shown as below.

Table-2: Effect of Time on Degradation of Dye

Time (min)	Absorbance (A _λ)	X (%)	%D
0	0.742	100.00	0.00
15	0.742	100.00	0.00
30	0.742	100.00	0.00
45	0.742	100.00	0.00
60	0.696	93.80	6.20
75	0.676	91.11	8.89
90	0.607	81.81	18.19
105	0.537	72.37	27.63
120	0.468	63.07	36.93
135	0.399	53.77	46.23
150	0.331	44.61	55.39
165	0.259	34.91	65.09
180	0.193	26.01	73.99
195	0.125	16.85	83.15
210	0.056	7.55	92.45
225	0.056	7.55	92.45
240	0.056	7.55	92.45

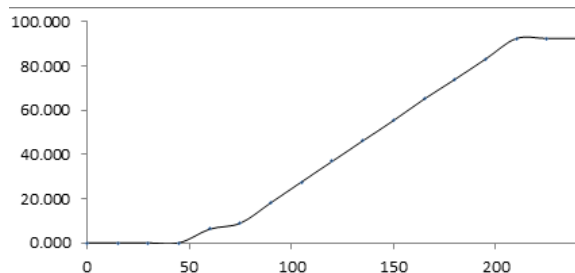


Fig.5: Effect of Time on Dye Degradation

EFFECT OF AMOUNT OF CATALYST:

The maximum amount of catalyst required for optimum degradation of the TYG dye for optimum equilibration time of three and half hours was determined by carrying out the experiments in absence of the catalyst and gradual increase in amount of catalyst up to 250mg. The findings are tabulated (Table-3) and represented in the graph (Fig.6) shown below.

Table-3: Effect of Amount of the catalyst on dye degradation

Amount of catalyst (g)	Absorbance (A _v)	X(%)	%D
0.000	0.742	100.00	0.00
0.025	0.115	15.50	84.50
0.05	0.056	7.55	92.45
0.075	0.056	7.55	92.45
0.1	0.056	7.55	92.45
0.125	0.056	7.55	92.45
0.15	0.056	7.55	92.45
0.175	0.056	7.55	92.45
0.2	0.056	7.55	92.45
0.225	0.056	7.55	92.45
0.25	0.056	7.55	92.45

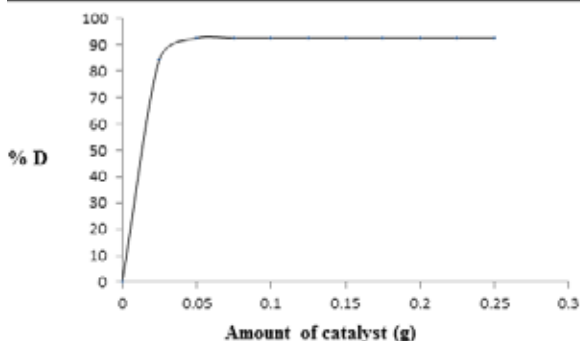


Fig.6: Effect of Amount of Catalyst

PART-II: COBALT SULPHIDE NANOPARTICLES

EFFECT OF TIME:

The time required for optimum degradation of the TYG dye using Cobalt sulphide nanoparticles was studied and tabulated (Table-4) and represented graphically (Fig.7) as shown below.

Table-4: Effect of Time on Dye Degradation

Time (min)	Absorbance (A _v)	X (%)	%D
0	0.742	100.00	0.00
15	0.742	100.00	0.00
30	0.742	100.00	0.00
45	0.742	100.00	0.00
60	0.731	98.52	1.48
75	0.708	95.42	4.58
90	0.641	86.39	13.61
105	0.568	76.55	23.45
120	0.502	67.65	32.35
135	0.431	58.09	41.91
150	0.365	49.19	50.81
165	0.293	39.49	60.51
180	0.227	30.59	69.41
195	0.159	21.43	78.57
210	0.089	11.99	88.01
225	0.089	11.99	88.01
240	0.089	11.99	88.01

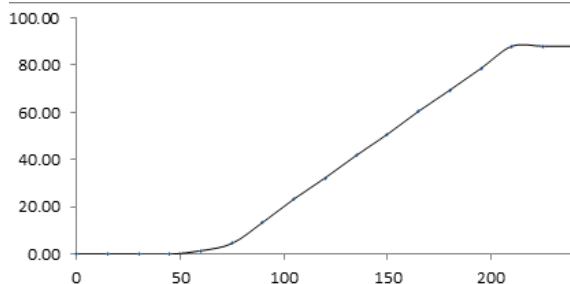


Fig.7: Effect of Time on Dye Degradation

EFFECT OF AMOUNT OF CATALYST:

The maximum amount of Cobalt sulphide nanoparticles required for optimum degradation of the TYG dye for optimum equilibration time of three and half hours was determined and the findings are tabulated (Table-5) and represented in the graph (Fig.8) shown below.

Table-5: Effect of Amount of Catalyst on Degradation of Dye

Amount of catalyst (g)	Absorbance (A _v)	X(%)	%D
0.000	0.742	100.00	0.00
0.025	0.146	19.68	80.32
0.05	0.089	11.99	88.01
0.075	0.089	11.99	88.01
0.1	0.089	11.99	88.01
0.125	0.089	11.99	88.01
0.15	0.089	11.99	88.01
0.175	0.089	11.99	88.01
0.2	0.089	11.99	88.01
0.225	0.089	11.99	88.01
0.25	0.089	11.99	88.01

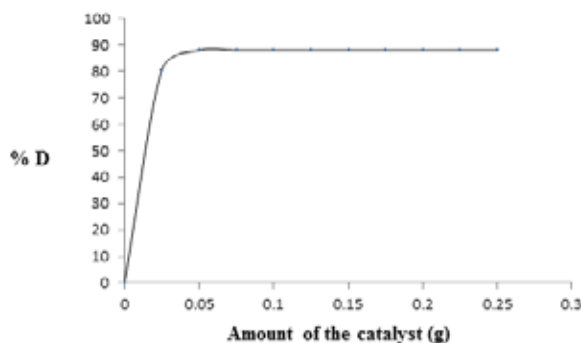


Fig.8 Effect of Amount of the catalyst

The Cobalt oxide and Cobalt sulphide nanoparticles in the present study obtained from CML-Metal complexes were used for their photocatalytic activity and percentage degradation of TYG dye for various nanoparticles given below.

Table-6: Percentage Degradation of TYG for different nanoparticles

Sr.No.	Precursor Complex	Nanoparticles Obtained	Absorbance(A _v)	X (%)	%D
1	[Co(MINAP)(Ala).2H ₂ O]	Cobalt Oxide	0.075	10.11	89.89
2	[Co(MINAP)(Val).2H ₂ O]	Cobalt Oxide	0.056	7.55	92.45
3	[Co(MINAP)(Leu).2H ₂ O]	Cobalt Oxide	0.070	9.43	90.57
4	[Co(MINAP)(Met).2H ₂ O]	Cobalt Sulphide	0.089	11.99	88.01
5	[Co(MINAP)(Phe).2H ₂ O]	Cobalt Oxide	0.063	8.49	91.51

REUSABILITY OF THE CATALYST:

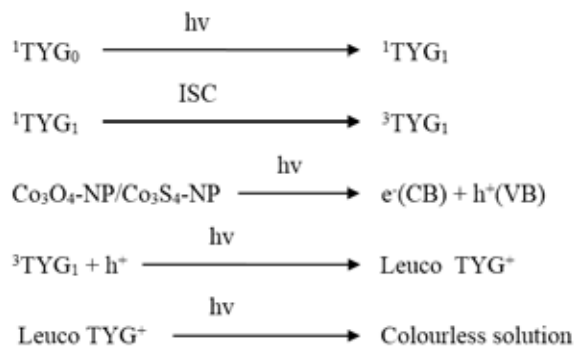
The reusability of the present catalysts were checked to find the sustainability of the catalysts for number of catalytic cycles and it was found that the representative Cobalt oxide nanoparticles obtained from [Co(MINAP)(Val).2H₂O] complex were effective till four catalytic cycles and after which only very little loss in catalytic activity has been observed.

Table-7: Reusability of the catalyst

No. of Catalytic Cycles	Absorbance (A ₀)	X (%)	%D
1	0.056	7.55	92.45
2	0.056	7.55	92.45
3	0.056	7.55	92.45
4	0.056	7.55	92.45
5	0.082	11.05	88.95
6	0.098	13.21	86.79

REACTION MECHANISM OF DECOMPOSITION OF TYG DYE:

The probable mechanism of decomposition of TYG dye using present nanomaterials as catalyst may be represented as follows.



The Thiazole Yellow G (¹TYG₀) absorbs radiations in the visible region and generate its excited singlet state (¹TYG₁). This excited singlet state undergoes intersystem crossing (ISC) and gives the triplet state (³TYG₁) of TYG. The Co₃O₄ and Co₃S₄ nanoparticles absorb the light energy to excite its electron (e⁻) from valence band (VB) to the conduction band (CB) of nanoparticles (Co₃O₄-NP/Co₃S₄-NP) and a hole (h⁺) is created in valence band. The holes in the valence band of semiconducting nanoparticles oxidize the dye molecules to its leuco form (TYG⁺) and as a consequence, decomposition of the dye results to the bleaching of TYG dye.

CONCLUSIONS

The present study deals with the synthesis, characterization and successful application of Co₃O₄ and Co₃S₄ nanoparticles for a potentially hazardous Thiazole Yellow G an azo dye. The physicochemically characterized Cobalt oxide and Cobalt sulphide nanoparticles obtained by decomposition of M-CML complexes at 700°C which were found to be potential photocatalysts for degradation of the dye in present study. Various parameters such as Time of contact, Catalyst selectivity, amount of catalyst were set for optimum dye degradation conditions. It was found that Co₃O₄ nanoparticles obtained from oxidative decomposition of [Co(MINAP)(Val).2H₂O] complex gives higher value of degradation of TYG dye.

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