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2-(2'-hydroxy-3'-methoxy phenyl)-4-bromo-6 methylbenzothiazolyl hydrazones and its metal complexes of Cr^{+++}, Mn^{++}, Fe^{+++} act as a catalyst in alcohol fermentation

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Abstract

A new hydrazine ligand, 2-(2′-hydroxy-3′-methoxyphenyl)-4-bromo-6-methylbenzothiazolyl hydrazone, has been synthesized and its coordination complexes with Cr(III), Mn(II), and Fe(III) ions have been prepared and characterized. The ligand and its metal complexes were characterized using elemental analysis, molar conductance, magnetic susceptibility, and spectroscopic techniques such as UV–Visible and FT-IR spectroscopy, confirming the proposed structures and coordination behavior. The catalytic efficiency of the synthesized metal complexes was investigated in alcohol fermentation reactions. Compared to the free ligand, the metal complexes exhibited enhanced catalytic activity, which is attributed to the presence of transition metal ions facilitating redox processes and improving reaction kinetics. Among the studied complexes, the Fe(III) and Mn(II) complexes demonstrated superior catalytic performance, suggesting their potential role in promoting fermentation efficiency. The results indicate that coordination of the hydrazone ligand with transition metals significantly influences catalytic behavior. These findings highlight the potential application of benzothiazole-based hydrazone metal complexes as effective catalysts in alcohol fermentation processes and related biochemical transformations.

1. Introduction

Hydrazones constitute an important class of Schiff base compounds formed by the condensation of hydrazides or hydrazines with carbonyl compounds. Owing to the presence of azomethine nitrogen and additional donor atoms such as oxygen or sulfur, hydrazones exhibit strong chelating ability toward transition metal ions, resulting in stable coordination complexes with diverse geometries and properties [1–3]. These complexes have attracted significant attention because of their applications in catalysis, analytical chemistry, and biological systems.

Benzothiazole-containing hydrazones represent a particularly interesting subclass due to the presence of a heterocyclic sulfur–nitrogen system that enhances electronic delocalization and metal-binding capacity. Benzothiazole derivatives have been reported to possess notable chemical stability and functional versatility, making them suitable for catalytic and biochemical applications [4,5]. Substituents such as hydroxyl, methoxy, bromo, and methyl groups further influence the ligand's electron density and coordination behavior, thereby affecting the catalytic performance of their metal complexes.

Transition metal ions such as chromium(III), manganese(II), and iron(III) are widely studied in coordination chemistry because of their variable oxidation states, redox activity, and ability to participate in electron-transfer reactions [6,7]. Metal complexes of hydrazone ligands incorporating these ions have shown promising catalytic activity in oxidation–reduction reactions and other organic transformations. In particular, iron and manganese complexes are of interest due to their relevance in biological systems and enzymatic processes [8].

Alcohol fermentation is a vital biochemical process employed in the production of ethanol and other industrially important products. The efficiency of fermentation depends on several factors, including enzyme activity, redox balance, and availability of catalytic species [9]. The use of metal complexes as catalysts or catalytic promoters in fermentation has gained attention as a strategy to enhance reaction rates and improve alcohol yield. Metal ions and their complexes are known to influence fermentation pathways by facilitating redox reactions and stabilizing intermediate species [10].

In the present work, the synthesis of **2-(2′-hydroxy-3′-methoxyphenyl)-4-bromo-6-methylbenzothiazolyl hydrazone** and its coordination complexes with Cr(III), Mn(II), and Fe(III) is reported. The ligand and its metal complexes were characterized using appropriate analytical and spectroscopic techniques. Their catalytic activity in alcohol fermentation was investigated to evaluate the effect of metal coordination on fermentation efficiency. This study aims to contribute to the understanding of benzothiazole-based hydrazone metal complexes as potential catalysts in alcohol fermentation processes.

2. Material and methods

Microorganism:
The yeast used in this study was Saccharomyces cerevisiae, obtained from the local market. The culture was maintained on solid yeast medium.

Molasses:
Molasses were obtained from Bhaurao Co-op. Sugar Industries, Laxmi Nagar, Nanded. The molasses contained approximately 40% reducing sugars and were diluted to prepare media with different sugar concentrations. The production medium was supplemented with nitrogen and phosphate sources, and the pH was adjusted to 5.

Media Composition:

- KH_2PO_4: 0.1%
- $(NH_4)_2SO_4$: 0.5%
- $MgSO_4 \cdot 7H_2O$: 0.05%
- Yeast extract: 0.1%
- pH: 5 (adjusted dropwise using dilute sulfuric acid)

Metal Chelates and Salts:

Cr^{+++}, Mn^{++}, Fe^{+++} metal ion and one chelates is used in the study:

1. 2-(2'-Hydroxy-3'-methoxy phenyl)-4-bromo-6-methylbenzothiazolyl hydrazone (HMPBMBTH)

Metal salts and these metal chelates were added to different experimental fermentation containers.

Fermentation Process:

A batch fermentation process was adopted. Fermentation flasks were prepared, labeled, and supplemented with yeast, metal salts, or metal chelates. The pH of each flask was carefully adjusted before incubation.

Experimental: - To study the effect of the metal ions and metal chelates different experiment were carried out. All the fermentation flask were sterilized. All solution which are used for the experiment were also sterlised . 8 fermentation flask (sterlised) were arranged and they were labeled from 1 to 8.

Fermentation flask no.1 is used as control, Fermentation flask no. 2 $CrCl_3$ salt 0.05 gm were added.

Flask no 3 is used to study the effect of 2-(2'-hydroxy-3'-methoxy phenyl) -4-bromo-6-methyl benzothiazolyl hydrazones on fermentation process. In conical flask no.4 [Cr (HMPBMBTH) 2Cl H_2O] Cl In flask no. 5, 0.05 gm $MnCl_2$ where flaske 6, [Mn $(HMPBMBTH)_2$] $Cl_2.H_2O$ 0.05 gm complex were added flask no7 , FeCl2 0.05gm FeCl2 were added. In flask no. 8, [Fe (HMPBMBTH) 2Cl H_2O] Cl 0.05 gm were put.

Solution like 0.05 % $KHSO_4$, 0.5% $(NH_4)_2SO_4$, 0.05 % $MgSO_4$ $7H_2O$ and as mentioned above different metal ion were added . the pH of the experiment is adjusted by putting drop by drop dil. H_2SO_4. The fermentation reaction were carried out for 24 hours. In each fermentation flask 10 ml 1% molasses solution and media

Estimation of biomass.:-

The quantity of biomass depends upon yeast growth takes place.
The dry biomass were measured by transferring the content of conical flask through the filter paper. The residue of biomass which is collected on the filter paper is dried by keeping it in oven at 100°C. The mass of biomass were recorded and it is given in the table.

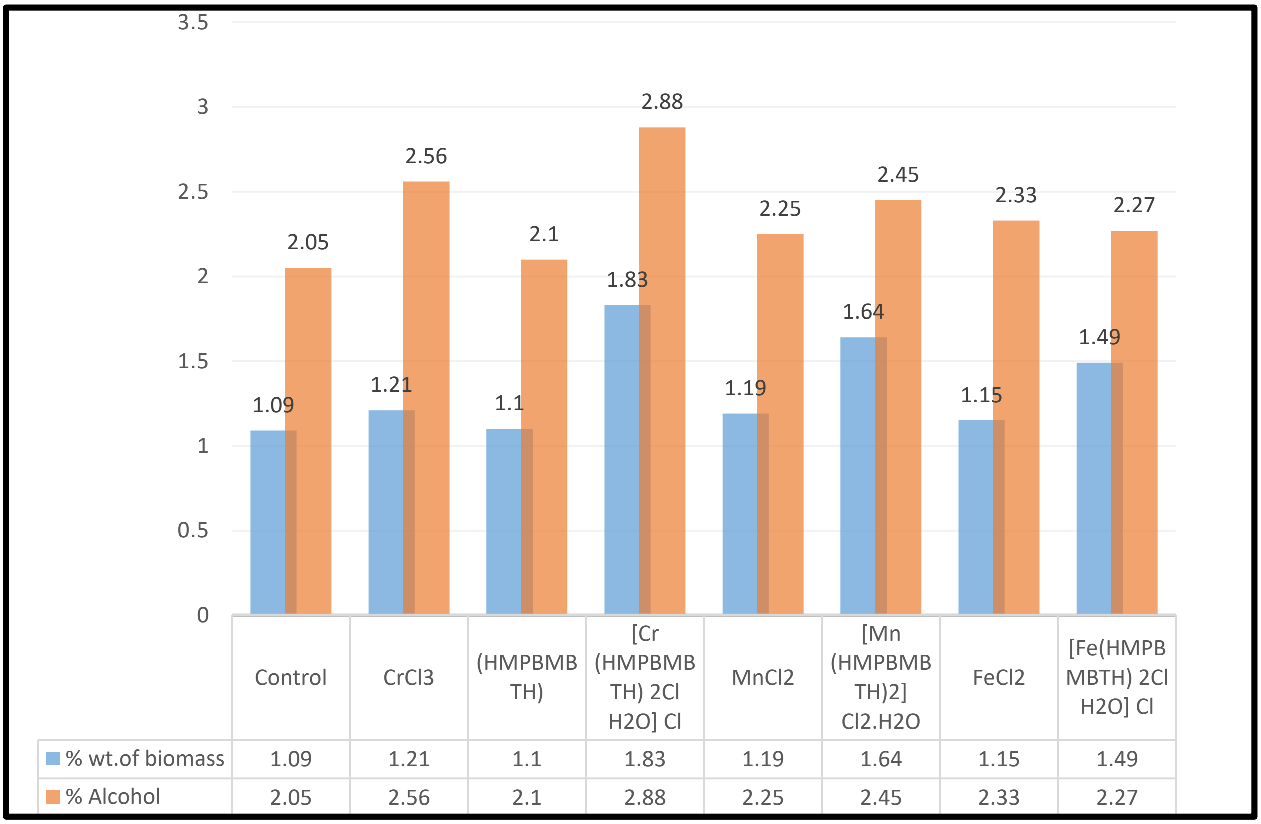
Estimation of ethyl alcohol:-

Spectroscopic method is used to determine the alcohol generated in the fermentation process. Fermented wash were taken in distillation flask. 15 ml distillate were collected in the conical flask. 5 ml $K_2Cr_2O_7$ (0.1N) in 0.1N H_2SO_4 solution were added it is warmed at 60°C. The color obtained. The optical density of solution were measured from standard graph. The ethanol generated during fermentation were determined.

Sr. No.	Flask No.	Compounds	%wt. of biomass	% Alcohol

1	1	Control	1.09	2.05
2	2	CrCl3	1.21	2.56
3	3	(HMPBMBTH)	1.10	2.10
4	4	[Cr (HMPBMBTH) 2Cl H_2O] Cl	1.83	2.88
5	5	MnCl2	1.19	2.25
6	6	[Mn (HMPBMBTH)2] Cl2.H2O	1.64	2.45
7	7	FeCl2	1.15	2.33
8	8	[Fe(HMPBMBTH) 2Cl H2O] Cl	1.49	2.27

Graphical representation of result



3. Result Interpretation.

The given data show the effect of different metal salts and their complexes on biomass formation and alcohol production in comparison with the control.

The control flask recorded a biomass of 1.09% and alcohol production of 2.05%, which represents the normal growth and fermentation level. Addition of $CrCl_3$ increased both biomass (1.21%**)** and alcohol content (2.56%) compared to the control, indicating that chromium ions enhance metabolic activity. The ligand HMPBMBTH alone did not produce any significant change, as biomass (1.10%) and alcohol (2.10%) remained almost similar to the control.

A marked improvement was observed with the chromium complex $[Cr(HMPBMBTH)_2Cl \cdot H_2O]Cl$, which showed the highest biomass (1.83%) and alcohol production (2.88%) among all treatments. This suggests that complex formation with chromium greatly enhances microbial growth and alcohol synthesis.

In the case of manganese, $MnCl_2$ caused a slight increase in biomass (1.19%) and alcohol (2.25%) over the control. Its complex $[Mn(HMPBMBTH)_2]Cl_2 \cdot H_2O$ further enhanced biomass (1.64%) and alcohol production (2.45%), showing a positive synergistic effect of manganese with the ligand, although the effect was less than that of the chromium complex.

For iron, $FeCl_2$ resulted in biomass of 1.15% and alcohol content of 2.33%, indicating moderate stimulation. The iron complex $[Fe(HMPBMBTH)_2Cl \cdot H_2O]Cl$ showed higher biomass (1.49%) but slightly lower alcohol production (2.27%) compared to $FeCl_2$, suggesting that iron complexation favors growth more than alcohol formation.

Overall, the data indicate that metal complexes are more effective than the control, metal salts, or ligand alone in improving biomass and alcohol production. Among all treatments, the chromium complex exhibited the strongest enhancement, followed by manganese and iron complexes.

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