Research Article

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Synthesis, Structural Elucidation and Photocatalytic Studies of some 4-Aminoantipyrine-based Ruthenium (III) Complexes

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ABSTRACT

Photo-catalytic studies are considered as the effective process of organic pollutants degradation, which decrease the impacts on human health and the environment. The present study was conducted to evaluate the photo-catalytic activities of some 4-aminoantipyrine-based Ru (III) complexes against methylene blue dye. A series of five novel Schiff base ruthenium complexes (RuL_2Cl_2) have been synthesized by the reaction between five types of 4-aminoantipyrine derived Schiff base ligands and ruthenium trichloride by direct condensation method. The synthesized ligands and metal complexes were characterized using analytical and various spectral techniques. The rate of photo-catalytic degradation of methylene blue using the synthesized metal complexes was calculated using UV light. As the number of active sites on the catalyst's surface increased with the increasing amounts of catalyst, the degradation rate increased. Additionally, an increase may result in the accumulation of free catalyst, as well as an increase in opacity and a reduction in UV light penetration. The formation of hydroxyl radicals was the cause for successful degradation of methylene blue dye. The synthesized Ru (III) complexes have shown highest percentage of degradation on photo-catalytic activity.

Keywords: 4-aminoantipyrine; Photo-catalytic activity; Ruthenium (III) complexes.

1. INTRODUCTION

Schiff bases derivatives prepared from 4-aminoantipyrine show wide variety of applications in many fields such as biological, inorganic and analytical chemistry (Deshmuk *et al.* 2015). Recent studies confirmed that ruthenium complexes act as a good catalyst for the oxidation of organic compounds. The developing environmental restrictions to reduce pollution in industrial processes have initiated the development of substitute technologies as replacement to the conventional and harmful approaches. In catalysis, water pollution is a major problem all over the world. Presence of toxic dye materials in water may be harmful to animals and plants. Disinfection of water is one of the applications of photocatalytic activity.

2. MATERIALS AND METHODS

2.1 Synthesis of Schiff base

To an alcoholic solution of higher amides, a 4-aminoantipyrine solution was added. The solution was vigorously stirred and allowed to cool after being refluxed for 5 hours. The solid intermediate was added to the alcoholic solution of phenylenediamine. The mixture was refluxed and poured into crushed ice. The brown solid ligand (L) product was separated, filtered and recrystallized from the alcohol. The synthesized ligand on condensation reaction with ruthenium trichloride formed RuL^1Cl_2, RuL^2Cl_2, RuL^3Cl_2, RuL^4Cl_2 and RuL^5Cl_2 complexes.

2.2 Photo-catalytic activity

The photocatalytic decomposition of methylene blue (MB) was used to test the sample's recycling ability under UV light irradiation, with a 300 W ultraviolet lamp as the light source. The photocatalytic experiment was carried out by mixing 50 mg of prepared sample with 100 mL of MB aqueous solution (0.5 mg/L). After irradiation with ultraviolet light, the suspension was stirred in the dark for 20 minutes to achieve adsorption and desorption equilibrium. The 5 mL solution was sampled and centrifuged at 20-minute intervals during the photocatalytic reaction. Before measurement, 5 mL of the suspension was removed and centrifuged (10000 rpm; 2 min.) to remove the photocatalyst. An UV-Vis. spectrophotometer was used to monitor the supernatant at the characteristic absorption wavelength of MB (662 nm) (John and Joseyphus, 2019). The photo-catalytic efficiency (%) was calculated using the formula:

$$\% \text{ Degradation} = \frac{(A_0 - A_t) \times 100}{A_0}$$

where, A_0 and A_t are the absorbances of MB solution before and after the photo-catalytic reaction.

3. RESULTS

The photocatalytic activity of the prepared samples was evaluated by degradation of MB under ultraviolet light irradiation ($\lambda < 400$ nm) with different intervals of time. The irradiation time photocatalytic degradation of MB was calculated from 0 to 90 min. with a concentration of 40 mg/L at neutral pH. It was observed that RuL^1Cl_2, RuL^2Cl_2, RuL^3Cl_2, RuL^4Cl_2 and RuL^5Cl_2 complexes have given degradations of 69.7, 70.0, 78.5, 80.7 and 87.3, respectively. It was clear that RuL^5Cl_2 complex has registered maximum degradation as compared to the other compounds. In general, increase in the amount of catalyst, increases the degradation because it increases the number of active sites on the catalysts surface (John and Joseyphus, 2019). Metal complexes absorb photons when they are irradiated with sunlight. The difference in charges increases the photocatalytic activity. Here Ru (III) complexes have produced –OH radicals during the reaction. Formations of these radicals were the reason for the colour change of MB. The mechanism for the reaction is:

$$[RuLCl_2] + \text{UV-light} \longrightarrow [RuLCl_2]^* + {}^3O_2 \longrightarrow OH^-$$

$$OH^* + \text{Dye} \longrightarrow \text{Oxidative products}$$

4. CONCLUSION

The photo-catalytic activities of some 4-aminoantipyrine-based Ru (III) complexes against methylene blue dye were investigated. Analytical and spectral techniques were used to synthesize and characterize Ru (III) complexes. Under UV light, photocatalytic degradation of methylene blue was successfully carried out using the synthesized complexes. It was found that the dye has been degraded due to the formation of hydroxyl radicals. The increasing order of degradation of Ru (III) complexes was found to be: $RuL^1Cl_2 < RuL^2Cl_2 < RuL^3Cl_2 < RuL^4Cl_2 < RuL^5Cl_2$.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

REFERENCES

Deshmukh, P., P. K Soni, A. Kankoriya, K. Anand, R. Dixit., 4-Aminoantipyrine: A Significant Tool for the Synthesi of Biologically Active Schiff Bases and Metal Complexes, *Int. J. Pharm. Sci. Rev. Res*., 34(1), 162-170 (2015).

John, L., R.S Joseyphus, I.H Joe., Synthesis, spectral characterization, DFT, and molecular docking studies of metal (II) complexes derived from thiophene-2-carboxaldehyde and 2-amino-6-picoline, *J. Coord. Chem.*, 72(16), 2669-2687 (2019). https://dx.doi.org/10.1080/00958972.2019.1668929