Plumeria rubra f. rubra: A Natural Chelating Ligand for Cu2+ ion

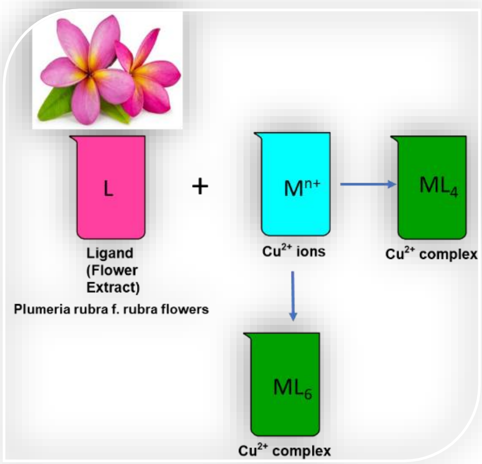
Ankur Dwivedi and Amita Chaudhary

Abstract- **Numerous parts of natural plants, especially flowers, can be used as pH sensors. Anthocyanins, which are found in numerous plants and are pH-sensitive, can be employed to measure the amounts of acids and bases. Flowers from Plumeria rubra come in a range of vibrant colours. One of these, the pinkish-red Plumeria rubra f. rubra flower, has been studied for its capability of detecting Cu2+ ions and their complex coordination entities. It has been observed that the cupric ions in the methanolic extract of Plumeria rubra f. rubra petals create an observable, acute, and distinct wavelength shift in the UV-VIS spectrophotometer. The effects of several counterions, such as sulphate, chloride, nitrate, and acetate, are also studied using the same cupric ion under equivalent experimental conditions. This observation suggests that Plumeria rubra f. rubra petals may contain compounds that can interact with cupric ions, potentially leading to the development of new analytical methods for detecting these compounds. Further research is needed to fully understand the mechanism behind this interaction and its potential applications.**

Indexed Terms- **Plumeria rubra; Cupric ion; Complexing Agent; Natural Indicator**

INTRODUCTION

The ability of many flowers to alter the colour of an acidic or basic medium makes them useful natural indicators for acid base titration[1], [2]. This is due to the fact that the natural pigments in these flowers can



Produce a variety of colours depending on the structural changes they undergo in both acidic and basic media[3]. These pigments have the ability to accept the electron pairs. From ligands into their empty d-orbitals, which enables them to function as ligands and can result in the formation of complex compounds with various transition metal ions. Plumeria rubra blooms come in four different varieties: Plumeria rubra f. acutifolia, Plumeria rubra f. lutea, Plumeria rubra f. rubra, and Plumeria rubra f. tricolor. [4] Plumeria rubra flowers are well known for their medicinal properties [5]–[7] as well as an acid-base indicator[8]. Earlier heavy metal detection with the help of plumeria rubra latex has been reported for Fe, Cr, Cd, and Pd metals[9]. In this short article, authors have discussed the result of first-hand investigations of complex formation between the cupric ion and pinkish red coloured Plumeria rubra f. rubra flower (Figure 1) extract with different anions, which has not been published to date. Currently, a detailed study is being carried out, and it will be published at a later stage.

Fig. 1. Photographs of Plumeria rubra f. rubra flowers

II. MATERIALS AND METHOD

A. Chemicals

About 25 g fresh Plumeria rubra f. rubra flower’s petals, HPLC grade methanol and double distilled water, have been used for the current investigations. Different cupric ion salts such as cupric sulphate pentahydrate: $CuSO_4.5H_2O$, cupric

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Corresponding author: Dr. Amita Chaudhary, Chemical Engineering Department, Institute of Technology, Nirma University, Ahmedabad-382481, INDIA (e-mail: amita.chaudhary@nirmauni.ac.in)

First Author: Dr. Ankur Dwivedi, Chemical Engineering Department, School of Engineering, Institute of Technology, Nirma University, Ahmedaba-382481, INDIA (e-mail: ankur_dwivedi@nirmauni.ac.in).

chloride dihydrate: $CuCl_2.2H_2O$, cupric acetate monohydrate: $Cu(CH_3COO)_2.H_2O$ and cupric nitrate trihydrate: $Cu(NO_3)_2.3H_2O$ have been used of AR grade quality.

B. Method of extraction and stock solution preparation

250 ml methanol and 25 g freshly crushed Plumeria rubra f. rubra flower's petals were mixed in a 500 ml iodine flask. The mixture was stirred and covered with an airtight stopper, and then it was kept for 24 hours. The next day, almost all the pigment content from crushed flower petals was extracted in methanol, and the petals became almost white. This methanolic flower extract was then filtered and stored in a sample bottle and kept in cold conditions at about 4-6 °C for further use. The schematic diagram of the preparation of natural Plumeria rubra f. rubra flower extract is depicted in Figure 2. Stock solutions of 5000 ppm concentration equivalent to copper ion concentration for each cupric salt were prepared in double distilled water.

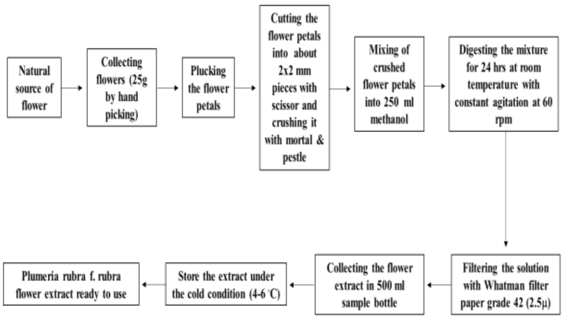

Fig. 2. Schematic methodology for preparing the natural Plumeria rubra f. rubra flower extract

C. Method of complex formation

In separate 10 ml test tube, 5 ml solution of cupric salt was taken. In these solution, 1 ml of Plumeria rubra f. rubra flower extract was added to develop the coloured complex. It was kept for about 15 minutes for the completion of the process of complex formation. All the salts are acidic in nature so the pH of the solutions was maintained acidic.

D. Spectrophotometric analysis

Spectrophotometric wavelength measurement was carried out using a Test Right Nanosystem, INDIA; equipped with Prizm SpectroSmart software. The spectrophotometer was calibrated with the standard US Pharmacopeial method before the use for the measurement[10].

III. RESULTS AND DISCUSSION

A. Colour of complex

Due to the different counter ions present in different cupric salts, the colours of cupric complexes were found to be different. In a basic medium with ammonia, there is a chance of the formation of light blue cupric hydroxide, which is insoluble in water and will precipitate. Furthermore, the addition of ammonia solution causes the copper ion to go back into the solution due to the deep blue ammonia complex formation. Hence, a basic medium cupric complex formation with Plumeria rubra f. rubra flowers is not possible. Hence, complex formation takes place in an acidic medium. The different coloured complexes are shown in Figure 3.

B. Wavelength Shift

As the colours are different than the initial colour for the different cupric complex formations, the shift in wavelengths has also been observed and is shown in Table 1. These shifts in wavelength may be due to the effect of the counterion present, as the central metal ion is the same in all the complexes, but the peaks of 465nm have been shifted to the higher wavelength for each salt. In all the cupric complexes, a Bathochromic shift (Redshift) is observed, which is shifted towards the higher wavelength. The counter ions were also checked for their standard qualitative tests, such as sulphate, chloride, nitrate and acetate, with classical wet chemistry methods, and the results confirm the ionisable state of the counter anionic entity.

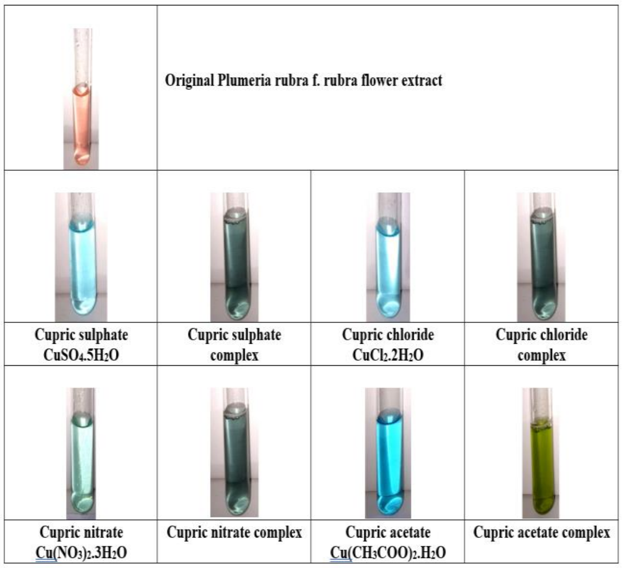

Fig. 3. Cupric ion complex formation with the methanolic extract of Plumeria rubra f. rubra flowers

TABLE 1
SHIFT IN WAVELENGTHS DUE TO THE COMPLEX FORMATION BETWEEN CUPRIC ION - PLUMERIA RUBRA F. RUBRA

Name of the cupric salt	Characteristic colour before complex formation	Characteristic wavelength before complex formation (nm)	Characteristic colour after complex formation	Characteristic wavelength after complex formation (nm)
Cupric sulphate	Light sky blue	465	Dark green	576
Cupric chloride	Light sky blue	465	Dark Green	576
Cupric nitrate	Light sky blue	465	Dark Green	576
Cupric acetate	Dark sky blue	465	Parrot green	597

In all the salts except cupric acetate, the colour and wavelength change for the complex observed is the same, i.e., from light sky blue (465 nm) to dark green (576 nm), but in cupric acetate, the colour and wavelength change observed was from light sky blue (465 nm) to parrot green (597 nm). As acetate is an organic counter anion, all other counter anions are inorganic, and that may be one of the reasons for the different colours due to the resonance in acetate ions. The studies reveal that the difference in the colour of inorganic ions (Sulphate, chloride
and nitrate ion) and organic (acetate ion) types of counter anions due to their chemical nature.

Researchers have identified the presence of different compounds such as tannins, alkaloids, flavonoids, saponins, gums and terpenoids in Plumeria rubra flowers. [5] Out of these, many compounds may behave as ligands with cupric ions and may lead to complex formation. The proposed mechanism is shown in Figure 4.

$CuSO_4 + 4L \rightarrow [Cu(L)_4]SO_4$

$CuCl_2 + 4L \rightarrow [Cu(L)_4]Cl_2$

$Cu(OAc)_2 + 4L \rightarrow [Cu(L)_4](OAc)_2$

$Cu(NO_3)_2 + 4L \rightarrow [Cu(L)_4](NO_3)_2$

Mechanism A

$CuSO_4 + 6L \rightarrow [Cu(L)_6]SO_4$

$CuCl_2 + 6L \rightarrow [Cu(L)_6]Cl_2$

$Cu(OAc)_2 + 6L \rightarrow [Cu(L)_6](OAc)_2$

$Cu(NO_3)_2 + 6L \rightarrow [Cu(L)_6](NO_3)_2$

Mechanism B

Fig. 4. Proposed mechanism: **(A)** with coordination number 4 **(B)** coordination number 6

C. Stability of flower extract solution

The methanolic extract of Plumeria rubra f. rubra flowers was stored in the refrigerator and studied its stability for two months (8 weeks); it was found to be reasonable of the same quality by giving consistent results and checking the complex formation after every week for up to two months. The complexes have shown almost the same wavelength with all cupric salts for up to two months, and no major changes in the composition of methanolic extract were observed (Figure 5), which shows that the flower extract has very good stability for up to two months. A detailed long-term stability study of this flower extract at different temperatures is being conducted.

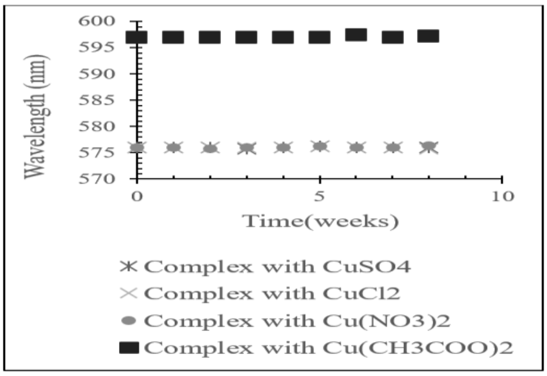

Fig. 5. Stability study of Plumeria rubra f. rubra flower extract by measuring the change in wavelength with time due to the degradation of flower extract

C. Proposed mechanism

As cupric ion is a transition metal ion with coordination number 4 or 6, it can accommodate four or six pairs of electrons donated by ligand in its empty d-orbitals and makes coordination bonds with it and can result into complex formation. In our case the ligand is the natural compounds present in Plumeria rubra f. rubra flower extract. The proposed mechanism is shown in Figure 4.

D. Future plan

In this short article, only complex formation and its colours, wavelengths, and effects of counterions are discussed, but the compound(s) responsible for complex formation have not been identified from the flower extract, and the work is in progress. The detailed study after the isolation of all the complexes with their characterisation data, as well as the method validation data, will be separately carried out and published in our forthcoming article. The identification of the compounds responsible for complex formation in the flower extract is a crucial step towards understanding the potential applications of these complexes. Once identified, further research can be conducted to explore their potential use in various fields such as medicine, agriculture, and materials science.

IV. CONCLUSION

Plumeria rubra f. rubra is a very good acid-base indicator, showing different colours in acidic and basic mediums due to the presence of natural pigments. These pigments can also act as ligands and can lead to the complex formation of cupric ions with different colours due to the presence of different counter ions. The flower extract has good stability for up to two months. If this property of complex formation of a cupric ion with Plumeria rubra f. rubra can be utilised to identify the presence of cupric ions in a wastewater sample, it will definitely be a very easy and economical tool to minimise the water and soil pollution, which is generally caused by using synthetic chemicals and will protect our environment as it is a natural and biodegradable compound. In the future, Plumeria rubra f. rubra will be the best naturally available cost-effective alternative due to its abundant availability for the identification and quantification of cupric ions with the help of visible spectrophotometer by measuring the absorbance of the samples followed by the comparison with the standard solutions of different concentrations of cupric ion.

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Dr. Ankur Dwivedi (Ph.D.) currently holds the position of Assistant Professor in the Department of Chemical Engineering, Institute of Technology, Nirma University. He earned his doctorate from the Department of Chemistry, Gujarat University, Ahmedabad, Gujarat. Dr. Dwivedi has authored multiple national and international journal papers, books and book chapters in the fields of Analytical Chemistry, Photochemistry, Material Chemistry and Waste Water Treatment. He has extensive experience in analytical research within the pharmaceutical industry and academia. His research interests include Chromatographic techniques, Pharmaceutical method development & method validation, Characterization of bulk drugs, Natural indicators, Water treatment, Waste management and Photochemistry. He is also a life member of several esteemed organisations, including ISTE, ACT, ISCA, and SPER. Dr. Dwivedi is a reviewer and an editorial board member of international refereed journals in the field of Chemistry. He also holds an MBA degree in Industrial Management from the National Institute of Management, Ahmedabad and an LL.B degree from Gujarat University, Ahmedabad.

Amita Chaudhary (Ph.D.) is currently working as an assistant professor at the Department of Chemical Engineering, Institute of Technology, Nirma University. She has completed her doctoral studies at the Chemical Engineering Department at the Indian Institute of Technology, Delhi. She has published a number of papers in the area of ionic liquid synthesis, CO_2 sequestration, corrosion science, waste management, etc., in International and nationally referred Journals. She has edited three research books with reputed publishers like Elsevier and Taylor & Francis, along with eight book chapters. She has a patent on the synthesis of ionic liquid for carbon capture in collaboration with IIT Delhi and FITT, Delhi. She is a member of various prestigious organisations like ISTE, IIChE, and ACT.