



# UV–Visible Spectroscopic Evaluation of Citric Acid Isolated from Lime Juice as Optical Chemosensor for Cadmium Ions

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## Abstract

## Original Research

The development of simple and cost-effective chemosensors for detecting heavy metal ions is of significant environmental importance. Herein, this article describes Citric acid isolated from lime juice as optical chemosensor for Cd<sup>2+</sup> ions using UV–Visible spectroscopy. The isolated citric acid was characterized using UV-Visible, <sup>1</sup>H-NMR and FT-IR spectroscopy. The absorption spectrum exhibited a characteristic peak around 285–295 nm corresponding to n → π\* transitions of carbonyl groups. Upon addition of Cd<sup>2+</sup> ions, change in absorbance intensity was observed, indicating complex formation. The results showed that absorption intensity was concentration-dependent, that is when the concentration of Cd<sup>2+</sup> increased from (0.01–0.08 ppm), the intensity increased. This trend indicates that the citric acid-based system responds proportionally to changes in cadmium concentration. The results demonstrate that citric acid can serve as a low-cost and eco-friendly optical probe for cadmium detection.

**Keywords:** Citric acid, Chemosensor, UV-Visible spectroscopy, Lime, cadmium ions.

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## 1. Introduction

Cadmium (Cd<sup>2+</sup>) is particularly hazardous heavy metals and is associated with severe health problems [1]. It is widely used in various industrial applications, such as the fabrication of metal alloys, electroplating films, nuclear reactor control rods and batteries [2]. The effect of Cd<sup>2+</sup> pollution has significant health concerns. Cadmium accumulates in the human body through contaminated water, air, soil, or other sources, leading to a variety of disorders of the kidney, liver, heart, lung, or other organs [3]. Conventional analytical techniques such as

atomic absorption spectroscopy (AAS) and ICP-MS are highly sensitive but require sophisticated instrumentation and skilled operation complicated sample preparation [4,5]. Optical chemosensing method provides a rapid, simple, and cost-effective alternative for sensing metal ions [6,7]. Recently, a large number of optical chemosensors with diverse scaffolds, such as rhodamine, quinolone, boron-dipyrromethene (BODIPY), pyrene and anthraquinone, etc. have been developed with sensitivity, selectivity, for detection of Cd<sup>2+</sup> [8,9]. However, only a few examples of chemosensors have been reported with UV-Visible absorption



intensity increase is observed upon  $\text{Cd}^{2+}$  ion binding [10]. In addition, the synthesis of these materials involved high cost of chemicals, difficult synthetic protocol, environmental concern due to toxic effects of these chemicals, and tedious purification steps.

The need for sustainable chemical processes have directed significant attention towards green chemistry [11]. Therefore, this study focuses on the utilization of plant-based material as eco-friendly alternatives for the production of optical chemosensor for cadmium ions. Citric acid, a naturally occurring tricarboxylic acid, exhibits strong chelating ability due to its multiple donor groups, making it suitable for metal ion sensing [12]. One of the plants rich in citric acid is the lime plant (*Citrus aurantiifolia*), it is produced in large quantity in tropical Africa, most of it is sold as fresh fruits in a domestic wet markets, the key problem is economic loss due to spoilage and poor preservation. Therefore, the extraction of citric acid from the lime fruits juice and its utilization as functional material will harness its economic and scientific potentials. Herein, we report low cost, eco-friendly Citric acid optical chemosensor derived from lime juice for detection of cadmium ions ( $\text{Cd}^{2+}$ ) using UV-Visible spectroscopy.

## 2.0 Materials and Methods

### 2.1 General

The lime fruits were collected in Gombi Orchard Adamawa State Nigeria. All chemicals were obtained from Aldrich and used as received without further purification unless otherwise stated.  $^1\text{H-NMR}$  spectra were recorded on a Bruker Ultra-Shield 400 MHz spectrophotometer. Samples were dissolved in  $\text{CDCl}_3$  as solvent and chemical shifts are reported in ppm. FT-IR spectra were recorded on a Perkin Elmer spectrophotometer in the range of  $4000\text{--}400\text{ cm}^{-1}$  and UV-Visible spectra were recorded on GENESYS 10S Spectrophotometer in range of 200nm to 400nm. Further purification of the sample was carried out using preparative liquid chromatography (prep LC) JAI Recycling LC PREP 9110 Model.

### 2.2 Collection and Preparation of the Sample

The lime fruits was collected from Gombi Orchard Adamawa State, Nigeria. The fruits was washed with clean running tap water. It was then peeled and blended for the extraction of the juice. The extract was filtered using muslin cloth to collect the liquid juice.

### 2.3 The Isolation of Citric Acid from Lime Juice

1000ml of lime juice was diluted with an equal volume of distilled water, and 10% NaOH solution was gradually added until the pH reached 9. 25g of Calcium chloride was dissolved in 100 ml of distilled water, and the solution was added to the mixture, it was then boil for 2 minutes which results in the formation of white precipitate. The white precipitate was collected by filtration using filter paper, and was washed with distilled water. Then 2%  $\text{H}_2\text{SO}_4$  solution was added and stirred. The mixture was filtered using filter paper to collect the filtrate. And it was boiled down to about 10% of its initial volume and was allowed to cooled and kept in a freezer for crystal growth [13,14]. Further purification of the sample was carried out using preparative liquid chromatography to obtained 3.5g of pure crystals of citric acid in 75% yield.

### 2.4 Preparation of the Cadmium ions Solution

The solution of the cadmium ions was prepared using salts of the element. A stock solution of 1000 ppm of the metal salt was prepared. From this stock solution, a standard solution of 100 ppm was prepared with the simple dilution principle ( $C_1V_1 = C_2V_2$ ). Then, working standards were prepared of varying concentrations range, 0.01, 0.02, 0.04, 0.06, 0.08 ppm.

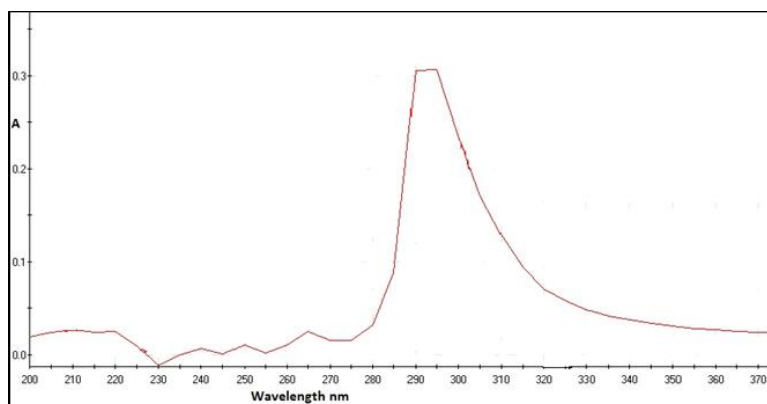
## 3.0 Results and Discussion

### 3.1 Spectroscopic Studies

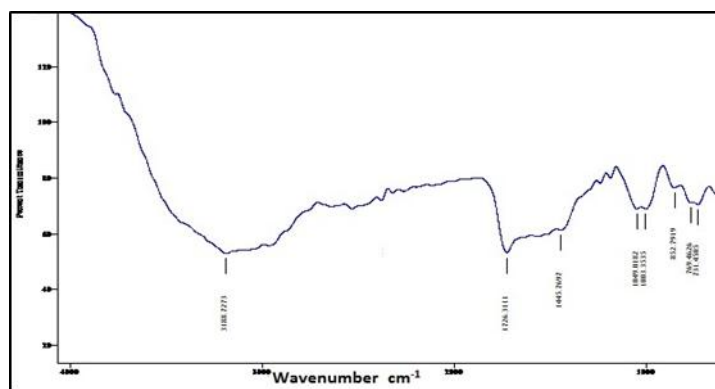
The UV-Visible absorption spectra of the citric acid were investigated, and maximum absorption wavelength appeared at 295 nm, which was

attributed to the  $n-\pi^*$  electronic transition as shown in (Figure 1). The electronic transition observed was due to the three carbonyl groups in Citric acid, specifically resulting from the transition of non-bonding  $n$  electrons to the anti-bonding  $\pi^*$  orbitals. The IR spectrum of the citric acid is depicted in (Figure 2). The IR spectrum gave the characteristic carbonyl (C=O) stretching vibration peak at  $1726.31\text{ cm}^{-1}$ , and  $3100-3188.72\text{ cm}^{-1}$  corresponded to O-H(c) stretching vibration. This band broadens because of the extensive hydrogen bonding in citric acid molecules [15]. It also exhibited characteristic C-O carboxylic stretching band at  $1049.76\text{ cm}^{-1}$ . The

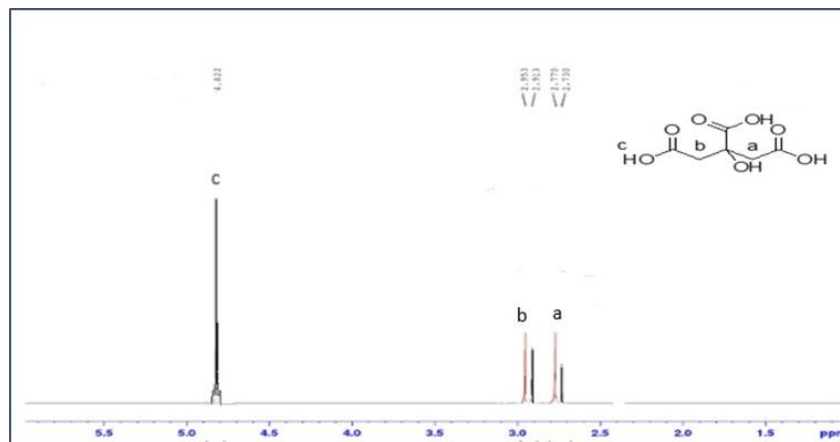
$^1\text{H-NMR}$  spectral studies as shown in (Figure 3), have been carried out to confirm the isolation of the citric acid. A downfield singlet seen around  $\delta$  4.8–5.0 ppm, is attributed to the hydroxyl ( $-\text{OH}$ ) proton attached to the tertiary carbonyl in the citric acid structure. The deshielded aspect of this proton arises from the very strong electron-withdrawing character of all three neighboring carbonyl groups and extensive intermolecular hydrogen bonding [16]. Also observed was peaks at  $\delta$ (a) 2.7 ppm doublet and (b) 3.0 ppm doublet upfield, attributed to methylene ( $-\text{CH}_2-$ ) protons of the citric acid.



**Figure 1.** UV-Visible absorption spectrum of isolated citric acid



**Figure 2.** FT-IR absorption spectrum of isolated citric acid

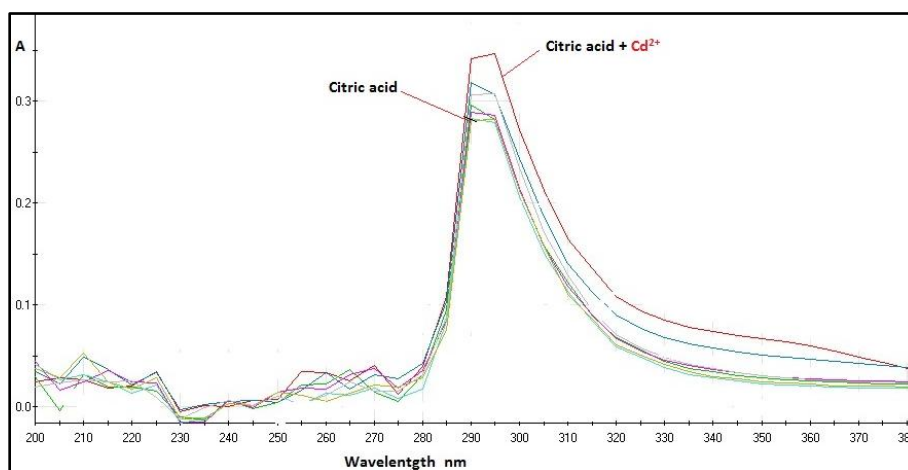


**Figure 3.**  $^1\text{H}$ NMR spectrum of isolated citric acid

### 3.2 UV-Visible Chemosensing Study

The chemosensing ability of citric acid towards  $\text{Cd}^{2+}$  was investigated through UV-Visible spectroscopy as indicated in (Figure 4). The maximum absorption wavelength of the citric acid appeared at 295 nm, which was attributed to the  $n-\pi^*$  electronic transition as shown in (Figure 1). Upon the addition of  $\text{Cd}^{2+}$  ions to the citric acid solution, a pronounced increase in absorbance intensity was observed. This enhancement indicates the formation of a citric acid-cadmium complex. The interaction occurs primarily through coordination bonding between  $\text{Cd}^{2+}$  ions and the oxygen atoms of the carboxylate and hydroxyl

groups of citric acid. Cadmium ions are known to form stable complexes with multidentate ligands containing oxygen donor atoms. Citric acid acts as a chelating agent, binding  $\text{Cd}^{2+}$  through two or more coordination sites, which alters the electronic structure of the ligand and results in changes in UV absorption [17]. The citric acid chemosensor was applied for the detection of  $\text{Cd}^{2+}$  in a different concentration ranges, from (0.01-0.08) ppm. As the concentration of the  $\text{Cd}^{2+}$  increase the absorption intensity also increases. This trend indicates that the citric acid-based system responds proportionally to changes in cadmium ions concentration.



**Figure 4.** UV-Visible chemosensing study of citric acid against  $\text{Cd}^{2+}$  with conc. (0.01-0.08) ppm

#### 4.0 Conclusion

This study investigated the chemosensing ability of citric acid isolated from lime juice toward detection of Cd<sup>2+</sup> using UV-Visible spectroscopy. The citric acid was successfully isolated, and the identity and purity of the isolated citric acid was confirmed by spectroscopic characterization, including UV-Visible, Fourier Transform Infrared, and proton nuclear magnetic resonance (<sup>1</sup>H-NMR) Spectroscopy. The study revealed that the UV-Visible chemosensing capability of citric acid on cadmium ions was concentration-dependent, as the concentration of the Cd<sup>2+</sup> increase the absorption intensity also increases. This indicated that the lime-extracted citric acid may be an alternative, low-cost and eco-friendly chemosensor for sensing cadmium ions.

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