Original Research Article

A new Pyrrole-2-Carboxaldehyde Functionalized Chitosan-Cu(II) Complex-based Chemosensor for Iodide Anion in Aqueous Media

Abstract

Iodine is an essential ingredient in thyroid hormones of which both low and high intakes may cause thyroid disease. This study develops a Pyrrole-2-Carboxaldehyde functionalized chitosan-Cu(II) Complex [PCAFC-Cu(II)] chemosensor, for quick and easy detection of iodide ions from its aqueous solutions. PCAFC-Cu(II) complex was synthesized from a simple condensation reaction of chitosan (CS) and pyrrole-2-carboxaldehyde (PCA) along with an aqueous solution of copper(II) salt. The starting materials and the products were characterized by spectroscopic (FT-IR and UV-Visible), X-ray powder diffraction, and microscopic methods (Scanning Electron Microscopy). The PCAFC-Cu(II) colorimetric sensing of I^- revealed a color change adduced to the formation of a hydrogen bond or deprotonation of the complex matrix. Colorimetric detection for I^- ions was obtained with a detection limit (LoD) of 0.005 M and the complex has high specificity for I^- ions detection from a solution consisting of several anions. The synthesized complex [PCAFC-Cu(II)] could serve as an on-site reagent for the qualitative detection of iodide ions.

KEYWORDS: Chemosensor, colorimetric detection, complex, anions, condensation, deprotonation.

1.0 Introduction

Anions are essential to numerous processes and are becoming increasingly important in the biological, chemical, industrial, and environmental spheres of existence. Rapid industrialization has resulted in the introduction of numerous species that are harmful to all living things, including humans [1]. Therefore, the development of sensors for anionic species is a subject of intense research [2].

Anions have a variety of important functions in both industrial and living systems. For instance, hypochlorite is used to disinfect water, and fluoride helps to prevent tooth decay. Genetic information is contained in DNA, a polyanion. Anionic cofactors are common in enzymes; one example is carboxypeptidase A. In metallurgical processes, cyanide is used to extract valuable metals like gold and silver [3, 4]. Goiter can be prevented by using iodide. An excess of these anions in the living tissues, however, poses a health risk that, if untreated, can be fatal. The consequences of iodide ions are a significant global conundrum, according to earlier reported research [5-7].

Considerable attention has been drawn to the design of colorimetric hosts that can selectively recognize anion species through visible color changes with the advantage that responses and immediate qualitative signal can be easily detected by the naked eye upon complexation[7, 8]. The design of anion receptors has frequently used hydrogen-containing polar groups as hydrogen-bond donors, such as ureas and thioureas[7]. Metal coordination leads to the development of anion-responsive surfaces, partial charge transfer, and a striking shift in color as a result of the establishment of a sensor-anion complex [2, 9].

The pursuit for effective schemes for recognition of physiologically and environmentally significant of different anion analytes prompted Kauret al.[10] to synthesized and reported achemosensorwith NH-binding sites for anions sensing and variations in selectivity as a result of structural modifications and mechanism of actions.

The promising characteristics of chitosan, such as its availability, affordability, biodegradability, great film-forming capacity, and nontoxic nature, are responsible for itssuitability as electrochemical sensors, biosensors, gas sensors, and volatile organic compound sensors [11, 12]. On the other hand, pyrrole is a flexible building block for macrocyclic dyes because it possesses an NH moiety that can be used to bind anions. In fact, the use of pyrrole-based macrocyclic dyes as cation and anion-binding agents is widely established [7].

In microbial investigations, the Schiff base metal complexes offer a wide range of applications, but there has been a new movement toward using them as electrocatalytic sensors. When compared to other detection techniques, electrochemical detection is one of the most sensitive and selective techniques of detection because it has a quick timeframe, is inexpensive, has low detection limits, and is simple to use [13, 14]. In order to produce sensing signals, Schiff bases, and ions must interact chemically. Schiff bases are synthetic chemicals that are used in a wide range of applications, such as fluorescent turn-on/turn-off sensors for the detection of various analytes, as flexible instruments. As a result, they can provide a method for identifying hazardous ions in environmental media and/or revealing their speciation [6].

Schiff bases and their transition metal complexes are widely used as electrode modifiers in sensors to identify analytes of forensic, pharmacological, and environmental significance [15]. Li et al.[16]reported a Schiff base which was employed as a sensor to distinguish between In^{3+} and Fe^{3+} through fluorescence 'off-on-off' behavior, while three Schiff bases with benzothiazolefunctionalizations used as colorimetric sensors for fluoride and acetate ions in acetonitrile were synthesized and reported by Borah et al. [17]

The sensing signal is generated in Schiff base-based chemosensors by altering their electrical characteristics using various charge transfer methods. A wide variety of Schiff bases are used for sensing anions in many forms of environmental and biological media. Schiff bases have also mostly been investigated as optical ion sensors. [6].

For anion sensors to work effectively, achromophorethat translates binding-induced modifications into an optical signal, such as the appearance of color, and an anion binding component, such as (CH=N), hydroxyl (-OH), or pyrrole (-NH) must be directly linked or intramolecularly connected [18]. Essentially therefore, chitosan and pyrrole-2-carboxaldehyde were condensed to form a Schiff base ligand for the complexation of copper ions employed for the sensing of iodide ions. The results obtained are herein presented.

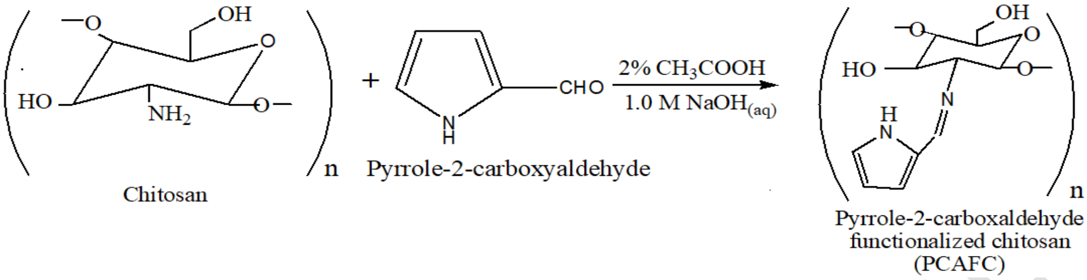
2.0 Experimental Method

2.1 Materials and Instrumentation

Chitosan powder with a molecular weight of 100,000–300,000, degree of deacetylation: 85%, and Pyrrole-2-carboxaldehyde: 98% were obtained from Bristol Scientific-Sigma-Aldrich, Lagos, Nigeria, All the other chemicals used for this research work were of analytical grade. They were obtained commercially and used without further purification. IR spectra of KBr disc pellets of the samples were recorded on SHIMADZU FTIR-8700 (Kyushu Preference, Japan) in the range of 4,000–400 cm^{-1} with a resolution of 4[1/cm] and apodization of Happ-Genzel. The electronic spectra of the samples were recorded with a UV-visible spectrophotometer of UV-1600 Series PC, (Shanghai, China) from 190 to 800 nm range. The X-ray powder diffraction determinations were made using a diffractometer with a parabolic filter, and a scan rate of 5.0/60.0/0.05/1 (sec). The patterns were run with Cu/K-alpha1 radiation, and wavelength to compute d-spacing = 1.54056 A, voltage = 40 kV, current = 30 mA. The surface morphology was determined using a JOEL-JSM-7600F field emission scanning electron microscope (SEM) operating at an accelerated voltage of 5.0 kV after gold sputter coating. The colorimetric sensing of I$^-$ was monitored by visual (naked) eye and UV-visible spectrophotometer.

2.2 Synthesis of pyrrole-2-carboxaldehyde functionalized chitosan (PCAFC)

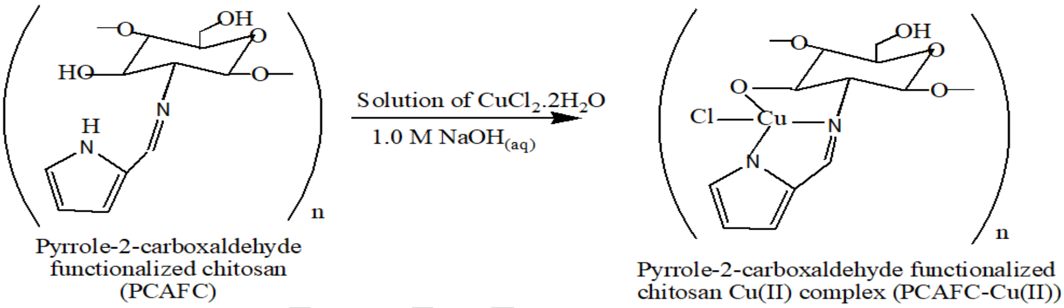
PCAFC was synthesized following a literature method byArh-Hwang et al.[19]; Olugbemi et al. [20]. The solution of chitosan was prepared by dissolving 0.5 g of chitosan into 10.0 mL of acetic acid (2 %, v/v), and 60 mL of distilled water was added. The resulting solution of the chitosan was mixed with pyrrole-2-carboxaldehyde, (PCA) (0.5 g). The solution was mixed and thoroughly stirred for 4 h to yield a viscous and colorless solution. Thereafter, sodium hydroxide solution (1.0 M, 30 mL) was added to the mixture to form the precipitate. The precipitate was filtered, washed, and then dried in the oven for 6 h at 60 °C. The percentage yield of the product from the reactants was 94.38%. The reaction scheme is shown in Scheme 1 as presentedin a previous study by Olugbemi et al. [20].



Scheme 1. Synthesis of Pyrrole-2-carboxaldehyde Functionalized Chitosan (PCAFC) Schiff base

2.3 Preparation of copper(II) complex [PCAFC-Cu(II)]

The Cu(II) complex was synthesized following a modified literature method by Anan et al.[21]. In a typical preparation, to10 mL of PCAFC solution, 10 mL of 0.1 M of Cu^{2+} ions was added and stirred thoroughly to achieve a homogenous mixture. 10 mL of 1.0 M sodium hydroxide solution was added to form the precipitate. The precipitate was filtered, washed, and then dried in the oven for 6 h at 60 °C (Scheme 2).



Scheme 2. Synthesis of Cu(II) Complex

2.4 Colorimetric sensing of the anion using PCAFC-Cu(II)

Colorimetric sensing has gained significant ground in the recent past as the observer detects species of importance through the naked eye and without any expertise on behalf of the user [4]. For visual detection studies, 0.1 g of PCAFC -Cu(II) complex was added to 5.0 mL of 0.1 M solution of the anions (Cl^-, Br^-, I^-, CO_3^{2-}, NO_3^- and SO_4^{2-}) in separate test tubes and change in color of the anion solutions was monitored visually (naked eye). The effect of different concentrations of I^- ions on the PCAFC-Cu(II) complex was investigated by preparing five (5) different concentrations of I^- ions in different test tubes labeled A, B, C, D, and E representing 0.01, 0.02, 0.10, 0.20 and 0.50 M respectively. Thereafter, 0.1 g of PCAFC-Cu(II) complex was introduced into each of the test tubes. Likewise, the effect of different pH of I^- ions on the PCAFC -Cu(II) complex was also studied by preparing six (6) different pH of I^- ions in different test tubes labeled A, B, C, D, E, and F representing pH 2, 4, 6, 8, 10 and 12 respectively. Afterward, 0.1 g of PCAFC-Cu(II) complex was introduced into each of the test tubes. The Change in color of the solutions of I^- ions was monitored by both visual and UV-Visible spectroscopic (200 – 800 nm) methods for different concentrations and pH.

The selectivity study of I^- ions by PCAFC -Cu(II) complex from a mixture of different anions was investigated by preparing a solution comprising of six different anions with 0.01 M for each of anions -(Cl^-, Br^-, I^-, CO_3^{2-}, NO_3^-, and SO_4^{2-}). PCAFC-Cu(II) complex (0.1 g) was transferred into a 5.0 mL of the solution in a test tube to verify the effect of selectivity of I^- ions from the mixture. The change in color of the solution was monitored visually.

3.0 Results and Discussion

3.1 Infra-Red Analysis

The FTIR spectra of the ligand materials and the corresponding metal complex [PCAFC-Cu(II)] are depicted in Figure 1. The spectrum of chitosan, (CS), showed strong broad absorption bands at 3283 and 3460 cm^{-1} which could be attributed to the stretching vibrations of N-H and O-H groups respectively while the absorption band at 1656 cm^{-1} tentatively assigned to C=O [22-24]. However, the spectrum of pyrrole-2-carboxaldehyde, (PCA) showed a broad absorption band at 1651 cm^{-1}adduced to C=C stretching frequency, while the band at 1722 cm^{-1} could be associated withthe C=O group. Comparatively, in the spectrum of the resulting ligand, pyrrole-2-carboxaldehyde functionalized chitosan, (PCAFC), a new absorption band at 1639 cm^{-1}ascribed to *v*(C=N) stretching suggests the formation of azomethine functionality [21, 22].

Furthermore, the absorption band observed at 1639 cm^{-1} from the ligand (PCAFC) showed a shift to a lower frequency at 1627 cm^{-1}in PCAFC-Cu(II)) complex. This could be a result of the interaction between nitrogen lone pairs of electrons with the metal ions that are electron deficient, suggesting the participation of the nitrogen of the imine group in coordination with the metal ions [13, 25 - 27].

In addition, weak bands in the region of the fingerprint might be assigned to the modes of *v*(M-N) at 513 cm^{-1} and *v*(M=O) at 457cm^{-1} [23, 28, 29]. These metal-ligand vibration bands occur at 500 - 650 cm^{-1} for *v*(M-N) and 400 - 500 cm^{-1}forv(M=O) [13, 29 - 22].

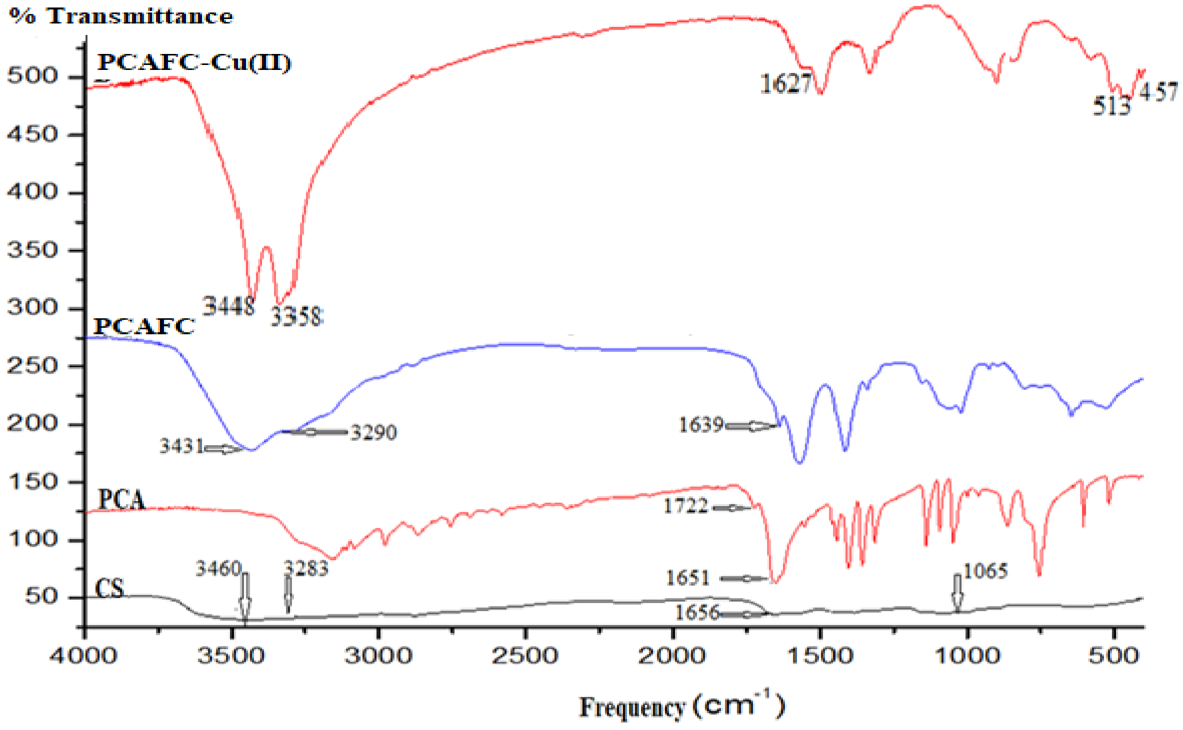


Figure 1. Infra-red spectra of CS, PCA, PCAFC, and PCAFC-Cu(II)

3.2 UV-Visible Analysis

The electronic transitions of the ligand materials and the corresponding metal complex [PCAFC-Cu(II)] were measured within the range of 200 nm and 800 nm using UV-Vis spectrophotometer and the spectra are presented in Figure 2. The UV-Visible spectrum of chitosan revealed no peak in the range of 300 – 800 nm in tandem with the previous studies by Adewuyiet al. [24]; Kumar et al.[33];Viveket al. [34]; Annaduzzaman[35]. However, the band around 260 nm can be attributed to the $n\rightarrow\pi^*$ intra-ligand electronic transition due to the C=O of the N-acetyl group in chitosan. The absorption band observed at 380 nm in the synthesized PCAFC experienced a red shift and hypochromic effect when compared with the CS and PCA. The absorption band at 380 nm in PCAFC was due to the transition between the π orbital localized on the azomethine, (C=N), that is, the existence of n- π^* transition of the azomethine group [18]. Transitions below 400 nm are assigned to intra-ligand charge transfer (n-π^*) and (π -π^*) bonds [21, 33].

In the complex, PCAFC-Cu(II), the intense bands shown in the electronic spectrum were due to ligand-to-metal charge transfer (LMCT) and weaker bands assigned to d-d transitions [36, 37]. Cu(II) is a d^9 system with a term symbol of ^2D and the electronic spectrum of the PCAFC-Cu(II) complex revealed two bands at 545 and 476 nm. The two transitions are due to $^2E_g \rightarrow {}^2T_{2g}$ and $^2B_{1g} \rightarrow {}^2A_{1g}$. Additionally, the spectrum showed a band at 326 nm which may be attributed to ligand-to-metal charge transfer.

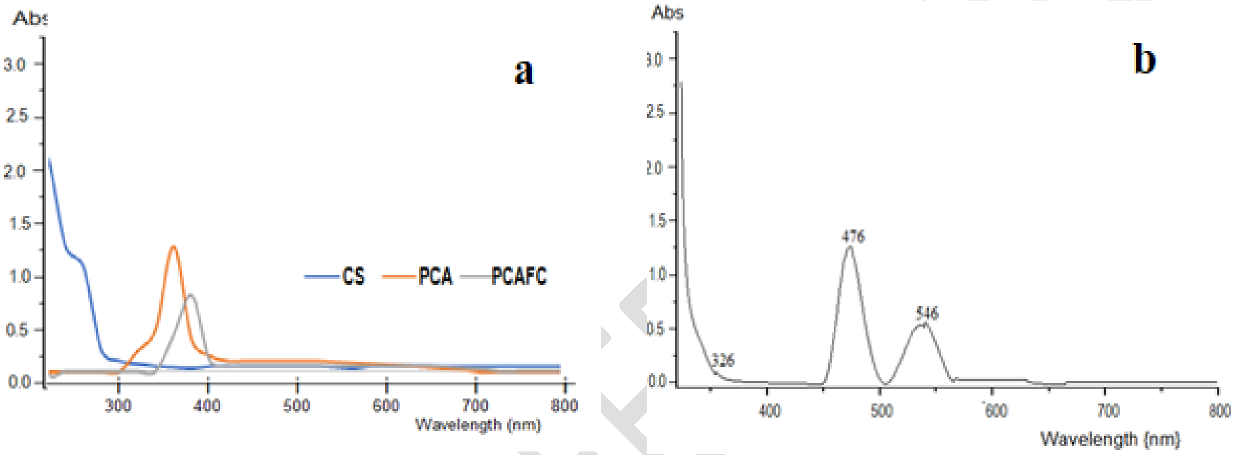


Figure 2: UV-Vis spectra of **a** = [CS, PCA, and PCAFC] and **b** = PCAFC-Cu(II).

3.3 Scanning Electron Microscopy (SEM) Analysis of PCAFC and PCAFC-Cu(II)Complex

In order to obtain information about the surface topology and compositions of the ligand and the metal complex, the surface morphology of the ligand, PCAFC, and the PCAFC-Cu(II) complex was studied using scanning electron microscopy (SEM) to have a clear insight into the surface interaction between the ligand, PCAFC, and the PCAFC-Cu(II) ions as presented in Figure 3. The SEM micrograph of the ligand, indicated a highly irregular and rough surface when compared to the smooth surface of chitosan indicating good homogeneity from the previous studiesby Olugbemi et al. [20]; Adewuyiet al. [24]; Annaduzzaman[35];Deyet al.[38].

The rough and more irregular surface of the ligand with large particle sizes and non-homogenous when compared with PCAFC-Cu(II) complex could bedue to the chemical modification of the ligand surface which is attributable to the formation of azomethine group (C=N). The holes and caves-type openings on the surface of the ligand would definitely have increased the surface area available for adsorption [39].The SEM monographof the PCAFC-Cu(II) complex showed a significant morphological change with fibril structures. The change in the morphology of the complex in relation to the ligand suggests that the imprinting of the Cu(II) ions on the ligand, PCAFC could leave footprints, thus increasing the porosities on the surface. This feature may be assigned to the coordination of the Cu(II) ions to the ligand active sites. The pores present in the ligand contributed to the adsorption capacity of the Cu(II) ions through complex formation [21].

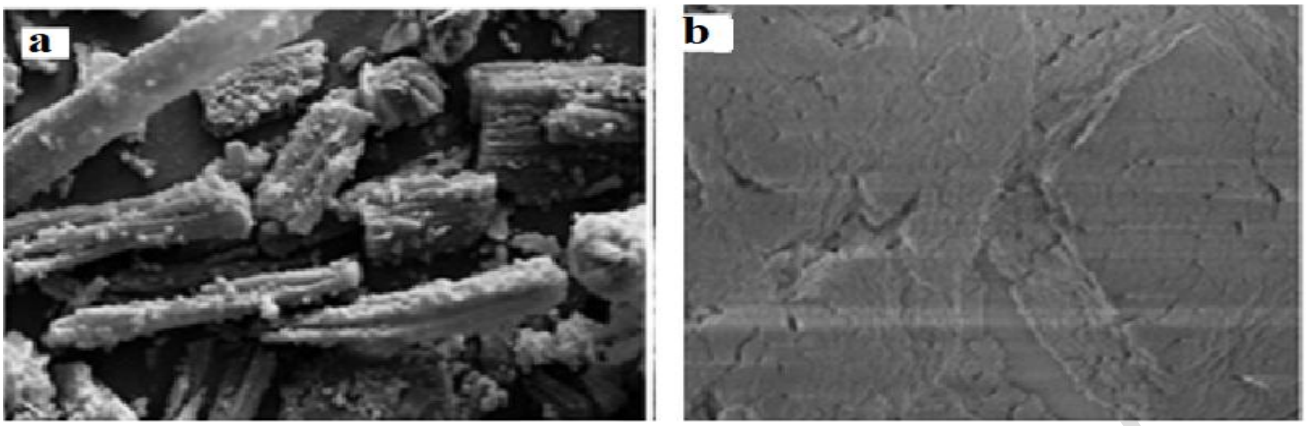


Figure 3. SEM monographs of **a**- PCAFC and **b** – PCAFC-Cu(II) (Source of **a**: [17].

3.4 X-Ray Diffraction Analysis of CS, PCAFC, and PCAFC-Cu(II) Complex

The XRD diffractograms of the compounds, CS, PCAFC, and PCAFC-Cu(II) complex are shown in Figure 4. The diffractograms of CS, PCAFC, and PCAFC-Cu(II) complex ranged from broad to sharp intense peaks. In the presence of free amino groups, CS exhibits two broad characteristic peaks at 2θ of 10 ° and 20 ° that are typical fingerprints of semi-crystalline nature and indicate the formation of inter- and intra-molecular hydrogen bonds [21, 22, 24]. The PCAFC ligand has two broad, amorphous distinctive peaks at 2θ of 7 ° and 20 °. When compared to the CS peak, which is located close to 10 °, the peak near 7 ° appears to be diminished. The shift in the crystallinity can be attributed to the formation of an azomethine group (C=N) in the ligand [20].

The XRD diffractogram of the PCAFC-Cu(II) complex showed several strong and sharp peaks. The amorphous nature of the ligand changed to a highly crystalline PCAFC-Cu(II) complex. The change in the crystallinity of the PCAFC-Cu(II) complex when compared with that of the ligand could be attributed to the coordination of Cu(II) ions to the ligand. The fine particles and high crystallinity of the PCAFC-Cu(II) complex are reflected in their XRD sharp intense peaks [22, 24]. The polymorph gave many peaks characteristic which are of crystalline regions.

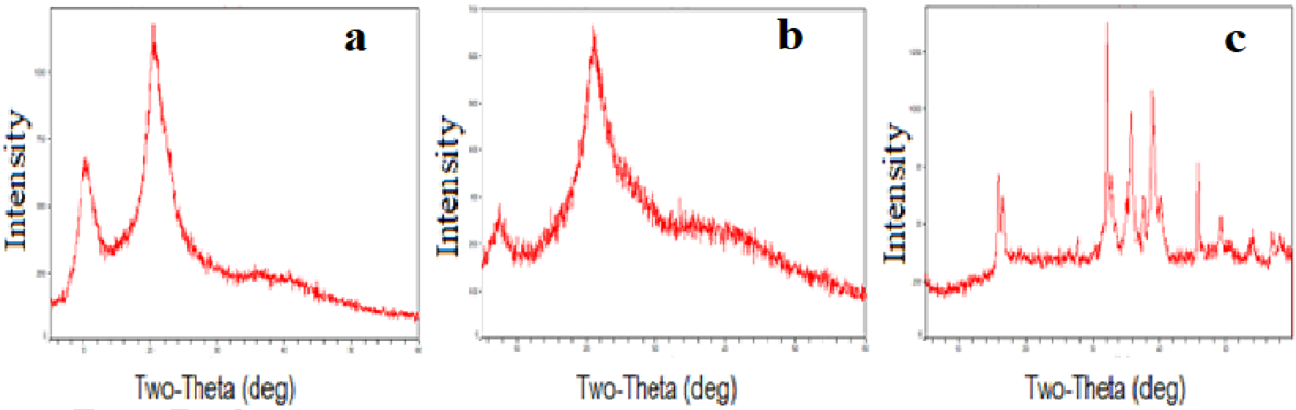


Figure 4. XRD diffractograms of a = CS, b = PCAFC and c = PCAFC-Cu(II) (Source of aand b: [17]).

3.5 Colorimetric Sensing Studies

The colorimetric sensing ability of the synthesized PCAFC-Cu(II)) with anions (Cl^-, Br^-, I^-, CO_3^{2-}, NO_3^- and SO_4^{2-}) was monitored by both visual (naked eye) method and UV-Visible spectroscopic method (Figure 5). The PCAFC-Cu(II) complex (0.1 g) was added to the solutions of the anions (Cl^-, Br^-, I^-, CO_3^{2-}, NO_3^- and SO_4^{2-}) in separate test tubes and change in the color of the anions was monitored. Upon the addition of PCAFC-Cu(II) to the solution of I^-ions, the solution turned brownish yellow while there was no color change in the solutions of the other anions.

The formation of a hydrogen bond or deprotonation of the complex could be a plausible explanation for the color change withthe addition of the complex to the anion solutions [18]. The I^- ions hashigh basic characters and acted as a strong base in the deprotonation of the complex proton. The interaction of PCAFC-Cu(II) with I^- ions induced a color change, thereby making the detectionof the presence of I^-ions with the naked eye possible [4, 18].

PCAFC-Cu(II) + anion solutions (a = Cl^-, b = Br^-, c = I^-, d = CO_3^{2-}, e = NO_3^-, f = SO_4^{2-} solutions
Figure 5: colorimetric sensing of anions by the PCAFC-Cu(II)

3.5.1 Effect of different concentrations of I^- ions on PCAFC-Cu(II) complex.

Five (5) different concentrations of I^- ions were prepared in different test tubes labeled a, b, c, d, and e representing 0.01, 0.02, 0.10, 0.20, and 0.50 M respectively. The PCAFC-Cu(II) complex (0.1 g) was introduced into each of the test tubes labeled a, b, c, d, and e. The color of I^- ions changed from colorless to greenish yellow in test tube a (0.01 M I^-). The yellow color gets more intense as the concentration of the ions increases even to brownish yellow in test tube E (0.5 M). (Figure 6).

3.5.2 Effect of different pH of I^- ions on PCAFC-Cu(II) complex.

Six (6) different pH of I^- ions were prepared in different test tubes labeled a, b, c, d, e, and f representing pH 2, 4, 6, 8, 10, and 12 respectively. (pH 2, 4, and 6 represent acidic medium while pH 8, 10, and 12 represent alkaline medium). The PCAFC-Cu(II) complex (0.1 g) was introduced into each of the test tubes labeled a, b, c, d, e, and f. (Figure 7).

In the acidic medium, the color of I^- ions changed from colorless to brownish yellow in test tube C with pH 6 of I^-ions. The brownish color gets more intense as the acidity increases from pH 6 to pH 4 and to pH 2. With pH 2, almost every part of the solution in the test tube turned brown color, On the other hand, in the alkaline medium, the color of I^- ions changed from colorless to yellow in test tube d with pH 8 of I^-ions. The yellow color gets more intense as the alkalinity increases from pH 8 to pH 10 and to pH 12.

3.5.3 Selectivity Study

The selectivity of I^-ions by PCAFC-Cu(II) complex from a mixture of different anions (Cl^-, Br^-, I^-, CO_3^{2-}, NO_3^-, and SO_4^{2-}) was investigated. A solution comprising of six different anions with 0.01 M each was prepared in a test tube and 0.1 g of PCAFC-Cu(II) complex was introduced into the test tube to verify the effect of selectivity of I^- ions from the mixture of the different anions in the solution.

From Figure 8, the result showed a change in the color of the mixture of anions from colorless to yellow upon the addition of 0.1 g of PCAFC-Cu(II). This implies that PCAFC-Cu(II) complex can still detect the presence of I^- ions from the mixture of different anions as it does when the solution was solely I^- ions.

3.6 UV-Visible spectral studies

In order to understand the interaction between PCAFC-Cu(II) complex and I^- ions, the UV-visible spectrophotometry analysis was carried out on the resulting solutions from the effect of concentrations and the effect of different pH in the visual sensing method.

3.6.1 Effect of different concentrations of I^- ions on PCAFC-Cu(II) complex

The UV-Visible spectroscopic analysis was carried out by varying the concentrations of the iodide I^- ions. The concentrations of the I^- ions used for the study ranged from 0.01 to 0.50 M.

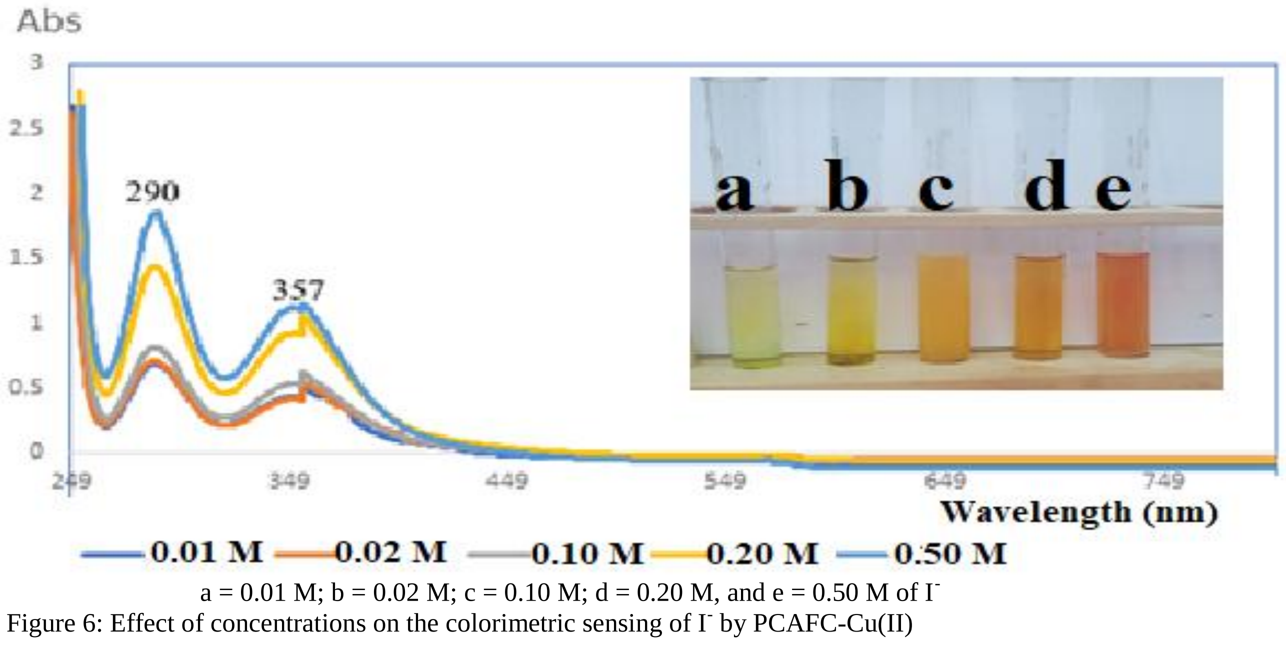
The electronic spectra of all the varying concentrations of the I^- ions with the PCAFC-Cu(II) complex (Figure 6) showed strong and broad absorption bands in the regions of 290 nm and 357nm. Increasing the concentrations of the I^- ions solution increases the intensities of the peak. This can be attributed to the hydrogen bonding interaction between the PCAFC-Cu(II) complex and the I^- ions [4]. Two isosbestic points were observed at 290 nm and 357 nm respectively confirming the equilibrium existing between the PCAFC-Cu(II) complex and the I^- ions [18, 23]. This is an indication that it is only one type of complex that exists in the solution.

3.6.2 Effect of varying the pH of I^- ions on PCAFC-Cu(II) complex.

The interaction of the PCAFC-Cu(II) complex with different pH of I^- ions showed similar behavior in the electronic spectra when compared with that of varying concentrations. The study was done in both acidic and alkaline media. pH 2 - 6 represents the acidic medium while pH 8 - 12 represented the alkaline medium.

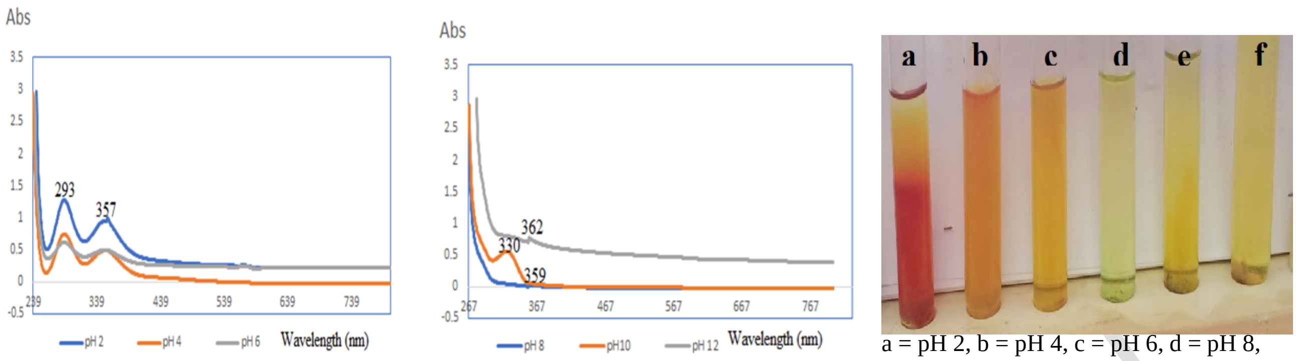
In an acidic medium, the electronic spectra showed two strong and broad absorption bands at 293 nm and 357 nm respectively. As the acidity of the anion solutions decreases, the absorption peak intensities also diminished gradually (Figure 7) and this can be attributed to the hydrogen bonding interaction between the PCAFC-Cu(II) complex and the I^- ions. Two clear isosbestic points were also observed at 293 nm and 357 nm respectively confirming the equilibrium existing between the PCAFC-Cu(II) complex and the I^- ions. This also is an indication that it is only one type of complex that exists in the solution.

In the alkaline medium, the electronic spectra exhibited similar spectra behaviors as seen in the acidic medium except for the fact that the absorption band is just one and weak, observed around 355 nm. As the alkalinity of the anion solution decreases the absorption peak also diminished. The isosbestic point observed around 355 nm confirms the equilibrium existing between the PCAFC-Cu(II) complex and the I^- ions.



a = 0.01 M; b = 0.02 M; c = 0.10 M; d = 0.20 M, and e = 0.50 M of I^-

Figure 6: Effect of concentrations on the colorimetric sensing of I^- by PCAFC-Cu(II)



Acidic medium

Alkaline medium

a = pH 2, b = pH 4, c = pH 6, d = pH 8, e = pH 10, f = pH 12 of iodide ions

Figure 7: Effect of pH on the colorimetric sensing of I^- by PCAFC-Cu(II)

Mixture of solutions ofCl^-, Br^-, I^-, CO_3^{2-}, NO_3^-, SO_4^{2-} Ions

Figure 8: Effect of selectivity on the colorimetric sensing of I^- ions by PCAFC-Cu(II)

4.0 Conclusion

A new Schiff base derived from chitosan and pyrrole-2-carboxaldehyde and its copper (II) complex were successfully synthesized. The new product was characterized by conventional methods of analysis. The functionalization of the chitosan structure to form the Schiff base allows Cu^{2+}ions in its aqueous solution to complex with the Schiff base. The synthesized Cu(II) complex was used to sense the presence of anions (Cl^-, Br^-, I^-, CO_3^{2-}, NO_3^- and SO_4^{2-}) in their solutions and it was found to detect the presence of iodide,I^- ions at different concentrations and pH. In addition, the complex showed the ability to select the presence of iodide ions even in the presence of other anions.

Statements of Declarations

Ethical Approval

“Not applicable as there was no transgression of ethical standards during the preparation of this manuscript.”

Consent to Participate

“Not applicable as the research work does not involve human participants or animals.”

Consent to Publish

“Not applicable.”

Availability of Data and Materials

“Not applicable.”

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