Cosmos Multidisciplinary Research E-Journal
Online Available at www.cmrj.in
Recognized International Peer Reviewed Journal
Impact Factor 5.3
ISSN No. 2456-1665

Spectrophotometric Approach to Quantify the Iron(II) Ions in the Synthesis of Polypyrrole

B.K. Sakhare[1], V.S. More[2*] T.N. Ghorude[2]
1. S.D.S.M.s Dandekar College, Palghar, Maharashtra, India
2. G.E.S.s N.B. Mehata Science College, Bordi, Maharashtra, India
*Corresponding author: vinod13570@gmail.com

Abstract: The present study discusses the development of Polypyrrole (PPy) nanomaterials through the implementation of a chemical oxidative technique. The pyrrole monomer is used to synthesize PPy nanoparticles, which are subsequently oxidised by anhydrous iron (III) chloride ($FeCl_3$). Over the period of six hours, the experiment was carried out at low temperature about 5 ^oC with varying molar ratios of oxidant to monomer, ranging from 0.5 to 3.0. A spectrophotometer (EQ 820D) was utilised to measure the iron (II) (Fe) ion content in PPy solution using a colorimetric technique and to ascertain the maximum wavelength (λmax) resulting from the interaction of PPy with o-phenanthroline. The correlation between optical absorbance and Iron(II) concentration was established by producing a series standardised Fe solutions. The presence of Iron(II) ions confirmed the process that resulted in the formation of PPy from its monomer.

Key words: *Polypyrrole, PPy, o-phenanthroline, Iron(II), Spectrophotometer*

1.Introduction:

In the contemporary landscape of scientific and technological exploration, nanomaterials have surged to the forefront, igniting unprecedented interest and curiosity[1]. These diminutive wonders captivate us with their extraordinary size-dependent properties, unlocking a realm of uncharted possibilities across a diverse array of domains, ranging from groundbreaking advances in medicine to transformative environmental solutions and cutting-edge innovations in energy-related fields, among others. Among these pioneering materials[2]. Polypyrrole (PPy) stands out as a renowned conducting polymer with immense potential, owing to its exceptional electrical conductivity and environmental resilience. The synthesis of PPy is a versatile alchemy, achieved through either electrochemical or chemical oxidation of pyrrole, thus endowing it with the flexibility to address a multitude of challenges[3]. While electrochemical polymerization may present limitations in terms of large-scale production, the chemical approach emerges as an attractive, uncomplicated, cost-effective, and readily scalable alternative, promising to further expand the horizons of PPy's applicability[4]. In this article, we delve into the multifaceted world of PPy nanomaterials, shedding light on their potential to drive innovations across a spectrum of disciplines, and the various avenues that beckon for exploration and exploitation[5].

In our quest to enhance PPy synthesis, we introduced $FeCl_3$ as an oxidant. We meticulously formed PPy solutions by varying $FeCl_3$ concentrations, exploring a range of oxidant to monomer ratios from 0.5 to 3.0. By introducing Iron Fe(III) ions to the pyrrole monomer, we provoke a chemical reaction that converts them into Iron Fe(II) ions, a crucial milestone in the PPy synthesis. Our primary objective was to pinpoint the Fe(II) concentration within the PPy solution, a tangible indicator for the completion of the synthesis process[6].

To achieve this, we employed a colorimetric approach, harnessing the power of color changes to decipher concentration variations. For this, our main apparatus is spectrophotometer (EQ 820D) operating in the visible range from 350 nm to 650 nm[7]. Spectrophotometry relying on the formation of complex species that absorb visible light, provided us with a reliable means to quantify the Fe(II) concentration in the colored solution, where color intensity was in direct proportion to the Fe(II) content. In the realm of iron (II) determination

in aqueous solutions, we harnessed the reactivity of o-phenanthroline ($C_{12}H_8N_2$), a ligand that forms vividly colored complexes with Fe(II). In an aqueous medium, these two entities engage in a precise 1:3 ratio to generate an intensely orange-red complex, $[(C_{12}H_8N_2)_3Fe]^{2+}$, as depicted in the equation[8].

$$Fe^{2+} + 3\ Phen \longrightarrow Fe(Phen)_3^{2+}$$

As we observed the striking shift in color, we diligently recorded the absorbance of the resulting solution at its λ_{max}, which we precisely identified by monitoring the absorbance at various wavelengths of standardized solutions. In the final stretch, we leveraged the data collected from the absorbance measurements of standard solutions with known concentrations to construct a calibration curve[6]. This critical curve allowed us to estimate the concentration of an unknown sample based on its spectrometer-derived absorbance value.

Within this paper, we introduce a dazzling innovation in the world of Polypyrrole (PPy) synthesis. By harnessing the power of chemical oxidative polymerization with $FeCl_3$ as our catalyst, we start innovation into conventional methods. Yet, our research is not confined to mere process improvement, it's a gateway to a user-friendly method for quantifying the amount of Iron(II) ions, converting it into a colorful solution where intensity mirrors the substance concentration. This innovation is a testament to the boundless possibilities presented by nanomaterials and their impact on various domains[8].

2. Theoretical Background:

In the mid-19th century, pioneering researchers embarked on an exploration of natural polymers, such as cellulose, silk, and rubber, delving into their unique characteristics[3]. The study of polymers remains a vibrant field today, with scientists continually pushing the boundaries by developing novel polymer forms. A significant breakthrough occurred in 1963 when Japanese chemist Shirakawa Hideki unveiled the astonishing potential of certain organic polymers, like PPy, which displayed electrical conductivity when doped with specific compounds[9]. This discovery ignited a wave of research interest, leading to an intensive investigation of the electrical properties of conductive polymers, including PPy, in the 1970s. Remarkable contributions came from researchers like Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa, culminating in the Nobel Prize in Chemistry being awarded to MacDiarmid and Shirakawa in 2000[10].

This remarkable journey brings us to our current investigation, where we focus on the process of polymerization in which pyrrole reacts with iron(III) from $FeCl_3$, resulting in the formation of iron(II) ions. Once this reaction is completed, our primary objective is to estimate the composition of Fe(II) within the PPy solution[11]. Our pursuit is deeply rooted in historical developments, such as the pioneering discovery by Blau, who first observed the formation of a complex between iron(II) and o-phenanthroline. This complex, a key milestone, has since served as an internal indicator for oxidimetric titration of iron and has been explored by distinguished scientists like Walden, Hammett, and Chapman[12]. Notably, Fortune and Mellon contributed by devising a method for spectrophotometrically measuring iron, depends on the synthesis of the iron(II)-o-phenanthroline complex. Over the years, various techniques have been employed to measure the concentration of Fe(II), with spectrophotometry emerging as a prominent option due to its simplicity, speed, and high sensitivity[13].

The spectrophotometer, an indispensable tool in our research, operates based on the fundamental principles of photometric techniques. It functions by sending an incident beam of light with an intensity of I_0 through a solution, where it is partially reflected, partially absorbed, and partially transmitted. If we denote the portions of light as I_r (reflected), I_a (absorbed), and I_t (transmitted), the relationship can be expressed as follows:

$$I_0 = I_r + I_a + I_t \qquad \ldots\ldots(i)$$

In the spectrophotometer, I_r is intentionally kept constant, as measuring I_t and I_0 is sufficient for determining I_a. The Beer-Lambert law is a pivotal factor in this context, establishing the connection between the amount of light absorbed and the concentration of the absorbing species[14]. It can be articulated as:

$$A = \varepsilon c l \qquad \ldots (ii)$$

where, A represents the absorbance, ε symbolizes the molar absorptivity or extinction coefficient, c denotes the concentration of the absorbing species, and *l* signifies the path length of light through the solution. This law is widely embraced in the realm of analytical chemistry for quantifying substance concentrations within solutions[6].

3. Materials and Methods:

3.1. Materials:

3.1.1. Chemicals:

Pure Pyrrole (C_4H_5N) monomer of reagent grade purchased from Spectrochem Pvt. Ltd. Its stored in dark at 0°C. Iron(III) chloride hexahydrate (analytical grade) was purchased from Loba Chemie Ltd. To remove any possible impurities, Pyrrole was distilled under reduced pressure before use. The solutions of Pyrrole (monomer) and $FeCl_3.6H_2O$ (oxidant) were synthesized in deionized water. Other chemicals o-phenanthroline, Potassium Hydrogen Phthalate (KHP), Sulphuric acid (H_2SO_4) used in standard form.

3.1.2. Instruments:

Digital Spectrophotometer (EQ 820D): the optical system consists of lamp, grating monochromator, Photodiode, Lens system and cuvette holder.

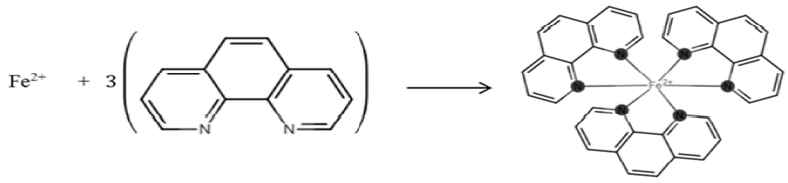
3.2. Methods:

3.2.1. Synthesis of Polypyrrole:

PPy nanomaterials was synthesized by In Situ chemical oxidative technique[11]. In summary, 10 mL of $FeCl_3$ was drop by drop added to 1 mL of aqueous Pyrrole solution (1 M). Using a magnetic stirrer, the solution was constantly stirred for eight hours at 5 ^{0}C. A black precipitate of PPy was produced once the reaction was finished. After being vacuum-filtered, the precipitate was repeatedly cleaned with deionized water. This generate a filtrate, which was then used for further analysis. The six distinct $FeCl_3$ concentrations underwent the same process. The ratios of oxidant to monomer were 0.5 to 3.0, S_1, S_2, S_3, S_4, S_5 and S_6 are the names of these six samples.

3.2.2. Analysis of Iron(II) ions:

At first, 100 ppm of Iron(II) solution was prepared by using Ferrous Ammonium Sulphate (FAS) [0.176 g of FAS + few mL of concentrated H_2SO_4 dissolved and diluted to 250 mL]. Pipetted out 0, 0.5, 1.0, 1.5, 2.0, 2.5 cm^3 of 100 ppm Iron(II) solution in 50 cm^3 of standard measuring flask labelled from 1 to 6. To each flask, we added 5 cm^3 of 0.5 M the KHP and 5 cm^3 of 0.25% o-phenanthroline. Each of this flask diluted up to the mark by double distilled water. The reaction of Iron(II) is shown in Figure 1. The previously obtained PPy filtrate, which contains high iron percent was diluted to the suitable quantity and treated in a same manner as other solutions. Then, we utilized flask-1 as a blank and flask no. 4 solution for maximum wavelength (λ_{max}) quantification using spectrophotometer. Set the wavelength at λ_{max} and measure the absorbance of each solution using flask-1 as blank solution.



1,10-phenanthroline Fe^{2+}(Phenanthroline)$_3$ complex

Figure 1: Reaction of formation of $Fe^{2+}(Phen)_3$ complex

4. Result and Discussion:

4.1. Recording the visible spectrum of the iron-o-phenanthroline complex:

Table 1: Absorbance of the iron-o-phenanthroline complex obtained from 3 ppm standard solution of Iron(II)

Sr. No.	Wavelength (nm)	Absorbance
1.	410	0.05
2.	425	0.08
3.	440	0.10
4.	455	0.12
5.	470	0.14
6.	485	0.18
7.	500	0.22
8.	515	0.25
9.	530	0.23
10.	545	0.18
11.	560	0.08
12.	575	0.04
13.	590	0.02
14.	605	0.01
15.	620	0

4.2. Graph between wavelength and absorbance for the standard solution (from Table 1).

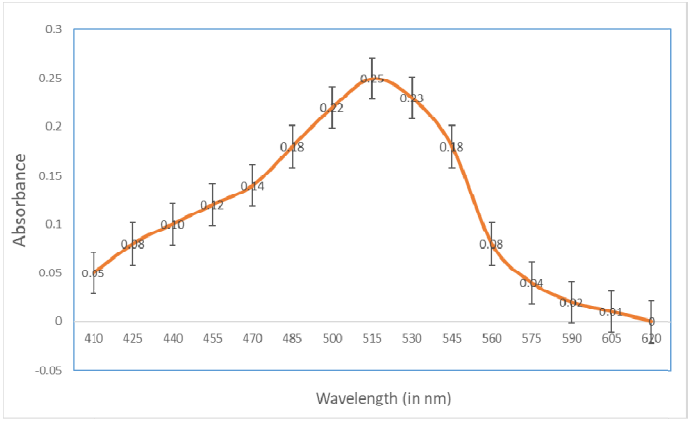


Figure 2: Visible spectrum of the Iron-o-phenanthroline complex

Based on the aforementioned spectrum, λ_{max} = 515 nm is determined to be the wavelength of maximum absorption.

4.3. Collecting absorbance data for the Beer-Lambart Plot:

Table 2: Absorbance values of the phenanthroline-complexes of standard and sample solutions of Iron(II) ions

Sample No.	Concentration of Fe(II) in PPM	Absorbance at λ_{max}
1	0.5	0.125
2	1.0	0.173
3	1.5	0.235
4	2.0	0.248
5	2.5	0.364
S1	Unknown (M.R. = 0.5)	0.051
S2	Unknown (M.R. = 1.0)	0.083
S3	Unknown (M.R. = 1.5)	0.102
S4	Unknown (M.R. = 2.0)	0.223
S5	Unknown (M.R. = 2.5)	0.291
S6	Unknown (M.R. = 3.0)	0.384

4.4. Plotting the calibration curve: The graph between the absorbance and the concentration of Iron(II) ion in the standard solution

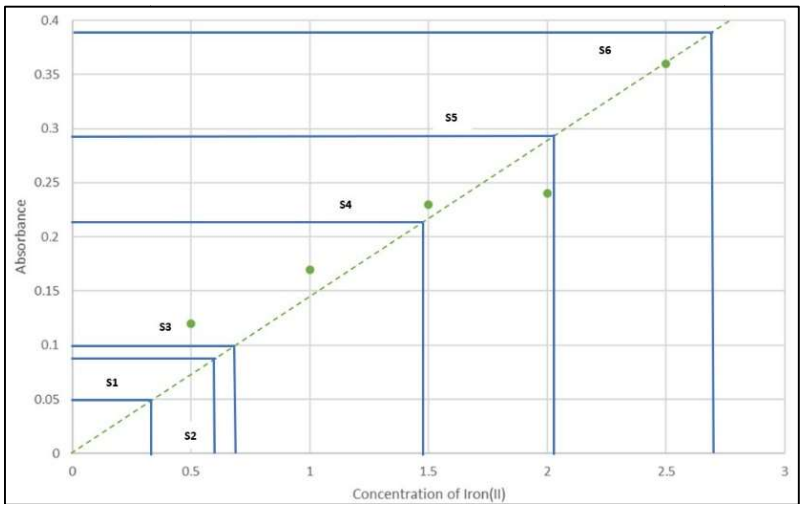


Figure 4: Calibration plot of absorption with the function of concentration

4.5. Determining the concentration of the Iron(II) ions present in the sample from calibration curve:

We plotted the value of absorbance of the sample solution on the calibration curve and determined the corresponding concentration value (in ppm).

$$\text{The concentration of Iron (II) ions in the given sample} = \text{(Value obtained from the calibration curve)} \times 10000 \text{ ppm}$$

The factor of 10000 comes from the fact that we took 1 cm^3 of the sample solution and first diluted to 100 cm^3. From this diluted solution, we have taken 0.5 cm^3 and finally diluted it to 100 cm^3.

The result by using above formula is shown in the table as:

Table 3: Concentration of Fe(II) ions for different M.R.

Sample No.	Molar Ratio of Oxidant to Monomer (M.R.)	Concentration values obtained from the graph	Concentration of Iron(II) ions (in g/L)
S1	0.5	0.3	3
S2	1.0	0.505	5.05
S3	1.5	0.515	5.15
S4	2.0	1.405	14.05
S5	2.5	2.113	21.13
S6	3.0	2.756	27.56

This illustrates that the concentration of Iron(II) ion in the PPy sample depends on the amount of $FeCl_3$ added to it.

Conclusion:

The current research used a modified simple chemical oxidative polymerization approach to successfully synthesize PPy nanocomposites in an aqueous media. The iron-o-phenanthroline complex's wavelength of maximum absorption was found to be 515 nm. We have displayed the calibration curve for this wavelength, which indicates that the PPy synthesis reaction is complete and estimates the Iron(II) concentration from the PPy solution. The result indicates that the amount of Iron(II) content rises with the incorporation of $FeCl_3$ to the PPy synthesis.

References:

[1] A. L. Pang, A. Arsad, and M. Ahmadipour, "Synthesis and factor affecting on the conductivity of polypyrrole: a short review," *Polym. Adv. Technol.*, vol. 32, no. 4, pp. 1428–1454, Apr. 2021, doi: 10.1002/pat.5201.

[2] M. Šetka, R. Calavia, L. Vojkůvka, E. Llobet, J. Drbohlavová, and S. Vallejos, "Raman and XPS studies of ammonia sensitive polypyrrole nanorods and nanoparticles," *Sci. Rep.*, vol. 9, no. 1, p. 8465, Jun. 2019, doi: 10.1038/s41598-019-44900-1.

[3] J. Wen, Y. Tian, Z. Mei, W. Wu, and Y. Tian, "Synthesis of polypyrrole nanoparticles and their applications in electrically conductive adhesives for improving conductivity," *RSC Adv.*, vol. 7, no. 84, pp. 53219–53225, 2017, doi: 10.1039/C7RA09725E.

[4] N. K and C. S. Rout, "Conducting polymers: a comprehensive review on recent advances in synthesis, properties and applications," *RSC Adv.*, vol. 11, no. 10, pp. 5659–5697, 2021, doi: 10.1039/D0RA07800J.

[5] M. Paúrová, I. Šeděnková, J. Hromádková, and M. Babič, "Polypyrrole nanoparticles: control of the size and morphology," *J. Polym. Res.*, vol. 27, no. 12, p. 366, Dec. 2020, doi: 10.1007/s10965-020-02331-x.

[6] T. G. Jo, K. H. Bok, J. Han, M. H. Lim, and C. Kim, "Colorimetric detection of Fe3+ and Fe2+ and sequential fluorescent detection of Al3+ and pyrophosphate by an imidazole-based chemosensor in a near-perfect aqueous solution," *Dyes Pigments*, vol. 139, pp. 136–147, Apr. 2017, doi: 10.1016/j.dyepig.2016.11.052.

[7] M. G. Mellon and D. F. Boltz, "Light Absorption Spectrometry," *Anal. Chem.*, vol. 28, no. 4, pp. 559–576, Apr. 1956, doi: 10.1021/ac60112a001.

[8] M. V. Martínez, C. R. Rivarola, M. C. Miras, and C. A. Barbero, "A colorimetric iron sensor based on the partition of phenanthroline complexes into polymeric hydrogels. Combinatorial synthesis and high throughput screening of the hydrogel matrix," *Sens. Actuators B Chem.*, vol. 241, pp. 19–32, Mar. 2017, doi: 10.1016/j.snb.2016.10.013.

[9] H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, "Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, (CH) x," *J. Chem. Soc. Chem. Commun.*, no. 16, p. 578, 1977, doi: 10.1039/c39770000578.

[10] C. K. Chiang *et al.*, "Electrical Conductivity in Doped Polyacetylene.," *Phys. Rev. Lett.*, vol. 40, no. 22, pp. 1472–1472, May 1978, doi: 10.1103/PhysRevLett.40.1472.

[11] S. Dey and A. Kumar Kar, "Morphological and Optical Properties of Polypyrrole Nanoparticles Synthesized by Variation of Monomer to Oxidant Ratio," *Mater. Today Proc.*, vol. 18, pp. 1072–1076, 2019, doi: 10.1016/j.matpr.2019.06.566.

[12] L. Yang and G. Yao, "A modified spectrophotometric method for the determination of ferrous ion during the Fenton process," *Int. J. Environ. Anal. Chem.*, vol. 102, no. 14, pp. 3194–3206, Nov. 2022, doi: 10.1080/03067319.2020.1766034.

[13] L. G. Saywell and B. B. Cunningham, "Determination of Iron: Colorimetric o-Phenanthroline Method," *Ind. Eng. Chem. Anal. Ed.*, vol. 9, no. 2, pp. 67–69, Feb. 1937, doi: 10.1021/ac50106a005.

[14] A. E. Harvey, J. A. Smart, and E. S. Amis, "Simultaneous Spectrophotometric Determination of Iron(II) and Total Iron with 1,10-Phenanthroline," *Anal. Chem.*, vol. 27, no. 1, pp. 26–29, Jan. 1955, doi: 10.1021/ac60097a009.