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**Research Article**

## Investigation and Evaluation of the structure, morphology, and reduction of the activity of homo and Copolymer aniline/pyrrole by tripyridyltriazine ligand

Nafiseh Hajiabdollah

Department of Chemical Engineering, Abadan Branch, Islamic Azad University, Abadan, Iran

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✉: N. Hajiabdollah  
: [hajiabdollah.n@gmail.com](mailto:hajiabdollah.n@gmail.com)

### ABSTRACT

In this research, homo and copolymer electrosynthesis of Aniline/Pyrrole changed into performed at the tip of a graphite pencil in phosphoric acid containing KCl as electrolyte support. The ability of electro-synthesized homo and copolymers to reduce  $\text{Fe}^{3+}$  turned into compared and evaluated. Fe is a ferromagnetic material that exhibits magnetic properties in the absence of a magnetic field.  $\text{Fe}^{3+}$  ions are very pale due to the unauthorized mutation of the electrons, and with the reduction and conversion to  $\text{Fe}^{2+}$ , there is a permissive electron mutation, which means that the chelates are rapidly attached to the authorized ligands and increase the color Fe (III), as an oxidant, tends towards the antioxidants found in the sample and makes contact with them and turns electrons into Fe (II) and tripyridyltriazine (TPTZ) is an electron binder in which by the electron donor antioxidant. The consequences show that the poly-aniline decreasing assets are better than the copolymer and that the copolymer is higher than the polypyrrole. The FTIR and UV-visible spectra indicated that the aniline ring increase in the polymer chain escalated the reduction. The structure and morphology of the homo and copolymer have been confirmed by SEM and FTIR.

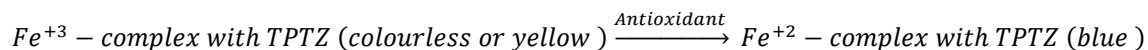
**Keywords:** Polyaniline; Poly pyrrole; Copolymer; Cyclic voltammetry; Conducting polymer; tripyridyltriazine.

## 1. Introduction

Conductor polymers are a subset of the large and older institutions of organic and mineral electric conductors that have electrical, magnetic, and optical properties of metals. In recent years, research has been achieved on polymers with conjugated twin bands[1-3]. polypyrrole and polyaniline are conductive polymers. Copolymers are polymers wherein one-of-a-kind monomers inside the chain are randomly disbursed and interconnected, and the structure of every copolymer relies upon the method and conditions of synthesis[4, 5]. A massive number of chemical and electrochemical techniques had been proposed for the synthesis of copolymers; all are based totally on the oxidation of monomers, formation of radical cations, chain linking of those radical cations to every different, and the formation of polymers. Among those, electrochemical techniques have a unique position due to their simplicity and repeatability. The technique of forming a copolymer starts with its nucleation and ends with the formation of a film on the surface of the electrode[6, 7].

Fe plays an important role in catalyzing the physiological and biochemical processes in the body, although as a vital element for natural physiological functions. On the other hand, Fe overload inside the body reasons many miss radicals in cell damage and loss of life. The severity of cell harm relies upon the number of losses radicals produced, and extra Fe can gather in vital organs, causing liver, heart, kidney, and neurological and endocrine illnesses [4, 8].  $\text{Fe}^{+3}$  ions are very faded due to the unauthorized mutation of the electrons, and with the reduction to  $\text{Fe}^{+2}$ , there is a permissive electron mutation, which means that the chelates are hastily connected to the authorized ligands and increase the color[9-11]. Fe (III), as an oxidant, tends closer to the antioxidants discovered within the sample and makes contact with them and turns electrons into Fe (II). Seeing that electrochemistry relies on the quick transfer of electrons, and tripyridyltriazine (TPTZ) is an electron binder wherein the electron donor antioxidant, speeds up the conversion of (Fe (III) –TPTZ) to ((Fe (II) –TPTZ) the complex.

(Fe (III)-TPTZ) is decreased in proportion to the antioxidant strength of the sample to the complex formed (Fe (II) -TPTZ), the decreased quantity of Fe is measured through absorbance at 593 nm [12-15].



As a result, as the antioxidant energy of the sample is reduced, the absorption is improved at 593 nm. One of the quantitative measurements of ionic ferric is its discount in a complex, which is a degree of the power and capability of the antioxidant of the lowering pattern [4]. Exam of electrodes with conductive polymer coatings which have the potential to reduce ionic ferric is an exciting area for studies. In this study, electrodes covered with homo and copolymer aniline and pyrrole have been observed to study the reduction of  $Fe^{+3}$  in a complex, which implies the antioxidant ability of those polymeric coatings. Moreover, for quantitative and qualitative assessment of electrochemical techniques in conductive polymers film, cyclic voltammetry (CV) was used.

## 2. Experimental

### *Materials, Equipment, and Method*

Aniline (sigma chemicals, USA) becomes purified by using distillation beneath a nitrogen environment at reduced strain. The resulting colorless liquid changed into stored inside the darkish at 5C°. Pyrrole (py) (Merk, Germany) became vacuum distilled earlier than used. Potassium chloride (KCl), phosphoric acid ( $H_3PO_4$ ), and 2, 4, 6- tripyridyl-s- triazine (TPTZ) were of analytical grade and used as acquired. Potassium ferricyanide ( $K_3[Fe(CN)_6]$ ) and ferrocyanide ( $K_4[Fe(CN)_6]$ ) (Shanghai No.1 Reagent manufacturing facility, China) were used as acquired. All aqueous solutions have been freshly organized with the usage of ultra-natural water from Milli – Q plus (Millipore Corp., united states of America).

The electrochemical system includes compact state potentiostatic (Ivium technology, Netherlands) managed by a private computer geared up with the Ivium soft. The 3-electrode cellular includes a 2B pencil graphite (1.8 mm diameter) (Staedtler Lumograph, Germany) as a working electrode and a Pt electrode became used because of the counter electrode in opposition to a pseudo-Ag/AgCl reference electrode. The FT-IR spectrophotometer device 2000 of PerkinElmer USA and the UV/ visible spectrophotometer V-500 (JASCO Japan) were extensively utilized for structural evaluation and characterization purposes. The scanning electron microscopy (SEM) prepared with an Oxford INCA four hundred power become used to explain the morphology of the homo and copolymer Ani and Py.

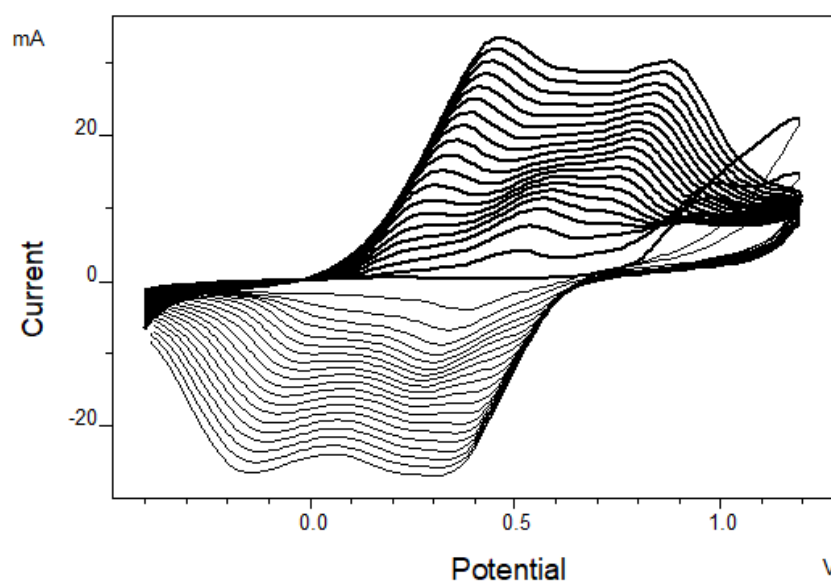
The electrosynthesis of homo and copolymer of Ani and Py on the surface of composite 2B pencil graphite become carried out in a 10 mL solution mixture of 50 mM Ani and Py, 1 M H<sub>3</sub>PO<sub>4</sub>(medium) and 1M KCl (supporting electrolyte) via sequentially sweeping the ability between  $-0.4$  and  $+1.2$  V, scan rate  $100 \text{ mV/s}^{-1}$ , under OFN atmosphere and at  $25 \pm 2^\circ\text{C}$ . The complex of  $0.001 \text{ M Fe}^{+3}$  was produced in  $0.01 \text{ M TPTZ}$  containing  $1 \text{ M H}_3\text{PO}_4$  and their maximum absorbance was obtained at  $593 \text{ nm}$  after  $30 \text{ min}$  exposure to  $0.15 \text{ g}$  of PAni, Ppy, and Copolymer Ani /py electropolymerized. Cyclic voltammetry (CV) became carried out with the use of a Potentiostat/Galvanostat (Iviumsoft, Netherlands) with the aid of a computer prepared with the IviumSoft software program package.

## 1. Results and Discussion

### *Electrochemical synthesis of polyaniline*

Figure 1 indicates cyclic voltammograms of  $50 \text{ mM}$  aniline in  $1 \text{ molar}$  phosphoric acid containing  $1 \text{ M}$  potassium chloride at the graphite pencil tip at a potential range of  $-0.4$  to  $1.2$  V, with up to  $20$  cycles, and scanning rate of  $100 \text{ mV/s}$ . Within the radical acidic environment, the aniline cations produced at the beginning of oxidation are paired within the polymerization process, and the binding of aniline monomers creates special configurations

which might be powerful in the residences of polyaniline. 3 peak pairs have been determined at a capacity variety of -0.2 to 1 V. The primary height pair is in the variety of -0.2 to 0.3 when it comes to the conversion of Leucoemeraldine (LE) to emeraldine salt (ES). The second pair is within the capacity range of 0.6 V because of ES oxidation to PN (pernigraniline). Pair of peaks in the range of 0.3 to 0.6 V is related to the degradation of hydroquinone products to quinones[11].

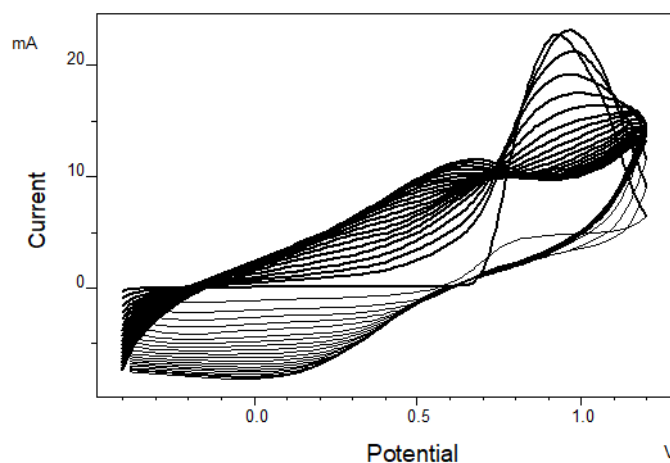


**Fig1.** The schematic of cyclic voltammograms received all through electropolymerization of aniline in 1 M  $\text{H}_3\text{PO}_4$  containing 1 M KCl. The potential is cycled between -0.4 to 1.2 V at a scan rate of 100mV/s for the 1st-20th cycle.

### *Electrochemical synthesis of poly-pyrrole*

Figure 2 suggests cyclic voltammograms of 50 mM Pyrrole in 1 M phosphoric acid containing 1 M Potassium chloride on the graphite pencil tip, inside the variety of -0.4 to 1.2 V, with up to 20 cycles and a scan rate of 100 mV/s. Typically, pyrrole and pyrrole circle of relatives' cyclic voltammetry does not have a giant margin for configuration, and best height synthesis may be used to interpret their electrochemical properties. The poly-pyrrole synthesis peak shift is in the direction of the greater negative potentials due to the simpler oxidation of pyrrole's monomer and the simpler formation of pyrrole cation radicals. Because

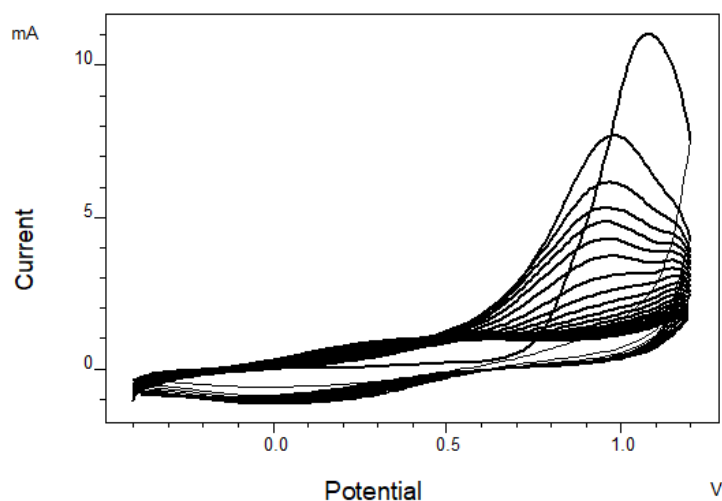
of the reduced conductivity of the changed electrode compared to graphite, the peak-synthesis flow in the next surveys is reduced. Inside the polypyrrole synthesis voltammogram, in the initial cycles, a configuration cycle became located which disappeared in subsequent cycles; it changed into pronounced that the peak is related to the impurities of the composite mattress[4].



**Fig2.** The schematic of cyclic voltammograms was obtained through electropolymerization of pyrrole in 1 M H<sub>3</sub>PO<sub>4</sub> containing 1 M KCl. The potential is cycled between -0.4 to 1.2 V at a scan rate of 100mV/s for the 1st-20th cycle.

### ***Electrochemical synthesis of aniline/pyrrole copolymer***

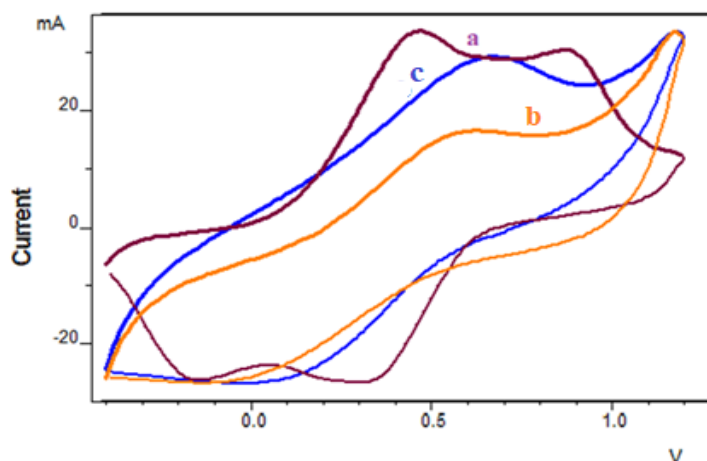
Figure 3 shows cyclic voltammograms of 50 mM Pyrrole and Aniline in 1 M phosphoric acid containing 1 M potassium chloride on the tip of a graphite pencil, inside the capability variety of -0.4 to 1.2 V, with up to 20 cycles and a scan rate of 100 mV/s. The primary degree of the copolymerization manner begins with different anodic oxidation of the two monomers, which can both be adsorbed on an electrode or appear in a thorough cationic answer. The relative speed of oxidation of monomers depends on the nature of each monomer, copolymerization ability, material, and apparent shape of the electrode. Within the 2nd step, the binding reaction of the radical cations to each other happens with the purpose to form copolymers[7, 11].



**Fig3.** The schematic of cyclic voltammograms acquired for the duration of electropolymerization of copolymer aniline/pyrrole in 1 M H<sub>3</sub>PO<sub>4</sub> containing 1 M KCl. The potential is cycled between -0.4 to 1.2 V at a scan rate of 100mV/s for the 1st-20th cycle.

## 2. Investigation of Fe voltammogram cycle the usage of modified electrodes with homo and copolymer aniline/pyrrole

Fig. 4 indicates the cyclic voltammograms of 0.001 M Ferro/ferricyanide of potassium Fe (CN)<sub>6</sub><sup>-4/3-</sup> at 1 molar phosphoric acid, within the range of -0.8 to 1.2 V and a scan rate of 100 mV s<sup>-1</sup>, the usage of changed electrodes (a) poly-aniline, (b) poly-pyrrole, and (c) aniline/pyrrole copolymer.



**Fig4.** The CVs acquired during electropolymerization of a) PAni, b) Ppy, and c) Copolymer PAni/PPy in 1M H<sub>3</sub>PO<sub>4</sub> containing 0.001 M potassium Ferro / ferricyanide [Fe (CN)<sub>6</sub><sup>4-/3-</sup>], The potential is cycled between -0.8 and +1.2 V (vs. Ag/AgCl) at an experiment charge of 100 mV/s.

The graphite electrode modified with poly aniline due to homogeneity shows a high electric-powered conductivity and unique redox property in comparison to poly-pyrrole, and whilst it converts Fe (III) to Fe (II), it demonstrates a greater current (34 mA). As proven in discern 4a, there may be a coupling of oxidation peaks and discount which have impacts on the reversibility of the reaction. Graphite electrode changed with aniline/pyrrole copolymer has higher conductivity compared to that changed with poly-pyrrole, and because copolymers exhibit the properties of each polymer, copolymer exhibits a greater current (28 mA) as compared to poly-pyrrole (13 mA).

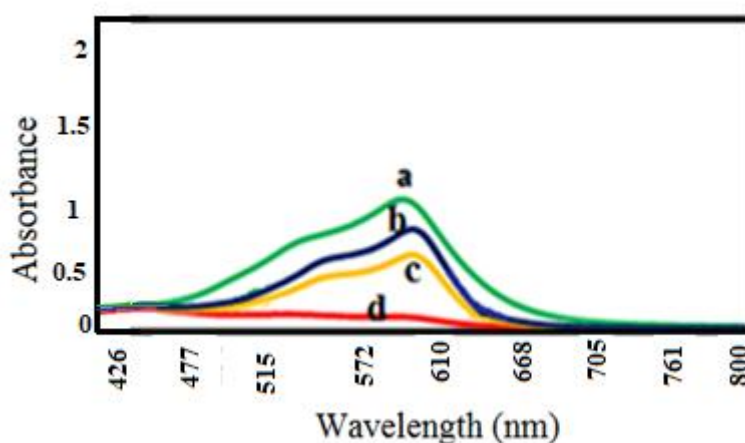
### **3. Investigation of Fe (III) reduction in the usage of electro-synthesized homo and copolymer of aniline/pyrrole**

There are one-of-a-kind techniques for measuring Fe (III), and those encompass, Potentiometry, amperometry, Coulometry, gravimetry, and spectroscopy. In these studies, spectrophotometry became used to measure the rate of Fe. Because the absorption of Fe (III) in spectroscopy is very small, a colored complicated is synthesized from it and it has a significant absorption within the UV-visible variety in proportion to the quantity of Fe and has an excessive sensitivity in measuring Fe values. One of the spectroscopy's most widely used ligands is tripyridyltriazine 2, 4, 6(TPTZ) [14, 15].

Fig. 5 indicates the UV- visible spectrum of 10 cc reduction of the 0.001 molar Fe (III) complicated, uncovered to 0.15 g of (a) poly aniline, (b) aniline/pyrrole copolymer, and (c) poly-pyrrole electro-synthesized for 30 min. In conductive polymers, the charge transfer is investigated thru the depth of the UV-visible adsorbing tapes in polymeric solutions. Graph d suggests the UV-visible spectrum of the Fe (III) complex without being exposed to homo and copolymer. Due to the strength of electron transfer, homo and copolymer aniline/pyrrole are electro-synthesized and the conversion of the Fe (III) complicated to Fe (II) adsorption increases. In different words, the extra electron is launched, the greater the awareness of the



Fe (II) complicated, and thus effects in growth in absorption, and the Fe (III) complex may additionally in all likelihood lower more. Diagrams: (a) The more impact of poly-aniline on electron release with the best absorbance (1.2) and color (tint blue); (b) the much less powerful effect of aniline/pyrrole copolymer on the launch of the electron in comparison to poly aniline and the more impact of copolymer on the launch of the electron in assessment with poly-pyrrole; and c) the lesser impact of a poly-pyrrole on the release of electrons with a minimum absorption depth (0.6) and color (pale blue) in a 593 nm wavelength. These consequences suggest the ability of the polymer to reduce Fe (III) and the formation of a complicated Fe (II) with the TPTZ ligand.

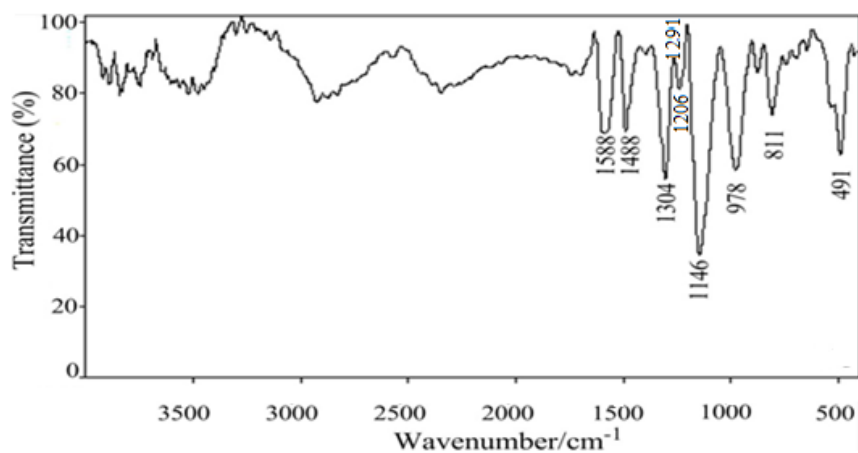


**Fig 5.** UV-vis spectra of 0.001 M complex  $\text{Fe}^{3+}$  in 1 M  $\text{H}_3\text{PO}_4$  after 30 min exposure to 0.15 g of a) PANi, b) CoAni /py, and c) Ppy electropolymerized. d) The absorbance of Ion  $\text{Fe}^{3+}$  in the absence of homo and copolymer is 0.1

#### *Electro-synthesized polyaniline FT-IR spectrum*

Fig. 6 suggests the FT-IR spectrum of electro-synthesized polyaniline. The presence of a C-C vibratory tensile band in the range of  $1588\text{ cm}^{-1}$  is related to the quinoidal (Q) and benzoinated (B) polymer earrings, respectively, even as the C-N stretching band inside the range of  $1488\text{ cm}^{-1}$  belongs to the configurations (ES) of the poly-aniline conductive form. The observed absorption band at  $1146$  to  $978\text{ cm}^{-1}$  corresponds to interstitial aromatic rings

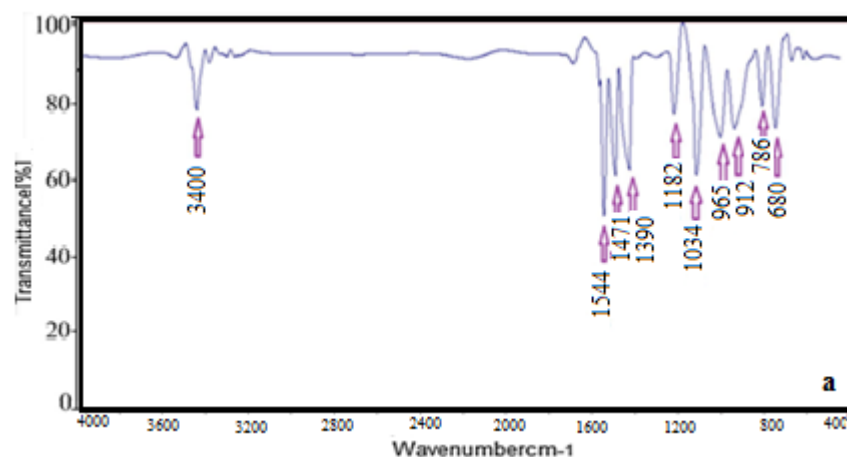
and outside the plane of the CH bond, respectively, and additionally, the absorption band ranged from 811 to 491  $\text{cm}^{-1}$  for the group  $(\text{PO}_4)^{-3}$ [6].



**Fig 6.** Baseline corrected FTIR spectra ( $2000\text{-}400\text{ cm}^{-1}$ ) of PANi electropolymerized in  $1\text{M H}_3\text{PO}_4$  containing  $1\text{ M KCL}$ .

#### *Electro-synthesized poly-pyrrole FT-IR spectrum*

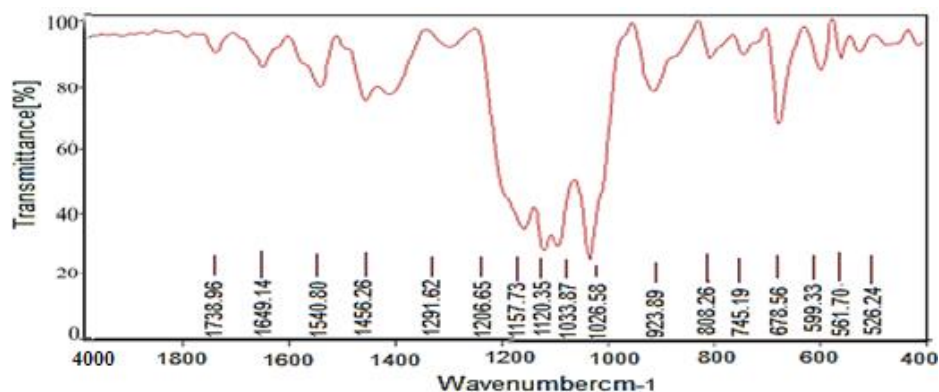
Fig 7 indicates the FT-IR spectrum of electro-synthesized polypyrrole. The absorption band found in  $1544\text{ cm}^{-1}$  is associated with the C-C tensile vibration bond within the poly-pyrrole ring structure. Every other absorbance band of  $1471\text{cm}^{-1}$  is the C-N tensile vibration bond inside the pyrrole ring shape. The absorbance band of  $1390\text{ cm}^{-1}$  is attributed to the plate's vibratory deformation of the C-H and N-H. The absorption band of approximately  $1182\text{ cm}^{-1}$ , A peak within the  $1038\text{ cm}^{-1}$  location of the vibratory deformation of the C-C outdoor hoop plate is discovered. Every other peak change into found in the absorption location of  $786\text{ cm}^{-1}$  in terms of the out-of-plane deformation of the C-H ring. In areas of  $680\text{ cm}^{-1}$ , it becomes determined that absorption bands are related to flexural C-C deformation and C-H out of the plate vibrations of the pyrrole ring[7].



**Fig 7.** Baseline corrected FTIR spectra ( $2000\text{--}400\text{ cm}^{-1}$ ) of Ppy electropolymerized in  $1\text{ M H}_3\text{PO}_4$  containing  $1\text{ M KCL}$ .

### ***Electro-synthesized poly aniline/poly pyrrole FT-IR spectrum***

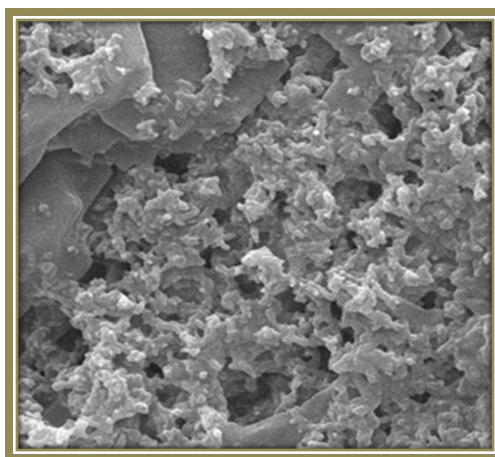
Fig 8 shows the FT-IR spectrum of electro-synthesized aniline/pyrrole copolymer. Peak shapes characterize homo-polymers of poly-aniline and poly-pyrrole in copolymer formation. The presence of peaks at  $1206$  and  $1291\text{ cm}^{-1}$  corresponds to the presence of polyaniline, and the tensile peaks of  $\text{C}=\text{C}$  at  $1540\text{ cm}^{-1}$  and the  $\text{C-H}$  vibrational height at  $1033\text{ cm}^{-1}$  reveal the presence of polypyrrole. The  $923\text{ cm}^{-1}$  peaks may be attributed to a fragment ring outside the  $\text{C-H}$  poly-pyrrole plate. The  $\text{C-N}$  tensile bands are observed at  $1250\text{ cm}^{-1}$  wavelength, even though they may be not located in copolymers, and are discovered in a decreased wavelength of  $1206\text{ cm}^{-1}$ [4]. Regarding the spectrum, it may be concluded that after two distinct monomers are within the shape of a copolymer, although the spectrum is very close to the spectrum of homo-polymers received from every one of the monomers, it is not an easy mixture in their spectra.



**Fig 8.** Baseline corrected FTIR spectra ( $2000\text{--}400\text{ cm}^{-1}$ ) of copolymer Ani and py electro-polymerized in 1M  $\text{H}_3\text{PO}_4$  containing 1 M KCL.

### *Morphology analysis*

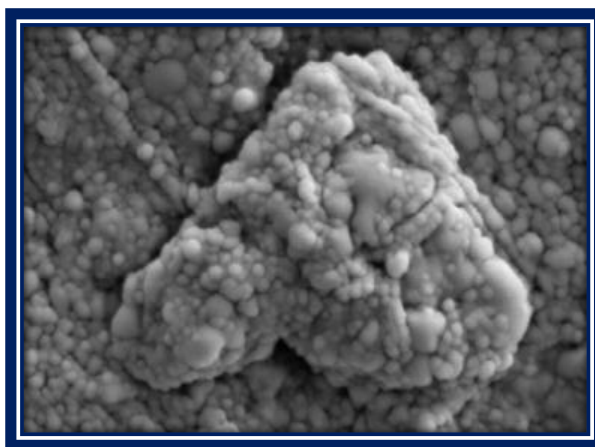
The images obtained from the scanning electron microscope indicate the different morphologies of the electro-synthesis of the copolymer and homo aniline/pyrrole films in the presence of potassium chloride support. Fig. 9 indicates the SEM image of the poly-aniline obtained from the 50 mM aniline electro-synthesis in 1 M phosphoric acid containing 1 M potassium chloride. The SEM photograph acquired from electro-synthesized polyaniline on the tip of a graphite pencil suggests a dense mass-shaped morphology.



**Fig 9.** SEM photograph of PANi obtained using electrochemical synthesis at  $-0.4$  to  $1.2\text{ V}$  in 1 M  $\text{H}_3\text{PO}_4$  containing 1 M KCl on Composite 2B pencil graphite.

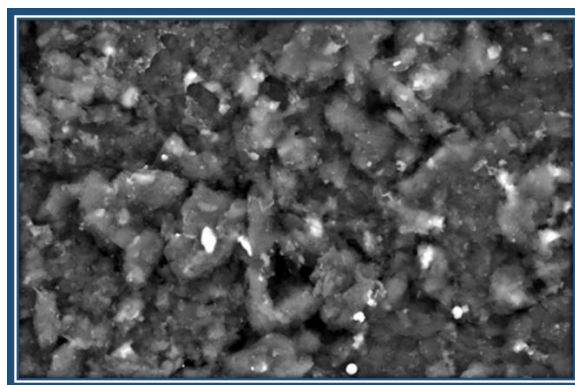
Fig.10 suggests the SEM photograph of the poly-pyrrole received from 50 mM pyrrole electro-synthesis in 1 M phosphoric acids, along with 1 M potassium chloride. The SEM

photograph received from the electro-synthesized polypyrrole at the graphite pencil tip indicates cluster morphology.



**Fig 10.** SEM photograph of Ppy obtained using electrochemical synthesis at -0.4 to 1.2 V in 1 M  $\text{H}_3\text{PO}_4$  containing 1 M KCl on Composite 2B pencil graphite.

Fig. 11 suggests the SEM image of aniline/pyrrole copolymer obtained from 50 mM aniline and 50 mM pyrrole in 1 M phosphoric acid containing 1 M potassium chloride. The SEM photo received from electro-synthesized aniline and pyrrole copolymer on the tip of graphite pencil shows a granular and difficult morphology.



**Fig 11.** SEM photograph of copolymer Ani/py obtained using electrochemical synthesis at -0.4 to 1.2 V in 1 M  $\text{H}_3\text{PO}_4$  containing 1 M KCl on Composite 2B pencil graphite.

#### 4. Conclusion

The results show that the electro-synthesized homo and copolymer of aniline and pyrrole in phosphoric acid in the presence of KCl have electrical conductivity and structural evaluation with FT.IR and SEM are constant with the aniline and pyrrole homo, and copolymer

formulas. The effects showed a high sensitivity of electro-synthesized homo and copolymer of aniline and pyrrole proportional to Fe content material. The higher the amount of absorption, the extra the antioxidant impact. Fe (III) to Fe (II) reduction using homo and copolymer aniline and pyrrole turned no longer only investigated, but, according to biotechnology researchers, it could be concluded that homo and copolymer aniline/pyrrole have a good antioxidant effect.

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