



Enhancement of Conductivity and Productivity of Polyaniline Emeraldine Salt Using Diverse Treatment Solutions



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Abstract

Polyaniline is considered one of essential materials used widely in technologies of solar cells, sensors, batteries and membranes. The preparation of polyaniline using chemical polymerization has many essential parameters that have to be controlled during the synthesis process. These parameters include temperature, time of polymerization, type of dopant, type of oxidant, and washing solution treatment. The washing step is an important factor for the removal of short chains produced during polymerization (oligomers), which are concomitant with the polyaniline during polymerization. Moreover, the washing treatment step is vital for getting rid of residual monomer and excess oxidant. polyaniline samples were prepared by using aniline monomer, ammonium persulfate as an oxidant, and acid dopant (hydrochloric acid or phosphoric acid). The prepared polyaniline was washed using different solutions such as water, acid, acetone, and alcohol. FTIR and XRD analyses confirmed the preparation of polyaniline emeraldine salt in all samples. The results showed an improvement in electrical conductivity and yield when two steps treatment by water and acid solutions were used, while acetone and ethanol showed no change in conductivity. The higher conductivity obtained was 7.95×10^{-2} S/cm when using hydrochloric acid dopant and two-step treatment by water then phosphoric acid.

Keywords: polyaniline, emeraldine salt, preparation, treatment, conductivity

1. Introduction

Polyaniline (PANI) has a wide variety of modified qualities that come from its structural flexibility; it is the most promising choice among various conducting polymers, such as polypyrrole, polythiophene, polyacetylene, and their derivatives. Due to its distinct redox chemistry and high spin density, PANI has intriguing electrical and magnetic characteristics. Additionally, it is highly environmentally stable, easily synthesized in both organic solvents and aqueous solutions, and the monomer is readily available at a reasonable price. Because of the special characteristics of PANI and its essential uses, it has drawn a lot of interest. According to the literature on the synthesis of conducting polymers using various techniques, the properties of the polymers are mostly determined by the dopant type, the degree of doping concentration, and the structure of the polymer that was produced [1–3].

Different studies were performed to investigate the effect of processing parameters on PANI production. These parameters are temperature, dopant type, oxidant type, dopant concentrations, oxidant/aniline ratio, and time of polymerization. Research has been done on the effects of temperature and time on the yield, conductivity, and morphology of PANI. It has been shown that the yield and conductivity of PANI increased with increasing polymerization time and decreasing temperature. In addition to these structural and conductivity changes, the particle size of polyaniline can be related to its conductivity, which varies from 0.5 S/cm to 11.1 S/cm. The shape changes from rod-like particles to globular. The increase in conductivity may stem from the rise of crystallinity and molecular weight [4]. Using low temperature has an advantage in chemical polymerization that can create fine particle size and uniform size distribution of PANI, indicating a high surface area of the

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PANI produced [5], while another study used ambient temperature in performing chemical oxidative polymerization. At low temperature, a high molar mass of PANI was produced, and its experiments showed no great effect on electrical conductivity. In this study, HCl and acetone were used in washing the PANI. In HCl solution, PANI is protonated more uniformly with chloride counterions; nevertheless, some sulphate or hydrogen sulphate anions from the breakdown of peroxydisulfate also function as counterions. Low-molecular oligomers are eliminated by washing step with acetone. Additionally, it keeps PANI agglomerates from forming while drying, resulting in a fine powder product [6].

PANI nanorods synthesized using different oxidants (APS, FeCl_3 , or $\text{H}_2\text{O}_2/\text{Fe}^{2+}$). As the polymerization period was extended, particularly from 12 to 24 hours, the yields of PANI nanomaterials rose but their specific capacitances and electrical conductivities declined. Furthermore, PANI nanorods with the best overall performance were those that synthesized using APS in less than 12 hours [7]. The effect of acid dopants on conductivity of PANI-ES electrical conductivity, doping agents of various strong acids were employed, namely nitric acid (HNO_3), formic acid (HCOOH), hydrochloric acid (HCl), and perchloric acid (HClO_4). HClO_4 showed the best enhancement in conductivity when compared with other acids. The protons of HClO_4 acid contributed in enhancing electrical conductivity [8]. The impact of oxidant/monomer molar ratio on prepared PANI, were carried out using different ratios of 0.25 to 1.50. The results showed the rise in yield by increasing oxidant/monomer ratio, then, electrical conductivity was declined, which may result from a high oxidant concentration [9].

The final step of the polyaniline synthesis procedure is the washing step, which is essential for achieving pure polyaniline and its subsequent physical and electronic properties. This is obvious in a number of research papers on washing and purifying polyaniline before its application and indicates the importance of ensuring the quality before testing any application. The washing step affects the particles in terms of both their purity and their properties [10–13]. Stejskal et al. recommended using acid and acetone in PANI synthesis and avoided using distilled water to eliminate the possible iron (III) ion content in water that could hasten the oxidation of aniline. They used HCl in washing the PANI to dislodge remaining monomer, oxidant, and oligomers. Hydrochloric acid solution has the advantage of obtaining more homogeneous protonation of PANI with chloride counterions. Oligomers and low-molecular-weight organic intermediates are eliminated by a final acetone washing and it keeps the PANI precipitate from clumping together while drying, resulting in a fine powder product [14]. On the other hand, Al-Daghman et al. used distilled water in washing to remove excess APS in the PANI product, and then acetone to get rid of any organic impurities [15,16]. Deng et al. used ethanol in the washing step and was regarded as an unfavorable due to a drop in yield, conductivity, and capacitance [9].

There are few studies conducted on the importance of washing step and didn't mention the effect of washing on PANI produced; therefore, this article highlights it and reveals its importance. The effect of different washing procedures was investigated to explore the influence on the yield and conductivity of the prepared PANI.

2. Experimental

2.1. Chemicals

The following materials were purchased: ortho-phosphoric acid (H_3PO_4) (85% from Specialty Chemicals Seelze, GmbH), hydrochloric acid (HCl) (37%) and ethanol (95%) from EL-Nasr Pharmaceutical Chemicals Company), and aniline (AN) (99% from S D Fine-Chem Limited, India). Acquired 98% of ammonium peroxydisulfate (APS) from Merck KGaA in Germany. Acetone (99.3%) from PIOCHEM laboratory chemicals and ethanol (95%) from NRC.

2.2. Chemical oxidative polymerization

Polyaniline was synthesized using the oxidative chemical polymerization method. 0.05 mole of aniline monomer was added to 50 ml of 1M acid and sonicated for 30 minutes. HCl and H_3PO_4 were used as the acid dopant. Then a second solution of 0.0625 moles of ammonium persulfate and another 50 ml of HCl. The polymerization was performed in an ice bath (4-5 °C). To achieve the dark green color of the emeraldine salt, drops of the second mixture were added to the sonicated solution and stirred for 15 minutes. This indicates the formation of the conductive form of polyaniline. To ensure complete polymerization, the polymerization was kept for 1hr in an ice bath (4-5°C) with stirring and then left-over night at 4°C. The solution was then filtered and washed. The samples dried in a vacuum dryer at 70°C until the weight was constant.

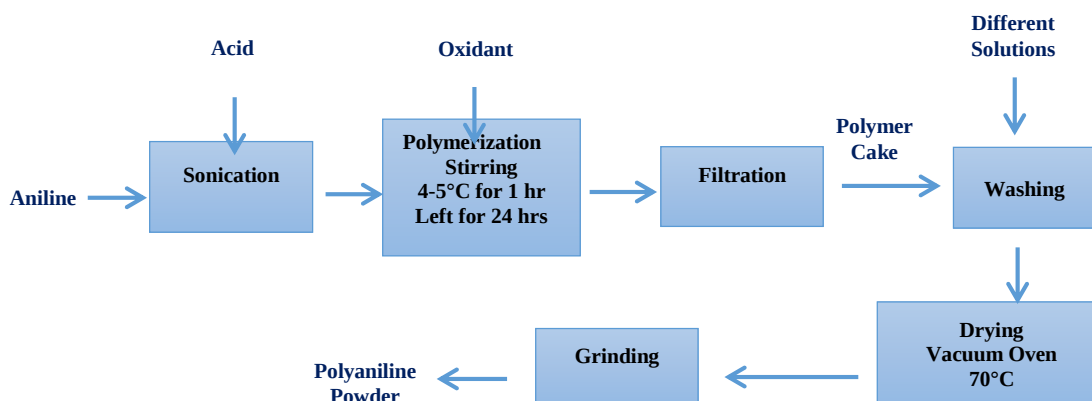


Fig. 1: Flow diagram of PANI preparation steps.

2.3. Washing procedure

In the washing step after filtration, organic and inorganic solutions (distilled water, ethanol, acetone, and acid) were used in the washing step to study its effect on polyaniline emeraldine salt (PANI-ES) produced. The washing was performed in one-step or two-step washing at room temperature. In one-step washing, samples were washed three times with 100 ml of water or 1 M acid (HCl or H₃PO₄), and other samples were washed many times (2 L) with water until the filtered solution became colorless. In two-step washing, first washing H₂O 100 ml three times (300 ml) and then 1 M acid solution or ethanol or acetone (300 ml). Table 1 summarized the two washing solutions. The samples were then dried to obtain polymeric powder and compacted into pellets with a 10 mm diameter and 3 mm thickness to be tested. Fig. 1 presents the preparation steps of PANI-ES.

Table 1. Two solutions used for washing step.

1 st washing solution	2 nd washing solution
H ₂ O	HCl
H ₂ O	H ₃ PO ₄
HCl	Acetone
H ₃ PO ₄	Acetone
H ₂ O	Ethanol

2.4. Characterization

2.4.1. Fourier-transform infrared spectroscopy (FTIR)

Using an absorbance approach and TGS detector, FTIR spectrometer (FT/IR-6100, JASCO, Japan) was used to characterize the PANI samples. The resultant FTIR spectra, which were acquired in the 400–4000 cm⁻¹ range, were utilized to determine the chemical groups and bonds present in each sample.

2.4.2. X-Ray diffraction analysis (XRD)

The manufactured samples were measured at 25 °C to determine the crystallinity using XRD (EMPYREAN, DY 1007, Netherlands). Cu anodic electrode material was employed, along with 30 mA and 45 kV generator settings, and the position [°2 Theta] ranged from 4.0150 to 79.9610.

2.4.3. Energy Dispersive X-Ray Analysis (EDX)

Utilizing the EDX instrument that is connected to the scanning electron microscope (SEM, JEOL JCM-6000 Neoscope) equipment. PANI samples were subjected to an x-ray spectrum utilizing a high vacuum mode and a 15 V high current probe. The structural appearance and elemental analysis of each sample under various conditions were examined using SEM and EDX.

2.4.4. Electrical conductivity measurement

Using a manual hydraulic press set at 20 MPa, the generated polyaniline was compressed into a pellet with a diameter of 10 mm and a thickness of 3 mm. Broad-band dielectric spectroscopy was used to examine the electrical conductivity. Using a Novo-Control Alpha analyzer, the PANI-pressed discs were analyzed at room temperature and in the frequency range of 10^{-1} to 10^{-7} Hz.

2.4.5. Yield of polyaniline (productivity)

The yield of polyaniline produced was calculated using the equation below [17,18]:

$$\text{Yield (y)} = \frac{\text{Mass of polyaniline produced}}{\text{Mass of aniline monomer}} \times 100$$

3. Results and Discussion

Aniline oxidized with APS to form non-conducting aniline oligomers in alkaline conditions. While in very acidic conditions ($\text{pH} < 2.5$), aniline oxidized to produce the conducting form of PANI [19]. p-benzoquinone can also result from the oxidation of aniline in a very acidic media [20–22]. Also, it has been demonstrated that the reaction of p-benzoquinone with aniline forms oligomers that resemble 2,5-dianilino-p-benzoquinone [23]. Fig. 2 shows The mechanism of aniline oxidation in acidic medium and the formation of PANI and oligomers in acidic medium [24,25].

Therefore, the washing step is important for producing highly pure PANI-ES. It is considered essential for the removal of oligomers, and the remaining oxidant may still be present. So, different washing solutions such as water, HCl, H_3PO_4 , ethanol, and acetone can be used. Washing performed either one washing solution using H_2O or acid or two washing solutions using H_2O or acid followed by acetone or ethanol. Two washing solutions are preferred, particularly when remaining excess oligomers are formed.

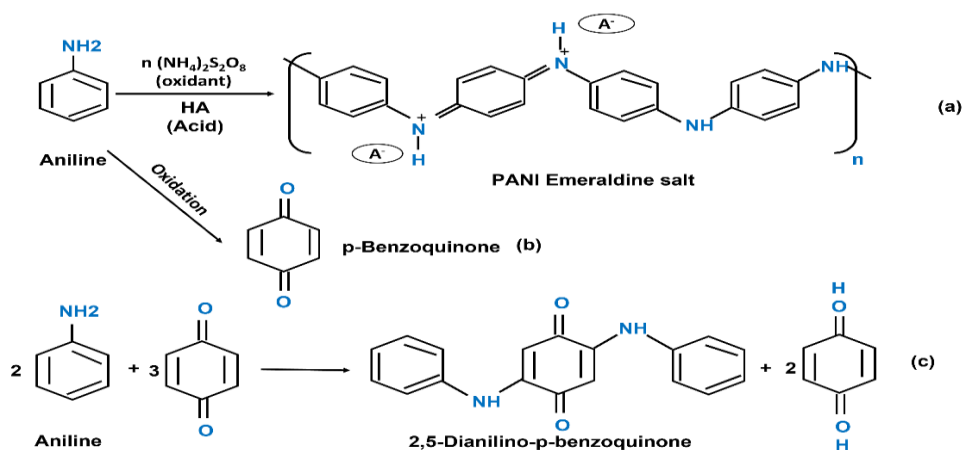


Fig.2. The oxidation of aniline in acidic medium (a) first reaction to form PANI-ES, (b) second reaction to form p-benzoquinone, and (c) the formation of oligomer 2,5-dianilino-p-benzoquinone.

3.1. Productivity and conductivity measurements

Different washing solutions were used after the preparation of PANI, such as water, HCl, H_3PO_4 , acetone, and ethanol. The study was carried out using two different acids, hydrochloric acid and phosphoric acid, as dopants. Generally, the yield produced in the case of phosphoric acid dopant is higher than hydrochloric acid dopant, as shown in Fig. 3. In both dopants, it was obvious that using both solutions, one washing by H_3PO_4 (1M) only and two washing by $\text{H}_2\text{O} + \text{H}_3\text{PO}_4$ (1M) are giving the higher amount of PANI-ES.

In the case of hydrochloric acid dopant, the yields were 191.15 and 221.69% for one washing H_3PO_4 and two step washing ($\text{H}_2\text{O} + \text{H}_3\text{PO}_4$), respectively. While the yield using H_3PO_4 as dopant was 242.61 and 271.26% after using one washing H_3PO_4 and two step washing ($\text{H}_2\text{O} + \text{H}_3\text{PO}_4$), respectively. These may be due to the tri-protonic of phosphoric acid (3H^+) stimulating the polymerization of aniline. It was also noticeable that the yield of PANI was a small amount in case of using one washing (H_2O), so it is required to be acidified with multiprotonic acid like H_3PO_4 . The yield was also a small amount when using one HCl or two-step washing ($\text{H}_2\text{O} + \text{HCl}$) due to the presence of mono-protonic acid (H^+). Furthermore, in the case of all organic washing solutions used in this study, like acetone and ethanol, the yield produced was a little less than the cases mentioned

above, particularly in the case of HCl as a dopant, where two-step washing (water + acetone) produced a yield 119.85%. Also, two-step washing (water + ethanol) produced a yield 111.68%, while two-step washing (acid + acetone) produced the minimum amount of 103.52%.

The reason for increasing the yield above 100% in all PANI samples is the existence of counterions like sulfonate anion [26]. Also at lower reaction temperatures (0–5°C), PANI is produced in high molar mass, which can increase the yield of PANI polymer [6]. This is consistent with prior research that produced high yields of PANI preparations exceeding 100% [27,28]. The reason for increasing the yield after washing by acid, may be due to the more protonation and increasing the counter ions of Cl in case of HCl washing and Phosphorous ions in case of H₃PO₄ washing that confirmed by EDX analysis.

The conductivity values of PANI-ES when HCl is used as a dopant are higher than in H₃PO₄ dopant in all samples. Since the acidic dopants protonated the imine nitrogen's, electron pairs located at imine nitrogen's were injected into the closest quinonoid ring and converted it to benzenoid form. The residual unpaired electrons act as charge carriers and produce a conduction path along the polymer chain. It means an increase in the degree of protonation leads to a higher conductivity [29,30]. The conductivity depends on the nature of the dopant, and in the present case, it remains maximum for monovalent ion dopant (hydrochloric acid) [31].

Using one washing solution (H₃PO₄) and two washing solutions (H₂O+H₃PO₄) are giving the higher conductivities among the other washing solutions in both dopants: phosphoric acid and hydrochloric acid. These indicate that the formation of polarons and di-polarons formed in the PANI-ES chain is favored in the case of hydrochloric dopant more than phosphoric acid dopant. These may be attributed to the high polarity of HCl. Also, it's completely ionized in one step, giving chlorine anion (Cl⁻) and proton (H⁺).

Conductivity is dependent on the type of dopant used, and in this case, monovalent ions, or hydrochloric acid dopant, continue to have the highest conductivity. The higher conductivity using hydrochloric acid dopant was 7.95×10^{-2} S/cm using two-step washing (H₂O + H₃PO₄), while the conductivity was decreased to 7.40×10^{-2} S/cm using one washing (H₃PO₄).

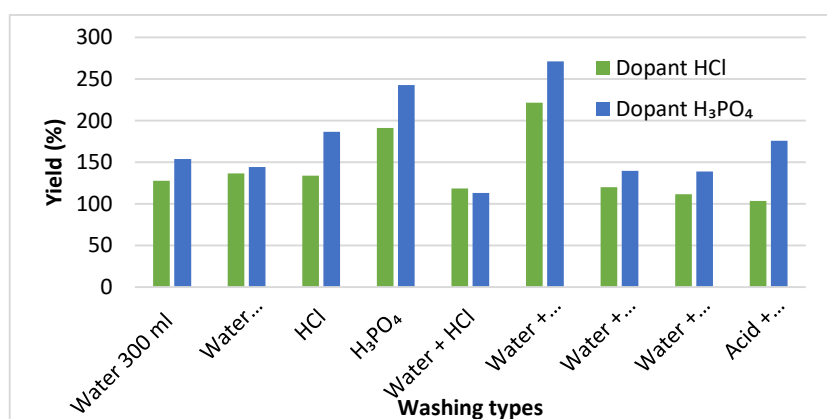


Fig. 3. The yield percentage using HCl and H₃PO₄ as dopants and different washing solutions

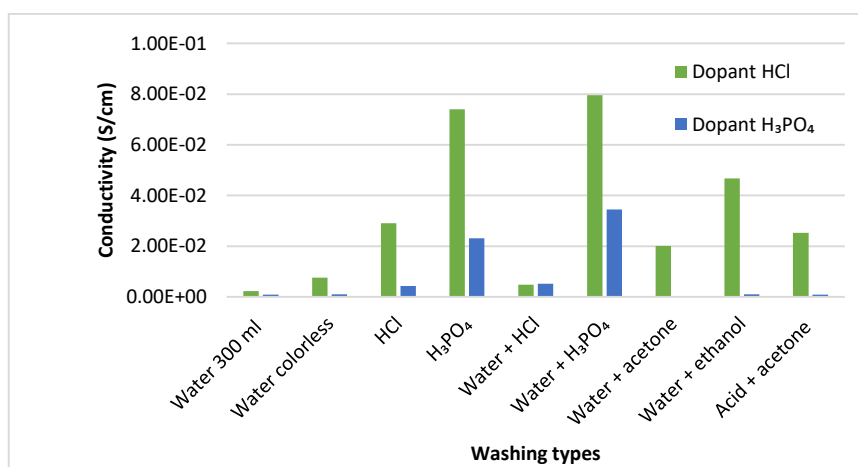


Fig. 4. The conductivity values using HCl and H₃PO₄ as dopants and different washing solution.

The conductivity was highly increased to 7.59×10^{-3} S/cm when compared with using one washing (H_2O). In the case of phosphoric acid dopant, the higher conductivities were 3.46×10^{-2} , 2.31×10^{-2} S/cm for two-step washing ($\text{H}_2\text{O} + \text{H}_3\text{PO}_4$) and one-step washing (H_3PO_4), respectively. Fig. 4 shows the effect of different washing solutions on conductivity for both dopants. From these findings, we can conclude that H_3PO_4 is more favorable as a washing solution than other solutions, and this indicates that H_3PO_4 is safer to keep the product of polyaniline without deterioration with highly conductive.

The conductivity values of prepared PANI-ES are dependent on the conditions of preparation, washing, and purity of raw materials. Thus, some publications showed higher values of conductivity [32,33], while, other publications showed lower values [34–39]. It is noteworthy to mention that the results of conductivity in this work showed a moderate range of conductivity according the conditions we used.

3.2. Chemical composition analysis

The higher yield of PANI using one-step washing (H_3PO_4) or two-step washing ($\text{H}_2\text{O} + \text{H}_3\text{PO}_4$) was confirmed with the results of EDX analysis. The results revealed that the presence of oxygen content was 45.16 and 44.07 wt. and phosphorus 7.66 and 8.75% wt., respectively, as shown in Table 2. This indicates the formation of negative anions, H_2PO_4^- ; these anions represented (A^-) of the chemical structure in emeraldine salt as shown in Fig. 2 above. Table 2 showed that using HCl as washing solution led to the presence of Cl⁻ content, as confirmed by EDX analysis. The presence of a low content of sulfur may be attributed to the remaining traces of APS (oxidant), which is the main oxidant of polymerization reactions. Mineral acids like HCl and H_3PO_4 are capable of removing the remaining sulfur, while the organic solution failed to remove sulfur. The EDX results indicated the presence of C, N, O, S, Cl, and P, and the peak intensity of each element was varied according to the conditions of polymerization, like dopant type and washing solutions. In addition to the chloride anions, larger counterions such as sulfate hydrogen sulfate anions might also be involved in the protonation of PANI in all samples doped or washed by HCl. The yield would seem to rise as a result of this [40]. The same in H_3PO_4 , sulfate hydrogen sulfate anions also might be obtained besides phosphate ions.

3.3. PANI morphology

The SEM images revealed distinct morphological features of PANI samples based on the dopant and washing solutions used. The H_3PO_4 doped samples showed more aggregation and less uniform structure compared with HCl-doped samples [27]. The washing step influences the morphology of PANI including surface structure, porosity, and particle size. The washing types used in PANI samples doped with H_3PO_4 are shown in Fig. 5, the morphology may show variations that reflect the impact of H_3PO_4 on the polymer structure. Some washing can make the structure monodisperse or even less uniform and such variation in the structure will lead to variation in the electrical properties. For HCl-doped Samples in Fig. 6, It is expected that more uniform and well-defined morphology are present, which could correlate with higher conductivity. The images may demonstrate better dispersion and less aggregation compared to H_3PO_4 -doped samples.

Table 2. Chemical composition of PANI samples using different washing solutions.

Dopant Type	Washing type	C%	N%	O%	S%	Cl%	P%
H₃PO₄	Water 300 ml	39.43	29.69	28.13	2.75	/	/
	Water (colorless)	40.87	31.84	23.91	3.37	/	/
	H ₃ PO ₄	28.52	17.57	45.16	1.09	/	7.66
	Water + H ₃ PO ₄	28.76	17.51	44.07	0.91	/	8.75
	H ₃ PO ₄ + Acetone	35.83	24.44	33.05	1.63	/	5.05
	Water + Acetone	40.76	32.79	22.96	3.49	/	/
	Water + Ethanol	41.52	30.18	23.06	4.69	/	0.55
	HCl	44.77	32.68	16.89	1.13	4.35	0.17
	Water + HCl	43.47	32.54	18.1	1.29	4.32	0.28
HCl	300 ml water	39.05	30.08	25.88	3.75	1.24	/
	Water (colorless)	42.73	29.57	23.59	2.41	1.70	/
	H ₃ PO ₄	30.88	19.83	42.63	1.59	/	5.06
	Water + H ₃ PO ₄	31.08	15.24	44.9	0.53	/	8.24
	HCl + Acetone	45.23	31.94	17.85	1.17	3.81	/
	Water + Acetone	40.57	30.04	23.60	3.55	2.46	/
	Water + Ethanol	43.26	27.93	23.11	4.07	1.63	/
	HCl	40.46	28.92	25.91	2.05	2.66	/
	Water + HCl	47.09	32.08	13.97	0.47	6.39	/

In the case of the washing with water, large particles and aggregates are formed, and this may be an indication for the incomplete removal of the dopant or residual impurities. However, in the case of the washing using acidic solutions (HCl or HPO), the dispersion of PANI enhanced and more refined structures were obtained. ($\text{H}_2\text{O} + \text{H}_3\text{PO}_4$) and ($\text{H}_3\text{PO}_4 + \text{Acetone}$) may exhibit better morphology, indicating that these techniques removed excess dopant and contaminants well.

The presence of aggregates during washing may negatively effect on polymerization and impacting PANI characteristics. To enhance conductivity, smaller and more uniform particles are generally desirable, as they can provide better surface area for charge transfer. Two step washing ($\text{H}_2\text{O} + \text{HCl}$) showed better morphology as it can effectively maintain the conductive properties of PANI. These conditions succeeded to remove excess dopant and enhancing the overall structural integrity of the polymer.

3.4. XRD analysis

The results of X-ray diffraction (XRD) indicate the presence of PANI-ES [41]. The patterns of PANI confirm the amorphous structure and semi-crystalline nature of PANI samples due to the presence of benzenoid and quinonoid groups. The characteristic distance between the ring planes of the benzene and quinoid rings in adjacent chains, respectively, may alternatively be represented by the peaks at ($2\theta=20^\circ$, 25.19°) and agreed with other literature [42–44].

The variation of peaks sharpness and peaks height is due to the different conditions used of preparation and washing, such as dopant type and washing solutions. It was observed that washing solutions with water and organic solutions led to wide peaks and amorphous aspects. While crystalline aspects and sharp peaks appeared in some samples when HCl and H_3PO_4 washing solutions were used. This phenomenon was strongly clear in the sample prepared in the conditions of dopant H_3PO_4 and washing solution ($\text{H}_2\text{O} + \text{HCl}$) where sharp peaks were formed indicating high crystallinity of emeraldine salt. Figs. 7 and 8 showed the pattern peaks of XRD analysis using different washing solutions using HCl and H_3PO_4 as dopants.

The samples doped with HCl exhibited a higher degree of crystallinity compared to the sample doped with H_3PO_4 . This variation in crystallinity could be explained by the different ionic sizes of the dopants and acid strengths. H_3PO_4 , with its greater ionic size, could disrupt the polymer chain packing and result in a more disordered arrangement, whereas HCl, being a stronger acid, may aid in the creation of a more ordered structure. This is consistent with the conductivity results, which show that samples doped with HCl are more conductive

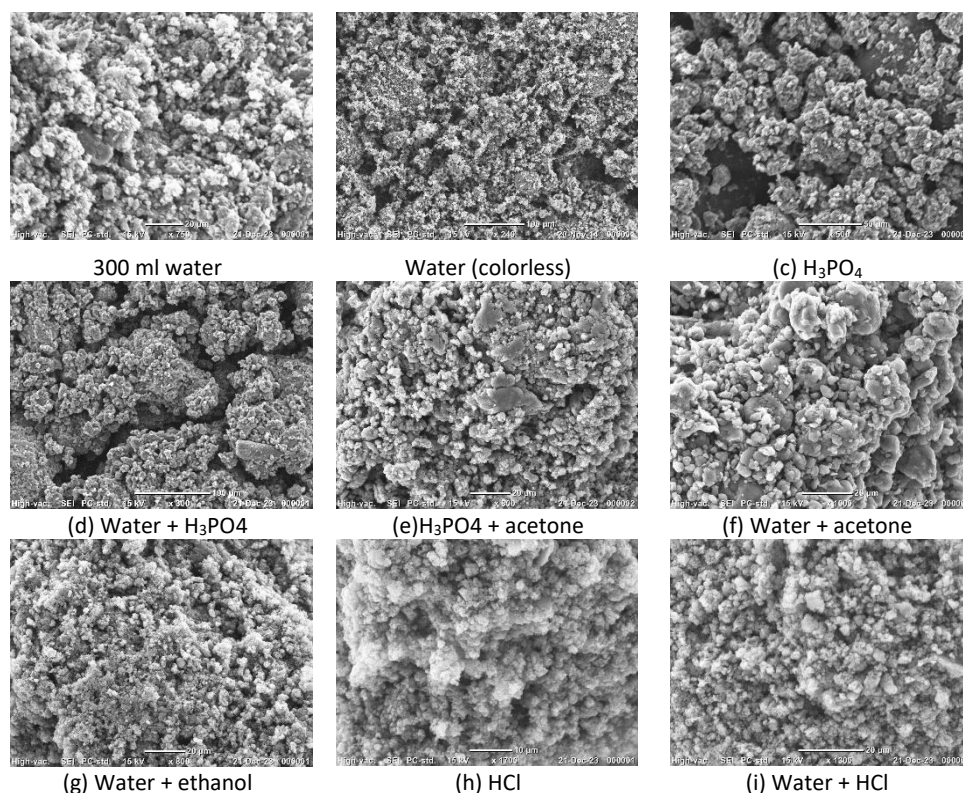


Fig. 5. SEM of PANI samples using different washing solutions (dopant H_3PO_4).

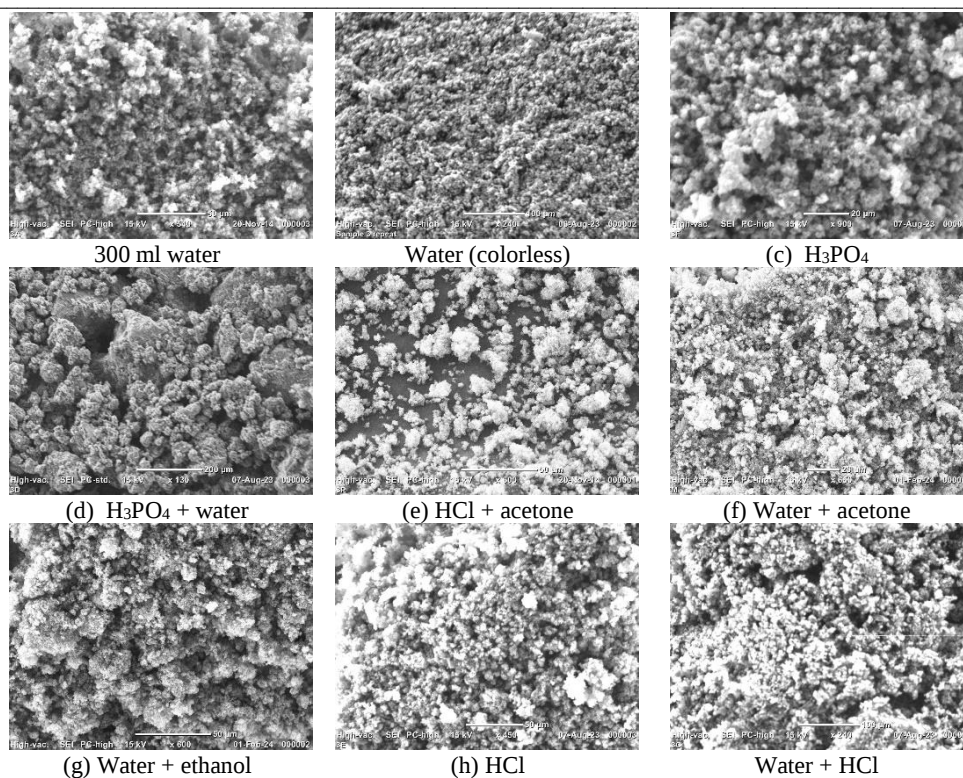


Fig. 6. SEM of PANI samples using different washing solutions (dopant HCl).

than samples doped with H_3PO_4 . Due to the increased conductivity and crystallinity of HCl-doped samples, they are more suited for use in optoelectronic devices and electrochemical sensors. The amorphous structure produced by H_3PO_4 doping might be advantageous for uses like energy storage and catalysis requiring for high surface area and porosity.

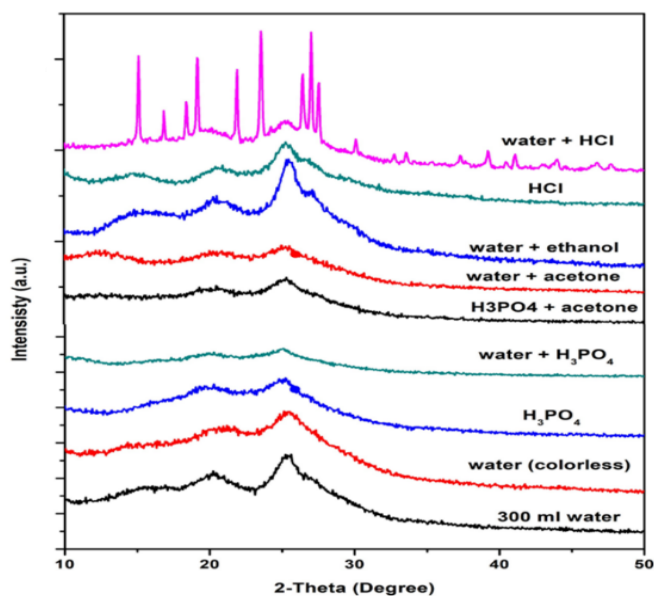


Fig. 7. XRD graphs of PANI using different washing (H_3PO_4 dopant).

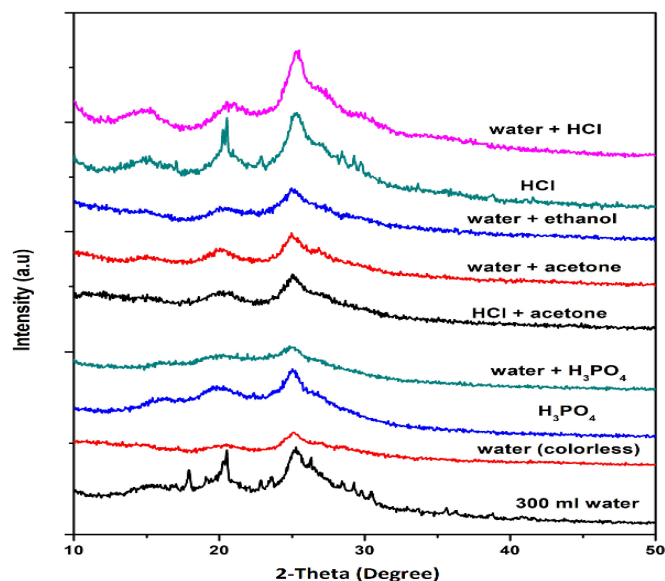


Fig. 8. XRD graphs of PANI using different washing (HCl dopant).

3.5. FTIR analysis

FTIR analysis showed that all samples revealed the main peaks characteristic of PANI-ES structure using two dopants, HCl and H_3PO_4 . In the case of HCl dopant, FTIR analysis of PANI-ES samples is displayed in Fig. 9, using different washing solutions. The peaks in the range of $777\text{--}785\text{ cm}^{-1}$ represent aromatic C–H out-of-plane bending vibrations. The secondary aromatic ring's C–N stretching peaks are located in the range $1230\text{--}1286\text{ cm}^{-1}$. Stretching vibration of the benzenoid (B) ring (N–B–N) at peaks in the range $1425\text{--}1468\text{ cm}^{-1}$ for C=C is observed. At $1532\text{--}1556\text{ cm}^{-1}$, the quinoid (Q) ring (N=Q=N) exhibits a C=C stretching, and the peaks range at 3207 and 3065 cm^{-1} from the secondary amine's N–H stretching vibrations. FTIR analysis for HCl dopant using different washing types is shown in Fig. 10.

On the other hand, in the case of H_3PO_4 dopant, as shown in Fig. 10, bands located at $610\text{--}690\text{ cm}^{-1}$ and at $739\text{--}777$ are indicated of out-of-plane bending vibrations of aromatic C–H. In-plane bending vibrations of the aromatic C–H are indicated by the peaks at $1024\text{--}1032\text{ cm}^{-1}$. The secondary aromatic ring's C–N stretching is shown by the bands that appear at ranges $1215\text{--}1239$ and $1277\text{--}1286\text{ cm}^{-1}$. The broad bands at 3041-- and $3215\text{--}323\text{ cm}^{-1}$ can be attributed to the N–H stretching vibrations of secondary amines; the quinoid (Q) ring (N=Q=N) exhibits a C=C stretching at $1539\text{--}1556\text{ cm}^{-1}$, and the benzenoid (B) ring (N–B–N) exhibits a C=C stretching vibration at $1412\text{--}1460\text{ cm}^{-1}$. All the peaks of the PANI-ES sample are almost the same peaks positions using H_3PO_4 dopant, and the data for two acid dopants agreed with other literature [45–47].

From analysis, there is no peaks in the range from $1650\text{--}1700\text{ cm}^{-1}$ to represent the carbonyl (C=O) stretching from the quinone structure of 2,5-dianiline-p-benzoquinone or p-benzoquinone. That means the washing solutions are perfectly removed them in the washing step and the only PANI-ES we obtained.

The intensity ratio between quinoid (I_Q) and benzenoid (I_B) absorption (I_Q/I_B) bands represents the relative content of quinone and benzene structures in polymers [47]. A greater value indicates a longer conjugation length along the molecular chains. Long conjugation generally promotes electron delocalization along backbones, which results in increased conductivity [48]. All samples showed an intensity value ≈ 1 , as shown in Table 3. Degree of oxidation (X) was calculated using the formula below.

$$X = \frac{I_Q}{I_B} = 1$$

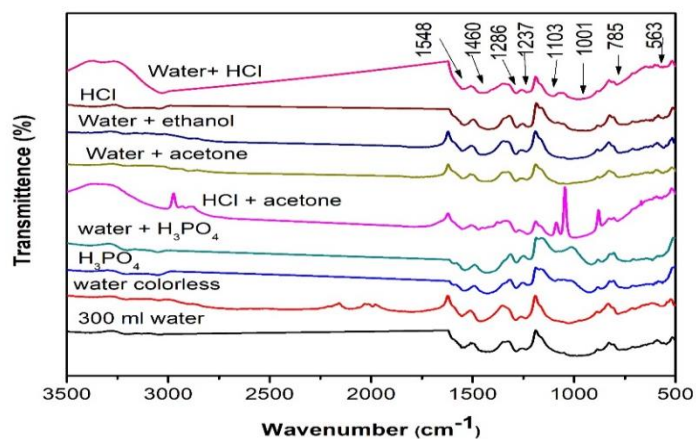


Fig. 9. FTIR peaks of PANI samples using different washing (HCl dopant).

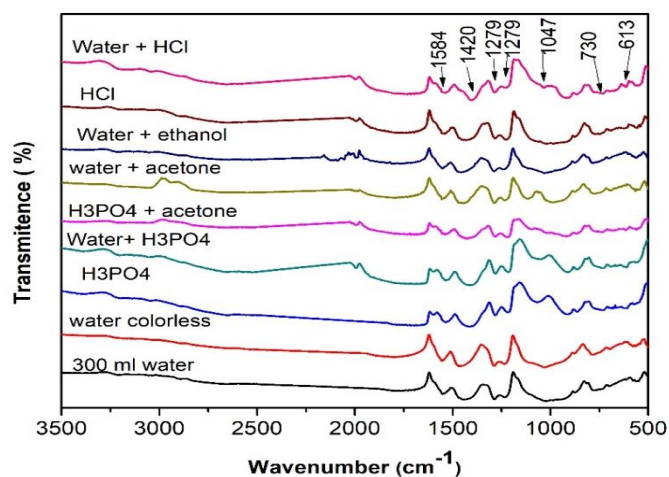


Fig. 10. FTIR peaks of PANI samples using different washing (H₃PO₄ dopant).

Table 3. Intensity absorption ratio and degree of oxidation for PANI samples using hydrochloric and phosphoric acid dopants

Washing type	Hydrochloric acid dopant		Phosphoric acid dopant	
	IQ/IB	Degree of oxidation	IQ/IB	Degree of oxidation
Water (300 ml)	1.05	0.49	1.05	0.49
water (colorless)	1.09	0.49	1.06	0.49
H ₃ PO ₄	1.04	0.49	1.05	0.49
Water + H ₃ PO ₄	1.05	0.48	1.07	0.48
HCl+ acetone	1.00	0.49	1.04	0.49
Water + acetone	1.06	0.49	1.05	0.49
Water + ethanol	1.05	0.48	1.06	0.48
HCl	1.07	0.48	1.07	0.48
Water+ HCl	1.06	0.47	1.11	0.47

Degree of oxidation is closer to the ideal value of 0.5 in all PANI samples [49]. This explains that all samples prepared are in conductive forms due to the presence of quinoid and benzenoid rings in the emeraldine salt structure. While the reason for variation in conductivity between samples is the existence of different counterions, as mentioned before.

From the findings, the washing step is vital for the chemical polymerization of polyaniline. It is essential to evaluate the appropriate washing solution used and suitable for the dopant type. In this study, washing solution ($\text{H}_2\text{O} + \text{H}_3\text{PO}_4$) was found to be the most favorable in the case of dopant H_3PO_4 , where the highest amount of productivity (271.26%) and the highest conductivity value obtained ($3.46 \times 10^{-2} \text{ S/cm}$) were achieved. Furthermore, washing solution ($\text{H}_2\text{O} + \text{H}_3\text{PO}_4$) revealed the highest productivity (221.69%) and the highest values of conductivity ($7.95 \times 10^{-2} \text{ S/cm}$) in case of HCl. The washing step is highly necessary for the removal of dimers or oligomers that may still be present as well.

4. Conclusion

PANI-ES was prepared using two different dopants, hydrochloric acid and phosphoric acid. The study focused on the investigation of using different washing procedures on the conductivity of the prepared PANI samples. Water, HCl, H_3PO_4 , acetone, and ethanol were used as the washing solutions for PANI precipitate before the drying step. The XRD confirmed the semicrystalline structure of PANI polymer salt and achieved improvements in conductivity and yield. In the case of HCl dopant, the conductivity was increased from $7.95 \times 10^{-3} \text{ S/cm}$ when using one washing solution (300 ml water) to $7.95 \times 10^{-2} \text{ S/cm}^{-1}$ when washed with two washing solutions ($\text{H}_2\text{O} + \text{H}_3\text{PO}_4$). Also, the conductivity measured of prepared PANI was 2.91×10^{-2} using one washing solution (HCl) and $7.4 \times 10^{-2} \text{ S/cm}^{-1}$ using one washing solution (H_3PO_4). While, in the case of H_3PO_4 dopant, the conductivity increased from $9.54 \times 10^{-4} \text{ S/cm}$ when using one washing solution (300 ml of water) to 3.46×10^{-2} when washed with two washing solutions ($\text{H}_2\text{O} + \text{H}_3\text{PO}_4$). Moreover, the conductivity measured of prepared PANI was 2.31×10^{-2} using one washing solution (H_3PO_4). The higher yield obtained in both dopants was obtained using two washing solutions (H_3PO_4 + water) and one washing (H_3PO_4). The EDX analysis indicated the presence of C, N, O, S, Cl, and P in PANI samples.

Conflicts of interest

The authors have no conflict of interest.

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