Electrically conductive fabric coated with polyaniline: physicochemical characterisation and antibacterial assessment

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Abstract

The present study investigated the potential antibacterial property of conductive cotton and polyester (PES) fabric coated with polyaniline (PANI). Phytic acid (10, 20, and 30% v/v) was used as a dopant. The fabricated fabric was produced via immersion technique with an immersion time of 30 minutes. The structural identification, conductivity, and morphological properties of prepared fabric were characterised with Fourier transform infrared spectroscopy (FT–IR), electrochemical impedance spectroscopy (EIS), and field emission scanning electron microscope (FESEM), respectively. The optimum conductivities of 2.28×10^{-4} S/m (for cotton) and 2.15×10^{-2} S/m (for PES) were recorded when doped with 30% (v/v) phytic acid. The antibacterial test showed that the fabricated fabric had relatively high antibacterial activity against *K. pneumoniae*, *S. aureus*, and *E. coli* strains.

Keywords Polyaniline · Conductive fabrics · Phytic acid · Antibacterial properties

1 Introduction

The development of fabric with enhanced functionalities, e.g., electrical conductivity, has been receiving attention in recent years due to the increasing demand for high-performance fabric. Despite the efficacy of the previous method by combining metal

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nanoparticles with textile substrates to produce such fabricated fabric, this approach comes with its set of risks for its end users and the environment [1]. Alternatively, conducting polymers (CP) such as polyaniline (PANI) or sometimes can be referred to as aniline black can be deposited on the fabric surface through a chemical or electrochemical method to produce conductive fabric [2, 3]. PANI-coated fabrics are versatile, which are proven from their applications as ammonia sensor [4], electronic devices [5], and precious metal recovery [6, 7]. The ability of CPs to conduct electricity is due to the presence of conjugated double bonds along the backbone. Dopant ions are introduced into the structure of these polymers to impart conductivity. These charged ions neutralise the unstable backbone of the polymer in its oxidised state by donating or accepting electrons [8]. The level of doping is crucial in CPs as this will indicate its oxidation state. Textile substrates such as cotton, nylon, polyester, silica, acrylics, glass, and quartz have been coated with PANI [9–11].

Various types of acid have been used to dope PANI such as H_2SO_4, HNO_3, HCl, and others to achieve high conductivities [12–14]. However, the use of phytic acid (PA) as the dopant in PANI is not widely reported. Previously, PA was used to enhance the stability of PANI. It works as the cross-linker between the substrate and PANI [15, 16]. The ability of dopant to stay in the backbone is highly important to retain its conductivity properties especially in pH media more than 7 (for

biomedical uses), in fact in water. This stability is vital to ensure its extended functionality in biological and physiological system. In this study, PA was used to dope PANI (Fig. 1), later incorporated in fabrics to induce the conductivity. This acid has multivalent anions to encourage the cross-linking activity. Moreover, it is stable enough to prevent the leaching out of the charge carrier from PANI system.

Even though the particular antibacterial activity of PANI has been reported before, studies on the potential antibacterial activity of PANI-embedded fabric are still limited. It was suggested that PANI triggers the production of hydrogen peroxide that forms hydroxyl radical. This radical can destroy cells, such as the case when tested against *E. coli* [17]. In another study by Robertson et al. (2018) [18], when PANI was incorporated into thin film surfaces, the modified surfaces exhibited similar antibacterial activity against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*). Excellent antibacterial performance of polyaniline (PANI) against *E. coli* and gram-positive *S. aureus* microorganisms has been demonstrated under both dark and visible light conditions [19]. The electrostatic adherence between the PANI molecules and the bacteria plays a very important role for the antibacterial reaction of the PANI. In this paper, conductive fabric-based PANI doped with phytic acid (PA) were fabricated by immersion technique. The effect of dopant percentage on the conductivity of the fabricated fabric was studied. The antibacterial activity of these fabric against gram-positive *Staphylococcus aureus* (*S. aureus*) and gram-negative *Escherichia coli* (*E. coli*) and *Klebsiella pneumoniae* (*K. pneumoniae*) was also investigated. The chemical characterisation of the fabricated fabric was performed with Fourier transform infrared spectroscopy (FTIR), while electrochemical impedance spectroscopy (EIS) was employed to characterise its electrical properties. Morphological changes of the doped and undoped fabric were analysed with field emission scanning electron microscope (FESEM).
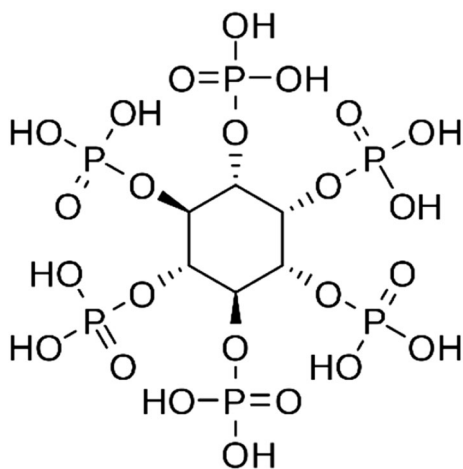
2 Experimental

2.1 Materials

Polyaniline emeraldine base (PANI–EB, 50 kDa), phytic acid, and dimethyl sulfoxide (DMSO) were sourced from Sigma-Aldrich. The polyester and cotton fabric were purchased from a local fabric retailer, Kamdar Sdn. Bhd.

2.2 Sample preparation

Doped polyaniline was prepared by dissolving 0.3 wt% PANI–EB (0.18 g) in DMSO solution (60 ml). 10 v/v% phytic acid (6 mL) was prepared. For doped solution, phytic acid was added into the solution. The solution was confirmed to be in a conductive state (emeraldine salt) when its colour changed from blue to green. This step was repeated for the rest of the volume percentage of dopant (20 v/v% and 30 v/v%). A nonconductive solution of dissolved 0.3 wt% PANI–EB without phytic acid acted as the control solution (blue colour). The solutions were centrifuged for 30 minutes at 2000 rpm to separate the solutions from the precipitate. The precipitate was filtered from the solutions to collect phytic acid-doped PANI solutions that were free from any undissolved particles. The polyester fabric was trimmed to a dimension of 5 cm × 5 cm. These trimmed fabrics were immersed in the doped and undoped PANI solutions for 30 minutes. Then, the samples were dried at room temperature and kept in the dark before use. The similar steps were repeated for cotton fabric. In this study, the range of concentration of phytic acid was varied within 10 v/v%, 20 v/v%, and 30 v/v%. The concentration at 30 v/v % has reached at the highest value in which we used 9 mL of phytic acid. In this case, the concentration of dopant was controlled with the aim to get the optimum concentration.

2.3 Material characterisation

All the fabric were analysed with Fourier transform infrared spectroscopy (FTIR), electrochemical impedance spectroscopy (EIS), and field emission scanning electron microscope (FESEM) to investigate the changes in their functional group, conductivity, and morphology, respectively.

2.3.1 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy analysis was carried out with a Perkin–Elmer spectrometer (model spectrum RX-1) in the range of 400 cm^{-1}–4000 cm^{-1} and with a resolution of 2 cm^{-1}. Each peak corresponds to a functional group in the PANI fabric.

Fig. 1 Molecular structure of phytic acid (PA)

Fig. 2 Visual assessment of the bare fabric (A) and immersed fabric in the undoped (blue colour) (B) and doped PANI (green colour) (C)
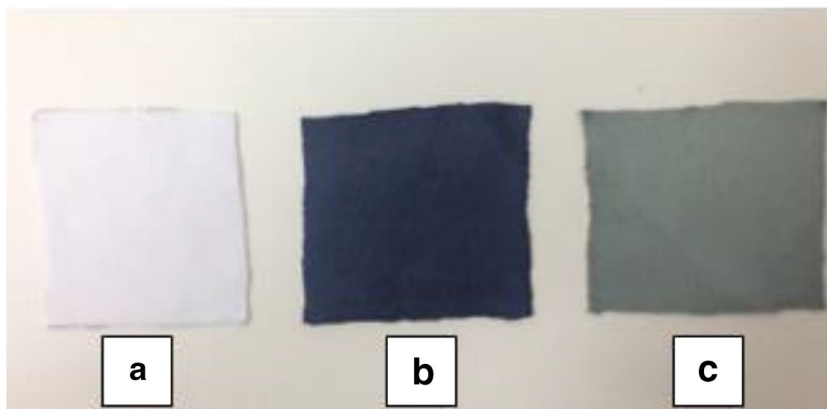
2.3.2 Electrochemical Impedance Spectroscopy (EIS)

In this study, the conductivity of the undoped and doped PANI samples was determined with a HIOKI 3520 LCR Hi-Tester electrochemical impedance spectroscopy (EIS) with a frequency range of 100 Hz to 1000 kHz at room and elevated temperature. Two stainless steel disc electrodes with a diameter of 2 cm were used to clip the samples of PANI-embedded polyester and cotton fabric. The dimension of each fabric was 5 cm × 5 cm. The thickness of the fabrics was measured using digital thickness gauge (see Supplementary 1). A small sinusoidal potential or voltage across the sample together with the current through the sample is measured. The impedance was recorded for each operating frequency. The value of conductivity was determined from the value of impedance plots, giving the resistance values. Then, tht e value of conductivity was obtained by using this formula,

$$\sigma = \frac{t}{RbA}$$

where

σ	conductivity
t	thickness
Rb	resistance
A	area

2.3.3 Field emission scanning electron microscope (FESEM)

The morphology of doped and undoped PANI was examined with a field emission scanning electron microscope (FESEM). The undoped and doped fabrics were sputter coated with a thin layer of Au (gold) to impart conductivity. The samples were scanned with magnification of 200× and 500× to capture the images.

2.4 Measurement of antibacterial activity

Three bacterial strains were selected for this study, which were *Klebsiella pneumoniae* (*K. pneumoniae*), *Staphylococcus*

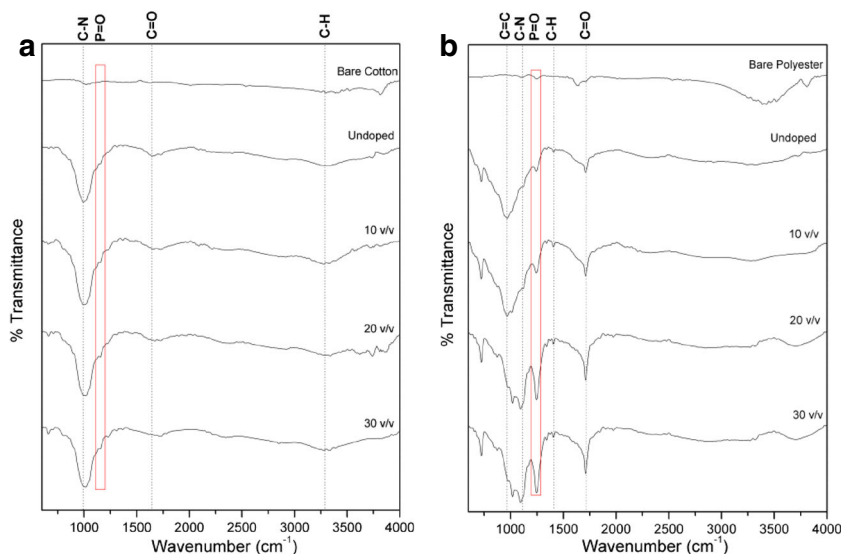**Fig. 3** FTIR spectra of A) PANI cotton fabric B) PANI polyester fabrics

Functional group	PANI cotton fabric (cm–1)	PANI polyester fabric (cm^{-1})
C–N	1152	1152
C=C	–	969
P=O	1228	1238
C=O	1725	1711
C–H	3282	1374

aureus (*S. aureus*), and *Escherichia coli* (*E. coli*). The assessment of antibacterial activity was based on the following observations:

1. The absence or presence of bacterial growth within the contact zone between agar and specimen (inhibition zone)
2. The appearance and size of the inhibition zone around the specimens
3. The evaluation of bacterial growth under the sample

Before the assessment, the samples were disinfected by being exposed to a UV-radiation source (258 nm) from a low-pressure Hg lamp. *K. pneumoniae*, *E. coli*, and *S. aureus* were inoculated with 4.0×10^{-7} colony-forming unit (CFU) mL^{-1} and incubated at 37 °C for 24 h. Five test specimens were placed onto an agar layer with sterilised tweezers, including the control antibiotic and undoped 10, 20, and 30 v/v% sample. The petri dishes with the specimens were incubated at 37 °C for 18 h.

3 Results and discussion

3.1 Visual assessment

The bare fabric (Fig. 2A) displayed standard white shading. However, the fabric turned blue upon immersion in undoped PANI (Fig. 2B). On the other hand, immersion in doped PANI resulted in green fabric, as shown in Fig. 2C. The difference between blue and green shading was a testament to successful doping due to the protonation of the PANI backbone by phytic acid. According to Nicholas and Poncin (2003) [20], the blue shading reflected emeraldine base condition while the green shading is a sign of emeraldine salt state. In the latter state, the acid dopant has protonated the PANI backbone.

3.2 Fourier transform infrared spectroscopy (FTIR)

The functional groups in PANI fabric were identified using Fourier transform infrared spectroscopy (FTIR) spectroscopy. Figure 3 shows the FTIR spectra of PANI cotton fabric and PANI polyester fabric. In general, all spectra show similar bands and peaks. The only significant difference in the FTIR analysis is the spectra of types of fabric, which reflect both PANI cotton fabric and

PANI polyester fabric [21]. We found small peaks at 1228 cm^{-1} and 1238 cm^{-1} for PANI cotton fabric and PANI polyester fabric, respectively. These peaks attributed to P=O from the dopant. As expected, this peak was absent in the undoped sample, except for polyester fabrics that carry the extent of oxidised functionality. This observation has proved that phytic acid has successfully doped in the PANI solution. By increasing the concentration of dopant, polyester fabrics have shown increase of peak intensity at the P=O segment.

A C=C bond stretching of vibration for benzene unit of the PANI polyester fabric was found at 969 cm^{-1}. However, this peak was not visible for the PANI cotton fabric. In this case, the thickness of the coating seems to be smaller than the PANI polyester fabric, which explains the difficulty in spotting this band (see Supplementary 1). The bands at 1725 cm^{-1} were

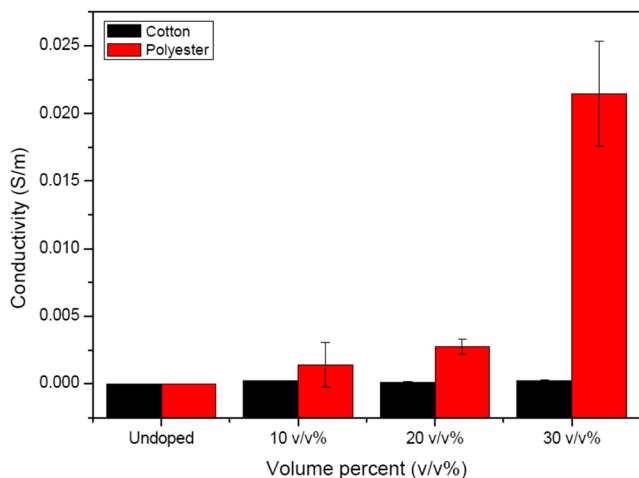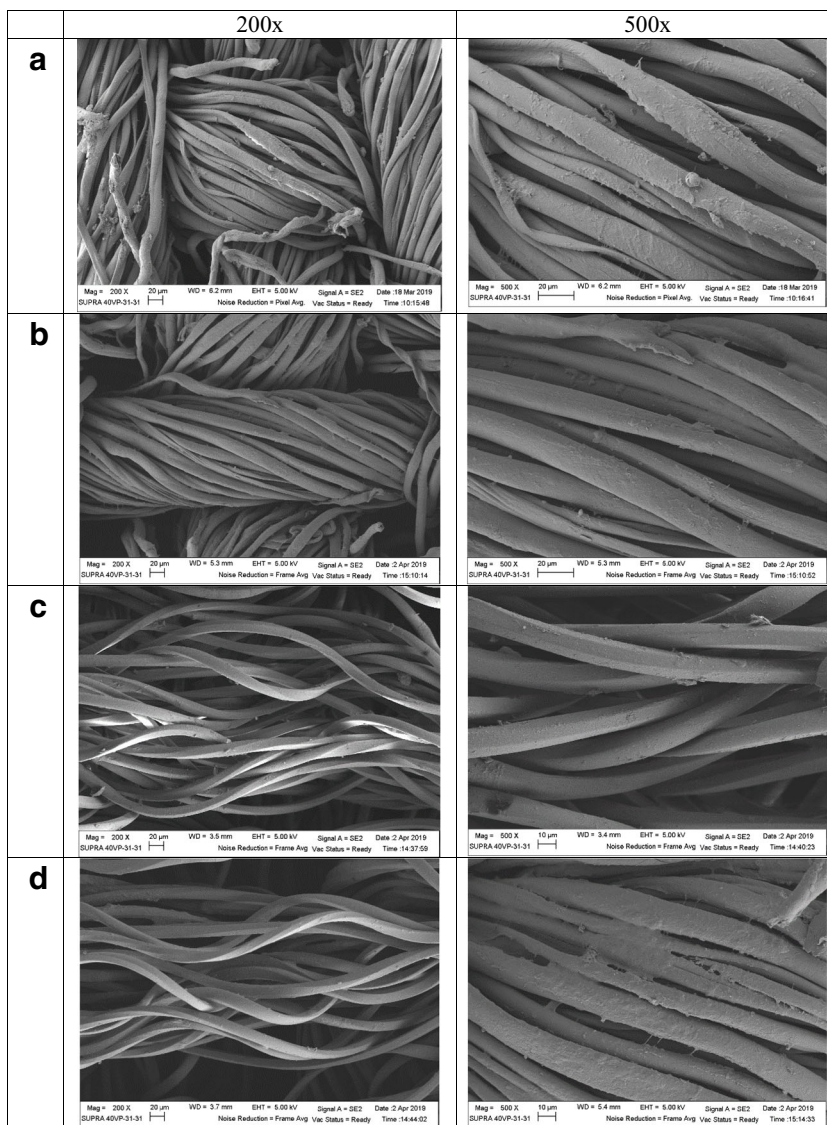| Sample	Volume percentage (v/v%)	Conductivity (S/m)
PANI + cotton fabric	Undoped	$2.04 \times 10^{-6} \pm 1.68 \times 10^{-7}$
	10	$2.06 \times 10^{-4} \pm 4.61 \times 10^{-5}$
	20	$1.04 \times 10^{-4} \pm 3.67 \times 10^{-5}$
	30	$2.28 \times 10^{-4} \pm 4.87 \times 10^{-5}$
PANI + polyester fabric	Undoped	$2.93 \times 10^{-6} \pm 7.20 \times 10^{-7}$
	10	$1.39 \times 10^{-3} \pm 1.66 \times 10^{-3}$
	20	$2.75 \times 10^{-3} \pm 5.70 \times 10^{-4}$
	30	$2.15 \times 10^{-2} \pm 3.86 \times 10^{-3}$

Fig. 4. Conductivity graph of PANI in cotton and polyester fabric.

Fig. 5 FESEM micrographs of A) undoped cotton fabric B) doped PANI cotton fabric C) undoped polyester fabric D) doped PANI polyester fabric

attributed to C=O stretching of aromatic ester for the PANI cotton fabric. Meanwhile, the PANI polyester fabric, the peak for C=O, was located at 1711 cm^{-1}. The bands at 3282 cm^{-1} were attributed to C–H for the PANI cotton fabric, while for the PANI polyester fabric, this peak showed up at 1374 cm^{-1}. The main feature of PANI could be observed at C–N stretching mode of benzenoid units [22]. This peak was found at 1152 cm^{-1}, behaving to be identical, and reflected similar bands for both types of fabrics. Table 1 summarised the comparison of FTIR analysis for PANI cotton fabric and PANI polyester fabric.

3.3 Conductivity

The conductivity of the PANI fabric was measured with an Electrochemical Impedance Spectroscopy (EIS) at ambient room temperature. Table 2 shows the conductivity of the

PANI cotton fabric and PANI polyester fabric. Important distinctions in conductivity were discovered for both fabrics. Fig. 4 shows that the conductivity of cotton fabric and polyester fabric from PANI undoped solution was $2.04 \times 10^{-6} \pm 1.68 \times 10^{-7}$ S/cm and $2.93 \times 10^{-6} \pm 7.20 \times 10^{-7}$ S/cm, respectively. Notably, these samples had a relatively poor conductivity due to the absence of acid within the PANI that acts as a dopant to impart conductivity [23]. The conductivity values of PANI doped with phytic acid in cotton fabric were $2.06 \times 10^{-4} \pm 4.61 \times 10^{-5}$ S/cm, $1.04 \times 10^{-4} \pm 3.67 \times 10^{-5}$ S/cm, and $2.28 \times 10^{-4} \pm 4.87 \times 10^{-5}$ S/cm for 10v/v%, 20v/v% and 30 v/v%, respectively. Meanwhile, for the PANI doped with phytic acid in polyester fabric, the results were $1.39 \times 10^{-3} \pm 1.66 \times 10^{-3}$ S/cm, $2.75 \times 10^{-3} \pm 5.70 \times 10^{-4}$ S/cm and $2.15 \times 10^{-2} \pm 3.86 \times 10^{-3}$ S/cm for 10v/v%, 20 v/v% and 30 v/v%, respectively. A large difference in conductivity value between the two fabrics was evident from Fig 3. The PANI polyester fabric had a higher conductivity when compared to the PANI cotton fabric. The range of conductivity for the PANI cotton fabric was 10^{-4} S/cm to 10^{-3} S/cm, while it was 10^{-3} S/cm to 10^{-2} S/cm for the PANI polyester fabric. These conductivity values proved that the acid dopant was a factor in the conductivity of PANI-EB [24]. This result was corroborated by Mostafaei and Zolriasatein [25] who postulated that the average conductivity range for PANI is 10^{-3} S/cm to 10^{3} S/cm.

The highest conductivity for all samples was recorded at 30 v/v%, suggesting that the ideal composition of PANI EB with acid dopant is 30 v/v%. Table 2 shows that the polyester fabric performed better as a substrate than cotton fabric, which is evident for its higher conductivity values. The contribution of protons from the acidic dopant increased the polar in the backbone of PANI [18], which subsequently improved the conductivity of the PANI fabric.

3.4 Morphology

FESEM micrographs of PANI surfaces are shown in Fig. 5. The micrographs demonstrated that the polyaniline particles were uniformly deposited on the surfaces of PANI undoped cotton fabric, PANI doped cotton fabric, PANI undoped polyester fabric, and PANI doped polyester fabric [26].

The significant amount of PANI precipitates that are noticeable on the surface of have affected the conductivity of the fabric [27]. According to Perumalraj (2015) [28], the conductivity of fabric is expected to be higher when there is an abundance of precipitates on its surface. Polyester fabric has high coating deposition on PANI fabric because polyester hold dye well to prevent from fading and it also holds it shape well and does not shrink when exposed to sunlight, washing and drying. Unlike cotton fabric, it has less coating deposition on PANI fabric because it easy to fade and shrink when exposed to the sunlight, washing and drying. It proved that polyester PANI fabric did not faded during the drying time that made it

give higher coating deposition compared to cotton fabric which then it can affect the conductivity and antibacterial results [29]. Doped PANI polyester fabric displayed greater aggregation of PANI precipitates on its surface when compared to undoped PANI polyester fabric, undoped PANI cotton fabric, and doped PANI cotton fabric (Fig. 5).

3.5 Antibacterial activity of PANI

Three bacterial strains were selected for this study, which were *K.pneumaniae*, *S.aureus,* and *E.coli*. Table 3 shows the inhibition zones that have been measured upon exposure to PANI cotton fabric and PANI polyester fabric that was incubated for 18 hours at 37°C. Inhibition zones were found around around PANI polyester fabric, however PANI cotton fabric did not exhibited as much inhibition zones as PANI polyester fabric (Fig. 6).

As shown in the tabulated data for *K.pneumaniae*, PANI polyester fabric gave the largest inhibition zones of 6.3±

Table 3 Measurements of inhibition zones of PANI cotton and polyester fabric in contact with *K.pneumaniae*, *S.aureus* and *E.coli*

Sample	Volume percent (v/v%)	Inhibition zone (mm)
K.pneumaniae		
Cotton	Undoped	0
	10	0
	20	4.3±0.21
	30	3.5±0.170
Polyester	Undoped	0
	10	0
	20	6.3±0.082
	30	10.3±0.048
S.aureus		
Cotton	Undoped	0
	10	0
	20	0
	30	0
Polyester	Undoped	0
	10	0
	20	1.5±0.082
	30	3.5±0.170
E.coli		
Cotton	Undoped	0
	10	0
	20	0
	30	0
Polyester	Undoped	0
	10	0
	20	2.0±0.17
	30	5.0±0.14

Fig. 6 The inhibition zones of PANI fabric against bacterial strains; *K.pneumoniae* against A)PANI polyester fabric and B) PANI cotton fabric, *S.aureus* against C) PANI polyester fabric and D) PANI cotton fabric and *E.coli* against E) PANI polyester fabric and F) PANI cotton fabric.
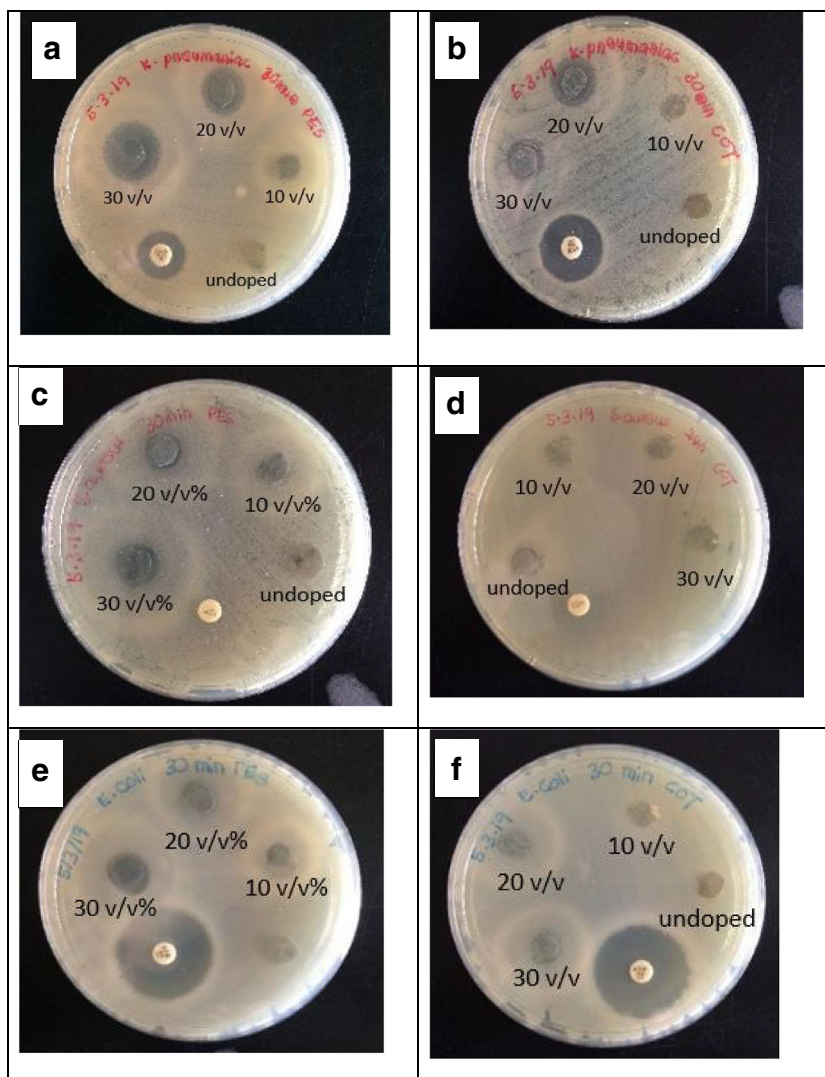
0.08165mm and 10.3± 0.04714mm for 20 v/v% and 30 v/v%, respectively. PANI cotton fabric had inhibition zones of 4.3± 0.20548mm and 3.5± 0.169967 mm for 20 v/v% and 30 v/v%, respectively. Undoped and 10 v/v% fabric demonstrated negative response towards the bacteria. No inhibition zone appeared around these samples. For *S.aureus*, all PANI cotton fabric had no inhibition zone. However, PANI polyester fabric displayed inhibition zones at 20 v/v% and 30 v/v%, which were 1.5±0.082 mm and 3.5±0.17 mm, respectively. The undoped and 10 v/v% samples had no inhibition zone. For *E.coli*, PANI polyester fabric at 20 v/v% and 30 v/v% showed a positive response towards the bacteria, with inhibition zones of 2.0 ±0.17 mm and 5.0±0.14 mm, respectively. However, no response towards *E. coli* was recorded for undoped polyester fabric, polyester fabric with 10 v/v% and all PANI cotton fabrics.

We found that PANI polyester fabric with the volume percentage of 30 v/v% had the highest resistance against the bacterial activity. This particular fabric produced an inhibition

zone with a dimension of 10.3±0.047 mm. No inhibition zone was detected for both types of undoped PANI fabric, which further proved their unreliability to inhibit bacteria. According to Gizdavic-Nikolaidis *et al.* (2011) [30], the inhibition zone was formed due to the reactivity of the acid in the fabric. When the acid leaches out, the fabric will inhibit any pathogen on its surface. In terms of charges, the positive ions from the acid (H^+) repel the charge of the bacteria that are attempting to colonise the fabric. This clash of opposite charges can cause damages to the cell wall of the bacteria which is a fact that is reflected in the study of Mashkour, Rahimnejad, & Mashkour, (2016) [31]. Their results postulated that PANI could destroy bacteria by disrupting its microbial cell membranes and walls via electrostatic contact. The interaction between cationic antimicrobial peptides (CAMP's) and anionic bacterial membranes leads to the death of the cell [32]. Therefore, it was concluded that doped fabric with inhibition zones has a potential application as an anti-infection agent for fabric.

4 Conclusions

The fabrication of conductive PANI fabric with phytic acid as a dopant was prepared with the immersion technique. FTIR results affirmed that the PANI fabric were doped effectively. The morphology of these textures demonstrated small contrast with significant changes in electrical conductivity. Furthermore, this study reinforces the correlation between higher fabric conductivity with higher amount of PANI particles on the fabric surface. Conductivity was the highest at 30 v/v % with polyester fabric as the substrate. In terms of antibacterial properties, it was proven that PANI single-handedly played a role in the repelling of bacteria. The largest inhibition zone for PANI against the bacterial strain is 10.3 ± 0.04714 mm. Finally, it is confirmed that PANI polyester fabric is the best bacteria-resistant material in this study.

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