



Preparation and Evaluation of PANI/PVA/Cu Bionanocomposite Hydrogel via Green Route



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Abstract

Novel biodegradable and biocompatible conductive bionanocomposite hydrogels comprising of polyaniline, polyvinyl alcohol, and copper nanoparticles (PANI/PVA/Cu) were synthesized using aniline hydrochloride instead of aniline and hydrochloric acid in a green manner to reduce the use of hazardous chemicals. Also, copper nanoparticles were prepared using green method, the process is based on the chemical reduction of copper salt in aqueous solution utilizing ascorbic acid as a reducing and capping agent. Addition of insulating polymeric components and inorganic particles improves the physical properties of conducting polymers. Fourier transform infrared spectroscopy and UV-Visible analyses were used to confirm the structural confirmation of the prepared hydrogels. The morphology of the prepared hydrogels was investigated by scanning electron microscopy (SEM). The X-ray diffraction (XRD) and transmission electron microscope (TEM) were used to study the morphology and particle size of nanoparticles; the obtained results demonstrated that the average particle size of nanoparticles was about 43.2 nm. The conductivity measurements revealed that PANI exhibited higher electrical conductivity than PANI/PVA hydrogel, and PANI/PVA/Cu bionanocomposite hydrogels. However, the bionanocomposite hydrogels showed very small increase in electrical conductivity with an increase in Cu-NPs concentration. Additionally, swelling tests were conducted in distilled water for the prepared hydrogels of different compositions and showed good swelling properties for PANI/PVA hydrogel, and PANI/PVA/Cu bionanocomposite hydrogels.

Keywords: Conductive bionanocomposite; Hydrogels; Polyaniline; Copper nanoparticles; Polyvinyl alcohol.

1. Introduction

Conducting polymers or intrinsically conducting polymers (ICPs) are conjugated polymer systems that exhibit high electrical conductivity due to the presence of polarons which provide charge mobility along the polymer chain's backbone [1]. ICPs, including polypyrrole (PPy), polyaniline (PANI), polythiophene (PT), poly(3,4-ethylenedioxythiophene) (PEDOT), and poly(paraphenylene-vinylenes) (PPV) [2], have various advantages, such as tunable electric conductivity, excellent stability [3] and resistance to corrosion, lightweight, low cost, and easy synthesis [1]. Polyaniline (PANI) a prominent semiconducting polymer has high and controllable electrical conductivity on the order of 10 S/cm controlled by type of dopant and doping process [4], easy synthesis from low-cost monomer, high absorption coefficients in the visible light, reversible protonation, unique redox behavior, different structural morphology, high crystallinity, and good stability [5, 6]. Initially, PANI was known as black aniline.

The oxidative polymerization of aniline or aniline

hydrochloride monomers produces polyaniline in different forms depending on the degree of oxidation; (a) emeraldine (Half oxidized PANI, green/baseblue), (b) leucoemeraldine (completely reduced PANI, white/clear), and (c) pernigraniline (completely oxidized PANI, blue/violet), Emeraldine is the most stable and conductive form of them. The synthesis process and protonation degree affect the conductivity of PANI [7]. However, PANI has drawbacks, including poor mechanical properties, processability in solvents especially aqueous solvents [4], solubility, and fusibility. Enhancing the drawbacks of polyaniline can be done by blending PANI with inorganic materials or polymers having better mechanical and optical properties, or by creating composites and nanocomposites for aniline. Conductive hydrogels produced from blending PANI with water-soluble polymers such as polyacrylic acid (PAA), polyvinyl alcohol (PVA), polystyrene sulfonic acid (PSSA), and polyvinylpyrrolidone (PVP) [8] have improved properties of both conductive polymers and hydrogels.

Hydrogels are three-dimensional cross-linked

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networks having the ability to absorb and retain large amounts of water without dissolving in it. Hydrogels are prepared from either natural or synthetic sources [9-11], and possess excellent stretchability, mechano-biological properties, analyte diffusivity, flexibility, and good biocompatibility [12,13]. Conducting polymer hydrogel is a unique material that combines the electrochemical properties of conducting polymers with the soft-wet nature of hydrogels [9,14]. These distinct properties have made conducting hydrogels the perfect choice for biomedical applications such as wearable/ implantable biodevices like intelligent skins, health recording electrodes, biomedical patches [15], and substrates for neural prostheses [16], protein and DNA adsorbents [6], electro-stimulated drug release systems, biorecognition membranes in biosensors [17], strain/stress sensors, tissue engineering including arterial phantom, cartilage tissue substitutes, corneal implants, and heart valves [18], bioelectronics, and medical electrodes [13]. In addition, they are used in gas sensors, light-emitting diodes, antistatic materials [8], Water treatment and dyes adsorbents [6], flexible supercapacitors [9], energy storage devices [10], fuel cells, soft robots, and rechargeable lithium batteries. One of the common conductive hydrogels is PVA/PANI copolymer hydrogel. Polyvinyl alcohol (PVA), nontoxic, biodegradable, biocompatible, hydrophilic, inexpensive, synthetic polymer can form films, and blend easily with other polymers. It also possesses excellent mechanical strength, high thermal and chemical stability, and perfect optical properties [8,19,20].

Composites are multiphase materials composed of two or more solid components that have different chemical and physical properties [21]. Nanocomposites contain a component in nanoscale (range 1-100 nm in size) [19]. The incorporation of nanoparticles in conductive hydrogels could effectively improve the physicochemical properties including optical, thermal, and mechanical properties [11]. In addition, Nanocomposite conductive hydrogels have attracted the interest because they have both organic and inorganic properties [8].

Nanoparticles have gained special interest due to enhanced activity compared to macro molecules, and larger surface area to volume ratio. They possess distinctive physical and chemical properties not found in macro molecules because of their small size effect, quantum effect, interface effect, and surface effect [22]. Copper nanoparticles (Cu-NPs) attracted a lot of interest among different metal nanoparticles due to their chemical, physical, magnetic, catalytic, optical, mechanical, and heat transfer properties. Also, Cu-NPs have relatively low costs in contrast with other metal nanoparticles such as silver, gold, and platinum, antifungal and antibacterial properties with biocidal nature, availability, and excellent electrical

conductivity. As a result, Cu-NPs have been considered for numerous applications, including sensors, catalysts, degradation of dyes, biomedical, super-strong materials, and as antimicrobial, bactericidal coatings for medical equipment [23,24].

Green synthesis techniques are gradually replacing physical and chemical techniques because of nontoxicity and avoiding hazardous chemicals. In this work, we suggest a green approach for the synthesis of (PANI/PVA/Cu) bionanocomposite hydrogels. Harmless polymerization of PANI has been occurred in the presence of PVA and inclusion of green synthesized copper nanoparticles in order to produce a compatible three-component system with enhanced physical properties more than PANI. In this three-component system, PVA is used to increase the processability in aqueous solvents and solubility, and Cu NPs are supposed to enhance the electrical conductivity. PVA, PANI and Cu NPs have been used owing to their biodegradability, biocompatibility, high electrical conductivity, low cost, facile synthesis, eco-friendly, non-toxicity, and thermal stability.

2. Materials and Methods

2.1. Materials:

Aniline hydrochloride and ammonium persulfate (APS) were purchased from SRL, India. Polyvinyl alcohol (PVA), copper chloride dihydrate, and L-ascorbic acid (vitamin C) were obtained from Sigma-Aldrich Co. Acetone and ethanol were purchased from El-Nasr Pharmaceutical Chemicals Co. All chemicals were of analytical grade and utilized without further purification.

2.2. Preparation of Polyaniline (PANI)

50 ml aqueous solution of 1 M aniline hydrochloride was cooled in ice bath at 0-4°C and a 50 ml solution of 0.75 M APS was added dropwise while stirring over 2h. A dark green color was developed indicating the formation of PANI. The reaction mixture was kept in the fridge overnight for complete polymerization. PANI was obtained by filtration. The powder of PANI was washed successively with deionized water and 30% acetone, then left to dry at room temperature.

2.3. Preparation of PANI/PVA Hydrogel

Aniline hydrochloride was dissolved in 5% solution of the assigned amount of PVA and stirred in ice bath. An aqueous solution of 0.75 M APS per 1 M of Aniline hydrochloride was added to the cooled mixture dropwise over 2h. The polymer blend was collected into a Petri dish and left to dry at room temperature then washed with 30% acetone and re-dried at room temperature. The assigned amount of PVA in Wt % to Aniline hydrochloride was 60 %.

2.4. Preparation of Copper Nanoparticles (Cu-

NPs)

An amount of 1.705 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 50 ml deionized water and 50 ml of 1M L-ascorbic acid solution (acted as both reducing and capping agent) was added dropwise while stirring and heating at 70°C . The reaction was stirred at 60°C for 20 h further until a dark brown color was developed (the reaction mixture has become colorless when adding L-ascorbic acid and gradually turned to yellow, orange, brown and finally dark brown). The dispersed Cu-NPs were separated by centrifugation and washed by deionized water then ethanol and left to dry at room temperature [25,26].

2.5. Preparation of PANI/PVA/Cu nanocomposite hydrogel

About 0.4 g aniline hydrochloride was dissolved in 12 ml 5% PVA aqueous solution and the assigned amounts of synthesized Cu-NPs (0.1, 0.15, 0.2 %) were added. The reaction mixture was stirred in ice bath till Cu nanoparticles were dispersed. An aqueous solution of 0.528 g APS was added dropwise over 2h. The mixture was poured into Petri dish and left to dry at room temperature. The formed film was washed by 30% acetone and re-dried at room temperature.

2.6. Characterization

2.6.1. X-Ray diffraction (XRD) Analysis.

The X-ray diffraction spectra of Cu NPs were recorded on a Philips X-ray diffractometer (PW 1930 generator, PW 182 goniometer). The scan was run in a 2θ range of 5° to 80° . The average size of nanocrystals was estimated from the diffraction peaks' broadening, nanoparticles' crystallite size was calculated by using Debye-Scherrer formula in Eq. (1).

$$D = \frac{K\lambda}{\beta \cos\theta} \quad \text{Eq. (1)}$$

where **D** is the particle diameter size, **K=0.9** which is the Scherrer constant, λ is the X-ray wavelength = 0.154 nm, β is the full width at half maximum intensity (FWHM) in radians, θ (diffraction angle) is the Bragg's angle in radians.

2.6.2. Microscopic Analysis (TEM, SEM, EDX)

The micrographs of the prepared samples were taken using a control scanning electron microscope with an acceleration voltage of 30 kV which was attached to Energy Dispersive X Ray spectrometer (EDX). Imaging was performed without any coating as samples are conductive. TEM images were applied on Cu NPs to confirm the shape and size distribution.

2.6.3. FTIR Spectroscopy.

FTIR spectra of the prepared samples were analyzed in the range of $4000\text{-}400\text{ cm}^{-1}$ on Thermo scientific FTIR spectrometer (NICOLET IS 10, USA).

2.6.4. UV-Visible Spectroscopy

The absorption spectrum was recorded at spectral range from 200 nm to 1100 nm on UV/Vis spectrometer t80+ (16-1884-18-0030) at room temperature.

2.6.5. Electrical conductivity

The conductivity of the samples was measured by Hioki LCR 3535-Hi Tester meter (Hioki Co., Japan).

2.6.6 Swelling Measurements

A weighed gel sample was immersed in distilled water at room temperature for definite time intervals. The swollen gel was pressed gently between two filter papers and reweighed. The swelling % was calculated using Eq. (2).

$$\text{Swelling \%} = \left(\frac{W_s - W_d}{W_d} \right) \times 100 \% \quad \text{Eq. (2)}$$

Where, **W_d** and **W_s** are the weights of the dry and swollen gel, respectively.

3. Results and Discussion

In the current work conductive hydrogel nanocomposites were prepared by using a green method. The obtained materials were characterized with the suitable techniques.

3.1. X-ray Diffraction (XRD)

From diffraction pattern, the size and shape of the unit cell can be determined from Peak Positions and the location of the atoms can be determined from Peak Intensities. Diffraction patterns also provide information on the electron density within the unit cell. The nanoparticles' size and crystal structure were verified by XRD measurements. **Figure 1** shows the XRD pattern of the synthesized nanoparticles. The 2θ values were observed at the peaks of 44.8, 50.36, 76.7 corresponding to (111), (200) and (220) planes of Cubic metallic copper nanoparticles. These peaks agree with those of the standard JCPDS Card No. 00-004-0836 for the standard spectrum of the cubic metallic Cu-NPs. Besides the metallic Cu peaks, other additional diffraction peaks appeared at 28.5, 33.03, 47.2, 56.4, 69.45, 76.6 representing (111), (200), (220), (311), (400) and (331) planes of cubic copper chloride (CuCl) nanocrystals which matched well with the JCPDS Card No. 00-006-0344. It is revealed that the synthesized nanoparticles are a mixture of metallic Cu and CuCl. The experimental and standard diffraction angles of Cu and CuCl nanoparticles were measured, and a comparison of the values of 2θ given in JCPDS cards with those obtained for the acquired samples is represented in (**Table 1**). The average particle size of Cu and CuCl nanoparticles was estimated from the major diffraction peaks using Debye-Scherrer equation and it was about 43.2 nm.

3.2. TEM

The morphology and size distribution of the synthesized copper nanoparticles were examined by Transmission electron microscopy (TEM). The typical TEM images are depicted in (**Fig. 2**) which shows that the particles are spherical in shape with high degree of monodispersity. Also, TEM topography of the prepared Cu-NPs was clean as spherical particles in nanosized between 25 - 70 nm as shown in (**Fig. 2a, b**).

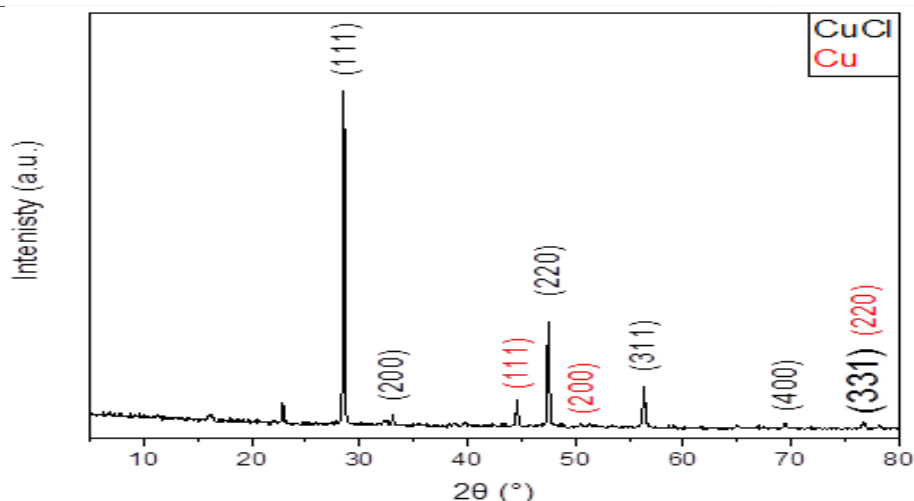


Fig. 1: XRD patterns of the synthesized Cu and CuCl nanoparticles

Table 1: Experimental and standard diffraction angles of Cu and CuCl nanoparticles

Cu 2θ	Standard 2θ, JCPDS Card No. 00-004-0836 (degree)	Value of hkl (planes)	CuCl 2θ	Standard 2θ, JCPDS Card No. 00-006-0344 (degree)	Value of hkl (planes)
44.80	43.298	(111)	28.50	28.522	(111)
50.36	50.434	(200)	33.03	33.027	(200)
76.70	74.133	(220)	47.20	47.437	(220)
			56.40	56.291	(311)
			69.45	69.348	(400)
			76.60	76.590	(331)

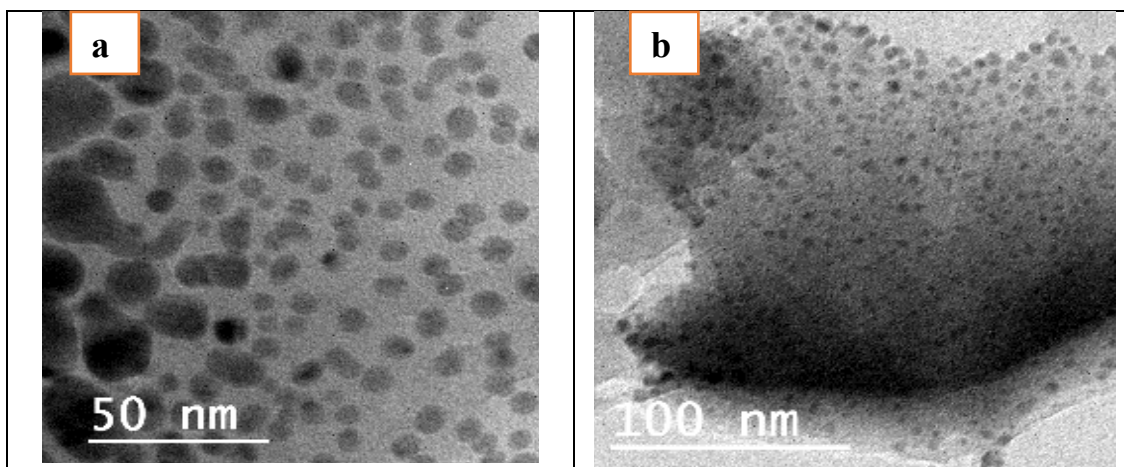


Fig. 2: (a, b) TEM images of the synthesized copper nanoparticles (different magnifications)

3.3. SEM and EDX Analysis

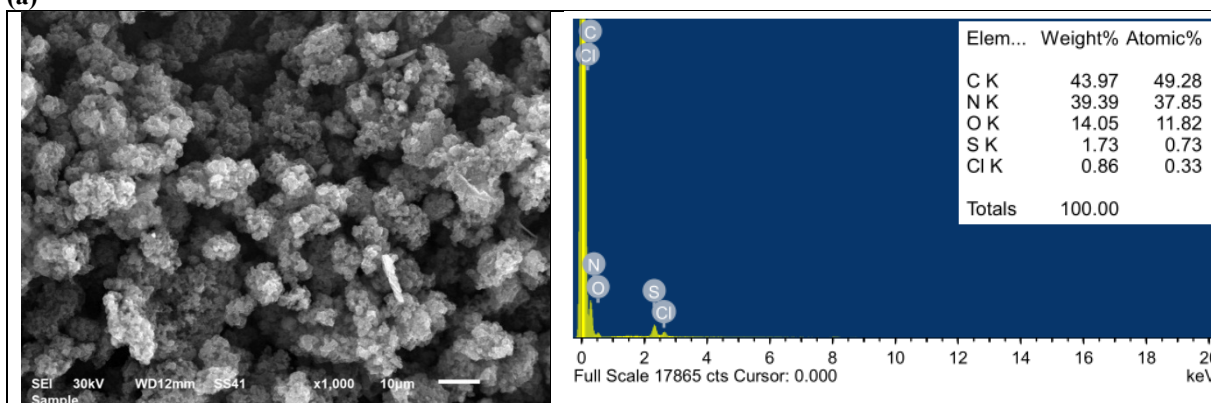
The morphological features of the prepared samples have been studied by recording SEM and the EDX images. **Figure 3** exhibits SEM and EDEX images of the prepared PANI, PANI/PVA, and PANI/PVA/Cu bionanocomposite hydrogels containing different concentrations of Cu-NPs (0.1, 0.15, and 0.2). Inspection of the micrographs, PANI possess an irregular granular morphology (**Fig. 3a**), PANI/PVA has a compatible and uniform distribution (**Fig. 3b**), micrographs of PANI/PVA hydrogel and

PANI/PVA/Cu bionanocomposite hydrogels reveal that they have porous morphology which is influencing their water sorption behavior. Correspondingly, in case of the addition of Cu-NPs to PANI and PVA hydrogel has effect on the topography of the fabricated bionanocomposite hydrogels where the Cu accomplished as metallic luster with random spreading on the bionanocomposites surfaces where the combined nanomaterials in composite matrices produced the non-homogeneous and coarse surface of the prepared bionanocomposites (**Fig. 3c, d, e**).

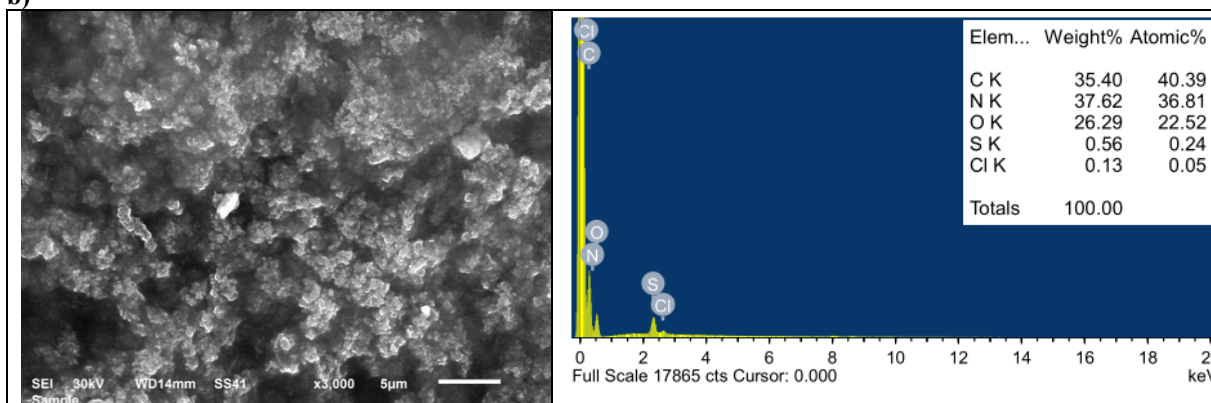
In addition, the EDX charts (Fig. 3c, d, e) of bioactive films illustrated the slightly equal intensity

of Cu peaks which increase with the addition ratio of Cu-NPs

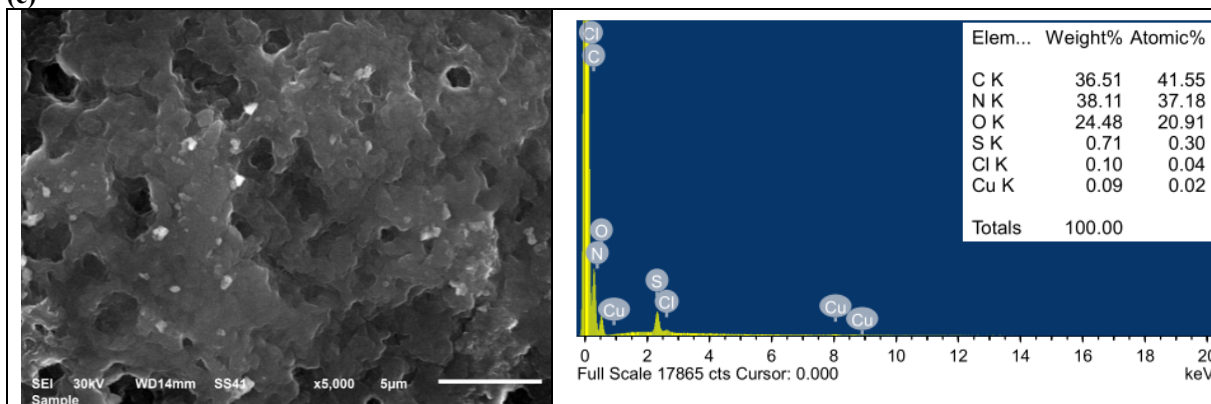
(a)



(b)



(c)



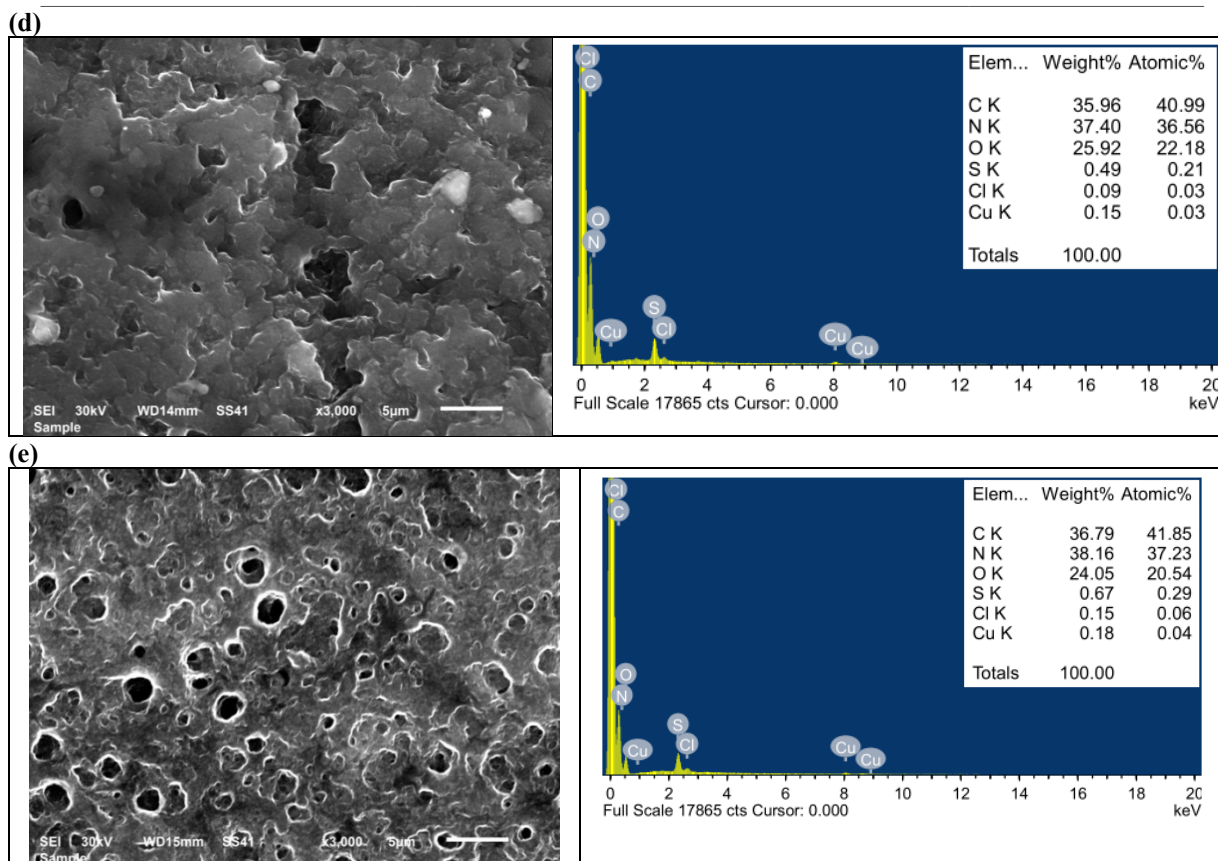


Fig. 3: SEM images of (a) PANI, (b) PANI/PVA, as well as PANI/PVA/Cu bionanocomposite hydrogels containing different concentrations of Cu-NPs, c) 0.1, d) 0.15, and e) 0.2 and their corresponding EDX data

3.4. FTIR Spectroscopy

Figure 4 represents the FTIR spectra of synthesized Cu-NPs, PANI, PANI/PVA hydrogel, as well as PANI/PVA/Cu bionanocomposite hydrogels containing different concentrations of Cu-NPs (0.10, 0.15, and 0.20). PANI powder has characteristic peaks at around 3447 cm^{-1} due to the free and hydrogen bonded N-H stretching vibrations of amino group. It showed also peaks at 1565 cm^{-1} and 1472 cm^{-1} corresponding to quinonoid and benzenoid ring-stretching vibrations beside a peak at 1294 cm^{-1} for N-H bending and at 1241 cm^{-1} for asymmetric C-N stretching vibrations of a secondary aromatic amine, a very strong peak at 1096 cm^{-1} attributed to B-NH⁺=Q stretching vibrations indicating the presence of the conductive emeraldine salt form of polyaniline, which also can be assigned to a strong inter-chain NH⁺...N hydrogen bonding. The peaks around 877 cm^{-1} and 793 cm^{-1} are assigned to out-of-plane and in-plane aromatic C-H ring bending vibrations and C-Cl stretching vibrations.

For the PANI/PVA hydrogel as well as PANI/PVA/Cu bionanocomposite hydrogels containing different concentrations of Cu-NPs, the peak of free N-H stretching vibrations of amino group is blue shifted which indicates interaction of amino group in PANI with PVA. The peak at 1140 cm^{-1}

corresponds to C-O stretching of PVA, 2921 cm^{-1} corresponds to C-H in the PVA structure [27]. For the prepared nanoparticles, the peaks at 3450 , 1705 , 1620 , 1360 , 1319 cm^{-1} are related to dehydroascorbic acid resulting from transformation of ascorbic acid during reduction process [25].

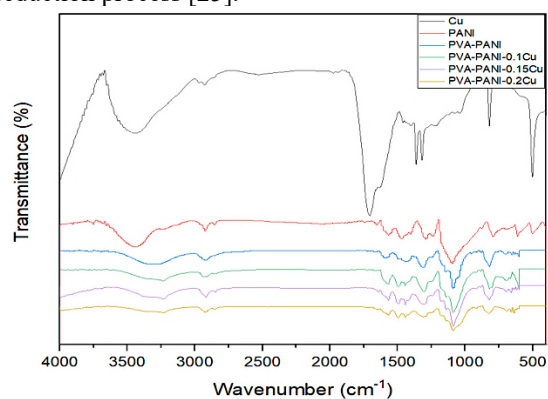


Fig. 4: FTIR spectra of synthesized Cu and CuCl nanoparticles, PANI, PANI/PVA hydrogel, as well as PANI/PVA/Cu bionanocomposite hydrogels containing different concentrations of Cu-NPs

3.5. UV-Visible Spectroscopy

UV-Vis absorption spectra of sensitized Cu nanoparticles, PANI, PANI/PVA hydrogel, as well as PANI/PVA/Cu bionanocomposite hydrogels containing different concentrations of Cu-NPs are

provided in (Fig. 5). Figure 5 displays, copper nanoparticles have absorption band at around 476 nm which is in accordance with the literature data reported for the copper nanoparticles (Jing Xiong et al. 2011) indicating the presence of small separated Cu-NPs. The plasmon peak of small particle size CuNPs has higher energies and shorter wavelength. Another absorption peak is observed at 396 nm corresponding to CuCl nanoparticles. PANI has absorption band at 346 nm corresponds to the $\pi-\pi^*$ transition of the benzenoid units of PANI, another band located at 376 nm is attributed to the transition of localized polarons and characterizing the protonated PANI, a weak peak at 540 nm represents the excitation absorption of the quinoid rings ($n-\pi^*$ of N-Q-N). For the PANI/PVA hydrogel, PVA exhibits one absorption peak at 245 nm, the $\pi-\pi^*$ transition of the benzenoid units of PANI, the transition of localized polarons, and the excitation absorption of the quinoid rings are red shifted as compared to PANI at approximately 477 nm, 524 nm, 915 nm, respectively. After adding Cu-NPs and CuCl NPs, a blue shift occurs in the $\pi-\pi^*$ transition of the benzenoid units and the excitation absorption of the quinoid rings as compared to PANI/PVA hydrogel at approximately 460 nm, 810 nm, respectively. Also, the intensity of the peak at around 460 nm increases due to the surface plasmon resonance of Cu-NPs, and extra beak appears at around 396 nm related to CuCl NPs.

3.6. Electrical Conductivity

PANI is a conjugated polymer and responsible for conductivity, as shown in (Table 2) the addition of PVA decreased the conductivity of PANI also the conductivity of the bionanocomposite hydrogels shows very small increased with the increase in the concentration of Cu-NPs.

This behavior was relatively unexpected, but it may be due to the possible partial distortion of the conjugation in PANI matrix after incorporation of Cu-NPs. This may lead consequently to hinder the π -electrons delocalization. The results of electric conductivity of PVA, PANI, PANI/PVA hydrogel, and PVA/PANI/Cu bionanocomposites with different concentrations of Cu-NPs are shown in (Table 2).

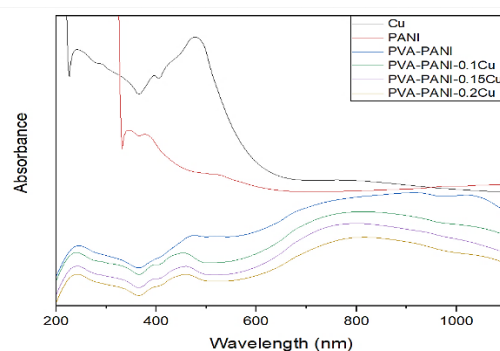


Fig. 5: UV-Visible spectra of synthesized Cu and CuCl nanoparticles, PANI, PANI/PVA hydrogel, as well as PANI/PVA/Cu bionanocomposite hydrogels containing different concentrations of Cu-NPs

Table 2: Electric conductivity of PVA, PANI, PANI/PVA, and PVA/PANI/Cu bionanocomposites with different concentrations of Cu-NPs

Sample	Conductivity (Scm^{-1})
PVA	4.34E-11
PANI	3.72E-04
PANI/PVA	1.36E-08
PANI/PVA-0.10 Cu	4.31E-07
PANI/PVA-0.15 Cu	7.46E-06
PANI/PVA-0.20 Cu	8.76E-06

3.7. Swelling Measurements

Swelling measurements were applied to evaluate the effect of Cu nanoparticles content on swelling % as shown in (Fig. 6). The presence of Cu nanoparticles leads to the decrease of swelling % and by increasing the concentration of it (0.10, 0.15, 0.20 %) the swelling properties of PANI/PVA/Cu nanocomposite hydrogel decreased. This decrease may be because the space in hydrogel's pores is occupied by Cu nanoparticles which also unable to absorb water molecules. However, PANI/PVA hydrogel and PVA/PANI/Cu bionanocomposite hydrogels both have good swelling properties.

3.8. Physical appearance

Figure 7 depicts the appearance of PANI, PVA, PANI/PVA hydrogel, and PVA/PANI/Cu bionanocomposites. From the photographs, PVA film is transparent while PANI, PANI/PVA hydrogel, PANI/PVA/Cu bionanocomposite hydrogel appear dark green in color, thus formation of PANI is clearly observed in hydrogels.

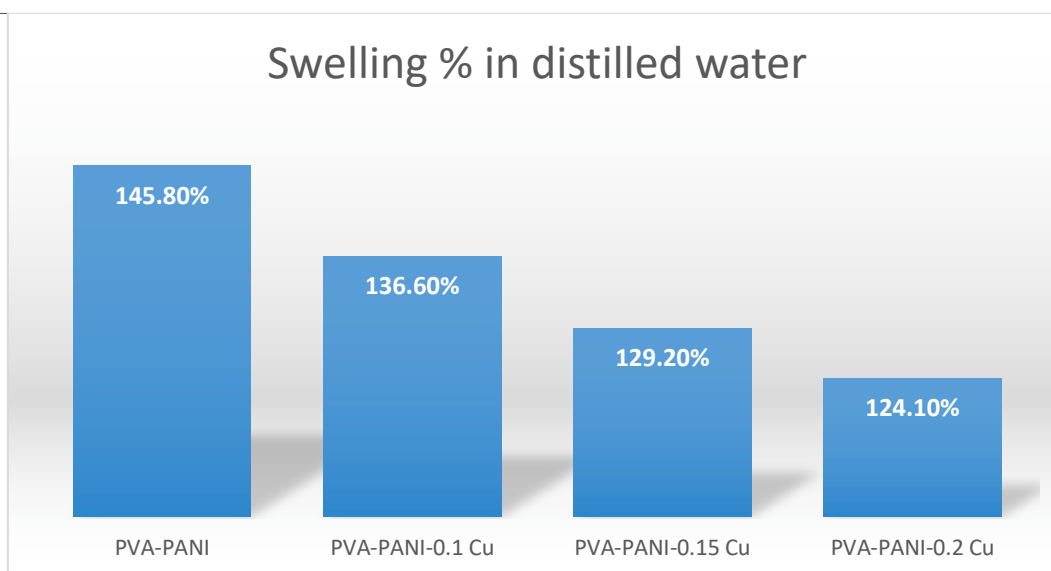


Fig. 6: Effect of Cu nanoparticles content on swelling %

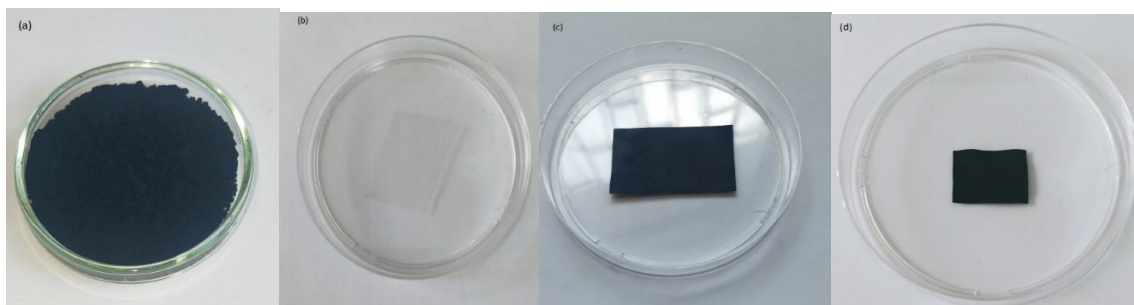


Fig. 7: Physical appearance of (a) PANI (b) PVA (c) PANI/PVA (d) PANI/PVA/Cu bionanocomposites

4. Conclusion

PANI, PANI- PVA hydrogel, and PANI/PVA/Cu bionanocomposite hydrogels with different concentrations of nanoparticles have been prepared using simple and nontoxic method. PVA and nanoparticles were blended with PANI in order to improve the processability in aqueous solvents, solubility and electrical conductivity. Polymerization of aniline hydrochloride in aqueous PVA solution has produced uniform, compatible and crosslinked conductive hydrogels. By using FTIR and UV/Vis spectroscopy, the chemical structures of the produced PANI, PANI/PVA hydrogel, and PANI/PVA/Cu bionanocomposite hydrogels have been confirmed. UV and XRD data show that the synthesized nanoparticles are a mixture of metallic Cu and CuCl. According to XRD and TEM analysis, the average particle size of nanoparticles estimated from the major diffraction peaks using Debye-Scherrer equation is about 43.2 nm. The presence of Cu and CuCl nanoparticles in the hydrogels was confirmed by SEM, EDX, UV, FTIR analysis. The resultant nanocomposite hydrogels were found to have porous morphology. The electrical conductivity shows very small increased with the increase in the concentration

of Cu and CuCl NPs. Finally, the swelling experiments performed in distilled water for the prepared hydrogels of different compositions revealed that all hydrogels show good swelling properties, however, the Swelling % decreased by increasing nanoparticles concentration.

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