Advanced X-ray shielding and antibacterial smart multipurpose fabric impregnated with polygonal shaped bismuth oxide nanoparticles in carbon nanotubes via green synthesis

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ABSTRACT
Synthesis of multifunctional hybrid materials for X-rays’ attenuation is attracting more recognition recently because of several superiorities over the conventional radiation shielding materials made using toxic lead-based compounds. For the first time, the present study investigates the microwave irradiation based green synthesis and in-situ stabilization of bismuth oxide (Bi₂O₃) nanoparticles on multiwalled carbon nanotubes (MWCNT) by a novel approach for making advanced material. TEM and XRD studies have shown that nanoparticles have a uniform size with polygonal morphology and are impregnated on MWCNT. The developed hybrid nanocomposite’s physical appearance is gel-like. It was then applied on a cotton fabric piece to create a multifunctional material and valuable for the fabrications of aprons, bandages, and X-ray shielding caskets. The porous nature of cotton fabric has facilitated the adhesion and stabilization of the nanocomposite. The elemental composition and topology of the hybrid material were further analyzed by XPS, EDX and AFM studies, respectively. The higher attenuation characteristics and shielding efficiency of the developed material are due to the dual shielding effect of polygonal nanoparticles and MWCNT. Availability of metal atoms with higher valency allowed the higher photoelectric effect followed by the Compton effect during X-ray shielding.

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1. Introduction
X-rays find extensive applications in diagnostic and therapeutic medicine. Some of the typical diagnostic applications include diagnostic radiology, CT scan imaging, microscopy, and fluoroscopy. However, X-rays are associated with severe health concerns. Their ionizing behavior can damage growing cells, induce tumors, alter DNA and result in gene mutations. It has been observed that frequent or prolonged exposure to these radiations, especially by the individuals who handle the X-ray instruments, may get momentary or permanent health disorders (1).

The adverse radiation effects may be minimized by attenuating the X-ray radiation energy to ~60–100 kVp (peak kilovoltage) before they reach the human body (2). Hence, attempts are made to develop shielding materials or equipment that can attenuate X-ray radiation energy. Nanostructured materials are appropriate for radiation shielding purposes because they provide a wide surface area distribution, which causes X-ray radiation to dissipate at a faster rate. Some of the nanostructures include nanofibers, nanoribbons, quantum dots and nanotubes. Among the above, nanotubes have gained much attention in the last decade. Carbon
nanotubes (CNT) are of extensive interest in X-ray shielding applications in recent years \( (3–5) \). CNT are categorized into two types, namely, single-walled CNT (SWCNT) and multiple-walled CNT (MWCNT). The SWCNT exhibits a monolayered structure, while the MWCNT exhibits multiple layers of nanotubes. Since SWCNT have only a single wall, they are inefficient to dissipate the X-ray radiation energy compared to MWCNT. The presence of numerous layers enhances the interaction between the radiation and MWCNT, thereby increasing the radiation’s scattering, which leads to faster energy attenuation. Secondly, being lighter in weight, the MWCNT accelerates the quicker dissipation of X-rays. Further, these carbon nanostructures’ shielding performance can be enhanced when incorporated with the salts of heavy metals like zinc, bismuth, iron, cerium, thallium, americium, gadolinium etc. \( (6,7) \). These metals have several free electrons in their outer shells, which increases the probability of Compton scattering of X-ray photons from the surface of the shielding materials \( (8) \). Since carbon atoms are present in a sp2 hybridized state in a planar form in the nanotubes, they make weak Van der Waals interaction with their neighboring nanotube structures current in the same plane. However, \( r \) orbitals form stronger bonds with metals through a perpendicular plane to the CNT axis \( (9,10) \). Aghaz et al. \( (11) \) have reported that the nanoparticle-based composites exhibited better shielding as compared to the micro particle-based composites at higher energy levels (>80 keV) \( (11) \). In a recent study, Mahmoudian et al. \( (12) \) have reported that the cerium-oxide and CNT-based composites exhibited synergistic effects against X-ray radiations in diagnostic applications \( (12) \).

Recently, lead (Pb) has been widely utilized to develop aprons and other protective equipment for doctors, patients, and operators. Unfortunately, lead aprons are relatively heavy (>11 pounds) and hence are difficult to handle. Also, the aprons undergo cracks and bend easily, which makes the lead-based aprons less durable. Considering these disadvantages, in recent times, lead-polymer composites have been proposed as shielding materials. Hosseini and co-workers \( (13) \) reported that lead-polypropylene composite that contained 40% of lead could attenuate ∼80% of the X-rays \( (13) \). Unfortunately, lead is highly toxic and a known carcinogen. Due to this reason, bismuth salts and oxides have been proposed as a safer and lighter alternative to lead \( (14–23) \). Bismuth oxide nanoparticles have been used to coat textile surfaces. It makes the fabric more durable. Electrospun bismuth oxide/polyactic acid nanofiber mats have been prepared by Azmanab et al. \( (24) \). The developed mats showed good X-ray attenuation properties. In short, bismuth oxide-based nanocomposites have been used to establish high-energy radiation shielding materials. Maghrabi et al. \( (25) \) reported that bismuth oxides could be used for the textile coatings, making the fabric more durable and efficiently attenuating the x-ray radiations \( (25) \).

Further, carbon nanotubes (CNTs) and bismuth oxide nanoparticles individually are good antibacterial agents as they suppress bacteria’s growth, as reported by a few researchers. Ahmed A and co-workers investigated a review on antimicrobial properties of carbon nanostructures \( (26) \). Abeer A. et al. \( (36) \) reported the determination of the antimicrobial activity of Bi2O3 nanospheres against multi-drug resistant pathogenic bacteria. Y-Rene Hernandez-Delgadillo et al. \( (28) \) reported bismuth oxide aqueous colloidal nanoparticles to inhibit *Candida albicans* growth and biofilm formation \( (27,28) \).

Considering this, the current study’s objective is to develop radiation shielding nanocomposite materials of CNT and bismuth oxide. For this purpose, an *in-situ* method for synthesizing bismuth oxide and MWCNT based nanocomposite has been proposed. The modified microwave oven reactor was used for developing the product. The use of microwave synthesis, which is considered the potential tool for green chemistry, is used in the reported work. Microwave-irradiated chemical reactions processing is attractive, which includes less pollution, cost-effective and high yields product generation. It is easy to handle and process. During the chemical processing, the particle collisions are accelerated, due to which the sample dispersed as well-crystallized properly. This reduces the reaction time for the synthesis of the product. The developed nanocomposite was coated over a textile cloth to prepare advanced X-ray radiation shielding garments. The spacing between the molecular structure of nanocomposite coated textile and its X-ray radiation shielding attenuation properties were characterized by X-ray diffraction (XRD) studies. The textile’s structural patterns, binding states, and elemental composition were confirmed through X-ray Photoelectron Spectroscopy (XPS) and Energy Dispersive X-Ray Analysis (EDX). Scanning Electron Microscopy (SEM) was used to study the surface topography of textiles. The disc diffusion assay was performed to obtain information about their antibacterial property against gram-positive bacteria (*Lactobacillus planatarum, Enteroxoccus faecalis)*.

### 2. Materials and methods

#### 2.1. Materials

MWCNT (>95% in purity, 20–25 μm in length) were utilized from NanosolutionCo., Korea. The reagent hexamethylenetetramine (C6H12N4HMTA) was procured from...
Rankem, polyethylene glycol (PEG), cytosine, sodium hydroxide (NaOH), tinopal and bismuth nitrate pentahydrate were procured commercially from companies namely Sigma-Aldrich, Himedia and Merck, respectively. 1M Nitric acid (HNO₃) was used with double distilled water (DDW) to dissolve bismuth nitrate. All these chemicals were used as received. 0.5 mm thick cotton bandage was procured from the local market of Bhopal, Madhya Pradesh, India.

2.2. Methods

2.2.1. Preparation of solutions

Cytosine solution: 0.5 M cytosine solution was prepared by dissolving 1.6 g of cytosine to 30 ml of distilled water. Solution-A: Solution A was prepared by dissolving 15 g of HMTA in 20 ml of water. The pH of the solution had a pH of 9.5.

NaOH solution: 1M NaOH solution was prepared by dissolving 4 g NaOH pellets to 100 mL distilled water. Solution-B: Initially,20 ml of PEG and 30 ml of cytosine solution were mixed. 5 g of citric acid was then dissolved in the PEG-cytosine solution. 100 mL of NaOH solution was mixed to the resulting PEG-cytosine-citric acid solution under constant stirring to form solution-B.

HMTA solution: 18.5 g of HMTA was dissolved in 25 mL water.

2.2.2. Synthesis of the jelly-like nanocomposite material

36.3 g of Bi(NO₃)₃.5H₂O was dissolved in HNO₃ (150 mL of 0.5 M) to form a clear solution. To the resulting solution, 5 g of MWCNT were added. The suspension was then homogenized in a bath ultrasonicator (Product code: MUB-33; Metrex Scientific Instruments Pvt. Ltd.) for 3.5 h. Then, 35 g of solution-A was added dropwise to this suspension, kept at room temperature, under constant stirring on a magnetic stirrer at 500 rpm. Further, solution-B was added to the resulting suspension that led to the material formation with a jelly-like texture. It was then irradiated in a modified microwave oven reactor (model: Sineo Wave 100s0 with rotating tray), operated at 300 W for 10 min to complete the gelification process. Finally, the bismuth oxide-incorporated MWCNT (BOCNT) nanocomposite material was obtained in the form of a gel.

2.2.3. Preparation of bismuth oxide impregnated MWCNT based bandage (BOCNT-impregnated fabric)

A 0.5 mm thick cotton fabric of 240 cm length and 10 cm width was thoroughly washed with distilled water and sun-dried. Then, it was rubbed mechanically using a fine metal brush on both sides. Consequently, naps were formed on both sides over the spun yarns. The jelly-like nanocomposite material (500 g) obtained in section 2.2.2 was then manually spread on the fabric using a brush. After that, the coated fabric was treated with HMTA solution (25 mL), which was used as a fixing agent to coat the material. This was followed by the treatment with tinopal solution (10 mL) to prevent the fabric’s discoloration. Subsequently, the textile was compressed using a heavyweight iron roller (length:17 cm; diameter: 12 cm), which helped in the adhesion of the BOCNT to the fabric. The fabric was then folded, and the compression process was done two more times. The BOCNT-impregnated fabric was then air-dried. This resulted in the formation of the radiation shielding bandage (length: 60 cm, width: 10 cm, and thickness: 5 mm).

2.3. Characterization of BOCNT-based bandage

2.3.1. X-ray radiation shielding attenuation properties

The X-ray radiation shielding attenuation properties of the developed shielding bandage were studied using Nomex Multimeter from PTW, the Dosimetry Company. The readings were taken with X-ray photons of energies 50–80 kVp. The X-ray machine used for testing was a DX 525–500 mA, 125 kVp X-ray machines of Wipro GE make.

2.3.2. X-ray diffraction studies

XRD studies were conducted to identify the various phases present in MWCNT and the developed dry gel sample. This was performed by using Cu Kα radiation obtained from the D8 advance X-ray diffractometer. The X-ray diffraction intensity was recorded as a function of Bragg’s 2θ in the angular range of 5°–70°.

2.3.3. X-ray photon studies

To quantify the elemental composition and chemical states in the developed sample, X-ray photoelectron spectroscopy (XPS) was performed. The acquisition parameters were total time 25.2 sec, the total number of scans, source gun-type Al Kα (Monochromatic) with 6 mA beam current and 12 kV, spot size 400 µm, lens mode standard CAE: Pass Energy 100.0, Analyser Mode Ev Energy Step Size 1,000 Ev and number of energy steps 1261 respectively.

2.3.4. Transmission Electron Microscopy

TEM of the developed dry gel sample was performed using the standard method. 4 ml of sample suspension in water was pipetted gently on to a formvar coated copper grid and was allowed to evaporate at room
temperature. Sample analysis was done under FEI Tecnai G2sprit twin transmission electron microscope armed with Gatan digital CCD camera (Netherlands) operated at 80kv.

### 2.3.5. Scanning electron microscopy

The untreated bandage and the developed smart multi-functional bandage were examined using a JEOL model JEM-35-CF scanning electron microscope. These samples were first seated on aluminium stubs with the help of carbon tape. They later were kept for coating with a thin layer of platinum to prevent charging before taking the microphotographs.

### 2.3.6. Atomic force microscopy

An atomic force microscope (AFM) NOVA Px instrument was used to study the surface topographical information about the developed dry gel sample in the air at room temperature. The tips were made up of silicon and mounted on a cantilever with a spring constant of ca 7.4 N m⁻¹ and a scanning range of 0.4 Hz. Scanning was carried out at the free cantilever oscillation frequency and different amplitudes, depending on the stability and contrast obtained. For the confirmation that the microscope was operating in intermittent contact mode, the amplitude was fixed higher than 90 nm. The setpoint was confirmed at 10–30% of the free oscillation. The sample for AFM analysis was prepared by making a film using a spin coater. A drop of the sample was treated for 90 s at 2000 rpm in the spin coater and kept drying in the air. It was then fixed on the double-sided adhesive bandage.

### 2.3.7. Viscosity

The viscosity of the developed gel was measured in brookfield, DV-II, Viscometer using spindle no. 4 at 50 rpm.

### 2.3.8. Antibacterial studies

A modified disc diffusion assay was used to study the antibacterial activity of developed dried gel against gram-positive bacteria. *Lactobacillus planatarum* (MTCC 1325) and *Enterococcus faecalis* (MTCC 439 and MTCC 7345) were procured from Microbial type culture collection (MTCC), Institute of Microbial Technology (IMTECH), Chandigarh, India. Muller Hilton agar plates were swabbed with the respective broth culture of organisms. The bacterial culture was diluted to 0.5 McFarland Standard with saline and kept for 15 min for absorption. Sterile filtered paper discs (Whatman no. 1, 6 mm in diameter) were impregnated with 100 µl of each diluted gel (10 mg/ml) to give a final concentration of 1 mg/disc. The discs were pre-dried and then placed on the seeded agar plates. Each disc was tested in triplicate with streptomycin in DMSO (1 mg/disc) as standard for bacteria and was kept for 1 h at 4°C for the diffusion of a compound. It was then incubated at 37°C for 24–48 h. The antibacterial screening was evaluated after the incubation by measuring the inhibition zone (mm) around the disc.

### 3. Results and discussion

Huda Ahmed Maghrabi et al. (25), investigated the use of bismuth oxide (Bi₂O₃) coating for textiles and can be used as a good substitute for toxic lead-based materials. A clear comparison with all main characteristics chemical/physical vs commercial showing advantages over the new approach has been shown in Table 1 below.

#### 3.1. Nature, density and viscosity of the tailored material

The developed advanced black colored jelly material was alkaline with pH 11. The density and viscosity of the material were evaluated using the standard...
methods. A capillary tube was used to measure the material’s transverse through the Ostwald Viscometry technique. The developed tailored material density was found to be 3.5 g/cm³ and viscosity was found to be 88.5 cP (centipoise) at 50 rpm and 27.5°C, respectively.

3.2. X-ray diffraction studies

Identifying various phases present in MWCNTs and the developed dried gel sample was studied using JCPDS standard XRD data files. The 2θ angle and intensities of the peaks obtained were compared with those of the respective likely substances (29) and are depicted in Figure 1. The characteristic peaks for MWCNTat 25.9° and 43.2°2θ were seen (30,31). The XRD pattern of Bi₂O₃–MWCNT nanocomposite also exhibits identical peaks at the same 2θ with similar intensities as alpha-Bi₂O₃ nanoparticles (PDF # 140699). Thus, the synthesized Bi₂O₃ nanoparticles in this work have a monoclinic symmetry with a space group of P 21/c (14). The sample also contains other bismuth-sodium-based crystalline phases. This confirms the presence of Bi₂O₃ nanoparticles along with MWCNT in the developed organic–inorganic hybrid nanocomposite.

3.3. X-ray photoelectron studies

XPS measurements were performed to determine the elemental composition and binding states of bismuth oxide in the developed material. Figure 2(a) presents the XPS spectra of the Bi 4f region of the nanocomposite showing the formation of two firm peaks at 159 and 165 eV, which can be assigned to Bi 4f7 and Bi 4f5, respectively. It indicates the bismuth ion’s trivalency state (Bi³⁺) in Bi–O bonds corresponding to Bi₂O₃, which is in good agreement with the database (32,33). Figure 2(c) shows the spectrum corresponding to the O1s region with two peaks at 532 and 535 eV, which is attributed to the Bi–O bond, confirming the formation of Bi₂O₃. An intense C1s peak located around 284 eV resulted from sp² hybridized graphitic carbon present in MWCNT. The Na1s spectrum for this composite appears as two peaks at 1072.5 and 1074 eV. Figure 3(e) clearly shows that the developed composites majorly consist of Bi, C, N, O and a minor Na in the nanocomposite.

3.4. Transmission electron microscopy

The dried gel was examined by TEM, and the images at 30000X magnification at three different places of the developed nanocomposite are shown in Figure 3(a–c), respectively. The microscopy reveals a unique hybrid organic–inorganic morphology possessing nano-sized bismuth oxide nanoparticles with unusual, irregular blob-like morphology on the surface of MWCNT. The long, convoluted MWCNT are seen along with the unique morphology of bismite nanoparticles. One of the irregular blob-like shapes is 44.83 nm, as depicted in Figure 3(a). The figure also seems to be nanoparticles are present in the polygonal bunch, which are densely firmly and tunefully impregnated on the surface of MWCNT. The TEM microphotograph reflects the honeycomb structures identical appearance with polygonal morphology with spherical cell structures inside, holding and hanging down from a tree’s stem. This unique hybrid organic–inorganic material containing MWCNT impregnated with desirable high-density nano metal oxide possesses a polygonal morphology. The dual shielding effect is obtained using multiple scattering morphology when the radiations fall on this distinctive structure.
3.5. Scanning electron microscopy

The surface of the pure cotton bandage and the developed smart multifunctional bandage were examined using SEM, and the images were shown in Figure 4. The SEM image of the pure cotton fiber at 85X magnification depicts very smooth and ribbon-like threads (Figure 4(a–c)). The fibers’ distinct uncoated/untreated surface is seen along with tiny spaces between the fibers (34). These spaces allow the jelly material to percolate easily into the fabric and impregnate the fabric’s nanocomposite. Thus, it helps provide high mechanical strength and the X-ray shielding capabilities in the developed intelligent multifunctional bandage (35).

The proper impregnation of the developed jelly material on the cotton fabrics surface was confirmed by visualizing the coated fabric. The SEM of developed BOCNT-impregnated fabric/bandage shown in Figure 4(d–f) were investigated to study morphology and the adherence between cotton fiber and the developed jelly material. The SEM micrographs confirm an excellent dispersion of gel on the cotton fiber. At higher magnification (Figure 4(f)), it can be envisaged that the developed gel has been appropriately adsorbed on the fiber and formed a durable adhesion, thereby imparting higher strength and radiation shielding characteristics in the developed smart BOCNT-impregnated fabric/bandage. Also, as the developed jelly material is alkaline consists of a nano-sized structure with polygonal morphology, a strong chemical bonding between (-OH) group of the cellulosic component in the cotton fiber and the gel during the formation of smart multifunctional bandage.

3.6. Atomic force microscopy (AFM)

The AFM images for the study of surface morphology of developed dried gelly sample was also performed. The typical 2d and 3d AFM images in three scanning areas were 3 µm x 3 µm, 1 µm x 1 µm and 200 nm x 200 nm respectively, and shown in Figure 5. The topographical images showed small grain-like structures in the sample, which predominantly indicates the Bi$_2$O$_3$ nanoparticles and MWCNT in the developed BOCNT nanocomposite. AFM studies also confirm the formation of nanoparticles in the developed sample. The results of AFM studies complement and supporting TEM.
Radiation attenuation characteristics of the developed smart multifunctional bandage were studied by exposing 50–80 kVp of X-ray energy for 200 ms time at 100 mA, respectively. Three different samples, namely control or untreated bandage (sample A), treated bandage with MWCNT (sample B) and the BOCNT coated bandage (sample C), were tested and compared for their respective attenuation characteristics (Figure 6 (a)). The attenuation percentage is inversely proportional to transmitted X-rays or unabsorbed X-rays through the sample. The lower the transmittance value, the higher is the X-ray absorption, indicating the higher radiation shielding attenuation characteristics. Sample A showed negligible radiation shielding effect, whereas sample B and C showed sufficient radiation attenuation from 50 to 80 kVp. The results depict the lesser radiation attenuation characteristics in sample B, which majorly consists of MWCNT. On the other hand, sample C showed higher and better radiation attenuation characteristics due to the presence of polygonal Bi$_2$O$_3$ nanoparticles impregnated MWCNT in the developed sample and are responsible for radiation shielding characteristics. This confirms the impregnation of Bi$_2$O$_3$ nanoparticles on MWCNT, further enhancing the developed sample’s radiation shielding property.

To understand the effect of concentration of Bi$_2$O$_3$ nanoparticles, another experiment was performed by developing samples with different percentage of bismuth source, i.e. 70, 75 and 80 w%, by keeping other chemical constituents and process parameters constant. The results of these three different materials are shown in Figure 6(b), which indicate that the increase in the concentration of Bi$_2$O$_3$ nanoparticles enhances the X-ray shielding nature of the material irrespective of the type of (different energized) X-rays. This

Figure 3. (a),(b) and (c)TEM of the developed BOCNT nanocomposite at different places of the developed nanocomposite.
attributes to the fact that higher polygonal bismuth oxide nanoparticles impregnated in MWCNT yield multiple scattering of X-rays. The presence of more polygonal nanoparticles facilitates more scattering structural phases and thus helps enhance the dissipation of X-ray radiation energy and thereby increased the shielding effect of the developed material.

Being flexible and moldable in nature, the developed smart bandage can be easily folded and conveniently used. With the increase in the fold, the thickness of the developed bandage also increases. The amount of X-ray radiation that can zestfully cross the material indicates the efficiency of the material. The crossing of X-rays through the material is inverse of its capability to attenuate the X-rays, which also depends on X-ray photons’ energy and physical dimensions. Thus, the thickness of the material is also a crucial parameter and plays a significant role during the fabrication of radiation shielding materials. Another set of radiation attenuation study was performed by increasing the number of layers of radiation shielding bandage C from one to five folds. The single-layered bandage showed relatively lesser attenuation from 50 to 80%, but it increases with the number of layers (Figure 6(c)). This is attributed to the fact that with the increase in layers, there will be an increase in the number of bismuth oxide nanoparticles in MWCNT. This kind of arrangement is responsible for imparting shielding characteristics in the developed bandage.

Based on the attenuation characteristics (Figure 6), it is concluded that the untreated bandage showed negligible attenuation of X-rays against the treated bandage with MWCNT which showed less shielding attenuation property, and BOCNT treated bandage showed maximum attenuation properties. Though the metal oxide and MWCNT are individually known for their X-ray radiation shielding properties, they complemented each other and provided a greatly enhanced dual shielding effect. Thus, the dual shielding effect can be obtained using multiple scattering morphology by designing these hybrid organic–inorganic materials containing MWCNT impregnated with desirable high-density nano metal oxides possessing a polygonal morphology. The shielding efficiency of

![Figure 4. SEM of (a-c) uncoated cotton fibers and (d-f) coated fibers.](image-url)
hybrid organic–inorganic materials containing MWCNT and desired metal oxides can be further augmented by developing morphologies of these materials capable of providing multiple scattering necessary for shielding by a dual mechanism. The use of hybrid materials also reduces the shielding material’s weight because of the effective reduction of inorganic metal content. Thus, the dual mechanism in the developed novel lightweight radiation shielding bandage enhances the photoelectric effect many times and increases the complementary effect of absorption limits. This may be attributed to the multiple scattering of X-rays that pass through the polygonal bismuth oxide nanoparticles, which were uniquely attached to the cylindrical CNT walls. X-rays consist of photons of both low and moderate energy. When they incident upon the developed material, the shielding mechanism primarily occurs due to photoelectric and Compton scattering effects. The more significant the number of free electrons in the outer shells of the atoms of the shielding material, the greater the probability of the Compton effect and hence more helpful is the shielding capability of the material. The shielding mechanism of the material was schematically depicted in Figure 7 below.

This hypothesis for shielding mechanism wherein multi-elementally and nano morphologically designed MWCNT-based hybrid organic–inorganic material provides higher attenuation of X-rays. The chemistry behind the formation of higher X-ray shielding by the organic–inorganic hybrid material is explained below.
Figure 6. (a) The radiation attenuation characteristics of Untreated bandage, Treated bandage with carbon nanotubes, Lightweight radiation shielding bandage at different kVp of energy. The purple label corresponds to the composite containing both MWCNT and Bi$_2$O$_3$. (b) Radiation attenuation characteristics of the developed material with an increased percentage (70, 75 and 80%) of bismuth oxide nanoparticles in the developed smart bandage (c) % attenuation characteristics of radiation shielding bandage C at a different thickness.

Figure 7. Schematic sketch of X-ray shielding mechanism in the developed bandage.
3.8. Probable mechanism for the formation of the nanocomposite

Based on the above obtained experimental results, a probable mechanism for the formation of smart multifunctional lightweight bismuth oxide impregnated MWCNT based bandage for X-ray radiation shielding and antibacterial applications can be expressed as follows:

At the initial stage of reaction, i.e. at Time $T = 0$, the chemical reaction is less vigorous. Bismuth nitrate pentahydrate, when dissolved in the water, produces bismuth (III) dihydroxonitrate and nitric acid, followed by the development of Bi(OH)$_3$, which is essential for the growth of BiO crystallites. Thus, at the beginning of the chemical processing, it functioned as the foundation blocks for final products' formation according to the chemical reaction (equation i).

\[
\text{Bi(NO}_3\text{)}_3 \cdot 5\text{H}_2\text{O} + 2\text{H}_2\text{O} \rightarrow \text{Bi(OH)}_2\text{NO}_3 + 2\text{HNO}_3 \rightarrow \\
\text{Bi(OH)}_3 + 2\text{H}_2\text{O} + 3\text{HNO}_3 \rightarrow \\
\text{Bi}^{3+}(\text{aq.}) + 4\text{NO}^{3-} + 5\text{H}_2\text{O} \\
(i)
\]

Further, at appropriate heating, Bi(OH)$_3$ leads to the formation of Bi$_2$O$_3$ crystallites. In the aqueous acidic solution, the formed bismuth ions are readily hydrolyzed to form bismuth hydroxide, as reported in the literature. Thus, so-formed nitrate ions decompose into nitrogen dioxide and oxygen gas during the dehydration process, as mentioned in the literature.

Then, MWCNT were added to the above solution and kept for ultrasonication.

\[
\text{Bi}^{3+}(\text{aq.}) + 4\text{NO}^{3-} + 5\text{H}_2\text{O} + \text{MWCNT}
\]

To the above solution, HMTA C$_6$H$_{12}$N$_4$ was added dropwise along with continuous stirring and heating. During the chemical reaction, HMTA plays a dual role; first, it hydrolyzed and produced OH$^-$ ions (as at increased temperature HMTA hydrolyses in the distilled water and generates the OH$^-$ ions) as shown in chemical reaction (ii) mentioned below. Secondly, HMTA serves as an effective additive for controlling the morphology of the nanostructures.

\[
\text{C}_6\text{H}_{12}\text{N}_4 + \text{H}_2\text{O} \rightarrow 6\text{H}_2\text{CO} + 4\text{NH}_3 \\
(ii)
\]

Thus, the probable chemical reactions (iii) become

\[
\text{Bi}^{3+}(\text{aq.}) + 4\text{NO}^{3-} + \text{MWCNT} + 6\text{H}_2\text{CO} + 4\text{NH}_3 + 5\text{H}_2\text{O} \\
\rightarrow \text{Bi}^{3+}(\text{aq.}) + 4\text{NO}^{3-} + 5\text{H}_2\text{O} + \text{MWCNT} + 6\text{H}_2\text{CO} + \text{NH}^{4+} + \text{OH}^- \\
(iii)
\]

Hence, from these chemical equations, it is seen that the step-growth of polygonal morphology of bismite nanoparticles in the presence of MWCNT was followed by the generation of hydroxyl ions from HMTA. The regular supply of Bi$^{3+}$ ions and OH$^-$ ions occurs from the bismuth precursor and HMTA, respectively, followed by Bi(OH)$_2$ units' continuous formation, which later converts into Bi$_2$O$_3$ crystallites and thus finally develops the nanoparticles of Bi$_2$O$_3$ with polygonal nano morphology impregnated in MWCNTs.

Further, into the above chemical reaction, the solution containing sodium hydroxide in polyethylene glycol along with aqueous cytosine and citric acid was added dropwise and finally, the material was heated using microwave irradiation. It is a familiar fact that NaOH is a very strong electrolyte that may help in the neutralization of the surface charges of the Bi$_2$O$_3$ due to the formation of sodium ions from sodium hydroxide and thus affects the aggregation process as well. Therefore, it acts as a vital component for the formation of the polygonal structure of bismite nanoparticles due to electrostatic attraction. Sodium hydroxide and polyethylene glycol, citric acid, and cytosine enhance the reaction system's jelly matrix formation.

However, it has been mentioned that the concentration of OH$^-$ ions affect the nucleation and growth behaviors (i.e. the quantity of the nuclei and the concentrations of growth units, too) of bismuth nanocrystals. Thus, OH$^-$ ions’ formation plays a significant role in deciding and framing advanced material’s morphology. Therefore, selecting and utilizing suitable and appropriate chemicals under specific reaction conditions is crucial to obtain the desired results. The simultaneous use of NaOH and HMTA leads to the intensification of the reaction due to the increase in the availability of OH$^-$ ions’ availability, resulting in a color change. This may be due to Bi(OH)$_2$ nuclei’s instant formation, which later transformed into Bi$_2$O$_3$ via chemical reactions. With the due course of time, the BiO nuclei assembled and formed the polygonal morphology. However, more detailed investigations are still required to obtain absolute confirmation for the formation and growth of the developed material’s unique morphology.

3.9. Determination of antibacterial efficiency

The antibacterial effect of the developed dried gel sample was tested against Lactobacillus plantarum and Enterococcus faecalis (MTCC 439 and MTCC 7345) using the disc diffusion method. The antibacterial activity was tested against selected microorganisms and was studied in terms of the inhibition zone (mm) of the sample. Figure 8(a) depicts the assays’ picture, and 8(b) represents the antibacterial activity of the developed sample on these bacteria, wherein the positive control used was streptomycin. The sample showed suitable antibacterial
property against all the tested bacteria at a 100 µg/ml concentration. The sample is more efficient against Enterococcus faecalis (MTCC 439) with an inhibition zone of 21 mm. On the other hand, the sample showed less and similar antimicrobial nature against Enterococcus faecalis (MTCC 7345) and Lactobacillus plantarum with an inhibition zone of 13 mm. This result agrees with other antibiotics activity done by Abdulkadir et al. (36–38).

The developed material’s effective antibacterial potential may be attributed to bismuth oxide and MWCNT in the produced material. The result reveals that the developed material’s unique morphology has allowed prohibiting these bacteria’s growth. When bacteria have come into contact with the developed material, the latter might have permeated through its cell membrane and effectively suppressed the respective bacteria’s viability. The high surface area to volume ratio of the nanocomposite might have triggered the hybrid material’s strong interaction with the biological systems.

4. Conclusion
In this study, smart multifunctional lightweight bismuth oxide impregnated MWCNT based bandage was developed using the microwave synthesis green process. The developed bandage is antibacterial and capable of attenuating X-ray radiations by an advanced dual mechanism. XRD studies confirmed the in-situ generation of bismite nanoparticles impregnated on MWCNT. The XPS spectra further confirm the presence and bonding of bismuth oxide nanoparticles with MWCNT. The TEM micrographs revealed the presence of polygonal morphology of bismite nanoparticles and their impregnation in MWCNT. The appropriate adhesion of the developed gelly material (BOCNT) on cotton fabrics was illustrated in SEM micrographs. The topographical images by AFM showed grain-like structures in the sample, which predominantly indicate polygonal-shaped Bi₂O₃ nanoparticles along with MWCNT. The detailed attenuation characteristics confirm the importance of in-situ generation of bismite nanoparticles in MWCNT. The antibacterial nature of the developed gel sample was confirmed by testing against Lactobacillus plantarum and Enterococcus faecalis using the disc diffusion method. Thus, the use of developed advanced multifunctional X-ray radiation shielding hybrid bandage possesses a broad application spectrum ranging from attenuating emergency radiation leakages, transport of casks and sealing of complex shielding installations in the public domain such as X-ray scanner, CT scanner rooms, medical equipment in biomedical applications and bunkers of army personnel, nuclear power plants, etc. of strategic nature.

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No potential conflict of interest was reported by the author(s).

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References

[1] Adrian, B.; Risteárd, Ó.L.; Peter, M.; Ronan, M.D. Discrepancy and Error in Radiology: Concepts, Causes and Consequences. *Ulster Med. J.* 2012, 81 (1), 3–9.

[2] Verma, S.; Amritphale, S.S.; Das, S. Properties of a Non-Toxic, Self-Healing X-ray Radiation Shielding Bandage Developed Using the Smart Gel. *Cellulose* 2017, 24 (7), 2939–2951.

[3] Fujimori, T.; Tsuruoka, S.; Fugetsu, B.; Maruyama, S.; Tanioka, A.; Terrones, M.; Dresselhaus, M.; Endo, M.; Kaneko, K. Outstanding X-ray Shielding Effects of Carbon Nanotubes; 2012.

[4] Fujimori, T.; Tsuruoka, S.; Fugetsu, B.; Maruyama, S.; Tanioka, A.; Terrones, M.; Dresselhaus, M.S.; Endo, M.; Kaneko, K. Enhanced X-Ray Shielding Effects of Carbon Nanotubes. *Materials Express* 2011, 1 (4), 273–278. DOI: 10.1166/mex.2011.1043.

[5] Al-Saleh, M.H.; Sundararaj, U. Electromagnetic Interference Shielding Mechanisms of CNT/Polymer Composites. *Carbon* 2009, 47 (7), 1738–1746.

[6] Verma, S.; Amritphale, S.S.; Das, S. Synthesis and Characterization of Advanced Red Mud and MWcnt Based EM Shielding Material via Ceramic Processing. *Materials Sciences and Applications* 2016, 7, 192–201. DOI: 10.4246/msa.2016.74019.

[7] Singh, R.; Kulkarni, S.G. Nanocomposites Based on Transition Metal Oxides in Polypyrrole for EMI Shielding Application. *Polym. Bull.* 2014, 71, 497–513. DOI: 10.1007/s00289-013-0576-7.

[8] Sayyed, M.J.; Akman, F.; Kaçal, M.R.; Kumar, A. Radiation Protective Qualities of Some Selected Lead and Bismuth Salts in the Wide Gamma Energy Region. *Nuclear Engineering and Technology* 2019, 51 (3), 860–866. DOI: 10.1016/j.net.2018.12.018.

[9] Rodriguez-Manzo, J.A.; Janowska, I.; Pham-Huu, C.; Tolvanen, A.; Krasheninnikov, A.V.; Nordlund, K.; Banhart, F. Growth of Single-Walled Carbon Nanotubes from Sharp Metal Tips. *Small (Weinheim an der Bergstrasse, Germany)* 2009, 5 (23), 2710–2715. DOI: 10.1002/smll.200900590.

[10] Banhart, F. Interactions between Metals and Carbon Nanotubes: At the Interface Between old and new Materials. *Nanoscale* 2009, 1 (2), 201–213. DOI: 10.1039/B9NR00127A.

[11] Aghaz, A.; Faghhihi, R.; Mortazavi, S.; Haghparast, A.; Meh dizadeh, S.; Sina, S. Radiation Attenuation Properties of Shields Containing Micro and Nano WO3 in Diagnostic X-ray Energy Range. *International Journal of Radiation Research* 2016, 14 (2), 127.

[12] Zohdiahghdam, R.; Mahmoudian, M.; Salimi, S. Evaluation of Synergistic Effects of the Single Walled Carbon Nanotube and CeO2-Hybrid Based-Nanocomposite Against X-ray Radiation in Diagnostic Radiology. *Radiat. Phys. Chem.* 2020, 168, 108562. DOI: 10.1016/j.radphyschem.2019.108562.

[13] Hosseini, S.H.; Noushin Ezzati, S.; Askari, M. Synthesis, Characterization and X-Ray Shielding Properties of Polypyrrole/Lead Nanocomposites. *Polym. Adv. Technol.* 2015, 26 (6), 561–568. DOI: 10.1002/pat.3486.

[14] Sayyed, M.J.; Akman, F.; Kaçal, M.R.; Kumary, A. Radiation Protective Qualities of Some Selected Lead and Bismuth Salts in the Wide Gamma Energy Region. *Nuclear Engineering and Technology* 2019, 51 (3), 860–866. DOI: 10.1016/j.net.2018.12.018.

[15] Halimah, M.K.; Azuraida, A.; Ishak, M.; Hasnimulyati, L. Influence of Bismuth Oxide on Gamma Radiation Shielding Properties of Boro-Tellurite Glass. *J. Non-Cryst. Solids* 2019, 512, 140–147. DOI: 10.1016/j.jnoncrysol.2019.03.004.

[16] Winter, H.; Brown, A.L.; Goforth, A.M. Bismuth-Based Nano-and Microparticles in X-Ray Contrast, Radiation Therapy, and Radiation Shielding Applications. *Bismuth: Adv. Applications Defects Characterization* 2018, 71. DOI: 10.5772/intechopen.76413.

[17] Yashkina, S.; Dorogovan, V.; Evtushenek, E.; Gavshina, E. O. Phase Changes in Radiation Protection Composite Materials Based on Bismuth Oxide, Sysa (2019) International Congress on Applied Mineralogy ICAM 2019: 14th International Congress for Applied Mineralogy (ICAM2019); 2019, 296–299.

[18] Hamid, S.; Mostafa, S.; Seyed, M.A.; Mehdi, R. Novel Semisolid Design Based on Bismuth Oxide Nanoparticles for Radiation Protection. *Nanomedicine Research Journal* 2017, 2 (4), 230–238. DOI: 10.22034/nrrj.2017.04.004.

[19] Tijani, S.A.; Al-Hadeethi, Y. The use of Isophilic-Bismuth Polymer Composites as Radiation Shielding Barriers in Nuclear Medicine. *Mater. Res. Exp.* 2019, 6, 055323. DOI: 10.1088/2053-1591/ab0578.

[20] Fontainha, C.C.; Baptista Neto, A.T.; Faria, L.O. Radiation shielding with Bi2O3 and ZrO2: Y composites: Preparation and Characterization. *International Nuclear Atlantic Conference - INAC 2015 São Paulo, SP, Brazil*; 2015.

[21] Kang, J.H.; Oh, S.H.; Oh, J.-I.; Kim, S.-H.; Choi, Y.-S.; Hwang, E.-H. Protection Evaluation of non-Lead Radiation-Shielding Fabric: Preliminary Exposure-Dose Study. *Oral. Radiol.* 2019, 35 (3), 224–229. DOI: 10.1007/s11282-018-0338-8.

[22] Rogers, J.L.; Ernat, J.J.; Yung, H.; Mohan, R.S. Environmentally Friendly Organic Synthetic Using Bismuth Compounds. Bismuth(III) Bromide Catalyzed Synthesis of Substituted Tetryhydroquinoline Derivatives. *Catal. Commun.* 2009, 10 (5), 625–626. DOI: 10.1016/j.catcomm.2008.11.004.

[23] Chen, S.; Nambiar, S.; Li, Z.; Osei, E.; Darko, J.; Zheng, W.; Sun, Z.; Liu, P.; Yeow, J. Bismuth Oxide-Based Nanocomposite for High-Energy Electron Radiation Shielding. *J. Mater. Sci.* 2013, 48 (6), 147. DOI: 10.1007/s10853-018-3063-0.

[24] Noor Azman, N.Z.; Siddiqi, S.A.; Haroosh, H.J.; Albetran, H.M.M.; Johannessen, B.; Dong, Y.; Lowa, I.M. Characteristics of X-ray Attenuation in Electrospun Bismuth Oxide / Polylactic Acid Nanofibre-Mats. *J. Synchrotron Radiat.* 2013, 20 (5), 741–748. DOI: 10.1107/S0909049513017871.

[25] Maghrabi, H.A.; Vijayan, A.; Deb, P.; Wang, L. Bismuth Oxide-Coated Fabrics for X-ray Shielding. *Text. Res. J.* 2016, 86 (6), 649–658. DOI: 10.1177/2040451715592809.

[26] Ahmed, A.; Surjith, A.; Kateryna, B.; Mohan, V.J. Review on the antimicrobial Properties of Carbon Nanostructures. *Materials (Basel)* 2017, 10, 1066. DOI: 10.3390/ma10091066.
[27] Savunthari Kirankumar, V.; Sumathi, S. Photocatalytic and Antibacterial Activity of Bismuth and Copper Co-Doped Cobalt Ferrite Nanoparticles. J. Mater. Sci.: Mater. Electron. 2018, 29, 8738–8746. DOI: 10.1007/s10854-018-8890-x.

[28] Cabral-Romero, C.; Hernandez-Delgadillo, R.; Arias, V.; Sanmiguel, M.; Diaz, D.; Dubé, Z.; Arevalo, N. Bismuth Oxide Aqueous Colloidal Nanoparticles Inhibit Candida albicans Growth and Biofilm Formation. Int. J. Nanomed. 2013, 8, 1645–1652. DOI: 10.2147/IJN.S38708.

[29] Powder Diffraction File Alphabetical Index. Inorganic Phases, Swarthmore, PA: JCPDS, International Center for Diffraction Data, 1984.

[30] Rojas, J.V.; Toro-Gonzalez, M.; Molina-Higgins, M.C.; Castano, C.E. Facile Radiolytic Synthesis of Ruthenium Nanoparticles on Graphene Oxide and Carbon Nanotubes. Material Science and Engineering, B 2016, 205, 28–35. DOI: 10.1016/j.mseb.2015.12.005.

[31] Balasubramanian, K.; Burghard, M. Carbon Nanotubes: Methods and Protocols. Methods Mol. Biol. 2010, 625, 2.

[32] Bu-Jong, K.; Jong-Pil, K.; Jin-Seok, P. Effects of Al Interlayer Coating and Thermal Treatment on Electron Emission Characteristics of Carbon Nanotubes Deposited by Electrophoretic Method. Nanoscale Res. Lett. 2014, 9, 23630. doi:10.1186/1556-276X-9-236.

[33] Escobar-Alarcón, L.; Morales-Mendez, J.G.; Solís-Casados, D.A.; Romero, S.; Fernández, M.; Haro-Poniatowski, E. Preparation and Characterization of Bismuth Nanostructures Deposited by Pulsed Laser Ablation. J. Phys. Conf. Ser. 2013, 582 (1), article id. 012013.

[34] Mousavi, M.P.; Ainla, A.; Tan, E.K.; Abd El-Rahman, M.K.; Yoshida, Y.; Yuan, L.; Sigurslid, H.H.; Arkan, N.; Yip, M.C.; Abrahamsson, C.K.; Homer-Vanniasinkam, S. Ion Sensing with Thread-Based Potentiometric Electrodes. Lab Chip 2018, 18 (15), 2279–2290. DOI: 10.1039/C8LC00352A.

[35] Li, Y.; Yang, C.Y.; Chen &., S.M. Photoelectrocatalysis of Hydrogen Peroxide at Functionalized Multiwalled Carbon Nanotubes (f-MWCNT) with Brilliant Blue Modified Electrode. Int. J. Electrochem. Sci 2011, 6, 4829–4842. DOI: 10.3390%2Fs90402289.

[36] Abeer, A.A.; Wasna’a, M.A.; Zuhair, S.A.; Abd, A.N. Determination of Antimicrobial Activity of Bi2O3 Nanospheres Against Multi-Drug Resistant Pathogenic Bacteria. AL-Qadisiyah Medical Journal 2018, 14, 25. Iraq.

[37] Hernandez, D.; Velasco-Arias, D.; Martinez-Sanmiguel, J.J.; Diaz, D.; Zumeta-Dube, I.; Arevalo-Niño, K.; Cabral-Romero, C. Bismuth Oxide Aqueous Colloidal Nanoparticles Inhibit Candida albicans Growth and Biofilm Formation. Int. J. Nanomed. 2013, 8, 1645. DOI: 10.2147%2FIJN.S38708.

[38] Motakef-Kazemi, N.; Yaqubbi, M. Green Synthesis and Characterization of Bismuth Oxide Nanoparticle Using Mentha Pulegium Extract. Iran. J. Pharm. Res. 2020, 19 (2), 70–79. DOI: 10.22037/IJPR.2019.15578.13190.