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Design, Synthesis and Antimicrobial Activities of New Carbon Nanotubes Derivatives

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ABSTRACT: Even though natural products or crops have been more common and popular in the recent, the chemicals without side-effects have been also addressed in various fields of industries due to possibility obtaining the large quantity and more bio-efficacy. In that context, many drugs have been developed for antibacterial activities but the over-uses of those relevant drugs have caused that microorganisms have adapted and evolved resistance against those drugs. Those lead to the researchers to focus on newly synthesized or functionalized molecules. In that context, nanotechnology, especially modified nanocarbon tubes (NCTs), are of the great interest of the various industries. Along with the current study, multi-walled carbon nanotubes (MWCNTs) were functionalized with three steps. Firstly, the carbon nanotube with a carboxylic acid tip on its surface was commercially purchased and then converted into acyl chloride, and later converted into a more reactive group. Then, the nucleophilic amino group such as diethylene triamine is bonded onto the carbon nanotube. Finally, after the carbon nanotube material with amine groups was functionalized with boric acid, carbon nanotube molecules carrying boric acid molecules were synthesized. Following modification and functionalization of MWCNTs, the newly synthesized molecules were characterized using FT-IR, SEM, TEM and XPS. After chemical characterization, the relevant molecules were screened for their anti-bacterial activities in comparison to those of well-known antibiotics. For anti-bacterial assays, molecules were tested against K. pneumoniae, E. coli, P.aeruginosa, S. aureus and B. subtilis. Concerning the findings of the antibacterial assays, concentrations of 40 and 80 µg /mL exhibited a range of activities but in parallel with those of standard antibiotics whereas the lower concentration, viz. 5, 10 and 20 µg / mL did not exhibit any activities. The highest activity was noted for 80 µg / mL, in comparison to those of antibiotics and other concentrations, against B. subtilis, with a 23 mm inhibition zone.

Keywords: Carbon nanotube, disc diffusion method, primary amine, antibacterial activity

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INTRODUCTION

Infectious diseases have been of the main causes of death due to enhanced resistance of bacteria to drugs available which, in turn result in higher rate of morbidity and mortality (Allahverdiyev et al., 2011). The relevant evolved resistance of the bacteria has been attributed to excessive uses of the current available drugs, causing a big and substantial threat to the health worldwide. To be compatible with the possible emergence of increasing global alarming of microbial diseases or to develop new compounds with augmented biological activities are of the great concerns. Furthermore, the well-known compounds might be also improved in their biological activities with the nanotechnology, especially modified nanocarbon tubes (NCTs) (Khabashesku et al., 2006; Amiri et al., 2012; Aslan et al., 2012; Zardini et al., 2012; Mocan et al., 2014; Salam et al., 2017; Sah et al., 2018). Indeed, a very high antibacterial activity of carbon based nanoparticles has been well-known and disseminated in that context. Of the first relevant researches, fullerenes, single-walled CNTs and graphene oxide (GO) nanoparticles have been clearly reported to possess anti-bacterial activities toward pathogenic microorganisms (Sah et al., 2018). However, in the last decades, allotropes of this new carbon have been discovered and applied in many fields (Sokolov and Stankevich, 1993; Cataldo and Da Ros, 2008; Wang et al., 2014).

A newly synthesized, modified and consequently functionalized carbon-based material are, in general, equipped with different properties rather than other conventional materials, being exclusive in its chemical structure, tubular arrangement, modifiable surface, stability and strength (Hu et al., 2009; Sah et al., 2018). Herewith the acquired unique and distinguishable properties, CNTs are of the mostly investigated allotropes of carbon, being prime candidates to be assessed in various disciplines ranging from medicine (Eatemadi et al., 2014; Amenta and Aschberger, 2015; Alshehri et al., 2016) to agriculture (Mondal et al., 2011; De La Torre-Roche et al., 2013; Chhipa, 2017).

Specifically, in order to combat with the possible emergence of new infectious diseases or their variants or microbial problems available, a wide range arrays of studies relating with enhancing the antibacterial capacity of the conventional compounds have been great interest studied (Chen et al., 2013; Seo et al., 2014; Dizaj et al., 2015; Kassem et al., 2019). For that reason, in the current study, we assessed the antibacterial activities of functionalized MWCNTs using diethylene triamine and boric acid. The structural modifications were revealed using FT-IR, SEM, TEM and XPS. Then, the successfully-obtained and conjugated compounds were assayed for their activity with five different microorganisms such as *K. pneumoniae, E. coli, P.aeruginosa, S. aureus and B. subtilis*. Then, compared with the common and well-known standard antibiotics Entamicin, Erythromycin, Amikacin, Ampicillin, and Cloxacill.

MATERIALS AND METHODS

Functionalization and Characterization

Materials

Thionyl chloride ($SOCl_2$), dimethylformamide (DMF), anhydrous tetrahydrofuran (THF), Diethylene Triamine, and boric acid were purchased from Sigma–Aldrich. Multi-walled carbon nanotubes (MWCNTs) were purchased from Nanografi Nano Technology with -COOH Functionalized MWCNT, Purity>96%, Outside Diameter: average diameters of 8-18 nm.

Functionalization of MWCNTs with Acylchloride

Figure 1 shows the schematic diagram of the surface acylation of multi-walled CNT with carboxylic acid tip. Following that acylation, 100 mg of MWCNTs (MWCNTs–COOH) was stirred in 10 mL of thionyl chloride ($SOCl_2$) in the presence of 1mL of dry dimethylformamide (DMF) at 70^{o}C

for 24 h. Then, a filtration process was followed for removal of solid from the solution using Gooch crucible (No: 3 or 4). The filtrate was firstly washed using dry diethylether, dry THF and finally with dry DMF and dried at 25 ºC temperature in a vacuum oven.

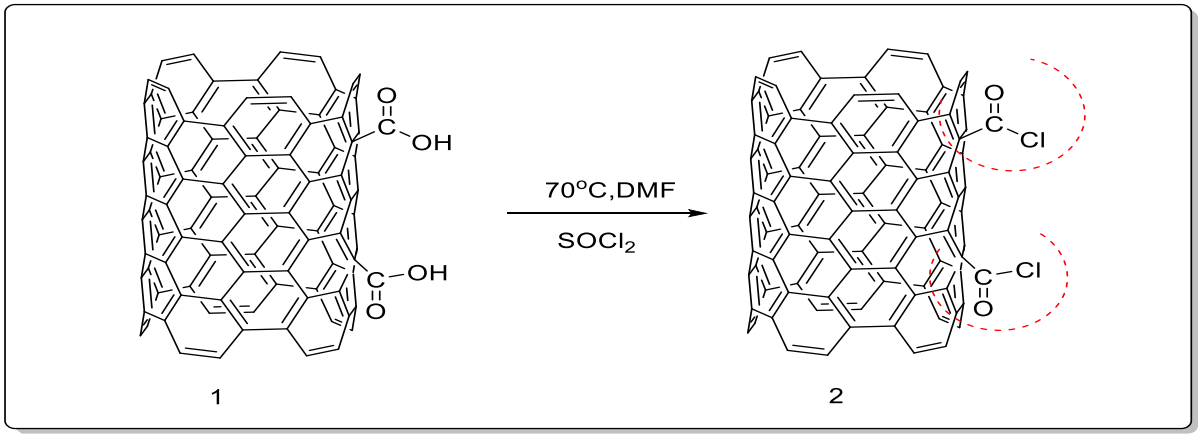

Figure 1. Schematic diagram of the surface acylation of multi-walled CNT with carboxylic acid tip

Functionalization of MWCNTs with Diethylenetriamine

Figure 2 shows the functionalization procedure of MWCNTs–Cl with diethylene triamine. In that context, MWCNTs–Cl (250 mg) was mixed with 4 mL of diethylene triamine and stirred for 24 h at 204ºC.Then, the procedure was followed by the filtration of the resulted material for removal of solid particles from the solution. Ultimately, the filtrates were washed using dry THF and dried at 25 ºC temperature in a vacuum oven.

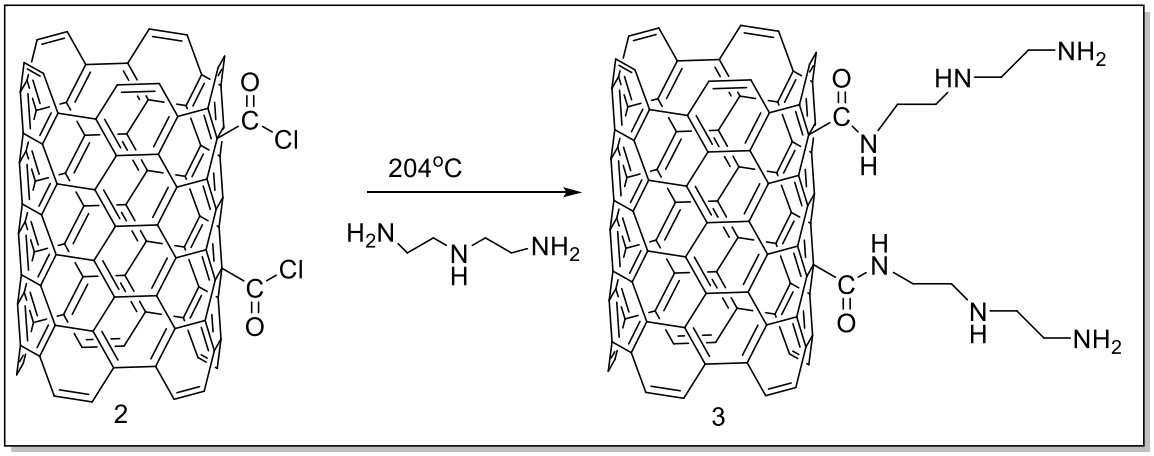

Figure 2. Schematic diagram of the tip of acylated multi-walled CNT with Diethylene Triamine groups.

Functionalization of MWCNTs-NH_2 with boric acid

Figure 3 shows the functionalization procedure of MWCNTs-NH_2 with boric acid. Briefly, MWCNTs-NH_2 (50 mg) was mixed with boric acid (150 mg) in 5 mL dry DMF and then mixture was allowed for stirring at 150ºC for 24 h. The stirring was followed by the removal of solid particles from the solution using Gooch crucible (No: 3 or 4). The filtrate was firstly washed using pure water, THF and finally with ethyl alcohol and dried at 25ºC temperature in a vacuum oven.

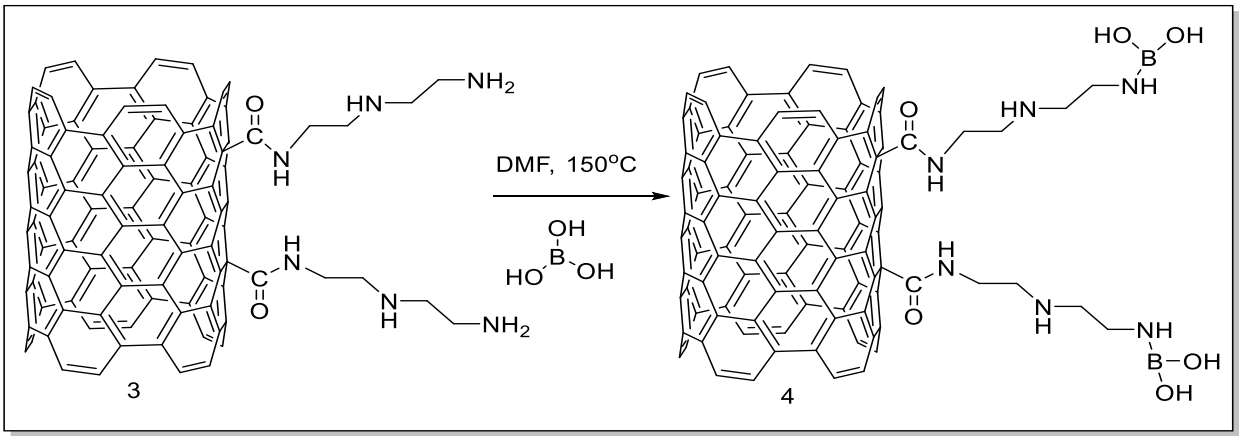

Figure 3. Schematic diagram of boric acid functionalization at the end of Diethylene Triamine modified multi-walled CNT

Characterization İnstrument

FT-IR studies

FT-IR spectra were obtained using KBr pellets (4000–400 cm^{-1}) on Bio-Rad-Win-IR Spectrophotometer.

Scanning Electron Microscope (SEM)

The structure characterization of the samples was carried out using a Zeiss Sigma 300 scanning electron microscope (SEM) with SE detector at 10 kV acceleration voltage.

Transmission Electron Microscope (TEM)

Hitachi HT7700 transmission electron microscope (TEM) device was used for surface information in the modification processes.

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was used to identify atomic and molecular information about the surface of the material, providing information on the composition and electrostatic level of the sample surface by analyzing the core levels and subsequent analysis of the emitted core photoelectrons. Herein, for the present study, we analyzed MWCNTs-NH-B $(OH)_2$ using XPS by taking data at a depth of 10 nm from the surface. The operating conditions of the spectroscopy were as follows: X-ray source: AI Kα Monochromatic (1486.68 eV), X-ray spot size: 300 μm, sampling area: 60x60 mm, analyzer: 180 ° hemispherical analyzer-128 channel detector, 200 eV transition energy for general scanning and 50 eV transition energy for partial scanning, Scan number: XPS device surface analysis was performed in 3 operating parameters.

Antimicrobial Studies

Microorganisms

The microorganisms were kindly provided from bacterial collection of Van Dursun Odabaş Medical Faculty Hospital (Van, Turkey). Three of the test microorganisms were Gram-negative bacteria (*Klebsiella pneumoniaee* AATC 13883, *Escherichia coli* ATCC 36218, *Pseudomonas aeruginosa* ATCC 9027), and two Gram-positive bacteria (*Staphylococcus aureus* ATCC 25923, ATCC 6633 *B. subtilis*) were assayed for anti-bacterial activities. For comparison of the functionalized MWCNTs with the standard and common antibiotics, Gentamicin, Erythromycin, Amikacin, Ampicillin, and Cloxacill were used as positive control groups. DMSO (Dimethylsulfoxide) was used as a negative control group

for antibacterial activity assays. Disk diffusion and hollow agar methods were used to determine the antimicrobial activities of multi-walled CNTs in which amine groups and different functional groups function. In the negative control group, in order to determine the effect of dimethyl sulfoxide (DMSO) used on microorganisms, four different concentrations (5, 10, 15 and 20 µl) were studied and no activity was found.

Determination of antibacterial activity by disk diffusion method

For the activity studies, microorganisms kept at -30 ° C were activated, then inoculated into MHB liquid medium with the help of a loop in a sterile cabinet and left for 24 hours incubation at 37 ° C (Anar et al., 2016). The bacterial suspension prepared at the end of the period was adjusted according to the Mac Farland standard density (İlçim et al., 1998; Berber et al., 2013). The discs used in the disc diffusion method (Whatman No: 1) are 6 mm and sterilized before use. The substances were prepared by dissolving in DMSO, and in the same way in dilutions, they were prepared with DMSO in four different concentrations (0.025, 0.05, 0.1 and 0.2 mg/µl) and absorbed on discs. Discs were placed at equal intervals on the cultivated media. Likewise, the substances (DMSO 10 mg/ml) were dissolved and 5 µl, 10 µl, 20 µl, 40 µl and 80 µl concentrations were prepared and studied in the well agar method. Furthermore, for positive control groups in their standard quantities, Gentamicin (CN: 10µg), Erythromycin (E: 15 µg), Amikacin (AK: 30 µg), Ampicillin (AMP: 10 µg), Cloxacill (CX: 5 µg) were used. Then it was left at room temperature for 15 minutes and incubated at 37 ºC for 24 h. After incubation, the results were measured in mm, inhibition diameters around the cavity and discs (Onbaşılı et al., 2011).

RESULTS AND DISCUSSION

FT-IR studies

Herein, the relevant functional groups of MWCNTs-NH-B(OH)$_2$ we used for the present study were evaluated using FT-IR spectroscopy. Figure 4 shows that the spectra of MWCNTs-NH-B(OH)$_2$, revealing that 3365 cm^{-1} vibration band (N-H) groups, Carbonyl (C = O) groups in vibration band amide groups of 1678 cm^{-1}, 1427, 1365, 921cm^{-1} vibration band (B-O) groups, and 920 cm^{-1} vibration band (C = C) groups (Amiri et al., 2012).

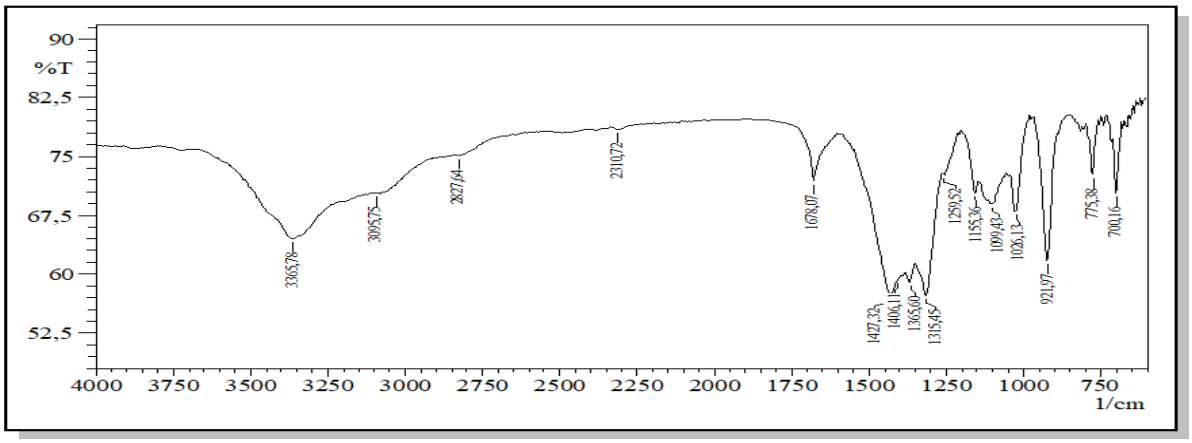

Figure 4. FT-IR spectra of MWCNTs-NH-B(OH)$_2$

Scanning Electron Microscope (SEM)

Figure 5 a-b represents the SEM images of MWCNTs-NH$_2$, MWCNTs-NH-B(OH)$_2$ molecules, respectively, suggesting a diameter of the multi-walled carbon nanotube modified with the amine group varied between 1-2 micrometers (Figure 5 a). Herein, a homogenous, clear and transparent image on the

surface of the MWCNT due to the covalently bonded amine group was observed. In addition, functionalization of CNTs with amine group resulted in contraction. Regarding modification with boric acid, the diameter of MWCNTs-NH-B $(OH)_2$ obtained through functionalization with boric acid on MWCNTs-NH_2 was slightly smaller than MWCNTs-NH_2 and a more rough surface was observed (Figure 5 b) (Cao et al., 2020)

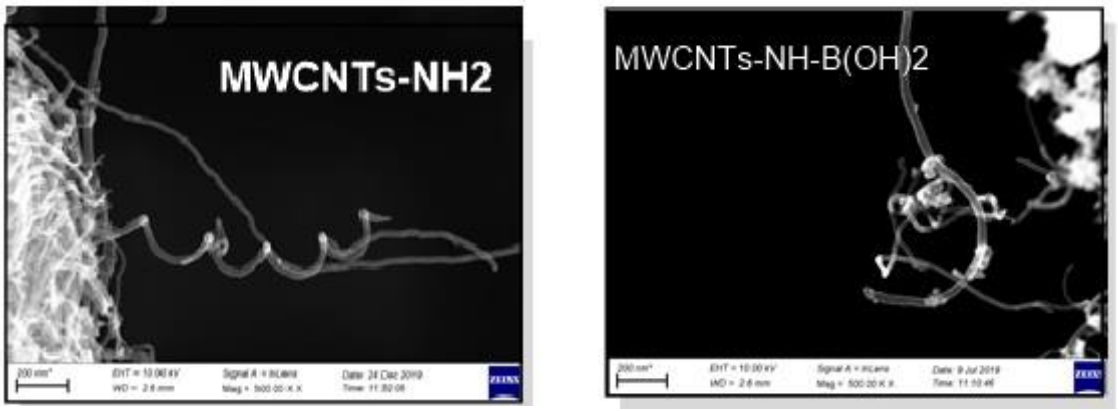

Figure 5. SEM images of MWCNTs-NH_2 and MWCNTs-NH-B $(OH)_2$ molecules

Transmission Electron Microscope (TEM)

EM images of MWCNTs-NH_2, and MWCNTs-NH-B $(OH)_2$ are given in Figure 6 a-b, respectively. As seen in Figure 6 a, in the characterization, inner pore size of MWCNTs-NH_2 was about an average with 10 nm and outer capsule size of MWCNTs-NH_2 was determined as an average of 8.5-12 nm. In addition, the inner pore size MWCNTs-NH-B $(OH)_2$ was about an average of 10 nm while the outer capsule size was determined to be between 8-11 nm (Cui et al., 2020).

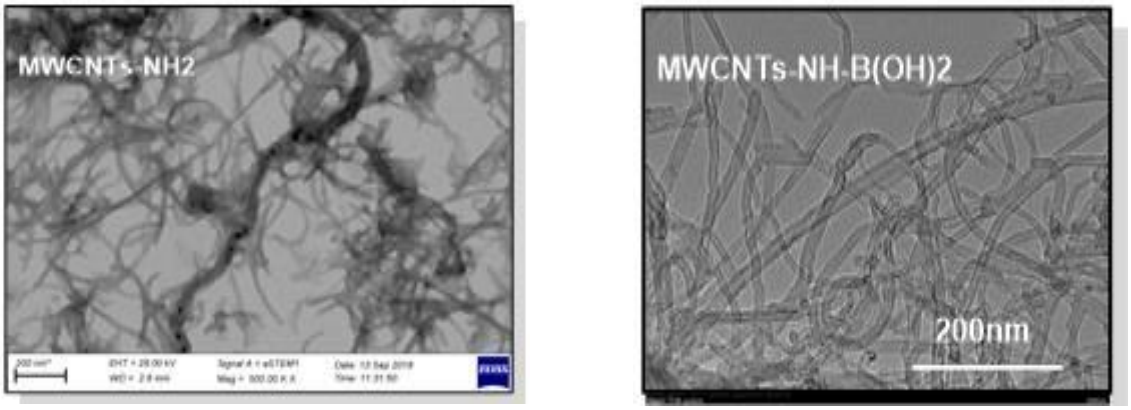

Figure 6. TEM image of MWCNTs-NH_2 and MWCNTs-NH_2-B$(OH)_2$.

XPS analysis of MWCNTs-NH-B $(OH)_2$

Figure 7 shows the spectra of MWCNTs-NH-B$(OH)_2$, revealing that MWCNTs-NH-B$(OH)_2$ exhibited the C1s and O1s peaks at the binding energies of 284.4 and 532.0 eV, respectively. Functionalization of MWCNTs with diethylene triamine and boric acid exhibited two new peaks of B1s and N1s at the binding energies of 192.0 and 401.0 eV, which they did not exist in MWCNTs-Cl. The deconvolution of the C1s spectra shows the following binding energy values corresponding to 284.4 eV for C-C (sp^2) / C-H and C=C, 285.19 eV for C-C(sp^3)/C-H, 287.16 eV for N-C=O, and 290.76eV for π-π interactions. Two peaks of N1s region demonstrate that 400.33 eV and 401.83eV values are responsible

for CO-NH and CH_2NH, respectively. Presence of two different peaks in O1s region can be explained by N-C=O (532.13 eV) and C=O (for carboxyl groups) (532.91eV). Furthermore, B1s region shows two peaks which are responsible for B-N (192.57eV) and B-OH (193.17 eV). Those relevant regional data prove that MWCNTs are properly functionalized with diethylene triamine and boric acid (Ma et al., 2014; Arumugasamy et al., 2020).

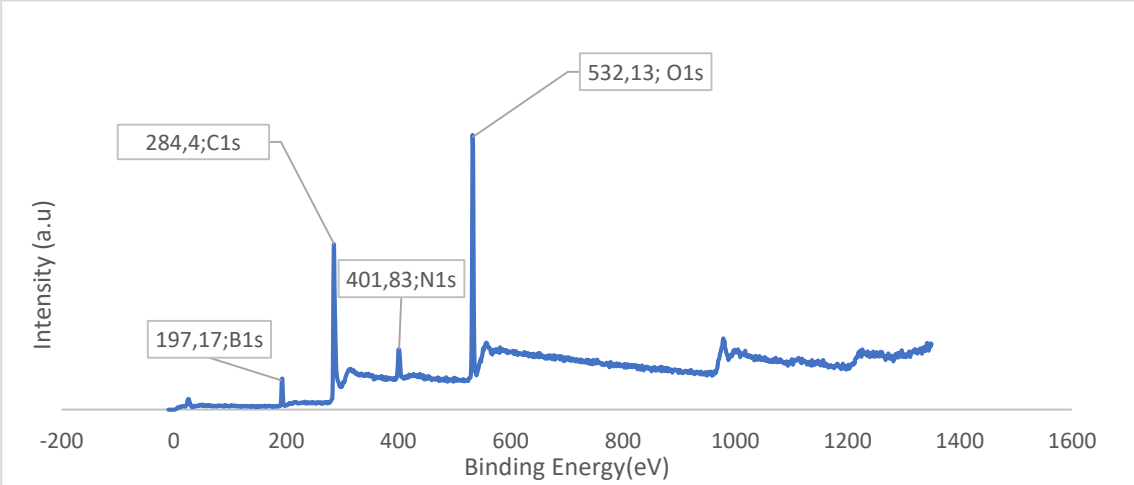

Figure 7. XPS spectrum for MWCNTs-NH-B(OH)2

Anti-bacterial activities of the common antibiotics and functionalized molecules

The findings relating activities of Gentamicin, Erythromycin, Amikacin, Ampicillin and Cloxacill are collectively presented in Table 1. Of those antibiotics, ampicilin did not exhibit any activities against P. aeruginosa and eritromisin were not substantially effective against L. monocytogenes (Table 1). For activities of MWCNTs-NH-B $(OH)_2$, a concentration ranging 5 to 80 µl was bio-assayed against the pathogenic bacteria. Of the tested concentrations, only 40 µg / mL and 80 µg / mL exhibited inhibitory activities, being active against E. coli (16 mm) and B. subtilis (14 mm) at concentration of 40 µg / mL and E. coli (20 mm), P. aeruginosa (15 mm), S. aureus (18 mm), and B. subtilis (23 mm) at concentration of 80 µg / mL (Table 2). The tested concentrations of the molecules ranged similar inhibition zones with those of relevant antibiotics. The highest activity was noted for 80 µg / mL, in comparison to those of antibiotics and other concentrations, against B. subtilis, with a 23 mm inhibition zone, leading more researches to be addressed on the inhibitory activities of the molecules against B. subtilis.

In the relevant reports, functionalized MWCNTs were more effective against E. coli than S. aureus (Zardini et al., 2012). Those results are consistent with the present findings. Lysine functionalized MWCNTs were also assayed against Escherichia coli and Klebsiella pneumonia, being bactericidal on both microorganisms whereas MWCNT- NH-B $(OH)_2$ did not exhibit any inhibitory effects on K. pneumonia (Amiri et al., 2012). We should herein utter that the volume and concentration of each solution of the present study was higher than those of Amiri et al. (2012). Those findings suggest that the activity might not be dependent on concentration but related and linked with the interaction between bacterial membrane and molecules (Liu et al., 2010), electronic structure of the CNTs (Vecitis et al., 2010), size (diameter) of the CNTs (Kang et al., 2008), and nature of the target organism (Al-Jumaili et 2017). Overall, the bactericidal activity of the MWCNTs is addressed on the complete surface phenomena involving leakage of the bacterial cellular components and coupling with the relevant enzyme activations (Li et al., 1997; Sah et al., 2018).

Table 1: Antibacterial activities of some common antibiotics

Antibiotics	*K. pneumoniae*	*E. coli*	*P. aeruginosa*	*S. aureus*	*B. subtilis*
Gentamisin	17 mm	17 mm	18 mm	18 mm	18 mm
Amikasin	10 mm	20 mm	25 mm	16 mm	11 mm
Eritromisin	19 mm	19 mm	19 mm	21 mm	20 mm
Ampicillin	16 mm	13 mm	-	24 mm	14 mm
Cloxacillun	10 mm	12 mm	12 mm	25 mm	15 mm

mm corresponds to the inhibition zone and (-) represents "no inhibition zone with 6mm disc diameter"

Table 2: Antibacterial activities of MWCNT- NH-$B(OH)_2$

MWCNT- NH-$B(OH)_2$ (µg / mL)	*K. pneumoniae*	*E. Coli*	*P. aeruginosa*	*S. aureus*	*B. subtilis*
5 µl	-	-	-	-	-
10 µl	-	-	-	-	-
20 µl	-	-	-	-	-
40 µl	-	16 mm	-	-	14 mm
80 µl	-	20 mm	15 mm	18 mm	23 mm

mm corresponds to the inhibition zone and (-) represents "no inhibition zone with 6mm disc diameter"

CONCLUSION

Along with the current study, MWCNTs were successfully modified with diethylene triamine and boric acid with a three-step procedure. Those relevant modifications of MWCNT- NH-$B(OH)_2$ were clearly revealed using FTIR, XPS, SEM, and TEM analysis. Functionalized molecules were then assayed for their anti-bacterial activities. At two high concentration, a range of activities were noted for specific bacterial collections but also concentration dependent activity from 40 and 80 µg / mL was reported herein. Novel findings of the study might be deduced as that 80 µg / mL concentration of the MWCNT-NH-B $(OH)_2$ were more effective against *B. subtilis*, with a-23 mm inhibition zone, in comparison to those of common antibiotics. Those findings might lead to the more specific studies to be addressed on the inhibitory activities of the molecules against *B. subtilis*.

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Conflict of Interest

The article authors declare that there is no conflict of interest between them.

Author's Contiıbutions

NM conceived and designed the experiments, discussed the data, and wrote the manuscript. AY has progressed experiments; YA and MHA have recorded and interpreted the DTA, SEM, TEM and XPS. All authors read and approved the manuscript.

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