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Copper and silver impregnated carbon nanotubes incorporated into cyclodextrin polyurethanes for the removal of bacterial and organic pollutants in water

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ABSTRACT

Increasing demand for safe drinking water and the problems associated with some existing water treatment methods have made it vital for the development of new technologies to address these challenges. This study explores the use of nanosized silver and copper impregnated on polyurethanes for possible use in water disinfection. It also investigates the adsorption of organics by the metal impregnated polyurethanes in water. Copper and silver nanoparticles were immobilized on carbon nanotube and embedded in water-insoluble cyclodextrin polyurethane polymers. The polyurethanes were characterized by various techniques such as BET, TEM, SEM and EDX and evaluated for their adsorption and bacteria reduction capacity using spiked water samples containing bacteria (*Escherichia coli* and *Salmonella typhi*) and a model organic pollutant (*para*-nitrophenol) in water. The metal impregnated polyurethanes inactivated up to 3 logs of bacteria but had a maximum adsorption of 55% of the model organic pollutant.

Keywords: Bacteria; Carbon nanotubes; Cyclodextrins; Nanoparticles

1. Introduction

Metal nanoparticles with antibacterial properties are emerging as alternative biocides in water treatment [1]. Metals such as gold, copper and silver have been previously used for antibacterial purposes including water purification [2]. The antibacterial activity of metals such as copper and silver has been attributed to several modes of action such as protein inactivation, blockage of DNA replication pathways and weakening of bacteria cell membranes that later leads to cell membrane disintegration [3,4]. Copper and silver nanoparticles have been immobilized on a wide range of substrates such as zeolites, carbon nanotubes, activated carbon fibres and carbon aerogels and have been found to be highly efficient in water treatment [5–7].

Silver nanoparticles cause irreparable damage to the cellular membrane [4,8,9] which enables the accumulation of nanoparticles in the cytoplasm 414. It is suggested that the action of silver nanoparticle arises due to this damage and not its toxicity [8]. Particle size has been reported to have an effect on the antibacterial properties of nanoparticles. In an analysis regarding the effect of silver nanoparticles in a size range of 1–100 nm, particles in the 1–10 nm size range were found to have the strongest antibacterial properties than other

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size fractions. It is therefore expected that smaller size nanoparticles are able to easily penetrate across membranes and accumulate in the cytoplasm [3,8]. At nano dimensions, the surface area to volume ratio of the metal particles is increased compared to their bulk forms. This leads to the availability of high numbers of nanometallic particles on the adsorbent surface for its interaction with contaminants [3,8].

Widely used disinfection methods include chlorination, chloramination, ozonation and UV disinfection [10]. These disinfection processes effectively inactivate or destroy bacteria and viruses that can be found in water during treatment. The chlorination process, for instance, can be further enhanced such that there is disinfection by residual chlorine species within the distribution system to prevent re-growth of bacteria and also combat biofilm formation. Chlorination and ozonation often yields disinfection by-products (DBPs) such as trihalomethanes (THMs), chlorinated biphenyls and other halogenated hydrocarbons [11] which can be a health risk. It is therefore imperative that research be undertaken into bacteria removing technologies that do not release potentially toxic by-products. In this paper, the use of metal nanoparticles embedded on a polymer substrate is being proposed as a potential solution although its cost-effectiveness in bulk water treatment has still not yet been determined.

Conventional drinking water treatment methods currently employed in water treatment, while very effective in the removal of turbidity, natural organic matter (NOM), metal species and organic micropollutants, have some limitations and drawbacks. For example, in coagulation and flocculation processes, various types of adsorbents and membranes are used effectively for such purposes. Methods involving the use of granulated activated carbon as an adsorbent or as a filter remove many organic pollutants but often fail to remove such compounds at parts-per-billion levels and also in instances where there is competition with NOM for adsorption sites. Therefore, the challenge is to develop a water treatment method that can reduce bacterial loading in water while at the same time having some capacity to remove organic micro-pollutants to desired levels without compromising the quality of water [12].

We have previously reported that cyclodextrin (CD) polymers incorporated with carbon nanotubes exhibit the ability to remove priority organic pollutants from water at concentrations as low as parts per million (ppm) [13]. These polymers could be recycled and reused several times without losing their structural integrity [14]. In extending this work, we now report on the anti-bacterial properties of these polymers after the carbon nanotubes in the polymer matrix have been impregnated with bioactive silver and copper nanoparticles. This study therefore evaluates the adsorption and disinfection capacity of the metal impregnated cyclodextrin based polyurethanes. Model pollutants such as *Escherichia coli* (*E. coli*) and *S. typhi*, which are indicators for faecal coliform contamination were used together with a model organic pollutant *p*-nitrophenol (PNP), an organic pollutant originating from industrial effluent. The polyurethanes are expected to effectively reduce bacterial counts in contaminated water without introducing disinfection by-products. What is also critical is that the metal nanoparticles should not leach into the water thus causing a secondary challenge with respect to toxicity.

There are several advantages of using a polymer-based system, including the ease with which different forms (beads, fibres, and films) can be synthesized and processed. This is not the case with many other adsorbent technologies such as activated carbon. In addition, the use of polyurethanes allows for the regeneration of the materials, thereby reducing costs. These materials have also been tested for their biodegradability at the end of their useful life [15].

2. Experimental

2.1. Functionalization of multi-walled carbon nanotubes (MWNTs)

Commercial MWNTs (Sunnano®), 1.0 g, were functionalized in a mixture of nitric and sulphuric acids (40 cm^3) at the ratio of 1:3 at 55 °C for 30 min under reflux. This was carried out to introduce hydroxyl and carboxylic groups on to the MWNTs [13]. The mixture was diluted with distilled water to 1000 cm^3 and the MWNTs were filtered using Teflon filter paper with pore size of 0.45 μm and a diameter of 47 mm. The functionalized MWNTs were then washed with distilled water and the pH was adjusted to 7.0. The MWNTs were then dried under vacuum at room temperature.

The dried functionalized MWNTs were then characterized using infrared (IR) spectroscopy and transmission electron microscopy (TEM).

2.2. Synthesis of silver nanoparticles onto functionalized MWNTs

Aqueous solutions containing 0.01 M silver nitrate (60 cm^3), 20 mm polyvinylpyrrolidone (PVP) (40 cm^3), a dispersant, and ethanol (20 cm^3) were stirred at 50 °C for 2 h in a foil-covered beaker, protected from light [10]. Functionalized MWNTs (1 g) were then immersed in these solutions followed by the addition of ascorbic acid (3.5 g), a reducing agent, and stirring for a further 2 h [16]. The resultant products were filtered, washed with double distilled water (1 l) and then dried in an oven at 150 °C for 3 h.

Characterization of these products was performed using FT-IR spectroscopy to confirm the presence of the carboxyl and hydroxyl groups required for polymerization. Transmission electron microscopy (TEM) was also used to determine whether the silver nanoparticles had been loaded onto the functionalized MWNTs.

2.3. Synthesis of copper nanoparticles onto functionalized MWNTs

Aqueous solutions containing 0.01 M copper nitrate ($Cu(NO_3)_2$) (40 cm^3), 4 mm polyvinylpyrrolidone (PVP) (20 cm^3) and ethanol (40 cm^3) were stirred at room temperature for 10 min. Functionalized MWNTs (0.50 g) were then immersed in the aqueous mixture and an aqueous solution of dilute hydrazine hydrate (HH) (1:1 with respect to $Cu(NO_3)_2$) was added to the reaction mixture [17]. The end of the reaction was marked by the disappearance of the blue colour which was replaced by a brown colour of the solution. The Cu/MWNTs composites were filtered and washed with distilled water then dried under vacuum. The metal/MWNTs nanocomposites were then characterized using transmission electron microscopy, scanning electron microscopy, emission dispersive spectroscopy and infrared spectroscopy.

2.4. Polymerization of metal impregnated MWNTs with β-cyclodextrin (CD)

β-CD (4.00 g) was dissolved in *N,N*-dimethylformamide (DMF) (36 cm^3) by stirring. Metal impregnated MWNTs (0.04 g) were added to the cyclodextrin mixture. These masses represented a 1% nanotube composition with respect to the mass of CD. The metal/MWNTs had previously been suspended in DMF (4 cm^3) by sonication for 10 min using a Selecta ultrasonic bath. The mixture of the cyclodextrin and carbon nanotubes was heated to about 70 °C at constant stirring. The bifunctional linker (hexamethylene diisocynate), 7.5 times mole equivalents (i.e., in excess) with respect to CD, was added dropwise into the mixture. The temperature for the reaction was maintained at 70 °C under an inert atmosphere for 24 h [13]. The progress of the reaction was monitored by the presence and intensity of the isocyanate peak on the IR spectroscopy at 2270 cm^{-1}. The disappearance of the isocyanate peak after 24 h marked the completion of the reaction. The polymer formed was precipitated by addition of acetone (~100 cm^3) and then filtered off to remove the solvent. The polymer was further washed with acetone to remove the residual solvent on the polymer. The polymer was subsequently dried under vacuum to remove the excess acetone after washing.

The polymers were then characterized by scanning electron microscopy using a Joel, JSM-840 and Brunauer–Emmett–Teller (BET) analysis was employed using the N_2 in a Trister 3000 V6.05 analyzer to measure surface area and pore volumes of the samples.

2.5. Sample preparation for UV–Visible spectroscopy

p-Nitrophenol (0.025 g), a model organic pollutant was transferred into a volumetric flask (500 cm^3) containing distilled water (100 cm^3). The contents were mixed until the *p*-nitrophenol had dissolved. The volume was made up to 500 cm^3 with distilled water. This stock solution had a concentration of 50 mg/l. From the stock solution, a dilution of 10 mg/l was prepared by pipetting 50 cm^3 of stock solution into a 250 cm^3 volumetric flask and made up to the mark with distilled water.

p-Nitrophenol (30 cm^3, 10 mg/l) was passed through the polymers (0.30 g) that were packed in empty solid phase extraction (SPE) C-18 cartridges connected to a collection flask. The flow rate for the *p*-nitrophenol solution was approximately 3–5 cm^3/min. The eluent was collected and its absorbance was measured using a UV–Visible spectrophotometer.

p-Nitrophenol standards (for the production of the calibration curve) and samples were analyzed using a Cary UV (50 Scan). Samples were placed in 1 cm^3 cuvettes. The absorbance of the sample was measured and recorded at 318 nm (the wavelength where there is maximum absorption by *p*-nitrophenol). Distilled water was used as a reference sample to zero the instrument. All measurements were taken at room temperature.

2.6. Growth of biomass

Two loops of *E. coli* ATCC 25925 were grown in sterile nutrient broth (200 cm^3) under constant aeration on a rotary shake incubator (117 rpm) at 37 °C for 24 h. The harvested cells were then washed by centrifuging using phosphate buffered solution (PBS) for several times. The washed cells were then re-suspended in tetra sodium pyrophosphate [10]. The cells in each centrifuge tube were enumerated by serially diluting the concentrated suspension 25 times in sterile saline solution. The same procedure was followed in cultivating *S. typhi* (ATCC 14029) cells.

2.7. Preparation of spiked water sample

Bacteria cells harvested and suspended in sodium pyrophosphate were used to spike sterile distilled water. To obtain different concentrations of bacterial contamination, different volumes of the suspension of known bacterial concentration were added to sterile distilled water. The concentrations of spiked water were confirmed by the standard spread plate procedure.

2.8. Disinfection of test waters

Polymers (multi-walled carbon nanotubes polymer cyclodextrin (MWNT/CD) (0.3 g), silver impregnated carbon nanotubes cyclodextrin polymer (Ag MWNT/CD) (0.3 g), copper impregnated carbon nanotubes cyclodextrin polymers (Cu MWNT/CD) and cyclodextrin hexamethylene diisocyanate polymer (CD/HMDI) (0.3 g) were packed in separate empty SPE cartridges. For the removal of bacteria from water, the set up used for the removal of PNP was used. The polymer filled cartridges were connected to a filtering set-up that comprised of a separatory funnel and a collecting funnel. The flow of water samples at 5 ml/min through the polymer cartridges was controlled by gravity and adjustment of flow through the tap on separatory funnel. The residual bacteria were collected in the collection flask. The eluent was cultured according to standard methods [18].

2.9. Nanoparticle leaching studies

Metal impregnated carbon nanotubes and cyclodextrin polymers were packed in SPE cartridges and were connected to the experimental set-up used for removal of the pollutant. Distilled water (100 ml) was passed through the polymers at flow rates of 5, 30 and 85 ml/min. The eluted water was then analyzed by atomic absorption spectroscopy for the presence of any silver or copper that could have leached out [18].

2.10. Effect of nano-material on cell surface morphology by scanning electron microscopy (SEM)

Five millilitres of *E. coli* cultured in nutrient broth for 24 h were centrifuged at 13,000 rpm for 5 min, the pellet obtained was mixed with 0.6 g of metal impregnated MWNTs in 20 ml of sterile distilled water. The mixture was then centrifuged and a small sample portion was placed on a copper grid. The grid was then placed in an oven at 37 °C for about an hour to dry the sample. After drying, the grid was mounted on the aluminium stub using a carbon tape. Low vacuum mode of the SEM at 5.00 kV was then used to analyze the sample. *E. coli* cells and nanomaterials were also incubated separately and considered as controls.

2.11. Statistical analysis

Statistical analysis was done using the SPSS computer statistical software (version 13.0). Test of significance was carried out using the Student's independent *T*-test at 95% confidence limit.

3. Results and discussion

3.1. Functionalization of MWNTs

FT-IR analysis of MWNTs that were treated with sulphuric and nitric acids confirmed the presence of carbonyl and hydroxyl peaks at 1730 cm^{-1} and 3437 cm^{-1}, respectively (Fig. 1). This confirmed that the oxidation of MWNTs had been achieved. After functionalization, confirmed by comparing with the spectrum of pristine nanotubes, the MWNTs were suspendable in water due to the presence of the carboxyl groups on the surfaces of the MWNTs.

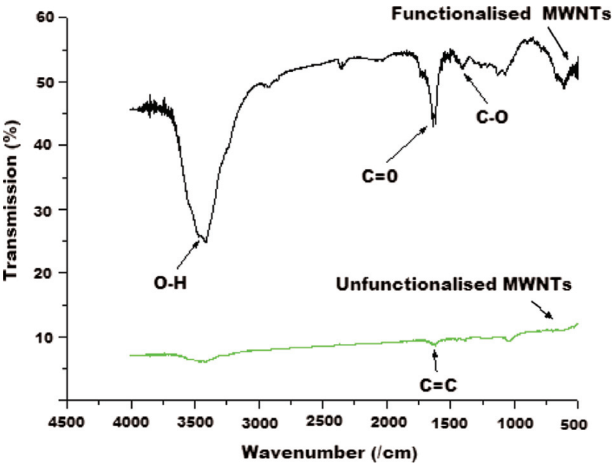

Fig. 1. FT-IR spectrum of unfunctionalized and functionalized MWNTs.

3.2. Metal nanoparticle impregnation

The synthesis of silver nanoparticles using ascorbic acid as a reducing agent in the presence of polyvinylpyrrolidone as a surfactant and 0.01 M silver nitrate solution yielded particles in the nanometer range according to TEM images. The TEM images in Figs. 2 and 3 show the successful loading of the nanoparticles onto the MWNT. From the TEM images, the presence of dark spots on the outer wall of the carbon nanotubes confirmed the successful impregnation of the metal nanoparticles of silver and copper, into MWNTs.

3.3. Nanoparticles size and distribution

The size of the metal nanoparticles was determined to be in the nanoscale range. Several electron micrographs or electronic images were obtained for each of these products and measured using Coreldraw™ (version 10). The diameter range of silver nanoparticles was 8–35 nm whilst copper nanoparticles ranged between 6 and 19 nm

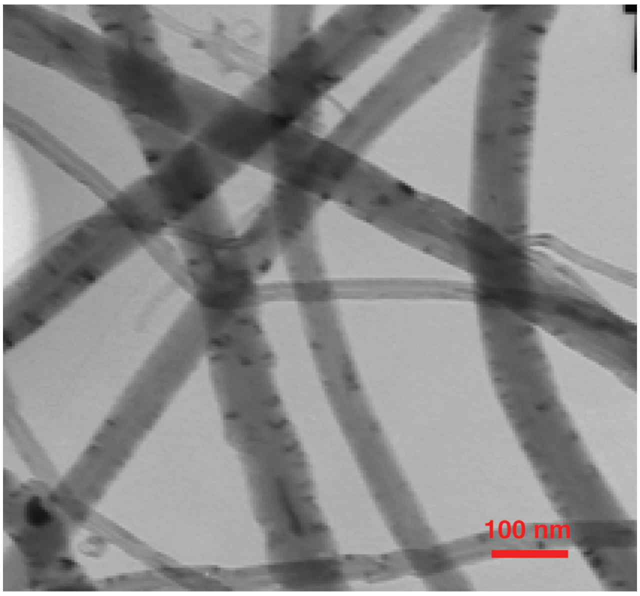

Fig. 2. TEM image of silver impregnated MWNTs.

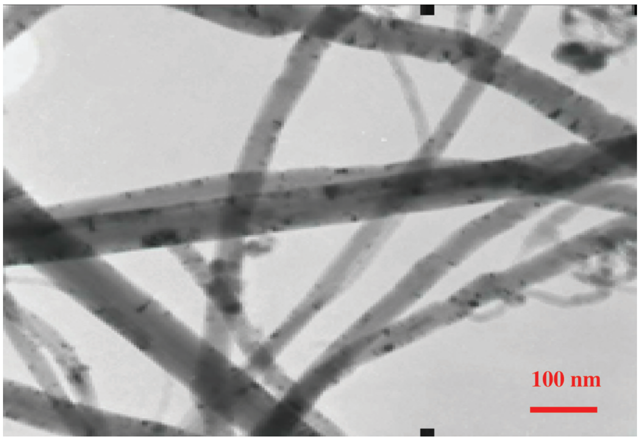

Fig. 3. TEM image of copper impregnated MWNT.

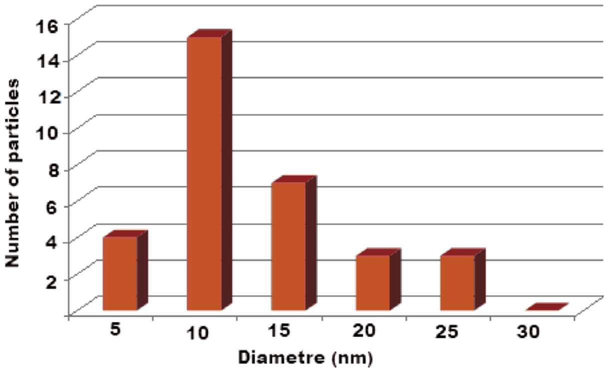

Fig. 4. Silver nanoparticle size distribution.

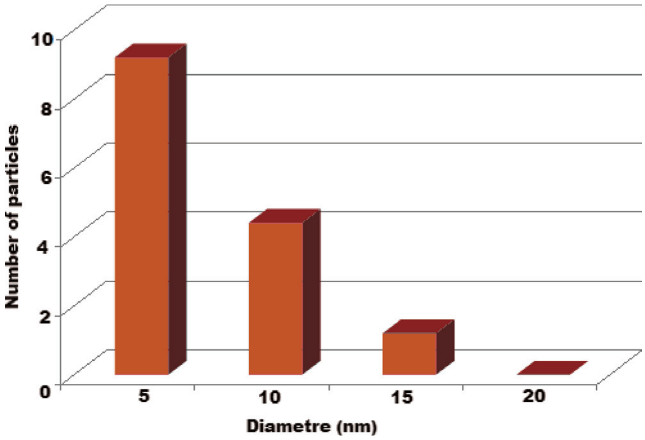

Fig. 5. Graph showing size distribution of copper nanoparticles.

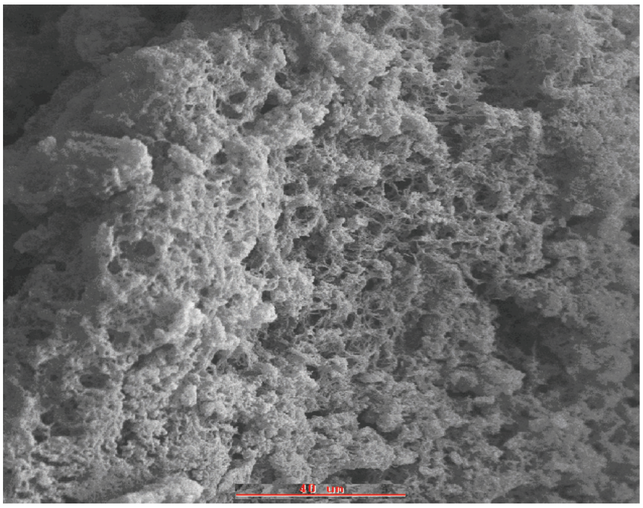

Fig. 6. SEM image of 1% Ag MWNT/CD polymer.

(Figs 4 and 5). From the TEM images in Figs. 2 and 3, it can be noted that the nanoparticles were evenly distributed with little or no agglomeration.

3.4. Synthesis of metal MWNT–CD polymer

The disappearance of the N=C=O peak after 24 h in the FT-IR spectrum indicated the completion of the reaction. After precipitating with acetone, water insoluble grey polymers were obtained. These were characterized using scanning electron microscopy (SEM) (Figs. 6 and 7) in order to determine their surface morphology. The polymers had a spongy surface appearance, which should allow for efficient contact between polluted water and the metal nanoparticles. The elemental composition of the polymer was also determined using energy dispersive X-ray spectroscopy (EDS) and the interpretation of the spectrum confirmed the presence of silver and copper in the polymers (Figs. 8 and 9).

3.5. Surface area analysis by Brunauer–Emmett–Teller (BET)

From the BET analysis it is apparent that the larger surface area allows for a wider distribution of the metal nanoparticles on the surface of the polymers. This should in theory provide a higher probability with respect to the interaction between the nanoparticles and the bacterial cell membrane. However in this study, probably as a result of metal loading, there was an observed decrease in the adsorption of *p*-nitrophenol (52–55%), the test pollutant, compared to the native polymers (with no metal nanoparticles) as shown in Table 1. The reason for this unexpected decrease is currently under scrutiny, but we speculate that the metal nanoparticles are partly obstructing some of the cyclodextrin cavities, and hence while the overall surface area has increased, the available sites for adsorption of organic pollutants have actually decreased.

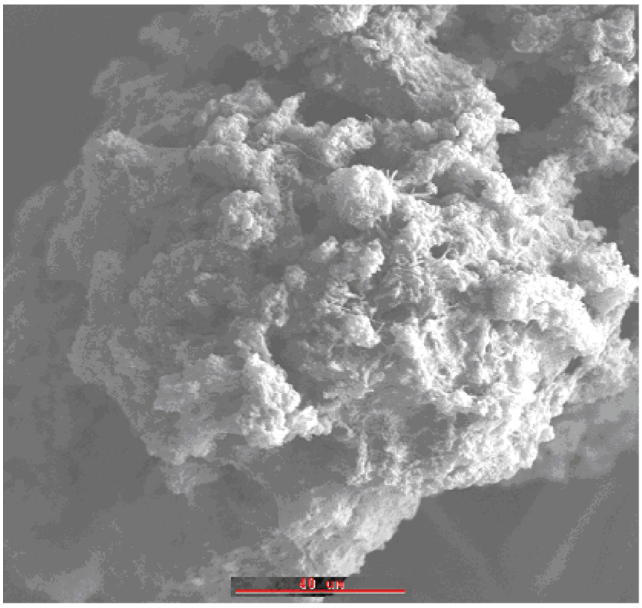

Fig. 7. SEM of Cu MWNT/CD.

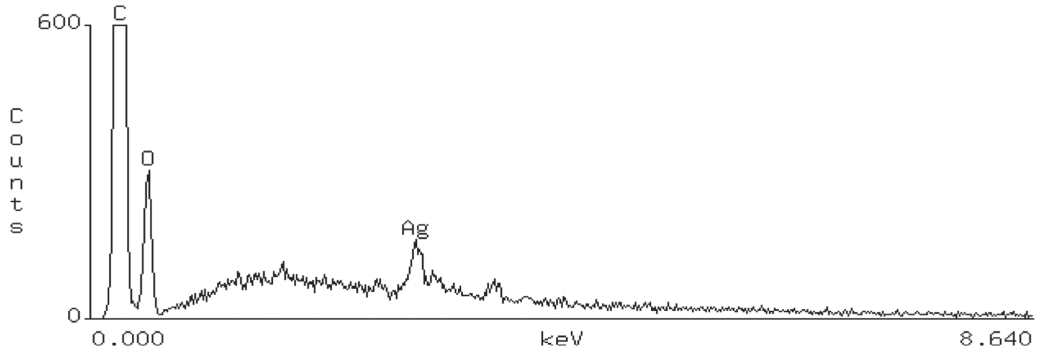

Fig. 8. EDX spectrum of Ag CNT/CD polymer.

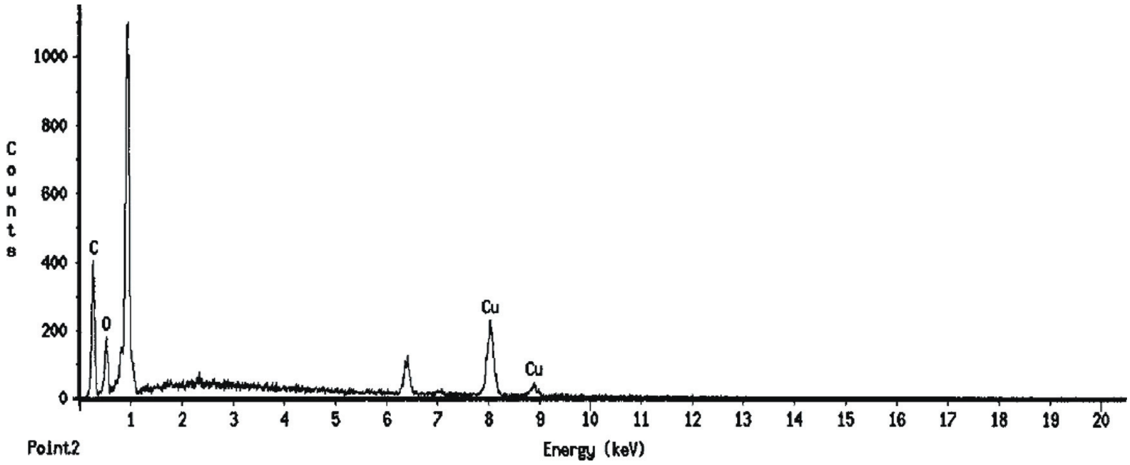

Fig. 9. EDX spectum of Cu MWNT/CD polymer.

Table 1
BET characterization of native cyclodextrin polyurethanes and their metal impregnated analogues

Sample name	BET surface area (m^2/g)	Pore volume (cm^3/g)
CD/HMDI	1.72	0.0087
MWNT/CD	5.72	0.0074
Ag MWNT/CD	0.78	0.00031
Cu MWNT/CD	0.3383	0.00194

Note: CD/HMDI – Cyclodextrin hexamethylene dii*so*cyanate, MWNT/CD – Multiwalled carbon nanotubes cyclodextrin polymer, Ag MWNT/CD – Silver impregnated carbon nanotubes and cyclodextrin polymer. Cu MWNT/CD – Copper impregnated carbon nanotubes and cyclodextrin polymer.

Table 2
PNP removal by native cyclodextrin polyurethanes and their metal impregnated analogues

Polymer	Initial PNP concentration (ppm)	Residual PNP ± standard deviation (ppm)	% Removal
CD/HMDI	10	3.8 ± 0.47	62
MWNT/CD	10	2.2 ± 0.44	88
Ag MWNT/CD	10	4.8 ± 0.63	52
Cu/MWNT/CD	10	4.5 ± 0.66	55

Table 3
Colony forming unit counts of spiked water samples

Sample	Mean (cfu/ml) ± standard deviation
E. coli	$8.5 \times 10^5 \pm 1.5 \times 10^5$
S. typhi	$1.1 \times 10^5 \pm 3.5 \times 10^4$

The primary goal of this study was to determine the bacterial count reduction capabilities of the nanoparticle impregnated polymers. In a typical water treatment system, the use of activated carbon would necessarily account for the removal of organic micro-pollutants. Activated carbon adsorption usually precedes chlorination disinfection in most water treatment trains. It is worth noting that the nano-metal impregnated polymers also showed some capacity to remove a typical contaminant such as *p*-nitrophenol. This is useful because while reducing the bacterial count, this system can still adsorb any residual organic micro-pollutant that would not have been removed by the activated carbon.

3.6. Bacterial count reduction of test waters

Test waters used were water samples spiked with *S. typhi* and *E. coli*. Table 3 shows the bacterial counts for the initial concentrations of spiked water prepared during the studied period.

Table 4 illustrates the resultant bacteria counts after treatment with the various types of polymer samples. Generally a reduction in bacterial counts was observed with all polymers. For example, the CD/HMDI polymer reduced *S. typhi* by one log reduction of in the first 30 min was observed whereas the silver impregnated polymer resulted in a 3 log reduction of the same bacteria. In conventional water disinfection and household treatment, a contact time between 20 and 30 min between water and the disinfectant is considered sufficient for significant bacterial reduction. The metal impregnated polymers showed a 2 log reduction of *E. coli* in the first 30 min whereas the metal-free polymers only had a 1 log reduction. After 90 min, the *E. coli* counts were 88 cfu/ml in silver polymer treated water and a 190 cfu/ml in copper polymer treated water. These metal impregnated polymers exhibited 3 log reduction of *Salmonella* at 90 min. The MWNT/CD polymer exhibited a 2 log reduction of *Salmonella* and a 1 log reduction for *E. coli* at 90 min.

From the results obtained, it can be deduced that the metal impregnated polymers exhibited a higher log reduction compared to polymer species with no

Table 4
Viable *E. coli* and *S. typhi* counts after treatment with cyclodextrin based polymers

Count in time (cfu/ml)		Polymer			
Time (min)	Sample	CD/HMDI	MWNT/CD	Ag MWNT/CD	Cu MWNT/CD
30	*S. typhi*	1.2×10^4	2.0×10^3	7.8×10^2	1.36×10^3
	E. coli	1.7×10^4	5.1×10^4	4.1×10^3	7.3×10^3
60	*S. typhi*	1.3×10^4	2.7×10^3	1.6×10^2	4.1×10^2
	E. coli	2.1×10^4	4.4×10^4	3.1×10^3	2.1×10^2
90	*S. typhi*	2.3×10^4	4×10^3	1.24×10^2	2.7×10^2
	E. coli	2.6×10^4	6.0×10^4	8.8×10	1.9×10^2

metal nanoparticles. The antibacterial mechanism of silver and copper is based on the interaction of the bacterial cell membrane and the metal surface [4]. Metal nanoparticles interact with the lipopolysaccharide layer on the exterior of the Gram negative cell wall of *E. coli.* These lipopolysaccharides contain covalently linked lipids and polysaccharides that lack strength and rigidity; hence their interaction with metal nanoparticles leads to the disintegration of the cell wall followed by the leakage of cellular contents leading to cell death [9]. However, the reduction of bacterial counts by metal-free polymers was a result of the adhesion of bacteria cells onto polymer surfaces. The adhesion is due to weak electrostatic forces between the carbon surface and the bacterial cell wall [20]. The adhesion is weak and short-term hence the material can be classified as weakly bacteriostatic, and the amounts of viable bacteria in the effluent water increases with time. Also, there is a significant difference between the performance of metal impregnated polymers and the metal-free polymers.

The ratio of bacterial cells inactivated per gram of polymer does affect the polymers efficiency at removing bacteria from water. For the two metal impregnated polymers the ratio was slightly different. For the copper polymer, the bacterial cells inactivated per gram ratio is in the region of 10^3 cfu/ml while for the silver polymer, the ratio is in the 10^4 cfu/ml region.

3.7. Interaction of nanomaterial with E. coli bacteria

Fig. 10 clearly reveals that the *E. coli* bacterium is entrapped on the surface of the carbon nanotubes (CNTs) while still maintaining its cell structure. Therefore, the multiwalled CNTs interact less with the outer membrane of *E. coli* (bacteristatic) [21]. One possible explanation for the less sensitivity of Gram-negative bacteria such as *E. coli* is that they contain an outer membrane that is predominantly made of tightly packed phospholipids and lipopolysaccharide (LPS) molecules which face into the environment that help provide an effective resistive barrier against the MWCNTs [22–24].

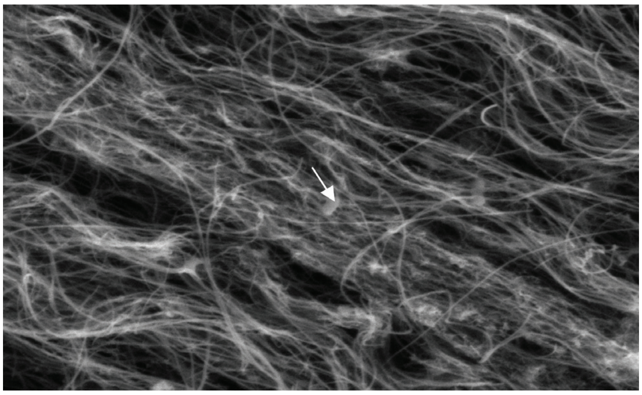

Fig. 10. A SEM image of *E. coli* cells on MWNTs. The arrow shows an *E. coli* cell on MWNTs.

However, when copper is supported on the MWCNTs there is direct interaction with the copper nanoparticles that results in the bactericidal effect of copper against the *E. coli* as observed in Fig. 11. The inhibitory mechanism of copper nanoparticles against the bacteria involves microbial cell wall chelation, DNA cleavage and enzyme inhibition due to the leaking of intracellular substances that eventually leads to the disturbance of the respiration process and death of the microorganism [22,25–27]. Moreover, the CNTs aid in the transportation of the electrons away from the copper surface and enhances the antibacterial effect.

3.8. Nanoparticle leach-out studies

In addressing nanomaterials' toxicity towards the environment and humans, it was necessary to assess the leachability of the metal nanoparticles immobilized onto the polymers [28]. Water treated with both metal impregnated polymers was found to contain less than 0.1 mg/l concentration levels of copper and silver in the treated water which was below the instrument's detection limit. According to the World Health Organization's drinking Water Quality Guidelines, silver levels of 0.1 mg/l and 2mg/l of copper can be considered not to be a health risk. These concentrations give a total dose over 70 y of half the human NOAEL (no-observed-adverse-effect-level) of 10 g of silver [29]. Copper is an essential trace element in the human diet and its presence in water in trace amounts does not pose a health risk but can be advantageous. There were therefore no detectable metal nanoparticles in the water that could pose a significant health risk since their levels were below the NOAEL stipulated by the WHO.

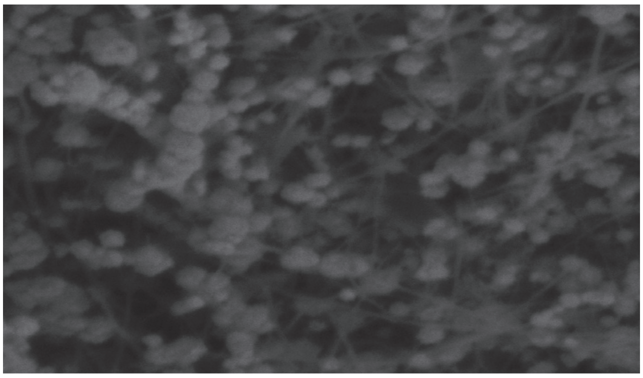

Fig. 11. A SEM image of *E. coli* cells on Cu/MWNTs.

4. Conclusions

The synthesis of metal impregnated polymers was achieved and confirmed by the various characterization techniques. The surface area and pore sizes of the metal impregnated polymers were quite low when compared to the MWNT/CD and CD/HMDI polymers. This could be attributed to the processing of the polymer involved during the loading of metal nanoparticles. The metal loaded polymers were able to reduce bacterial counts in spiked water to as low as 88 cfu/ml. Comparing the MWNT/CD polymer and CD/HMDI polymer, it can be concluded that metal nanoparticles loading enhanced the polymers' antibacterial property. Copper impregnated polymers possess lower antibacterial activity compared to the silver impregnated polymer. Also, the copper impregnated polymer has a lower bacterial-cells-per-gram of polymer ratio. Factors such as differences in nanoparticle size and surface interaction can be the reason why the two metal loaded polymers have different antibacterial performances. However, the removal of organic pollutants from water by these metal polymers was lower compared with the metal-free polymers.

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References

[1] J. Theron, J.A. Walker and T.E. Cloete, Crit. Rev. Microbiol., 34 (2008) 43–69.
[2] T.P. Anshup, Thin Solid Films, 517 (2009) 6441–6478.
[3] J.R. Morones, J.L. Elechiguerra, A. Camacho, K. Holt, J.B. Kouri, J.T. Ramirez and M.J. Yachman, Nanotechnology, 16 (2005) 2346–2353.
[4] I. Sondi and B.S. Sondi, J. Colloid Interf. Sci., 275 (2004) 1170–1782.
[5] K. Yoon, J. Byeon, J. Park and J. Hwang, Sci. Total Environ., 373 (2007) 572–575.
[6] A. Top and S. Ulkun, Appl. Clay Sci., 27 (2004) 13–19.
[7] B.J. Kim and S.J. Park, J. Colloid Interf. Sci., 325 (2008) 279–299.
[8] S. Pal, Y.K. Tak and J.M. Song, Appl. Environ. Microbiol., 73 (xxxx) 1712.
[9] S.K. Gorgoi, P. Gopinanth, A. Paul, A. Ramesh, A. Ghosh and A. Chattopathyay, Langmuir, 22 (2006) 9322.
[10] M.N.B. Momba and T.E. Cloete, Water Res., 30 (1996) 364–370.
[11] S.D. Freese and D.J. Noziac, Water SA, 30(5) (2004) 18–24.
[12] B. Genthe and R. Kfir, Water Res., Commission Report, 469/1/95, 1995.
[13] K.L. Salipira, B.B. Mamba, R.W.M. Krause, T.J. Malefetse and S.H. Durbach, Environ. Chem. Lett., 5 (2007) 13–17.
[14] K.L. Salipira, B.B. Mamba, R.W.M. Krause, T.J. Malefetse and S.H. Durbach, Water SA, 34(1) (2008) 113–118.
[15] B.B. Mamba, R.W. Krause, T.J. Malefetse and S.P. Sithole, S. Afr. J. Chem., 61 (2008) 133–140.
[16] K. Dai, L. Shi, J. Fang and Y. Zhang, Mater. Sci. Eng., 465 (2007) 283–286.
[17] A.L. Wang, H.B. Yin, M. Ren, X.N. Cheng, Q.F. Zhou and X.F. Zhang, Acta Metall. Sinica., 19 (2006) 362–370.
[18] L.S. Clesceri, A.E. Greenberg and R.R. Trussel, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, Washington, DC, (1989).
[19] H.O. Ibarra, N. Casillas, V. Soto, B.M. Soto, R.T. Vitela, W. Cruz and S.G. Salazar, J. Colloid Interface Sci., 31 (2007) 562–571.
[20] S. Shrivastava, T. Bera, A. Roy, G. Singh, P. Ramachendraro and D. Dash, Nanotechnology, 18 (2007) 225103–225112.
[21] L.R. Arias and L. Yang, Langmuir, 25 (2009) 3003–3012.
[22] K. Yoon, J.H. Byeon, J. Park and H. Hwang, Sci. Total Environ., 373 (2007) 572–575.
[23] R. Brayner, R. Ferrari-Iliou, N. Biivois, S. Djediat and M.F. Benedetti, Nano Lett., 6 (2006) 866–870.
[24] L. Fan, J. Song and P.D. Hildebrand, J. Appl. Microbiol., 9 (2002) 144–148.
[25] M. Tumer., H. Koksal, M.K. Sener, et al., Transition Met. Chem., 24 (1999) 414–420.
[26] S.A. Ibrahim, H. Yang and C.W. Seo, Food Chem., 1009 (2008) 137–143.
[27] S. Khan, S.A.A. Nami, K.S. Siddigi, E. Husain and I. Naseem, Spectrochimica Acta Part A: Mole. Biomol. Spectrosc., 72 (2009) 421–428.
[28] C.F. Schutte and W. Focke, Water Research Commission Report, KV 195/07, (2007).
[29] WHO, Guidelines for Drinking-Water Quality, 3rd ed., World Health Organisation, Geneva, 1 (2006).