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COMPARATIVE STUDIES OF SILVER DOPED CARBON NANOTUBES AND β-CYCLODEXTRIN FOR WATER DISINFECTION

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Various nanocomposites consisting of silver nanoparticles (by reductive pre-treatment of Ag^+) coated on multi-walled carbon nanotubes/β-cyclodextrin (1wt.%Ag-MWCNTs/β-CD), multi-walled carbon nanotubes (32wt.% Ag-MWCNTs), β-cyclodextrin (10wt.% Ag/β-CD) and a series of various concentrations of multi-walled carbon nanotubes on β-cyclodextrin (1, 2, 3wt.% MWCNTs/β-CD) were prepared as confirmed by X-ray diffraction (XRD), Field emission scanning electron microscopy (FE-SEM) and Energy dispersive X-ray spectroscopy (EDX). The nanocomposites were investigated for removal of *p*-nitrophenol (PNP) and *Escherichia coli (E. coli),* ATCC 25922 bacteria from water samples. The XRD data revealed that the smaller crystallite size of Ag particles on MWCNTs/β-CD enhanced the antibacterial activity. A 100% antibacterial activity was recorded (on 1wt.%Ag-MWCNTs/β-CD) within 10 minutes of interaction, compared with 1wt.% MWCNTs/β-CD, 32wt.% Ag-MWCNTs and 10wt.% Ag/β-CD which showed 88%, 95% and 97%, respectively. The high surface area of 1wt.% MWCNTs on β-CD correlated with high PNP absorption efficiency, as compared to high concentration of MWCNTs on β-CD and all Ag containing nanocomposites. The study revealed that 1wt.% MWCNTs on β-CD and smaller Ag crystallites on MWCNTs/β-CD played a significant and specific role on organic and bacterial contaminants, respectively.

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1. Introduction

Pure drinking water is an essential need for human survival. Every human requires sufficient uncontaminated water every day for drinking, food preparation, and bathing [1]. Microorganisms are accountable for many diseases initiated by consumption of contaminated water. Common treatment methods for removing harmful biological species from water involve ozone, or strong oxidants containing halogens, peroxides, or related compounds [2]. However dispersion of chemicals in water leaves undesirable chemical by-products that can be harmful in many ways [2].

Nanoporous polymers such as cyclodextrin alone and its combination with MWCNTs have demonstrated the ability to remove organic compounds in water through the formation of inclusion complexes of the guest-host type [3-5]. Salipira *et al.*,[4] have reported a removal of 99% of *p*-nitrophenol using cyclodextrin polymer that have been copolymerized with carbon nanotubes. A report by Lukhele *et al*., [6] has shown that Cyclodextrin polymerised with silver impregnated MWCNTs, removes 95% of the bacteria within 90 min. They further noted that possible leaching of silver when using silver impregnated polymers does not pose any significant health risk since levels are below 0.1 mg/L (World Health Organization acceptable levels). On the toxicity of MWCNTs, studies by Aillon *et al*., [7] have reported conflicting and inconsistent data,

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while others [8, 9] have noted that it is biocompatible. However, none of the above studies have investigated the surface properties of Ag particles and the combine effects of MWCNTs and β-CD on both organic and bacterial contaminants in water.

Herein; the paper has focus on comparative studies of various nanocomposites for their effectiveness in removing both organic and bacterial contaminants in water. A series of MWCNTs on β-CD were successfully prepared and compared with Ag-MWCNTs, Ag/β-CD and Ag-MWCNTs/β-CD. The study aimed at investigating the surface properties and comparing the effects of different concentrations of MWCNTs on β-CD and the role of Ag on MWCNTs/β-CD during the removal of PNP as well as *E-coli* bacteria.

2. Experimental

2.1 Materials and preparation methods

Silver nanoparticles were synthesised by a wet chemical method [10]. Polymerisation of carbon nanotubes with cyclodextrin was undertaken following the method used by Salipira *et al*., [4] Silver containing MWCNTs, β-CD and MWCNTs/β-CD were synthesised following the method described in our previous studies [9].

2.2 Removal of contaminants in water samples

Different concentrations of PNP were prepared in distilled water. Solid-phase extraction was carried out to determine the concentrations of PNP that can be absorbed by different nanocomposites. Approximately 100 mg of nanocomposites were packed on the column for extraction of PNP. The filtrates were collected and their absorbance was measured at 318 nm using an Ultraviolet-visible (UV-Vis) spectrophotometer. Disinfection of water contaminated with *E. coli* bacteria (ATCC 25922) were carried out following the method described previously [9]. The percentage inactivation of the bacteria was calculated from the visible number of colonies.

3. Results and discussion

3.1 Characterisation of nanocomposites

The Field emission scanning electron microscopy (FE-SEM) image of 32 wt.% Ag-MWCNTs (Fig.1b) show the presence of flower-like, silver particles (Fig. 1a) attached on the surface of carbon nanotubes. The FE-SEM image of 10 wt.% Ag/β-CD (Fig.1c) displayed a spongy cyclodextrin polymer randomly attached to the silver particles. The FE-SEM image of 1wt.%Ag-MWCNTs/β-CD (Fig. 1d) shows silver particles attached to both MWCNTs and β-CD.

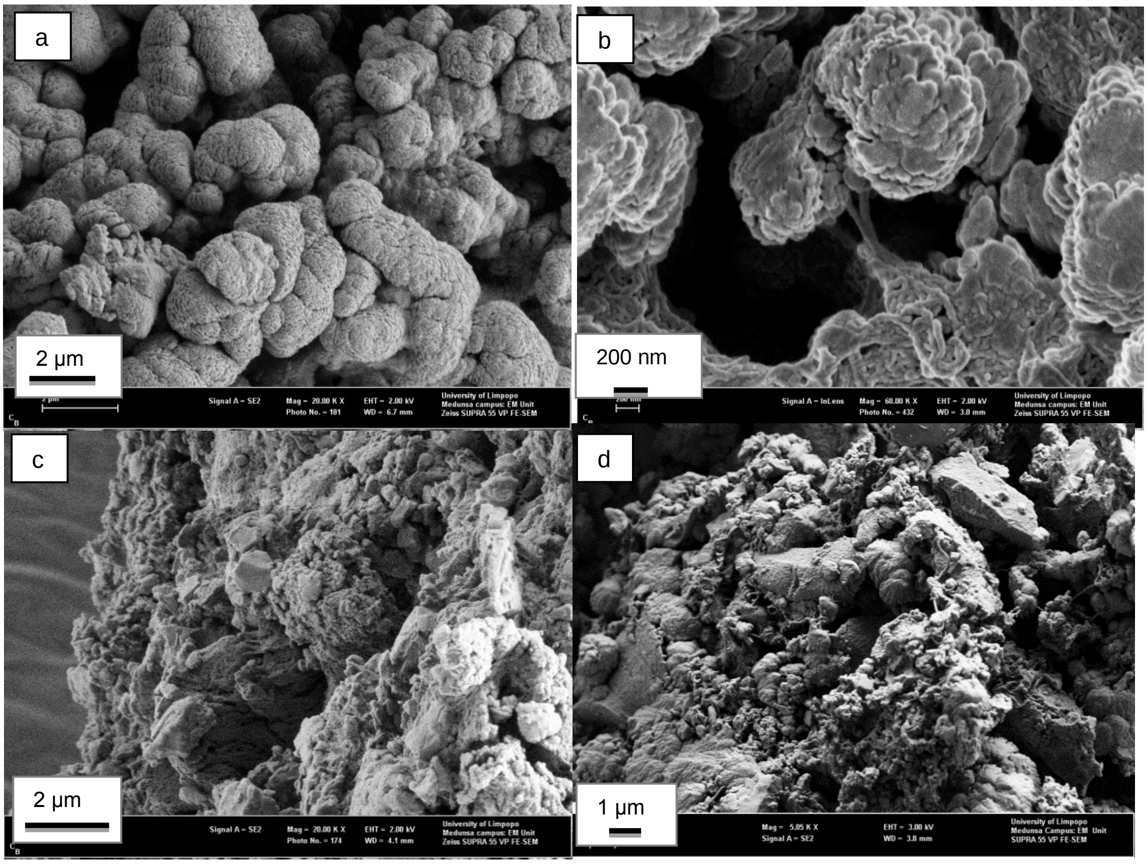

Fig. 1. FE-SEM micrographs of (a) silver (b) 32wt.% Ag-MWCNTs (c) 10wt.% Ag/β-CD and (d) 1wt.% Ag-MWCNTs/β-CD nanocomposites.

Fig. 2b shows the XRD patterns of 1wt.%Ag-MWCNTs/β-CD, 32wt.% Ag-MWCNTs and 10wt.% Ag on β-CD nanocomposites. The data confirms the presence of silver particles in all nanocomposites and the intensity of (111) plane increased with amount of silver. Higher silver loading reduced the intensity of the (002) plane, corresponding to carbon reflection of both cyclodextrin polymer and carbon nanotubes. Similar results were observed by Ma *et al*., [11]. The calculated crystallites sizes of Ag [using the width at half height of (111) plane peak intensity] was 4.67 nm for 32wt.%Ag-MWCNTs, 5.25 nm for 10wt.%Ag/β-CD and 2.93 nm on 1wt.%Ag-MWCNTs/β-CD. This data shows that smaller Ag particles were deposited throughout the organic frameworks of either MWCNTs and/or β-CD. Hence, the leaching of Ag nanoparticles was reduced [12]. The Energy dispersive X-ray spectroscopy (EDX) of 32wt.% Ag-MWCNTs and 1wt.%Ag-MWCNTs/β-CD, confirms the deposition of Ag particles on both nanocomposites (Fig.2a).

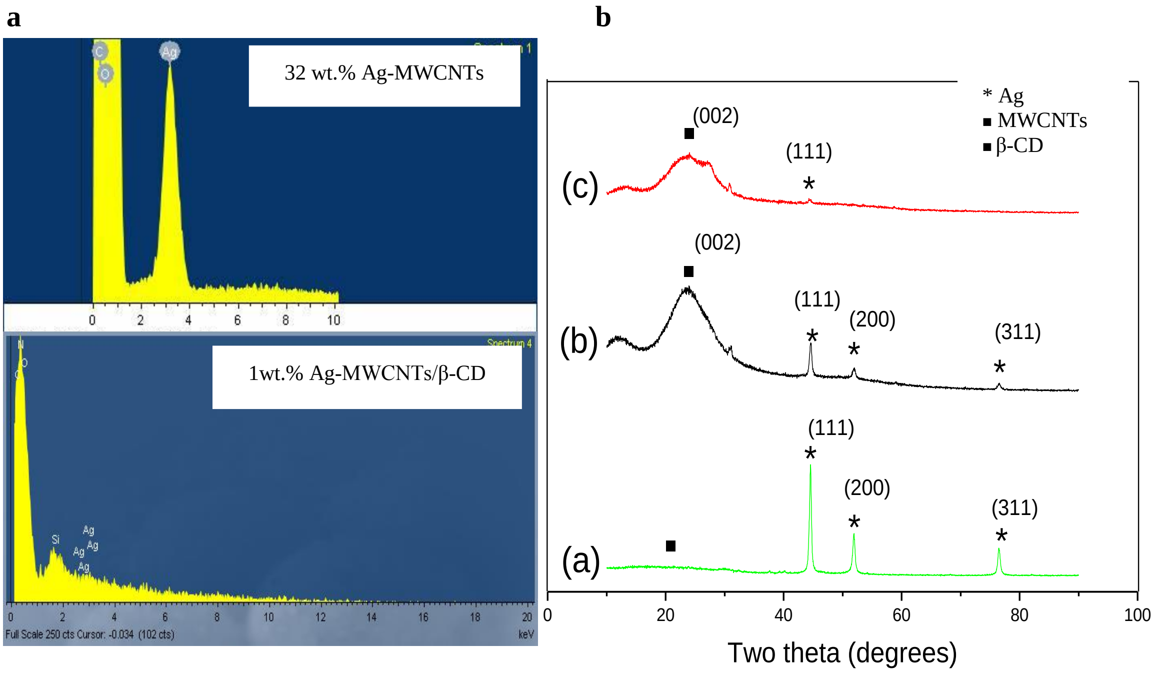

Fig. 2a. EDX of 32wt.% Ag-MWCNTs and 1wt.%Ag-MWCNTs/β-CD nanocomposites. Fig. 2b. XRD profiles of (a) 32wt.%Ag-MWCNTs (b) 10wt.% Ag/β-CD and (c) 1wt.%Ag-MWCNTs/β-CD nanocomposites.

3.2 Disinfection of water contaminated with *p*-nitrophenol (PNP)

The data in table 1 shows the percentage absorption of PNP in water samples and Brunauer-emmet-teller (BET) surface area analysis of the nanocomposites. The data shows that all three series of MWCNTs/β-CD nanocomposites are capable of removing higher PNP levels, as reported by Salipira *et al.*, [4]. The surface area and PNP absorption percentage of sample 1 to 3, decreased with an increase in carbon nanotubes loading. These results suggests that a small amount of carbon nanotube addition in cyclodextrin polymers is generally required in order to achieve a high surface area of the nanocomposite materials. This also ensures that the MWCNTs are not easily leached out into the environment, [12] since MWCNTs are incorporated on β-CD. The role of surface area was noted and not undertaken by Salipira *et al.*, [4].

The table also shows that 1wt.% Ag-MWCNTs/β-CD, 32wt.%Ag-MWCNTs and 10wt.% Ag/β-CD nanocomposites had lower PNP absorption compared to the combined series of MWCNTs and β-CD composites. These reveals that silver particles lowers the PNP absorption efficiency of MWCNTs/β-CD nanocomposites. The occupation of the available absorption sites by silver particles is noted to be the main hindrance and as a result reduced the surface area of the mixture of MWCNTs/β-CD and silver particles (Sample 6), as confirmed by BET surface area analysis (Table 1).

Table 1 BET surface area and absorption analysis of PNP using nanocomposite materials.

Sample no:	Sample name	Surface area (m^2/g)	Initial concentration (mg/L)	Final concentration (mg/L)[a]	PNP absorbed (%)[b]
1	1wt.% MWCNTs/β-CD	3.65	10	0.34	97
2	2wt.% MWCNTs/β-CD	2.23	10	0.44	96
3	3wt.% MWCNTs/β-CD	1.76	10	0.52	95
4	32wt.%Ag-MWCNTs	4.73	10	6.9	31
5	10wt.% Ag/β-CD	0.039	10	6.6	34
6	1wt.%Ag-MWCNTs/β-CD	0.652	10	4.2	58

[a]The absorption studies were repeated three times. [b] The % PNP was calculated as follows: % PNP = $[(C_{in}-C_{fin})/(C_{in})]$ *100

3.3 Disinfection of water contaminated with *E. coli* bacteria

Fig. 3 shows the effects of different nanocomposite materials on inactivation of *E. coli* bacteria. Interesting to note is that the combination of MWCNTs and β-CD doped with 1wt.% Ag (i.e., 1wt.%Ag-MWCNTs/β-CD), gave better antibacterial activity compared to 32wt.% Ag-MWCNTs, 10wt.% Ag/β-CD and 1wt.% MWCNT/β-CD. The 1wt.%Ag-MWCNTs/β-CD nanocomposite was able to inactivate all the bacteria within 10 minutes of contact. The bactericidal effect of the nanocomposite is highly enhanced as compared to the results reported by Lukhele *et al.*, [6] on related nanocomposite. The findings are attributed to the deposited smaller crystallite sizes of Ag, as confirmed by XRD data. This is clearly due to the differences in preparation method of silver nanoparticles [9]. Thus the study reveals that the Ag particle size plays a significant role on the bactericidal effects of 1wt.%Ag-MWCNTs/β-CD nanocomposites. Hence, the nanocomposite is mainly effective at removing bacteria in water.

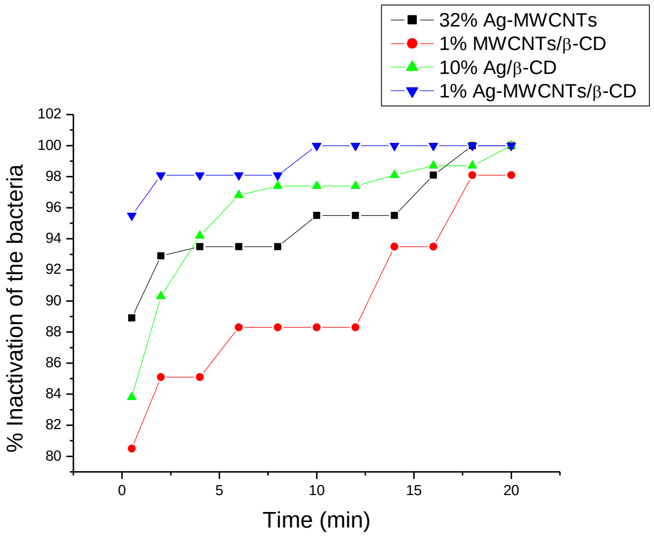

Fig. 3. Effects of different nanocomposites on the E-coli bacteria in contaminated water samples.

4. Conclusions

Different nanocomposites were successfully prepared as confirmed by XRD, FE-SEM and EDX. The high surface area of 1wt.% MWCNT/β-CD correlated with the high absorption of PNP. Silver based nanocomposites had lower PNP absorption efficiencies which were attributed to their low surface area; however they performed well in antibacterial studies due to the antibacterial properties of Ag nanoparticles. It is believed that the smaller crystallite size of Ag particles contributed to high bactericidal activity of 1wt.% Ag-MWCNTs/β-CD. Based on these results the 1wt.% MWCNTs/β-CD and 1wt.% Ag doped MWCNTs/β-CD nanocomposites can be used simultaneously to disinfect water contaminated with both organic and bacterial contaminants.

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