

# Characterization and Detection of Cadmium Ion Using Modification Calixarene with Multiwalled Carbon Nanotubes

Amira Shakila Razali, Faridah Lisa Supian, Muhammad Mat Salleh, Suraini Abu Bakar

**Abstract**—Water contamination by toxic compound is one of the serious environmental problems today. These toxic compounds mostly originated from industrial effluents, agriculture, natural sources and human waste. These studies focus on modification of multiwalled carbon nanotube (MWCNTs) with nanoparticle of calixarene and explore the possibility of using this modification for the remediation of cadmium in water. The nanocomposites were prepared by dissolving calixarene in chloroform solution as solvent, followed by additional multiwalled carbon nanotube (MWCNTs) then sonication process for 3 hour and fabricated the nanocomposites on substrate by spin coating method. Finally, the nanocomposites were tested on cadmium ion (10 mg/ml). The morphology of nanocomposites was investigated by FESEM showing the formation of calixarene on the outer walls of carbon nanotube and cadmium ion also clearly seen from the micrograph. This formation was supported by using energy dispersive x-ray (EDX). The presence of cadmium ions in the films, leads to some changes in the surface potential and Fourier Transform Infrared spectroscopy (FTIR). The nanocomposites MWCNTs-calixarene have potential for development of sensor for pollutant monitoring and nanoelectronics devices applications.

**Keywords**—Calixarene, Multiwalled Carbon Nanotubes, Cadmium, Surface Potential.

## I. INTRODUCTION

ONE of basic needs of life is water. Without water, all plants, human and animal will perish. The contamination of water by heavy metal is one of the most serious environmental problems today. The main sources of this metal are industrial effluents, agriculture runoffs, natural sources and human activities [1]. The effect of heavy metals such as cadmium (Cd), lead (Pb), zinc (Zn) and copper (Cu) on human health have been investigated [2]. Cadmium (Cd) is one of the potentially toxic heavy metals when absorbed into the body. The presence of Cd in drinking water even at low concentration level may cause disease such as osteoporosis, osteomalacia and bone defects [3].

Therefore, effective techniques and material can be used to remove of heavy metal from water need to be developed. Several methods such as reduction, reverse osmosis and ion

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exchange have been used to remove heavy metal from water [4]. Most of these methods are not effective in removing heavy metal to extremely safe levels. Adsorption techniques have many advantages and shown great potential in removing heavy metal and some organics in wastewater especially at medium to low ion concentration [5].

Thin film of calixarene derivatives have been widely used in sensor. Calixarene is a macrocyclic or cyclic oligomer based on hydroxyalkylation product of phenols and aldehyde, where phenolic sub-units are bridged by methylene spaces forming a ring with upper rim, lower rim and central annulus as illustrated in Fig. 1 [6]. Besides that, it is known that calixarene can form host-guest complexes with metal ions.

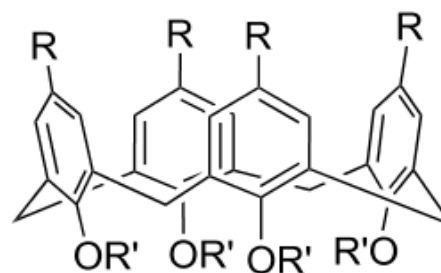


Fig. 1 Division of calixarene (applicable to all calixarene)

In this study, we used a type calix[8]arene incorporating with carbon nanotube (CNT) and indicate their ability in removing heavy metal such Cd from water. In following section we present the experimental details of sample preparation and characterization result obtained FTIR, STEM, FESEM, EDX and surface potential ( $\Delta V$ ).

## II. EXPERIMENTAL METHOD

### A. Materials

Chloroform ( $\text{CHCl}_3$ , >99.8% purify) were purchased from Fisher Scientific. Multi-walled carbon nanotubes (MWCNTs) prepared by chemical vapor depositions (CVD) were purchased from Shenzhen Nanotech, China. The MWCNTs have a purify >95% and diameter of tubes average (10-20) nm and length of >1  $\mu\text{m}$ . 5,11,17,23,29,35,41,47-p-tert-butyl-49,50,51,52,53,54,55,56-Oktakis[(carboxy)-pentoxy]-calix[8]arene was obtained from Institute of Technology, Tallaght, Dublin, Ireland and named as calix[8]arene. The molecular structure of calix[8]arene is shown in Fig. 2.

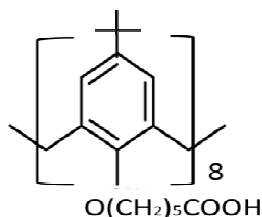


Fig. 2 Molecular structure of 5,11,17,23,29,35,41,47-p-tert-butyl-49,50,51,52,53,54,55,56-Oktakis[(carboxy)-pentoxy]-calix[8]arene

### B. Modification of MWCNTs with Calix[8]arene and Preparation of Films

For the fabricated of MWCNTs-calix[8]arene nanocomposite films, the following procedure was used. There are two categories of sample needed to be prepared. Category A is MWCNTs-calix[8]arene on substrate of quartz without the presence of Cd and the other is with the presence of Cd, category B. The solution of materials, concentration of 0.2 mg/ml was prepared by dissolving 2 mg of calix[8]arene powder in 10 ml of chloroform ( $CHCl_3$ ) under 1 hour sonication process. 2 mg MWCNTs were added into each perfectly solved calix[8]arene solution and also sonication process 3 hours was applied into these mixture nanocomposite solutions. Long sonication process, it's mechanically cutting off long MWCNTs structure [7].

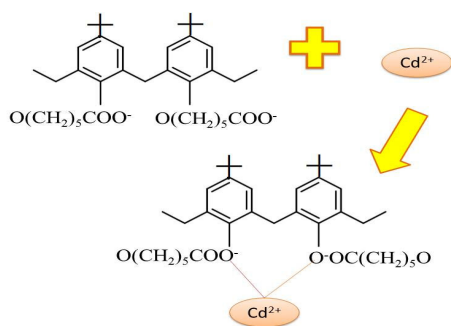


Fig. 3 The mechanism of calix[8] detection  $Cd^{2+}$  ions

MWCNTs-calix[8]arene nanocomposite were deposited layer by layer on silicon wafers (2.5x2.5) cm and quartz substrate with 3000 rpm and 15.0 s using spin coating process. Finally, the substrate was heated in the oven with the temperature of  $80^\circ C$  for 20 minutes. For sample with presence of Cd (category B), the stock solutions of  $Cd^{2+}$  were prepared by dissolving of 125.5 mg  $CdCl_2$  respectively in 10 ml of deionized water (DI) and sonication process 30 minutes. The substrate that has been deposited with MWCNTs-calix[8]arene by spin coating technique was immersed in Cd stock for 15 minutes then was reheated at the temperature of  $80^\circ C$  for 20 minutes. The mechanism calix[8]arene detected  $Cd^{2+}$  as shown in Fig. 3.

### C. Characterization of MWCNTs-calix[8]arene Nanocomposite with Cd and without Cd

The MWCNTs-calix[8]arene nanocomposites films with the presence Cd and without the presence Cd were used for

analysis and characterization. Fourier transform infrared (FTIR) spectroscopic measurements were performed by using Thermo Nicolet 6700 Nexus with attenuated total reflectance method. For the measurement of Surface potential ( $\Delta V$ ), KSV Surface Potential Meter (SPOT) as shown in Fig. 4 with a vibrating plate condenser connected to the counter electrode which was place at the bottom of the trough. The vibrating plate is placed approximately 1-2 nm from the substrate to achieve an accurate reading of surface potential. High resolution field emission scanning electron microscope (FESEM) enables to visualize the morphology of the surface model Hitachi SU 8020 UHR.

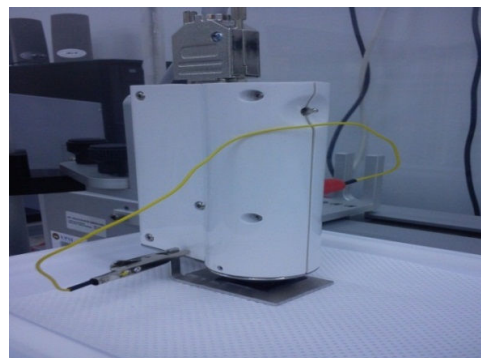


Fig. 4 KSV Surface Potential Sensor (SPOT)

## III. RESULT AND DISCUSSION

### A. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy gives more information about the vibrational properties and functional group present on the sidewall of functionalized sample in IR range [8]. The IR transmittance spectra of all functionalized sample calix[8]arene are shown in Fig. 5. Spectra (a) in Fig. 5 show the FTIR spectrum of calix[8]arene with an absorption at  $3676\text{ cm}^{-1}$  is attributed  $-OH$  of phenol which usually adsorbs strongly in range of  $3680\text{--}3584\text{ cm}^{-1}$  region [9]. The peak at  $2260\text{ cm}^{-1}$  can be assigned to the  $C\equiv C$  stretch mode from medial alkyne of aromatic ring calix[8]arene.

In Fig. 5 (b), the MWCNTs-calix[8]arene nanocomposite show IR spectra at  $2916\text{ cm}^{-1}$  and  $2845\text{ cm}^{-1}$  are due to the  $-CH_2$  stretch mode which is indicative of the presence of MWCNTs. By doing this analysis, it is proven that calix[8]arene has successfully incorporated with MWCNTs by identification of functional group present on the sidewall of the functionalized sample. FTIR analysis for MWCNTs-calix[8]arene nanocomposite immersed in  $Cd^{2+}$  solution at concentration  $10 \times 10^{-2}\text{ mM}$  was done. Figs. 5 (b) and (c) show IR spectra of MWCNTs-calix[8]arene nanocomposite and MWCNTs-calix[8]arene with  $Cd^{2+}$ . By comparing both spectra, there is an extra peak at  $3064\text{ cm}^{-1}$  for MWCNTs-calix[8]arene with  $Cd^{2+}$  which is attributed the interaction of  $Cd^{2+}$  and  $-COOH$  of carboxyl group of calix[8]arene [10].

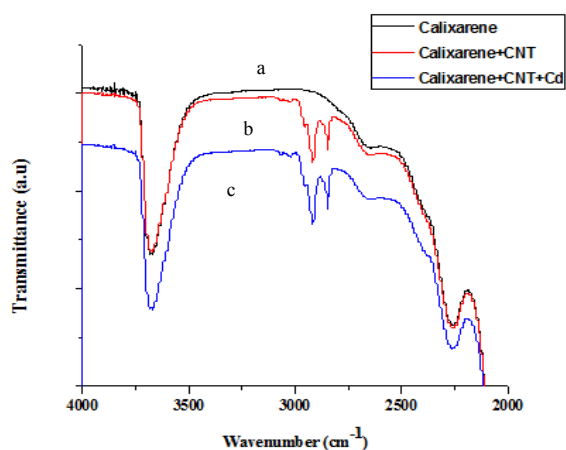


Fig. 5 FTIR spectra of (a) calix[8]arene, (b) MWCNTs-calix[8]arene nanocomposite and (c) MWCNTs-calix[8]arene with  $\text{Cd}^{2+}$

### B. Surface Potential ( $\Delta V$ )

Table I present the relationship between  $\Delta V$  max and the thickness of film, 10 layers and 20 layers. The thickness of films is referred to the number of layer deposited on silicon substrate by spin coating technique. The relationship can be seen at  $\Delta V$  max increase when the number of layer increases. Besides that,  $\Delta V$  max of nanocomposite MWCNTs-calix[8]arene nanocomposite film is much higher than calix[8]arene film. This indicates the presence of interaction between the MWCNTs and calix[8]arene decorated on the surface. MWCNTs are the ideal material to composite with calix[8]arene because MWCNTs are useful in improving thermal and mechanical strength as well as increase overall conductivity of calix[8]arene [11]. By these results, it is confirmed that the MWCNTs was successfully incorporated with calix[8]arene in thin films.

TABLE I  
 $\Delta V$  MAX OF CALIX[8]ARENE AND MWCNTS-CALIX[8]ARENE NANOCOMPOSITES

Sample	$\Delta V_{\text{max}}$ (mV)	
	10 Layers	20 Layers
Calix[8]arene	35	76
MWCNTs-Calix[8]arene	171	218

The  $\Delta V$  max of calix[8]arene and MWCNTs-calix[8]arene nanocomposite complex with  $\text{Cd}^{2+}$  ions are present in Table II. From the table, we noticed that the  $\Delta V$  max of calix[8]arene and MWCNTs-calix[8]arene nanocomposite increase and this indicates that both sample formed complexes with  $\text{Cd}^{2+}$  ions. Comparing the  $\Delta V$  max of calix[8]arene and MWCNTs-calix[8]arene presence  $\text{Cd}^{2+}$  in Table II, it is found that  $\Delta V$  max of MWCNTs-calix[8]arene nanocomposite is higher than sample calix[8]arene. Addition of CNT to calix[8]arene molecule improved the adsorption capacities of calix[8]arene. This may be due to the fact that the cavity of calix[8]arene opens up as more functionality are attached to the lower rim resulting in a larger cavity that can accommodate more  $\text{Cd}^{2+}$  ion. The result report quite similar with author [2], [12]

showed that MWCNTs-calix[8]arene are effective in capturing  $\text{Cd}^{2+}$  from water.

TABLE II  
 $\Delta V$  MAX OF 10 LAYERS AND 20 LAYERS FILMS INCORPORATED WITH  $\text{Cd}^{2+}$

Sample	$\Delta V_{\text{Max}}$ (mV)	
	10 Layers	20 Layers
Calix[8]arene	35	76
Calix[8]arene With $\text{Cd}^{2+}$	56	81
MWCNTs-Calix[8]arene	171	218
MWCNTs-Calix[8]arene with $\text{Cd}^{2+}$	208	231

### C. Morphology and Structure Analysis by FESEM, TEM and EDX

The morphology of the MWCNTs-calix[8]arene nanocomposite was detected by field emission scanning electron microscope (FESEM) are illustrated in Fig 6. The FESEM images of MWCNTs show the smooth surface and with diameter 30 nm (Fig. 6a). After modify MWCNTs with calix[8]arene, MWCNTs smooth surface change into rough surface as presented in Fig. 6b. Meanwhile the diameter enhanced to 60 nm. This indicates that calix[8]arene interaction on the exterior walls of MWCNTs. This indicates that calix[8]arene interaction on the exterior walls of MWCNTs. FESEM observation also showed that the homogenous sonication process (3 hour) of MWCNTs-calix[8]arene nanocomposite.

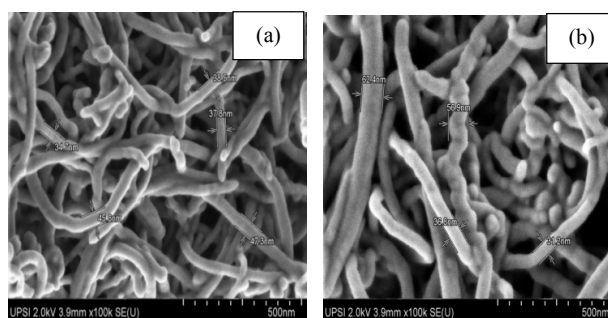


Fig. 6 FESEM images of (a) MWCNTs and (b) MWCNTs-calix[8]arene nanocomposite

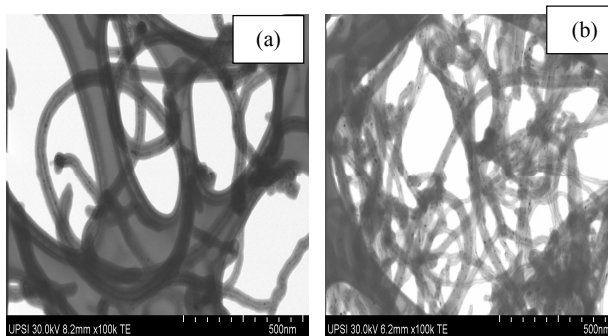


Fig. 7 STEM images of (a) MWCNTs and (b) MWCNTs-calix[8]arene nanocomposite

This may also be evident by the change of morphology in STEM measurement as shown in Fig. 7. The uniform surface of MWCNTs was observed, the perfect lattice structure of

carbon-carbon bonds while the modified MWCNTs showed some defects in carbon-carbon bonding associated with the formation of calix[8]arene on the surface [13].

Besides that, the formation of  $\text{Cd}^{2+}$  on the exterior walls of MWCNTs-calix[8]arene nanocomposite can be seen from FESEM micrograph shown in Fig. 8. This formation of  $\text{Cd}^{2+}$  on the surface of MWCNTs-calix[8]arene nanocomposite was supported by using energy dispersive x-ray (EDX) as shown in Fig. 9. The presence of the peak of Cd and  $\text{Cl}_2$  indicated that the MWCNTs-calix[8]arene had been incorporated with  $\text{Cd}^{2+}$  ions into the film.



Fig. 8 FESEM images of MWCNTs-calix[8]arene with  $\text{Cd}^{2+}$

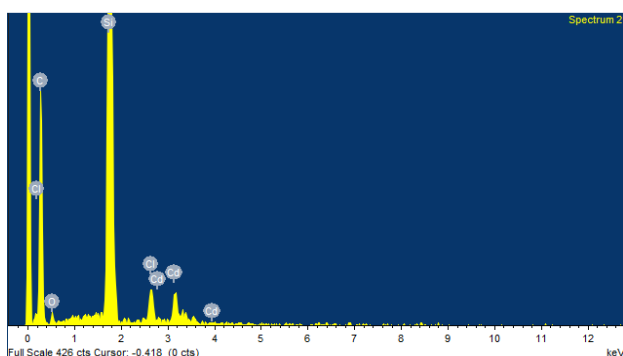


Fig. 9 EDX analysis of MWCNTs-calix[8]arene with  $\text{Cd}^{2+}$

#### IV. CONCLUSION

Preparation and characterization of nanocomposite MWCNTs-calix[8]arene was successfully achieved. The nanocomposites MWCNTs-calix[8]arene were prepared by dissolving in  $\text{CHCl}_3$  under sonication, followed by spin coating technique to fabricated films. The composite material has nanoparticle of calix[8]arene arranged on the surface of the MWCNTs. This approach has shown on FTIR, FESEM and TEM. From FTIR result shown two peaks is observed at  $2916\text{ cm}^{-1}$  and  $2845\text{ cm}^{-1}$  are due to the  $-\text{CH}_2$  stretch mode of MWCNTs which is overlapping MWCNTs on calix[8]arene surface. FESEM and STEM observation showed that the formation of amorphous (calix[8]arene) on outer walls of MWCNTs. The nanocomposite MWCNTs-calix[8]arene make it possible to form host-guest interaction in the adsorption of

$\text{Cd}^{2+}$  metal ions. The outstanding adsorption abilities for  $\text{Cd}^{2+}$  ion have exhibit good prospects for sensor application.

#### ACKNOWLEDGMENTS

The financial support (RACE Research Grant) of this work by Universiti Pendidikan Sultan Idris is gratefully acknowledge. The authors thank the Chemistry Department, Universiti Pendidikan Sultan Idris, Malaysia for providing all research facilities.

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