RESEARCH ARTICLE

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Multiwalled Carbon Nanotube Based Solid- Phase Extraction Cartridges and its Application in Waste Water Analysis

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ABSTRACT

Isolation of different organic impurity from industrial waste water was carried out using solid phase extraction (SPE) cartridges and analyzed by reverse phase high performance liquid chromatography.

Kalonji oil-a rich source of carbon, easily available in nature and cheap is used as a naturally occurring precursor for the synthesis of Multiwalled Carbon Nanotubes (MWCNTs) in laboratory by chemical oil vapor deposition technique (COVD) by direct pyrolysis at 800°C in an inert gas (Hydrogen) atmosphere. The obtained MWCNTs were purified by acid treatment and characterized by different analytical tools such as XRD (X-ray diffraction), SEM (Scanning Electron Microscope) and FTIR (Fourier Transform Infra-Red Spectroscopy), BET surface area analyser.These MWCNTs used directly to prepare solid phase extraction cartridges in laboratory and studied its application in isolation of organic impurities (Aniline and Phenol) from industrial waste water followed its identification by RP - HPLC (Reverse phase High performance liquid chromatography analysis).

Keywords: Solid-Phase Extraction, Multiwalled Carbon Nanotubes, Water Analysis, Organic Impurities.

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INTRODUCTION

Industrial waste water quality determination before directly pouring it to natural resources is very important now days which is directly or indirectly affecting health of human being and aquatic environment [1]. Different organic and inorganic impurities are the outputs of different chemical and pharmaceutical industries. Industrial effluent quality is determined by physical, chemical and biological parameters [2].Use of naturally occurring precursor for the manufacturing carbon nanotubes by in-house, simple and efficient method is utmost important to get multiwalled carbon nanotubes in laboratory [3]. Aniline is aromatic amine widely used in many chemicals, pharmaceutical, rubber and dye industries as chemical feedstock [4]. Aniline and phenols are carcinogens and are highly toxic to aquatic life even in trace amount [5]. Presence of Aniline in concentration of Synthesizing metallic ppm range will kill 50 % of exposed organisms within 96Hrs [6].

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Traditional methods of water purification such as liquid extraction, distillation, adsorption can be used for removal of many organic and inorganic impurities [7]. Now a day many chemical, dye making and pharmaceuticals industries are looking for alternative and reusable cheap material technologies for the purpose which can be used to overcome the disadvantages. As multiwalled carbon nanotubes

having highest surface area as compared to that of activated charcoal which is currently used in many industries for removal of organic and colored impurities from industrial effluents, the multiwalled carbon nanotubes have better performance abilities and advantages over the conventional methods. Functionalization of MWCNTs carried out with different functional groups and with different API's (Active Pharmaceutical Ingredients) [8] [9]. is also found to be useful in separation. Carbon Nano beads are also synthesized from naturally occurring oil [10] and can be used for multiple applications. The research objectives of this research is to execute the chepest, simple and reusable technology for treatment of industrial waste of chemical, dye making, pharmaceutical industries before pouring it to natural resources.

The adequate column sizes of such multiwalled carbon nanotubes once used till its loading capacity and can be reused after unloading the separated contaminants using some special treatments which will be found suitable over a conventional method of treating industrial effulents.

MATERIALS AND METHODS

Materials used for research work

Kalonji oil	: Purchased from local market
Aniline	: LR Grade (ACS chemicals)
Phenol	: AR Grade (Rankem)
Sodium dihydrogen orthophosphate	: AR Grade (Merck)
Formic acid	: AR Grade (Loba Chemie)
Water	: Deionized Milli Q
Methanol	: HPLC Grade (Rankem)
Industrial waste water	: Collected from MIDC Area

Synthesis Methodologies

Synthesis of Multiwalled Carbon Nanotubes: The MWCNTs was synthesized from Kalonji oil using a nickel catalyst, (detail method of synthesis of nickel catalyst is discussed elsewhere [11].) by COVD method by direct pyrolysis at 800°C in an inert atmosphere. In COVD synthesis [12], as represented herewith schematically in figure:1 where 'A' and 'B' are two electric furnaces (vaporizing furnace and pyrolysing furnace respectively). 10 g of Kalonji oil placed in quartz boat 'C' and 200 mg of nickel catalyst in other quartz boat 'D' and both the boats are kept e boats in furnance 'A' and furnace 'B' respectively. The inert gas hydrogen is allowed to pass through quartz tube 'Q' for 5 min with constant flow rate of 10cc/min so as to remove oxygen from the tube. The temperature of pyrolysing furnace 'B' was set to 800°C. Once the furnace 'B' reaches the desired temperature. The furnace 'A' was turned on and temperature was set to boiling point of Kalonji oil. The heating of furnance 'A' was continued till all oil gets vaporized. The heating of furnance 'B' was continued for one hour. The furnance 'B' is allowed to cool at room temperature and material was collected from boat 'D'.

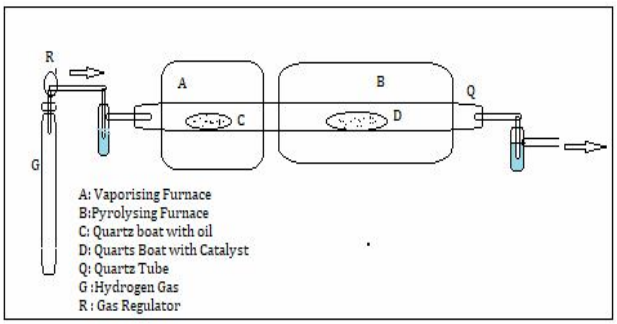

Figure 1: Schematic Diagram of Lenton's Split Tube Furnace

Purification of Multi Walled Carbon Nanotubes

As obtained MWCNTs from boat 'D' was soaked in Hydrochloric acid (50%) followed by Nitric acid (50%) solution for 24Hrs and sonicated for about 2.0 Hrs. The material is filtered using whatmann filter paper, collected and dried at 200°C for 3Hrs in drying air oven.

Characterization of Multi walled Carbon Nanotubes

Purified MWCNTs were characterized by ATR method of Shimadzu Spectrometer with IR Affinity model. X-ray diffraction (XRD) analysis was performed using Phillips analytical X-ray diffractometer with Cu Kα radiation running at 45 KV/40 mA in the 2θ range 2°–100° with step size of 0.02. Specific surface areas were measured using SmartSorb-92/93 model of Smart Instruments Co. Pvt. Ltd. by low temperature nitrogen adsorption using the Brunauer-Emmett-Teller (BET) single point method. The samples were degassed at 150°C for 2 hours prior to analysis. The morphological analysis was performed with a Phillips SEM 505 scanning electron microscope.

Fabrication of Solid-phase Extraction Cartridges

Figure 2 represents as prepared solid phase extraction cartridge in laboratory and it is prepared by handmade method. Weighed accurately about 0.5 g of purified MWCNTs and transferred to a plastic syringe of 5.0 cm length and 5.7 mm diameter

containing cotton plug at the bottom. This syringe containing MWCNTs was tapped for 10 minutes and vortexed for 10 minutes later. Once this material is packed, washed it with milli Q grade water followed by methanol and henceforth referred as MWCNTs based SPE cartridge.

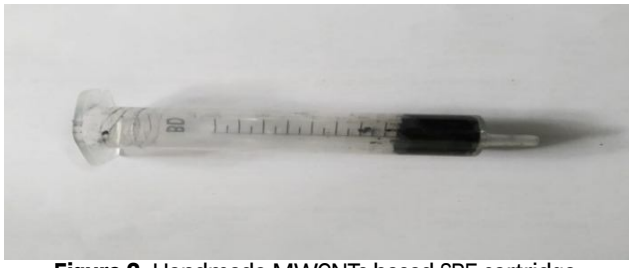

Figure 2: Handmade MWCNTs based SPE cartridge

Application of MWCNTs based SPE cartridge in waste water sample

Industrial waste water sample (1 L; 5.8 pH) were collected from MIDC area dombivali, Kalyan MS, India. This sample is centrifuged for 10 minutes to remove any solid suspended particles. The blank sample is analyzed for identifying the presence of any Aniline and phenol using RP-HPLC with photo Diode Array detector (PDA). The water sample was spiked with Aniline and phenol to get the concentration of each compound as 100 mg/L. The prepared sample was kept for overnight. On next day sample is sonicated and shake well before use, taken 10 ml of this sample and allowed to pass through the conditioned cartridge and allow to adsorb the added impurities on the surface of MWCNTs. Later the impurities were desorbed using Methanol (0.1 % Formic acid) The eluent was collected and concentrated using rotary evaporator and injected 20ul volume to HPLC, identified against standard solution chromatograms.

RP-HPLC Methodologies for Peak Identification

Thermoscientific RP-HPLC model 'Ultimate 3000' was used for the identification of isolated impurities. HPLC equipped with Quaternary low pressure gradient pump, PDA detector, column oven and autosampler is used for this analysis with HPLC column (Inertsil ODS 3V, 250mmX4.6mm and 5.0um particle size). Gradient elution was performed with 0.01M sodium dihydrogen orthophosphate buffer in water as mobile phase 'A' and Methanol as an organic eluent and constant flow rate 1.0 ml/min.

The gradient programme is maintained throughout the run as mentioned in below table1.

Table-1: HPLC Gradient Programme

Time (min)	Flow Rate (ml)	% Mobile Phase A (Buffer)	% Mobile Phase B (MeOH)
0	1.0	70	30
15	1.0	30	70
20	1.0	70	30
25	1.0	70	30

Aniline and phenol individual standard solutions are prepared in methanol (200 ppm each) and injected 20ul volume of each compound along with neat Blank and spiked samples and monitored using PDA detector at 230 nm wavelength.

Results and Discussions

Multiwalled Carbon Nanotubes

Figure 3(a) shows FTIR spectrum of as obtained MWCNTs. Spectra which shows significant band at 2870cm^{-1},2881cm^{-1}, 2924cm^{-1}and moisture related bands 3436 cm^{-1}.

Figure 3 (b) represents FTIR spectra after treatment with acid mixture i.e. after purification, significant increase in peak at 2924 cm-1 and peak related to –OH group at 3436 cm-1 is observed.

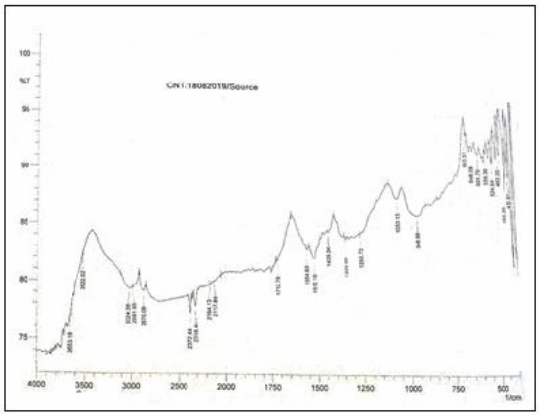

Figure 3(a): FTIR Spectrum of MWCNTs before Purification

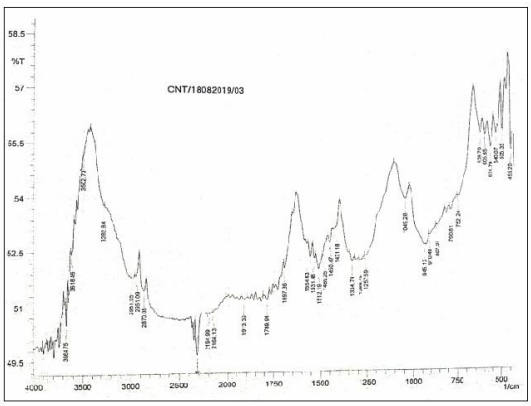

Figure 3(b): FTIR Spectrum of MWCNTs after purification

Characterization by Powder XRD Technique: Figure 4 X-ray Diffractogram of purified MWCNTs shows crystalline pattern which itself indicates the characteristic peaks one at about 2θ value 26° is a characteristic peak of MWCNTs and other represents the presence of trace level metallic impurities present in it.

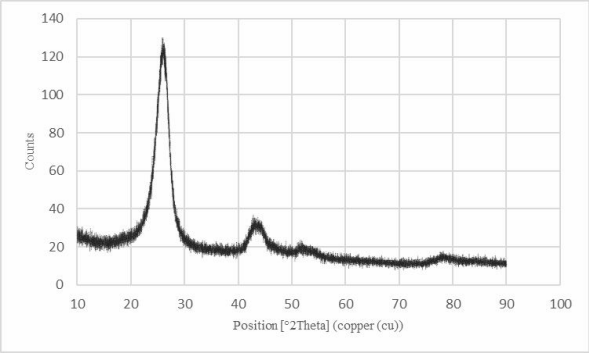

Figure 4: X-Ray Diffractogram of MWCNTs

Surface Area Measurement by BET Technique: Figure 5 indicates the surface area of purified MWCNTs. The higher surface area value was 102.42m^2/g which also proves the formation of nanosize.

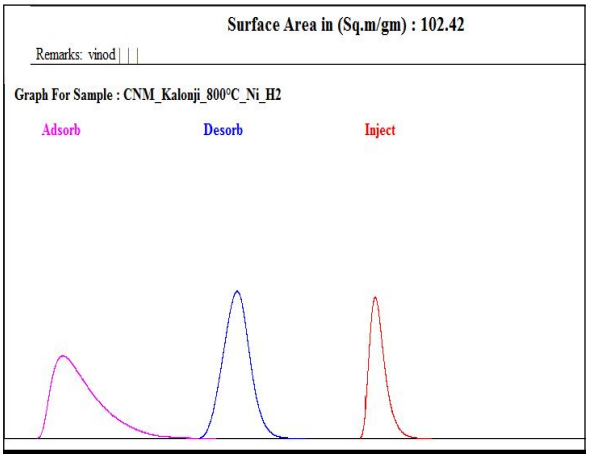

Figure 5: BET Surface Area of MWCNTs obtained from Kalonji oil

Morphology by Scanning Electron Microscopy : Figure 6 shows SEM image of purified MWCNTs obtained from Kalonji oil by COVD method. The SEM image shows the formation of MWCNTs with diameter in the range of 28-82nm.

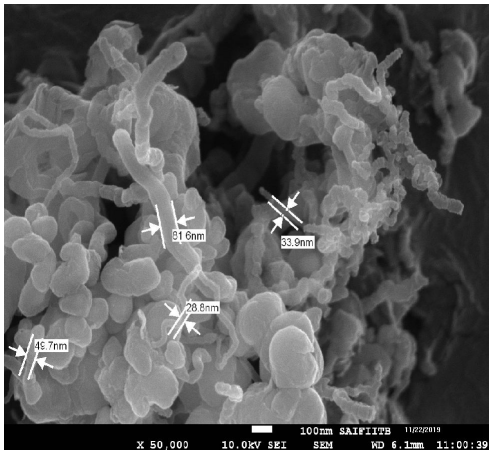

Figure 6: Scanning Electron Microscope Image of MWCNTs

Identification by using RP-HPLC: The obtained chromatograms of HPLC shows the presence of Aniline and phenol peaks collected post MWCNTs based SPE cartridge and confirms the proper isolation capacity of respective analyte as shown in figure 7.

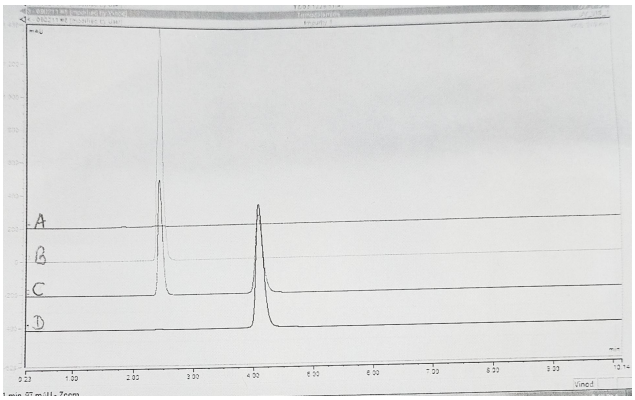

Figure 7: Overlay chromatograms by RP-HPLC

Where A: HPLC chromatogram of Blank (Neat water),
B: HPLC Chromatogram of Aniline
C: HPLC chromatogram of mixture of aniline and Phenol isolated from SPE Cartridges.
D: HPLC chromatogram of Phenol

Values on X axis of chromatogram represents Retention time of respective analyte in minutes while Y axis values represents absorbance in mAU.

CONCLUSION

MWCNTs based SPE cartridges prepared at lab scale are simple, reusable and cost effective as it is synthesized from natural precursor which is cheapest and easily available source. These MWCNTs based

SPE cartridges can be modified to industrial scale which will be a best alternative material for chemical, dye making and pharmaceutical industries to separate different aromatic compounds like aniline and Phenol from industrial effluent before pouring it to natural resources.

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