

## Summary of Thesis

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Carbon nanotubes (CNTs) are wonder materials and new allotropes of carbon and have a very high aspect ratio. These cylindrical carbon molecules have unusual properties, which are valuable for nanotechnology, electronics, optics and other fields of materials science and technology. Due to their extraordinary thermal conductivity and mechanical and electrical properties, carbon nanotubes find applications as additives to various structural materials. CNTs can be used to prepare novel materials such as hydrogen storage materials, super conductors, reinforced materials etc.

They have very large surface areas, and large exposed surface areas show tremendous adsorption ability. Adsorption heterogeneity and hysteresis are two widely recognized features of organic chemical-CNT interactions. Different mechanisms mainly hydrophobic interactions, pi-pi bonds, electrostatic interactions, hydrogen bonds, and adsorption of organic chemical adsorption on CNTs may account for adsorption behavior. Adsorption mechanisms will be better understood by investigating the effects of properties of both CNTs and organic chemicals along with environmental conditions. Due to their adsorption characteristics CNTs have potential applications in separation sciences and water treatment.

This thesis describes the various methods of synthesis of various types of CNTs and their basic properties, basically related to adsorption behavior.

This thesis also explains the water crises in India and the available water recourses. The various technologies used for water purification as sulfide precipitation, carbonate precipitation, solvent extraction, cementation, ultrafiltration and nanofiltration membrane processes, reverse osmosis etc. have been described. Thus use of nanotubes as an advancement over conventional methods has been described.

The use of carbon nanotubes in pure or composite forms the major base of present study. The nanosize materials also have the capacity of altering the pore diameters of polymeric membranes. This property has been used for heavy metal rejection studies using only carbon nanotubes and CNT/Polysulfone nanocomposite membranes, where effect of addition of CNTs to polysulfone has been recorded in terms of porosity and hydrophilicity variation.

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## ***Chapter 2***

This chapter describes the metal rejection behavior of CNT's without functional groups and with different functional groups such as oxidized, acylated, reduced, amide and azide functionalized CNT's. Cleaned nanotubes were treated with various chemical reagents to introduce  $-\text{COOH}$ ,  $-\text{OH}$ ,  $-\text{COCl}$ ,  $-\text{CONHCH}_2\text{CH}_2\text{NH}_2$  groups respectively onto CNT surface. The overall rate constant for physisorption reaction for all metal ions onto CNT's with varying functional groups have been studied and compared.

Batch adsorption isotherm studies have been conducted by using five concentrations (900, 1000, 1500, 1750 and 2500  $\mu\text{g/L}$ ) of Chromium solution at pH 3.5 and  $25 \pm 1^\circ\text{C}$ . The amount of metal ion adsorbed by amide and azide functionalized CNTs per gram ( $Q_e$  mg/g) was calculated.

It was confirmed that % removal is a function of time and continuously increases with time of contact, upto a point where equilibrium is reached. At equilibrium the adsorption process becomes steady and does not increase with increase in contact period. Maximum adsorption and thus percentage removal is observed for Chromium followed by that of Lead. It has been observed that the Freundlich model is more suitable to fit the adsorption data than Langmuir model since the correlation coefficients are higher.

### ***Chapter 3***

In this chapter, we perform a systematic analysis of the chemical oxidation of MWNT's treated by various reagents that possess different degrees of oxidation power. The cleaned graphitic surfaces were treated with acid mixture ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ), acid piranha ( $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}_2$ ), base piranha ( $\text{NH}_4\text{OH}$ ,  $\text{H}_2\text{O}_2$ ) and  $\text{KMnO}_4$ ,  $\text{CH}_3\text{COOH}$  in presence of a phase transfer catalyst. All the reactions were performed at room temperature for 1-2 h. All these processes gave different results in respect to degree and type of functionalization, cutting of lengths and damage of sidewalls, which have been reported in this chapter. The surface morphology and surface concentration of functional groups were determined by various analytical techniques such as SEM, FT-IR, Raman and titration analysis. The functionalized CNT's material were quantitatively analyzed by titration analysis using a standard strong acid-base titration procedure to determine the --COOH concentrations on their surface of the treated CNTs. TGA curves with different degradation points were obtained, according to various functional groups and have been included in this chapter to account for the presence variation in degree and type of functionalization. Oxidation with  $\text{H}_2\text{SO}_4/\text{HNO}_3$  under extreme conditions (reflux) increases the defect formation, shortens the length and gives highest degree of functionalization. The degree of defect formation and functionalization followed the trend  $\text{H}_2\text{SO}_4/\text{HNO}_3 > \text{Base piranha} > \text{Acid piranha} > \text{KMnO}_4$ . Use of non-acidic treatments such as the mixture of  $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{O}_2$ , facilitates the complete removal of carbonaceous materials and gives good number of functional groups, though less as compared to treatment with acid mixture but better as compared to acid piranha.

## ***Chapter 4***

In this chapter various studies related to flux improvement, pore structure and size control have been done on polysulfone/CNT composite membranes. In the present study modified CNT's (oxidized, amide and azide functionalized) were used to enhance the interaction with the polysulfone matrix. The prepared composite membranes were characterized by FT-IR, SEM, TGA.

Pore size and contact angle measurements have been carried out to show that presence of MWNT's remarkably decrease the pore size and contact angle, and increase the hydrophilicity of membranes. The FTIR spectra of blend membranes have been shown to confirm the presence of hydrogen bond interaction between functional groups of CNT's and sulfonic groups of polysulfone membrane. MWNTs owing to their high mechanical and heat resistance, offer increased heat tolerance to composite membranes. Heavy metal rejection studies have been carried out for  $\text{Cr}^{+6}$ ,  $\text{Cd}^{+2}$ ,  $\text{Pb}^{+2}$ ,  $\text{Cu}^{+2}$  and  $\text{As}^{+3}$  at different pressures for all composite membranes.

Amide and azide functionalized carbon nanotubes gave better results as compared to oxidized CNTs at acidic pH 2.6 and pressure 4.90 bars, which was better than plain unfunctionalized CNTs. All the observations with results make an important part of this chapter.

## Chapter 5

In present study we report the use of novel initiators acylated carbon nanotubes and acetyl chloride for ATRP of PMMA and polystyrene.

In a typical experiment, CuCl and bidentate ligand 2,2'-bipyridyl were mixed in RBF, equipped with a magnetic stirring bar and to this, emulsion of monomer was transferred by means of cannula using vacuum. To this system initiator was injected dropwise under nitrogen purging. The reaction mixture was stirred at room temperature and at 60°C. The reaction was quenched by intensive cooling and diluted with tetrahydrofuran (THF). The formed polymer was recovered by precipitation in a non-solvent.

PMMA as well as polystyrene have been prepared and analyzed by FT-IR,  $^{13}\text{C}$  NMR, TGA, SEC and DSC techniques. The number average molecular weights ( $M_n$ ), weight average molecular weights ( $M_w$ ) and polydispersities were determined by GPC. The GPC results show that formed polymers have high molecular weights as compared to  $M_{\text{theo}}$ . The linear plots of  $\ln[M]_0/[M]$  with time confirm the process to follow first order kinetics. The linear variation of polydispersity and average molecular weight with %conversion also account to formation of a polymer with good molecular weight distribution. It concludes that Acylated carbon nanotubes" and acetyl chloride can be used as initiators for ATRP, and that reducing the surfactant concentration gives a better control over molecular weights.