Synthesis of Carbon Nanomaterials and Effects of Post-Treatment on Removal of Heavy Metals from Water

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Abstract-- **Carbon nanomaterials (CNMs) can be synthesized and used for various applications. In this study, two CNMs of different surface morphology were synthesized using chemical vapor deposition (CVD) by altering the process parameters. Different post-treatments were given to CNMs for removal of the catalyst. The effect of post-treatment on CNMs was observed by monitoring the carbon content and the contact angle. The treatment time of CNMs was optimized based on sorption potential of selected heavy metals. Treatment of CNMs resulted in removal of amorphous carbon and change in hydrophobicity of the samples. In addition to surface morphology of the CNMs, post-treatment processes also played an important role in affecting the heavy metal sorption characteristics.**

***Index Terms*—Carbon nanomaterials, Nanoporous carbon, sorption.**

I. INTRODUCTION

Heavy metals are released into the environment by natural or anthropogenic sources through waste disposal, smelter stacks, and the disposal of sewage sludge. Heavy metals are ubiquitous in the environment, since they are not biodegradable. Moreover, heavy metals pose potential risk due to their bioaccumulation tendency. While the pollutant levels in our water resources are increasing, the drinking water guidelines are also becoming more stringent [1]. Clean water, free of toxic chemicals and pathogens is essential for human health. Moreover, water is also an essential utility used in most industries, such as, food processing, pharmaceuticals and electronics. Most of the countries in the world are facing an uphill task in meeting the rising demand for clean water since many of the available freshwater resources are contaminated. Sustainable supply of clean water is an increasingly important national and international issue, and there is an urgent need to conquer the situation with novel technologies [2]. It is thus, important to develop competent technologies with the help of recent advancement in research for delivering clean water to the public and industry to ensure uninterrupted progress of mankind.

Nanotechnology is about synthesizing structures, devices and systems at nanoscale. As the size of the substances are reduced to nanoscale, the properties of substances may change dramatically and relatively inert substances may become more reactive. At nanoscale surface properties become more important, because the surface area to mass ratio increases and the proportion of the total number of atoms at the surface of a structure are larger. This phenomenon eventually alters the properties, such as, chemical reactivity, thermal and electrical conductivity, optical and magnetic behavior and tensile strength. The change in properties of nanomaterials make them vibrant for research. Different nanomaterials with their exceptional properties may be utilized for developing novel techniques which may help in environmental remediation [3].

CNMs can be synthesized by several techniques, such as, Arc-discharge method, Laser ablation method and Chemical Vapor Deposition (CVD) method [4]. However, the CVD method was reported to be highly promising for scale-up of defect-free and controlled synthesis of CNMs [5]. CNMs synthesized using CVD may exist in several forms, such as, singlewalled carbon nanotubes (SWCNTs), multiwalled carbon nanotubes (MWCNTs), carbon beads, carbon fibres, nanoporous carbon, etc. CNMs have been studied widely for potential applications in catalyst supports, optical devices, quantum computer, and biochips. However, their sorption potential has not been studied extensively. CNMs are engineered materials targeted to exhibit unique surface morphologies, hence, they may prove to be good sorbents [6]. Carbon nanotubes (CNTs) have shown exceptional adsorption capability and high adsorption efficiency for various organic pollutants such as, benzene [7], 1, 2-dichlorobenzene [8], trihalomethanes [9] and polycyclic aromatic hydrocarbons (PAHs) [10]. CNTs were found to be superior sorbents for inorganic pollutants such as fluoride [11], and several divalent metal ions [12], [13], [14] and [15]. CNTs with more defects and poor quality possessed higher surface area and exhibited better lead sorption capacity compare to aligned CNTs [13]. Post-treatment of CNTs play an important role in enhancing the maximum sorption capacity. Post-treatment causes removal of catalyst and amorphous carbon in CNMs. Moreover, alteration of surface

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morphology and addition of surface functional groups due to post-treatment of CNTs under oxidizing conditions with chemicals such as, HNO_3, $KMnO_4$, H_2O_2, NaOCl, H_2SO_4, KOH, and NaOH have been widely reported [11], [16], [17] and [18]. The few studies to date indicate that CNTs have a great potential for removal of contaminants from water. However, studies on adsorption of trace pollutants on CNMs are still very limited in the literature. In this work, CNMs synthesized by CVD were characterized and the effect of post-treatment on heavy metal sorption was evaluated. Further, the sorption potential of CNMs is also compared with commercial activated carbon (AC).

II. MATERIALS AND METHODS

Different types of CNMs were produced in the laboratory using a CVD unit (Fig 1). The detailed synthesis process was described by [19], [20] and [21]. A brief process description follows. A quartz reactor was designed to pass through a vaporizing furnace and a pyrolising furnace. The organic precursor was kept inside the vaporizing furnace. Simultaneously, the catalyst was kept inside the pyrolising furnace. The process parameters play an important role for structure and surface morphology of CNMs. Nanocarbon (NC) was synthesized by pyrolysis of organic precursor in the furnace under nitrogen environment with cobalt as catalyst. Similarly, nanoporous carbon (NPC) was synthesized by pyrolysis of organic precursor in the furnace under hydrogen environment with silica as catalyst. Synthesis of CNMs was carried out by pyrolysis of the organic precursor at high temperature.

After deposition of NC on the cobalt catalyst, cobalt was removed by digestion with strong HNO_3 (70%) for 3 h and subsequently activating with 30% KOH solution for opening the pores [11], [16] and [20]. A similar treatment was also given to NPC, although it was synthesized using silica as catalyst, to evaluate the effect of treatment with HNO_3. After treatment with HNO_3, the NPC was further treated with 30% KOH for different time duration (1h, 5h and 10h) for optimization of the post-treatment time. Similarly, after HNO_3 treatment, the NC was further treated with 30% KOH for the optimized time to evaluate the effect of treatment with 30% KOH. Hence, both NC and NPC were treated with similar post-treatment protocols (i.e., with 70% HNO_3 for 3h and 30% KOH for 1h) and their potential for removal of different heavy metals were evaluated.

CNMs were characterized using X-ray diffractometer (XRD, Philips PW3040/60 X'pert PRO, Netherlands) employing Cu/K_α radiation. The XRD patterns were interpreted with standards from International Centre of Diffraction Data. Surface morpholgy was analysed using Scanning Electron Microscopy (SEM, Hitachi S3400N, Netherlands). Elemental analysis of CNMs were carried out by CHNSO Analyser (Thermo Finnigan FLASH EA 1112 series, Italy) and surface hydrophobicity of CNMs were analysed by Powder Wettability Instrument (GBX Instrumentation CAP26, France). Equilibrium studies were carried out in polypropylene vials at room temperature and at constant ionic strength (0.01 M), pH (7.0) and fixed CNM loading (0.5 g/L). Nitrate salts of Pb, Ni, Zn and Cd were used for preparing the solution and the initial heavy metal concentration was 1 meq/L. The vials were tumbled for 12 h to allow sufficient time for equilibration. The solutions were filtered and the final aqueous phase concentration (C_e) of metal ions were determined by an Atomic Absorption Spectrophotometer (AAS, GBC-902 Scientific Equipments Pvt. Ltd., Australia).

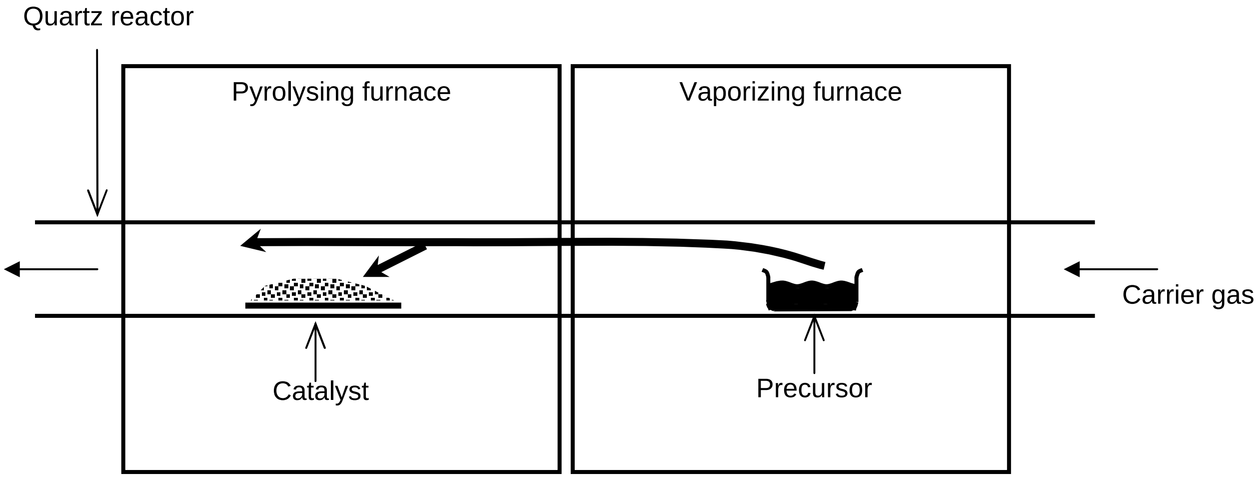


Fig 1. Schematic of the CVD setup

III. RESULTS AND DISCUSSIONS

The XRD pattern of AC, NC and NPC revealed characteristic peaks for all the samples at 12.05, 24.01 and 39.28 which correspond to the (002), (004) and (200) graphitic planes. SEM images of AC, NC and NPC are reported by [21]. These images reveal vast differences in surface morphology among the three carbon samples. AC mainly consists of flake-like material in which the pore structure was not visible. The porous structure was not evident in NC, however its surface was filled with verically grown nanorods. In contrast, NPC exhibited a highly porous honeycomb-like structure. Uniform porosity was clearly observed at high magnification throughout the sample. Its structure was unique and distinctly different from AC and NC. Post-treatment of synthesized CNMs is necessary, because it contain catalyst and amorphous carbon, which may fill-up the pores and block the active sites for soption (Fig 2a).

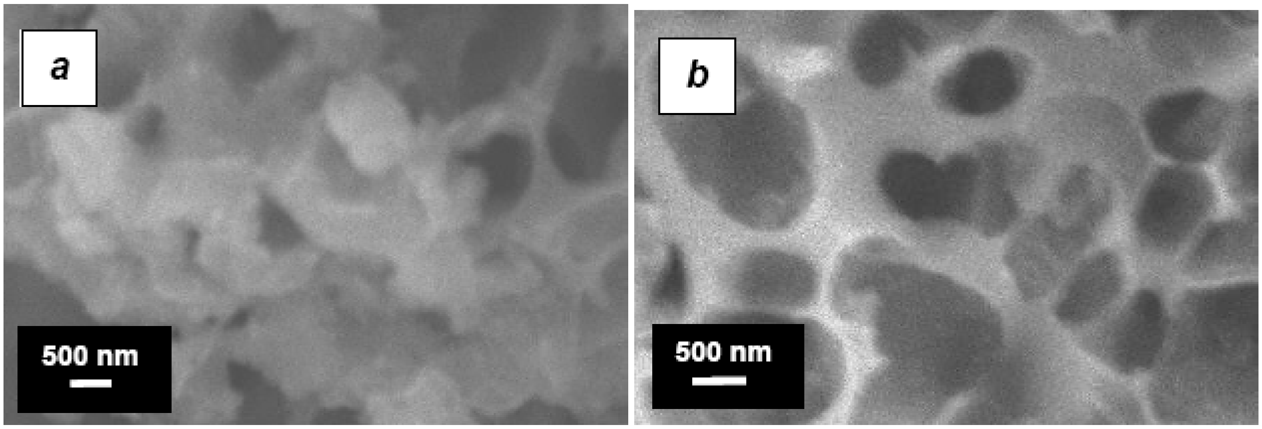
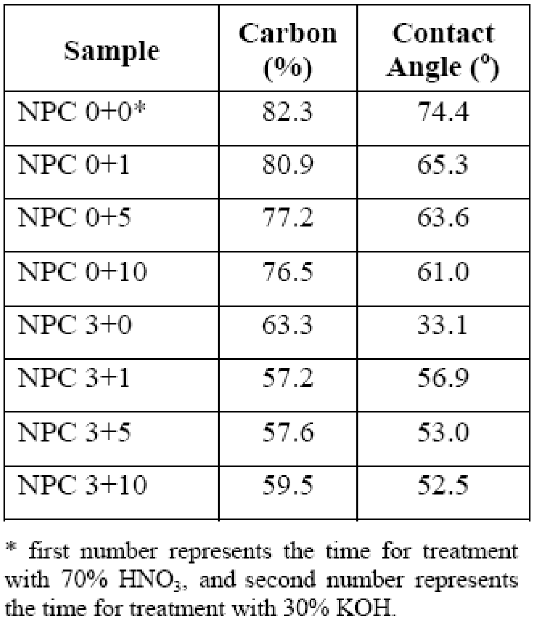


Fig 2. SEM images of (a) NPC before treatment and (b) after treatment

Post-treatment of CNMs can remove catalyst particles as well as amorphous carbon, which also results in removal of blockages, and consequently increases the availability of active sites for sorption (Fig 2b). The characterization of NPC after post-treatment with 70% HNO_3 followed by 30% KOH for different time duration is illustrated in Table 1. It is observed that NPC without treatment (0+0) has relatively higher carbon content. Furthermore, the untreated NPC has higher contact angle, which implies a hydrophobic nature of the sample.

The untreated sample of NPC exhibited poor sorption potential for sorption of the selected heavy metals (Fig 3). This could be due to the hydrophobic nature of the sample. The carbon percentage in CNMs was moderately reduced after post-treatment with KOH for different time duration (0+1, 0+5 and 0+10). The reduction in the contact angle of NPC was not very significantly reduced after the alkaline treatment. The sorption potential of the NPC samples treated only with KOH did not demonstrate much improvement (Fig 3). Acidic treatment of NPC resulted in significant reduction of carbon percentage and contact angle. This implies that amorphous carbon and hydrophobicity of the sample is reduced. However, slight improvement in sorption potential of the NPC (3+0) was observed. The observation could be due to blockage of active sites on NPC by the silica particles which were used as catalyst for NPC synthesis. For a post-treatment process consisting of acidic treatment followed by alkaline treatment, the carbon content of the sample and contact angle were reduced significantly. It was observed that sorption potential of NPC (3+1, 3+5 and 3+10) was significantly higher (Fig 3).

TABLE 1: EFFECTS OF POST-TREATMENTS ON NPC



Sample	Carbon (%)	Contact Angle (°)
NPC 0+0*	82.3	74.4
NPC 0+1	80.9	65.3
NPC 0+5	77.2	63.6
NPC 0+10	76.5	61.0
NPC 3+0	63.3	33.1
NPC 3+1	57.2	56.9
NPC 3+5	57.6	53.0
NPC 3+10	59.5	52.5

* first number represents the time for treatment with 70% HNO_3, and second number represents the time for treatment with 30% KOH.

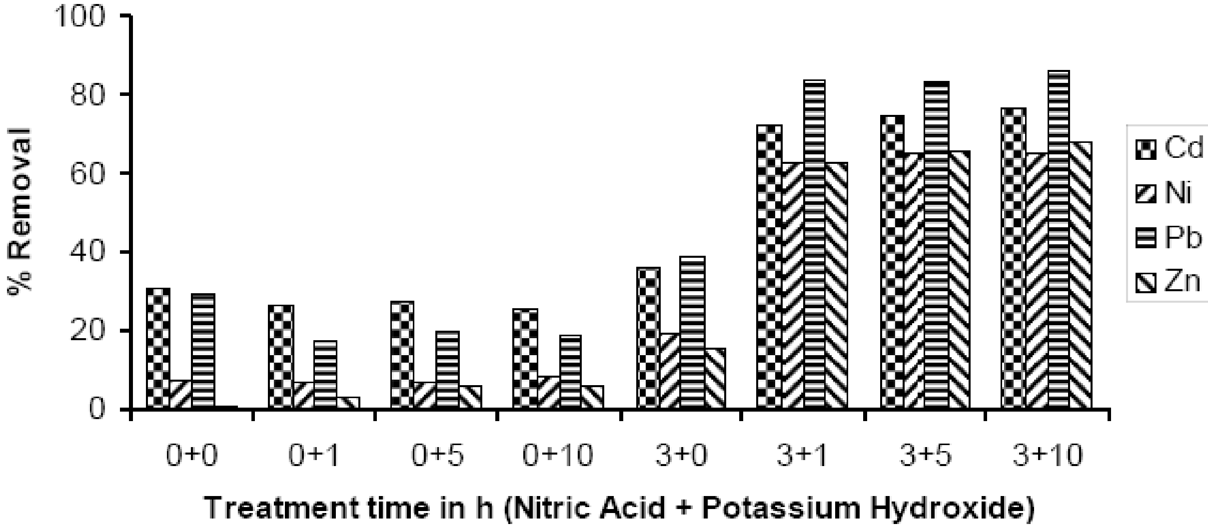


Fig 3. Optimization of post-treatment time for NPC

Sorption efficiency of NPC was observed in similar range for all combinations of acid and alkali treatment. Therefore, 3h treatment with 70% HNO_3 followed by 1h treatment with 30% KOH was considered as the optimized treatment for NPC. The results of sorption experiments of the selected heavy metals with AC, treated NC and NPC are discussed by [21]. For solution containing 1 meq/L of heavy metals (Cd, Ni, Pb and Zn), AC and NC exhibited heavy metal removal efficiency around 15-30% and 25-45% respectively. NPC was found to have greater sorption capacity (70-80%) for all the selected metal ions compared to AC and NC. Heavy metal removal efficiency was possibly higher in NPC, due to its unique structure and uniform surface morphology. Moreover it is also possible that oxygen containing functional groups were introduced during the post-treatment processes. Similar observations have been reported by various researchers [11], [14] and [22]. for oxidation of CNTs with oxidizing agents. These surface modifications are also reported to enhance the sorption of metal (M^{2+}) ions. Therefore, both the porous structure of the sorbent and the post-treatment applied, determines the sorption efficiency. A unique combination of both may provide an efficient sorbent for specific applications.

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