Potential of carbon nanomaterials for removal of heavy metals from water

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Abstract

Heavy metals, such as, cadmium, lead, nickel and zinc can be removed from water using sorbents. The rate and extent of removal may be enhanced by choice of appropriate sorbents. In this study heavy metal sorption was studied on indigenously synthesized carbon nanomaterials (CNMs). Two CNMs differing in surface morphology were synthesized using turpentine oil in a chemical vapour deposition (CVD) setup by varying the process parameters. Activation and catalyst removal were achieved by post-treatment with HNO\(_3\) and KOH. Characterization of the CNMs produced revealed that both comprised of graphitic amorphous carbon, however, while the nanocarbon (NC) produced using cobalt catalyst in N\(_2\) atmosphere comprised of varying grain sizes indicative of soot, the nanoporous carbon (NPC) produced using silica catalyst in H\(_2\) atmosphere had a distinctive uniformly porous surface morphology. Comparative sorption studies with cadmium, lead, nickel and zinc also revealed greater sorption on NPC compared to NC. Batch isotherms for the various heavy metals using NPC and a commercial activated carbon (AC) widely used for metal sorption revealed that NPC is characterized by significantly higher metal sorption capacity and more favourable sorption energetics. The superior performance of NPC as a sorbent may be due to its unique nanoporous structure.

Keywords: Heavy metal; Adsorption; Sorption; Carbon nanotubes; Nanoporous carbon
1. Introduction

Extensive industrialization and improper disposal are attributed to be a prime factor responsible for the release of heavy metals into the ecosystems. Once released, the heavy metals tend to bioaccumulate in higher trophic levels of the food chain. Almost all heavy metals are toxic to living beings and excessive levels are known to cause both acute and chronic toxicity [1]. Heavy metals cannot be degraded or destroyed; moreover, the natural process of metal mineralization is very slow. Hence, removal of heavy metals from water and wastewater is best accomplished by immobilization and concentration on suitable sorbents. The sorbed metals can be removed and reused as raw materials [2].

Cadmium, lead, nickel and zinc were chosen for this study due to their widespread use in industries and potential water pollution impact. Cadmium exposure may cause nausea, salivation, muscular cramps and anaemia. Extended exposure to cadmium may also cause cancer [3]. Lead poisoning is associated with gastrointestinal disorders, constipation, abdominal pain, and central nervous system effects [4,5]. Exposure to nickel may cause cancer of lungs, nose and bones. Moreover, it may cause extreme weakness, dermatitis, headache, dizziness and respiratory distress [6]. Zinc toxicity from excessive ingestion is less common, however, it may cause damage to various systems in the human body [7,8].

Sorbents which have been studied for adsorption of metal ions include activated carbon, fly ash, crab shell, coconut shell, zeolite, manganese oxides, and rice husk. However, these adsorbents have poor removal efficiencies for low concentrations of metal ions. Moreover, the slow removal rates often fail to meet pollution control requirements [9–12]. To prevent deteriorating surface water quality, legislation governing the levels of heavy metals, such as cadmium, lead, nickel and zinc discharged from industries is becoming progressively more stringent. Thus, there is a need for exploring alternative adsorbents, with better metal removal efficiency for low aqueous concentrations.

With the emergence of nano science and technology in the last decade, research has been initiated to exploit the unusual and unique properties of carbon nanomaterials (CNMs). CNMs may exist in several forms, such as, single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), carbon beads, carbon fibres and nanoporous carbon. 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 [13].

Carbon nanotubes (CNTs) have shown exceptional adsorption capability and high adsorption efficiency for various organic pollutants such as benzene [14], 1,2-dichlorobenzene [15], trihalomethanes [16] and polycyclic aromatic hydrocarbons (PAHs) [17]. CNTs were found to be superior sorbents for inorganic pollutants such as fluoride [18], and several divalent metal ions [7,8,19–25]. Li et al. [24] reported that CNTs with more defects and poor quality possess higher surface area and exhibit better lead sorption capacity compared to aligned CNTs. Activation of CNTs plays an important role in enhancing the maximum sorption capacity. Activation causes modification in the surface morphology and surface functional groups and causes removal of amorphous carbon. Activation of CNTs under oxidizing conditions with chemicals such as HNO₃, KMnO₄, H₂O₂, NaOCl, H₂SO₄, KOH, and NaOH have been widely reported [8,21,26,27]. During activation, the metallic impurities and catalyst support materials are dissolved and the surface characteristics are altered due to the introduction of new functional groups [24,26].

Both Langmuir and Freundlich adsorption models have been used for representing sorption
of heavy metals on CNTs. Maximum sorption capacity for heavy metals determined based on Langmuir model varies based on the type of metal. The maximum sorption capacity for cadmium, lead, nickel and zinc is reported to be in the range of 10–11 mg/g [21], 49–97 mg/g [20,22,24], 9–47 mg/g [19,25] and 11–43 mg/g [7,8] respectively. Hence, with CNTs as sorbent, metal ion uptake followed the order Pb$^{2+}$ > Ni$^{2+}$ > Zn$^{2+}$ > Cd$^{2+}$.

Characteristics of CNTs synthesised by chemical vapor deposition (CVD) process depend upon the type of catalyst and carrier gas used [28–32]. Ryoo et al. [33] proposed a novel silica template-mediated approach for synthesis of nanoporous carbon using CVD. The resulting high surface area materials with uniform pores were suitable for a wide variety of applications: as adsorbents, catalyst supports, and materials for advanced electronics applications. Han et al. [34] used the NPC synthesized using silica template for dye adsorption. The adsorption capacity of nanoporous carbon was found to be 10 times higher than that of commercial activated carbon for removal of direct blue-78 dye. Apart from the template-mediated method, another nanoporous carbon synthesis approach involves functionalization and introduction of nanopores in activated carbon by chemical oxidation and heat treatment. Such functionalized activated nanoporous carbon has been used for adsorption of Ca$^{2+}$, Cd$^{2+}$, Pb$^{2+}$, and Hg$^{2+}$, however, surface morphological analysis has not been reported. The maximum amount adsorbed decreased in the order Hg$^{2+}$ > Pb$^{2+}$ > Cd$^{2+}$ > Ca$^{2+}$ [35].

The current study discusses the synthesis, treatment and characterization of CNMs, i.e., nanocarbon (NC) and nanoporous carbon (NPC) produced by variation of process parameters in CVD. Investigations were further carried out to determine the sorption potential of NC and NPC. Sorption isotherms were generated for removal of cadmium, lead, nickel and zinc from aqueous solution. The objective was to compare heavy metal sorption capacities of novel carbon materials synthesized in the laboratory with traditionally used activated carbon.

2. Experimental procedure

2.1. Preparation of purified CNMs

CNMs were produced in the laboratory using a CVD unit consisting of two furnaces joined side by side with a quartz tube traversing both of them (Fig. 1). Detailed catalyst preparation, synthesis and treatment methods have been described elsewhere [36,37]. Pyrolysis of organic precursors at high temperature facilitated by catalyst leads to CNM formation. In the CVD process, 7 g of crude turpentine oil was filled in a quartz boat and kept in the vaporizing furnace. Two quartz boat each containing 0.5 g of catalyst were kept in the pyrolysing furnace. After inserting the quartz boats within the quartz tube, one end was connected to the carrier gas inlet and the other end was connected to the gas bubbler through which the gas was vented. Initially, carrier gas flow was initiated (500 mL/min) to ensure an oxygen-free environment inside the quartz tube. The pyrolysing furnace set at a predetermined temperature was switched on after 15 min. The vaporising furnace also set at the desired temperature was switched on after the temperature of the pyrolysing furnace was stabilized. As the turpentine oil started vaporizing, dark brown fumes were observed to emerge through the gas bubbler. After 2–3 min, the dark brown vapour was no longer observed, thus indicating complete vaporization of turpentine oil. Both furnaces were then switched off and allowed to cool. Throughout the process, the carrier gas flow rate was maintained constant. After cooling of the furnace, the catalyst boats and precursor boat were taken out. The carbon deposited on each boat was weighed and stored for further purification.

By varying the process parameters, i.e., catalyst (cobalt/silica), type of gas (N$_2$/H$_2$) and the
pyrolysis temperature (600°C/700°C), CNMs with different characteristics were deposited and these were designated as nanocarbon (NC) and nanoporous carbon (NPC), respectively. The vaporization temperature was kept constant at 500°C. Nanocarbon and the cobalt catalyst were separated by treating with strong HNO₃ for 3 h. Purification involved a 3 h reflux in 65% nitric acid at 80°C where approximately 1 L of acid was required per 50 g of raw material. Subsequently, the black solution was centrifuged (10000 rpm, 10 min) and the nanocarbon pellet was recovered after decanting off the acid. The nanocarbon pellet still contained substantial trapped acid which was removed by repeatedly re-suspending the pellet in DI (deionized) water (by shaking vigorously), centrifuging, and decanting the supernatant liquid. This process was repeated until the solution attained neutral pH. Metal catalyst particles were digested with strong HNO₃ and washed away. The NC was further treated with 30% KOH solution (80°C in a reflux set-up) and repeatedly washed with DI water until neutral pH was attained. Purified NC was oven dried and stored in a dessicator. The same procedure was applied to NPC deposited on silica catalyst. Post-treatment time for removal of catalyst was optimized and 3 h of 65% HNO₃ treatment followed by 1 h of 30% KOH treatment was found to be sufficient. With crude turpentine oil as precursor, the yield for NC and NPC was about 40–45%.

2.2. Characterization

Crystallinity and purity of CNMs were determined by X-ray diffraction (XRD, Philips PW3040/60 X’pert PRO, Netherlands) employing Cu/Kₐ radiation. Surface morphology was analysed using scanning electron microscope (SEM, Hitachi S3400N, Japan). Surface hydrophobicity of CNMs were analysed by powder wettability instrument (GBX Instrumentation CAP26, France). The aqueous phase heavy metal concentration was determined using an atomic absorption spectrophotometer (AAS, GBC-902 Scientific Equipments Pvt. Ltd., Australia).

2.3. Metal sorption experiments

A kinetic study was performed for cadmium, lead, nickel and zinc using the nitrate salt (S.D.
Fine-Chem Ltd., Mumbai, India) of each metal. The sorbents used were NC, NPC and commercially available AC (Loba Chemie Ltd., Mumbai, India). A kinetic study was conducted to decide the contact time required for the adsorption process to reach equilibrium. Polypropylene batch reactors were filled with 100 mL of aqueous solution containing the metal ion (M$^{2+}$) at a concentration of 1 meq/L and 0.5 g/L sorbent. The aqueous solution in all experiments contained 0.01 M NaNO$_3$ for maintaining constant ionic strength. The initial pH was adjusted to 6.5 using 0.01 N NaOH. The reactors were capped and kept in a tumbler set at 15 rpm and maintained at room temperature. Over a period of 30 min–48 h, a pair of samples were removed and analyzed at predetermined time intervals. The sorbent was separated out by centrifugation (12000 rpm, 15 min), pH of aqueous phase was measured and aqueous samples were stored at 4ºC until analysis was conducted. A study was carried out at a fixed initial concentration ($C_o$ for M$^{2+} = 1$ meq/L) to check the sorption potential of each sorbent. Sorption of all metals was compared on AC, NC and NPC. Subsequently, the equilibrium studies were conducted over the initial metal concentration range 0.5–5.0 meq/L, while maintaining a constant sorbent dose of 0.5 g/L. For the equilibrium isotherm studies all samples were extracted and analyzed similarly after allowing sufficient time for equilibration. For all studies, controls devoid of sorbent were maintained and analyzed. All experiments were carried out in triplicate.

### 3. Results and discussion

#### 3.1. Characteristics of carbon materials

The AC, NC and NPC samples were characterized using XRD. The XRD patterns (Fig. 2) of AC, NC and NPC samples were compared and interpreted with standard data of the International Centre of Diffraction Data (ICDD). The peaks at 12.05° and 24.01° can be attributed to (002) and (004) graphitic planes. The wide peaks indicate the presence of amorphous nanocarbon [38]. The XRD pattern further reveals that the cobalt and silica catalysts were efficiently removed from NC and NPC, respectively, by the post-treatment process.

The SEM images of the carbon samples at various magnification are shown in Fig. 3. The morphology of the AC sample is fairly heterogeneous and comprised of grains with particle sizes greater

![Fig. 2. XRD pattern of AC, NC and NPC.](image-url)
Fig. 3. SEM images of AC (a–d), NC (e–h) and NPC (i–l) at various magnifications.
than 5 μm. Porosity was not observed even at a higher magnification (Figs. 3a–d). The NC powder exhibits a porous structure as compared to AC powder (Figs. 3e–h). Multi-folded graphene sheets and cylinders are observed in NC. However, the structural uniformity is lacking and grains of varying particle sizes, indicative of the presence of soot and the related substances are observed. In contrast, the NPC sample demonstrates a highly porous morphology (Figs. 3i–l). This unique structure of NPC is distinctly different from AC and NC. At a high magnification, a unique honeycomb-like structure with a uniform porosity and interconnected pores is observed throughout the NPC sample. The average pore dimension is about one micron. The difference in the morphology of NC and NPC discussed above can be attributed to the difference in the process parameters used for synthesis of CNMs. The use of hydrogen as a carrier gas in NPC synthesis may lead to less soot formation. Various researchers have reported that the hydrogen concentration inside the CVD reactor has an effect on the nature and quality of the deposited materials [32,39].

The water contact angle of any powder reflects its surface hydrophobicity. The greater the water contact angle, the greater the surface hydrophobicity of the powder. The water contact angle measured for AC was 50°. The water contact angles of NC and NPC as produced were 68° and 74°, respectively, representing hydrophobic surfaces. Post-treatment with HNO₃ and KOH reduced the contact angle values of NC and NPC to 55° and 57°, respectively. This transition to hydrophilic surfaces is possibly due to the introduction of acidic oxygen containing functional groups. Similar observations were reported by various researchers [7,19,21,25] for oxidation of CNTs with HNO₃. These surface modifications are also reported to enhance the sorption of metal (M²⁺) ions.

3.2. Metal sorption studies

Kinetic study conducted with lead, cadmium, nickel and zinc with all carbon types AC, NC and NPC indicated that the samples essentially reach equilibrium after 1 h as shown in Fig. 4 for lead sorption. Similar time scale, i.e., 1 h equilibration time, for sorption of metal ions on CNTs has been reported by various researchers [7,19] although longer time periods have also been reported [21,22] for lead, copper and cadmium sorption on CNTs.

The equilibrium sorption studies were set-up for 12 h in all cases to allow sufficient time for achieving equilibrium. The metal loading on the sorbents (qₑ, meq/g) was determined by mass balance. The results of a single point sorption study (at a fixed initial concentration of 1 meq/L) shown in Fig. 5 indicated that the removal efficiency of NPC is much higher compared to AC and NC.

NPC could sorb all the heavy metals studied such that a high degree of removal was observed. The objective of this preliminary study conducted at a fixed initial concentration was to identify the better sorbent amongst the two CNMs. Subsequently, isotherm studies were conducted with NPC, and sorption on NPC was compared to that of AC.

3.3. Isotherm studies

The sorption isotherm data (Cₑ vs. qₑ) were fitted to the Langmuir and Freundlich isotherm
models. The Langmuir model [Eq. (1)] assumes monolayer coverage on sorbent whereas the Freundlich model [Eq. (2)] is an empirical model allowing for multilayer adsorption on sorbent [40].

\[
q_e = \frac{Q^o_a b C_e}{1 + b C_e}
\]  

(1)

\[
q_e = K_F C_e^n
\]  

(2)

where \(q_e\) = loading of adsorbate on adsorbent at equilibrium (μeq/g); \(Q^o_a\) = maximum capacity of adsorbent for adsorbate (μeq/g), \(b\) = sorption energy (L/μeq), \(K_F\) = indicator of sorption capacity (μeq/μeq/L g⁻¹), \(n\) = adsorption energetics and \(C_e\) = aqueous concentration of adsorbate at equilibrium (μeq/L).

Isotherms generated for selected heavy metals using AC and NPC as sorbents are shown in Fig. 6 along with the Langmuir and Freundlich model fit to the data. The Langmuir and Freundlich model parameters are listed in Table 1. The parameter values for the Langmuir and Freundlich isotherm models were obtained by linear regression based on the experimental data.

The \(R^2\) value of the Langmuir and Freundlich models reveals that none of the models fits well to the experimental data. However, from Fig. 6 it is observed that the model fits are relatively good and may be used to make comparison across the two sorbents and the various heavy metals. A comparison of the Langmuir model parameter \(Q^o_a\) representing the sorption capacity reveals that sorption on NPC is significantly more than on AC for sorption of all metals. Moreover, the sorption energetics represented by the Langmuir parameter \(b\) is also more favourable as indicated by the significantly higher \(b\) values for NPC (except for zinc sorption studies). The larger \(b\) values in NPC indicate that utilization of the sorption capacity of NPC is likely to be higher in any treatment scenario since 50% monolayer coverage would be achieved at lower \(C_e\) (=1/b) values. The unique structure and uniform surface morphology of NPC may have facilitated heavy metal sorption.

NPC demonstrates high sorption capacity for all the metals studied. Sorption of heavy metals on NPC may occur due to ion exchange with the acidic oxygen containing functional groups intro-
Fig. 6. Freundlich (- - - ) and Langmuir (——) model fits to experimental sorption data on NPC and AC for cadmium (a), lead (b), nickel (c) and zinc (d).

Table 1
Isotherm model parameters for heavy metal sorption on AC and NPC

<table>
<thead>
<tr>
<th>Metal</th>
<th>Sorbent</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$Q_e$ (μeq/g)</td>
<td>$b$ (L/μeq)</td>
</tr>
<tr>
<td>Cd</td>
<td>AC</td>
<td>217.4</td>
<td>0.0031</td>
</tr>
<tr>
<td></td>
<td>NPC</td>
<td>1428.6</td>
<td>0.0092</td>
</tr>
<tr>
<td>Pb</td>
<td>AC</td>
<td>909.1</td>
<td>0.0025</td>
</tr>
<tr>
<td></td>
<td>NPC</td>
<td>2000</td>
<td>0.01</td>
</tr>
<tr>
<td>Ni</td>
<td>AC</td>
<td>909.1</td>
<td>0.0004</td>
</tr>
<tr>
<td></td>
<td>NPC</td>
<td>1428.6</td>
<td>0.0075</td>
</tr>
<tr>
<td>Zn</td>
<td>AC</td>
<td>625</td>
<td>0.0043</td>
</tr>
<tr>
<td></td>
<td>NPC</td>
<td>2000</td>
<td>0.0035</td>
</tr>
</tbody>
</table>
duced by activation during the post-treatment process. The sorption capacity (expressed in μeq/g) is comparable for lead and zinc. The sorption capacities for cadmium and nickel are comparable but lower than for lead/zinc. The lower capacity for cadmium and nickel sorption may be due to the lower penetration and their inability to reach all the sorption sites that are accessed by lead and zinc. For lead, the ionic radius is the largest (1.19 Å), hence, due to its lowest hydrated ionic radius it is likely to penetrate effectively into the porous matrix. However, this consideration alone cannot explain the lower penetration of cadmium (ionic radius 0.97 Å) compared to zinc (ionic radius 0.74 Å). Moreover, the electronegativity of zinc is significantly lower compared to the other metals. Thus, comparable sorption capacity for lead and zinc is an unexpected result. It may be noted that the $R^2$ values for the Langmuir fit (Table 1) are significantly lower for cadmium and nickel compared to those for lead and zinc.

In this study, the sorption capacity is reported over the equilibrium concentration range 10–4000 μeq/g and pH 6.5 for all the metals. Although a direct comparison with the literature reported studies for CNTs cannot be made due to differences in pH, $C^*$ range and other parameters, the sorption capacity on NPC needs to be reviewed in comparison to that reported for CNTs. Li et al. [21] treated CNTs with different oxidizing agents and generated isotherms for cadmium sorption at pH 5.5 over the equilibrium concentration range 10–130 μeq/L. For the various CNTs studied, the sorption capacity of cadmium was significantly lower than for NPC (1428 μeq/g) and was reported to be in the range of 35–200 μeq/g. A lead sorption study with CNTs was carried out by Li et al. [20] at pH 7 and equilibrium concentration range of 10–80 μeq/L where the sorption capacity was reported as 482 μeq/g. In another study, Li et al. [24] reported that the lead sorption capacity of CNTs at pH 5 was 797 μeq/g. The lead sorption capacity on NPC is significantly higher (2000 μeq/g) than on these CNTs. Lu and Liu [19] and Lu and Chiu [7] reported nickel and zinc sorption capacity on CNTs as 1630 μeq/g and 1335 μeq/g, respectively, at pH 7 over the equilibrium concentration of 200–2200 μeq/L which is comparable to that observed in this study for NPC (1428 and 2000 μeq/g, respectively). It is thus established that, by virtue of its unique morphology, NPC has a significant sorption potential for heavy metals which is superior or comparable to the literature reported values for CNTs.

4. Conclusions

Surface morphology plays an important role in sorption. Two types of CNMs differing in surface morphology were synthesized by CVD by varying the process parameters, i.e., catalyst, carrier gas and temperature of the furnace. XRD analysis demonstrated that both CNMs were graphitic in nature. SEM images revealed that nanoporous carbon (NPC) prepared using silica catalyst in a hydrogen atmosphere had a distinctive surface morphology comprised of uniform porosity with interconnected pores of average pore diameter 1 μm. In contrast, the nanocarbon (NC) prepared using cobalt catalyst in a nitrogen atmosphere comprised grains with varying particle sizes which indicated the presence of soot and related particles. The porous NPC with distinctive surface morphology exhibited superior sorption of heavy metals compared to NC and AC, a commercially-available activated carbon. The sorption capacity and energetics for heavy metal sorption on NPC were more favourable compared to AC. This implies that at a low aqueous concentration of heavy metals, the sorption capacity of NPC will be efficiently utilized for the removal of heavy metals. NPC exhibited a high sorption capacity for all the heavy metals — lead, cadmium, nickel and zinc — used in this study. These values were significantly higher or comparable to those reported for carbon nanotubes by various researchers. Thus, nanoporous carbon has a good potential for use in water treatment applications.
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