Synthesis, Characterization and Adsorption Studies of Chlorine–doped Carbon Nanotubes

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Abstract-Chlorine doped carbon nanotubes (CNTs) are synthesized to introduce dipole moment into the lattice of the CNTs to enhance interaction with cationic species in adsorption. Cobalt and silver co-catalyst supported on magnesium oxide (MgO) is used as growth promoter and their morphological features were studied using Raman spectroscopy, energy dispersive spectroscopy (EDX), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD) spectroscopy. Equilibrium and thermodynamic batch adsorption experiments were carried out by studying the concentration, time and temperature effects. The morphological images of the doped carbon materials showed amorphous multiwall nanotubes with some crystalline regions that are attributable to the doping of the chlorine. The adsorption studies recorded a rapid uptake of Cr³⁺ by the carbon nanotubes h was mainly diffusion controlled. The thermodynamic studies suggested relatively low temperature (low energy) favoured sorption was exothermic with a physic-sorption mechanism.

Keywords- Adsorption; Carbon Nanotubes; Chlorine; Synthesis

I. INTRODUCTION

Carbon nanotubes (CNTs) are cylindrical allotropes of carbon consisting of hexagonally arranged sp² hybridized carbon atoms [1-3]. This cylindrical honey comb-like carbon structures possesses length to diameter ration of up to 1,000,000 (high aspect ratio) [4]. CNTs may consist of one to hundreds of graphitic carbon cylinders and are thus classified as either single walled carbon nanotubes (SWCNT) or multi walled carbon nanotubes (MWCNT) [5-8]. Although carbon nanotubes are basically made up of concentric graphitic carbon cylinders, the differences in the number of graphitic layers, thickness of the layers, helical structures and length causes them to have either metallic or semi conducting properties [9-10]. CNTs generally possess outstanding physical, mechanical and electrical properties, according to Peng et al. [10] and De Volder et al. [11], they possess elastic modulus of up to 1 TPa, and a tensile strength of about 100 Gpa thus making CNTs over 10-fold stronger than any industrial fibre, also a typical MWCNT has been reported to carry a current of up to 10⁹ A cm⁻² and individual SWCNT can have a thermal conductivity of about 3500 W m⁻¹ K⁻¹ at room temperature [10]. These outstanding properties coupled with the high aspect ratio of up to 1,000,000 makes CNTs ideal for a lot of uses and applications such as: drug delivery, genetic engineering, non-metallic catalyst material, anti-oxidant material, artificial implant material field emission transistors, probe sensors, polymer composite materials, anti-rust coating composite materials, gigahertz diode, and conductive fillers in rechargeable batteries and lately as an adsorbent for the removal bio-fouling and toxic materials from the environment [10-18]. Over the past few years, several method have been developed for the synthesis of CNTs, but the most commonly used methods are: electric arc discharge method, laser ablation method and the chemical vapour deposition (CVD) method. The CVD method, however, utilises lower synthesis temperature than the electric arc-discharge and the laser ablation methods, and it is, therefore, the most preferred synthetic route than the other methods. Also additionally, the CVD method is scalable (for commercial purposes), cost effective and offer the opportunity to control the size and shape of the synthesized carbon nanotubes [4, 12].

Doping of CNT is the deliberate introduction of foreign atoms (and consequently defects) into the lattice of the CNT in order to tune, control and improve the properties of the CNT for specific purposes [19], the introduction of foreign atoms usually introduces a hole as in the case of doping with boron, or introduces an extra electron, leading to the formation of positive or negative (p or n) type doped CNT [18, 19]. In a general term, there are three types of doping, namely: endohedral doping which involve the filling of the inner cavity of the pure substance with foreign species; secondly exohedral doping, which involves intercalation or insertion of the foreign material in between the concentric rings or layers of the pure substance; and thirdly substitution doping, which in the case of CNTs involves the replacement of a carbon atom in the lattice of the CNT with a foreign atom [19]. Mostly, doping of CNTs usually involves substitution doping.

Nanoadsorbents have found a wide range of applications in engineering fields as they are efficient bio-compatible adsorbents having large specific surface area, more attractive sites and low intra particle resistances. Nano-adsorbents have nanoscale pores, high selectivity, high surface area, high permeability, good mechanical stability and good thermal stability. Nano particles have greater surface area to volume ratios than micro particles. This makes the latter to be more reactive than
other materials. Nano particles have vast applications in the fields of biomedical, electrical, environmental engineering. There are many more attractive phenomena hid within the tiny, mysterious world that exist inside the carbon nanotubes [1, 20-22].

Osikoya et al. [1, 20] studied the adsorption, equilibrium and thermodynamic properties of the removal of chromium ion from aqueous systems using doped carbon nanotubes. Information on the use of chloride doped carbon nanotubes for the removal of metal ions from solution is very scanty which has necessitated this study. The conventional methods for the removal of metals from aqueous solution and waste water are precipitation, flocculation, filtration, ion exchange reverse osmosis, etc. These methods are very much capital intensive, but some renewable adsorbents have been used for the removal of metals from solutions which include polyvinylchloride, polystyrene, polymethylmethacrylate, seaweeds, medicago sativa (alfafa) and manihot sculenta cranz [23-27].

In this study, chlorine doped carbon nanotubes were synthesized using Co – Ag bi-catalyst prepared on magnesium oxide support, with acetylene carbon source in a horizontal chemical vapour deposition (CVD) reactor. The resultant carbon materials are characterized with EDX, SEM, TEM and XRD and subsequently used to conduct adsorption and thermodynamic studies for chromium.

II. EXPERIMENTAL

A. Chemicals Used and Level of Purity

Silver nitrate (AgNO₃) Merck 99.5 %; cobalt II sulphate (CoSO₄) Labchem 99.5 %; sodium bi-carbonate (NaHCO₃) Univar 99.0 %; sodium chloride (NaCl) Univar 99.5 %; acetylene (C₂H₂) Afrox 99.0 %; argon (Ar) Afrox 99.999 %; nitrogen (N₂) Afrox 99.999 %; 1-chlorobutane (CH₃(CH₂)₂Cl) Sigma-Aldrich 99.0 %; nitric acid (HNO₃) Promark Chemicals 55.0 %. All the chemicals used were of the laboratory reagent grade, no further purification was performed, and all the reagents were used as purchased from the manufacturers.

B. Preparation of Catalyst

The catalyst used in this study was Co – Ag metals impregnated on magnesium oxide support. This bi-metallic catalyst was prepared by reacting 500 ml of 1M CoSO₄ solution with 1000 ml of 1M NaHCO₃ solution at about 55°C to obtain CoCO₃ according to Eq. (1):

\[ \text{CoSO}_4(aq) + 2\text{NaHCO}_3(aq) \rightarrow 55^\circ\text{C} \rightarrow \text{CoCO}_3(s) + \text{Na}_2\text{SO}_4(aq) + \text{CO}_2(g) + \text{H}_2\text{O}(l). \]  

The precipitated CoCO₃ obtained in this reaction was mixed with 59.5 g of MgO while still in the reaction solution, the mixture was then filtered, washed thoroughly with distilled water, and finally dried in the oven at 70°C for about 48 hours and allowed to cool to room temperature. In the same vein, 500 ml of 1M AgNO₃ was reacted with 500 ml of 1M NaCl according to Eq. (2):

\[ \text{AgNO}_3(aq) + \text{NaCl}(aq) \rightarrow \text{AgCl}(s) + \text{NaNO}_3(aq) \]  

The reaction product in Eq. (2) was mixed with 71.66 g of MgO and the mixture was filtered, washed thoroughly with distilled water and dried in the oven at 120°C for about 48 hours and allowed to cool to room temperature. The catalysts prepared were respectively grinded into very fine powder with mortar and pestle and stored for usage in the carbon nanotubes synthesis experiments. They were referred to respectively simply as cobalt catalyst and silver catalyst.

C. Preparation of Carbon Nanotubes

CNTs were synthesized in a horizontal CVD reactor using the prepared catalysts. The fabrication and experimental setup of this equipment have been described elsewhere [28, 29]. The carbon nanotubes were chlorine-doped by pyrolysis of acetylene gas (primary carbon source) and 1-chloro butane (chlorine source) via the bubbling method in a tubular quartz reactor which was horizontally positioned within a furnace electronically controlled to produce accurate heating rate and reaction temperature. The bi-metallic catalyst of cobalt and silver were loaded into a 120 x 15 mm quartz boat at room temperature and placed in the centre of a horizontal quartz tube, which was also carefully placed in a horizontal furnace. The furnace (and its contents) was then heated while at the same time, the flow of nitrogen gas commenced first so as to purge the reactor of air and create an inert atmosphere for the synthesis reaction. The nitrogen gas flow was maintained at 40 ml/min for about 70 minutes until the reaction temperature of 800°C is attained. At the same time, acetylene gas flow at 50 ml/min and argon gas flow at 240 ml/min bubbling through 1-chloro butane were simultaneously introduced into the reactor to start the reaction. The reaction was allowed to proceed for 60 minutes after which the bubbling of the argon gas through 1-chloro butane and the acetylene gas flow stopped. The furnace was allowed to cool to room temperature at the end of reaction period under a continuous flow of nitrogen gas at 40 ml/min. The samples formed inside the boat were collected and characterized.

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D. Characterization of the Chlorine Doped CNTs

The structural, morphological and elemental analysis of the synthesized chlorine doped carbon nanotubes were carried out using Raman spectroscopy, FE-SEM, HR-TEM, EDS, and XRD. The Raman spectra were obtained by a Raman spectroscope, Jobin-Yvon HR800 UV-VIS-NIR Raman spectrometer equipped with an Olympus BX 40 attachment. The excitation wavelength was 514.5 nm with an energy setting of 1.2 mV from a coherent Innova model 308 argon-ion laser. The Raman spectra were collected using back scattering geometry with an acquisition time of 50 seconds. The surface morphology and EDS measurements were recorded with a JEOL 7500F Field Emission scanning electron microscope. The HR-TEM images of the sample were obtained by a CM 200 electron microscope operated at 100 kV. Powder X-ray diffraction (PXRD) patterns were collected with a Bruker AXS D8 Advanced diffractometer operated at 45 kV and 40 mA with monochromated copper Kα1 radiation of wavelength (λ = 1.540598) and Kα2 radiation of wavelength (λ = 1.544426). Scan speed of 1 s/step and a step size of 0.03°. UV-vis spectra were recorded on a Perkin-Elmer lambda 9 UV-vis spectrometer.

E. Batch Adsorption Experiment

The batch adsorption experiments were conducted to study the effects of concentration, time and temperature of the synthesized chlorine doped carbon nanotubes on chromium. A measured quantity of the chlorine doped carbon nanotubes (0.01 g) was weighed and placed in pre-cleaned test tubes. Five metal ion solutions with standard concentrations of 20, 40, 60, 80 and 100 mg/l were made from spectrophotometric grade standards of Cr\(^{3+}\) (from CrCl\(_3\)) and 20 ml of each metal solution were added to each tube containing the carbon nanomaterials and equilibrated for 1 hour by shaking at 29°C. The resultant carbon nanomaterial suspensions were centrifuged for 5 min at 4000 rpm. The supernatants were analysed to determine the metal content. In order to study the effect of time and temperature, this same experiment was repeated by equilibrating the chlorine doped carbon nanomaterials for each time intervals of 20, 30, 40, 50 and 60 min and at temperature interval of 25, 40, 60 and 80°C using a Compenstat Gallenhamp water bath. In each case, the resultant carbon nanomaterial suspensions were centrifuged for 5 min at 4000 rpm and the supernatants were analysed to determine the metal content. The metal analysis was performed with AAS using a Buck Scientific Atomic Absorption/Emission spectrophotometer 200A (AAES). The controls of one of the metal solutions were run to detect any possible metal precipitation or contamination.

F. Data Analysis

Various equilibrium, kinetic and thermodynamic models (equations) were employed to interpret the data and establish the extent of adsorption. The amount of metal uptake was computed using the material balance equation for batch dynamic studies (Eq. (3)) [25].

\[ q_e = \frac{V}{M}(C_o - C_e) \]  

with \( q_e \) as metal uptake capacity (mg/g carbon nanotube at equilibrium), \( C_e \) is metal ion concentration in solution (mg/l) at equilibrium, \( C_o \), the initial metal ion solution (mg/l), \( V \), the volume of solution in litres and \( M \), the dry weight of carbon nanotube used in (g). Langmuir plots were carried out using the linearized Eq. (4):

\[ \frac{M}{X} = \frac{1}{ab C_e} + \frac{1}{b} \]  

where \( X \) is the amount of Cr\(^{3+}\) adsorbed per mass \( M \) of carbon nanotube in mg/g. \( a \) and \( b \) are the Langmuir constants obtained from the slope and intercepts of the plots. The essential characteristics of the Langmuir isotherm were expressed in terms of a dimensionless separation factor or equilibrium parameter \( S_f \) (Eq. (5)) [30].

\[ S_f = \frac{1}{1 + aC_o} \]  

where \( C_o \) is the initial concentration of Cr\(^{3+}\) in solution, the magnitude of the parameter \( S_f \) provides a measure of the type of adsorption isotherm. If \( S_f > 1.0 \), the isotherm is unfavourable; \( S_f = 1.0 \) (linear); \( 0 < S_f < 1.0 \) (favourable) and \( S_f = 0 \) (irreversible). The adsorption intensity of the Cr\(^{3+}\) in the carbon nanotube was assessed from the Freundlich plots using the linearized Eq. (6):

\[ \ln \frac{X}{M} = \frac{1}{n} \ln(C_e) + \ln(K) \]  

where \( K \) and \( n \) are Freundlich constants and \( 1/n \) is approximately equal to the adsorption capacity.

The fraction of carbon nanotube surface covered by the Cr\(^{3+}\) was computed using Eq. (7):

\[ \theta = 1 - \frac{C_e}{C_o} \]
where $\theta$ is the degree of surface coverage. The effectiveness of the adsorbent (carbon nanotube) was assessed by the number of cycles of equilibrium sorption process required to reduce the levels of Cr$^{3+}$ in solution according to the value of the distribution (partition coefficient ($K_d$) in Eq. (8)).

$$K_d = \frac{C_{aq}}{C_{ads}}$$

where $C_{aq}$ is concentration of Cr$^{3+}$ in solution, mg/l; $C_{ads}$ is concentration of Cr$^{3+}$ in carbon nanotube in mg/l. The heat of adsorption ($Q_{ads}$) was obtained using the following Suzuki Eq. (9).

$$\ln \theta = \frac{\ln K_d C_a}{T^{0.5}} + \frac{Q_{ads}}{RT}$$

with $T$ as solution temperature (K); $K_d$ a constant and R gas constant (8.314 J/K.mol). The linear form of the modified Arrhenius expression was applied to the experimental data to evaluate the activation energy ($E_a$) and sticking probability $S^*$ as shown in Eq. (10).

$$\ln(1 - \theta) = S^* + \frac{E_a}{RT}$$

The apparent Gibbs free energy of sorption $\Delta G^o$ which is a fundamental criterion for spontaneity was evaluated using the Eq. (11):

$$\Delta G^o = -RT \ln K_d$$

$K_d$ is obtained from the Suzuki Eq. (11). The experimental data was further subjected to thermodynamic treatment to evaluate the apparent enthalpy ($\Delta H^o$) and entropy ($\Delta S^o$) of sorption using Eq. (12).

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}$$

The expression relating the number of hopping ($n$) and that of the surface coverage ($\theta$) as shown in Eq. (13) was applied to the experimental data.

$$n = \frac{1}{(1 - \theta)\theta}$$

with $C_i$ and $C_e$ as initial and equilibrium concentrations in mol/cm$^3$ $R$, the gas constant and $T$, the solution temperature in K.

III. RESULTS AND DISCUSSION

Generally, Raman spectral showed two major peaks of D and G bands appearing at around 1340 and 1580 cm$^{-1}$, deriving from the in-plane motion of the carbon atoms to provide a signature of carbon nanotubes [30]. The Raman spectral feature of chlorine doped carbon nanotubes (Fig. 1) has two major peaks at 1339 and 1583 cm$^{-1}$. Berciaud et al. [31] reported that the Raman spectral signature of carbon nanotubes (1340 and 1580 cm$^{-1}$) is very sensitive to strain effects as well as doping. The appearing of the band at 1583 and 13439 cm$^{-1}$ in the Raman spectral of our chlorine doped carbon nanotubes, assigned to the G and D band respectively, shifted because of the doping effect of chlorine. The obtained Raman spectral feature of chlorine doped carbon nanotubes could be assigned to the multiwall nanotube because of the absence (weakness) of radial breathing mode (RBM) to be observed, which normally appears between 120 and 250 cm$^{-1}$ in single wall nanotube [33-36]. Ferrari et al. [32] attributed these G and D peaks to sp$^2$ sites of the carbon based materials.

The X-ray powder diffraction is a powerful tool for characterizing a solid state sample. Each crystalline substance has a unique X-ray diffraction pattern. With a diffraction pattern, an investigator can identify unknown specie or characterize the atomic scale structure of an already identified substance. Fig. 2 shows the XRD results of the as-grown carbon nanotubes. The XRD patterns of chlorine doped carbon nanotubes shows major peaks at around $2\theta = 20$ and 40°. These peaks are attributed to the hexagonal graphite structures (0 0 2) and (1 0 0), respectively. Therefore, the as-grown carbon nanotubes are assumed to be amorphous, as also revealed by the TEM images. Similar results have been reported in the literature by Ci et al. [34] (who called their product amorphous carbon nanotubes) and Li et al. [35]. No explanation related to the small and sharp peak around $2\theta = 45^o$ and 80° could be found in the literature. However, we assumed that these peaks can be attributed to the crystalline region of chlorine doped carbon nanotubes.

Energy dispersive X-ray (EDX) was applied for elemental analysis of the carbon nanotubes. The EDX spectrum presented in Fig. 3 confirmed sharp peak due to the carbon atom (C), while Cl, and others are in trace quantities. The presence of these elements will produce charges on the surface of the nanotubes and create electrostatic forces of attraction between the sample and Cr$^{3+}$ in solution.

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In order to examine the morphology of the doped carbon nanotubes, scanning electron microscope (SEM), and transmission electron microscope (TEM) images of the sample were taken to respectively show the external and internal morphologies of the synthesized carbon nanomaterial. The SEM and TEM images show that the surface of the carbon
nanotubes had irregular small size particles which indicated a high surface area and porous nature as shown in Figs. 4 and 5. Large surface area of any adsorbent facilitates maximum adsorption.

The percentage sorption of Cr\(^{3+}\) by the carbon nanotube at different concentrations of the Cr\(^{3+}\) is presented in Fig. 6. The maximum adsorption of 52% took place at equilibrium concentration of 20 mg/l Cr\(^{3+}\). This is because at lower concentration more nanotube pore spaces were available for the Cr\(^{3+}\), but as the concentration of Cr\(^{3+}\) increased, the adsorption capacity of the carbon nanotubes decreased due to reduced availability of free pore spaces. The results indicated that the sorption of Cr\(^{3+}\) was very much dependent on the concentration of the Cr\(^{3+}\).

Time dependency studies show the amount of time needed for maximum adsorption to occur. The variation in percentage removal of Cr\(^{3+}\) with time has been presented in Fig. 6. It indicates that a maximum of 60% removal of Cr\(^{3+}\) was observed in 20 minutes and remained constant afterwards. The relatively short contact time required to attain equilibrium suggests that a rapid uptake of Cr\(^{3+}\) by the nanotube occurred to fill some of the vacant pores in the carbon nanotube and after which the remaining spaces were difficult to be occupied due to repulsive forces between the Cr ions.

Fig. 6 also presents the plot of percentage adsorption of Cr\(^{3+}\) by the carbon nanotubes at varying temperatures with optimum sorption of 61% occurring at 28°C. The plot showed that further increase in temperature resulted in a slight decrease in adsorption. This is in agreement with the general principle that physical adsorption decreases with increase in temperature [20]. This behaviour could be attributed to the weakening of the attractive forces between the nanotubes and Cr\(^{3+}\), the increased kinetic energy of the Cr\(^{3+}\) and the decrease in the thickness of the boundary layers of the carbon nanotube due to the higher tendency of the Cr\(^{3+}\) to escape from the pores.
The extent of adsorption can be correlated using an isotherm. Attempts were made to fit the data obtained from the adsorption experiments into various adsorption isotherms. The linear plots of the Langmuir and Freundlich isotherm models for the sorption of Cr\textsuperscript{3+} by the carbon nanotubes are presented in Fig. 7. These straight line plots confirmed the application of the Langmuir and Freundlich isotherm models to the adsorption of Cr\textsuperscript{3+} by the nanotube. The slopes and intercepts were used to compute the Langmuir constants and adsorption capacity. The fraction of the carbon nanotube surface covered by the Cr\textsuperscript{3+} is given as 0.72 (Table 1). This value indicates that 72\% of the pore spaces of the nanotube surface were covered by the Cr\textsuperscript{3+}, which means high degree of adsorption.
The equilibrium and thermodynamic batch adsorption studies recorded rapid uptake of the Cr\(^{3+}\) ion coefficient $S^*$ = 0 (indefinite sticking or energy which was exothermic with a physical mechanism was exothermic. A positive $\Delta S$ indicates that the sorption process was spontaneous. The value obtained for $\Delta H$ was less than -20 KJ/mol suggesting electrostatic interaction between the Cr\(^{3+}\) and the nanotube which supported physical sorption mechanism.

Table 1 also presents the Gibbs free energy $\Delta G^*$ for the sorption of Cr\(^{3+}\) by the carbon nanotubes which was calculated from Eq. (9). Gibbs free energy is the fundamental criterion of spontaneity. The $\Delta G^*$ value of -0.810 KJ/mol was negative indicating that the sorption process was spontaneous. The value obtained for $\Delta G^*$ was also less than -20 KJ/mol suggesting electrostatic interaction between the Cr\(^{3+}\) and the nanotube which supported physical sorption mechanism.

The values of the enthalpy change ($\Delta H^*$) and entropy change $\Delta S$ were calculated from Eq. (10) to be -169.3 J/mol and 1.75 J/molK respectively. A negative $\Delta H^*$ suggests that sorption proceeded favourably at a lower temperature and the sorption mechanism was exothermic. A positive $\Delta S$ suggests that the freedom of the adsorbed Cr\(^{3+}\) was not restricted in the carbon nanotubes, indicating that physical-sorption mechanism predominates.

The probability of Cr\(^{3+}\) finding a vacant site on the surface of the carbon nanotube during the sorption was correlated by the number of hopping ($n$) done by the Cr\(^{3+}\). The hopping number presented in Table 1 is 4. The lower the hopping number, the faster the adsorption [20]. The low value of $n$ obtained in this study suggests that the adsorption of Cr\(^{3+}\) on the nanotube was very fast.

### IV. Conclusions

Chlorine doped carbon nanotubes were synthesized using bi-metallic catalyst in a conventional horizontal CVD reactor, and the results of the characterization confirmed amorphous multiwall carbon nanotubes with some crystalline regions due to the doping with chlorine. The equilibrium and thermodynamic batch adsorption studies recorded rapid uptake of the Cr\(^{3+}\) by the chlorine doped carbon nanotubes which were diffusion controlled. The adsorption was favoured by low temperature and energy which was exothermic with a physical-sorption mechanism. The results from this study will add to the knowledge base on the synthesis, characterization and the use of carbon nanotubes for the sorption of metal ions from aqueous solutions.

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### Table 1 Equilibrium and Thermodynamic Parameters

<table>
<thead>
<tr>
<th>Heat of adsorption ($Q_{ads}$) KJ/molK</th>
<th>Sticking probability ($S^*$)</th>
<th>Activation energy ($E_a$) J/molK</th>
<th>Gibbs free energy of adsorption ($\Delta G^*$) KJ/mol</th>
<th>Apparent entropy ($\Delta S^*$) J/molK</th>
<th>Apparent enthalpy ($\Delta H^*$) J/mol</th>
<th>Surface coverage ($\theta$)</th>
<th>Separation factor ($S_f$)</th>
<th>Hopping number ($n$)</th>
<th>Sorption coefficient ($K_d$)</th>
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