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ADSORPTION AND DESORPTION OF NAPROXEN ON CARBON NANOTUBES: A THERMODYNAMIC APPROACH

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Abstract

We report the adsorption behavior of non-steroidal, anti-inflammatory drug, naproxen (NAP) on different carbon templates like multi-walled carbon nanotubes (MWCNT), and carboxylic acid functionalized MWCNT and activated carbon. In addition to the adsorption, the drug molecule desorbs simultaneously at neutral pH which is highly remarkable. Various thermodynamic parameters like change in free energy (ΔG), change in entropy (ΔS) and change in enthalpy (ΔH) were calculated and activation energies were determined to investigate the feasibility of drug adsorption process.

Keywords: *adsorption, carbon nanotubes, desorption, drug, thermodynamic properties*

I. INTRODUCTION

The process of adsorption depends on the adsorbate-adsorbent interaction and also on binding probability. Carbon nanotubes (CNTs) are the allotropes of carbon with cylindrical nanostructures classified into single walled (SWCNT) or multi-walled (MWCNT) according to their layers. Because of π- π electron systems, MWCNTs have a great affinity to the dyes, drugs, pesticides and others through either donor-acceptor interaction or hydrophobic interaction. Hydrogen bonding interaction and electrostatic interaction also plays a major role while interacting with MWCNTs [1-3]. Such interactions are responsible for the delivery of drugs and other biologically important molecules [4]. Since the CNTs possess cylindrical nature and also having unusual physiochemical and electrical properties, these materials have been successfully used in nanotechnology, electronics, optics and also in materials science [5]. In the direction of adsorption, MWCNTs are considered as extremely superior adsorbents towards drug molecules and also in the adsorption of metal ions due to high surface area [6-9] which makes CNTs amenable for molecular recognition and detection. Such an affinity of MWCNTs towards metal ion creates applications for both waste water treatment and water decontamination [10-14].

Adsorption/desorption phenomena, in general, a preferable choice for drug delivery due to its relative simplicity and minimal changes to a drug structure and properties. Also adsorption of drugs on the surface of MWCNT appears very attractive for overcoming their bioavailability, which is a common issue for many drugs. Non-steroidal drugs that are well known to reduce inflammation, pain and fever and naproxen is such a kind of non-steroidal anti-inflammatory drug (NSAID) [15-16]. Therefore, adsorption studies of such NSAIDs on CNTs

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need to be studied to understand the nature of the interaction. Adsorption and desorption studies of various drugs have been performed at neutral pH on different supports.

In the current manuscript, adsorption and desorption properties of NAP on MWCNTs were investigated systematically. The influencing factors such as concentration, the temperature on adsorption properties were studied. Analysis of the adsorption of NAP onto MWCNTs will benefit from understanding the interaction between adsorbate and adsorbent, which serves as a basis for the establishment of nanoscale drug delivery systems. The objectives of this work are to determine the adsorption affinity of the drug at different adsorbate/adsorbent combinations and also determine the activation energy, thermodynamic parameters like Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) for the adsorption of naproxen at neutral pH. Overall, our study demonstrates the potential of –COOH functionalized carbon nanotubes as an efficient drug delivery system and presents a functionalization scheme that is able to overcome many of the problems encountered in the area of application of other templates of CNTs.

II. EXPERIMENTAL SECTION

Activated charcoal were purchased from Aldrich and used as such. Analytical grade naproxen was received from IICT, Hyderabad. MWCNTs and -COOH functionalized MWCNT were purchased from Nano Shell Pvt. Ltd, Haryana. The solubility of the drug was tested in aqueous (water) and organic solvents like polyethylene glycol and methanol etc. In the current study water was taken as a choice of study for adsorption-desorption investigation. Phosphate buffer solutions were used to maintain the neutral pH (7.4).

III. CHARACTERIZATION OF MATERIALS

The surface morphology of MWCNTs was characterized by using Scanning Electron Microscope (SEM). The SEM measurements were carried out using a field emission SEM (LEO 1530VP) equipped with a field emission gun. The scanning electron microscope was operated at 20 kV.

3.1 High Performance Liquid Chromatography (HPLC) method

The adsorption and desorption experiments of NAP were carried out by HPLC method. High-performance liquid chromatography system was used, with UV-detector and stationary phase 4.6 x 150 mm C-18 HPLC column (Shimadzu, Japan). The binding coefficient of NAP on CNTs was calculated using calibration plots. The adsorption studies were carried out with different concentrations of NAP on different adsorbate. To get the adsorption profile, various samples of drug solution (NAP) with 1, 3, 5, 7, 9, 10 mg and 10 mg per 10 ml of CNT was used.

3.2 Ultraviolet Visible (UV-Visible) spectroscopic methods

NAP adsorption and desorption studies were analyzed by UV-Visible spectrophotometer. Shimadzu UV-Visible system was adopted for the calibration and analysis of NAP.

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3.3 Adsorption-desorption experiments

In a typical adsorption-desorption study, 10 mg of MWCNTs were added to 10.0 mL distilled water solutions of varied known concentrations of NAP in 10 mL glass vials. The vials were closed and shaken for half an hour at 298K at neutral pH to ensure equilibrium adsorption. The characteristics peak absorbance of non-adsorbed NAP in solution was measured at 232 nm for each trial. The concentration of NAP drug obtained by using Beers law with a linear calibration produced in a series of separate experiments on solutions with known concentrations of the drug (without any adsorbent). These experiments were carried out in the set of three at room temperature and also at higher temperatures *i.e*. at 308 K and 318 K. All experiments were carried out at neutral pH. Similarly, AC and –COOH functionalized MWCNTs were also used for the adsorption and desorption studies of naproxen.

IV. Results and Discussion

Fig. 1 shows the SEM and TEM image of the MWCNT before (Fig. 1 (a) and 1 (b). The images inform bundle-like structure consists of self-assembled one-dimensional nanowire with the diameter of 40-50 nm.

The adsorption of NAP on MWCNTs was monitored by using UV-Visible spectroscopic method. The chromatograms of NAP in UV-Visible were monitored at 232 nm. The concentration of NAP was identified by plotting the calibration curve. Initially, NAP was allowed to adsorb on different templates of carbon at neutral pH, and it was observed that adsorption takes place at 278 K (Fig 2). Measurement of drug concentrations in solution reveals that the drug is adsorbed by MWCNTs. Remarkably, higher NAP adsorption takes place on MWCNTs as compared to –COOH functionalized MWCNTs at 298 K. Interestingly, as the temperature increases the adsorption –COOH functionalized MWCNTs improved and became higher than pristine MWCNT. Further, it is supported by the decrease and increase of naproxen concentration with time suggested that adsorption and desorption processes are going simultaneously as shown in the Fig. 2. Adsorption typically depends on the concentration of adsorbed molecule. Thus, the effects of NAP with different concentrations were considered for adsorption study. The plots of percent of drug removed from the solution shows that 95-98% of NAP is adsorbed at lower concentrations by MWCNTs. However at higher concentrations, MWCNTs behave differently, and 0.4 units of adsorbate is the optimum concentration as shown in the Fig. 3. To the best of our knowledge, this is the first report to observe the adsorption and desorption phenomena simultaneously on any carbon template at neutral pH.

V. EFFECT OF TEMPERATURE

The effect of temperature on the sorption phenomena of NAP onto the different carbon templates was studied at different temperatures of 298, 308 and 318K. The results show that increase in the adsorption capacity of NAP onto –COOH functionalized MWCNTs with increasing temperatures whereas adsorption capacity decreases on MWCNTs with the increase in temperature. Notably, at all temperatures, AC was showing least tendency towards adsorption of NAP (Fig. 2).

The sorption phenomena allow the following order:

1. At 298 K pristine MWCNT> -COOH functionalized MWCNT >AC
2. At 308 K: -COOH functionalized MWCNT > pristine MWCNT >AC
3. At 318 K: -COOH functionalized MWCNT > pristine MWCNT >AC

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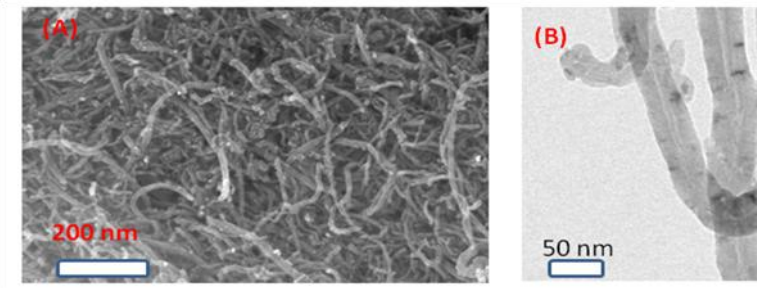
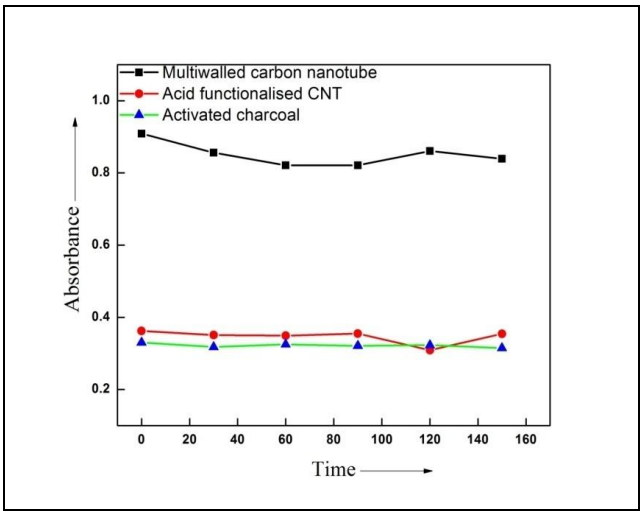


Fig. 1. (A) SEM of, (B) TEM of –COOH functionalized MWCNT



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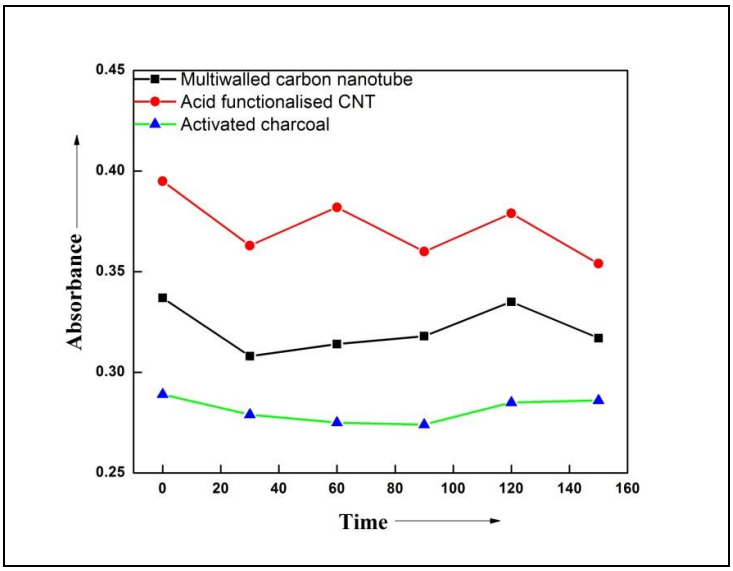

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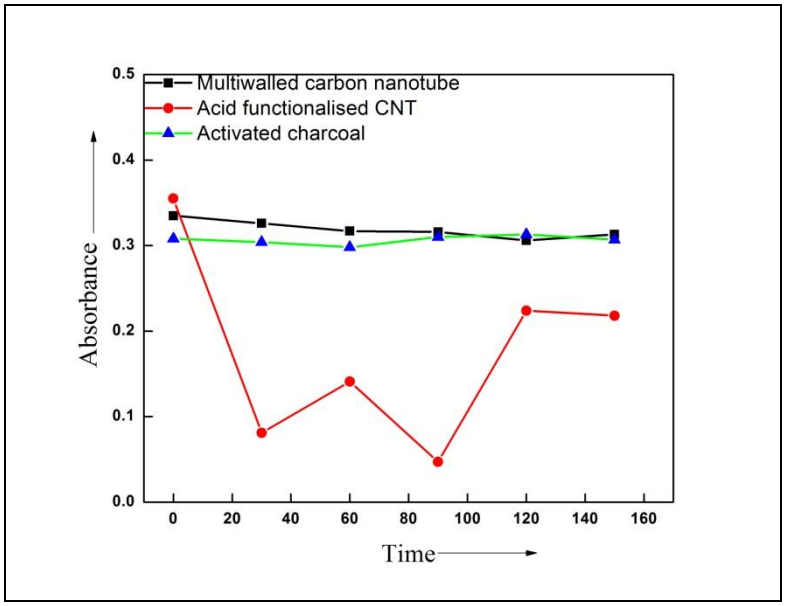

(C)

Fig. 2. Adsorption and desorption profile of Naproxen from carbon nanotubes (MWCNT, -COOH funtionalized MWCNT, and Activated charcoal). (A) At 298 K (B) At 308 K (C) At 318 K.

It is very important to understand the interaction between adsorbate and adsorbent in an adsorption and desorption process. To study the binding coefficient of NAP on the surface of MWCNT, method of continuous variation was considered and presented in the form of Jobs curve [20-22] (**Fig. 3**). The concentrations of NAP were identified by drawing calibration curve using HPLC (**Fig. S4**). This result clearly indicates that 0.4 units of adsorbate are the optimum concentration for the maximum binding value of NAP on the MWCNT quantitatively regarding peak area.

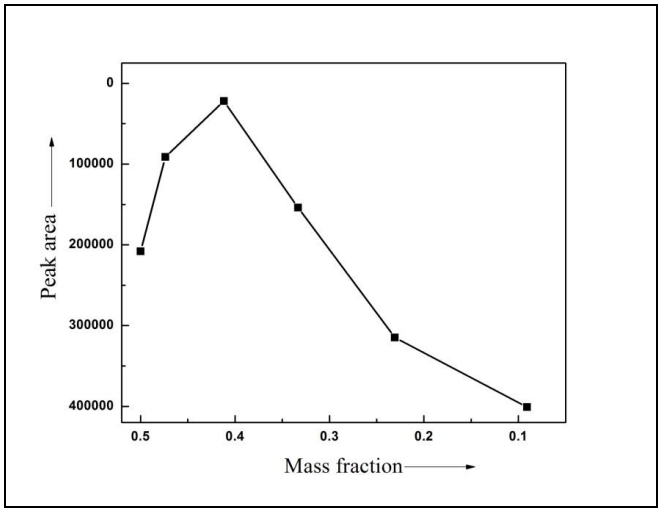

Fig. 3. Jobs plot for determination of binding coefficient of NAP on the –COOH functionalized CNTs.

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Thermodynamic parameters play a crucial role on adsorption - desorption process. Thus, evaluation of various thermodynamic parameters such as the change in Gibbs free energy (ΔG), enthalpy (ΔH), and entropy changes (ΔS) for the present study was considered. The above thermodynamic parameters were calculated with the application of optimum NAP concentration. The calculations were based on the equations as presented in Table 1. Moreover, activation energy (Ea) was also calculated for the adsorption process. Values of these parameters are compiled in Tables 2-4.

Table 1

Thermodynamic equations

$k = A\ exponential(-\frac{Ea}{RT})$	(1)
$\Delta G = -2.303RT \log k$	(2)
$\log\left(\frac{k2}{k1}\right) = \frac{\Delta H}{2.303R}\left(\frac{1}{T1} - \frac{1}{T2}\right)$	(3)
$\Delta G = \Delta H - T\Delta S$	(4)
$\Delta S = \frac{\Delta H - \Delta G}{T}$ [23]	(5)

VI. ACTIVATION ENERGY (E_a)

The comparative chart of adsorption activation energies of all the carbon templates under investigation indicates that the –COOH functionalized required least activation energy at room temperature. The corresponding values of E_a first increases with increase in temperature and then the sudden downfall of the value were observed with further elevation as shown in Table 4.

Table 2

Activation energy (E_a) in kJ.mol^{-1} of NAP on different templates of carbon and at different temperatures calculated from equation (1) and (2).

Entry	298 K	308 K	318K
MWCNT	-1.096	-2.284	-0.276
-COOH MWCNT	-0.372	-1.765	-0.757
Activated Charcoal	-0.807	-0.870	-0.753

VII. THERMODYNAMIC PARAMETERS: CHANGE IN FREE ENERGY (ΔG) AND CHANGE IN ENTROPY (ΔS)

The negative ΔG reveals that the adsorption process is spontaneous (Table 3). Also the ─COOH functionalized MWCNT shows a decrease of ΔG with increasing temperature whereas other two adsorbents show opposite trend. Moreover, the negative ΔS similarly in the case of MWCNT and AC indicated the decrease in randomness at the solid-solution interface during the sorption process of NAP on different carbon templates

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(Table 4) which is consistent with the fact that adsorption reduces the entropy while opposite behavior for –COOH functionalized MWCNT was observed i.e. positive ΔS. This signifies that (probably by the dipole-dipole interaction between NAP and carboxylate part of the –COOH functionalized MWCNT).

Table 3

Change in Gibb's free energy change (ΔG) in kJ.mol^{-1} of NAP on different templates of carbon calculated from equation (2).

Entry	298K	308K	318K
MWCNT	-15.355	-14.644	-18.325
-COOH MWCNT	-16.903	-14.895	-7.280
Activated Charcoal	-16.401	-17.028	-18.116

7.1 Change in enthalpy (ΔH)

The enthalpy change of adsorption process was found to be negative in case of MWCNT and AC, which indicates the exothermic nature of the adsorption process (Table 4). However ─COOH functionalized MWCNT shows opposite behavior that arises due to hydrophilic and hydrophobic interactions.

Table 4

Change in enthalpy (ΔH) in kJ.mol^{-1} and Change in entropy (ΔS) in kJ.mol^{-1}.K^{-1}of NAP on different templates of carbon calculated from equation (3) and (5) respectively.

Entry	ΔH (kJ.mol^{-1})	ΔS (kJ.mol^{-1}K^{-1})
MWCNT	-98.282	-0.376
-COOH MWCNT	248.864	0.753
Activated Charcoal	-16.359	-0.083

The adsorption on solids is classified into physical and chemical adsorption, but the exact dividing line in the present study is not very sharp. However, physical adsorption is usually non-specific, and the variation of energy on chemical adsorption is smaller than that of chemical adsorption in that is highly specific. Typically, ΔH for physical adsorption ranges from -4 to -40 kJ.mol^{-1}, compared to that of chemical adsorption ranging from -40 to -800 kJ.mol^{-1}**.** Generally ΔG for physisorption is between -20 and 0 kJ.mol^{-1} and for chemisorptions is between -80 and 400 kJ.mol^{-1} [24-25]. In a more clear way when the adsorption force is van der Waals force, the adsorption heat is (4 to 10) kJ.mol^{-1}, when the force is a hydrogen bonding force, the adsorption heat is (2 to 40) kJ.mol^{-1}. As the force is the exchange of dentate, dipole-dipole interaction, and chemical bonds force, the adsorption heat is about 40 kJ.mol^{-1}, (2 to 29) kJ.mol^{-1}, and above 60 kJ.mol^{-1}, respectively [25-26]. As shown in Table 3 and 4, ΔH and ΔG all implied that chemisorption might dominate the adsorption of naproxen onto MWCNT. Further functionalization and presence-absence of heteroatom may have some modification properties [26] of sorption on different carbon templates.

ISSN (O) 2454-9665
ISSN (P) 2454-0663

VIII. CONCLUSIONS

The potential of various carbon templates as adsorbents for the sorption of naproxen drug in the neutral pH has been examined, and the following conclusions are drawn:

1. The adsorption process is especially dependent on temperature and mild effect of pH is detected as process is simultaneously occurring. The values of ΔH, ΔS, and ΔG results show that the adsorbent employed has considerable potential as an adsorbent for the drug-delivery vehicle and release the molecule to the target surface.
2. Preferably, adsorption takes place when the drug is ionized, and even it is non-ionized. The ionized form is adsorbed more than non-ionized form. This study also showed that the sorption process of NAP is simultaneous and optimum at neutral pH on the different carbon templates. Moreover, the results showed –COOH functionalized MWCNT has maximum sorption capacity at higher temperatures, which is comparable with the other low-cost adsorbents.
3. The thermodynamic parameters like ΔH, and ΔG values of NAP sorption on MWCNTs and activated charcoal showed that the adsorption process is spontaneous, chemical and exothermic in nature (exceptionally for –COOH functionalized MWCNT where endothermic nature of adsorption is observed) and confirmed the affinity of various carbon templates for the drug NAP. The decreasing value of free energy changes with temperature for –COOH functionalized CNTs indicate that the adsorption capacity of the carbon increases at higher temperatures. The sorption of Naproxen on –COOH MWCNTs is a spontaneous physical adsorption process, and also an entropy-increasing process.
4. The present study also reveals that the optimum concentration for the maximum quantitative measure of binding of the adsorbate (NAP) on the surface of multiwalled carbon (MWCNT) is 0.4 units.
5. The thermodynamic description of the drug delivery and adsorbate-adsorbent complex is a complex task with the world of cellular thermodynamics, but further research is required into many different areas which includes increasing our fundamentals of reliable data on free energy of biomolecules in their environment, with a major emphasis on drugs with high specificity in active site and nature of cell as well. In addition, correlative approaches and cellular thermodynamics for open, closed and even irreversible systems, needs to be encouraged for therapeutic drugs and delivery. Surely, with this new generalization, concept of biothermodynamics is extended into new and challenging field for the cellular research.

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