Optimization of growth temperature of multi-walled carbon nanotubes synthesized by spray pyrolysis method and application for arsenic removal

S. Mageswari (A), P. S. Syed Shabudeen (B), S. Karthikeyan (C, *)

(A) Department of Chemistry, Vivekanandha College of Engineering for Women, Tiruchengode, Tamil Nadu, India.
(B) Department of Chemistry, Kumaraguru College of Technology, Coimbatore, Tamil Nadu, India.
(C) Department of Chemistry, Chikkanna Government Arts College, Tirupur, Tamil Nadu, India.

Multi-walled carbon nanotubes have been synthesized at different temperatures ranging from 550 °C to 750 °C on silica supported Fe-Co catalyst by spray pyrolysis method using Citrus limonum oil under nitrogen atmosphere. The as-grown MWNTs were characterized by scanning electron microscope (SEM), high resolution transmission electron microscope (HRTEM), X-ray diffraction analysis (XRD) and Raman spectral studies. The HRTEM and Raman spectroscopic studies confirmed the evolution of MWNTs with the outer diameter between 25 and 38 nm. The possibility of use of as-grown MWNTs as an adsorbent for removal of As (V) ions from drinking water was studied. Adsorption isotherm data were interpreted by the Langmuir and Freundlich equations. Kinetic data were studied using Elovich, pseudo-first order and pseudo-second order equations in order to elucidate the reaction mechanism.

1. Introduction: Nanotechnology is the creation of well-designed materials, devices and systems through control of matter on the nanometer scale and also the exploitation of novel phenomena and properties of matter (physical, chemical, biological, electrical etc.) at that length. Carbon nanotubes (CNT) have attracted growing interest owing to their distinctive physico-chemical and mechanical properties and plenty of potential applications. Majority of the synthetic methods such as arch-discharge, laser ablation, chemical vapor deposition (CVD) and spray pyrolysis are directly or indirectly based on the petroleum products [1, 2]. Considering the environmental effects and decreasing petroleum product sources, efforts are currently directed to away from them and switch over to reproducible natural carbon sources such as camphor [3], Turpentine oil [4], Eucalyptus oil [5], Coconut oil [6], Pine oil [7], Helianthus annuus oil [8], Jatropha curcas oil [9] and Glycine max oil [10] etc. as they are smart supply of hydrocarbons.

Transition metals are typically used as catalyst owing to their catalytic decomposition of carbon source, ability to form carbides and possibility for carbon to diffuse through and over the metals extremely rapidly [11]. Since it is catalyst that initiates the nucleation of carbon nanotube (CNT); it is imperative that the size of metal to be used as catalyst should be in nano scale. CNTs are tried to possess huge potential as superior adsorbents for removing many kinds of organic and inorganic contaminants due to their massive specific surface area, tiny size and capability to make each hollow, with high aspect ratio, and layered structures. Carbon nanotubes type aggregated pores due to the entanglement of hundreds of individual tubes that adhere to each other as a result of Van-der-Waals forces of attraction [12]. Heavy metals like lead, arsenic,
mercury etc. are glorious for an extended time to be serious water contaminants [13]. Arsenic is listed as a carcinogenic contaminant also liable for different health effects like stillbirth and polygenic disorder. Porous carbon adsorption has been cited by the US environmental protection agency (EPA) together of the most effective on the market environmental pollution control technologies [14].

In this article, we report the synthesis of MWNTs using Citrus limonum oil being a natural source that is renewable and low-cost. The possibility of the use of MWNTs as an adsorbent for the removal As (V) ions and adsorption capacity of chosen adsorbents was studied at various influencing factors such as temperature, pH, time and dosage of adsorbent.

2. Experimental Methods:
2.1 Synthesis of multi-walled carbon nanotubes: A silica supported Fe-Co catalyst (Fe: Co: SiO$_2$ = 1:0.1:4) was prepared by wet impregnation method [15]. Appropriate quantities of metal salts (Merck) i.e. Fe(NO$_3$)$_3$·6H$_2$O and Co(NO$_3$)$_3$·3H$_2$O were dissolved in methanol and mixed thoroughly with methanol suspension of silica support of Particle size 100-150 µm was procured from Merck (India). The solvent was then evaporated and the resultant cake heated to 90-100 °C for 3 h, removed from the furnace and ground in an agate mortar. The fine powders were then calcined for 1 h at 450 °C and then re-ground before loading into the reactor. The prepared catalyst was directly placed in a quartz boat and kept at the centre of a quartz tube which was placed inside a tubular furnace. The carrier gas nitrogen was introduced at the rate of 100 mL/min into the quartz tube to remove any oxygen from the quartz tube. The temperature was raised from room temperature to the desired growth temperature. Subsequently, Citrus limonum oil was introduced into the quartz tube through a spray nozzle and the flow was maintained at the rate of 0.5 mL/min. The deposition was conducted for 30 min for each process at different temperatures from 550 °C to 750 °C. Spray pyrolysis was carried out for 45 minutes and thereafter the furnace was cooled to room temperature. Nitrogen atmosphere was maintained throughout the experiment.

The morphology and degree of graphitization of the as-grown nanostructures were characterized by scanning electron microscopy, (Hitachi SU6600), high resolution transmission electron microscopy (JEOL-3010), Raman spectroscopy (JASCO NRS-1500W, green laser with excitation wavelength 532 nm) and thermo gravimetric analysis (TGA). Magnetic properties of the sample at room temperature were studied using a vibrating sample magnetometer. The as-grown products were subjected to purification process as follows [16]. The sample material was added to 5% HF solution to form acidic slurry. This slurry was heated to 60 °C and stirred at 600 rpm. The sample was filtered and washed with distilled water. The collected sample was dried at 120 °C in air for 2 h. The stock solution of As (V) was prepared by dissolving Na$_2$HAsO$_4$·7H$_2$O in distilled water. The residual As (V) concentration in the solution after adsorption was analyzed using a flame atomic adsorption spectrometer (AAS). The solution pH was adjusted with HCl and NaOH.

![Figure (1): Schematic diagram of the home-made spray-pyrolysis set-up. A - furnace, B - spray nozzle, C - separating funnel containing carbon feed stock, D - nitrogen gas cylinder, E - quartz boat containing catalysts with supporting material, F - rubber tube, G - outlet, H - flow meter.](image-url)

2.2. Adsorption process:
As (V) adsorption capacity of MWNTs was firm in a batch reactor. The As (V) solutions of required concentration were prepared by diluting appropriate volume of a stock solution. The solution was further diluted to the required
concentrations (10 - 100 mg/L) before its use. The pH of the solutions was adjusted by adding 0.1M HNO$_3$ or 0.1M NaOH. All the experiments were performed by agitating 50 mL of the As (V) solution at the desired concentration and 50 mg MWNTs in 100 mL bottles.

Agitation was performed for a predetermined time at room temperature in a reciprocating shaker. The suspension was filtered through 0.45 µm filters and the residual As (V) concentration was determined in the liquid phase using atomic absorption spectrometer (AAS, Shimadzu, Japan model AA-6800). The percentage of adsorption was calculated using the relationship:

$$R_\text{ads} = \frac{(C_0 - C_t)}{C_0} \times 100$$  \hspace{1cm} (1)

where $C_0$ and $C_t$ are initial (inlet) and final concentrations of arsenic at time t. Then the amount of arsenic adsorption per unit mass of adsorbent at time t ($q_t$) was calculated using the relationship:

$$q_t = \frac{C_0 - C_t}{W} \times V$$  \hspace{1cm} (2)

where $V$ is the volume of solution (L) and $W$ is the mass of the adsorbent (g).

2.3. Effect of pH on the removal of As (V) ions:
The effect of pH on the adsorption of As (V) ions on MWNTs was investigated. The pH value played an important role with respect to the adsorption of particular ions on MWNTs. The pH of solution affected the surface charge of the adsorbent and the degree of ionization. The Figure (2) shows that pH variations have some extent of influence on the As (V) adsorption. In order to evaluate the effect of pH on the adsorption of As (V) on CNTs, a series of sample solutions containing As (V) at a concentration of 50 mg/L was adjusted to pH in the range of 2-10 with 0.1N HNO$_3$ and 0.1N NaOH solutions. The pH of the solutions was measured by using an Elico pH meter (model L1-120-ISI, 1977). Figure (2) shows that the adsorption of As (V) decreases while there is an increase in the pH value. As (V) adsorption is strongly dependent on electrostatic parameters such as adsorbent surface charge, which are dependent on pH [17].

The adsorption potency at pH 2 was found to be 92.2 %. Therefore, during this study, the optimum pH value for As (V) adsorption was resolved to be 2. The pH$_{zc}$ is the value of pH at which the surface of an adsorbent has a net neutral charge [18]. At higher pH values the surface has a net negative charge and at lower pH values the surface has a net positive charge. As the pH of a system increases, the amount of negatively charged sites will increases [19]. A negatively charged surface site on the adsorbent does not favor the adsorption of As (V) ions due to the electrostatic repulsion. The isoelectric point value of 6.4 for MWNTs indicates that the surface of MWNTs is positively charged under acidic conditions and the positive charges facilitate the removal of As (V) ions.

3. Result and Discussion:
Figure (3) expressly presents the SEM images of MWNTs grown up at varied temperatures. Figure (3a) shows the formation of MWNTs is low at 550 °C. As a result of at this temperature the carbon decomposes partially leading to the carbonaceous materials. At 650 °C, as the temperature was appropriate for complete pyrolysis of carbon sources, pyrolysed carbon atoms diffused over the catalyst particles and helped to initiate the expansion of nanotubes so it was potential to get an even diameter within the grownup MWNTs Figure (3b). At 750 °C the
amount of MWNTs has decreased and thick nanotubes have been fashioned. The diameter of nanotubes enhanced with increasing the temperature.

Figure (3) : SEM images of MWNTs grown on Fe-Co catalyst supported on silica at various temperatures ranging from 550 °C (a), 650 °C (b), and 750 °C (c).

Figure (4): TEM images of MWNTs grown on Fe-Co catalyst supported on silica at various temperatures ranging from 550 °C (a), 650 °C, (b) and 750 °C (c).
The HRTEM images in Figure (4a) illustrate the tiny quantity of amorphous carbon present in the MWNTs with \( \approx 30 \) nm at 550 °C. The overall diameter of MWNTs has been found to be \( \approx 35 \) nm at 650 °C and \( \approx 40 \) nm at 750 °C. It is clearly seen that the diameter of the MWNTs will increases considerably with increasing temperature. At 650 °C, the MWNTs have tubular structure with inner and outer diameters creating a regular structure over entire length of the tube.

Figure (5): Typical Raman Spectrum of the MWNTs grown at 650 °C.

![Raman Spectrum](image)

**Table (1):** Langmuir and Freundlich models for adsorption of As (V) onto purified chosen MWNTs

<table>
<thead>
<tr>
<th>Adsorption isotherm models</th>
<th>Langmuir models</th>
<th>Freundlich models</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( Q_0 ) (mgg(^{-1}))</td>
<td>( b ) (L mg(^{-1}))</td>
</tr>
<tr>
<td>As (V)</td>
<td>32.66</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Table (1): Langmuir and Freundlich models for adsorption of As (V) onto purified chosen MWNTs

The results of Raman spectroscopy analysis in Figure (5) represent the MWNTs grown on the catalyst surface at 650 °C, indicating two characteristic peaks at 1354 cm\(^{-1}\) and 1582 cm\(^{-1}\) which correspond to D and G bands, respectively. The G bands are associated with stretching vibration within the basal plane of graphite crystal, which is normalized to an equivalent intensity. The D bands are associated with the disorder or defective planar graphite structure. The D peaks at 1354 cm\(^{-1}\) may be attributed to the defects in the curved graphene sheets. Therefore, the Raman spectrum provides definite proof that the MWNTs have graphitic structure.

![XRD Pattern](image)

**Figure (6):** XRD patterns of MWNTs grown at 650 °C.

Figure (6) shows that the MWNTs crystal structure was studied by X-Ray Diffraction method. The peaks are indexed as the (002) and (101) reflections of hexagonal graphite. Intense peaks are found at 26.35° and 44.44° can be indexed to the (002) and (101) planes, respectively.

### 4. Adsorption Isotherm:

The experimental data for As (V) adsorption onto MWNTs could be evaluated by the Langmuir and Freundlich isotherm models.

\[
Q = \frac{Q_0 b C_e}{1 + Q_0 C_e} \quad (3)
\]

\[
Q = K_F C_e^n \quad (4)
\]

where \( C_e \) is the equilibrium concentration of As (V) (mg/L), \( Q_0 \) (mgg\(^{-1}\)) and \( b \) (L mg\(^{-1}\)) are Langmuir constants and \( K_F \) (mg g\(^{-1}\)) and \( n \) are Freundlich constants. The constants of Langmuir and Freundlich models are obtained from fitting the adsorption equilibrium data and are listed in Table1. The correlation coefficients of Langmuir and Freundlich models are 0.993 and 0.967 respectively, indicating that the Langmuir model is more appropriate to describe the adsorption characteristics of As (V) onto chosen adsorbent.
4.1. Kinetics of adsorption:
Adsorption kinetics is used to investigate the mechanism and the rate controlling steps of adsorption. The kinetic information obtained is then applied to totally different models to explain the interaction between the As (V) and also the chosen adsorbents. The pseudo-first order, pseudo-second order and Elovich kinetic models were used to elucidate the complex dynamics of the adsorption process. To determine the equation that best describes the adsorption of As (V), a standard error of estimate was calculated for every kinetic equation, viz. pseudo first order, pseudo second order and Elovich equation. A relatively high value of the regression coefficient ($R^2$) was used as the criterium for the most effective work [20].

$$R^2 = \frac{\sum q^2 - (\sum q - \sum q')^2}{\sum q^2}$$  \hspace{1cm} (5)

where $q$ and $q'$ are the measured and calculated amounts of As (V) adsorbed on a chosen adsorbent at time $t$.

Pseudo-first order kinetic model:
The pseudo first order equation [21] is generally expressed as first order rate expression as shown below.

$$\frac{dq}{dt} = k_1(q_e - q_t)$$  \hspace{1cm} (6)

where $q_e$ and $q_t$ are the adsorption capacity (mg g$^{-1}$) at equilibrium and at time $t$ respectively, $k_1$ is the rate constant of pseudo-first order adsorption (min$^{-1}$).

Pseudo-second order kinetic model:
The pseudo-second order equation [22] has been considered for describing the adsorption of As (V) on chosen adsorbates. The linearized form of the pseudo-second order rate equation is given as

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (7)

where $k_2$ is the rate constant of pseudo second order adsorption (g mg$^{-1}$ min$^{-1}$), $q_e$ and $q_t$ are the values of the amount of As (V) adsorbed per unit mass of adsorbate at equilibrium and at any time $t$, respectively.

Elovich model: The Elovich equation is another kinetic model used to describe the adsorption As (V) on chosen solid adsorbents. The equation [20] is generally expressed by:

$$\frac{dq}{dt} = \alpha e^{-\beta q}$$  \hspace{1cm} (8)

where $\alpha$ and $\beta$ are the Elovich coefficients that represent the initial adsorption rate (mg g$^{-1}$ min$^{-1}$) and the desorption constant (g mg$^{-1}$) respectively.

4.2. Batch Adsorption studies:
All reagents used were of AR grade (E merck). 50mL of pH adjusted arsenic solution of known concentration ($C_0$) was taken in a 100 mL screw-cap conical flask with a required amount of adsorbent and was agitated at a speed of 200 rpm in a thermostatic shaker bath at 27 °C for a specified period of time. Then the solution was filtered through a 0.45 µm membrane filter.

4.3. Effect of adsorbent dosage on As (V) adsorption:
The effect of MWNTs dose in the range of 1 g/L to 10 g/L on As (V) adsorption was investigated at pH=3. The initial As (V) concentration was kept constant at 50 mg/L and the contact time used was 2.5 h. Figure (7) shows that the As (V) adsorption increased from 37 % to 80 % when the adsorbent dose increased from 1 g/L to 10 g/L. The adsorption capacity decreased from 17.7 mg/g to 3.9 mg/g. The increase in percentage of As (V) adsorption with the increase of adsorbent dose may be due to increased number of available adsorption sites and the decrease in adsorption capacity is mainly due to unsaturation of adsorption sites through adsorption reaction.
4.4. Effect of Temperature on kinetic rate constant and rate parameters:

Adsorption experiments were carried out with fixed initial As (V) concentration (50 mg/L) at pH 3 and at different temperatures, viz. 30 °C, 45 °C and 60 °C. The analysis of the data collected in Table 2, reveals that the increases in temperature on As (V) removal have a significant effect on the pseudo first order and Elovich rate constants. The results reveal also that the influence of temperature on pseudo second order rate constant is appreciable. The value of correlation coefficient $R^2$ (0.992) for pseudo second order rate equation, shows that the adsorption of As (V) ions by MWNTs was better than Elovich rate equation.

| Adsorbent | Initial Temperature | Pseudo first order | | \( K_1 \) (min) | R² | Pseudo second order | \( K_2 \) (g mg⁻¹ min⁻¹) | h (mg g⁻¹ min⁻¹) | R² |
|-----------|---------------------|-------------------| | | | | | | |
| MWNTs     | 35 °C               | 0.134             | R² | 0.91 | | 0.120 | 21.613 | 0.986 |
|           | 45 °C               | 0.137             | R² | 0.91 | | 0.014 | 14.212 | 0.994 |
|           | 60 °C               | 0.168             | R² | 0.92 | | 0.126 | 11.225 | 0.986 |

Table (2): The adsorption kinetic model rate constants for chosen MWNTs at different Temperatures.

4.5. Thermodynamic Parameter:

The thermodynamic parameters obtained for the chosen adsorbent-adsorbate system were calculated using the following equation [23].

\[
K_c = \frac{C_{ae}}{C_e} 
\]

\[
\Delta G = -RT \ln K_c 
\]

\[
\log K_c = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} 
\]

where $K_c$ is equilibrium constant, $C_{ae}$ is the solid phase concentration at equilibrium, $C_e$ is residual concentration at equilibrium, $R$ is gas constant (J/mole) and $T$ is the temperature in Kelvin, $\Delta G$ is Gibbs free energy (KJmol⁻¹), $\Delta H$ is enthalpy change (KJmol⁻¹) and $\Delta S$ is entropy change (KJmol⁻¹).

$\Delta H$ and $\Delta S$ were obtained from the slope and intercept of Van’t Hoff plot ($1/t$ Vs $\ln K_c$) and their values are presented in Table (3). The negative values of free energy change ($\Delta G$) indicate the feasibility and spontaneous nature of adsorption. The positive value of $\Delta S$ is due to the increased randomness during the adsorption and positive $\Delta H$ value indicates endothermic nature of adsorption.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$\Delta G \times 10^4$ (KJ mol⁻¹)</th>
<th>$\Delta H$ (KJ mol⁻¹)</th>
<th>$\Delta S$ (KJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNTs</td>
<td>-11.77</td>
<td>13.14</td>
<td>431.89</td>
</tr>
</tbody>
</table>
5. Mechanism of As (V) adsorption on to MWNTs:
The high correlation coefficients were obtained exploitation of pseudo first order, pseudo second order and Elovich kinetic models. It looks to be impossible to conclude that adsorption mechanism truly occurred in a trial to spot the precise adsorption mechanism.

In adsorption methods of As (V) on a solid surface, the As (V) species migrate towards the surface of the adsorbent. This kind of migration issue tills the concentration of the adsorbate species on the surface of the adsorbent reach most. Once equilibrium is attained, the migration of the solute species from the solution stops. In this situation, it is possible to measure the magnitude of distribution of the solute species at the solid-liquid interface. The magnitude of this kind of distribution is a measure of efficiency of the chosen adsorbent and adsorbate species.

When MWNTs are in contact with a solution containing As (V), the metal ions initial migrate from the bulk solution to the surface of the liquid film. This surface exerts a diffusion barrier which may be noteworthy. The involvement of a significant quantum of diffusion barrier indicates a dominant role of the film diffusion in the adsorption process. Furthermore, the rate of an adsorption process is controlled either by external diffusion, internal diffusion or by both types of diffusion.

The adsorption of an adsorbent on MWNTs is remarkably different from adsorption on other conventional porous carbons in several aspects. First, owing to their one-dimensional nanostructure, the external surface available for adsorption is considerably larger than the surface area arising from inner cavities. The predominance of outer cavity to inner cavity surface area determines the adsorption characteristics of As (V) on MWNTs. The adsorption on the external surface of MWNTs is more important than the adsorption inside the micro/mesoporous cavities. Another noteworthy difference can be ascribed to the interstitial space between individual nanotubes. The dimension of this space is determined by the relative positions among individual tubular structures.

In the batch mode contact time adsorption experiments, rapid stirring was maintained. This made As (V) migrate from the solution to the external surface of the adsorbent material and this step controlled the rate of the adsorption process [24]. To interpret the experimental data it is necessary to recognize the steps involved in the process of adsorption that govern the overall rate of As (V) removal. The mathematical treatments recommended by Boyd et al. have been applied [25]. These mathematical treatments were found to be useful to distinguish between particles diffusion and film diffusion.

The successive steps in the adsorption of As (V) by adsorbents include:
(i) Transport of adsorbates to the external surface of adsorbent (film diffusion);
(ii) Transport of the adsorbates within the pores of the adsorbent except for a small amount of adsorption, which occurs on the external surface (particle diffusion);
(iii) Adsorptions of the ingoing ion (adsorbate) on the interior surface of the adsorbent.

Only the third process can be considered as not limiting step in the uptake of As (V) on to MWNTs [26]. The remaining two steps impart the following three possibilities:
Case I: external transport < internal transport if the rate is governed by particle diffusion.
Case II: external transport > internal transport if the rate is governed by external diffusion.
Case III: external transport ≈ internal transport if the transport of adsorbate ions to the boundary is not possible at a reasonable rate; this may result in formation of a liquid film surrounded by the adsorbent particles with a proper concentration gradient.

As rapid stirring was maintained in the study, the transport of the adsorbed species, As (V), from the solution to the pores of the adsorbent material might control the rate of adsorption process. Hence, the author concludes that the mechanism of As (V) removal by the chosen adsorbents is complex. It indicates the probable occurrence of
both film diffusion and intraparticle diffusion. Therefore, the adsorption data were further analyzed by the kinetic expression given by Boyd et al.

\[
F = q_t / q_e = 1 - \frac{6}{\pi^2} \sum_{n=1}^{N-1} \frac{1}{n^2} \exp \left[ - \frac{D_i \pi^2 n^2}{r^2} \right]
\]  

(12)

\[
B_i = \frac{\pi^2 D_i}{r^2}
\]

(13)

In the present study, the quantitative treatment of the sorption dynamic was found in accordance with the observation made by Reichenberg [27], as described by the following equation.

\[
F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{N-1} \frac{1}{n^2} \exp \left[ - n^2 \beta_i \right]
\]

(14)

where \( F \) is the fractional attainment of equilibrium at time \( t \) and \( n \) is constant [28].

\[
F = \frac{Q_t}{Q_\infty}
\]

(15)

where, \( Q_t \) and \( Q_\infty \) are the amounts adsorbed after time \( t \) and after infinite time respectively.

\[
B = \frac{\pi^2 D_i}{r_0^2} = \text{time constant}
\]

(16)

where, \( D_i \) is the effective diffusion coefficient of adsorbate in the adsorbent phase and \( r_0 \) is the radius of adsorbent particles.

For every observed value of \( F \), corresponding values of \( B_i \) were derived from Reichenberg’s table. In each case, the plot of \( B_i \) vs. time distinguishes between the processes involving film diffusion and particles-diffusion, controlling the rate of adsorption.

Typical \( B_i \) vs. time plots at the concentration of 20 mg/L As (V) adsorbed on MWNTs at different temperatures are presented in Figure (8). The \( B_i \) vs. time plots for the adsorption of As (V) adsorbed on MWNTs found to be linear at the temperatures of 30, 45 and 60 °C, thus the process involved can be considered as film diffusion. At 30 °C the adsorbent exhibits linearity in \( B_i \) vs. time plots in the entire concentration range, but the straight lines obtained do not pass through origin, revealing thereby that the rate-determining process is film diffusion at this temperature for the chosen adsorbent.

\[
D_i = D_0 \exp \left[ - \frac{E_a}{RT} \right]
\]

(17)

\[
D_0 = (2.72 d^2 kT / h) \exp \left[ \frac{\Delta S^#}{R} \right]
\]

(18)

where, \( d \) is the average distance between the successive exchange sites and is taken as 5Å and \( R \), \( h \) and \( k \) are the gas, Planck and Boltzmann constants respectively. The values of \( E_a, D_i, D_0, \Delta S^# \) and other parameters are given in the Table 4. The negative values of \( \Delta S^# \) indicate that no significant change occurs in the internal structure...
of chosen adsorbents during the adsorption process.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>( D_i ) (m/s)</th>
<th>( D_0 ) (m/s)</th>
<th>( E_a ) (KJ/moI)</th>
<th>( \Delta S^# ) (JK°mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNTs</td>
<td>3.22 x 10(^{-13})</td>
<td>7.13 x 10(^{-13})</td>
<td>4.94 x 10(^{-4})</td>
<td>22.42</td>
</tr>
</tbody>
</table>

Table (4): Effective diffusion coefficient \( (D_i) \) pre exponential constant \( (D_0) \), activation energy \( (E_a) \), and entropy of activation for diffusion of As \((V)\) in chosen MWNTS.

6. Conclusions:
Multi-walled carbon nanotubes were obtained by chemical vapour deposition technique using *Citrus limonum* oil, an unconventional natural precursor. The experimental diameter of CNT was found to be about 20 - 40 nm and the achieved yield was 60 % at 650 °C, confirming the possibility and reliability of obtaining MWNTs as a major adsorbent source to be applied in the process of eliminating As \((V)\) from aqueous solution. Furthermore, the adsorption of As \((V)\) was found to be dependent on pH, temperature and dosage of the adsorbent. Thermodynamic parameters obtained for the adsorbents account for feasibility of the process at each concentration of As \((V)\). The kinetic study also revealed that elimination of As \((V)\) takes place through a film diffusion process at all the concentrations and temperatures of MWNTs obtained from *Citrus limonum* oil. The saturation percentage was found to be 93 % for the MWNTs and the As \((V)\) adsorption on adsorbent was found to follow the pseudo second-order rate equations. Furthermore, this research can be scaled up for mass production of MWNTs for multiple benefits.

Reference

***