Purification of Ethanol Produced by al Mosul State Company for Sugar Production Using Carbon Nano Tubes

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Abstract

Ethanol produced by AL Mosul state Company usually used for industrial uses contains impurities such as methanol and formaldehyde. In order to remove these impurities, functionalized MWCNTs were used as an adsorbent in batch process. In the present work, multi wall carbon nanotubes (MWCNTs) were prepared by catalytic chemical vapor deposition (CCVD) method, using tubular furnace in which thermal decomposition of acetylene gas has been done under 700 C° for 1 hour in quartz tube using argon as carrier and inert gas. Purification of carbon nanotubes from impurities of amorphous carbon and metal catalyst has been done by using ultrasonic path in the presence of 6M HCl. Functionalization of MWCNTs has been obtained by chemical treatment with a high concentration (69% - 72%) nitric acid under total reflux. MWCNTs were characterized by using a different technique. The result of SEM showed a well-defined CNTs with 75nm in diameter and several μm in length, this result was confirmed by XRD analyses in which two peaks were observed for MWCNTs at (2θ) 26.1° and (2θ) 42.9° which represent the hexagonal structure of MWCNTs. BET technique showed that carbon nanotubes have a specific surface area of 175m²/g and with pore volume of about 0.91cm³/g. Fourier Transfer Infrared Spectra (FTIR) was used to detect functional group, peak at 3429.34 cm^{1} characterized hydroxyl group and peak at 3394.72 cm^{1} characterized carboxyl group. In batch adsorption process experiments, the effect of MWCNTs dosage of (50, 100 and 150) mg/L, pH (3-12) with initial concentration of (10, 20 and 30) ppm for methanol and (20, 40 and 60) ppm for formaldehyde and contact time (5-35) min have been studied. The maximum removal efficiency was obtained under the following conditions (pH=5, CNTs dosage=100mg/l, contact time=35min and initial concentration=10, 20 for methanol and formaldehyde respectively). Adsorption isotherms were fitted with the Langmuir and Freundlich models. The equilibrium data were best represented by the Langmuir isotherm model with higher correlation coefficient R2 value of (0.9321, 0.9987) for formaldehyde and methanol respectively.

1 Introduction

The application of ethanol as a renewable, clean energy fuel for helps conserve petroleum and reduce emission, chemical solvent, medical and pharmaceutical agent, required purification for removal of very low concentration of impurities usually exist in ethanol during ethanol production. Accordingly, extensive researches on ethanol purification have done recently due to a rapid increase in world ethanol production [1].

Iraq is considered one of the main producers of date in the Middle East, in addition to sugar cane and sugar beet, now a large quantity of ethanol is produced by fermentation of juice extracted from the date which considered the main substrate of ethanol in Iraqi private and state companies. Meanwhile, remnants of the sugar industry (Molasses) are the dominant substrate of ethanol in Iraqi State Companies as in Mosul Sugar Production Company (north of Iraq) and Messan sugar production company (south of Iraq) [2].

The state company for sugar industry/Mosul city produces a large quantity of ethanol mainly uses for industrial purposes. The company is facing marketing problem due the undesirable odor irradiated from some organic impurities particularly formaldehyde. These impurities make ethanol unfit with the national and international standards of the medical and pharmaceutical industry uses.

In lecture various techniques have been used for organic impurities removal from ethanol such techniques are distillation, ozonation [3], gas stripping [4], and adsorption [5].

Distillation is one of the most efficient separation techniques. However, it contains several problems; one is the separation of volatile compounds. It is expected that impurities with similar boiling points to ethanol lodge in ethanol even after distillation, second is its cost [1].

Ozonation is one of the efficient methods used for decomposition and removed of ethanol impurities. Ozone is a tri-atomic molecule consisting of three oxygen atoms. Ozone could decompose various kinds of compounds using its strong oxidation potential. Decomposition of compounds could result in changes in physical and chemical properties of compounds such as increases in volatility, biodegradability, and a decrease in toxicity. Although oxidation of ethanol could be expected with oxidation, it does not happen under the atmospheric condition .Thus, ozone can remove impurities without a significant damage on ethanol. There are still some problems with non-oxidizable compounds and ozonolysis by-products. It is expected that some compounds cannot be oxidized by ozone. These compounds will remain after ozonation. Also; ozonation is an oxidation process and not remove compounds physically. Thus, ozonation could generate new compounds, ozonolysis by-products. These compounds should be removed after ozonation by post-Ozonation treatments [2].

Gas stripping is a separation technique utilizing the differences in volatilities among compounds. The separation efficiency is simply governed by Henry's law constant

$$H = \frac{P_{vap}}{C_{sat}} \quad (1)$$

Where H = Henry's constant (moles/L atm)

Pvap = the partial pressure of a pure compound (atm), and Csat = the saturation concentration of the pure compound in the liquid phase (moles or mg/L). Henry's law constant varies depending on the vapor and liquid phases. It is easily imagined that compound with low boiling points can be stripped more easily such as acetaldehyde, which is one of the major impurities in ethanol [6].

Therefore, we find necessary to suggest a new process to serve the problem. Recently great attention has been paid to CNTs because of its unique properties. CNTs have a high specific surface, large number of active sites by introducing different functioned groups, and ability to interact with other molecules, these properties make CNTs a favorable adsorbent material for environmental applications [7,8] and it was found to be more efficient adsorbents than the conventional activated carbons, with a higher adsorption capacity [9], [10], [11], [12], and shorter equilibrium time [10].

The aim of this work was to be treated of industrial ethanol produced from fermentation of Molasses using CNTs as an adsorbent in the batch experiment process. Removes impurities like formaldehyde aim to purify the ethanol from undesired odor, which is one of the major factor effects on ethanol medical and pharmaceutical specification.

2. Materials and Methods:

2.1 Materials

Acetylene 99% and argon (100%) was supplied by Alfurat Iraqi state company, nitric acid (69-70%), HCl (37%), and NaOH (98%) was supplied by Merk Germany. Industrial ethanol 96% was supplied by the Iraqi ethanol factory in Mosul (North of Iraq), it was consisted of 20ppm of formaldehyde. Absolute ethanol 99.9% and formaldehyde were purchased from J.T.Baker, Holland, all other chemicals were a chemical grade and purchased from Merk Germany.

2.2 Preparation Purification and Functionalization of Carbon nanotubes (CNTs)

CNTs were prepared, purified, and functionalized according to our previously published work [13]. Synthesis is carried out by Chemical Vapor Deposition system CVD shown in figure 1 by decomposition of acetylene gas in a horizontal quartz tube (2.5 cm in diameter and 150 cm length) at 700 0C in a presence of inert gas (argon) and alumina coated Fe nanoparticles used as a catalyst.

Prepared CNTs were purified to remove the metal catalyst; 2 grams of CNTs was dispersed into a flask containing 100mL of 6M hydrochloric acid and then shaken in ultrasonic cleaning bath for one hour. After that, it was rinsed with distill water for several times until the pH of the mixture was close to 7; the solution was filtered using millipore membrane filter 0.45 μm (Chmlab group, Spain). Finally, it was dried in air for 24 hours. For functionalization of CNTs 1 gram of purified CNTs powder was mixed with 150mL of 69% nitric acid under total reflux at 100^0C for 2 hours. Then the CNTs solution cooled, washed with deionized water several times until the pH reached 7; the solution was filtered using millipore membrane filter 0.45 μm. Then, CNTs dried in air for 24 hours and then dried in a furnace at 140^0C for 2 hours.

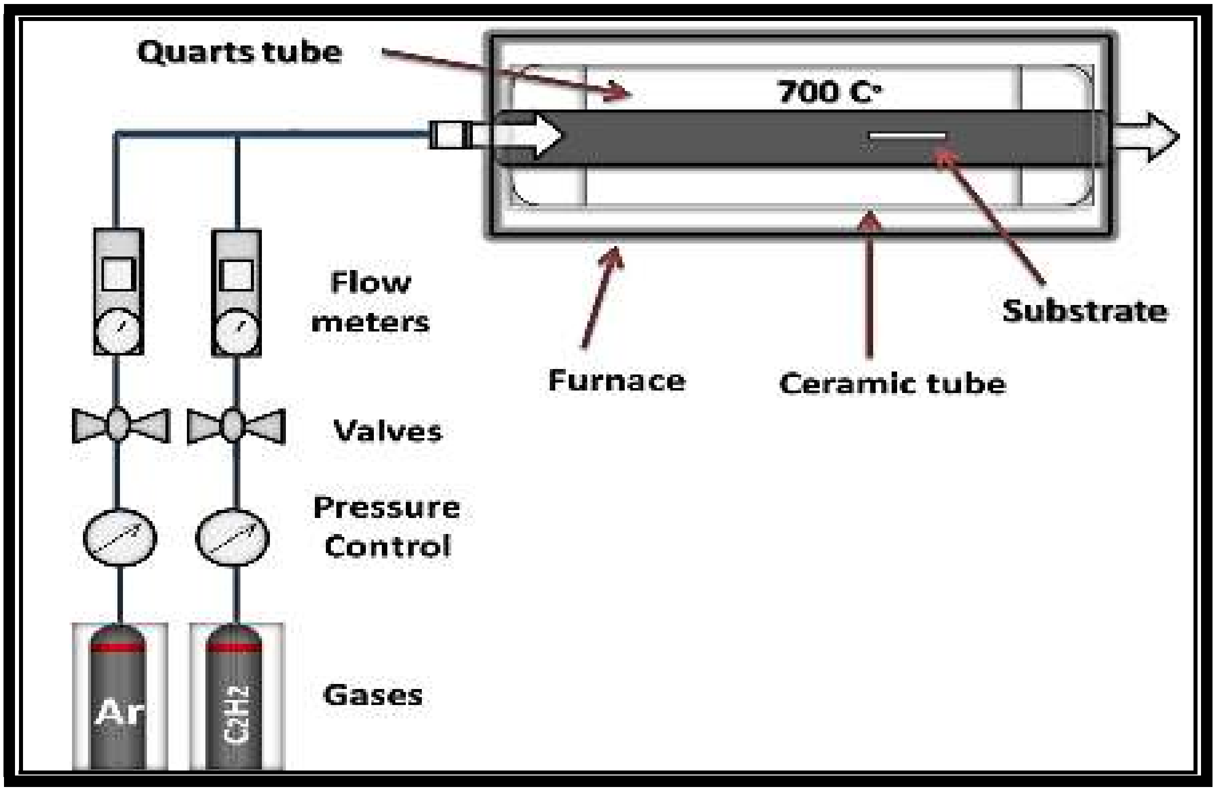

Figure 2: Schematic diagram of the CCVD system.

2.3 Characterization of the samples

The synthesis CNTS were characterized using Scanning Electron Microscopy (SEM) (Type TESCAN VEGA 3SB, Accelerating Voltage: 30kv, X-ray diffraction (type XRD-6000, Shimadzu), FT-IR instrument (Type Shimadzu 8400 S, Japan), and the measurement of the pore volume and specific surface area were done according to Brunauer, Emmett and Teller (BET) method using Instrument model Q-surf 9600 (USA).

2.4 Batch Adsorption Experiments:

Batch mode is used for removal of formaldehyde (FR) during the course of this work. The stock solution of formaldehyde was prepared by diluting 1 gm of FR in 400ml ethanol .The stock solution was then diluted to the desired initial concentrations. An amount of (50, 75,100,125 and 150 mg/l) adsorbent (CNTs) was added to 100 ml conical flask filled with an industrial ethanol solution of known concentrations. The conical flasks were placed inside the shaker and shakes at 200rpm for 30min at room temperature. After shaking, the mixtures were settled for 1 hour. The supernatants withdraw were immediately filtered using 0.45 um filter paper and analyzed by a U.V-1100 spectrophotometer (Chrom Tech / China). The effects of various variables affecting the adsorption of impurities in industrial ethanol over CNTs were determined. The pH of each solution was adjusted using 0.1 M HCL or o.1 M NaOH. Table 1 summarized the variables studied through the batch adsorption process.

Time (min)	5	10	15	20	25	30	35
CNTs dose (mg/L)	50	75	100	125	150		
Initial concentration of formaldehyde (mg/L)	20	30	40	50	60		
pH of the solution	3	5	6	8	12		

Table 2: the variables values of batch adsorption process

The equilibrium adsorption capacity was calculated using Eq. (2):

$$q = V * \frac{C_o - C_f}{m} \quad (2)$$

where q (mg/g) is adsorption capacity, m (g) is the mass of adsorbent, V (L) is the volume of solution, and C_0 and C_f (mg/L) are the formaldehyde solution concentration at initial and final, respectively. The removal efficiency (R %) of the formaldehyde was calculated by the following relationship:

$$R\ (\%) = \frac{C_o - C_f}{C_o} * 100 \quad (3)$$

3. Result and Discussion

CNTs were successfully synthesized using chemical vapor deposition method. The CNTs were characterized using Scanning Electron Microscopy (SEM), X-ray diffraction technique, and Fourier Transform Infrared (FTIR) spectroscopy.

SEM micrographs confirm the formation of multiwalled carbon nanotubes MWCNTs rather than single walled carbon nanotubes. The functionalized MWCNTs are showed in figure 3 well defined multiwall carbon nanotubes with average diameter of 10-25nm were obtained.

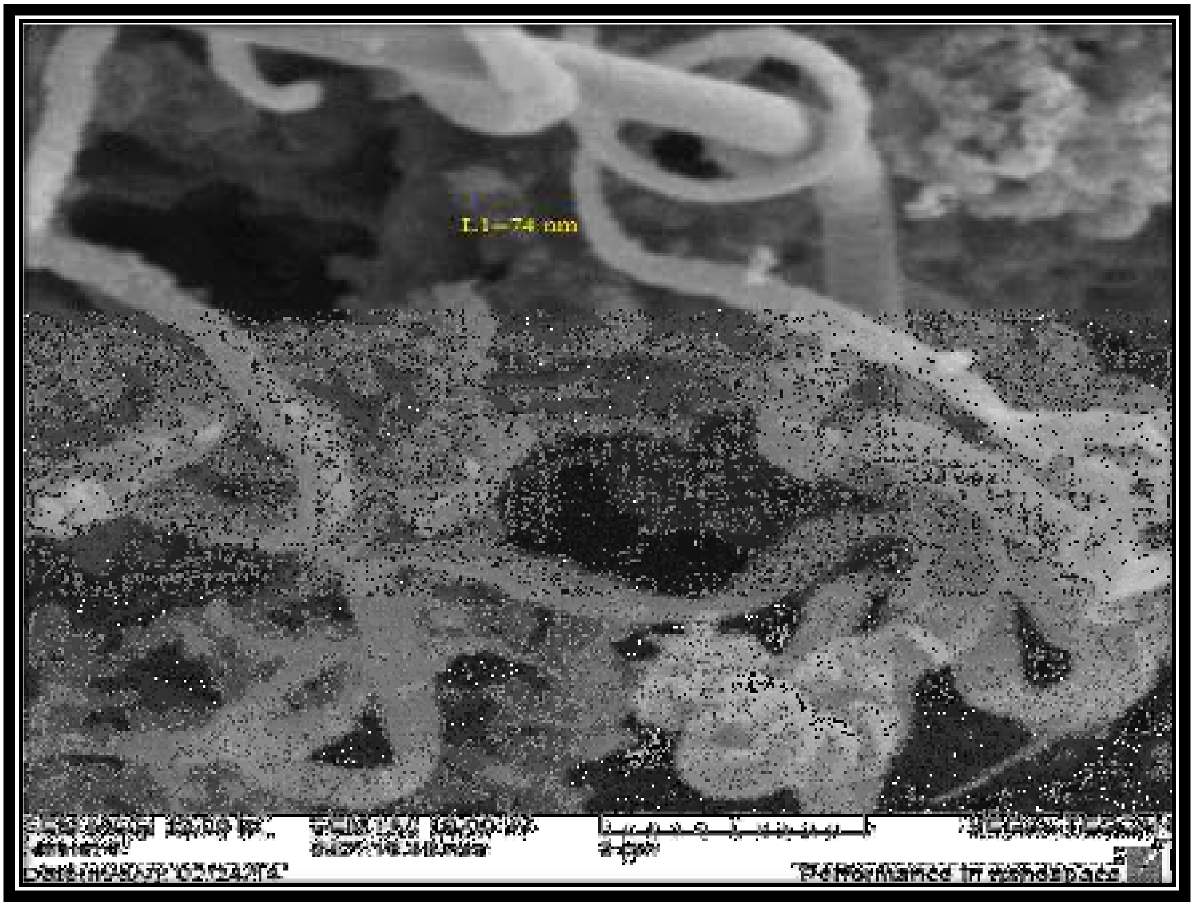

Figure 4 : SEM image of the prepared CNTs.

Figure 5 shows the x-ray diffraction of the functionalized MWCNTs. Peak at the angle (2θ) of 26.1° and peak at the angle (2θ) of 42.9° can be indexed as the C (002) and C (100) respectively. This can be ascribed to the hexagonal graphite structures. As can be gathered from this result the carbon nanotubes are free from impurities because no other peaks are shown in the diffraction pattern. These results are in good agreement with the result obtained by Louis et al. [14] and Gao et al. [15]

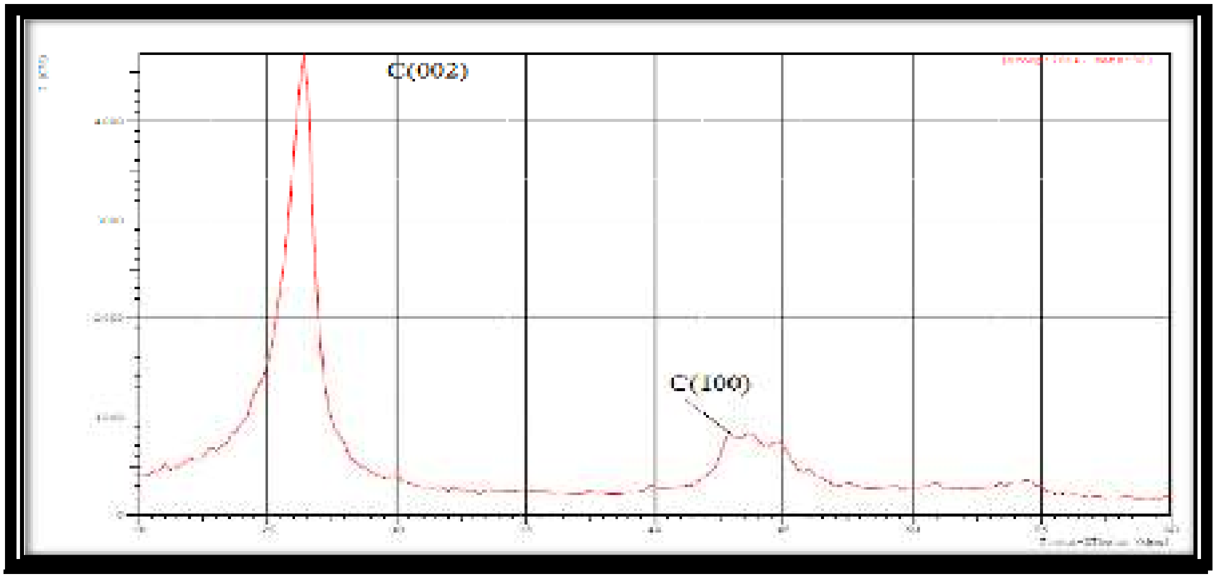

Figure 6 : X-ray diffraction of CNTs produced**.**

Figure 7a shows FTIR spectra of purified carbon nanotubes (CNTs) while the FTIR spectra of oxidized (functionalized) carbon nanotubes are shown in figure 8b, as can be gathered from the result of figure 4b, the treatment of CNTs with HNO_3 acid generates different functional groups on the surface of carbon nanotubes. Peak at the band 2348-2370 cm^{-1} characterizes –OH stretch from strong H-bonded-COOH , The band at 1741.78 can be attributed to the C=O groups , peaks at 3742.03 and 3439.19 cm^{-1} characterized hydroxyl groups and carboxyl groups respectively Gupta et al. 2011 [16] . The results of FTIR confirm the growth of carbon structure due to the observation of stretching C-C bond at 1585.49 cm^{-1}. These results are in good agreement with the results obtained by Atieh et al. 2010 [17].

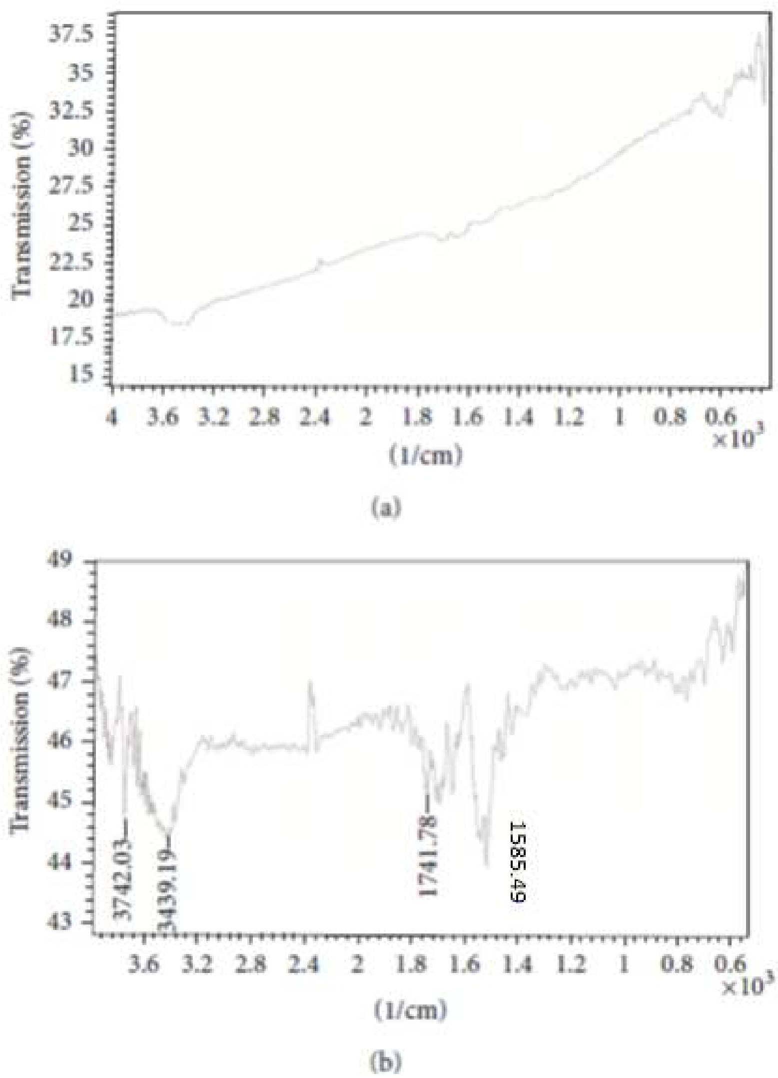

Figure 9: FTIR spectra of a) CNT and b) functionalized CNTs.

The surface area (175m^2/g) and pore volume (0.91cm^3/g) of CNTs was measured by BET method.

3.1 Batch Adsorption results

3.1.1 Effect of the pH

The effect of the pH of the solution on the adsorption of formaldehyde was studied in the range between 3 and 12 as shown in figure 10. It can be seen from the figure that the maximum removal efficiency was achieved at pH of 5 even with different concentration of formaldehyde in ethanol (i.e. 20,40,60 ppm). The increase in removal efficiency of formaldehyde at lower pH value (3-5) is due to the excessive in hydrogen ion concentration that competes with anionic impurities and gets higher removal efficiency [18, 19].While the decreasing in adsorption efficiency at pH less than 5 may attributed to the decrease of positive charge on the adsorbent surface and the negatively charged site increases.

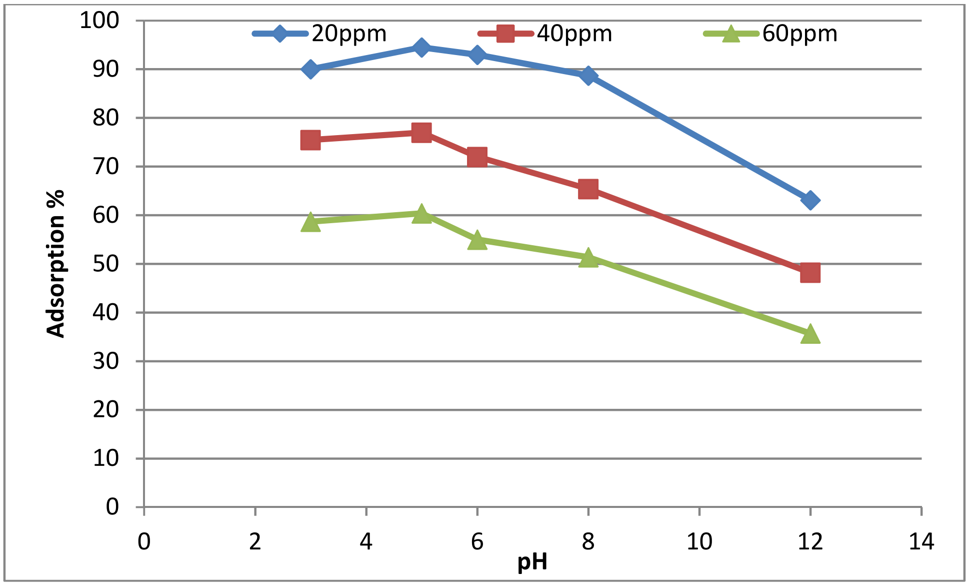

Figure 11: The effect of pH on the adsorption of formaldehyde.

3.1.2 Effect of Contact Time

The effect of contact time on removal efficiency (%adsorption) of (20, 40, 60ppm) formaldehyde concentration at pH 5, from ethanol is illustrated in figure 12. the results show that the removal efficiency increases gradually with increasing time until it reaches the equilibrium at 25min.

This can be explained that in the beginning of adsorption when the removal efficiency increases rapidly with time there are a large number of active sites (functional group) on the surface of carbon nanotubes and with increase in contact time surface active sites are decreased, saturated and then reached the equilibrium state.

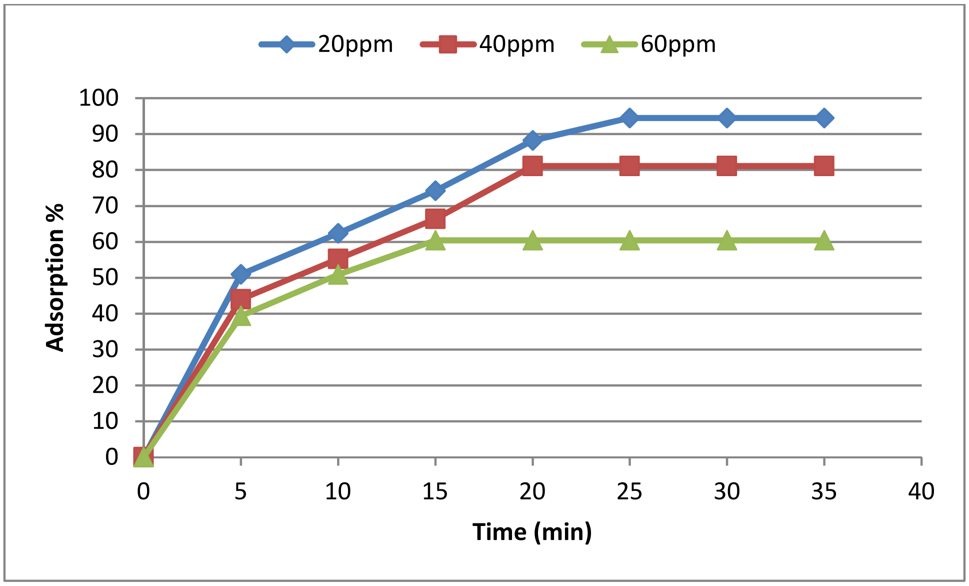

Figure 13 : The effect of contact time on formaldehyde adsorption % at (pH = 5, CNTs dosage = 100mg/L).

3.1.3 Effect of CNTs Dosage

CNTs dosage is one of the important factors on the removal efficiency of impurities in ethanol. Different amounts of CNTs dosage of (50, 100, and150mg/l) were used in batch experiment adsorption. Figure 14 shows the effect of CNTs dosage on removal efficiency (Re %). When pH=5 and contact time 35min. The result observed increase in the removal efficiency as the CNTs increased; this may be due to the increase in servant active sites of carbon nanotubes and the large surface area and pore volume [20].

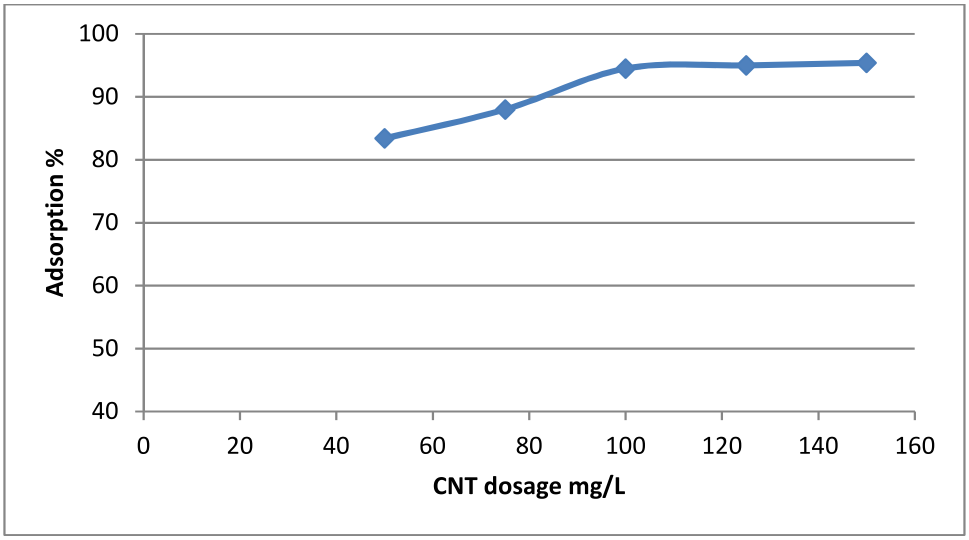

Figure 15: The effect of CNT dosage on formaldehyde adsorption % at (pH = 5, initial concentration = 20ppm initial concentration).

3.1.4 Effect of formaldehyde Concentration

The effect of initial concentration on removal efficiency of FR is illustrated in figure 16. The removal efficiency decreases with increasing FR concentration from 20 to 60 ppm. The maximum removal at initial concentration of FR (20ppm) was found to be 95% at CNTs concentration 100mg /L and pH of 3 and 82% for initial formaldehyde of 40ppm But decreases to about 60 % at 60ppm.

The decreases in removal efficiency with increase in formaldehyde concentration, may attributed to the increase of the ratio of cations impurities to the adsorbent dosage and the number of active sites which required to be adsorbate remain constant while the number of active site increase and hence the removal efficiency of the adsorption decrease. The same behavior has been obtained by Omid, 2011 [21].

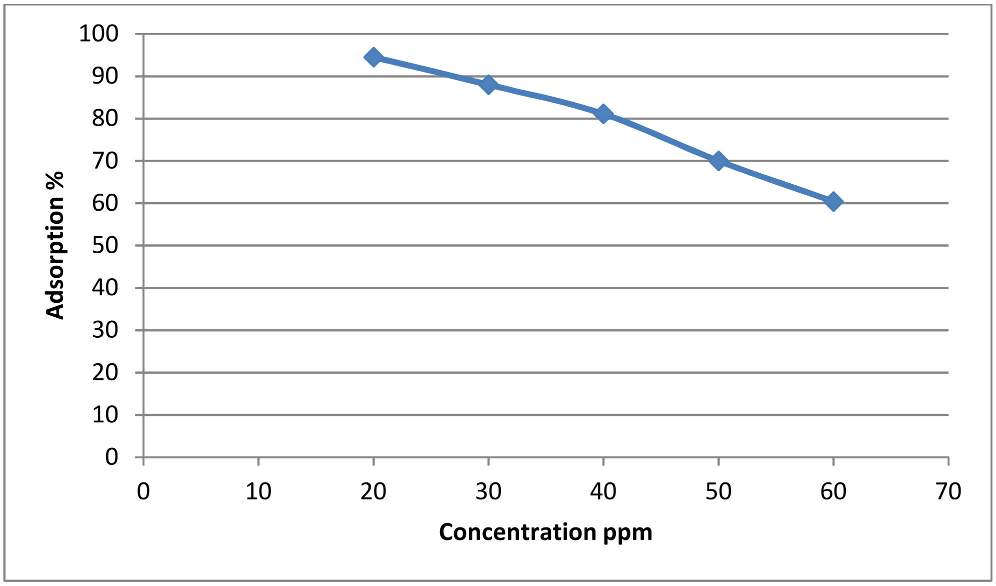

Figure 17: The effect of initial concentration on formaldehyde adsorption % at (pH = 5, CNTs dosage = 100mg/L).

3.2 Adsorption Isotherms

The adsorption data were fitted into Langmuir and Freundlich isotherm equations. The linearization form of the Langmuir equation is as follows [22, 23]:

$$\frac{C_e}{q} = \frac{1}{K_L\, q_m} + \frac{C_e}{q_m} \quad (4)$$

where q, Ce, qm and K_L are the amount of FR adsorbate equilibrium (mg/g), concentration of adsorbate at equilibrium (mg/L), maximum adsorption capacity (mg/g) and Langmuir constant (L/mg), respectively. qm and K_L constants were evaluated from the slope and intercept of the linear plots of Ce/q versus Ce, respectively, as shown in Figure 18 for CNTs. The Langmuir maximum adsorption capacity for CNTs was found to be 384.6 mg/g. It appears that the Langmuir model best fits the experimental results over the experimental range with good coefficients of correlation (R^2=0.9997). The values of qm , K_L and linear correlation R^2 are given in table 2

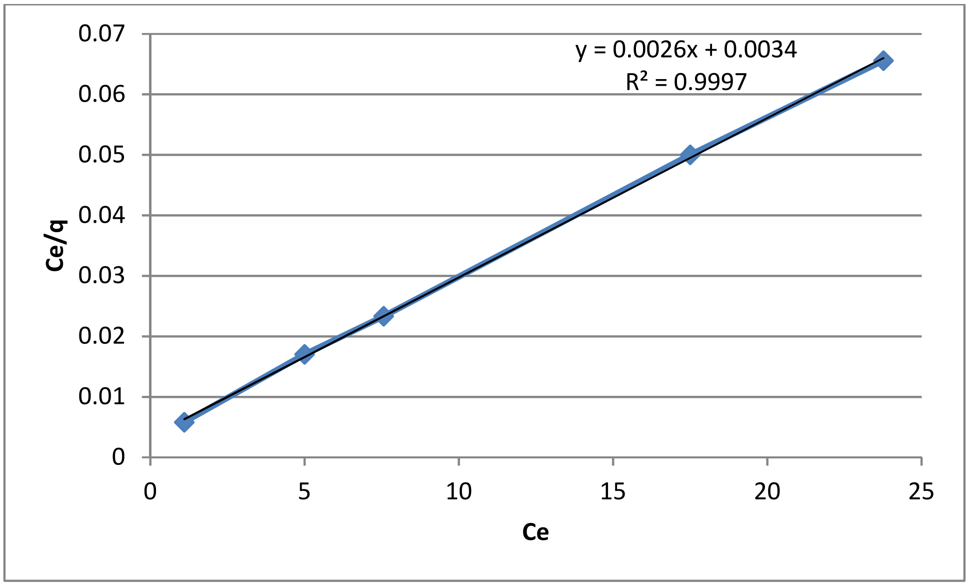

Figure 19: Langmuir isotherm of formaldehyde adsorption onto CNTs at (pH=5, CNTs =100 mg/L, Contact Time=35 min).

Freundlich parameters			Langmuir parameters		
K_f(mg/g)	n	R^2	q_m	K_L	R^2
196.4	4.74	0.939	384.6	1.3	0.9997

Table (2): Freundlich, Langmuir, constants for the adsorption isothermat (pH=5, contact time=35min).

The equilibrium adsorption data are also fitted to Freundlichs equation (24):

$$log\ q_e = \left(\frac{1}{n}\right) logC_e + logK_f \qquad (5)$$

Where K_f and 1/n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively, of the sorbent. The plot of log C_e versus log q in figure 20 is employed to evaluate the intercept K_f and the slope 1/n. The values of K_f, n, and a linear correlation

R^2 with Freundlich isotherms are given in Table 2. The best fit exhibited R^2 = 0.939. The magnitude of n was 4.74. From above results it is clear that the Langmuir isotherm with R^2 (0.939) represent the best fitting with the adsorption experimental data , the high correlation coefficient obtained indicates high affinity between adsorbent surface of CNTs and formaldehyde which plays the major role in the adsorption mechanisms .

Adsorption mechanisms are confirmed to Langmuir model rather than Freundlich model. This may be due to formation of a nonhomogeneous layer adsorbate on the outer surface of the CNTs adsorbent (25).

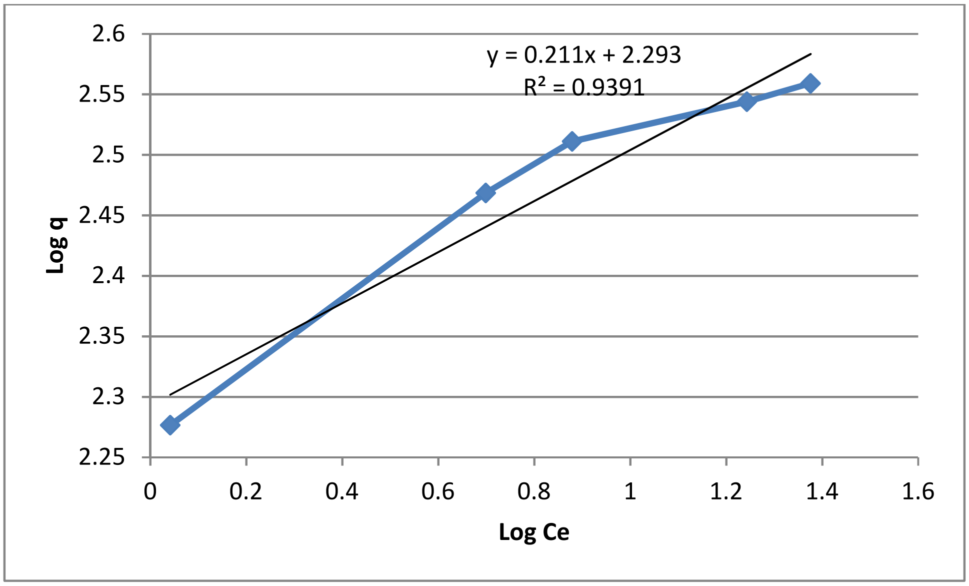

Figure 21: Freundlich isotherm of formaldehyde adsorption onto CNTs at (pH=5, CNTs =100 mg/L, Contact Time=35min).

4. Conclusions

Removal of trace impurities and undesirable material from industrial ethanol using CNTs is a new trend and consider as a first step in synthesis and treatment of ethanol for application in pharmaceutical and medical products industry. MWCNTs was prepared by CVD method, characterized and used as adsorbent for the removal of FR from industrial ethanol. CNTs were found to have great potential on removal of FR from ethanol in batch adsorption system.

1. Within the ideal condition of batch experiment process, CNTs was capable to achieving 95% of FR removal at pH5, contact time 25min and FR concentration 20ppm.The maximum adsorption capacity of CNTs for FR removal was 384.6mg/g.
2. Batch experiment showed that the percentage of removal of FR increases with the increase in the contact time and CNTs dosage, while it decreases with the increase initial FR concentration and pH .
3. The adsorption isotherms studies demonstrated that the adsorption processes can be well fitted by the Langmuir isotherm model with a correlation coefficient of 0.9997.
4. In batch experiment, removal of FR increased with increasing contact time (35 min of contact time was found to be the equilibrium time).
5. The increase in adsorption capacity for the CNTs sample was attributed mainly to the functionalized process of CNTs by which active sites have been increased and also due to high surface area of CNTs.

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