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The Study of Adsorption Characteristics of 1-Chloro-4-Nitrobenzene onto Multi-Walled Carbon Nanotubes Surfaces from Aqueous Solution: Equilibrium and Kinetics

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ABSTRACT

In this study adsorption of 1-chloro-4-nitrobenzene (CNB) from aqueous solutions onto multi-walled carbon nanotubes (MWCNTs) was surveyed. The effect of some key parameters such as pH (2-10), carbon nanotubes dosage (0.02-0.1 mg/250mL), CNB concentration (2-16 mg/L), and temperature (20,30,40,50°C) were investigated. The results showed that, the variation of initial pH and CNB concentration exhibits no considerable change onto MWCNTs adsorption process. Results showed that the adsorption is independent of temperature and reveals that the adsorption is physisorption. A trend of increment in adsorption capacity with increment in adsorbent dosage was observed. The adsorption kinetic data were analyzed using pseudo-first-order and pseudo-second-order models. It was found that the pseudo-second order kinetic model was the better model, describing the adsorption kinetics of CNB onto MWCNTs. Adsorption isotherm of CNB onto MWCNTs was determined at various concentration of CNB. Data were fitted to the Langmuir and Freundlich isotherm models and isotherm constants were determined. The equilibrium data for MWCNTs was best represented by the Langmuir isotherm model.

Keyword: Adsorption, MWCNTs, 1-Chloro-4-nitrobenzene, Isotherm, Kinetic

1. INTRODUCTION

Water contamination is caused by industrial effluents, such as agricultural and chemical industries which contain several substrates that can be harmful to the environment. So, it is importance to find an effective method for their elimination from different sources [1].

The presence of phenolic compounds even at low concentrations can cause unpleasant taste and odor. Chlorinated nitroaromatic compounds such as 1-chloro-4-nitrobenzene (CNB), which are important building blocks for the synthesis of industrial chemicals, are present in industrial wastes [2] and are serious environmental pollutants. CNB is used as an intermediate in the synthesis of

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certain drugs, dyes, pesticides and other substances in commerce. CNB causes methemoglobinemia in humans and animals and reportedly is weakly mutagenic and carcinogenic [3]. So, it is necessary to remove it from water.

Adsorption is a promising method for wastewater treatment compared to the other methods such as precipitation and coagulation [4], chemical oxidation [5], sedimentation [6], filtration [7], osmosis, and ion exchange [8]. This method is recognized for its high efficiency, low cost, simplicity, and reusability of the adsorbent and easy recovery. Sorbents which have been studied for adsorption of pollutants include activated carbon, fly ash, crab shell, coconut shell, zeolite, manganese oxides, and rice husk. However, these adsorbents have poor removal efficiencies for low concentrations of pollutants. One of the most recent studied materials is carbon nanotubes (CNTs). Carbon Nano Materials may exist in several forms, such as, single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), carbon beads, carbon fibers and nanoporous carbon. CNTs are engineered materials targeted to exhibit unique surface morphologies, hence, they may prove to be good sorbents [9]. Their high surface area, small diameter and easily functionalized surface are beneficial for CNTs to become a potential adsorbent for liquid adsorption. CNTs have shown high adsorption efficiency for various organic pollutants such as benzene [10], 1,2 dichlorobenzene [11], trihalomethanes [12] and polycyclic aromatic hydrocarbons (PAHs) [13].

The main objective of this research was to evaluate the adsorption of multi-walled carbon nanotubes for the removal of CNB as a model compound. The effects of pH, contact time, initial CNB concentration and MWCNTs dosage on adsorption capacity were investigated. Moreover, kinetic and equilibrium models were used to fit experimental data.

2. MATERIALS AND METHODS

2.1. Materials
1-Chloro-4-nitrobenzen (CNB) [$C_6H_4ClNO_2$,

$M=157.6$ g/mol, $\lambda_{max}=279$ nm] was purchased from Fluka company. A stock solution of CNB was prepared at a concentration of 16 mg/L. Multi-walled carbon nanotubes, which were purchased from Research Institute of Petroleum Industry, Iran with outer diameter in the range of 1-2 nm, surface area of 700 m^2/g and purity above 95%, was used as an adsorbent. The length of MWCNTs was in the range of 10 μm. All solutions were prepared by using deionized water. All other chemicals were supplied from Merck, Germany.

2.2. Methods
The adsorption experiments were conducted in an erlyne myer containing 250 mL of CNB solution of known concentration (16 mg/L). A given mass of multi-walled carbon nanotubes (0.1 g/250 mL) was added to solution. Then, the resultant suspension was stirred in a stirrer for 60 min. Samples were taken at predetermined time intervals and centrifuged to separate adsorbent particles. Then filtrated solution analyzed for residual CNB. The pH of each solution was adjusted at pHs of 2-10 with HCl or NaOH solution. The removal percentage (% Removal) was determined from eq. (1):

$$R(\%) = \frac{C_i - C_t}{C_i} \times 100 \qquad (1)$$

where C_i and C_t are the initial and at any time concentrations of CNB (in mg/L) in solution phase, respectively. The adsorbed CNB mount onto the MWCNTs (mg/g) at any time and at equilibrium, were calculated using the eqs.(2) and (3):

$$q_e = \frac{V}{m}(C_i - C_e) \qquad (2)$$

$$q_t = \frac{V}{m}(C_i - C_t) \qquad (3)$$

Here, C_i and C_e display initial and equilibrium concentrations (in mg/L), respectively and V is the volume of the sample solution (in L) and m is the mass of the adsorbent (in g).
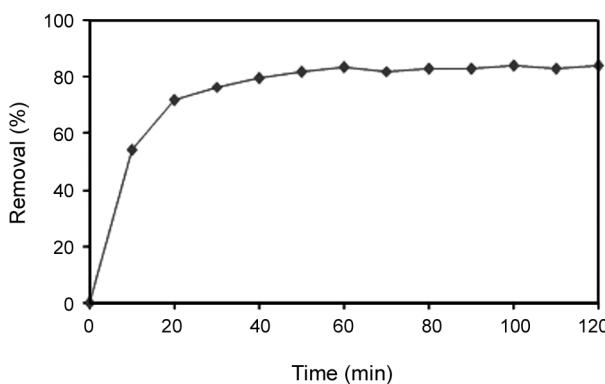
Salahi B et al

Int. J. Bio-Inorg. Hybd. Nanomat., Vol. 1, No. 2 (2012), 87-92

Figure 1: *Effect of contact time on adsorption of CNB onto MWCNTs. $[CNB]_0$=16 mg/L; $[MWCNTs]_0$=0.1 g/250mL; pH=5.4.*

3. RESULTS AND DISCUSSION

3.1. Effect of contact time

In order to determine the time of contact necessary for the establishment of adsorption equilibrium, the removal percent of CNB by MWCNTs is measured as a function of the time. The variation of % Removal according to the contact time is shown in Figure 1. As shown, after 60 min, the adsorption reached to equilibrium. So, the experiments were performed 60 min.

3.2. Effect of pH

The effect of solution pH on the equilibrium adsorption amount is shown in Figure 2. It demonstrates that the adsorption of CNB is
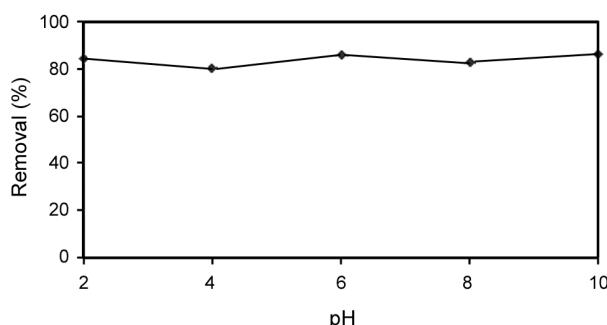

Figure 2: *Effect of pH on adsorption of CNB onto MWCNTs. $[CNB]_0$=16 mg/L; $[MWCNTs]_0$=0.1 g/250mL; Contact Time=60 min.*

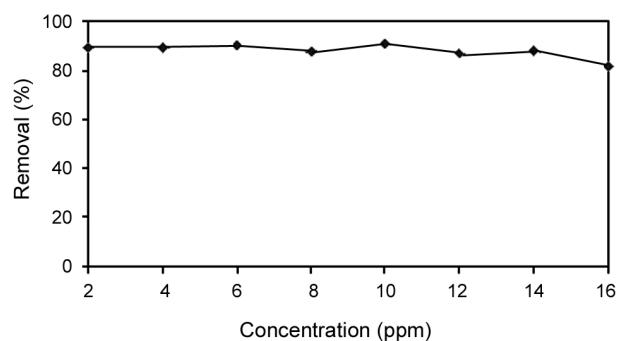**Figure 3:** *Effect of MWCNTs dosage on adsorption of CNB onto MWCNTs. $[CNB]_0$=16 mg/L; $[pH]_0$=5.4; Contact Time=60 min.*

relatively independent of pH and varied between 84 to 86%. In fact, CNB is a nonionizable compound and so the variation of pH has no significant effect on adsorption of it onto MWCNTs. It seems that CNB is an unionized compound, so the change of pH has no effect on removal of it from aqueous solution.

3.3. Effect of adsorbent dosage

In order to study the effect of adsorbent dosage on the adsorption of CNB, a series of adsorption experiments were carried out with different adsorbent dosages at initial CNB concentration of 16 mg L^{-1}. Figure 3 shows the effect of adsorbent dose on the removal of CNB. Along with the increase of adsorbent dosage from 0.02-0.1 mg/250 mL, the percentage of CNB removal increased from 38.18-83.5%. This was attributed to increased surface area and availability of more adsorption sites [14].

3.4. Effect of initial concentration

Various concentrations of CNB solutions (2, 4, 6, 8, 10, 12, 14, 16 mg/L) were used to study their effect on the percentage removal of CNB. Figure 4 shows the percentage removal of CNB at different CNB concentrations. As Figure 4 shows, CNB removal efficiency slightly decreased with the increase in initial CNB concentration. In fact, at higher concentrations, the available sites of adsorbent become fewer, and hence the percentage removal of CNB which depends upon the initial concentration,
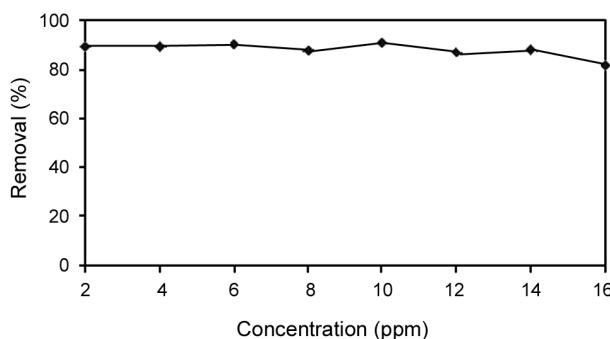
Int. J. Bio-Inorg. Hybd. Nanomat., Vol. 1, No. 2 (2012), 87-92

Salahi B et al

Figure 4: *Effect of CNB concentrations on adsorption of it onto MWCNTs. [MWCNTs]$_0$=0.1 g/250mL, [pH]$_0$=5.4; Contact Time=60 min.*

decreases [15] and subsequently the fractional adsorption becomes independent of initial concentration.

3.5. Effect of temperature

The effect of temperature on the sorption characteristics of CNB onto MWCNTs was investigated by determining the adsorption isotherms at 20, 30, 40 and 50°C. As can be seen from figure 5 adsorption of CNB generally is not sensitive to the temperature changes. It could be found that the adsorption of CNB onto MWCNTs is physisorption.

3.6. The analysis of adsorption isotherms

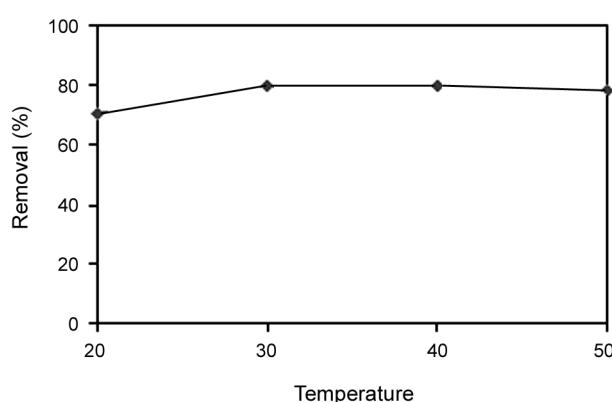The Langmuir and Freundlich models which are employed to analysis adsorption occurred in the experiment.

Figure 5: *Effect of temperature on adsorption of CNB onto MWCNTs. [CNB]$_0$=16 mg/L; [MWCNTs]$_0$=0.1 g/250mL, [pH]$_0$=5.4; Contact Time=60 min.*

Langmuir theory [16] is based on the assumption that the surface of the adsorbent is energetically homogenous, and that a monolayer surface coverage is formed with no interactions between the molecules adsorbed. On the other hand, the Freundlich model [16] is an empirical equation that was originally developed to overcome some limitations of the Langmuir theory, by taking into account the surface heterogeneity and that there might exist intermolecular interactions between the adsorbate molecules. The Langmuir linear eq. (4):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e} \tag{4}$$

where q_m (mg /g) and K_L (L/ mg) are the Langmuir constants, representing the maximum adsorption capacity for the solid-phase loading and the energy constant related to the heat of adsorption, respectively. q_e is the uptake capacity and C_e is the equilibrium concentration. The Freundlich linear eq. (5):

$$Lnq_e = LnK_F + \frac{1}{n}LnC_e \tag{5}$$

Parameters of K_F and n are Freundlich constants, whereby K_F is a measure of the adsorption capacity and n a measure of the adsorption intensity [17]. q_e and C_e are the uptake capacity and the equilibrium concentration, respectively.

The fitted parameters using two models are given in Figure 6 and Table 1. The results showed that the Langmuir adsorption isotherm was the best model for the CNB adsorption on MWCNTs with R^2 of 0.997.

The maximum sorption capacity q_m of MWCNTs for CNB attained from the intercept is 144.92 mg/g, reflecting that MWCNTs has good capacity adsorbing CNB.

3.7. Adsorption kinetic models

In order to define the adsorption kinetics of CNB onto MWCNTs, the kinetics parameters for the adsorption process were studied for contact times
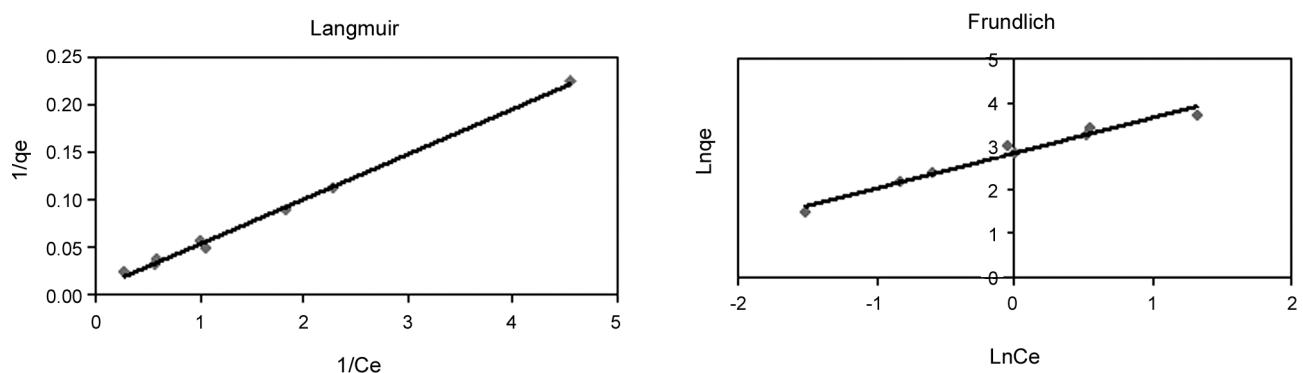
Salahi B et al

Int. J. Bio-Inorg. Hybd. Nanomat., Vol. 1, No. 2 (2012), 87-92

Figure 6: Langmuir and Frundlich isotherms for the adsorption of CNB onto MWCNTs.

Table 1: *Isotherm parameters for CNB adsorption onto MWCNTs.*

Langmuir model			Freundlich model		
q_m	K_L	R^2	n	K_F	R^2
144.92	0.14	0.996	1.24	17.35	0.969

ranging from 5 to 60 min by monitoring the removal percentage of the CNB. Both pseudo first and second-order models were used to describe the adsorption kinetics data [18,19]. Pseudo first-order model by using eq. (6):

$$Ln(q_e - q_t) = Lnq_e - K_1 t \qquad (6)$$

where q_t is the amount of solute adsorption at any

time (mg/g), and k (1/min) is the rate constant of pseudo-first-order model. Pseudo Second-order model; equation (7):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + (\frac{1}{q_e})t \qquad (7)$$

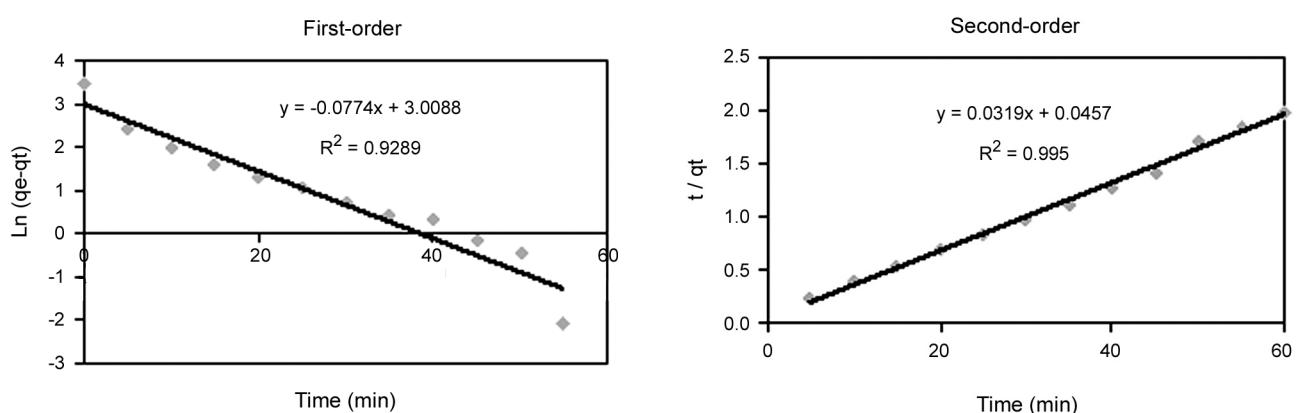where k_2 (g/mg.min) is the rate constant of pseudo-second-order adsorption.

Figure 7: First and second order kinetics for the adsorption of CNB onto MWCNTs.

Int. J. Bio-Inorg. Hybd. Nanomat., Vol. 1, No. 2 (2012), 87-92

Salahi B et al

Table 2: *Kinetics constants.*

First order		second order	
K_1	R^2	K_1	R^2
0.077	0.928	0.022	0.995

The pseudo first and second order kinetics plots are presented in Figure 7. The results indicated that the adsorption process follows pseudo second-order model (Table 2).

4. CONCLUSIONS

From the current study we can conclude that CNB can be significantly removed by MWCNTs from aqueous phase. The results show that equilibrium adsorption was attained within 60 min and the removal of CNB independent of pH, temperature and CNB concentration. But, increased by increasing dosage of MWCNTs. The adsorption phenomenon of the CNB onto MWCNTs well described by the Langmuir model and pseudo second order kinetic.

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