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Adsorption of 1-chloro-4-nitrobenzene from aqueous solutions onto single-walled carbon nanotubes

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ABSTRACT

In this study adsorption of 1-chloro-4-nitrobenzene on single walled carbon nanotubes has been investigated. The effect of contact time, pH, initial concentration of 1-chloro-4-nitrobenzene, adsorbent dosage and temperature on its adsorption has been carried out in order to find optimum adsorption conditions. Adsorption isotherms and related constants were also determined. Results showed that contact time to reach equilibrium was 60 min at 25°C and after that a little change of 1-chloro-4-nitrobenzene removal efficiency was observed. The results show that maximum 1-chloro-4-nitrobenzene removal (81.9 %) obtained at pH of 6 and it decreased at higher initial 1-chloro-4-nitrobenzene concentration, lower adsorbent doses and lower temperature. Langmuir, Freundlich and Temkin isotherm models were used to test the equilibrium data. Adsorption test results revealed that 1-chloro-4-nitrobenzene adsorption on the studied adsorbents could be better described by Freundlich isotherm.

Keywords: *Adsorption; 1-Chloro-4-nitrobenzene; Single walled carbon nanotube; Isotherms.*

INTRODUCTION

Water contamination is mainly caused by industrial effluents which contain several non-biodegradable compounds that can be harmful to the environment. Various industries are responsible for contributing these hazardous organic. One of the most important pollutants is benzene, which is produced extensively by chemical industry including production of materials such as colorants, coatings, plastics, food synthetic additives, etc. [1]. After entering an organism, benzene targets organs viz. liver, kidney, lung, heart, brain, etc [1]. So, it is important to removal it from aqueous solution by a simple and economical methods. Adsorption is one of the most commonly used methods in water treatment processes. It is interesting due to it easy operation and the availability of a wide variety of commercial adsorbents [2].

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Some common adsorbents are activated carbon, fly ash, crab shell, coconut shell, zeolite, manganese oxides and rice husk [3].

With the emergence of nano science and technology in the last decade, researchers have been initiated to use of carbon nanomaterials (CNMs) as adsorbents. CNMs have been found in several forms, such as, single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs) and nanoporous carbon. CNMs are engineered materials targeted to exhibit unique surface morphologies [3]. Carbon nanotubes (CNTs) have shown great adsorption capability and high adsorption efficiency for various organic pollutants such as benzene [4], 1,2-dichlorobenzene [5], trihalomethanes [6] and polycyclic aromatic hydrocarbons (PAHs) [7]. The interaction of SWCNTs with chemical species is the main ingredient for many of these applications. Limited numbers of studies have been conducted to understand the adsorption of organic contaminants by carbon nanotubes [8].

A common observation from these studies was that carbon nanotubes are very strong adsorbents for hydrophobic organic compounds. This is understandable considering the strong hydrophobicity and high surface area of carbon nanotubes. Additionally, an important implication from several of the studies is that electronic polarizability of the aromatic rings on the surface of carbon nanotubes might considerably enhance adsorption of the organic compounds to carbon nanotubes [8-11].

In this work, we study the role of some key parameters on the efficiency of single-walled carbon nanotubes for the removal of 1-chloro-4-nitrobenzene from aqueous solutions.

EXPERIMENTAL

Material

1-Chloro-4-nitrobenzene (4NCB) [$C_6H_4ClNO_2$, M=157. 6, λ_{max}=279] was purchased from Fluka company. A stock solution of 4NCB was prepared at a concentration of 15 mg/L. Single-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 550 m^2/g and purity above 95%, was selected as a catalyst because it is a very environmental friendly in nature and has a low solubility in water. The length of SWCNTs was in the range of 5 - 15 μm. All solutions were prepared by using deionized water. All other chemicals were supplied from Merck, Germany.

Methods

The process of adsorption on SWCNTs was conducted from water solutions of 4NCB of the following concentrations: 3.0, 6.0, 9.0, 12.0 and 15.0 mg/L. A desired value of SWCNTs was placed in an Erlenmeyer together with 250 cc of water solution of 4NCB of a given concentration. The system was stirred by a magnetic stirrer for 60 min. The samples were withdrawn every 10 min and centrifuged to removal of filtrate. Then analyzed spectrophotometrically, using UV-Vis spectrophotometer (Model DR-5000, Hach,USA). The pH of the solution was adjusted to between 2-12, using 0.1 and 3M of HCl and NaOH.

RESULTS AND DISCUSSION

The factors affecting the adsorption equilibrium include the solution pH, adsorbate concentration, adsorbent dosage, and temperature. In this research the influence of those parameters on the adsorption of 4NCB on surface of $SWCNT_S$ was studied.

Effect of contact time on 4NCB adsorption

Contact time is one of the effective factors in batch adsorption process [12]. Figure 1 shows the percentage of removed 4NCB onto SWCNTs. The adsorption process was rapid in the initial 20 min, and then gradually decreased until equilibrium was reached at 60 min. This progression is expected based on the large number of vacant surface sites available for adsorption during the initial stage, and, after certain amount of time, the remaining vacant surface sites are difficult to occupy due to repulsive forces between 4NCB molecules on SWCNTs and bulk phases [13]. There was no significant change in equilibrium concentration after 60 min up to 120 min and after 60 min, the adsorption phase reached to equilibrium.

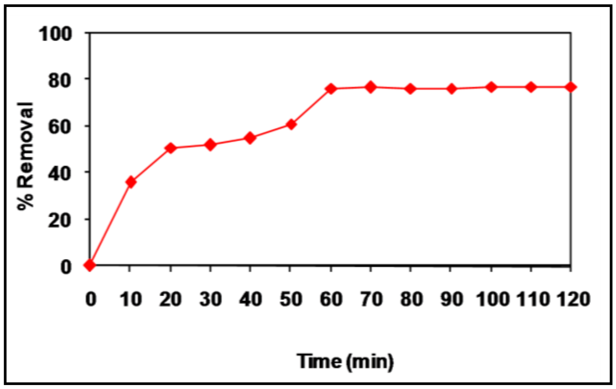

Fig. 1. Effect of contact time on 4NCB adsorption onto SWCNT surfaces [4NCB]0=15 mg/L; pH=6; [SWCNTs]=0.1 g

Effect of SWCNTs dosage

Figure 2 shows the effect of SWCNTs dosage on 4NCB adsorption at equilibrium of 60 min.. For 4NCB, the adsorption percentage increased from 32 to 79% when the SWCNTs dosage increased from 0.02 to 0.1g. The effect of adsorbent dosage on the adsorption of 4NCB showed that the percentage of 4NCB removed increased with increase in adsorbent dosage due to increased adsorption surface area, which increased the availability of adsorption sites [14].

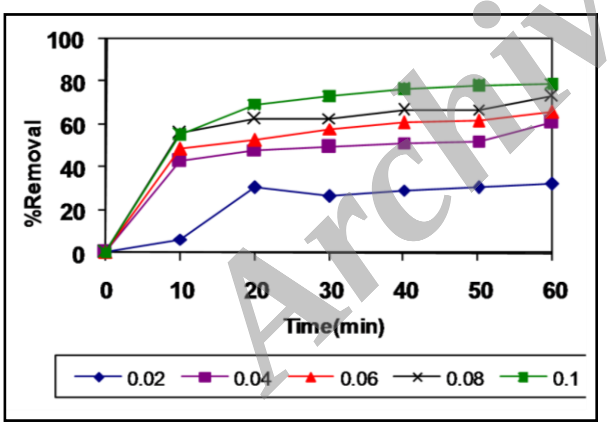

Fig. 2. Effect of adsorbent dose on 4NCB removal [4NCB]0=15 mg/L; pH=6

Effect of pH on adsorption

The pH of the solution is a key parameters on adsorption process. Figure 3 shows the equilibrium adsorption results of 4NCB onto SWCNTs at various pHs. As shown, there is no significant change in the removal of 4NCB during different pHs, but the recovery of 4NCB increases slightly with an increase in pH from 2 to 6 (76.85 to 81.92%) and then decreased by increasing pH from 6 to 10 (81.92 to % 79.45). The effect of pH on 4NCB adsorption can be explained by the following reasons. The surface charge is neutral at isoelectric point (IEP), where the pH_{IEP} value is obtained 6.8 for SWCNTs (not shown here). At pH values lower than the IEP, the net surface charge is positive whereas at pH values higher than the IEP the net charge is negative. Since 4NCB is a kind of unionizable compound, the high adsorption is occurred at pH_{IEP}, where the charge of SWCNTs surface is neutral and can support the adsorption of 4NCB[15].

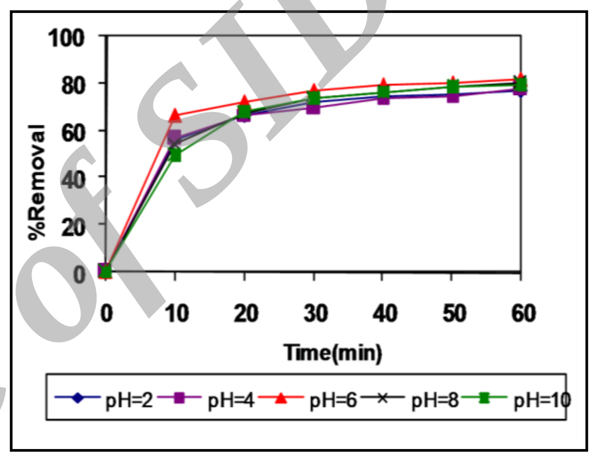

Fig. 3. Effect of pH for 4NCB adsorption onto SWCNTs [4NCB]0=15 mg/L; [SWCNTs]=0.1g

Effects of initial 4NCB concentration

Figure 4 shows the effect of initial 4NCB concentration on the amount of 4NCB adsorbed by SWCNTS under different initial 4NCB concentrations. As shown, % adsorption decreases with increasing of initial 4NCB concentration. As shown, the adsorption percentage of 4NCB onto SWCNTs decreases from 95.71 to 76.59% by increasing initial 4NCB concentration from 3 mg/L to 15 mg/L. In case of low 4NCB concentrations, the ratio of the initial number of moles of 4NCB to the available surface area of adsorbent is large and subsequently the fractional adsorption becomes independent of initial concentration. However, at higher concentrations, the available sites of adsorption become fewer, and hence the percentage removal of 4NCB which depends upon the initial concentration, decreases [16].

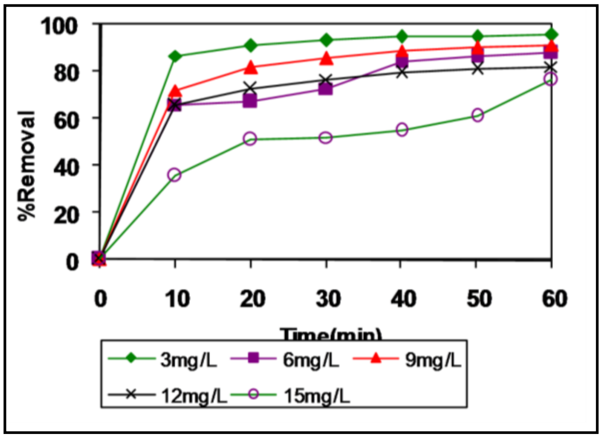

Fig. 4. Effect of 4NCB concentration on 4NCB adsorption onto SWCNTs [SWCNTs]=0.1 g; pH=6

Effect of Temperature

The effect of temperature was studied for 4NCB adsorption onto SWCNTs. % Removal–time profiles at different temperatures is illustrated in Figure 5 for 4NCB adsorption on SWCNTs.

Figure 5 shows that the adsorption of 4NCB slightly increases with an increase in temperature that might be due to the increase of diffusion on adsorbent surfaces with increasing activity of 4NCB[17].

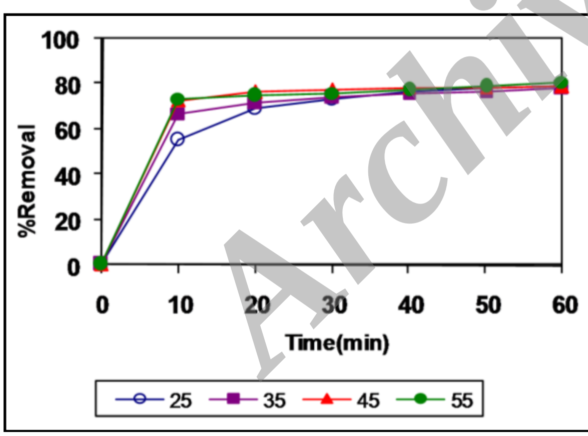

Fig. 5. Effect of temperature for 4NCB adsorption onto SWCNTs [4NCB]0=15 mg/L; [SWCNTs]=0.1 g; pH=6

Analysis of adsorption isotherms

Adsorption isotherm curves were obtained by plotting the amount of 4NCB adsorbed (qe) on the solid adsorbent versus equilibrium concentration (Ce) in solution for different concentration. The amounts of 4NCB adsorbed (qe) on SWCNTs were calculated from the differences between the C_0 and C_e.

Experimental adsorption isotherms obtained are compared with the very well-known three parameter models of Langmuir, Freundlich and Temkin which are in common use for describing adsorption equilibrium in many liquid phase applications together with wastewater treatment applications, as well [18]. The Langmuir model (equation 1) assumes monolayer coverage on sorbent whereas the Freundlich model (equation 2) is an empirical model allowing for multilayer adsorption on sorbent [3]. Temkin and Pyzhev considered the effects of some indirect sorbate/adsorbate interactions on adsorption isotherms (equation 3) and suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with coverage [18].

$$q = \frac{q_m b C_e}{1 + bC_e} \quad (1)$$

$$q_e = K_f C_e^{1/n} \quad (2)$$

$$q_e = \frac{RT}{b} Ln(k_T C_e) \quad (3)$$

where q (mg g^{-1}) and Ce (mgdm^{-3}) are the amount of adsorbed 4NCB per unit weight of sorbent and unadsorbed SWCNTs concentration in solution at equilibrium, respectively. q_m (mg g^{-1}) is the maximum amount of the 4NCB per unit weight of sorbent to form a complete monolayer on the surface bound and b (dm^3 mg^{-1}) is a constant related to the affinity of the binding sites. Where K_f and n are the Freundlich constants characteristic of the system. K_f and n are indicators of adsorption capacity and adsorption intensity, respectively. k_T is the equilibrium binding constant (L g^{-1}), b is related to heat of adsorption (J/mol), R is the universal gas constant (8.314 J/mol K) and T is the absolute temperature (K). Equilibrium adsorption isotherm data were analyzed according to the linear forms of Langmuir, Freundlich and Temkin adsorption isotherm equations (4-6), respectively and withdrawn in Figures 6, 7 and 8.

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

$$Lnq_e = (\frac{1}{n})LnC_e + LnK_F \quad (5)$$

$$q_e = B_1 LnC_e + B_1 LnK_T \quad (6)$$

Adsorption isotherm constants for 4NCB adsorption onto SWCNTs appearing in the Langmuir, Freundlich and Temkin isotherms models with the square of the correlation coefficients (R^2) were calculated and the results are given in Table 1.

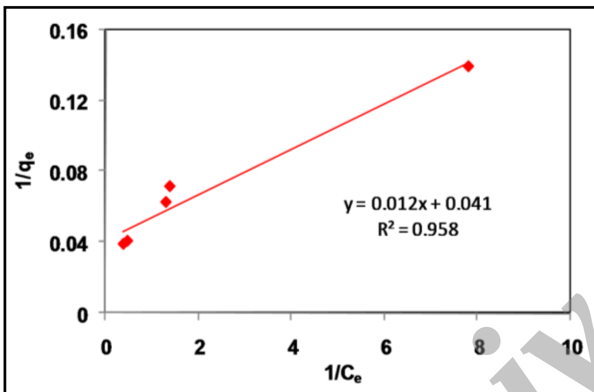

Fig. 6. Langmuir isotherm for 4NCB adsorption onto SWCNTs.

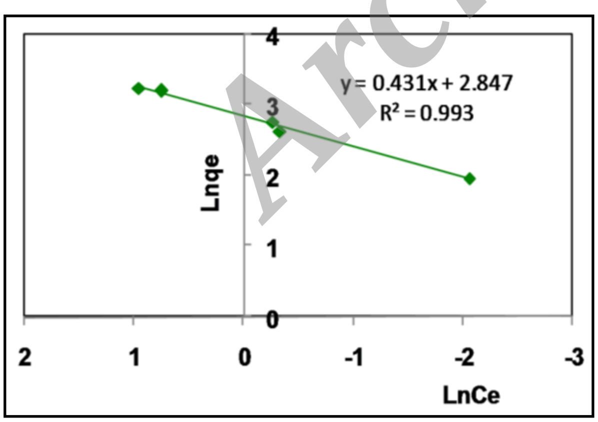

Fig. 7. Frundlich isotherm for 4NCB adsorption onto SWCNTs.

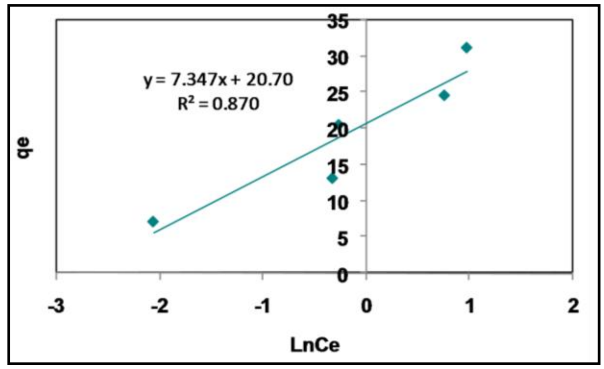

Fig. 8. Temkin isotherm for 4NCB adsorption onto SWCNTs.

From the results, it was seen that the best fit is obtained with the Freundlich model with an R^2 value of 0.993. This means that heterogeneous occupation of the surface may be predominated and also physisorption occurs rather than chemisorption [19]. The Freundlich parameters, K_F and n were found to be 17.11 and 2.32, respectively. A relatively $n<<1$ indicates that adsorption intensity is favorable over the entire range of concentrations studied, while n>1 means that adsorption intensity is favorable at high concentrations but much less at lower concentrations [20]. Therefore, in the present study, adsorption intensity is favorable at high concentrations.

Table 1. Isotherm parameters for 4NCB adsorption onto SWCNTs [SWCNTs]: 0.1 g, pH: 6, temp.: 25 °C, contact time: 60 min.

Langmuir model			Freundlich model			Temkin model		
q_m	K_L	R^2	n	K_F	R^2	B_1	K_T	R^2
24.39	3.41	0.958	2.32	17.11	0.993	7.347	16.73	0.870

CONCLUSIONS

The equilibrium adsorption of 4NCB onto SWCNTs was investigated for different adsorbate concentrations values. The results have shown that the adsorption rate was increased with decreasing pH and increasing temperature. The adsorption of 4NCB onto SWCNTs was highest at pH 6 and 55°C. The experimental adsorption equilibrium data of 4NCB on SWCNTs were compared with the Langmuir, Freundlich and Temkin isotherm models and adsorption capacities were determined. These results have shown that Freundlich isotherm model was best fitted.

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