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Optimization and Modeling of Ammonia Removal from Aqueous Solutions by Using Adsorption on Single-walled Carbon Nanotubes

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Highlights:

- The highest adsorption was obtained in alkaline conditions (pH = 9.5) with a yield of 90%.
- The Freundlich isotherm had the highest conformity with the data and is considered the best model for describing adsorbent properties.
- First-order kinetics had more conformity with the data compared with second-order kinetics.

Abstract. Due to the health effects of ammonia as an environmental pollutant, such as its odor, corrosion, algae phenomenon, etc., a method should be adopted to remove it from wastewater. In this study, removal of ammonia from hypothetical wastewater was investigated using adsorption on SWCNTs. The Design-Expert software was used to design the experiments and optimize the parameters that are effective in the adsorption performance of carbon nanotubes (CNTs), such as contact time, adsorbent dosage, pH, temperature, and ammonia concentration. The results revealed that the maximum adsorption with a performance of 90% was attained at a pH of 9.5. In addition, the adsorption performance was enhanced by increasing adsorption time and adsorbent dosage. Furthermore, increasing the temperature and the adsorbate quantity led to a decrease in the adsorption performance.

Keywords: *ammonia removal; carbon nanotubes; isotherm; kinetics; response surface methodology.*

1 Introduction

Urban development, the emergence of a variety of industries, the increased level of social welfare and other factors have caused irreparable damage to the environment. One of the major environmental sources that have been

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contaminated over time are water resources [1]. Among all types of environmental pollutants, urban and industrial wastewater is one of the most prominent sources of pollution, which if left untreated can cause irreparable damage to the environment, especially water resources [2-5]. Over time, environmental laws have been developed to protect the environment and exploit it sustainably for the present and future generations. With the rapid growth of industrial activities around the world, ammonia-induced pollution has become an important and serious phenomenon. Ammonia pollution is caused by numerous industries and industrial activities, such as industries manufacturing small- and large-scale electrical equipment, refineries, and petrochemical industries [6]. Ammonia is widely used in the chemical industry; approximately 113 to 244×10^6 tons of ammonia is released annually through agricultural and industrial activities and wastes in the world. Wastewater from industries such as petrochemical, pharmaceutical, fertilizer, food and paper industries contains large amounts of ammonia and must thus be treated before being discharged into the environment [1-7]. Ammonium nitrate is one of the most important environmental pollutants with high levels in the wastewater of petrochemical industries, especially those producing ammonia and urea [8].

So far, various methods have been identified for the removal of ammonia from industrial wastewater. These methods include physical, chemical, and biological approaches. Among them, one of the most commonly used methods is using adsorbent materials for removing ammonia. The adsorption process has been widely used for removing organic and inorganic pollutants from industrial wastewater and has attracted much attention from researchers [9-11]. Nanomaterials have been employed for their high specific surface area and the large fraction of atoms available for chemical interaction [12]. Carbon nanotubes (CNTs) as an adsorption media have a high potential for removing toxic pollutants such as heavy metals (chromium, lead, zinc, and arsenic compounds), organic substances such as polycyclic aromatics (PAHs) and atrazine, and a wide range of biological contaminants (bacteria and viruses), natural organic matters (NOM), and cyanobacterial toxins from aqueous solutions [13-17]. One of the adsorbents suitable for the removal of ammonia is CNT. These materials are cylindrical hollow structures comprised of carbon atoms that can be arranged in single or multi-walled form and have metallic and quasi-metallic properties. Nanotubes have unique features such as small size, high permeability, high specific surface area, hollow and tubular structure, high mechanical strength, high electrical conductivity, and good mechanical and thermal stability [18-21]. These materials are durable and resistant to heat. Moreover, they are easy to clean and reuse in water and wastewater treatment processes [18-21]. The reason for the interest of researchers in single-walled carbon nanotubes (SWCNTs) and their attempt to replace these nanotubes in industry is based on theoretical calculations of their experimental effects on mechanical properties and the electrical conductivity of their metalloids.

SWCNTs cost more to produce than multi-walled CNTs. However, due to advantages such as high porosity, high efficiency in adsorbing various types of pollutants such as heavy metals and organic compounds, and electrical properties that are not present in multi-walled CNTs, SWCNTs are considered as adsorbents in the absorption of ammonia from wastewater [22-25].

CNTs quickly attracted the attention of researchers due to the favorable physicochemical behavior of their active surface groups with both heavy metals and organic pollutants. In recent years, numerous studies have been conducted on using single-walled and multi-walled CNTs. In one study, a modified multi-walled CNT was used to investigate the efficiency of the removal of ammonia from a water sample from a domestic dam in Iran in the summer of 2012 [26]. The results indicated that under the condition of pH = 6, the efficiency of removing ammonia from water reached 88.3%. In addition, the researchers reported that under optimized conditions, 0.01 g of the adsorbent could reach a removal efficiency of 88.2% [26]. The results of a study that investigated the efficiency of multi-walled carbon in removing ammonia from aqueous solutions revealed the capacity of multi-walled CNTs to adsorb ammonia; their removal efficiency was 129 g/g and 95%, respectively [27]. The results of optical analysis of ammonia showed that La/Fe/TiO_2 had more catalytic activity than ammonia in wastewater compared with pure TiO_2 and TiO_2 with metal [28]. A study was conducted to investigate the efficiency of iron-loaded activated carbon in removing ammonia from wastewater. The results of this study indicated that the optimized conditions for the initial concentration of ammonia, carbon nano adsorbent dosage, contact time, and pH were 0.001 mol/L, 1.4 g/L, 240 min, and 7, respectively [29].

In another study the composition of carrageenan/multi-CNTs hybridized with nano-composite hydrogels was investigated for adsorbing violet crystals from wastewater. The results showed that the isotherm of the hydrogel adsorption equilibrium with the Langmuir adsorption isotherm was more consistent compared with the Freundlich adsorption isotherm model. According to this model, the maximum capacity for the adsorption of violet crystals was obtained by 118 mg/g nanoparticle hydrogels [30].

The aim of the present study was to evaluate the performance of SWCNTs removing ammonia from wastewater.

2 Methods and Materials

2.1 Materials and Instruments

In this study, synthetic effluent was first provided with different ammonia concentrations in double-distilled water. Then, using different amounts of adsorbent, the ammonia removal performance was investigated at different temperatures, pressures, times, and pH. In this work, SWCNTs (manufactured by US Research Nano Materials, as specified in Table 1) were used. The main materials and instruments used in this study are shown in Table 2. In addition, Figure 1 perfectly illustrates the internal spaces of these nano-carbons with microscopic images (SEM).

Table 1 Specifications of single-walled carbon nanotubes.

Specifications	Amount
Purity	More than 95%
Average diameter (nm)	1.1
Inner diameter (nm)	0.8 to 1.6
Outer diameter (nm)	1 to 2
Special surfaces(m^2/g)	380
Electrical conductivity (S/cm)	100
Thermal conductivity (W/m.K)	50 to 200

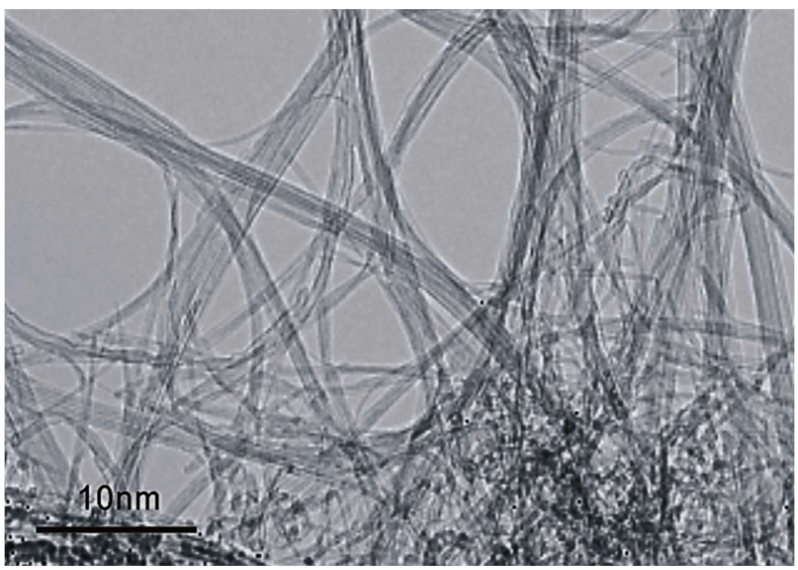

Figure 1 Microscopic Image (SEM) single-walled carbon nanotubes.

Table 2 Main materials and instruments used in this study.

Name	Producer company
Carbon nanotube (SWCNT)	US Research Nano Materials
Nitric acid (HNO3) 65%	Merck
Hydrochloric acid (HCl) 30%	Merck
Ammonia (NH3) 25%	Merck
Sodium hydroxide (NaOH) 97%	Merck
Double distilled water	Kimia Mavad
pH meter paper	Universal
Magnetic stirrer Hot Plate	Alpha
Avon	Aria Teb
Vacuum pump	PART-SHIMI
Spectrophotometer	PART-SHIMI

The design of the experiment was one of the most important tools for managing the quality and productivity of the processes, leading to designing and creating the product with the highest quality and lowest cost. In designing the experiment, some of the initial variables were manipulated to evaluate their effect on the response variable [31,32]. In this research, the Design-Expert software was used to design the experiment.

Based on the process used in the sources, to modify the SWCNTs, the nanotubes were washed with 10% nitric acid and double-distilled water; after that, they were oxidized in a solution containing 65% nitric acid at 120 °C for 48 h. The oxidized nanotubes were washed several times with double-distilled water, using a vacuum pump whose pHwas is equal to the pH of the double-distilled water used for washing. Then the nanotubes were dried at 105 °C for 2 h in an oven unit. In order to investigate the effect of pH on the adsorption of ammonia by SWCNTs, solutions with 100 mL of ammonia were prepared. Then the pH of these solutions was adjusted to values of 2 to 12 by using 0.1 M solutions of HCL and NaOH. Finally, the removal percentage of the adsorbing material was calculated using Eq. (1) [33-35].

$$R\ (\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{1}$$

where R is the percentage of adsorption, C_0 is the initial concentration of the adsorbent, and C_e is the equilibrium concentration.

In order to investigate the effect of the CNT adsorbent on the adsorption of ammonia from synthetic effluent, at the optimized pH and ambient temperature, different concentrations of the adsorbent sample from 0.13 to 2.63 mg/L were used in 100 mL of ammonia. In each experiment, different concentrations of the adsorbent with the initial concentration of the ammonia sample were placed in a 180-rpm mixer for 7 min at ambient temperature. After mixing and separating the adsorbent, the absorbance of each solution was read by a spectrophotometer at a wavelength of 200 nm. In order to evaluate the effect of contact time on the adsorption of ammonia by CNTs, solutions containing 100 mL of ammonia were prepared. The optimized amount of the adsorbent was added to each sample and then placed in a 180-rpm mixer at an optimized pH and ambient temperature at intervals of 20 to 180 min. In order to investigate the effect of temperature on the adsorption of ammonia by CNTs, samples with 100 mL of ammonia and the optimized amount of the adsorbent were tested at the optimized pH and time with adsorption temperature at 19.5 to 49.5 °C.

In order to investigate the effect of the concentration of ammonia on its adsorption by CNTs, the samples were tested under the optimized conditions regarding time, temperature, and pH as well as the optimized amount of the adsorbent in the range of 50 to 650 mg/L of the concentration of ammonia. Finally, after each test, the absorbance of each solution was read by a spectrophotometer at a wavelength of 200 nm and then Eq. (1) was used to calculate the adsorption percentage of the adsorbing substance.

2.2 Adsorption Kinetics and Adsorption Isotherms

The adsorption kinetics were studied in order to have a better understanding of the adsorption dynamics and provide a predictive model. These models allow estimating the amount of adsorption over the time of the process. To investigate the adsorption kinetics, pseudo-first order and the pseudo-second-order kinetic equations are used. Langmuir proposed a pseudo-first-order rate equation for expressing the rate of adsorption of a soluble aqueous medium, which is expressed as follows [36-39]:

$$\frac{dq}{dt} = k(qe - qt) => ln\frac{(qe-q)}{qe} = -kt \tag{2}$$

where $\boldsymbol{q}$ is the amount of adsorbed pollutant, $\boldsymbol{qe}$ is its value at equilibrium, $\boldsymbol{k_1}$ is the pseudo-first-order rate constant, and $\boldsymbol{t}$ is time.

The other equation used to analyze the adsorption kinetics was the following pseudo-second-order rate equation:

$$\frac{dq}{dt} = k_2(qe - qt)^2 => \frac{t}{qt} = \frac{1}{k_2 qe^2} + \frac{t}{qe} \tag{3}$$

where ***qe (mg/g)*** and ***qt (mg/g)*** are the pollutant amount adsorbed at equilibrium at any ***t(min)***, respectively, and $\boldsymbol{k_2}$ ***(g/mg min)*** is the constant rate of the pseudo-second-order equation.

The adsorption isotherm is one of the important factors in the design of adsorption systems. In fact, the adsorption isotherm explains how interaction occurs between the adsorbent and the adsorbed substrate. Therefore, these equations are always considered an essential factor in determining the adsorbent capacity and optimizing the adsorption capacity. The Langmuir, Freundlich, and Temkin isotherms were used in this research. Their equations are given below.

$$\frac{Ce}{qe} = \frac{1}{q_{max}k_L} + \frac{Ce}{q_{max}} \quad (4)$$

where Ce is the concentration of the adsorbate at equilibrium (mg/g), qe is the amount of the adsorbate at equilibrium (mg/g), and k_L is the Langmuir constant related to the adsorption capacity (mg/g).

$$\log(qe) = loge(k) + \frac{1}{n}\log(Ce) \quad (5)$$

where K is the adsorption capacity (L/mg) and $1/n$ is the adsorption intensity.

$$qe = \frac{RT}{b}\ln(Ce) \quad (6)$$

where b is the Temkin constant, which is related to the heat of sorption (J/mol), and R_T is the Temkin isotherm constant (L/g).

To prepare the ammonia solutions in the required concentrations, first, a 10 g/L stock solution of ammonia (0.588 M/L) was made. To prepare this stock solution, 40 mL of 25% ammonia was added to 960 mL of deionized water. Then the required concentrations were prepared by diluting the 10 g/L stock solution. After performing the adsorption process at the desired contact time, the sample was centrifuged at 4000 rpm and a certain volume of the sample was removed using a pipette. After the adsorption process is performed during the desired contact times, the sample was centrifuged at a speed of 6000 rpm and a certain volume of the sample was picked up using a pipette. This was passed through a strainer and prepared for measuring its concentration.

3 Results and Discussion

3.1 Statistical Analysis

As shown in Figures 2A to 2D, the accuracy and precision of the performed tests could be ensured. Moreover, these figures show the statistical quality of the data test. The internally studentized residual is displayed in Figure 2A, which shows the number of standard deviations (SDs) that separate the actual and the predicted response values.

The normal probability graph (Figure 2B) shows how the residuals follow a normal distribution. Figure 2C shows a Box-Cox curve. Box-Cox is a tool that helps to identify the most appropriate power transfer function in order to act on response. The lowest point in the Box-Cox shows the best value of the lambda, in which the minimum sum of squares of residuals is created. Figure 2D plots real values versus predicted ones. Therefore, the statistical section shows that the results of the tests performed in this study had good accuracy (lack of fit = 0.15, $R^2 = 0.9082$, adjusted $R^2 = 0.8449$, predicted $R^2 = 0.623$).

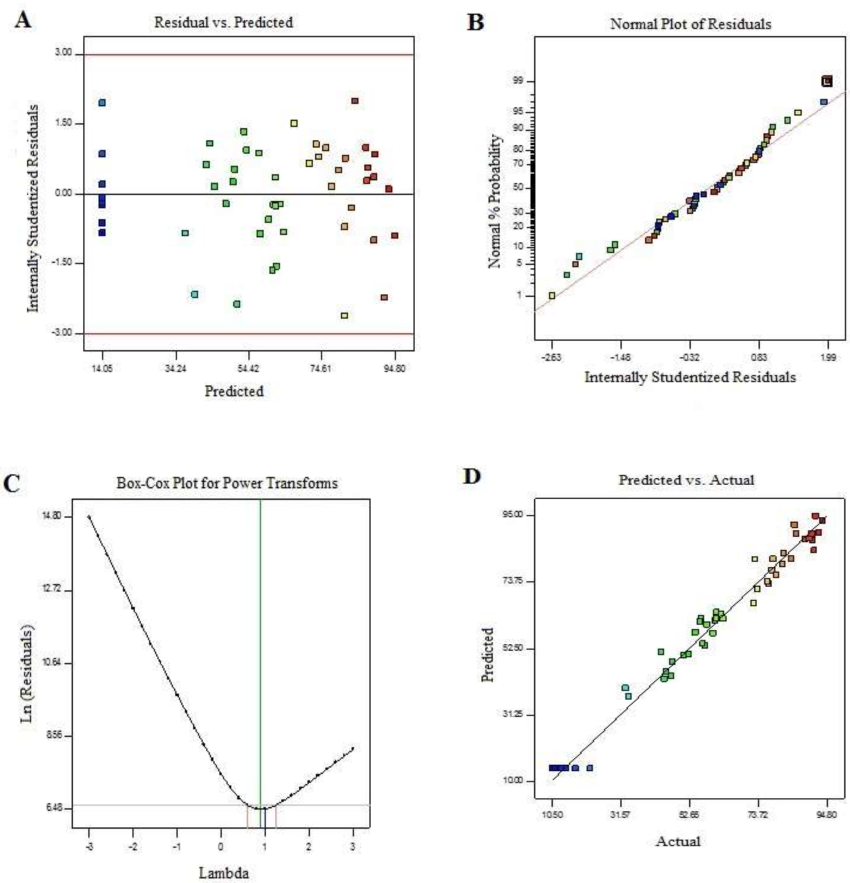

Figure 2 A: internally studentized residual, B: normal probability graph, C: Box-Cox plot, and D: predicted values versus actual values.

3.2 Effect of Operational Parameters

In Figure 3, the efficiency of ammonia adsorption is shown in terms of pH. As can be seen in the figure, it is clear that the adsorption efficiency increased by increasing pH. According to this figure, the adsorption performance at best was equal to 90%, which is due to the higher adsorption of SWCNTs in the alkaline solution. In Figure 5, the efficiency of ammonia adsorption is plotted in terms of the amount of input ammonia and pH. In this 3D figure, similar to what is shown in Figure 3, at low concentrations of ammonia, the adsorption efficiency increased with an increase of pH. On the other hand, at high concentrations of ammonia, adsorption increased with a more acidic or alkaline environment. According to the figure, to achieve the highest adsorption there should be a low concentration of ammonia and the highest alkaline pH in the environment. In Figure 5, the efficiency of adsorption is plotted versus the contact time of the adsorbent with the adsorbed material and pH. $R^2 = 0.9223$

It can be seen that adsorption increased with time. It should be noted that according to the results shown in Figures 4 and 5, the lowest adsorption was seen when pH was almost equal to 7. The pH at the zero point of charge (pHzpc) of single-walled carbon nanotubes is 6.9; at a pH above 6.9, the adsorbent has a negative charge and at a pH below 6.9 it has a positive charge. Since ammonia is found in the form of ammonium in aqueous media, at a pH higher than 6.9, where the adsorbent surface has a negative charge, the amount of ammonia adsorption increases [40,41]. In Figure 6, the removal efficiency is plotted in terms of the amount of the adsorbent and process temperature. Due to the exothermic nature of the adsorption process, the results of this graph show that adsorption increased at lower temperatures and greater amounts of adsorbent.

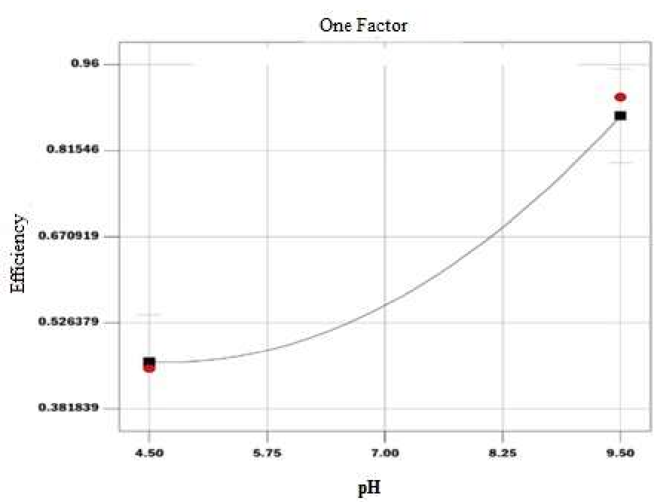

Figure 3 Effect of pH on the adsorption of ammonia on SWCNT.

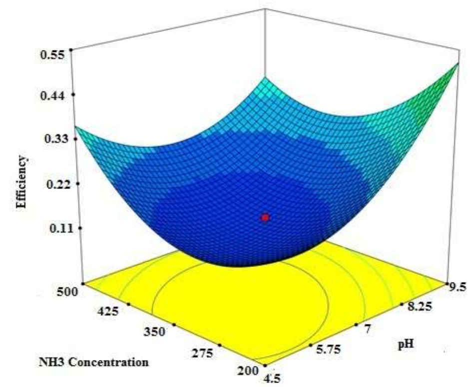

Figure 4 Efficiency versus pH and ammonia concentration.

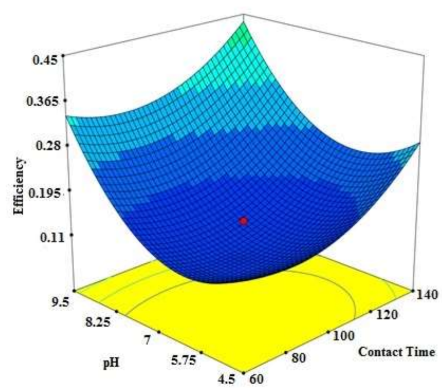

Figure 5 Efficiency versus contact time and pH.

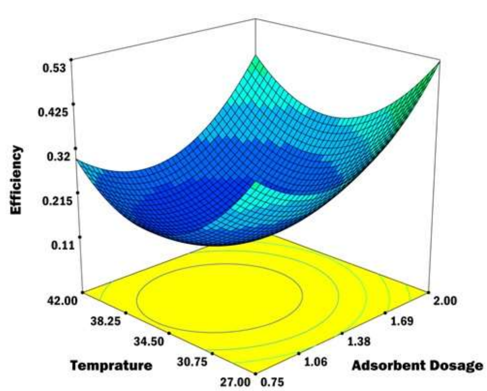

Figure 6 Efficiency versus adsorbent dosage and temperature.

3.3 Kinetics and Isotherms of Adsorption

To obtain information on the factors influencing the reaction rate, a kinetic assessment was necessary. Two kinetic models that are widely used in resources for the surface adsorption process include the first- and second-order kinetics. The results of kinetic simulations of the pseudo-first-order and pseudo-second-order models are shown in Figures 7 and 8. The results of this section show that first-order kinetics had more conformity with the data in comparison with second-order kinetics. Kinetic studies of ammonia adsorption on SWCNTs has shown that surface adsorption occurs by penetration within a layer.

There are many isothermal models, such as Longmuir, Freundlich, and Temkin models, for analyzing the experimental data and describing equilibrium in adsorption. These models are used to provide insight into the mechanism of adsorption, surface properties, adsorption, and descriptive adsorption data, so it is important to establish a proper relationship between the equilibrium curves to optimize the conditions and the design adsorption systems. Surface adsorption isotherms begin with weak forces such as vandalism and end with stronger forces such as ionic, metallic, and covalent forces. Covalent forces are associated with chemical reactions and act not only on the surface but also on the interior of the matter.

The results of the adsorption isotherms are presented in Figures 9 to 11 for Langmuir, Freundlich, and Temkin models, respectively. Based on the results presented in these figures, the Freundlich isotherm had the highest conformity with the data and is considered the best model for describing the adsorbent properties. In the Freundlich isotherm, the amount of adsorbed material depends on the specifications of the adsorbent material, its concentration in the solution as well as the temperature. This model can be used for adsorption on non-uniform surfaces with interactions between soluble molecules. The results showed that by increasing the equilibrium concentration of ammonia, the equilibrium adsorption capacity gradually increased, which can be attributed to the easy access of the adsorption sites in the early moments of the process.

Chemical and physical adsorptions are two important mechanisms for effective ammonia adsorption by SWCNTs [42,43]. Physical adsorption capacity depends on adsorbent properties such as pore size and adsorbent particle size, since the pollutant is captured through nonselective Van der Waals forces [42]. However, chemical adsorption depends on the properties of the contaminant as well as the functional groups present on the adsorbent surface. Based on the size of the SWCNTs and their high number of pores, the mechanism of physical adsorption has a greater role in the adsorption of ammonia on these nanotubes.

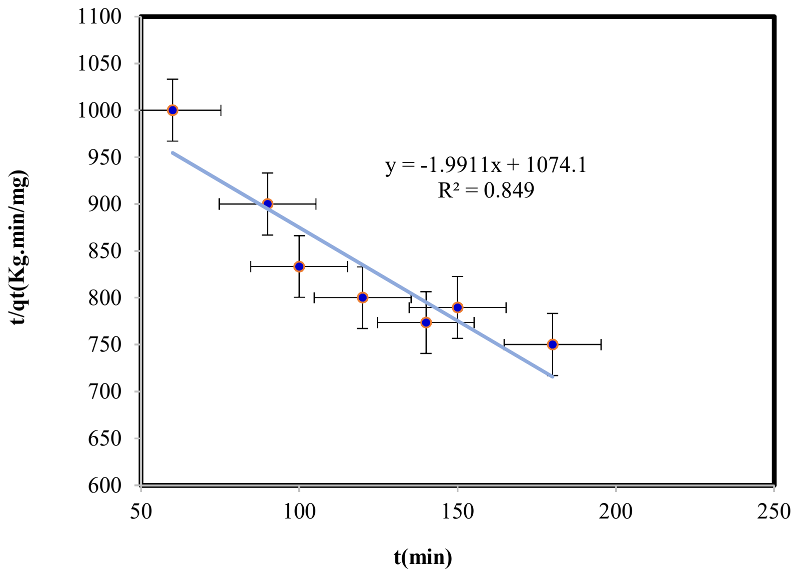

Figure 7 Pseudo first-order adsorption kinetics.

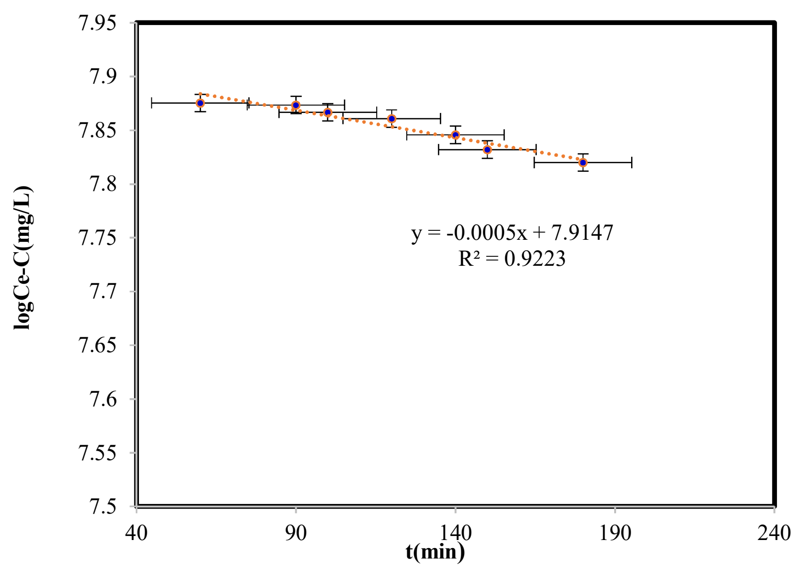

Figure 8 Pseudo second-order adsorption kinetics.

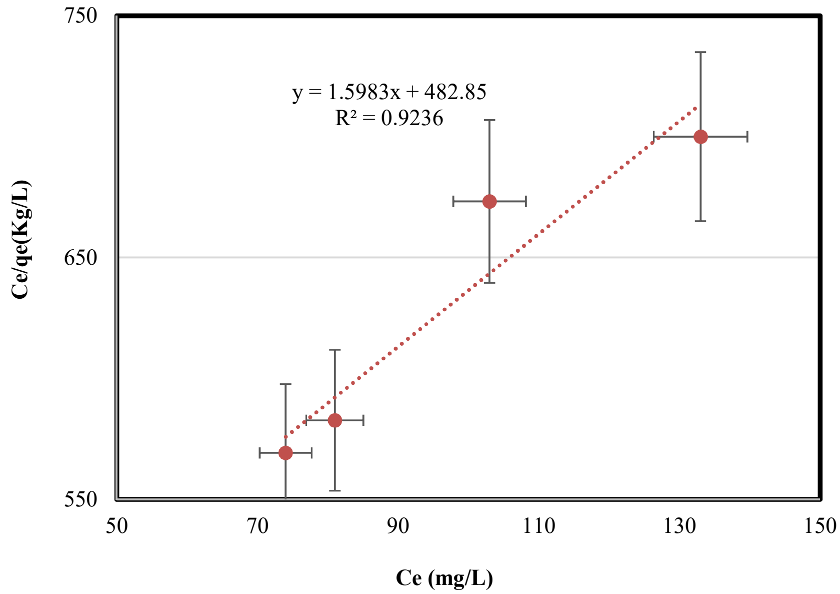

Figure 9 Langmuir isotherm.

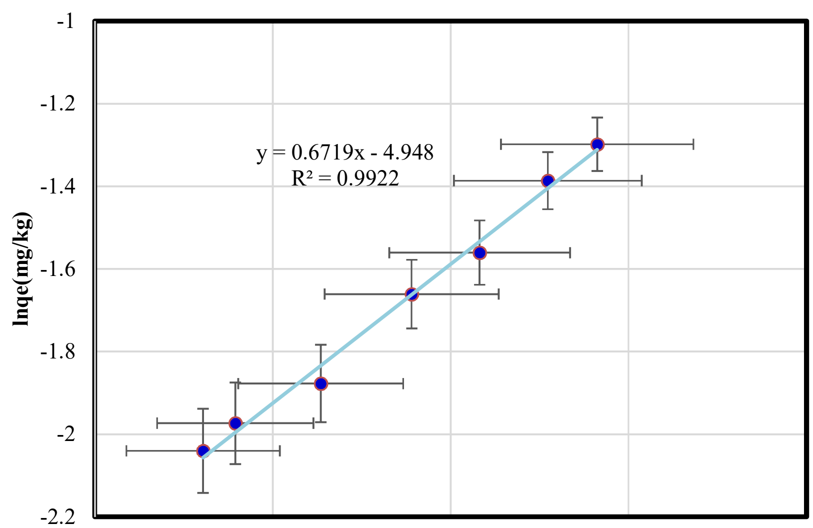

Figure 10 Freundlich isotherm.

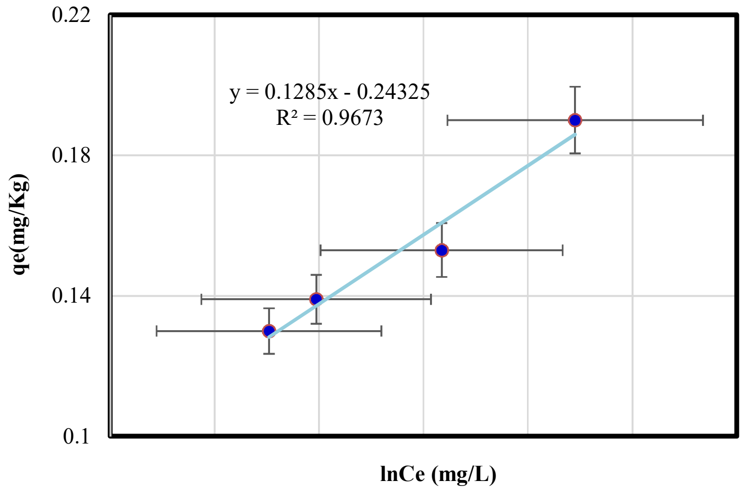

Figure 11 Temkin isotherm.

4 Conclusion

In this study, experiments on ammonia removal from an aqueous solution were carried out by using CNTs. For this purpose, after designing the experiments with the Design-Expert software, a synthetic wastewater solution was prepared and adsorption tests with nanotubes were performed. In these experiments, pH ranged from 2 to 12, the ammonia concentration was 50 to 560 mg/L, the adsorption temperature was 19.5 to 49.5°C, the adsorption time was 20 to 180 min, and the concentration of the adsorbent doses was 0.13 to 2.63 g/L. Finally, the experimental data showed the following results:

1. The highest adsorption was obtained at a pH equal to 9.5 with a yield of 90%.
2. Adsorption decreased with decreasing the pH (acidic solution).
3. Adsorption decreased with increasing temperature.
4. Adsorption increased continuously with increasing adsorption time.
5. Adsorption increased with increased adsorbent dose.
6. At a high pH, efficiency decreased with increasing concentration of ammonia, but at low pH, the efficiency increased with increasing ammonia concentration.
7. The most suitable model for the adsorption of ammonia on SWCNTs was the Freundlich isotherm.

Acknowledgments

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