Research Article

Chemical Review and Letters
journal homepage: www.chemrevlett.com
ISSN (online): 2645-4947 (print) 2676-7279

Removal of Copper (II) Ions from the Effluent by Carbon Nanotubes Modified with Tetrahydrofuran

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ARTICLE INFO

Article history:
Received 10 November 2021
Received in revised form 15 January 2022
Accepted 5 March 2022
Available online 13 March 2022

Keywords:
Adsorption
Heavy metals
Copper metal
Carbon nanotube
Tetrahydrofuran

ABSTRACT

In this study, a carbon nanotube modified with tetrahydrofuran was first synthesized. After preparing the adsorbent, discontinuous adsorption experiments of copper metal were performed on the adsorbent. Atomic absorption spectrometry was used to measure the concentration of copper metal. In this paper also, the effect of contact time, adsorbent amount, pH, initial metal concentration and temperature were investigated. The experiments were performed at concentrations of 2 ppm to 35 ppm and at temperatures of 303 to 343 Kelvin. The results showed that the highest removal efficiency was obtained at pH about 5. Equilibrium contact time for 6 ppm concentration was obtained in 30 minutes and the optimal adsorbent is 0.2 g. After optimizing these variables, the maximum absorption value was 96.33%. Kinetic studies of copper removal by synthesized adsorbent were performed. The results obtained for discontinuous experiments follow the quasi-quadratic kinetic model with (R^2 = 0.9931). Also, equilibrium studies of adsorption show that the adsorption process is better consistent with the Tamkin isotherm (R^2 = 0.9683). In thermodynamic analysis, it is observed that the adsorption process is an endothermic process due to the positive enthalpy changes 3287.32 ($\frac{j}{mol.o_K}$) , and the positive sign of Gibbs free energy at temperature 303 ^oK with value (1715.53 j) shows, the process is non-spontaneous. It is also a sign of positive and equal entropy changes (5.187 J * -K), which indicates an increase in entropy during the adsorption process in the system. Therefore, the absorption process is associated with an increase in irregularities.

1. Introduction

At the beginning of the growth of small communities, urban, industrial, industrial and service wastes and effluents were discharged into rivers and it was even thought that these wastes feed on fish and aquatic organisms and cause their growth and development. It was on this basis that the Mississippi River became a conduit full of municipal and industrial waste, and as a result, in 1928, the discharge of waste into the rivers of some American states was banned, and since 1965, special laws for the disposal of various pollutants and industrial and urban effluents were laid [1-4].
In developing countries, the lack of proper enforcement and regulation of laws and the decentralized growth of industry have caused water resources, especially rivers, to become more polluted every day. Surface runoff and groundwater are of great environmental importance due to their widespread human and industrial uses [5]. Any contamination of surface runoff upstream has many adverse effects downstream, so that all consumers, including humans, animals and industry, are exposed to environmental hazards [6]. Also, providing safe and hygienic water and protecting resources from pollution is one of the current concerns of the government and decision-making centers [7]. Therefore, the need to prevent the destruction of water resources and surface runoff, by identifying, measuring pollutants and setting and enforcing laws becomes more important. In this regard and in order to achieve this important, the project of measuring heavy metals lead, zinc and cadmium in sensitive rivers of the country, investigating the number

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of pollutants in rivers and identifying their sources of entry is important and vital. Experimental results have shown that the above agreement with the predicted conditions is favorable. In addition, the experimental results are modeled by Freundlich and Langmuir isotherms, which is more suitable for the Langmuir isotherm. MCN showed good adsorption capacity in which bisphenol-A, ketrophene and tonalid were the most vulnerable, which were 98%, 96% and 96% removed in 47 minutes, respectively.

Thermodynamic studies showed that the adsorption process for microprocessor ash is endothermic and spontaneous [8-14]. Adsorbate regeneration studies were performed with methanol, ethanol, HCl, NaOH and hydrogen peroxide in five regeneration periods. Methanol had the highest adsorbent rate. MCN can be studied as a stable adsorbent for delta micro-pole adsorption. Significant interest in sustainable and environmentally friendly methods is the renewal of nanomaterials spent in order to use resources more efficiently and minimize the cost of materials and techniques. In this paper, the possibility of using ozone to regenerate magnetic carbon nanotubes (MCNTs) after their use to remove organic pollutants from water is investigated. We performed MCNT through several regeneration cycles (magnetic collection, ozone regeneration, ethanol wash, and then water) to absorb atrazine. The results of our adsorption experiments show that the removal capacity of ATrazine MCNTs decreases from 57.8 to 7.6 mg/g in three cycles, if used only as a regeneration method. However, this capacity increases when MNCTs are washed with ethanol after ozone treatment [15, 20].

MCNTs retained 85-93% of their initial uptake even after ten consecutive recovery periods. In addition, we used a three-layer graphite sheet as a model system for CNTs and performed functional theory (DFT) calculations to calculate the free energy of the adsorption energy and the free energy of the atomization and its by-products in water and ethanol. The results of XPS and DFT measurements showed that the π-π interaction of MCNTs was not affected by pathology or ethanol leaching and that this method could remove degraded lesions on the surface. Overall, this is the first report to suggest the possibility of regenerating MCNTs spent using ozone by rinsing with ethanol as an effective and easy treatment. Carbon fiber nanotubes (CNT-g-CFs) were continuously fabricated by thermal CVD [21-29].

The use of an in-situ potential difference (V300) between the fibers and a cylindrical graphite foil crossover electrode enhances the growth and uniform coating of carbon nanotubes with a diameter of about 10 nm and a length of 125 ca. nm single-fiber tensile tests show that this method prevents a significant reduction in carbon fiber, which is commonly associated with kidney transplantation processes. Single-fiber epoxy fragmentation testing with on-site video fragment detection showed that CNT-g-CFs have the highest interphase shear strength for such systems (MPa5±101), which is comparable to advanced control sizes (8±8 Volt) 103. Single fiber sliding data show a similar trend. The short lengths of scattered CNTs are attractive for absorbing the volume fraction of primary fibers in composite applications. The results are compared with a brief comparison of interface data available in related systems. Composite polyanylene / polygon carbon nanotubes (PAnI/MWCNT, 1: 0.1 w/w) were developed with the aim of bonding the adsorbent properties of the two materials and using them for drug adsorption from aqueous media. PAni/MWCNT was determined by scanning electron microscopy, thermography, infrared spectroscopy, pH at zero point and the effect on material surface wetness. As proof of concept, adsorption studies were performed using meloxicam (MLX) as a drug and were evaluated as function of pH, temperature, ionic strength, contact time and concentration change [5, 30-39].

Kinetic and isothermal models were used to evaluate the mechanism of the adsorption process. The best result was MLX adsorption at pH 2 with 6 minutes of PAni/MWCNT contact. The kinetic models that contained the experimental information were pseudo-second and Elovich, respectively, and the Langmuir-Freundlich kinetic model was two-dimensional. Both models show that adsorption occurs by the chemical nature of the surface and in the interests of the heterogeneous energy composite. PAni/MWCNT shows an absorption capacity of 1mmg-221.2 compared to the literature, which is of great value and can be used to remove drugs from aqueous media [40-47].

2. Materials, equipment and test description

2-1. Solubilization

Five-aqueous copper sulfate (CuSo4.5H2o) was used to obtain the required concentrations of Cu (II). For adsorption experiments, ppm1000 copper (II) solution was used, which was calculated by the following method. We know that to prepare a standard solution of ppm 1000 copper, we have to dissolve 1 gram of copper in 1 liter of water, so we have to find out how much salt there is, i.e. copper sulfate.

MW (CUSO4.nH2O) =249.69g/mol

MW (Cu) =6 4gr/mol

Gr (CUSO4.nH2O) = (1gr CU* 249.69gr CUSO4.Nh2O)/ (64gr CU) =3.9014gr

Therefore, the amount of 3.9014 g of copper sulfate is poured into a 1000 ml/L balloon with distilled water to a volume of 1000 ml. To prepare thinner solutions, the same standard solution is used according to Equation 1.

$C_1V_1=C_2V_2$ (1)

C_1: Maternal solution concentration

V_1: The volume of solution from the mother solution to prepare a thinner solution

C_2: Concentration of the desired dilute solution

V_2: The volume of the desired dilute solution.

2-2. Measurement of copper ions by spectrophotometer

To measure the concentration of copper ions by standard solution method, prepare between 10 and 100 mg/L and add 25% by weight ammonia. Until the copper complex is formed and then we get the maximum wavelength of copper. The maximum wavelength obtained is 615 nm.

Set the wavelength of the spectrophotometer to 615 nm and give the device solutions of a certain concentration. And we read their absorption number. We give the data to Excel software and draw a calibration diagram. To measure solutions with unknown concentration, first we put them in the spectrophotometer and read the absorption number from the device, then we put the read absorption number in the calibration diagram and obtain the unknown concentration.

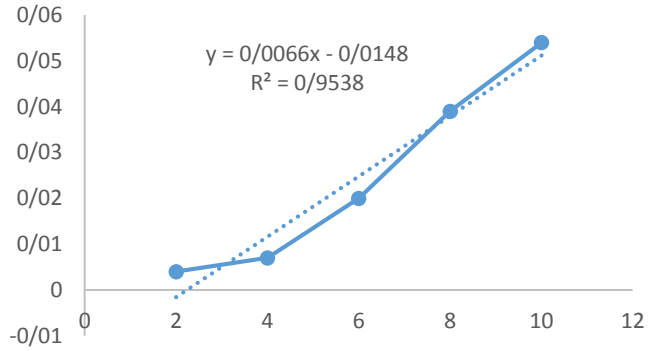

Figure 1. Absorption calibration curve in terms of different initial concentrations of copper (II) solution at temperature (298 K)

Activation of carbon nanotube surface:

To increase the activity of carbon nanotube, we modify the surface of the sample in acidic solutions or base. For this purpose, a certain amount of carbon nanotubes separately in the amount of 20 ml of each of the solutions of concentrated hydrochloric acid, concentrated nitric acid, concentrated phosphoric acid, 4 N sodium, and a solution of hydrochloric acid and nitric acid 1 to 1: 1 and stir for one hour at room temperature with a magnetic stirrer. After one hour, the mixture is centrifuged and washed once with 5 ml of deionized water and the sample is dried first at normal pressure and then in a vacuum oven.

2-3. Binding of tetrahydrofuran ligand to the activated surface of carbon nanotubes

To bind tetrahydrofuran ligand to the Nano-sorbent surface, pour a certain amount of its surface in the previous step by acid solution or modified base in 20 ml of tetrahydrofuran solvent and stir for 30 minutes with a magnetic stirrer (or by machine ultrasonic). Then, the sample is filtered after centrifugation with the help of filter paper and after drying, the solid phase is used to absorb and concentrate the desired ion.

3. Results and Discussion

3-1. Investigation of the effect of pH on the amount of adsorption

50 ml of copper (II) sulfate solution with a concentration of 6 ppm at different pHs is added to 0.1 g of adsorbent of carbon nanotube modified with tetrahydrofuran and placed at room temperature for 3 hours on a magnetic stirrer at a constant speed of 300 rpm. The solutions were then centrifuged and passed through a filter paper, and finally their adsorption was measured by an atomic absorption apparatus. The results showed that the highest percentage of copper (II) ion removal occurred using the adsorbent of carbon nanotube modified with tetrahydrofuran at pH = 5. So, pH = 5 was chosen as the optimal pH.

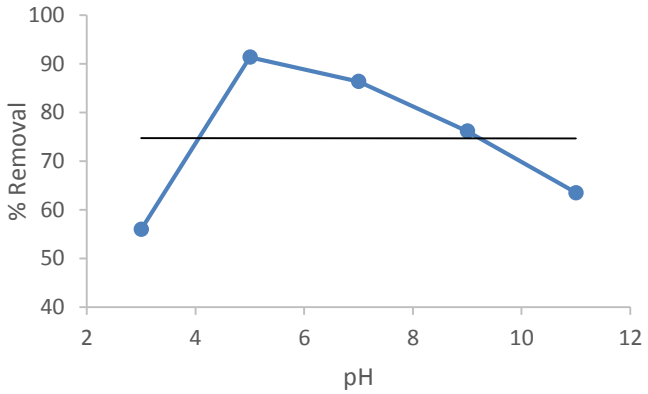

Figure 2. Effect of pH on the percentage of copper (II) ion removal by tetrahydrofuran-modified carbon nanotubes

3-2. Investigation of the effect of adsorbent on adsorption

Add 50 ml of copper (II) sulfate solution with concentration of ppm6 and pH = 5 to different amounts of adsorbent of tetrahydrofuran-modified carbon nanotube in grams and place at room temperature for 3 hours on a magnetic stirrer at a constant speed of 300 rpm. The solutions were then centrifuged and passed through a filter paper, and finally their adsorption was measured by an atomic absorption spectrometer. The results showed that the highest percentage of removal of divalent

copper ions with the amount of 0.2 g from the adsorbent of carbon nanotubes modified with tetrahydrofuran occurred.

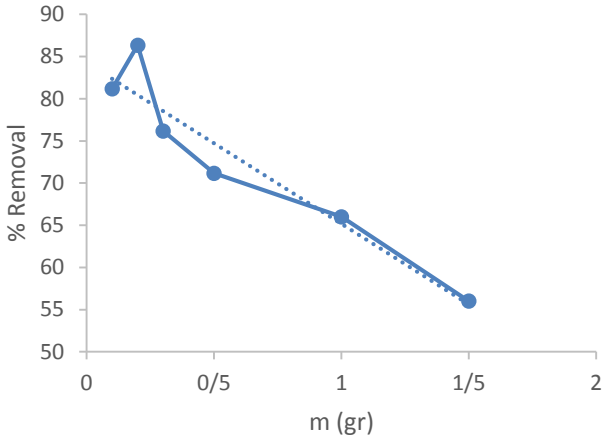

Figure 3. Effect of adsorbent amount on removal percentage of copper (II) ion by tetrahydrofuran-modified carbon nanotube

3-3. Investigating the effect of time on the amount of absorption

50 ml of copper (II) sulfate solution with a concentration of 6 ppm and pH = 5 was added to 0.2 g of the nanotube adsorbent modified with tetrahydrofuran at a temperature of 303 K and at different times per minute on a magnetic stirrer with a constant speed of 300. The solution was centrifuged and then centrifuged and passed through a filter paper, and finally their adsorption was measured by an atomic absorption spectrometer. The results showed that the highest percentage of removal of copper (II) ions by the adsorbent was done in 30 minutes.

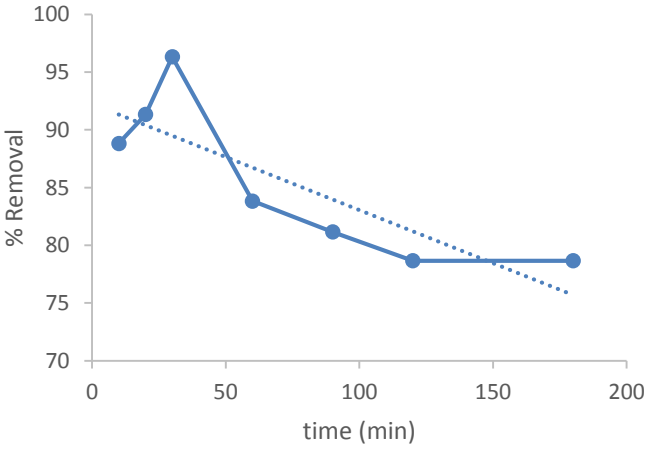

Figure 4. Effect of time on the percentage of copper (II) ion removal by tetrahydrofuran-modified nanotubes

The quasi-first-order and quasi-second-order kinetic diagrams at a concentration of 6 ppm are plotted as follows.

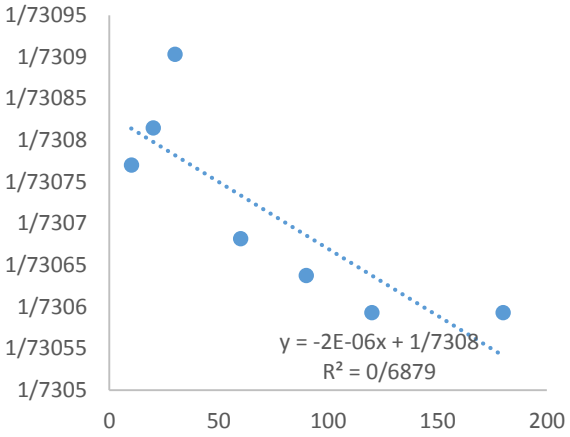

Figure 5. A quasi-first-order kinetic curve for an initial concentration of 6 ppm

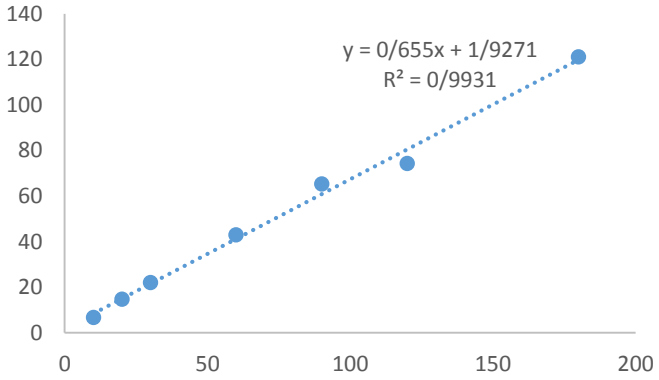

Figure 6. Quasi-quadratic kinetic curve for the initial concentration of 6 ppm

The least squares method has been used to investigate the agreement of kinetic models with experimental data. In this method, parameter R2 or correlation coefficient was used for comparison. Table (1) shows the R2 values for the adsorption kinetic models.

Table 1. R^2 values for quasi-quadratic and quasi-quadratic kinetic models

Kinetic models	Pesudo first order	Pesudo second order
R^2	0.6879	0.9931

Due to the fact that the value of R2 in the quadratic kinetic model is larger and closer to one, the experimental data at a concentration of 6 ppm are more consistent with this model and follow the quasi-quadratic kinetic model.

3-4. Investigation of the effect of temperature on the amount of adsorption

50 ml of copper (II) sulfate solution with a concentration of 6 ppm and pH = 5 was added to 0.2 g of the nanotube adsorbent modified with tetrahydrofuran and at different temperatures for 3 hours on a magnetic

stirrer at a constant speed of 300 rpm. The minutes were centrifuged and the solutions were centrifuged through filter paper, and finally their adsorption was measured by an atomic absorption spectrometer. The results showed that the highest percentage of removal of divalent copper ions by tetrahydrofuran-modified nanotube adsorbent occurred at 303 Kelvin.

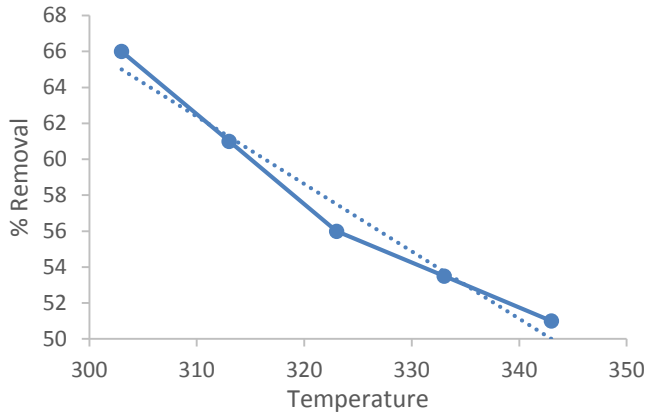

Figure 7. Effect of temperature on the percentage of copper (II) ion removal by tetrahydrofuran-modified nanotubes

As can be seen in Figure (7), the percentage of adsorption decreases with increasing temperature, which may indicate the physical nature of the adsorption. In fact, increasing the temperature increases the entropy and weakens the bond between the adsorbent and adsorbent species.

3-5. Investigation of the effect of concentration on the amount of adsorption

50 ml of copper (II) sulfate solution with different concentration but pH = 5 was added to 0.2 g of tetrahydrofuran modified nanotube adsorbent and placed at 303 K for 30 minutes on a magnetic stirrer at a constant speed of 300 rpm.

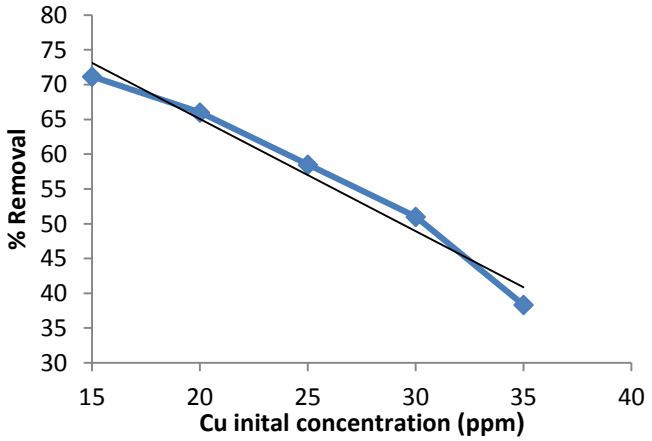

Figure 8. Effect of concentration on the percentage of copper (II) ion removal by tetrahydrofuran-modified nanotubes

The solutions were then centrifuged and passed through a filter paper, and finally their adsorption was measured by an atomic absorption apparatus. The results showed that with increasing concentration, the percentage of adsorption decreases.

4. Investigation of adsorption isotherms of copper (II) ions by tetrahydrofuran-modified carbon nanotubes

4-1. Langmuir surface adsorption isotherm study

Langmuir adsorption isotherm for concentrations of 15, 20, 25, 30 and 35 ppm of copper (II) sulfate solution is shown at 303 K and according to the obtained equation and line equation, Langmuir constants can be calculated. The results showed that the maximum adsorption capacity is 0.12 mg/g.

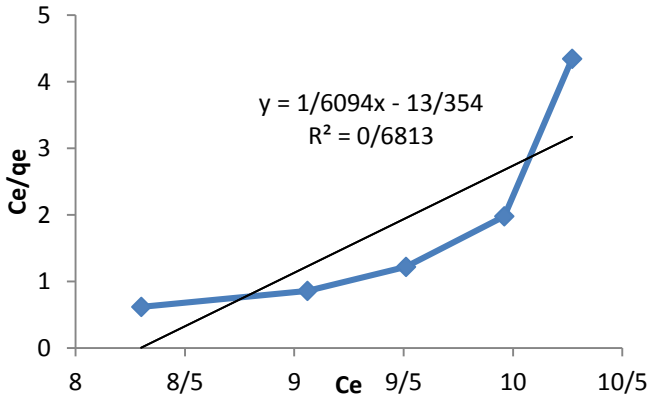

Figure 9. Langmuir surface adsorption isotherm for different concentrations of copper (II) sulfate solution on 0.2 g of carbon nanotube modified with tetrahydrofuran for 30 minutes, pH = 5 and at 303 K.

4-2. Investigation of Friendlich surface adsorption isotherm

The Fredlich surface adsorption isotherm diagram for concentrations of 15, 20, 25, 30, and 35 ppm of copper (II) sulfate solution at 303 K is shown.

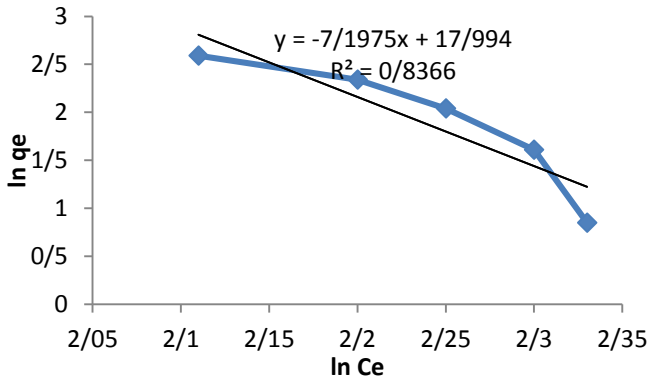

Figure 10. Friendliege adsorption isotherm for different concentrations of copper (II) sulfate solution on 0.2 g of carbon nanotube modified with tetrahydrofuran for 30 minutes, pH = 5 and at 303 K

4-3. Investigation of Tamkin ion adsorption isotherm

The isothermal adsorption diagram for the concentrations of 15, 20, 25, 30 and 35 ppm of copper (II) sulfate solution at 303 K is shown and according to the equation and the line equation obtained, the obedience constants can be calculated.

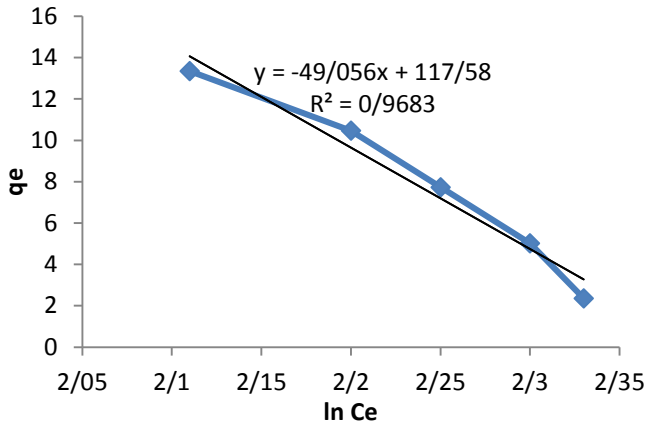

Figure 11. Adsorption isotherm of Tamkin for different concentrations of copper (II) sulfate solution on 0.2 g of carbon nanotube modified with tetrahydrofuran for 30 minutes, pH = 5 and at 303 K

4-4. Investigation of Dabinin-Raduskovich surface adsorption isotherm

Figure (12) shows the D-R adsorption isotherm for concentrations of 15, 20, 25, 30 and 35 ppm of copper (II) sulfate solution at 303 K, and the D-R constants can be calculated according to the equations and the straight-line equation.

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (2)$$

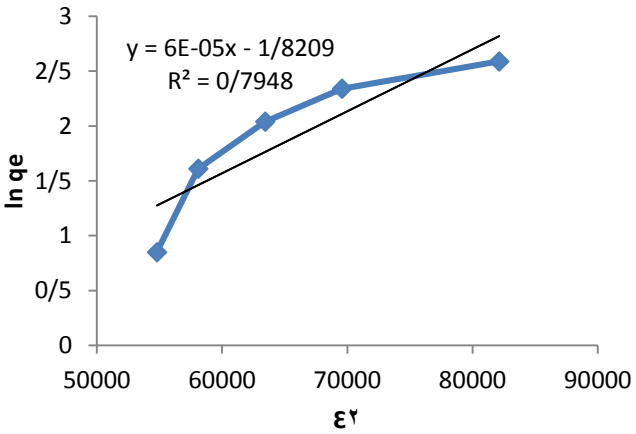

Figure 12. D-R adsorption isotherm for different concentrations of copper (II) sulfate solution on 0.2 g of tetrahydrofuran-modified carbon nanotube for 30 minutes, pH = 5 and 303 K

$$E = \frac{1}{\sqrt{2\beta}} \quad (3)$$

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \quad (4)$$

$$y = 6E\text{-}05x - 1.8209 \quad (5)$$

$\beta = 6\times10^{-5} mol^2\ J^2$

$q_m = 1.82.9$ mg/g

E = 0.091 KJ/mol

5. Calculation of thermodynamic parameters of copper (II)

5-1. Calculation of enthalpy of standard adsorption

In order to calculate ΔH ° ads, using the equations, the enthalpy can be calculated from the slope of the line equation.

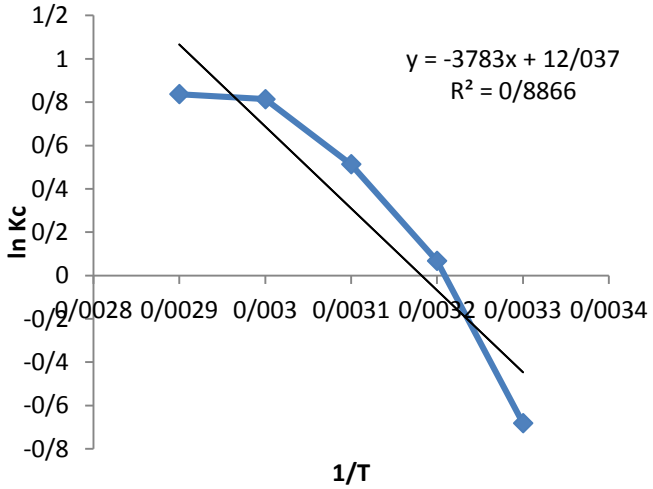

Figure 13. ln Kc curve in terms of 1/T slope of the indicator line/standard enthalpy of standard adsorption of copper (II) sulfate solution on 0.2 g of carbon nanotube modified with tetrahydrofuran for 30 minutes at pH = 5 303 Kelvin

$$\ln K_c = \frac{-\Delta H^\circ_{ads}}{RT} + D \quad (6)$$

$$K_c = \frac{C_0 - C_e}{C_e} \quad (7)$$

y = -3783 x + 12.037

$\Delta H^\circ_{ads} = 3287.32\ J\ mol^{-1}$

5-2. Calculation of free energy of standard desorption gases

The standard Gibbs free energy of adsorption (ΔG ° ads) can be calculated using Equation (8).

$$\Delta G^\circ_{ads} = -RT \ln K_c \quad (8)$$

The standard entropy energy of surface adsorption (ΔS ° ads) can be calculated using Equation (9).

$$\Delta S^\circ_{ads} = \frac{\Delta H^\circ_{ads} - \Delta G^\circ_{ads}}{T} \quad (9)$$

$S^\circ_{ads} = 5.187\ (J\ mol^{-1}\ K^{-1})$

6. Conclusion

- Equilibrium contact time for 6 ppm concentration in 30 minutes with adsorption percentage of 68.13% was obtained.
- In the study of kinetic models, the adsorption process follows the quasi-quadratic model with (R2 = 0.9931).
- The optimum pH at pH = 5 with an adsorption percentage of 91.33%. Also, at pHs above 7, the solubility of copper is very low and reduces the percentage of adsorption.
- The optimal amount of adsorbent is 0.2 g with an adsorption percentage of 86.33%.
- In the study of the effect of temperature, 303K temperature with an absorption percentage equal to 66% has the highest absorption rate.
- As the concentration increases, the adsorption percentage decreases and the maximum adsorption rate at 15 ppm is 71.16%.
- In thermodynamic analysis, it is observed that the adsorption process is an endothermic process due to the positive enthalpy changes $3287.32\frac{j}{mol.o_K}$, and the positive sign of Gibbs free energy for the optimal temperature of 303 K with the value (1715.53 j) indicates that the process is non-spontaneous.
- Also, the sign of entropy changes is positive and equal to ($5.187\frac{j}{o_K}$), which indicates an increase in entropy during the adsorption process in the system. Therefore, the absorption process is associated with an increase in irregularities.
- By examining the correlation coefficients of Langmuir (0.6813) and Freundlich (83.66), Tamkin (0.9683) and Rabinin-Radushkovich (0.7948) isotherms, the correlation coefficient of the Tamkin adsorption isotherm shows that the adsorption data correspond to the Tamkin isotherm.

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