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Reducing Nitrate from Aqueous Solutions Using CNT as a Powerful Adsorbent: Modification by Lanthanum

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Abstract

Carbon nanotubes (CNTs) and La/CNTs composite as adsorbents were synthesized and characterized by FTIR, SEM, and BET analysis and literally were applied for the removal of nitrate from aqueous solutions at different conditions. Taguchi's method of design of experiments was used to study the effect of each parameter at three levels on the total amount of nitrate adsorption on adsorbents. The effects of important variables such as pH, temperature, initial concentration of nitrate, and contact time on adsorption process were optimized by Taguchi approach. Optimum values of 3, 0^0C, 10 ppm and 210 min were obtained for pH, temperature, initial concentration of nitrate, and contact time, respectively. At the optimized condition, the removal efficiencies were found to be 65.15% and 93.37% for CNTs and La/CNTs, respectively. The experimental data were analyzed by the Langmuir, Freundlich and Temkin models of adsorption. Equilibrium data fitted well with the Langmuir model.

Keywords: Adsorption, Lanthanum, carbon nanotubes, Nitrate, Taguchi**.**

Introduction

In addition to the need for water to drink, water resources have a significant impact on various economic sectors including industrial activities, poultry, forestry, electricity, agriculture, and other related activities. The main source of water is nature, and it is clear that this a problem we face with a shortage of water supplies to meet the growing needs of our biological and industrial activities in the world (Effendi 2016, Mekonnen and Hoekstra 2014). Therefore, supply of healthy and safe water is one of the most important challenges for human societies, especially in developing societies (Dargahi, et al. 2016). Environmental contamination and the energy crisis have become two key issues for human society and seriously threaten the existence of terrestrial lives(Jiang, et al. 2016). Nitrate Pollution is one of the most important factors that lead to the loss of water resources (Asrari and Avatefinezhad 2017). In addition, Various diseases and harmful effects caused by drinking, fluoride and nitrate contaminated water have been a great anxious to our human society (Suriyaraj and Selvakumar 2016). Excess nitrate-nitrogen losses from agricultural watersheds generate a host of water quality problems around the globe, including eutrophication, algae blooms, and fish kills(Kuroki, et al., 2014) and These contaminants greatly endanger public health since the nitrite is a well-known precursor to cancer causing agents. In principle, removal of nitrate/nitrite from water (also called denitrification) can be achieved through a physicochemical method such as ion exchange, reverse osmosis, electrodialysis, or a biological route (Zhao, et al. 2016). Although Nitrate is an essential nutrient for the growth of plants and microorganisms(Nur, et al. 2015) but due to the elimination of livestock effluents, using various fertilizes in agriculture and the distribution of industrial and urban waste, the pollution caused by nitrate in surface and groundwater has been increased(Tong, et al. 2017). The long term health hazards and increasing levels of nitrate in drinking water through natural and anthropogenic sources are challenging and warrant the need for advanced technologies for abating these contaminants(Abo-El-Enein, et al. 2017). Adsorbents such as zeolites, activated carbon (AC), polymers, biomaterials, have been used widely for treating wastewater (Sadegh, et al. 2017).

Common methods such as electrodialysis, biological processes, and reverse osmosis are relatively costly (Wan, et al. 2012). Adsorption is regard as an appropriate technology of nitrate removal for less expensive and more flexible and its convenience, ease of operation, and simplicity of design. Selection of a proper adsorbent is the key to nitrate adsorption (Tong, et al. 2017, Xue, et al. 2016). Adsorption by

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solids decreases the toxicity of the wastewater or removes non-safe organic materials from industrial effluents, etc. (Malik 2004). In adsorption method, nitrate molecule is attached on the surface either through physisorption or chemisorption (Tyagi, et al. 2018).

The application of carbon nanomaterials such as carbon nanotubes (CNTs) in the field of adsorption is one of the emerging trends for the removal of dyes from wastewater, even at very low concentrations(Zare, et al. 2015). Polymer nanocomposite is a combination of polymer matrix and with a large range of filler materials. These fillers can be one dimensional, two- or three-dimensional**.** Carbonaceous nanofillers such as graphene, carbon nanotubes (CNTs) play a very promising role due to their better functional and structural properties such as high aspect ratio, high electrical properties, and high mechanical strength than others (Mittal, et al. 2015).

Carbon has the potential to be present in many molecular forms; which is known as allotropes of carbon. CNTs are cylindrical graphite sheets in a tube like structure (allotropic form of carbon) (Abbas, et al. 2016). Other properties of CNTs include controlled pore size distribution, high specific surface area, and great sorption capacity compared to conventional granular and powder activated carbon. Further studies show that the adsorption capacity of CNTs depends on both the nature of the sorbate and its surface functional groups (Bankole, et al. 2017).

The objective of this work is to study the nitrate adsorption behavior of the lanthanum loaded on CNTs. The present paper describes an experimental and theoretical investigation of nitrate adsorption on CNTs and modified CNTs. CNTs and La/CNTs composite (modified CNTs) were synthesized and characterized in details. The adsorption isotherms were also investigated. Equilibrium sorption experiments and isotherms were carried out, and the data were compared to activated carbon to evaluate the sorption behavior of nitrate by the synthesis composite.

Experimental

Chemical and materials

Lanthanum nitrate ($LaN_3O_9.6H_2O$, 99%), Hexamethylenetetramine ($C_6H_{12}N_4$), and Sodium nitrate ($NaNO_3$, 99%) were purchased from Merck and Multi Wall Carbon Nanotube (CNTs, 95%) was purchased from Mina Tajhiz Arya. Stock solution of Sodium nitrate containing 500 ppm Sodium nitrate was prepared by dissolving 0.677 g of $NaNO_3$ in Demineralized (DM) Water and this solution was completed up to the mark of 1L measuring flask. $NaNO_3$ solutions of lower concentrations were prepared by further dilution. Materials weights were calculated with digital balance with accuracy to 0.001 g. DM water was used in all over the experiment. All chemicals used in the investigation were of analytical grade.

Nitrate concentrations in solution were quantified via optical absorption using UV absorbance in a spectrophotometer JENVAY 7315.

Preparation of Lanthanum/carbon nanotubes

Before adsorbent synthesis, Lanthanum was loaded on carbon nanotubes. For this purpose, 3 gr of carbon nanotubes was mixed with 5 gr lanthanum nitrate ($La(NO_3)_3$), and 5 gr Hexamethylenetetramine, then it was transferred to 100 ml volumetric flask and dissolved in DM water and brought to volume with DM water. Then the volumetric flask was sonicated for 15 min in ultrasonic bath at room temperature, so the solutes would spread out well. After ultrasonic bath, the flask was stirred in oil bath (90^0C) for 1h because of the fact that reaction between carbon nanotubes and Hexamethylenetetramine, and Lanthanum nitrate requires high temperature and activation is more successful. The solution was transferred into a glass centrifuge pot and centrifuged for 5 min at 1500 rpm, supernatant was removed by Pipette, and the residue was rinsed with DM water, moved to the beaker and heated for 3 hours to provide a dry adsorbent. The weight of obtained adsorbent was 4.8 gr which was heavier than 3 gr carbon nanotubes indicating that lanthanum has loaded on carbon nanotubes successfully.

Characterizatio

The samples were characterized using following methods. The surface morphology of adsorbent was analyzed by using scanning electron microscopy (SEM). The specific surface areas of the adsorbents were calculated using the Brunauer–Emmett–Teller (BET) equation. FT-IR spectroscopy, which permits confirmation of the presence of the corresponding functional groups or chemical bonding of the related atoms in the structure of the molecule, for CNTs and La/CNTs were measured.

Experiments Design

Taguchi method for optimization was developed by Genichi Taguchi to improve the quality of product with a unique set of “orthogonal array” experiments which are balanced with respect to all control factors and yet are minimum in number (Kundu, et al. 2015).

It provides a simple, efficient, and systematic approach to optimize designs for performance, quality, and cost and leads to a more fully developed process. The key step in the Taguchi method is the parameter design to achieve high quality without increasing in cost. One another advantage of Taguchi method is the possibility of performing experiments in a parallel (Pourjavadi, et al. 2008, Rao, et al. 2008).

In addition, a complete investigation of the effects of experimental factors would require a large number of experiments. Thus, in this study, the Taguchi optimization approach was used to reduce total number of experimental runs by selecting an appropriate orthogonal array based on the required number of factors and levels(Rashidi, et al. 2013).

QUALITEK 4 software for automatic designing and analyzing of Taguchi experiments was used to study the ANOVA and optimum condition of nitrate adsorption on CNTs and La/CNTs. QUALITEK-4 (QT4) is the windows version software for Automatic Design and Analysis of Taguchi Experiments.

Selection of control factors is an important stage of Taguchi applications and design of the factors is generally set by experimenter's experience (Balak, et al. 2015). Full factorial approach will require 162 experiments to be conducted for optimizing a process while in fractional factorial using L9 orthogonal array the number of experiments reduces to 18. Three combinations of variables (levels) for each of the adsorption factors (pH, temperature, initial concentration, and time) were selected. The factors and their levels, and the standard L9 orthogonal array are presented in Table 1 and Table 2, respectively.

Adsorption studies

We have studied nitrate adsorption by adsorbents with nine conditions, which were derived by Taguchi. Adsorption process was conducted in glass beakers for adequate time to complete the adsorption and achieve equilibriums concentrations. 1M HCl and 1M NaOH were used to adjust the pH of the solutions. For each experiment, 20 cc of nitrate with specific concentration were added to 0.1 g of adsorbents in beaker. For experiments with 0^0C temperature, beaker were placed in water and ice container and in experiments with 60^0C the beaker was placed on heater. After specified contact time, samples were filtered and the solution adsorption was determined by a UV-visible spectrophotometer at a wavelength of 220 nm. Removal percentages were calculated by eq. (1) and adsorption capacities were determined by eq. (2)

$$Removal\ (\%) = (C_0 - C_e)/C_0 \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)\,V}{m} \quad (2)$$

Where C_0 and C_e are the initial and equilibrium nitrate concentrations in the solutions, respectively.

The adsorption isotherm studies were carried out by varying the nitrate initial concentrations in 0^0C. The adsorption data were fitted with three adsorption isotherms, namely, Langmuir, Freundlich and Temkin. The adsorption isotherm studies were repeated in 30 and 60^0C for CNTs and La/CNTs composite

Results and Discussion

Characterization of Adsorbents

The BET calculation obtains the sample surface area value by determining the monolayer volume of adsorbed gas from the isotherm data (Abbaslou, et al. 2017). The results of total pore volume for the carbon nanotubes and lanthanum/carbon nanotubes composite are given in Table 3. Table 3 shows the BET surface area, average Pore diameter, and total pore volume for La/CNT is smaller than commercial CNTs because of Lanthanum loaded on carbon nanotubes. Lanthanum, due to its placement on cavities and carbon nanotubes surfaces, would cause decreasing of mentioned parameters and on the other hand, due to its high adsorption capacity, would cause increasing of adsorption capacity. As a result, adsorption power of modified carbon nanotubes would increase significantly.

The surface morphology of adsorbents were analyzed by using scanning electron microscopy (SEM). Figures 1a and b show the SEM images of CNTs and La/CNTs, respectively. It is evident that the CNTs are homogenous and have cylindrical shapes with the specific diameter and cavity volume range. It can be seen that lanthanum (bright Granular) have been loaded homogenously on CNTs after modification.

Fig. 2a and b display FT-IR spectra of CNTs and modified CNTs, respectively. By comparing these spectrums, it can be found out that lanthanum has bonded to carbons successfully and have been added to the adsorbent structure. Weight percentage of adsorbent elements are given in Table 4.

Adsorption Studies

- *Effectiveness of the adsorbents in the removal of nitrate*

Table 5 and Table 6 show nitrate removal percentage and capacity at equilibrium in different conditions for the CNTs and La/CNTs, respectively. Removal percentage and capacity of CNTs and modified CNTs comparison are represented in Table 7.

Analysis of ANOVA under Taguchi design

After designing experiments by Taguchi approach, experimental data were analyzed using ANOVA since Taguchi approach uses ANOVA to investigate statistically significant parameters in finding the optimum levels.
Tables 8 and 9 represent ANOVA of the S/N ratios for the CNTs and La/CNTs composite. Figures 3 and 4 show the significant factors and interaction influences for nitrate adsorption on adsorbents. Optimum conditions determined based on the qualify character. DOF_R represents the degree of freedom for each factor, which is obtained by subtracting one from the number of the level of each factor (L). Each column of Tables 8 and 9 illustrate the effectiveness of each factor on nitrate adsorption in comparison with other factors and analyzes these data with statistical approach.
The total and factor sums of squares are the basic calculations needed for ANOVA. Four other quantities calculated as part of the ANOVA table information are all derived from the original sums of squares (Roy, 2001).

According to Table 8 and Fig. 3, initial concentration is the most significant (53.3%) factor on adsorption process. Effectiveness of contact time, pH, and temperature are approximately 20.4%, 14.14%, and 11.8%, respectively.

Optimization condition

Numerical experiments of Taguchi design for nitrate adsorption on CNTs and La/CNTs composite were applied and imported to Qualitek-4 to find the best optimum condition of nitrate adsorption on CNTs and La/CNTs (Table 10). Optimum point was found to be at Level (1, 1, 1, 3) which is related to (pH, T, C, t). These values are (3, 0^0C, 10 ppm, 210 min) for nitrate adsorption. Removal Efficiencies were found to be 65.15% and 93.37% for CNTs and La/CNTs, respectively.

Adsorption isotherms

Adsorption isotherms models were applied to study the maximum uptake capacity of nitrate on the CNTs and La/CNTs. The equilibrium adsorption of nitrate ions on the adsorbents were analyzed using Langmuir, Freundlich and Temkin adsorption isotherms.

The experimental data were fitted to the linear form of Langmuir (Eq. (3)), Freundlich (Eq. (4)) and Temkin (Eq. (5)) (Zong, et al. 2017).

$$\frac{c_e}{q_e} = \frac{1}{Q_{max}.b} + \frac{c_e}{Q_{max}} \quad (3)$$

$$\log\left(\frac{x}{m}\right) = \log(q_e) = \log(K_f) + \frac{1}{n}\log(C_e) \quad (4)$$

$$q_e = A + B.\,\mathrm{Ln}(C_e) \quad (5)$$

Where in eq. 3, C_e (mg/L) is the equilibrium concentration of the nitrate, q_e (mg/g) is the amount of the nitrate adsorbed at equilibrium, Q_{max} is the maximum adsorption capacity, and b is the Langmuir equilibrium.

In eq. 4, K_f = Freundlich adsorption capacity parameter, (mg/g) $(L/mg)^{1/n}$ and 1/n = Freundlich adsorption intensity parameter.

In eq. 5, A is Temkin isotherm equilibrium binding constant corresponding to the maximum binding energy (L/g), B is constantly related to the heat of sorption (J/mol), R is the universal gas constant (8.314 J/mol/K), T is absolute temperature at 298 K°, b is Temkin isotherm constant, which indicates the adsorption potential of the adsorbent (Dehghani, et al. 2016).

Tables 11 and 12 show the regression coefficients (R^2) for the fitting of the experimental data for CNTs and La/CNTs, respectively. The result is in an agreement with those reports of other lanthanum-modified adsorbents, such as lanthanum modified bentonite (Kuroki, et al. 2014).

The mean R^2 in 0, 30, and 60^0C for Langmuir, Freundlich and Temkin models were 0.99, 0.97 and 0.95 for CNTs, respectively. R^2 is about 1 in Langmuir, indicated that Langmuir gave the best fit for the nitrate adsorption by adsorbents with R^2 = 0.99, which shows that the nitrate adsorption onto CNTs was monolayer (Tang, et al. 2014)

The mean R^2 in 0, 30, and 60^0C for Langmuir, Freundlich and Temkin models were 0.99, 0.95 and 0.92 for La/CNTs, respectively.

Kinetic analysis

The sorption of ions onto CNTs is commonly correlated with the Langmuir or the Freundlich equations (Abbas, et al. 2016). As it said before, nitrate adsorption on CNTs and synthesis La/CNTs can be best described by Langmuir equation. Therefore, we used Langmuir isotherm to analyze the adsorption heat (eq. (6)).

$$\left(\frac{x}{m}\right) = q_{max}\left(\frac{b.C_e}{1+b.C_e}\right) \quad (6)$$

The isosteric heat of adsorption is a thermodynamic quantity that characterizes the enthalpy change associated with the adsorption of a molecule on a surface. Isosteric heat of adsorption, Q_{st}, is obtained from adsorption isotherms measured at different temperatures and is often used to characterize adsorption energetics (Anson, et al. 2004).

Eq. (7), (8) and (9) were used to determine ΔH, ΔG, and ΔS.

$$\Delta H = -R\ln\left(\frac{b_2}{b_1}\right)\left(\frac{T_1T_2}{T_1-T_2}\right) \quad (7)$$

$$\Delta G = -R.T.\mathrm{Ln}(Kc) \quad (8)$$

$$\mathrm{Ln}(Kc) = \frac{\Delta S}{R} - \frac{\Delta H}{R.T} \quad (9)$$

The results of kinetic studies of nitrate adsorption are represented in Table 13.

Conclusion

In the present study, CNT and synthesis La/CNTs as adsorbents for nitrate adsorption from aqueous solution were compared and investigated. It was found that synthesis La/CNTs is better adsorbent for nitrate removal. Effective parameters such as pH, contact time, temperature and initial concentration of nitrate were studied and it was observed that Adsorption decreases by increasing the pH and the optimum pH found to be 3 for both adsorbents. Increasing the reaction time would increase the contact time between adsorbents and nitrate ions in aqueous solutions and would increase removal efficiencies, the best contact time (equilibrium time) is 210 min for both adsorbents. Adsorption increases by increasing the initial concentration of nitrate and the optimum concentration found to be 10 ppm. Adsorption was studied in 0, 30 and 60 degree centigrade and 0^0C showed the highest adsorption since the adsorption is exothermic.
Removal capacity of nitrate adsorption were found to be 4.45 mg/f for CNTs and 6.48 mg/g for modified CNTs, respectively. The data were analyzed by the linear Langmuir, Freundlich and Temkin models of adsorption. Equilibrium data fitted well with the Freundlich and Temkin models but it has best fitted with Langmuir model. From kinetic study, it can be seen that enthalpy changes negatively which shows that adsorption is exothermic. Gibbs negative sign shows that the adsorption is spontaneous. Entropy sign is negative, so the adsorption is associated with decreasing disorder.

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Table 1. Levels of the control factors used as preparation parameters.

Investigating parameters	Level 1	Level 2	Level 3
pH	3	7	11
T	0	30	60
C_o	10	25	40
t	30	120	210

Table 2. L9 orthogonal arrays

run	pH	T	C_o	t
1	3	0	10	30
2	3	30	25	120
3	3	60	40	210
4	7	0	25	210
5	7	30	40	30
6	7	60	10	120
7	11	0	40	120
8	11	30	10	210
9	11	60	25	30

Table 3. Results of nitrogen adsorption analysis for the adsorbents

Sample Name	BET Surface Area (m^2/g)	Average Pore Dia. (4V/A) (nm)	Total Pore Vol. (cm^3/g)
CNT	145.17	54.678	1.9844
La/CNT	82.034	50.697	1.0397

Table 4. Weight percentage of adsorbent elements

element	%W (CNTs)	%W(La/CNTs)
C	97.30	59.35
O	2.70	17.35
N	-	10.00
La	-	13.30

Table 5. Nitrate removal percentage and capacity by CNTs

run	pH	T	C_o	t	a	C_e	Re	q_e
1	3	0	10	30	0.137	3.667	63.33	1.27
2	3	30	25	120	0.421	10.430	58.28	2.91
3	3	60	40	210	0.601	17.768	55.58	4.45
4	7	0	25	210	0.403	9.977	60.09	3.00
5	7	30	40	30	0.706	20.852	47.87	3.83
6	7	60	10	120	0.159	4.254	57.45	1.15
7	11	0	40	120	0.646	19.082	52.29	4.18
8	11	30	10	210	0.141	3.777	62.23	1.24
9	11	60	25	30	0.506	12.527	49.89	2.49

Table 6. Nitrate removal percentage and capacity by La/CNTs

run	pH	T	C_o	t	a	C_e	Re	q
1	3	0	10	30	0.041	1.099	89.01	1.78
2	3	30	25	120	0.23	5.693	77.23	3.86
3	3	60	40	210	0.364	10.753	73.12	5.85
4	7	0	25	210	0.137	3.391	86.44	4.32
5	7	30	40	30	0.428	12.644	68.39	5.47
6	7	60	10	120	0.109	2.922	70.78	1.42
7	11	0	40	120	0.256	7.562	81.09	6.49
8	11	30	10	210	0.077	2.064	79.36	1.59
9	11	60	25	30	0.362	8.960	64.16	3.21

Table 7. Removal percentage and capacity comparison of CNTs and La/CNTs

run	pH	T	C_o	t	Re (CNTs)	Re (La/CNTs)	Re Enhancement
1	3	0	10	30	63.33	89.01	28.85

2	3	30	25	120	58.28	77.23	24.54
3	3	60	40	210	55.58	73.12	23.99
4	7	0	25	210	60.09	86.44	30.48
5	7	30	40	30	47.87	68.39	30.01
6	7	60	10	120	57.45	70.78	18.83
7	11	0	40	120	52.29	81.09	35.51
8	11	30	10	210	62.23	79.36	21.59
9	11	60	25	30	49.89	64.16	22.24

Table 8. ANOVA-nitrate adsorption on CNTs

Col # / Factor	DOF (f)	Sum of Sqrs. (S)	Variance (V)	F - Ratio (F)	Pure Sum (S')	Percent P(%)
1 pH	2	33.678	16.839	-----	33.678	14.458
2 T	2	27.455	13.727	-----	27.455	11.786
3 C	2	124.215	62.107	-----	124.215	53.326
4 t	2	47.578	23.789	-----	47.578	20.425
Other/Error	0					
Total:	8	232.933				100.00%

Table 9. ANOVA-nitrate adsorption on modified CNTs

Col # / Factor	DOF (f)	Sum of Sqrs. (S)	Variance (V)	F - Ratio (F)	Pure Sum (S')	Percent P(%)
1 pH	2	45.294	22.647	-----	45.294	8.278
2 T	2	403.624	201.812	-----	403.624	73.768
3 C	2	47.713	23.856	-----	47.713	8.72
4 t	2	50.515	25.257	-----	50.515	9.232
Other/Error	0					
Total:	8	547.147				100.00%

Table 10. Optimum conditions of nitrate adsorption on adsorbents

adsorbent	pH	T	C_0	t	a	C_e	Re	Q
CNT	3	0	10	210	0.021	0.56	94.37	1.89
La/CNT	3	0	10	210	0.130	3.48	65.15	1.30

Table 11. Correlation coefficients (R2) obtained from Langmuir, Freundlich and Temkin isotherms for CNTs

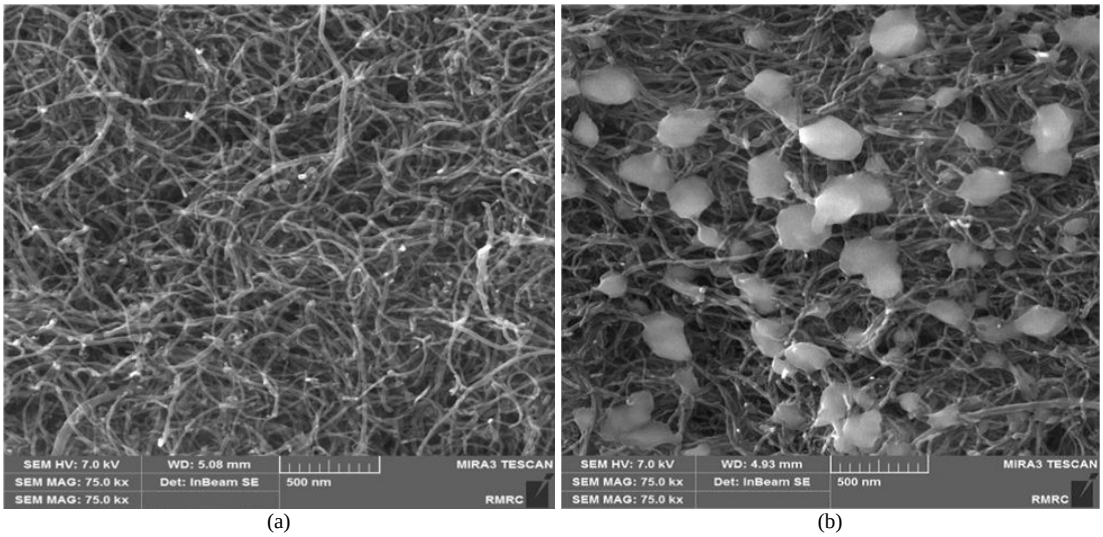
Temperature	R^2 Langmuir	R^2 Freundlich	R^2 Temkin
0	0.9977	0.9834	0.9998
30	0.9950	0.9680	0.9968
60	0.9789	0.9594	0.8540
Mean	0.9904	0.9703	0.9502

Table 12. Correlation coefficients (R2) obtained from Langmuir, Freundlich and Temkin isotherms for La/CNTs

Temperature	R^2 Langmuir	R^2 Freundlich	R^2 Temkin
0	0.9996	0.9869	0.9973
30	0.9951	0.9568	0.9992
60	0.9646	0.9094	0.7665
Mean	0.9864	0.9550	0.9210

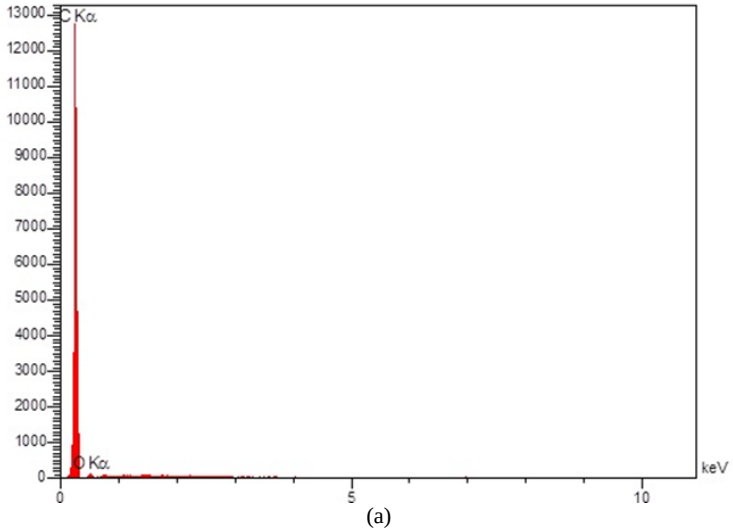
Table 13. Kinetic data

	T (℃)	T (K)	ΔH ($cal.mol^{-1}$)	ΔG ($cal.mol^{-1}$)	ΔS ($ca.lmol^{-1}.K^{-1}$)
CNTs	0	273.15	-1433	-189.4833	-4.5516
	30	303.15	-1433	-150.1831	-4.2308
	60	333.15	-1433	-144.7505	-3.9562
La/CNTs	0	273.15	-6183	-986.8733	-19.0590
	30	303.15	-6183	-670.5300	-18.1834
	60	333.15	-6183	-544.4472	-16.9245

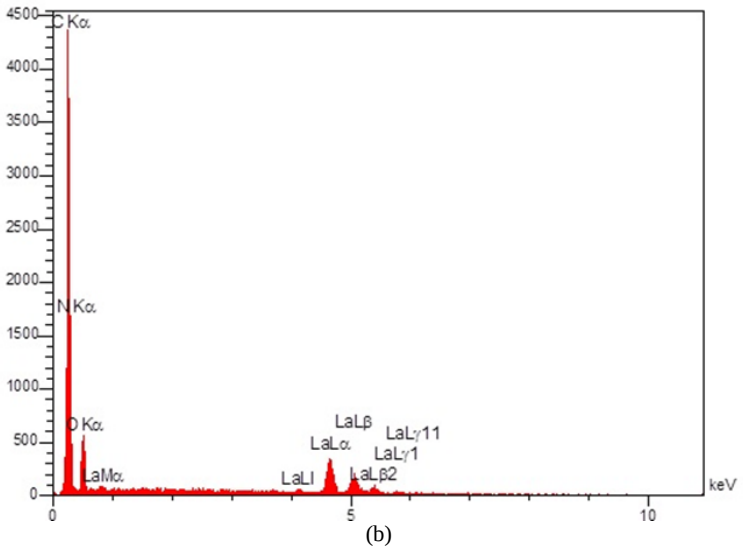


(a) (b)

Fig. 1. Scanning electron microscope images of (a) CNTs, (b) La/CNTs



(a)



(b)

Fig. 2. FT-IR of (a) CNTs carbon and (b) La/CNTs

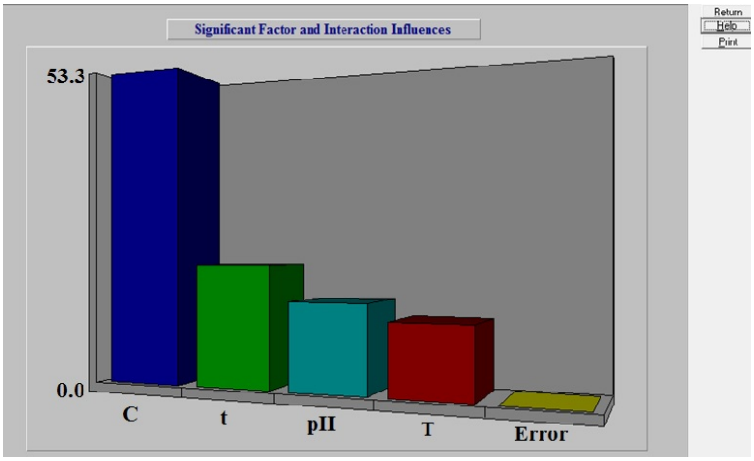


Fig. 3. significant factor and interaction influences for nitrate adsorption on CNTs

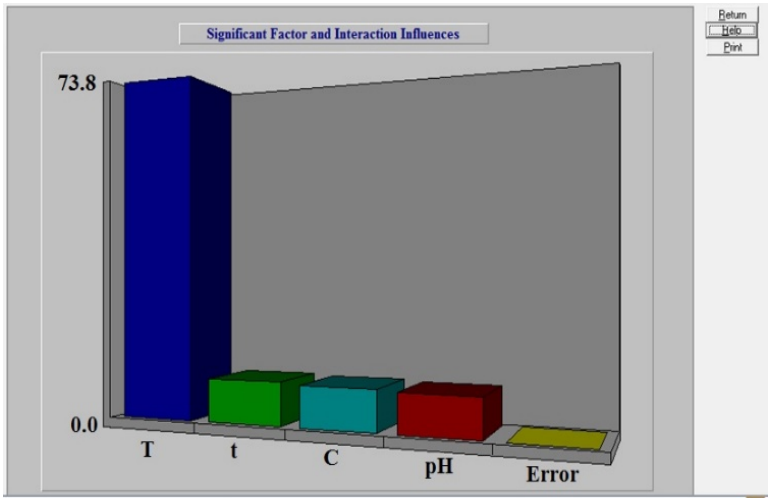


Fig. 4. significant factor and interaction influences for nitrate adsorption on modified CNTs