Artículo de investigación

Investigation of cod removal efficiency from wastewater of a refinery using carbon nanotubes

Investigación de la eficiencia de eliminación de bacalao de las aguas residuales de una refinería utilizando nanotubos de carbono

Investigação da eficiência de remoção de bacalhau de águas residuárias de uma refinaria usando nanotubos de carbono

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Abstract

Refineries are considered as one of the water consumers, and a significant amount of wastewater is produced at various stages of the process. The aim of this study was to determine the efficiency of carbon nanotubes in removal of organic matter in the refinery effluent. The experiments were performed discontinuously with changes in effective factors such as pH, organic matter concentration, nanotube content and process time. The purpose of this study was to determine the effect of effective parameters on the performance of nanotubes it is a carbon at removing organic matter from the wastewater. The results of the experiments and measurements indicated that the concentration of organic matter, pH, and the amount of carbon nanotubes increased and or the reduction of each one leads to a change in its efficiency and performance. The results of this study showed that the highest amount of organic matter removal from wastewater using carbon nanotubes was 89.87%. The results showed that optimum pH for testing was 5.5. The data provided by the central composition design method could well satisfy the test data.

Keywords: refinery, refinery effluent, cod, response procedure, carbon nanotubes.

Resumen

Las refinerías se consideran como uno de los principales consumidores de agua y productora significativa de aguas residuales en varias etapas del proceso. El objetivo de este estudio fue determinar la eficiencia de los nanotubos de carbono en la eliminación de la materia orgánica en el efluente de la refinería. Los experimentos se realizaron de forma discontinua con cambios en factores efectivos como el pH, la concentración de materia orgánica, el contenido de nanotubos y el tiempo de proceso. El propósito de este estudio fue determinar el efecto de los parámetros efectivos sobre el rendimiento de los nanotubos: es un carbono que elimina la materia orgánica del agua residual. Los resultados de los experimentos y las mediciones indicaron que la concentración de materia orgánica, el pH y la cantidad de nanotubos de carbono aumentaron o que la reducción de cada uno ocasionó un cambio en su eficiencia y rendimiento. Los resultados de este estudio mostraron que la mayor cantidad de remoción de materia orgánica del agua residual usando nanotubos de carbono fue de 89.87%. Los resultados mostraron que el pH óptimo para la prueba fue 5.5. Los datos proporcionados por el método de diseño de composición central bien podrían satisfacer los datos de prueba.

Palabras clave: refinería, efluente de refinería, bacalao, procedimiento de respuesta, nanotubos de carbono.

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Resumo

Refinarias são consideradas como um dos consumidores de água, e uma quantidade significativa de águas residuais é produzida em várias fases do processo. O objetivo deste estudo foi determinar a eficiência dos nanotubos de carbono na remoção de matéria orgânica no efluente da refinaria. Os experimentos foram realizados de forma descontínua com alterações em fatores efetivos como pH, concentração de matéria orgânica, teor de nanotubos e tempo de processo. O objetivo deste estudo foi determinar o efeito de parâmetros efetivos sobre o desempenho de nanotubos é um carbono na remoção de matéria orgânica da água residuária. Os resultados dos experimentos e medições indicaram que a concentração de matéria orgânica, pH e a quantidade de nanotubos de carbono aumentaram e ou a redução de cada um leva a uma mudança em sua eficiência e desempenho. Os resultados deste estudo mostraram que a maior quantidade de remoção de matéria orgânica do efluente utilizando nanotubos de carbono foi de 89,87%. Os resultados mostraram que o pH ótimo para o teste foi de 5,5. Os dados fornecidos pelo método de design da composição central podem muito bem satisfazer os dados do teste.

Palavras-chave: refinaria, efluente de refinaria, bacalhau, procedimento de resposta, nanotubos de carbono.

Introduction

Water is a mixture that covers three quarters of the Earth's surface and is a condition of life and increasing population and raising the level of culture and life will increase the need of human societies to water every day and human with the advances that have been made through much effort has been trying to provide better life and comfort but with the advent of these industrial, agricultural, medical and even scientific developments, environmental pollution and natural resources have increased and it has become one of the greatest human problems (Kavaz & Oztoprak, 2017, Nzilano, 2017). The increase in population and the expansion of industries on the one hand and the non-observance of environmental criteria, on the other hand, have prevented the spontaneous refinement of nature and there is a kind of mismatch between the spread of pollutants and the nature of water treatment (Ghasemi Z., Younesi H., Zinatizadeh A. 2015).

In the meantime, contamination of limited sources of fresh water is available to living organisms and is exposed to microbial and chemical contamination and solving this problem is very important. Therefore, it is necessary to look for suitable solutions for water treatment from pollutants (Keshtkar Talebizadeh, (2017)).

Refineries are water utilization centers that are often located in the vicinity of large cities and even in Iran and sometimes they are in the cities (Moslehyani, A., Ismail, A. F., Othman, M. H. D., & Matsuura, T. (2015), Laszlo, K. Podkoscielny, P. and Dabrowski, A.2003).

The main criteria for designing wastewater treatment units in refineries are the use of treated wastewater. The refined water in the refineries of the country has three applications: this water is used in cooling towers, either discharged in the river and the sea or used as water for irrigation (Terzyk, A. P. 2003).

Oil and petrochemical industries are one of the most widely used water industries, and wastewater produces high levels of organic pollutants that cannot be purified in common systems. Due to the rapid growth of these industries and the adverse effects of their entry into the environment, it is necessary to use low cost and high efficiency methods. Methods for removing organic pollutants from oil waste in refineries can be divided into physical, biological and chemical methods (Keshtkar Dadkhodazadeh, 2018).

Over the past two decades, extensive attention has been paid to environmental pollution by hazardous organic materials. Some common ways have been developed to remove organic matter from liquid wastewater: chemical deposition, ion exchange, membrane processes, electrochemical purification, and so on. However, these methods have various disadvantages, including the removal of unpredictable organic matter, the need for a large amount of reactants, toxic sludge production, and so on. Surface absorption is a process that represents innovation as well as an economical tool for removing organic matter from aqueous solutions (Kujawski, W. Warszawski, A. Ratajczak, W. Porebski, T. Capała, W. and Ostrowska, I. 2004).

If refinery wastewaters are released in nature, create irreparable environmental effects in nature so eliminating and removal of the toxicity of these materials has created a great challenge for the researchers. Therefore, to achieve this purpose a low-loss, high-efficiency, low-cost method is needed. The process of surface adsorption with carbon nanotubes, in addition to increasing the absorption capacity, reduces the reaction time and thus increases the absorption percent of toxic compounds in the wastewater (Kujawski, W. Warszawski, A. Ratajczak, W. Porebski, T. Capała, W. and Ostrowska, I. 2004).

The various industries produce wastewater that contain toxic aromatics and high organic load, these pollutants can pollute the environment, therefore, the treatment of these wastewater is a major problem for these industries and the release of them without a treatment is a serious threat to the environment (Gunasekara, A. S. Donovan, J. A. and Xing, B. 2000).

The wastewater in industries such as oil, petrochemicals, coal, textiles, pharmaceuticals and food, COD has high color and has to be refined. Three commonly used methods for wastewater treatment are: physical, chemical and biological methods. Most organic aromatic compounds are resistant to biological degradation, and physical and chemical processes such as chemical deposition, coagulation and electrocoagulation, only the pollutant is transferred from wastewater to another, and secondary waste is produced which requires further treatment (Jing, J. Li, J. Feng, J. Li, W. and Yu, W. W. 2013).

Progress in science and engineering at the nanoscale shows that many of the current problems related to water quality can be addressed or largely by the use of nanoscale absorbent materials, nanocrystals, bioactive nanoparticles, nanocatalysts and advanced nanoparticles will be improved among other products and processes that result from nanotechnology development. Innovation in the development of new technologies for sweetening water is one of these achievements. In addition, nano-manufactured products reduce concentrations of toxic compounds to less than one part in a billion in water; therefore, this technology is used to meet the standards used by water and sanitation consultants. Healthy water is essential for human health and is also a vital raw material in many key industries such as electronics, medicine and food. The world faces many challenges in increasing the demand for clean water as fresh water resources, which is declining due to the following: (A) spread of drought, (B) increase population growth, (C) intensifying and improving health regulations and finally (d) increasing water use growth. Nanomaterials have several key physico-chemical properties which makes them particularly attractive as separating filters for water purification. They have a much wider range of mass particles. Nanomaterials can also be combined with different chemical groups to increase the desire for a specific compound (Keshtkar 2018, J. B. 2001, Amosa, K., Jami, S. Maan, F. R. Dzun, N. and Suleyman, A. Muyibi. 2015).

They can also be used as high selectivity ligands, high capacity and recyclable materials for toxic metal ions, radionuclides, organic and mineral anions and salts are used as nano materials in aqueous solutions also offer unparalleled opportunities for the development of Redox's active catalysts and filters for more efficient water treatment, because it has more surface areas, size, optical, electrical properties and shape- dependent catalytic. Nanomaterials are used as chlorine-free materials by combining with chemical groups that are selectively key biochemical compounds; they target bacteria and viruses in the water. It is believed that the further improvements in the production of nano-materials are more cost-effective and more environmentally friendly; these nanomaterials can be used as key components of industrial and public water treatment systems (Keshtkar, 2017)).

Today, surface absorption is recognized as an effective and economical way to treat wastewater from aromatic substances. The absorption process is flexible in design and operation and in many cases produces a high quality refined output stream. Additionally, since surface absorption is sometimes reversible, adsorbents can be reconstructed using appropriate regeneration processes. The most important adsorbent in this field are activated carbon and carbon nanotubes. Activated carbon adsorbents are widely used to remove aromatic substances contaminants. The reason for their good performance in this field is due to the high volume of micro holes and meso holes in them and its high level (Mohd Hafizuddin, M. Siti Rozaimah, Sh. Abu Bakar, M. Rakmi, A. 2013).

Carbon nanotubes have also recently been used in this field. Carbon nanotubes were first discovered by Lijima in 1991. These relatively new adsorbents have great potential to absorb aromatics. Carbon nanotubes are divided into two types: 1) single-wall carbon nanotubes and 2) multi-wall carbon nanotubes. The mechanisms by which metal ions absorb carbon nanotubes are very complicated and it seems to be associated with processes such as electrostatic gravity, sediment absorption, and chemical interaction between metal ions and functional groups on the surface of nanotubes (Mohan D, Singh KP. 2002). Therefore, the purpose of this study was to evaluate the adsorption process of COD in wastewater using carbon nanotubes and compare the effect of different operating parameters on the absorption rate of refinery wastewater COD. In this research, process modeling is done in terms of COD absorption rate using the response procedure.

Experimental Section

Materials and equipment

The wastewater used in this paper is the actual wastewater from the Tabriz refinery. Table 1 shows the sample of wastewater from Tabriz refinery.

Table 1: Properties of wastewater sample without treat of Tabriz refinery

value	parameter
622	COD (mg/L)
204	BOD (mg/L)
56	TSS (mg/L)
44	VSS (mg/L)
25.3	$N-NH_3$ (mg/L)
7.9	pH
2.3	DO

In this experimental study the multi-wall carbon nanotubes (MWCNTs) were used as adsorbent. The purchased nanotubes from the research institute of the oil industry have the following characteristics: length 10µm, internal and outer diameter was 3.8 nm and 10-10 nm respectively, and purity was 95%. These nanotubes have been produced by a chemical vapor deposition (CVD) method. Acetic acid and sodium hydroxide was purchased for pH adjustment with a specific purity from the Merck of Germany Company. The UV-Vis spectrophotometer (DR 5000 model of HACH Company) was used to determine the amount of COD of the treated wastewater at maximum wavelength (600 nm).

Method

Method of testing

A 100 mL Erlen glass was used for testing, which 0.1 g of nanotube carbon was poured into it and 100 mL of wastewater added to it. Figure 1 shows the pilot general schema.

Figure 1: Pilot general schema

The initial concentration of wastewater (C0) was 400 mg/L at minimum concentrations of these compounds in the medium. The Erlen glass was placed on an orbital shaker (Model OS 625) and was stirred at a temperature of 25° C for mixing rate 240 rp 60° C for 60 minutes. All tests were repeated 1 time. In addition to the samples, a control sample was added to which no adsorbent was added to ensure that the reduction of wastewater COD in the solution was due solely to the absorption of carbon nanotubes and has not diminished due to absorption into the Erlen glass or through the evaporation of its concentration. The samples were then passed through a 0.45 micron fiberglass filter and its COD was measured by a spectrophotometer apparatus at a wavelength of 600 nm according to the standard method (closed reflux). The pH of the solution was recorded before and after contact with carbon nanotubes. The pH was adjusted with acetic acid 0.05 mole and sodium hydroxide 0.05 molar in neutral. Equation (1) was used to calculate the absorbed COD yield (R%) on carbon nanotubes.

$$\frac{\partial^2 T}{\partial x^2}+\frac{\partial^2 T}{\partial y^2}+\frac{\partial^2 T}{\partial z^2}+\frac{\dot{q}}{k}=\frac{\rho C_p}{k}\frac{\partial T}{\partial t}$$

(1)

$$\%R=\frac{C_0-C_t}{C_0}\times 100$$

(1)

In this equation, C0 and Ct are the initial COD concentrations and after contact with carbon nanotubes are in mg/L.

Absorbance correction method

In this study, hydrogen peroxide was used to modify carbon nanotubes, which are fully described below:

Correction method: Inside a human, 1000 ml, 10 g of carbon nanotubes and 990 g of hydrogen peroxide (10 g/LH2O2) were placed on the stirrer to mix for 2 minutes. After mixing the sample, the microwave was placed for 10 minutes (900 watts). It was then placed in an oven at 40° C for 48 hours.

Data analysis

To analyze the data and compare the results of carbon nanotubes in COD removal, the DOE Design of Experiment software was used. In this study, Response Surface Method (RSM) method was used. Design of experiment involves making targeted changes in the input characteristics or factors of a process to see changes to the output or response characteristic; in other words, knowledge is one that can help to measure the effectiveness of each of the effective factors (X1, X2, X3, ...) on the output characteristics (Y3, Y2, Y1, ...) in the form of an equation Yi = F (Xi) and also one of the most reliable statistical methods is to improve the target function (in this paper, the purification efficiency). Some objectives of the design of experiment are (Montagomery, D. C. 2001):

- Reduce the number of experiments,
- Reduce time,
- Reduce costs,
- Identify important variables,
- Determine optimum conditions.

Given to the above, the reasons for using the design of the experiment in this research can be, preventing the deviation in the target, reducing errors, taking into account the combined effect of operational parameters, more detailed analyzes and statistical descriptions of the results. Since the main purpose of the research is to examine the individual and interactive effects of the operating parameters on the output, so it is preferable, it is a methodology that takes into account maximum testing, the minimum error is created and the response procedure method is the best choice to achieve this goal (Pacheco et al., 2017). Based on the above, the purpose of the design of the experiment in this research is determining the relationship between the effective parameters and the responses obtained from the experiments, which can be expressed in equation (2).

Responses (COD Abs.%) = F (Time, $(CNT)_{\circ}$, pH, $(COD)_{\circ}$)

(2)

The number of experiments will vary according to the number of parameters. In order to evaluate the effect of operational parameters on the process of removal of wastewater COD and process modeling, four main factors including initial COD (mg/L), the amount of carbon nanotubes (g), pH and process time (min) were investigated. Then Minitab17 software designed the test based on these four factors, and 31 tests were repeated with a repeat program, which included six repetitions at the central point. The range of parameters and levels used in Table 2 is given .

Table 2: The range of parameters and levels of experimental variables for eliminating COD (2 = α)

variables	range and levels				
	2+	**1+**	**0**	**1-**	**2-**
$(COD)_{\circ}$ (mg/L) (X_1)	**800**	**700**	**600**	**500**	**400**
$(CNT)_{\circ}$ (g) (X_2)	**0.5**	**0.4**	**0.3**	**0.2**	**0.1**
pH (X_3)	**11**	**9**	**7**	**5**	**3**
Time(min) (X_4)	**90**	**70**	**50**	**30**	**10**

The quadratic equation of the following polynomials (3) was used for the relationship between dependent and non-dependent variables (16):

$$Y=\beta_{\circ}+\sum_{i=1}^{k}\beta_i X_i+\sum_{i=1}^{k}\beta_{ii}X_i^2+\sum_{1\le i\le j}^{k}\beta_{ij}X_iX_j \quad (3)$$

Where Y is the response variable (eliminating efficiency), Xi and Xj are the experimental levels of the variables, βi is the correlation coefficient of the linear factors, βii is the coefficient of correlation of quadratic factors, βij is the mutual correlation coefficient i and j, and k is the number of variables.

RESULTS AND DISCUSSION

The function of adsorbents

Table 3 shows the percentage of COD adsorption by crude and modified carbon nanotubes for the initial COD of 400 mg/L, concentration of adsorbent 0.5 g, the contact time is 90 minutes and the mixing rate is 240 rpm.

Table 3: Removal of COD by crude and modified carbon nanotube

Absorbent	COD Wastewater		
	(COD_0) (mg/L)	Secondary concentration (CODt) (mg / L)	Percentage of absorption (%)
Crude Carbon Nanotubes	0.1±400	0.2±239	40.25
Modified carbon nanotube	0.1±400	0.3±94	76.5

In order to investigate the efficiency of modified carbon nanotube by hydrogen peroxide in adsorption of COD wastewater, a certain amount of adsorbents in solution was added with a certain concentration of wastewater and was sampled at different times in the stirrer.

Figure 4-5 shows the performance results of modified carbon nanotube powder and crude carbon nanotubes as a percentage of COD absorption at different times.

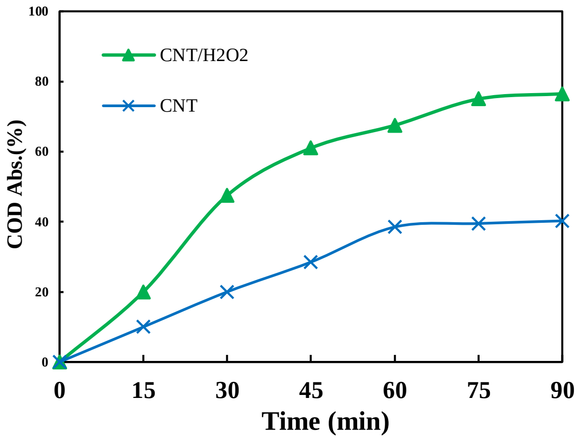

Figure 2: Percentage of absorption of COD wastewater using adsorbent

Regarding the high efficiency of carbon nanotubes modified by hydrogen peroxide, COD adsorption experiments were continued using this adsorbent.

Experimental design results to investigate the absorption of COD using modified carbon nanotubes

In this section, the absorption efficiency of COD as a response was introduced into the calculations. Then, using the process presented in the previous section, the results were analyzed. Table 4 shows the experimental results of the model design for COD absorption using carbon nanotube modified with hydrogen peroxide.

Table 4: Experimental results of COD absorption experiment design using CNT/H^2O^2

Percentage of absorption		Time (min)	pH	$(CNT)_o$ (g)	$(COD)_o$ (mg/L)	No
Model	Experimental					
39.52	38.69	30	5	0.2	500	1
17.23	18.20	30	5	0.2	700	2
62.58	59.24	30	5	0.4	500	3
37.50	40.18	30	5	0.4	700	4
20.02	18.18	30	9	0.2	500	5
1.99	3.47	30	9	0.2	700	6
37.99	35.21	30	9	0.4	500	7
17.18	13.54	30	9	0.4	700	8
58.49	61.26	70	5	0.2	500	9
36.40	38.27	70	5	0.2	700	10
78.06	75.67	70	5	0.4	500	11
53.18	54.15	70	5	0.4	700	12
41.48	37.89	70	9	0.2	500	13
23.66	26.14	70	9	0.2	700	14
55.97	54.14	70	9	0.4	500	15
35.36	35.28	70	9	0.4	700	16
64.44	70.47	50	7	0.3	400	17
21.54	17.29	50	7	0.3	800	18
27.10	24.56	50	7	0.1	600	19
61.85	66.17	50	7	0.5	600	20
37.45	35.21	50	3	0.3	600	21
0.12	4.14	50	11	0.3	600	22
29.34	32.11	10	7	0.3	600	23
66.48	65.49	90	7	0.3	600	24
52.50	52.58	50	7	0.3	600	25
52.50	52.47	50	7	0.3	600	26
52.50	52.59	50	7	0.3	600	27
52.50	52.31	50	7	0.3	600	28
52.50	51.89	50	7	0.3	600	29
52.50	53.21	50	7	0.3	600	30
52.50	52.47	50	7	0.3	600	31

In order to evaluate the validity of the model and the studies, the residual values (the difference between the experimental responses and the predicted responses) were calculated. In Fig. 3, the normal distribution curve and residual values are shown. As can be seen, the linearity of the normal distribution curve (frequency values by percentage) and the possibility of the distribution of residual values in terms of predicted absorption efficiency indicate that the model is suitable.

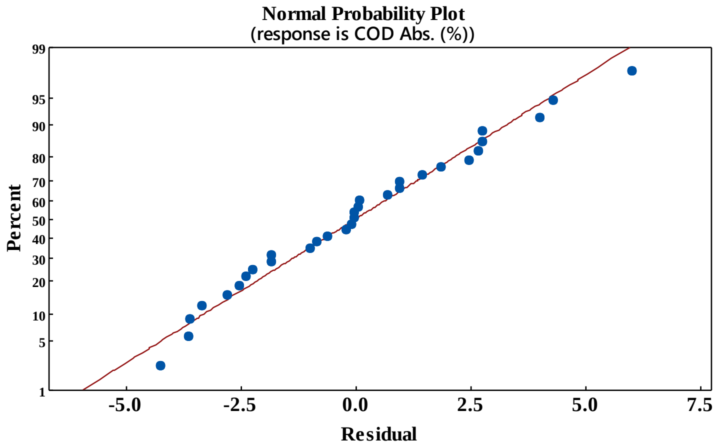

Figure 3: Normal Distribution Curve and Residual for COD absorption using CNT/H^2O^2

According to the results, it can be concluded that the resulting model can model the experimental results with acceptable accuracy and to predict the output variable in other circumstances. In this section, all experiments were performed with one repeat; then the results were analyzed in Table 5.

The polynomial quadratic equation (Equation 4) shows the relation between dependent and independent variables for the COD absorption percentage:

$$\text{COD Abs. (\%)} = -117.7 + 0.1605\,(COD)_o\,(mg/L) + 315.5\,(CNTs)_o\,(g) + 22.76\,pH + 0.757\,Time\,(min) - 0.000238\,(COD)_o{*}(COD)_o - 200.7\,(CNTs)_o{*}(CNTs)_o - 2.107\,pH{*}pH - 0.00287\,Time{*}Time - 0.0698\,(COD)_o{*}(CNTs)_o + 0.00533\,(COD)_o{*}pH + 0.000025\,(COD)_o{*}Time - 6.35\,(CNTs)_o{*}pH - 0.436\,(CNTs)_o{*}Time + 0.0156\,pH{*}Time \qquad (4)$$

Figure 4 also shows the effect of the main parameters on the COD absorption percentage.

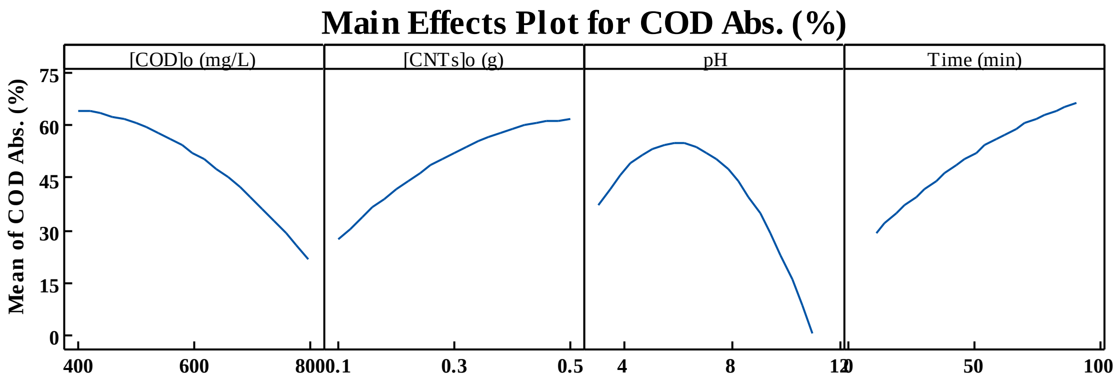

Figure 4: Main effects curve for COD absorption percentage

To form the table for analysis of variance, the relationships in the previous section were used to calculate the degree of freedom, sum of squares, mean squared, and value of F of each effect. The calculations performed for the percentage of COD absorption in Table 5 are presented.

Using the calculations, the table for analysis of variance can be made according to Table 5.

Table 5: Analysis of variance for COD absorption percentage for CNT/H^2O^2

Source of variability	Degrees of freedom	sum of squares	average of squares	F value	P value
(COD)o (mg/L)	1	2760.8	2760.83	224.23	0.000
(CNT/H2O2)o (g)	1	1811.9	1811.87	147.15	0.000
pH	1	2089.7	2089.73	169.72	0.000
Time(min)	1	2069.3	2069.26	168.06	0.000
(COD)o*(CNT/H2O2)o	1	7.8	7.8	0.63	0.438
(COD)o*pH	1	18.2	18.21	1.48	0.242
(COD)o*Time	1	0	0.04	0.0	0.955
(CNT/H2O2)o*pH	1	25.8	25.83	1.2	0.167
(CNT/H2O2)o*Time	1	12.2	12.16	0.99	0.335
pH*Time	1	6.3	6.26	0.51	0.486
Error	16	197	12.31		
Total	30	11121.8			
Summary					R^2 =98.23

According to Table 5, the following results and analyzes can be obtained:

Regarding the values of P and F, in the analysis of variance, the most effective parameters on the COD absorption rate are respectively:

- Primary COD
- pH
- reaction time
- The amount of modified carbon nanotube

Figure 5 shows two-dimensional and three-dimensional graphs showing the COD absorption efficiency as a function of the initial COD and the amount of carbon nanotube in a value of pH =7 and a duration of 50 minutes. The initial concentration of benzene is one of the most effective parameters in the efficiency of the absorption process.

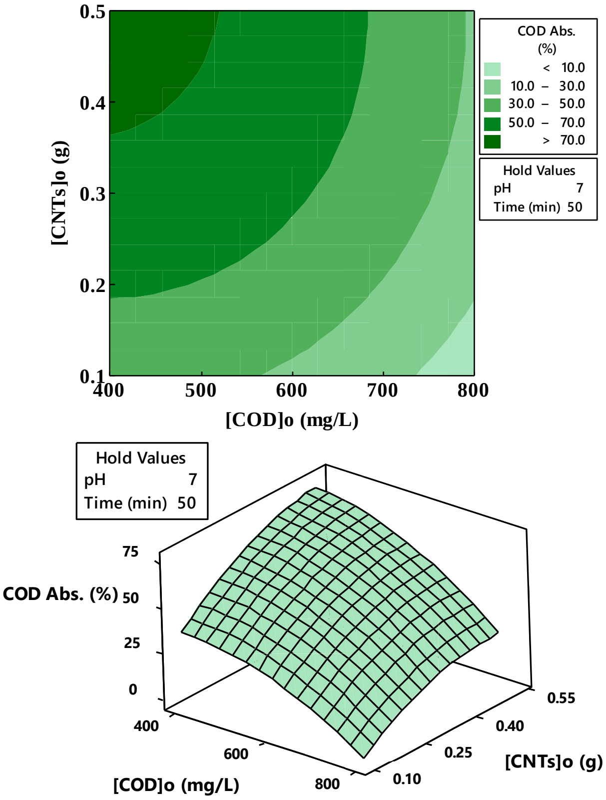

Figure 5: Two-dimensional and three-dimensional COD absorption efficiency (%) in terms of COD and time

As can be seen, with increasing COD, decreases the absorption efficiency. Under constant operating conditions, there is a certain amount of carbon nanotubes that are responsible for the absorption of wastewater, while increases the COD value. Consequently, the amount of hydrolysis will not be sufficient to absorb high concentrations of wastewater and reduce the absorption efficiency. Due to the constant amount of adsorbent, by increasing COD, there will be sufficient available adsorption sites for COD but with increasing COD, adsorption sites will be saturated with adsorbent and adsorption percentage decreased.

The amount of nanotube carbon is one of the most effective parameters in the efficiency of the adsorption process. These figures show that with increasing carbon nanotube up to about 0.5 grams increases the COD absorption efficiency. Increasing the COD adsorption efficiency by increasing the amount of adsorbent due to the surface area of the contact and thus increase the available positions (Antón Chávez, 2017).

Also, increasing the COD adsorption efficiency by increasing the amount of carbon nanotubes can be attributed to the higher hydrolysis of organic matter inside the carbon nanotube (Ernst, M. Lurot, F. Schrotter, J. 2004, Qu, Y., Ma, Q., Deng, J., Shen, W., Zhang, X., He, Z., ... & Zhou, J. (2015).).

Figure 6 shows two-dimensional and three-dimensional graphs of COD absorption efficiency as a function of pH and process time for COD, 600 mg / L, and carbon nanotube value of 0.3 g.

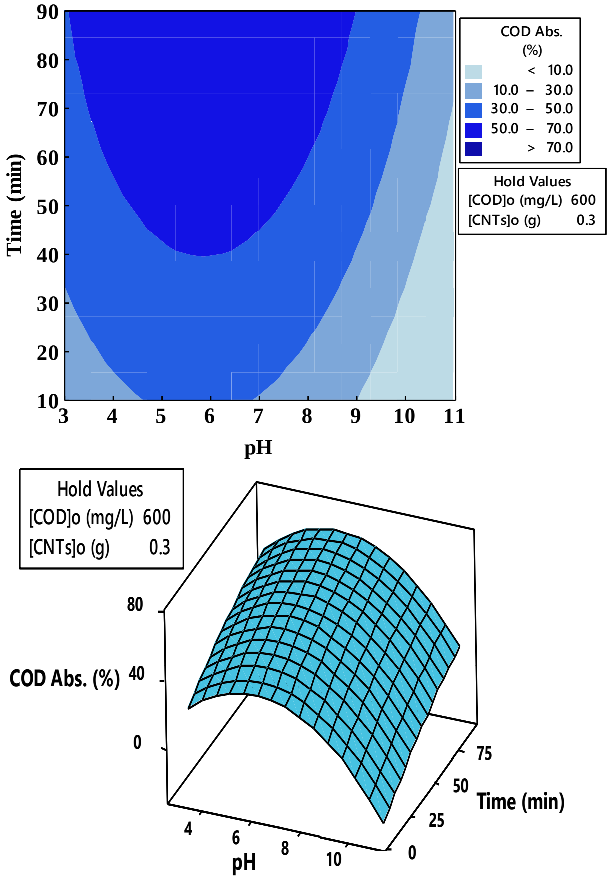

Figure 6: Two-dimensional and three-dimensional graphs of COD absorption efficiency (%) in terms of pH and time

As can be seen, with increasing pH, an optimal amount increases the absorption efficiency. The absorption efficiency increases in accordance with the figure at low pHs. The pH of the solution can affect the absorbent surface load, the degree of ionization of various pollutants, the separation of functional groups on active adsorbent sites, and the structure of organic wastewater. In fact, the pH of the solution affects the chemistry of the aqueous medium and adsorption surface bonds. Therefore, the solution pH is an important parameter during the absorption process.

The reason for increasing the efficiency of COD adsorption in low pH is that, according to Zeta's potential results, the level of adsorbent is positive. Because the organic matter contained in the refinery wastewater is an anionic substance, electrostatic gravity at lower pHs causes increased absorption efficiency. On the other hand, in alkaline pHs, due to the adhesion of hydroxyl groups in a superficial loaded environment, negative and thus the range between the negative charge of organic matter and the negative charge load absorption percentage is reduced (Shahrezaei, F., Pakravan, P., Azandaryani, A. H., Pirsaheb, M., & Mansouri, A. M. (2016).). Figure 7 also shows the optimal area diagram for performing a better COD absorption process.

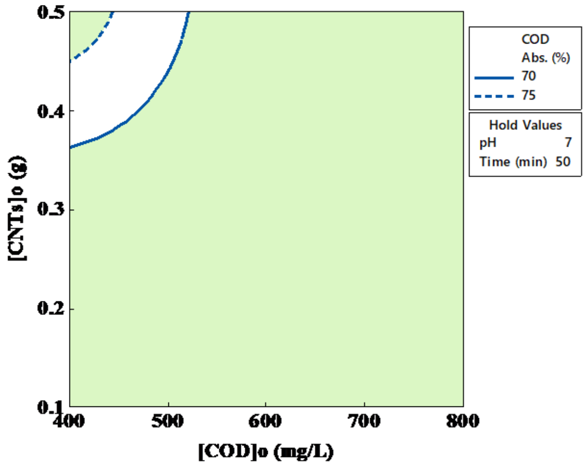

Figure 7: Optimal area curves for COD absorption percentage

The optimal mode of absorption of wastewater is to reach the maximum efficiency. Therefore, by using the Minitab17 software, the optimum test conditions were determined, as shown in Table 6. After obtaining optimum conditions, an experiment was conducted on actual wastewater in these conditions and the test result showed that there is a good match between the experimental value and the predicted value of the model. This shows the success of using the response procedure in modeling and optimizing the absorption process.

Table 6: Optimum conditions of operating parameters for synthetic wastewater absorption efficiency

variable	Percentage of absorption
$(COD)_o$ (mg/L) (X_1)	**400**
$(CNT/H_2O_2)_o$ (g) (X_2)	**0.5**
pH (X_3)	**5.5**
Time (min) (X_4)	**90**
Estimated absorption efficiency (%)	**91.69**
Experimental absorption efficiency in these conditions (%)	**89.87**

Conclusion

In this paper, the results of analyzes have been summarized and presented.

- The results of the evaluation of the carbon nanotube correction method show that the modified methods with hydrogen peroxide have a favorable absorption rate compared to the unmodified state.
- The results of COD percentage of absorption on hydrogen peroxide modified carbon nanotubes showed that the highest adsorption percentages occur in neutral pH, high adsorbent and high contact time and low COD.
- The results of the COD absorption modeling on carbon nanotube using the Minitab software show that this model is in good agreement with empirical absorbent data.
- The results of the experimental design showed that COD, pH and process time have the most effect on the amount of absorption.
- As it was observed, COD absorption percentage of refinery wastewater in optimal conditions was about 89.87%.

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