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# Treatment of TNT red water by chemical-modified carbon adsorbent prepared from cheap raw materials of pine tree wood

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## ABSTRACT

This work reports the treatment of trinitrotoluene (TNT) red water by chemical-modified carbon adsorbent. The pine wood was used for preparation of carbon particles. The chemical modification by solutions of $HNO_3$, $ZnCl_2$, and NaOH was made for activation of carbon adsorbent. The activated carbon particles were characterized by X-ray diffraction (XRD) pattern, FT-IR spectra, scanning electron microscope (SEM) images, BET, and CHNS analyses. The formation of amorphous carbon was confirmed by XRD pattern. The variation of pores of carbon particles before and after the treatment of TNT red water was seen from SEM images. The area and pores volume of activated carbon were obtained 197–211 $m^2/g$ and 0.149–0.157 $cm^3/g$, respectively. The considerable decrease of chemical oxygen demand amount was obtained after the treatment of TNT red water samples with activated carbon by $HNO_3$ solution. Treatment experiments were carried out using batch method. The treatment efficiency of 90% was obtained in optimized parameters of pH value of 3, adsorbent dose of 40 g/L, and contact time of 300 min. Adsorption process followed the pseudo-second-order kinetic model. Thermodynamic studies revealed that the adsorption process is spontaneous ($-\Delta G = 10.4$–$12.5$ kJ/mol) and endothermic ($\Delta H = 10.7$ kJ/mol) at temperature range of 25–55˚C. The sorption isotherm was in good agreement with the Freundlich isotherm for TNT red water diluted in range of 100–500 times. Desorption process using sodium hydroxide and boiling water for reuse of the adsorbent were studied and the removal efficiency of 48–72% was obtained in three times of reuse of carbon adsorbent.

*Keywords:* Activated carbon; TNT red water; Treatment; Sorption isotherms; Pine wood

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## 1. Introduction

Nitroaromatic explosives such as trinitrotoluene (TNT) have been extensively used for both military and civilian purposes for a much long time [1,2]. During the TNT manufacturing process, unsymmetrical TNTs produced from the nitration of toluene must be removed to meet military specifications. In the purification stage, sodium sulfite is added to react with unsymmetrical TNT to produce dinitrotoluene sulfonate (DNTS). The wastewater after the phase separation has a dark red color and is commonly called “TNT red-water” [1,2]. The TNT red water contains incomplete nitration products, such as 2,4-DNT and 2,6-DNT, and complicated toxic byproducts formed

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during the nitration and purification stages. Therefore, TNT red water is a highly hazardous and toxic wastewater. Direct discharge of untreated TNT red water into waterways or soils causes severe water and soil pollution [3,4].

The wastewater treatment method such as oxidation by air has been used for treatment of TNT red water [5]. Incineration was the most widely used process, but the cost of fuel is high and this process usually generates secondary pollution during treatment [6]. The vacuum distillation procedure for the treatment of TNT red water was reported by Zhao et al. [7]. Biological treatment has been widely applied in wastewater treatment such as explosive wastewater. However, biological methods are limited by toxicity top of TNT red water for micro-organisms and high concentrations of organic and inorganic compounds in red water [8]. One way to solve this would be for the TNT red water to undergo a cost-effective preprocess before biological treatment. Adsorption technique is widely used for wastewater treatment due to its versatility and efficiency in separating a wide range of chemical compounds and its easily operational procedure. Activated carbon is one of the main adsorbents that can be used for the treatment of TNT red water [9,10].

The use of activated carbon for treatment of water and wastewater in industrial-scale application has been widely progressed in last years [11,12]. The advantages of activated carbon are high porosity, high adsorption capacity, and high specific area, so that it is a good sorbent for removal of pollutants in wastewater samples [13,14]. However, large-scale use of activated carbon is not economically affordable [15,16]. Therefore, the use of cheap raw materials for the preparation of carbon adsorbent developed in recent years [17,18].

This study presents the preparation of carbon particles from cheap raw materials of pine tree wood. So far, the use of pine tree as an adsorbent for treatment of TNT red water has not been reported. The chemical-modified carbon adsorbent was used for treatment of TNT red water. The activation of carbon particles by NaOH, $ZnCl_2$, and $HNO_3$ and characterization of activated particles as well as the thermodynamic, kinetic, and sorption isotherms of adsorption process were studied in this research.

## 2. Experimental

### 2.1. Materials

All chemicals used in this study were analytical grade reagents with high purity. The pine wood was selected from Esfahan city. It is a soft wood easier to carve. It is cheaper than other woods because of quantity available. The only problem is that it is one of the lowest qualities of wood. The density of it is 350–500 $kg/m^3$. The TNT red water was obtained from the Esfahan Chemical Corporation. Stock solutions and other used solutions were prepared in distilled water.

### 2.2. Characterization of adsorbent

A UV–vis spectrophotometer Carry-100 using a paired 1.0-cm quartz cell was used to record the absorbance spectra and measurement of absorbance in UV–vis domain. The Fourier transform infrared (FT-IR) spectra of activated carbon were obtained on a Nicolet Impact 400D FT-IR spectrophotometer. The powder samples were mixed with KBr (spectroscopic grade) and prepared as disks with diameter of 10 mm and thickness of 1 mm. A diffractometer, Bruker D8ADVANCE Germany, with an anode of Cu ($\lambda$ =1.5406 Å of Cu K$\alpha$) and a filter of Ni was used for record of X-ray diffraction (XRD) pattern. A Philips XL 30 scanning electron microscope (SEM) was employed to examine the surface morphology of the activated carbon before and after adsorption. The surface of activated carbon was estimated by the B.E.T. method and $N_2$ adsorption isotherms. The nitrogen as an adsorption gas at 77 K using a Belsorp Mini Π instrument was used in this study. Samples were out gassed at 300˚C for 4 h prior to surface area measurements. A Metrohm 691 pH meter using a combined glass electrode was used for measurement of the pH of samples.

### 2.3. Activated carbon

Chemical activation [19] by NaOH, $ZnCl_2$, and $HNO_3$ were used to activate the raw material of pine wood. One gram of raw material as wood chips was weighed and was impregnated in 5 mL of activation solution with concentration of 1 mol/L for 1 h at room temperature. The mixture was transferred to a muffle furnace, where carbonization was carried out under an air atmosphere. The furnace was heated at 150˚C, and maintained at this temperature for 60 min in order to allow the free evolution of water. A black solid was obtained after this step. Then, the furnace was heated at 500 and 700˚C for 60 and 30 min., respectively. After cooling to room temperature, the solid was washed with distilled water at 25˚C to remove excess NaOH, $ZnCl_2$, and $HNO_3$. The activated carbon samples were dried at temperature of 100˚C.

For measuring of bulk density (g/ml) of prepared carbon powder, a glass cylinder was filled to a specified volume from activated carbon by $HNO_3$ and dried in an oven at 100℃ for 24 h. The dried carbon in cylinder was then compacted for 2 min.

### 2.4. The $pH_{PZC}$ of activated carbon

For determination of $pH_{PZC}$ (point of zero charge), the pH ($pH_i$) of 11 solutions of NaCl (0.1 mol/L) were adjusted in pH values of 2–12 by addition of solutions of 0.1 mol/L of HCl and/or NaOH. Then, 0.2 g of activated carbon was added to each solution and the obtained suspensions were shaken for 24 h. After the removal of carbon particles, the pH of NaCl solutions ($pH_f$) was determined after 24 h. The $pH_{PZC}$ of activated carbon was found from intersection of curve of $pH_f$ vs. $pH_i$ with the abscissa [20].

### 2.5. Treatment experiments

Batch treatment experiments were conducted using 10–50 g/L of activated carbon as adsorbent in a 100-mL flask containing 25 mL of TNT red water. The flasks were agitated at 150 rpm in a temperature-controlled shaker. The effect of pH of samples on the treatment efficiency was studied in the pH range of 2.0–12.0. The pH was adjusted using 0.1 mol/L NaOH and HCl solutions. For investigating the effect of the dilution ratios of TNT red water on adsorption, TNT red water was diluted from 100 to 500 times. The effect of contact time is studied on the treatment efficiency from 60 to 360 min with time intervals of 60 min for TNT red water samples that diluted 100 times.

The adsorption isotherms were studied using of red water samples diluted from 100 to 500 times. The thermodynamic and kinetic of adsorption process were studied using TNT red water with dilution 100 times. During the experiments, the adsorbent was removed by carefully filtering the supernatant liquids.

For calculation of treatment efficiency, the chemical oxygen demand (COD) of TNT red water was determined before and after adsorption by a colorimetric method. The HACH test vials containing potassium dichromate oxidant, catalyst, masking reagent, and TNT red water were put into digestion unit keeping 120 min at 150℃ [1]. After cooling and cleaning the vials, the COD of TNT red water was tested by measuring of absorbance at a wavelength of 620 nm in the range of 0–1,000 mg/L. The COD adsorption at equilibrium, $q_e$ (mg/g), and (%)COD removal were calculated as follows:

$$q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

$$(\%)\mathrm{COD}_{\mathrm{removal}} = \frac{(C_o - C_e)}{C_o} \times 100 \tag{2}$$

where $C_o$ (mg/L) is the initial COD of TNT red water and $C_e$ is the equilibrium COD of TNT red water, $V$ (L) is the volume of TNT red water, and $W$ (g) is the absorbent weight.

### 2.6. Adsorption isotherms

Langmuir, Freundlich, and Temkin isotherms (Eqs. (3)–(5), respectively) are the most common equations to represent the adsorption equilibrium data [21–23]:

$$C_e/q_e = \frac{1}{(q_{\max} \times b)} + \frac{C_e}{q_{\max}} \tag{3}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

$$q_e = B \ln K_T + B \ln C_e \tag{5}$$

where $C_e$ is the equilibrium concentration of pollutant in solution (mg/L), $q_e$ is the amount of pollutant absorbed by adsorbent at equilibrium (mg/g), $q_{\max}$ and $b$ are the Langmuir constants related to adsorption capacity and the energy of adsorption. A plot of $C_e/q_e$ vs. $C_e$ indicate a straight line with slope and intercept equal to $1/q_{\max}$ and $1/(q_{\max}b)$, respectively. In Eq. (4), $K_F$ (L/g) and $n$ are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. By plotting the $\log q_e$ vs. $\log C_e$, a straight line with slope of $1/n$ and intercept of $\log K_F$ is obtained. The $K_F$ and $n$ values show the adsorption capacity and adsorption effectiveness, respectively. In Eq. (5), $B$ and $K_T$ are constants, $K_T$ is the equilibrium binding constant corresponding to the maximum binding energy, and constant $B$ is related to the heat of adsorption. A plot of $q_e$ vs. $\ln C_e$ enables the determination of the isotherm constants of $K_T$ and $B$ [21–23].

### 2.7. Kinetic and thermodynamic parameters

Kinetic modeling was investigated to study the rate-controlling step in the removal of pollutant from samples by adsorbent. The pseudo-first-order, pseudo-second-order, and intraparticle diffusion equations (Eqs. (6)–(8), respectively) were used for indicate of kinetic rate modeling [24]:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \tag{6}$$

$$t/q_t = \frac{1}{K_2 \times q_e^2} + \frac{1}{q_e}t \tag{7}$$

$$q_t = K_i t^{1/2} \tag{8}$$

where $q_e$ is the amount of pollutant sorbed at equilibrium (mg/g), $q_t$ is the amount of pollutant sorbed at time $t$ (mg/g), $K_1$ is the rate constant of first-order sorption (1/min), $K_2$ (g/mg min) is the rate constant of the pseudo-second-order adsorption, and $K_i$ is the intraparticle rate constant (mg/g min$^{1/2}$).

Thermodynamic parameters such as enthalpy, $\Delta H$, entropy, $\Delta S$, and Gibbs free energy, $\Delta G$, for the sorption of adsorbate on the adsorbent were calculated using Eqs. (9) and (10):

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{9}$$

$$\Delta G = \Delta H - T\Delta S \tag{10}$$

where $R$ is the universal gas constant, 8.314 (J/mol K), $T$ is the adsorption absolute temperature, and $K_d$ (mL/g) is distribution coefficient ($K_d = q_e/C_e$) [25].

### 2.8. Recovery and regeneration of adsorbent

The recovery and reusing of used adsorbent was studied by NaOH 10 w/w% solution and boiling water. After 2 h of exposure, the samples were centrifuged and again adsorbent was washed several times with double-distilled water and dried at 100℃. Treatment experiments of TNT red water with reconstruction absorbent under optimal conditions were investigated.

## 3. Results and discussions

### 3.1. Characterization studies

Prior to carbonization, the raw material is impregnated with certain chemicals for chemical activation. The chemical is typically an acid ($HNO_3$), strong base (NaOH), or a salt ($ZnCl_2$). Then, the raw material is carbonized at lower temperatures (450–900℃). Chemical activation is preferred over physical activation owing to the lower temperatures and shorter time needed for activating material [26]. The first step is to enrich the carbon content and to create an initial porosity and the activation process helps in enhancing the pore structure. Chemical activation improves the pore development in the carbon structure, and because of the effect of chemicals, the yields of carbon are usually high [26]. Chemical agents used are dehydrating agents that influence pyrolytic decomposition and inhibit the formation of tar, thus enhancing yield of carbon and after washing, large amounts of is formed after elimination of chemical from product.

The surface area, pore volume, and average pore diameter of activated carbon were measured by $N_2$ adsorption isotherm. Also, the surface functional groups of activated carbon using different chemical activation were studied by Boehm's titration [27]. The obtained results and the point of zero charge ($pH_{PZC}$) are collected in Table 1. The obtained results show that chemical activation by nitric acid is due to the increase in surface area that is a basic parameter for an adsorbent. Also, the CHNS elemental analysis indicates the weight percent (%w) 37.6, 4.8, 1.1, 0.1, and 56.4% for C, H, N, S, and O elements, respectively, in activated carbon powder. Also, the bulk density of activated carbon powder is obtained 0.35–0.44 g/ml.

The FT-IR spectra of activated carbon by $ZnCl_2$, NaOH, and $HNO_3$ are shown in Fig. 1(a)–(c), respectively. As seen, in all spectrums, the activated carbon shows the absorption peaks of C=O and C=C groups and a broad band located around 3,300–3,600 cm$^{-1}$ that is attributed to the hydroxyl groups or adsorbed water. The bands around 1,612 and 1,730 cm$^{-1}$ are related to stretching vibration of conjugated C=O. For aromatic rings, peaks around 1,400 cm$^{-1}$ are seen in IR spectra. Also, active groups such as C=O and C=C is due to increasing of the intensity of peaks in IR spectrum [28,29].

Fig. 2 shows the typical XRD pattern of the activated carbon nanoparticle. A wide peak around 2$\theta$ of 18–32° indicates the presence of large amounts of amorphous carbon nanoparticles [30]. Broadening of a peak in XRD pattern is dependent on the size of

Table 1
The data of Boehm's titration, $pH_{PZC}$, and $N_2$ adsorption isotherm of activated carbon using chemical activation

| Parameter | $HNO_3$ | $ZnCl_2$ | NaOH |
|---|---|---|---|
| Carboxylic groups (mmol/g) | 0.218 | 0.189 | 0.197 |
| Phenolic groups (mmol/g) | 0.154 | 0.147 | 0.141 |
| Acid groups (mmol/g) | 0.612 | 0.587 | 0.432 |
| Basic groups (mmol/g) | 0.135 | 0.145 | 0.156 |
| BET (m$^2$/g) | 211.4 | 202.7 | 197.8 |
| Pore volume (cm$^3$/g) | 0.157 | 0.163 | 0.149 |
| Average pore diameter (nm) | 2.34 | 3.78 | 2.95 |
| $pH_{PZC}$ | 5.2 | 6.7 | 7.8 |

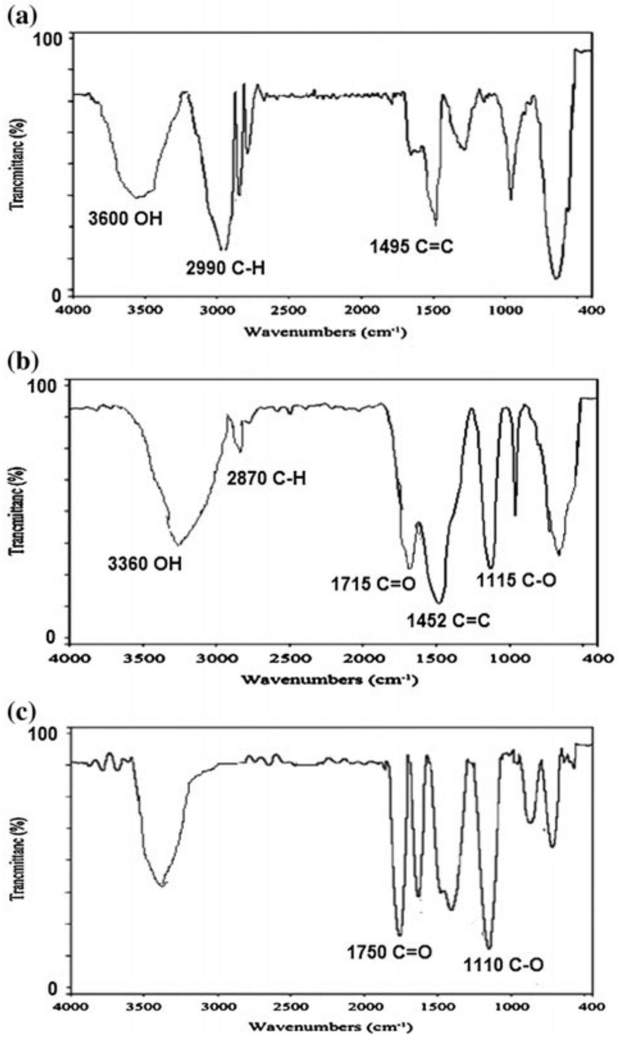

Fig. 1. FT-IR spectra of activated carbon with $ZnCl_2$ (a), NaOH (b), and $HNO_3$ (c).

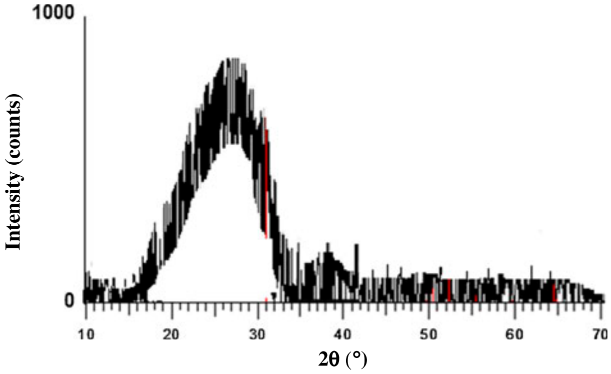

Fig. 2. The X-ray diffraction pattern of activated carbon nanoparticles.

powder particles. The peak width is used for estimation of the average dimensions of particles in a powder by the Scherrer equation [20]:

$$d = \frac{\kappa\lambda}{\beta \cos \theta} \tag{11}$$

where $\kappa$ is constant (0.89), $\lambda$ is X-ray wavelength (0.154 nm), $\theta$ is the Bragg angle, $\beta$ is full width at half maximum, and $d$ is size of powder particles. With respect to peak of XRD pattern, the size of particles of the activated carbon was approximately estimated less than 50 nm.

The SEM images of activated carbon before and after the treatment of TNT red water are indicated in Fig. 3(a) and (b), respectively. The porosity pores and cavities with various dimensions in activated carbon are shown in the micrographs. The pores and cavities provided a large exposed surface area for adsorption of adsorbate. So that, the adsorbate is trapped in the

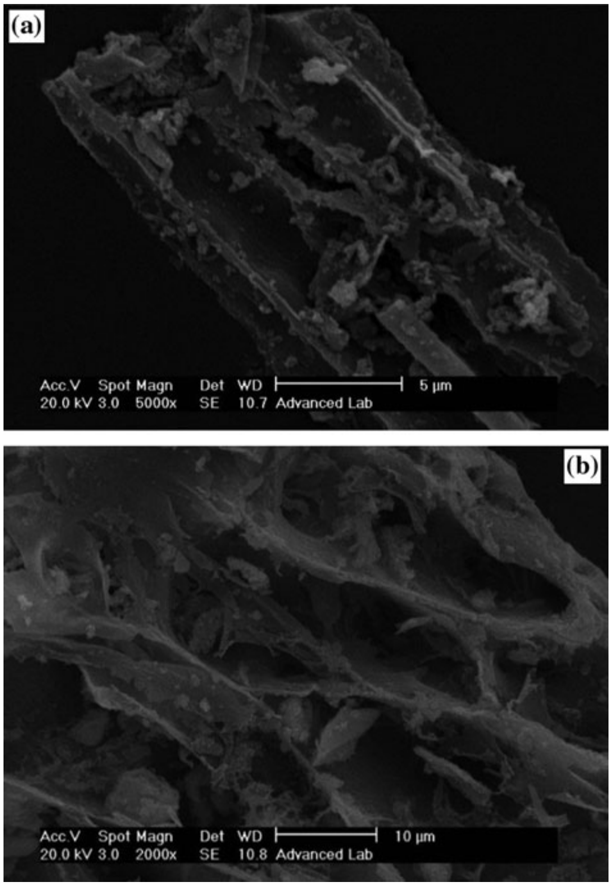

Fig. 3. SEM images of activated carbon before (a) and after (b) treatment of TNT red water.

pores and cavities and adsorbed onto the surface of the adsorbent. Also, these cavities are large enough to allow the adsorbate molecules to penetrate into the carbon structure and interact therein with the surface groups. However, the surface roughness of carbon adsorbent was changed significantly after adsorption of pollutants. The pores were completely filled and the pores appear to be prominently swollen after the adsorption of adsorbate. Therefore, adsorbate can be adsorbed to the functional groups present inside the pores [31,32].

### 3.2. Treatment of TNT red water

The chemical properties of TNT red water sample with dilution of 100 times are given in Table 2. The initial COD value is used as $C_o$ in equations of (1) and (2) for calculation of $q_e$ and %COD removal values. The TNT red water with dilution of 100 times was treated by chemical-activated carbon. Fig. 4 shows the treatment efficiency of TNT red water using activated carbon. The obtained results show that the treatment efficiency depends on the type of chemical activator. As seen from Table 1, activation by $HNO_3$ produces the carbon adsorbent with the highest specific surface area per unit weight. $HNO_3$ is the main factor for fracturing carbon aromatic band and also creating surface active groups such as –COOH and C=O [33]. The acid treatment can change the surface functional groups and pore structure. The acid activation increases the acidity of activated carbon [34]. Chemical activating reagents such as $ZnCl_2$ and alkali metal hydroxide were also used to prepare activated carbons.

Oxygen surface groups are very common in activated carbons and they may be easily introduced by oxidation with nitric acid. Chemical treatment will modify the pore structure and the chemical nature of the surface of an activated carbon. The extent of oxygen–carbon group formation will naturally affect the accessibility of the adsorbate to the oxidized active carbon [34]. Treatment of carbon with $HNO_3$ slightly increases its adsorption capacity, probably by dissolving some of the permeated inorganic matter and oxidizing deposited carbon that blocks pore openings, thus creating some micro and mesoporosity. Chemisorption in the pores of the carbon particles is due to the increase in elements of C, H, N, S, etc. in the adsorbent. So, according to the results, in other experiments $HNO_3$ was selected for carbon activation.

Table 2
The physical and chemical properties of TNT red water with dilution of 100 times

| | |
|---|---|
| pH | 3.5 ± 0.3 |
| COD (mg/L) | 760 ± 15 |
| Total solids (mg/L) | 1,680 ± 28 |
| TNT (mg/L) | 35.5 ± 2.5 |

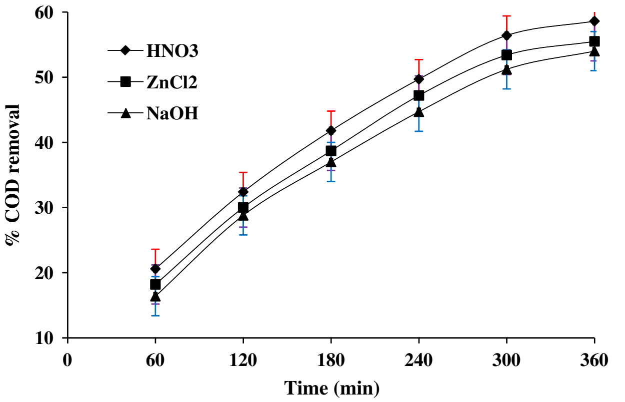

Fig. 4. Effect of chemical activation on the removal efficiency using activated carbon; TNT red water with dilution of 100 times, pH 3.5, $C_o$: 760 mg/L, sorbent dose: 20 g/L, 25°C.

Also, Fig. 4 shows the effect of the contact time in the treatment of TNT red water. The adsorption increases with contact time up to 300 min and then shows a slightly change in %COD removal (<3%). Thus, it can be concluded that the time of adsorption equilibrium is at contact time of 300 min. A large number of vacant sites on the surface of activated carbon are available in the initial stage of adsorption. In adsorption equilibrium, the decreasing of available sites on the surface of adsorbent is due to the steady state of adsorption process [9,10]. Therefore, the equilibrium time of 300 min is selected.

The pH value of point of zero charge of activated carbon using $HNO_3$ is obtained 5.2 (Table 1). At this point, the electrostatic force enhances the adsorption capacity of adsorbent. The functional groups with charges of positive and negative on the surface of activated carbon are due to the adsorption of different pollutants. The increase in removal yield for TNT treatment is observed with change of pH of samples from basic to acidic solutions and the maximum removal efficiency is obtained in pH value of 3 (Fig. 5). The positive charge on the surface of activated carbon in pH value of 3 is due to the increase in the removal efficiency by attraction of TNT molecules via the nitro groups. However, interference of $H^+$ ions in acidic samples with pH < 2 is due to the decrease in removal efficiency [17].

The effect of adsorbent dose on the treatment of TNT red water is shown in Fig. 6. The %COD removal

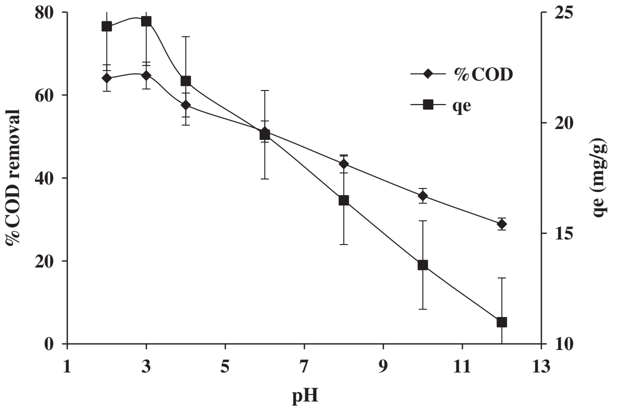

Fig. 5. Effect of pH on treatment of TNT red water and equilibrium adsorption capacity using activated carbon; TNT red water with dilution of 100 times, $C_o$: 760 mg/L, sorbent dose: 20 g/L, contact time: 300 min, 25˚C.

increased with the increase in adsorbent dose. This increment is related to an increase in the adsorbent surface area and availability of more adsorption sites. However, after the dose of 40 g/L, the %COD removal is nearly constant that is attributed to the non-availability of active sites on the adsorbent and establishment of equilibrium between the adsorbate and adsorbent. On the other hand, the equilibrium adsorption capacity showed an opposite trend. This may be due to the decrease in the total adsorption surface area available to adsorbate resulting from overlapping or aggregation of adsorption sites [35]. Therefore, maximum sorption achieved when 40 g/L of adsorbent was used.

The rate of adsorption is a function of the initial amounts of the adsorbate, which makes it an important factor to be considered for effective adsorption. The effect of dilution of TNT red water in range of 100–500 times was investigated on the treatment of wastewater samples (Fig. 7). The %COD removal increased with the dilution times of TNT red water that is related to the limited number of active sites. The active sites become saturated at a certain concentration of pollutant. However, the adsorption capacity at equilibrium decreased with increasing of dilution times. Increasing of adsorbate concentration is usually due to the increase in the driving force for mass transfer of adsorbate between the aqueous phase and the activated carbon [36].

Fig. 8 displays the effect of temperature on the treatment of TNT red water using activated carbon. As seen, the yield of treatment is increased with the increase in temperature in range of 25–45˚C. High temperature increases the efficiency of removal and elimination rates and also the active sites are expanded with the increase in temperature. However, the %COD removal is slightly increased from temperature 45 to 55˚C. Because, the attraction force in adsorption process is decreased in high temperatures [37].

### 3.3. Thermodynamic, kinetic, and isotherm of adsorption reaction

The effect of temperature on the treatment of TNT red water using activated carbon was studied in batch experiment at temperatures of 298, 308, 318, and 328 K. The values of $\Delta H$ and $\Delta S$ of adsorption process are obtained as 10.7 kJ/mol and 70.7 J/mol K using Eqs. (9) and (10). The distribution coefficient, $K_d$, and

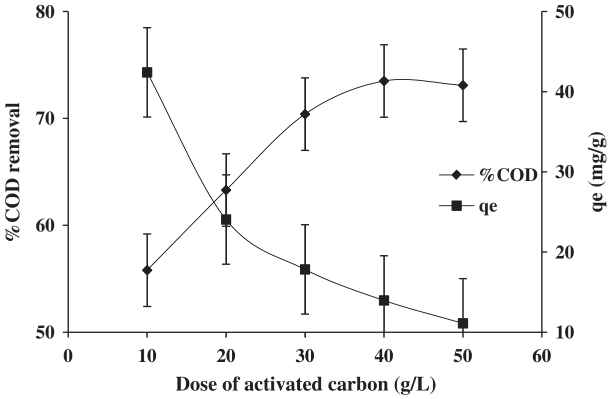

Fig. 6. Effect of activated carbon dose on treatment of TNT red water and equilibrium adsorption capacity; TNT red water with dilution of 100 times, $C_o$: 760 mg/L, pH 3, contact time: 300 min, 25˚C.

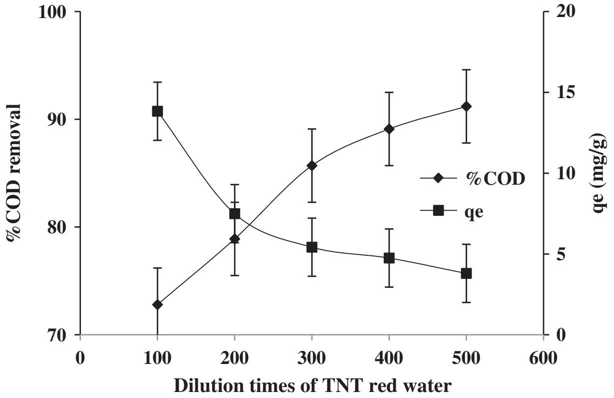

Fig. 7. Effect of dilution times of TNT red water on the removal yield and equilibrium adsorption capacity of activated carbon; sorbent dose: 40 g/L, pH 3, contact time: 300 min, 25˚C.

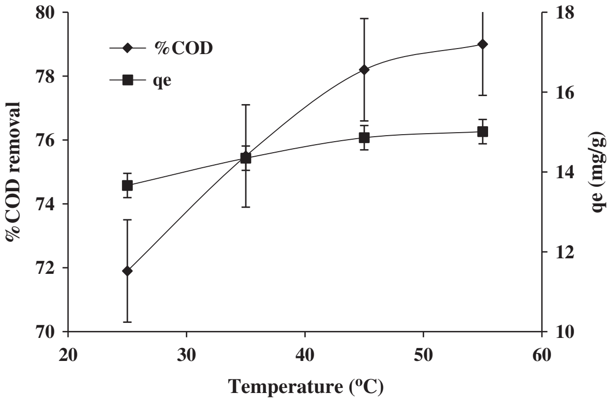

Fig. 8. Effect of temperature on treatment of TNT red water and equilibrium adsorption capacity; dilution times: 100, $C_o$: 760 mg/L, pH 3, contact time: 300 min, sorbent: 40 g/L.

Gibbs free energy, $\Delta G$, values are calculated as 63.9, 77.0, 89.7, and 94.0 mL/g; and −10.4, −11.1, −11.8, and −12.5 kJ/mol at temperatures of 298, 308, 318, and 328 K, respectively. Positive value of $\Delta H$ indicates that the adsorption of adsorbates on the surface of the adsorbent can be a chemical reaction such as deprotonation. Also, positive value of $\Delta S$ can be related to the desolvation and dehydration of adsorbate molecules [37].

Kinetic modeling was performed to investigate the rate-controlling step in the treatment of TNT red water by activated carbon. Kinetic models including the pseudo-first-order, pseudo-second-order, and the intraparticle diffusion were investigated. The obtained kinetics parameters are listed in Table 3. Comparing of the correlation coefficients of kinetic models indicates that the pseudo-second-order model described the data better than the first-order model which relies on the assumption that adsorption be a chemical reaction [38]. Also, the correlation coefficient of intraparticle diffusion model shows that the process is controlled by outer surface adsorption and intraparticle diffusion. That is, the adsorbent has the main responsibility in the adsorption process. Also, intraparticle diffusion has a role in adsorption process but it is not the only controlling stage of process [38].

Table 4
The Langmuir, Freundlich, and Temkin parameters and correlation coefficients of isotherm models; TNT red water with dilution of 100, 200, 300, 400, and 500 times, pH 3, contact time: 300 min, sorbent: 40 g/L, 25°C

| Model | Parameters | $R^2$ |
|---|---|---|
| Langmuir | $q_{\max}$ (mg/g) = 17.575, $b$ (L/mg) = 0.014 | 0.914 |
| Freundlich | $K_F$ (mg/g (L/mg)$^{1/n}$) = 1.138, $n$ = 2.206 | 0.975 |
| Temkin | $K_T$ (L/g) = 0.171, $B$ = 3.492 | 0.900 |

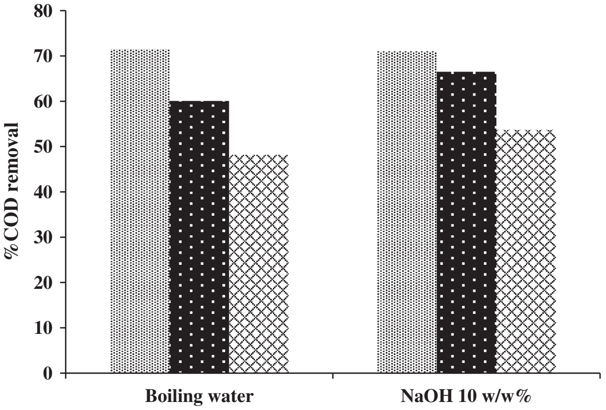

Fig. 9. The recovery of used activated carbon adsorbent by boiling water and solution of NaOH 10 w/w%. TNT red water with dilution of times: 100, $C_o$: 760 mg/L, pH 3, contact time: 300 min, sorbent dose: 40 g/L, 25°C.

Sorption equilibrium measurements were used to determine the maximum or ultimate sorption capacity and the obtained data were formulated into the most commonly models include Langmuir, Freundlich, and Temkin isotherms [39]. The treatment experiments were repeated and the average results (Table 4) were reported at temperature of 25 ± 2°C. Comparing the correlation coefficient values ($R^2$) of isotherm models, that is a measure of the fitting of experimental data on the isotherm's model, confirms that the Freundlich model is the best model to describe the sorption data. That is, a multilayer adsorption has been proposed by activated carbon in treatment of TNT red water. Value

Table 3
Kinetic parameters of treatment of TNT red water by activated carbon. Dilution times: 100, $C_o$: 760 mg/L, pH 3, sorbent dose: 40 g/L, contact time: 60, 120,180, 240, and 300 min

| Model | Regression equation | Kinetic rate constant | $R^2$ |
|---|---|---|---|
| Pseudo-first-order | $\log(q_e - q_t) = 1.390 - 0.006t$ (min) | $K_1 = 0.014$ 1/min | 0.945 |
| Pseudo-second-order | $t$ (min)/$q_t = 7.581 + 0.049t$ (min) | $K_2 = 0.109$ g/mg min | 0.997 |
| Intraparticle diffusion | $q_t = -0.284 + 0.815t^{1/2}$ | $K_i = 0.815$ 1/min$^{1/2}$ | 0.989 |

of $n > 1$ represents a favorable adsorption condition. The Freundlich adsorption isotherm is an empirical relation between the concentrations of adsorbate in the surface of adsorbent and in the liquid phase [39].

### 3.4. Recovery of activated carbon sorbent

The recovery of activated carbon is studied by treatment of used sorbent in boiling water and solution of NaOH 10 w/w%. The recovery cycles were repeated three times. The obtained results are given in Fig. 9. The treatment of TNT red water is optimized in acidic conditions, therefore, the NaOH solution and alkaline pH can be used for desorption of adsorbate molecules. However, the efficiency is reduced in following cycles. The competition of the hydroxide ions with pollutant molecules is due to the reduction in the removal efficiency [40]. Also, the more reduction of % COD removal is seen in repeated cycles using recovery by boiling water. The adsorbates can be solved in boiling water solutions and adsorbent can be reusable [40].

## 4. Conclusions

The pine wood can be used for preparation of carbon sorbent for treatment of TNT red water. The carbon sorbent was modified by chemical modification using $HNO_3$ and then was activated in a temperature programming. The kinetic and thermodynamic parameters of adsorption process were calculated at temperature range of 25–55˚C. Data of Langmuir, Freundlich, and Temkin adsorption isotherms were calculated in the range of dilution times of 100–500 of TNT red water sample. The adsorption process in treatment of TNT red water has indicated the pseudo-second-order kinetic model and Freundlich adsorption isotherm. The adsorption process was spontaneous and endothermic. The %COD removal was depended on the pH of sample, dose of adsorbent, contact time, and temperature. Optimization of effective factors indicated that the pH value of 3, 40 g/L of adsorbent, contact time of 300 min, and temperature of 55˚C were the optimized conditions. The process of desorption by sodium hydroxide solution and boiling water showed the reusability of sorbent in treatment of TNT red water.

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