Kinetic and multi-parameter isotherm studies of picric acid removal from aqueous solutions by carboxylated multi-walled carbon nanotubes in the presence and absence of ultrasound

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Abstract

Carboxylated multi-wall carbon nanotubes (MWCNTs-COOH) have been used as efficient adsorbents for the removal of picric acid from aqueous solutions under stirring and ultrasound conditions. Batch experiments were conducted to study the influence of the different parameters such as pH, amount of adsorbents, contact time and concentration of picric acid on the adsorption process. The kinetic data were fitted with pseudo-first order, pseudo-second-order, Elovich and intra-particle diffusion models. The kinetic studies were well described by the pseudo-second-order kinetic model for both methods. In addition, the adsorption isotherms of picric acid from aqueous solutions on the MWCNTs were investigated using six two-parameter models (Langmuir, Freundlich, Tempkin, Halsey, Harkins-Jura, Fowler-Guggenheim), four three-parameter models (Redlich-Peterson, Khan, Radke-Prausnitz, and Toth), two four-parameter equations (Fritz-Schlunder and Baudu) and one five-parameter equation (Fritz-Schlunder). Three error analysis methods, correlation coefficient, chi-square test and average relative errors, were applied to determine the best fit isotherm. The error analysis showed that the models with more than two parameters better described the picric acid sorption data compared to the two-parameter models. In particular, the Baudu equation provided the best model for the picric acid sorption data for both methods.

Key words: carbon nanotube, picric acid, kinetics, ultrasound, adsorption isotherms

1. Introduction

Nitrophenols are used as intermediates in the production of dyes, pigments, preservatives, pesticides, pharmaceuticals and rubber chemicals [1]. Hence, they usually are found in effluent wastes and rivers with input from munitions and textile factories [1,2]. Among the nitrophenols, 2,4,6-trinitrophenol (picric acid), which is synthesized with inherent stability until detonation, has been used in naval ordnance and was common in many other types of ordnance in the early part of this century [3,4]. Due to the various applications of picric acid in dyes, explosives, analytical reagents, germicides, fungicides, tissue fixatives, photochemicals, and pharmaceuticals as well as for the oxidation and etching of iron, steel, and copper surfaces [5], it could enter the water table or environment and effect the health of humans because picric acid is toxic even at low concentrations [6,7]. On the other hand, the World Health Organization (WHO) reported 0.001 mg/L as the permissible phenolic concentration in potable water [8]. In addition, US Environmental Protection Agency issued a permissible limit of 0.1 mg/L in wastewater [9]. Therefore, the removal of phenolic contaminants from aqueous solutions has become a major focus of research and is essential. The adsorption process is one of the major methods for the removal of phenols, nitrophenols and some of their derivatives from aqueous solutions [10]. The advantage of this technique over other methods, such as filtration, chemical precipitation and ion exchange, is that it is generally easy to handle, can be regenerated by a suitable desorption process, is insensitivity to toxic...
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2. Experimental

2.1. Materials and methods

Picric acid (Merck Chemical Inc., USA) and MWCNTs (%95 purity; OD, 30–50 nm; length, 0.5–2 μm; Neutrino Co., Ltd) were purchased and used as received. Analytical reagent-grade chemicals were used as well as deionized water from a Milli-Q system (Millipore). The concentration of picric acid was measured with a Unico UV-2100 (USA) variable-wavelength ultraviolet-visible spectrophotometer at 340 nm. Scanning electron microscope (SEM) measurements were taken using an KYKY-EM3200 model. Fourier-transform infrared spectroscopy (FTIR) spectrum was recorded using KBr tablets on a Thermo Nicolet 870 FTIR spectrometer (USA). The ultrasonic irradiation was carried out with an Elmasonic S 60 H (ELMA Ultrasonic, Germany) with a constant frequency of 37 kHz.

2.2. Batch sorption experiments

To study the effects of pH on the sorption of picric acid, 30 mg of MWCNT-COOH were dispersed into 15 mL solutions containing a picric acid concentration of 100 mg/L. The initial pH values were adjusted from 1.0 to 10.0 using nitric acid and NaOH at 25±1°C. The amounts of sorbed picric acid were calculated as the difference between the initial and final concentrations when equilibrium was reached. The results are based on at least three replicate experiments for each pH value. To estimate the sorption capacity, 30 mg of MWCNT-COOH were mixed with 20 mL of picric acid solution (concentration range, 10–100 mg/L). After 120 min, the picric acid concentration in the aqueous solutions was determined by ultraviolet-visible spectroscopy. The removal (%) and sorption capacity q (mg/g) were obtained as follows:

\[
\text{Removal\%} = \frac{C_0 - C_e}{C_0} \times 100\%
\]

\[
q_e = \frac{(C_0 - C_e) \times V}{m}
\]

where \(C_0\) and \(C_e\) are the initial and final concentrations (mg/L) of the picric acid in the aqueous solution, respectively; \(V\) (L) is the volume of the picric acid solution, and \(m\) (g) is the weight of the sorbent. The kinetic data were analyzed using four kinetic models to gain an understanding of the sorption process. The kinetic experiment was carried out under normal atmospheric conditions at 25±1°C. Initially, 30 mg of MWCNTs were contacted with a 10 mL solution containing a picric acid concentration of 100 mg/L in glass vials, and then, it was stirred for different times with both stirring and ultrasound methods. The adsorbent and solution were separated at predetermined time intervals, filtered using a 0.45 μm membrane filter and analyzed for residual picric acid concentrations as described above.

2.3. Non-linear regression analysis

The adsorption equilibrium data for picric acid on MWCNT-COOH were analyzed by non-linear curve fitting analysis using the MATLAB® software (MathWorks, USA) to fit the three-parameter, four-parameter, and five-parameter isotherm models. The optimization procedure requires an error function to be defined in order to be able to evaluate the fit of the equation to the experimental data [30]. Apart from the correlation coefficient \(R^2\), the chi-square \(\chi^2\) test and the average relative errors \(\text{ARE}\) were also used to measure the goodness-of-fit [30]. The chi-square test and ARE can be defined as follows:

\[
\chi^2 = \sum_{i=1}^{n} \frac{(q_{i,exp} - q_{i,cal})^2}{q_{i,cal}}
\]

\[
\text{ARE} = \frac{100}{N} \sum_{i=1}^{n} \left| \frac{q_{i,exp} - q_{i,cal}}{q_{i,exp}} \right|
\]

where \(q_{i,exp}\) and \(q_{i,cal}\) are the experimental and calculated values, respectively, and \(n\) is the number of measurements. The smaller chi-square and \(\text{ARE}\) values indicate a better curve fitting.

3. Results and discussion

3.1. Characterization of adsorbent

A SEM image was used to study the morphology of the MWCNT-COOH. Fig. 1a shows that the MWCNTs are curved, rope-like and highly tangled and agglomerated with each other. In addition, the obtained diameters of the MWCNTs were about 30–60 nm.

Fig. 1b shows the FT-IR spectrum of the MWCNT-COOH. The peaks at around 1400–1570 and 3100–3400 cm\(^{-1}\) are assigned to the C=C and OH stretching modes, respectively. In addition, the appearance of the absorption peaks at 1703 (C=O) and 1066 (C-O) cm\(^{-1}\) clearly shows the carboxylic groups on the MWCNTs. Additionally, the bands at around 2800–2900 could be related to the C-H stretch vibration of the MWCNTs defects.
Dosage studies were carried out to determine the adsorption percentage of picric acid from aqueous solutions at a picric acid concentration of 100 mg/L. According to Fig. 3, the experimental results revealed that the adsorption percentage of picric acid increased as the MWCNT dosage was increased for both methods. For example, the removal of picric acid was significantly enhanced from 20.3% to 96.29% by the MWCNT-COOH for stirring method and from 14.3% to 87.7% for the ultrasound method when the CNT dosage was increased from 0.01 to 0.07 g. This increase could be related to the greater surface area or more adsorption sites in the high dosage of the MWCNT-COOH. In other words, these values are noticeable for MWCNT-COOH which could be related to the presence of many accessible sites (external surface sorption) on the MWCNT-COOH surface which agrees with the fast transfer of the picric acid species to the surface of the CNTs.
Fig. 4. Effect of pH on the picric acid sorption onto the carboxylated multi-wall carbon nanotube.

3.4. Effect of pH

The effect of pH on the uptake of picric acid is shown in Fig. 4. Because adsorption studies on drinking water purification were more significant at a neutral pH, in this study, we calculated the adsorbed amount of picric acid after equilibrium at C_0=100 mg/L in a pH range between 1.0 and 10.0 for the purpose of comparison. In liquid-phase adsorption, the adsorption capacity of CNTs for aromatic compounds depends on a number of factors such as the physical nature of the adsorbent (pore structure, purity and functional groups), the nature of the adsorbate (its solubility, the presence of functional groups, polarity, molecular weight and size) and the solution conditions such as pH. The experimental results for adsorption in various pHs suggested that there is an increase in the uptake of picric acid at a pH lower than 5. This result could be related to the solubility of picric acid in aqueous solutions. In fact, the solubility of picric acid is dependent on the pH values. In other words, the solubility of picric acid diminishes as the pH value or $H^+$ concentration decreases or increases, respectively, because the adsorption of phenolic compounds on activated carbon is inversely proportional to the solubility [31]. Therefore, the adsorption percentage of picric acid by the MWCNTs increased as the pH value was decreased. On the other hand, the picric acid dissociates to picrate anion at the higher pH values in which the surface coverage decreases. In these conditions, the electrostatic repulsion between the identical charges decreases the adsorption capacities. In addition, because picrate anions are more soluble in aqueous solution, the stronger adsorbate-water bonds must be broken before adsorption can occur [18,32].

3.5. Kinetic studies

Four kinetic models, the pseudo-first-order, pseudo-second-order, Weber-Morris intra-particle diffusion and Elovich models were used to investigate the rate of the adsorption process and rate controlling step. The best-fit model was selected based on the correlation coefficient values ($R^2$) of the linear regression.

The pseudo-first-order equation, which was proposed by Lagergren [33], has been used for reversible reactions with an equilibrium being established between liquid and solid phases. This equation is expressed as follows:

$$
\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t
$$

where $k_1$ is the rate constant of the adsorption (min$^{-1}$); $q_e$ is the amount adsorbed (mg/g) at equilibrium, and $q_t$ is the amount adsorbed (mg/g) at time $t$. The plot of $\log(q_e - q_t)$ against $t$ gives a linear relationship from which $k_1$ and $q_e$ are determined from the slope and intercept of the plot, respectively. The pseudo-second-order model can be expressed as given in linear form [15,18]:

$$
\frac{1}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}
$$

where $k_2$ is the pseudo second-order rate constant of the adsorption (g/mg min), and the other terms have already been defined. The values of $q_e$ and $k_2$ can be estimated from the slope and intercept of the plot of $t/q_t$ versus $t$.

Elovich’s equation [34] assumes that the solid surfaces of an adsorbent are energetically heterogeneous, and there are no desorption and interactions between the adsorbed species at a low surface coverage. This model can be expressed in linear form as follows:

$$
q_t = \frac{a}{b\ln(ab)} + \frac{1}{b}\ln(t)
$$

Here, parameter $a$ in the equation is the initial sorption rate (mg g$^{-1}$ min$^{-1}$), while parameter $b$ is related to the extent of the surface coverage and the activation energy for chemisorption (g mg$^{-1}$). If this equation applies, it should lead to a straight line for which the $a$ and $b$ coefficients can be calculated from the plot of $q_t$ versus $\ln t$.

The adsorption parameters derived from the application of the pseudo-first-order equation ($K_1$ and $q_e$), the pseudo-second-order equation ($K_2$, $q_e$) and Elovich’s equation ($a$ and $b$) were calculated and are listed in Table 1. In addition, all plots of the adsorption kinetics are presented in the Supplementary information. The low correlation coefficients, $R^2$, of the pseudo-first-order and Elovich models for both methods suggest that both models are not applicable to fit the experimental data. In addition, there is no agreement between the $q_{cal}$ and $q_{exp}$ values calculated for the pseudo-first-order model (Table 1). The correlation coefficients of the pseudo-second-order model for the stirring and ultrasound methods were 0.9998 and 0.9975, respectively, which indicate the suitability of the pseudo-second-order equation for the MWCNT-COOH for both methods. In addition, the adsorbed values of picric acid at equilibrium ($q_e$) for the stirring and ultrasound methods were 28.01 and 19.53 mg g$^{-1}$, respectively, which were near to those from the experimental data. These results show that the sorption of picric acid from an aqueous solution onto MWCNT-COOH with both methods obeys the pseudo-second-order kinetic model and could be used to determine the equilibrium sorption capacity, rate
According to Fig. 5, it is clear that intra-particle diffusion of picric acid within the MWCNT-COOH with both methods occurred in two stages because the plots contain two different straight lines. The initial adsorption stage is approximately rapid for the MWCNT-COOH for both methods. It is from 0 to 50 min for the stirring method and from 0 to 60 min for the ultrasound method, which is due to the fast diffusion of the picric acid from the aqueous phase to the outer-surface of the MWCNTs. The second stage is a slow adsorption and is from 50 to 90 min for the stirring method and from 60 to 90 min for the ultrasound method which could be attributed to the intra-particle diffusion of the picric acid molecules into the porous structure of the MWCNT-COOH. In other words, when the adsorption on the exterior surface became saturated, the picric acid molecules entered into the pores of the adsorbent and were adsorbed by the interior surface of the mesopores. Thus, these results confirm that both external surface sorption and intra-particle diffusion participate in the process of picric acid adsorption by MWCNTs and that the intra-particle diffusion model is not the only rate-controlling step. The results are shown in Table 1.

### 3.6. Adsorption isotherms

Adsorption isotherms are the mathematical equations in which the ratio between the adsorbate concentrations in the solid phase and that in the liquid phase at a constant temperature and pH is studied. In fact, it indicates how a substance from aqueous media transfers to a solid phase when an equilibrium state is established in a system. In this study, the two-parameter (Langmuir, Freundlich, Halsey, Tempkin, Harkins-Jura, Fowler-Guggenheim), three-parameters (Redlich-Peterson, Khan, Radke-Prausnitz, Toth), four-parameters (Fritz-Schlunder and Baudu) and five-parameter (Fritz-Schlunder) isotherm models along with their constant values, which describe the surface properties and affinity of the adsorbent, were used to express the mechanism of adsorption. All plots of the adsorption isotherms are presented in Supplementary data.

#### 3.6.1. Two-parameter isotherms

**3.6.1.1. Langmuir isotherm**

The Langmuir model [30,36] assumes that the maximum sorption capacity corresponds to a complete monolayer coverage of the molecules on the adsorbent surface with no

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**Table 1. Parameters of the pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion models for picric acid sorption onto the MWCNTs-COOH**

<table>
<thead>
<tr>
<th>Methods</th>
<th>Pseudo-first-order model</th>
<th>Pseudo-second-order model</th>
<th>Intra-particle diffusion model</th>
<th>Elovich model</th>
</tr>
</thead>
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<tr>
<td></td>
<td>k_1 (min^{-1})</td>
<td>q_e (mg/g)</td>
<td>K_f (g mg^{-1} min^{-1})</td>
<td>q_e (mg/g)</td>
</tr>
<tr>
<td></td>
<td>R^2</td>
<td>K_f (g mg^{-1} min^{-1})</td>
<td>R^2</td>
<td>kid (mg g^{-1} min^{-0.5})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>a</td>
<td>b</td>
<td>R^2</td>
</tr>
<tr>
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<td>0.0767</td>
<td>5.86</td>
<td>0.9184</td>
<td>0.0392</td>
</tr>
<tr>
<td>Ultrasound</td>
<td>0.0516</td>
<td>7.92</td>
<td>0.9402</td>
<td>0.0162</td>
</tr>
</tbody>
</table>

Temperature, 298 K; initial picric acid concentration, 100 mg L^{-1}; mass of MWCNTs, 30 mg; volume of solution, 10 mL; and pH of the sample solution, 7.0. MWCNTs-COOH, carboxylated multi-wall carbon nanotube.

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In order to better understand the adsorption mechanism that affects the kinetics of adsorption, the kinetic data were fitted to the Weber-Morris intra-particle diffusion model [15,35]. In fact, it is described by external mass transfer and intra-particle diffusion. This model is expressed as follows:

\[
q_t = \frac{k_{id} t^{1/2}}{1 + C_i}
\]

where \( k_{id} \) (mole g^{-1}min^{-1/2}) is the rate constant of the intra-particle diffusion, and \( C_i \) is proportional to the boundary layer thickness. If the regression of \( q_t \) versus \( t^{1/2} \) gives a straight line, then intra-particle diffusion is involved in the adsorption process, and if this line passes through the origin, then intra-particle diffusion is the sole rate-limiting step, and the \( k_{id} \) can be calculated from the slope and \( C_i \) from the intercept. The intra-particle kinetic model of picric acid sorption by MWCNT-COOH for both methods is shown in Fig. 5. The nonzero intercepts of the plots in each case were a clear indication that intra-particle diffusion is not the rate-limiting step of the sorption mechanism. Hence, the intra-particle diffusion model is not the only rate-controlling step. The difference in the rate of mass transfer during the initial and final stages of adsorption could cause the deviation in the straight lines from the origin. According to Fig. 5, it is clear that intra-particle diffusion of picric acid within the MWCNT-COOH with both methods occurred in two stages because the plots contain two different straight lines. The initial adsorption stage is approximately rapid for the MWCNT-COOH for both methods. It is from 0 to 50 min for the stirring method and from 0 to 60 min for the ultrasound method, which is due to the fast diffusion of the picric acid from the aqueous phase to the outer-surface of the MWCNTs. The second stage is a slow adsorption and is from 50 to 90 min for the stirring method and from 60 to 90 min for the ultrasound method which could be attributed to the intra-particle diffusion of the picric acid molecules into the porous structure of the MWCNT-COOH. In other words, when the adsorption on the exterior surface became saturated, the picric acid molecules entered into the pores of the adsorbent and were adsorbed by the interior surface of the mesopores. Thus, these results confirm that both external surface sorption and intra-particle diffusion participate in the process of picric acid adsorption by MWCNTs and that the intra-particle diffusion model is not the only rate-controlling step. The results are shown in Table 1.

**Fig. 5.** Linearized intra-particle diffusion kinetic model of the picric acid sorption onto the multi-wall carbon nanotubes.
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The Langmuir equation in non-linearized form can be written as follows:

\[ \frac{q_e}{C_e} = \frac{1}{b q_m} + \frac{1}{b q_m C_e} \]  

(7)

interaction between the sorbed molecules. In addition, this empirical model refers to the same activation energy of adsorption when the adsorption of each molecule occurs at definite localized sites onto a homogeneous surface without transmigration of the adsorbate in the plane of the surface. The Langmuir equation in non-linearized form can be written as follows:

\[ q_e = \frac{b q_m C_e}{1 + b C_e} \]

where \( q_e \) (mg g\(^{-1}\)) and \( C_e \) (mg L\(^{-1}\)) are the amount of solute adsorbed per unit weight of adsorbent at equilibrium and the picric acid concentration at equilibrium, respectively. \( q_m \) (mg g\(^{-1}\)) is the maximum adsorption capacity, and \( b \) is the adsorption equilibrium constant (L mg\(^{-1}\)) that is related to the free energy of adsorption. The four linear forms of the Langmuir isotherm with its parameters are shown in Table 2. Among the four forms, the values for the obtained regression coefficients from the Type-1 and Type-2 equations for both methods indicate that the adsorption of picric acid on the MWCNTs follows the Langmuir isotherm. In other words, Type 1-2 equations are the best form for the interpretation of experimental data, which had the highest coefficient of correlation for the MWCNTs with the stirring and ultrasound methods compared to the other forms. In addition, the obtained Langmuir parameters (\( b \) and \( q_m \)) from the four linear models were different.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Langmuir (type 1)</th>
<th>The calculated parameters</th>
<th>Plot</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stirring</td>
<td>[ q_e = \frac{1}{b q_m} + \frac{1}{b q_m C_e} ]</td>
<td>( q_m ) (mg/g)</td>
<td>B (L/mg)</td>
</tr>
<tr>
<td>Ultrasound</td>
<td>28.49</td>
<td>0.531</td>
<td>0.999</td>
</tr>
<tr>
<td>Stirring</td>
<td>[ \frac{1}{q_e} = \frac{1}{1 + \frac{1}{b q_m C_e}} ]</td>
<td>22.03</td>
<td>0.2722</td>
</tr>
<tr>
<td>Ultrasound</td>
<td>26.52</td>
<td>1.036</td>
<td>0.9973</td>
</tr>
<tr>
<td>Stirring</td>
<td>[ q_e = q_m - \frac{q_m}{b C_e} ]</td>
<td>20.45</td>
<td>0.449</td>
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<tr>
<td>Ultrasound</td>
<td>26.91</td>
<td>0.9870</td>
<td>0.9713</td>
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<tr>
<td>Stirring</td>
<td>[ q_e = b q_m - b q_e ]</td>
<td>20.799</td>
<td>0.4253</td>
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<tr>
<td>Ultrasound</td>
<td>27.065</td>
<td>0.9586</td>
<td>0.9713</td>
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<tr>
<td>Stirring</td>
<td>Freundlich</td>
<td>[ K_f (mg/g) ]</td>
<td>(mg/L)</td>
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<tr>
<td>Ultrasound</td>
<td>10.604</td>
<td>3.77</td>
<td>0.9133</td>
</tr>
<tr>
<td>Stirring</td>
<td>Halsey</td>
<td>[ K_H ]</td>
<td>(mg/L/g)</td>
</tr>
<tr>
<td>Ultrasound</td>
<td>10.604</td>
<td>3.77</td>
<td>0.9133</td>
</tr>
<tr>
<td>Stirring</td>
<td>Tempkin</td>
<td>[ K_T (L/g) ]</td>
<td>( K_2 )</td>
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<tr>
<td>Ultrasound</td>
<td>4.0117</td>
<td>21.92</td>
<td>0.982</td>
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<td>Stirring</td>
<td>Harkins-Jura</td>
<td>[ A_H ]</td>
<td>( B_H )</td>
</tr>
<tr>
<td>Ultrasound</td>
<td>76.92</td>
<td>1.784</td>
<td>0.8479</td>
</tr>
<tr>
<td>Stirring</td>
<td>Fowler–Guggenheim</td>
<td>[ W (kJ/mol) ]</td>
<td>( K_f )</td>
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<tr>
<td>Ultrasound</td>
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<td>0.9791</td>
</tr>
<tr>
<td></td>
<td>-11.574</td>
<td>0.0003456</td>
<td>0.9984</td>
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</table>

Table 2. The parameters of the different isotherm models for picric acid removal from aqueous solutions by the MWCNT-COOH.
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of the Type 1 and 2 models were found to be around 0.0096–0.1585 for the stirring method and 0.02179–0.2687 for the ultrasound method indicating a favorable behavior toward picric acid adsorption.

3.6.1.2. Freundlich and Halsey isotherms

The Freundlich [37] and Halsey [18,38] isotherms can be used for multilayer adsorption and heterogeneous surfaces with non-uniform distribution of adsorption heat. The linearized form of the Freundlich equation is as follows:

\[ \ln q_e = \ln K_f + \frac{1}{n} \ln C_e \]  

(9)

where \( K_f \) is an empirical constant related to the sorption capacity of the adsorbent \((L \text{ mg}^{-1})(L \text{ g}^{-1})^{1/n}\), and constant \(n\) is a constant indicative of the intensity of the adsorption and varies with the surface heterogeneity and affinity. The values of \(K_f\) and \(n\) can be calculated by plotting \(\ln q_e\) versus \(\ln C_e\). Moreover, the Halsey equation can be given as follows:

\[ \ln q_e = \frac{1}{n_H} \ln C_e - \ln \left( \frac{1}{K_H} \right) \]  

(10)

where \(K_H\) and \(n_H\) are the Halsey constants, which can be obtained from the slope and intercept of the linear plot based on \(\ln(q_e)\) versus \(\ln(C_e)\), respectively. The related Freundlich and Halsey isotherm parameters were calculated and then tabulated in Table 2. The low correlation coefficients of the Freundlich and Halsey models for the stirring (0.9133) and ultrasound (0.9537) methods show that they are not suitable for the interpretation of the experimental data. In other words, these models could not interpret the data reasonably well for the adsorption of picric acid onto the MWCNT-COOH.

3.6.1.3. Tempkin isotherm

Tempkin [39] suggested that due to adsorbent-adsorbate interactions, the heat of adsorption of all molecules linearly decrease with the surface coverage. In addition, it assumes that the adsorption is characterized by a uniform distribution of the binding energies up to some maximum binding energy. The linearized form of the Tempkin model has generally been applied in the following form:

\[ q_e = K_1 \ln C_e + \frac{1}{b} \]  

(11)

where \(k_1\) is related to the heat of adsorption \((L/g)\), and \(K_2\) is the dimensionless Tempkin isotherm constant. The Tempkin parameters \((k_1\) and \(k_2\)) can be determined from the linear plots of \(q_e\) and \(\ln C_e\). As can be seen in Table 2, the values for the regression coefficients for the stirring and ultrasound methods were 0.982 and 0.9865, respectively, which relatively show good agreement with the picric acid adsorption on the MWCNT-COOH.

3.6.1.4. Harkins-Jura isotherm

The Harkin-Jura model assumes the existence of a heterogeneous pore distribution in the surface of adsorbents. It could be related to the transformations of the non-linear model to the linear forms which cause a change in the error structure of the standard least-squares method. Additionally, the dimensionless equilibrium parameter or separation factor, \(R_L\), is the essential characteristics of the Langmuir isotherm as follows [16,15]:

\[ R_L = \frac{1}{1 + bC_0} \]  

(8)

where \(b\) is the Langmuir constant, and \(C_0\) is the initial concentration of adsorbate in solution. These values show the type of isotherm to be irreversible \((R_L=0)\), favorable \((0<R_L<1)\), linear \((R_L=1)\) or unfavorable \((R_L>1)\). The calculated values of \(R_L\) for both methods are shown in Table 3. From Table 3, the \(R_L\) values

<table>
<thead>
<tr>
<th>Type 1</th>
<th>Langmuir models</th>
<th>The calculated (R_L) values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stirring method</td>
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<tr>
<td>10</td>
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</tr>
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<td>30</td>
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<tr>
<td>50</td>
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<td>0.068446</td>
</tr>
<tr>
<td>70</td>
<td>0.026199</td>
<td>0.049865</td>
</tr>
<tr>
<td>90</td>
<td>0.020496</td>
<td>0.039219</td>
</tr>
<tr>
<td>100</td>
<td>0.018484</td>
<td>0.035436</td>
</tr>
<tr>
<td>10</td>
<td>0.088028</td>
<td>0.182149</td>
</tr>
<tr>
<td>30</td>
<td>0.031172</td>
<td>0.069109</td>
</tr>
<tr>
<td>50</td>
<td>0.018939</td>
<td>0.042644</td>
</tr>
<tr>
<td>70</td>
<td>0.013602</td>
<td>0.030836</td>
</tr>
<tr>
<td>100</td>
<td>0.010611</td>
<td>0.024149</td>
</tr>
</tbody>
</table>

(continued)
applied to multi-layer adsorptions [40]. This model is written as follows:

\[
\frac{1}{q_e} = \frac{B_{ij}}{A_{ij}} - \frac{1}{A_{ij}} \log C_e
\]  

(12)

Here, the Harkins-Jura isotherm parameters, \(A_{ij}\) and \(B_{ij}\), can be obtained from the linear plot of \(1/q_e\) against \(\log C_e\). The values of the Harkins-Jura constants together with the regression coefficients are presented in Table 2 for the adsorption of picric acid onto MWCNT-COOH for both methods. The low regression coefficients of the MWCNTs-COOH for both methods show the inapplicability of this model for picric acid adsorption onto MWCNTs.

### 3.6.1.5. Fowler-Guggenheim isotherm

The Fowler-Guggenheim isotherm [41] describes the presence of lateral interactions between adsorbed molecules on MWCNTs. The linearized form of this model can be given as follows:

\[
\ln \frac{C_e(1-\theta)}{\theta} = -\ln K_{FG} + \frac{2W\theta}{RT}
\]  

(13)

where \(K_{FG}\) is the Fowler-Guggenheim equilibrium constant (L mg\(^{-1}\)); \(\theta=(1-C_e/C_0)\) is the degree of surface coverage; \(W\) is the interaction energy between adsorbed molecules (kJ mol\(^{-1}\)); \(R\) is the universal gas constant and is equal to 8.314 J mol\(^{-1}\) K\(^{-1}\), and \(T\) is the absolute temperature (K). The \(W\) sign determines the interactions between the adsorbed molecules. Therefore, if \(W\) is positive, the interaction between the adsorbed molecules is attractive and the heat of adsorption due to the increased interaction between the adsorbed molecules increases with the loading of adsorbates. Additionally, if \(W\) is negative, the heat of adsorption decreases with the loading of adsorbates, and hence, the interaction among the adsorbed molecules is repulsive. When there is no interaction between adsorbed molecules, \(W=0\). The values of \(K_{FG}\) and \(W\) were evaluated from the intercept and the slope, respectively, of the linear plot of \(\ln C_e/(1-\theta)\) versus \(\theta\) based on the experimental data. The adsorption data for the picric acid adsorption onto the MWCNT-COOH for both methods were calculated and summarized in Table 2. As can be seen in Table 2, the negative values of the interaction energy (\(W\)) for both methods indicate the presence of repulsion between the adsorbed molecules, and the regression coefficients of the MWCNTs-COOH for both methods were relatively good.

### 3.6.2. Isotherm models of more than two parameters

Generally, the parameters of isotherm models have been frequently obtained by linear regression. However, modifying the non-linear isotherm equations to linear forms violate the theories existing behind the model which can cause an estimation error. Hence, nonlinear regression is a more useful method to estimate the parameters of the model and that the calculated parameters with this method are more relevant than those obtained with linear regression. In addition, nonlinear regression can be applied to the isotherm model which cannot be linearized. Therefore, nonlinear regression was used for the isotherm models with more than two parameters. Table 4 presents the calculated parameters of the adsorption isotherms and their characterizations obtained using the non-linear fitting analysis. As can be seen from Table 4, the coefficients of correlation for all the models are very good (≥0.9921). Thus, the values of the chi-square test and the ARE will determine the better model. Among the three-parameter isotherms, the best representation of the experimental results for the adsorption was obtained with the Redlich-Peterson model for the ultrasound method because it has the minimum ARE and chi-square values and maximum regression coefficients. The characterization of the Redlich-Peterson model is presented in Table 2. This model reduces to the Langmuir equation when its heterogeneity parameter is \(g=1\). The obtained \(g\) values for both methods were close to unity (0.9245 and 0.901) which shows the adsorption tends to be a Langmuir behavior. In other words, the adsorption process is achieved by a homogeneous surface in a monolayer distribution.

The Khan model presents a better adjustment for the interpretation of the obtained data from the stirring method. The maximum uptake values (\(q_m\)) were well predicted by the model with high correlation coefficients and minimum ARE and chi-square values. Of course, this model shows that the maximum adsorption capacities are lower than those of the Langmuir model for both methods; however, the difference in the maximum adsorption capacities between the two methods was similar to those of the Langmuir model. The Radke-Prausnitz and Toth models have remarkable similarity in accuracy and fitness with the Redlich-Peterson and Khan models, respectively. The adsorption data of the five-parameter isotherm models of Fritz-Schlunder and Baudu are presented in Table 4. The obtained data from the Fritz-Schlunder model were similar to the Redlich-Peterson one for the stirring method which shows the characterization of the Langmuir model. However, for the ultrasound method, despite the high regression coefficients (0.997) and low ARE and chi-square values, this model cannot describe the experimental equilibrium data. The Baudu model provides an excellent description of the experimental results. The maximum adsorption capacities for both methods are slightly higher than those calculated by the Langmuir model which shows good agreement with this model. The adsorption data of the five-parameter isotherm model of Fritz-Schlunder were analyzed and presented in Table 4. From Table 4, the coefficients of correlation for both methods are very good (≥0.997), and the ARE and chi-square values for picric acid are relatively low. The values for the maximum adsorption capacity obtained with the Fritz-Schlunder equation were similar to those calculated by the Khan model. Comparing the three-parameter, four-parameter, and five-parameter models, it seems that Baudu is the most logical model for fitting the adsorption isotherms of both methods because the \(q_m\) is close to the experimental values. In addition, the fitting degree of the three-parameter isotherms for the stirring and ultrasound methods was as follows: Khan > Toth > Radlch-Prausnitz > Redlich-Peterson, and Redlich-Peterson > Radlch-Prausnitz > Toth > Khan, respectively.
Table 4. The calculated parameters of the isotherm models of more than two parameters for picric acid removal from aqueous solutions by MWCNT-COOH.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Isotherm models</th>
<th>The calculated parameters</th>
<th>Characterization</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stirring</td>
<td>Redlich-Peterson $q_i = \frac{k_R a_R C_i}{1 + a_R C_i}$</td>
<td>$k_R$</td>
<td>$a_R$</td>
<td>$g$</td>
</tr>
<tr>
<td>Ultrasound</td>
<td>Redlich-Peterson $q_i = \frac{k_R a_R C_i}{1 + a_R C_i}$</td>
<td>$k_R$</td>
<td>$a_R$</td>
<td>$g$</td>
</tr>
<tr>
<td></td>
<td>Khan $q_i = \frac{q_s a_K b_K}{1 + b_K C_i}$</td>
<td>$q_s$</td>
<td>$a_K$</td>
<td>$b_K$</td>
</tr>
<tr>
<td>Stirring</td>
<td>Radke-Prausnitz $q_i = \frac{C_i}{1 + C_i R}$</td>
<td>$k_T$</td>
<td>$a_T$</td>
<td>$t$</td>
</tr>
<tr>
<td>Ultrasound</td>
<td>Radke-Prausnitz $q_i = \frac{C_i}{1 + C_i R}$</td>
<td>$k_T$</td>
<td>$a_T$</td>
<td>$t$</td>
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<tr>
<td></td>
<td>Fritz-Schlunder $q_i = \frac{A B C_i^m}{1 + B C_i^n}$</td>
<td>$A$</td>
<td>$B$</td>
<td>$C_i$</td>
</tr>
<tr>
<td>Stirring</td>
<td>Fritz-Schlunder $q_i = \frac{A B C_i^m}{1 + B C_i^n}$</td>
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<tr>
<td>Ultrasound</td>
<td>Fritz-Schlunder $q_i = \frac{A B C_i^m}{1 + B C_i^n}$</td>
<td>$A$</td>
<td>$B$</td>
<td>$C_i$</td>
</tr>
</tbody>
</table>

ARE, average relative errors.
4. Conclusions

The study showed that MWCNT-COOH has the ideal performance for the adsorption of picric acid. The results showed that MWCNT-COOH has a higher sorption capacity for the stirring method relative to that for the ultrasound method. The sorption kinetics of picric acid by MWCNT-COOH was found to follow the pseudo-second-order model for both methods. Among the two-parameter models, the Langmuir model better described the isotherm data. In the case of more than two parameters, the Baudu model was found to provide the closest fit to the equilibrium experimental data with a high $R^2$ and relatively low ARE and chi-square values. In addition, the W values of both methods for MWCNTs were negative, which show the presence of the repulsion among the adsorbed molecules.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

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