INTRODUCTION

The huge increase in the number of vehicles on roads around the world has contributed to the growing problem of disposing of used car tires. The lack of appropriate disposal methods for waste rubber tires causes a concerning serious global problem for the environment [1]. Proper disposal of car tires is essential to minimize the negative impact on the environment. Unfortunately, one of the unacceptable practices is the illegal disposal of used tires, namely burning. Substances emitted during open burning have a negative impact on the environment (dioxins emitted during tire burning are one of the most toxic and poisonous substances among many other pollutants, e.g. PM10 and PM2.5) as also in humans on the circulatory system, brain function and nervous system [2]. Therefore, in Poland only certified disposal companies have the necessary knowledge and equipment to dispose of used tires in an environmentally friendly way. Among others, one approach to solve this issue is the recycling, namely pyrolysis process, which in turn may become to a source of producing char [3]. The use of pyrolysis opens up new possibilities for the sustainable processing of used tires. Thanks to this method, it is possible to use used tires in an effective and sustainable way. The use of the pyrolysis process will contribute to the pursuit of a circular economy and waste reduction. One of the products produced in the pyrolysis process is tire pyrolysis oil, which can be used as a direct replacement for many raw materials and oils based on fossil fuels. Another product is tire char which can be used in the production of rubber products, varnishes or paints, dyes, master-batches, replacing charish soot from fossil fuels [4].
The nitrate contamination occur worldwide (biogenic compounds such as nitrates and phosphates and ammonia, the source of which are mainly fertilizers that have been abundantly used in agricultural production for decades) therefore, it is important to monitor the sources of nitrate emissions and take actions to prevent their formation. Moreover, due to the fact that the environmental problem of increasing nitrate content in water concerns the entire European Union, and water pollution caused in one country may affect the waters of another country, the European Commission has taken remedial actions in this regard at the Community level [5, 6]. The effect of the directive is to impose on EU Members the obligation to designate waters sensitive to pollution by nitrogen compounds from agricultural sources and to designate particularly vulnerable areas from which the outflow of nitrogen from agricultural sources into these waters should be limited.

It’s harmful effect for human health such as disease methemoglobinemia and has been studied and reported frequently in literature [7, 8]. Methemoglobinemia is a condition of elevated methemoglobin in the blood and that cause symptoms, including headache, shortness of breath, dizziness, nausea, low muscle coordination, anemia, intestinal dysfunction, cancer (nitrosamines products derived from nitrates and nitrites increase the risk of gastrointestinal cancer) and cyanosis (blue-colored skin). Moreover for a long run the serious complications may take a place including seizures and heart arrhythmias [9, 10]. The currently applicable standard for the highest permissible concentration of nitrates in drinking water is 50 [mg/L] in accordance with Polish legislation [11]. Most common techniques for water treatment (to remove excessive amounts of contaminants from water) contain ion exchange (strong basic anion exchangers most often are used), chemical precipitation, reduction and membrane processes (including reverse osmosis, electrolysis or electrodialysis) and others. Anyway, the mentioned methods have certain disadvantages and limitations, including low efficiency, sensitive processing conditions, stern technological regime, and finally, further disposal and by-products may be expensive [1].

Moreover, the currently observed continuous increase in the number, diversity, complexity and amount of various substances constituting water pollution and contamination makes conventional individual water treatment methods ineffective. Another phenomenon used in water technology is the adsorption process, one of the most essential elementary processes in which the adsorbate (e.g. nitrate ions) attaches to the surface of the adsorbent (e.g. char or activated carbon) using physical, chemical or electrostatic forces [12].

Determination of equilibrium parameters of adsorption at the solid-liquid interface analysis can be realized through the stationary (batch conditions) or dynamic (flow conditions) experimental systems [13]. In order to determine the relationship between the amount of adsorbed substance and the concentration, adsorption isotherms are determined for the equilibrium solution. An essential part of the implementation of the adsorption process is the fitting of the obtained experimental data (empirical value) with the appropriate selected adsorption isotherm model (theoretical equation), that may allows to obtain e.g. information on the mechanism of the process, its nature and the type of interactions between the adsorbate and the adsorbent [14, 15, 16].

Based on the listed above problems, the main aim of this work was to evaluate the potential and assess the effectiveness of nitrites adsorption from aqueous solutions on different chars processed from tires and submitted for experiments. In this study, two types of char commercially available produced based on recycled wasted rubber tires were investigated as an adsorbent in order to remove nitrates from water solutions. Zero point of char surface were determined. Equilibrium data were mathematically calculated and modelled using ten adsorption equation models to describe the equilibrium isotherms. Interpreting the obtained results made it possible to assess the validity of using studied chars for water purification.

MATERIALS AND METHODS

Used materials

In this project there have been investigated potential evaluation of equilibrium adsorption isotherms for the removal of nitrates from water solutions using two types of char (CH-1 and CH-2) produced in commercial-scale pyrolysis based on recycled waste rubber tires. Investigated char was manufactured in thermal production process (waste tires pre-processing and pyrolysis) by different companies located in the Central Europe. The companies’ names have been reserved from public dissemination. CH-1 was manufactured by
company X and CH-2 – by company Y. Pyrolysis of waste tires at both companies was carried out using a slow method. Under such conditions, numerous reactions take place in the raw material, such as dehydration, dehydrogenation, isomerization, aromatization and others. Optimal process conditions were selected taking into account: the fragmentation of raw material, temperature, process time, heating rate and composition of the atmosphere. Medium-fragmented chars were processed in for 180 min and 900 °C for CH-1 and 90 min and 800 °C for CH-2. Studied chars were characterized by a high content of elemental carbon (reaching up to 90% for both CH-1 and CH-2) and sulfur (about 2–3%). The major proportion of other basic elements for CH-1 included: Si = 91.6, Zn = 50.5, S = 22.8, Al = 3.7, Fe = 2.6 and for CH-2: Si = 78.1, Zn = 64.5, S = 28.9, Al = 2.1, Fe = 3.7 (all expressed in g/kg). The specific surface area (BET) of CH-1 was 67 m²/g and for CH-2 char reached the value 66 m²/g. The ash content ranged from 8% for CH-1 to 11% for CH-2. It was related to the addition of metal (especially zinc) in the tire manufacturing process and the contamination present on used tires. Both companies processed char in similar oxygen-free atmosphere. All used chemicals - sodium hydroxide (NaOH), nitric acid (HNO₃), potassium nitrate (KNO₃), sodium nitrate (NaNO₃) were supplied in analytical grade.

**Used NO₃ determination method**

Determination of nitrates concentration were measured using laboratory UV-Vis spectrophotometer (UV-Vis model DR 5000 HACH LANGE according to reference method: SM 4500-NO₃-B) selecting program 355 N, Nitrate HR and 10 mL of sample. In brief, cadmium metal reduces nitrates in the sample to nitrite. The nitrite ion reacts in an acidic medium with sulfanilic acid to form an intermediate diazonium salt. The salt couples with gentisic acid to form an amber colored solution. Test results are measured at 500 nm [17].

**Experimental studies**

**Zero point of charge determination of CH-1 and CH-2 chars**

In order to determine zero point of charge (PZC) of the studied tire chars the suspension method was used which consist heterogeneous solution in the form of a suspension of solid particles (char) in a liquid dispersing these particles [18]. In order to do so, a total of 0.5 g of tire chars (CH-1 and CH-2) and 50 mL of 0.1 M NaNO₃ (to maintain ionic strength) were weighed (using laboratory scale: model DV314CM OHAUS ± 0.1 mg Discovery Analytical, Parsippany, NJ, United States) into ten flasks with a capacity of 100 mL. Using nitric acid (0.1M HNO₃) and sodium hydroxide (0.1M NaOH) the selected pH values were adjusted and obtained approximately 2; 3; 4; 5; 6; 7; 8; 9; 10 and 11 (pHₗ is the initial pH) using a magnetic stirrer (RCT basic IKA) until pH was stabilized with an accuracy of two decimal places at room temperature. Measurement of pH was conducted using a pH meter FiveEasy Plus FEP20 with combined glass LE438 electrode (METTLER TOLEDO, Zurich, Switzerland), according to the PN-90/C-045400/01 standard. Before pH determination, the electrode was calibrated using buffers (pH 4, 7 and 10) and the readings were taken with an accuracy of two decimal places. The samples were stirred for 24 h in orbital mechanical shaker (WL-2000 JW Electronic, Warsaw, Poland) at 120 rpm, then the final pH of the samples (pHₗ is the final pH after 24 h of stirring) were measured again.

**Adsorption equilibrium studies**

Derived chars from rubber waste tire were investigated towards nitrate ions removal from water solutions. In order to determine of the sorption isotherms, experimental studies were performed under batch conditions additionally using orbital laboratory shaker (Elektron, Parsippany, NJ, United States) into ten flasks with a capacity of 100 mL. Using nitric acid (0.1M HNO₃) and sodium hydroxide (0.1M NaOH) the selected pH values were adjusted and obtained approximately 2; 3; 4; 5; 6; 7; 8; 9; 10 and 11 (pHₗ is the initial pH) using a magnetic stirrer (RCT basic IKA) until pH was stabilized with an accuracy of two decimal places at room temperature. The stock nitrate solution with initial concentration 132.86 mgNO₃/L (after conversion to nitrate ion 30.00 mgN-NO₃/L) was prepared by dissolving 0.2166 g of KNO₃ using a laboratory scale in 1L of highly purified water (0.065 μS/cm SolPure-7, Bielsko-Biala, Poland). After the mixture was stirred for 10 min at room temperature, its initial concentration was measured using laboratory spectrophotometer (UV-Vis model DR 5000 HACH LANGE, reference method: SM 4500-NO₃-B). The required initial concentrations of used nitrate solutions were prepared by several dilutions in order to obtain
RESULTS AND DISCUSSION

Zero point of charge of CH-1 and CH-2 chars

In this paper we describe research on evaluation of the potential and additionally assess the effectiveness of nitrates adsorption from aqueous solutions on different chars processed from tires submitted for experiments. Additionally zero point of charge (PZC) determination of CH-1 and CH-2 chars for both types of studied chars was assessed. PZC was determined using suspension method. The method consist heterogeneous solution in the form of a suspension of solid particles (char) in a liquid dispersing these particles. The zero point of charge is the point at which the number of positively charged groups is equal to the concentration of negatively charged groups. However, this does not mean that the surface has no charge, but it does mean that the surface charge components become zero under given conditions.

Based on the obtained experimentally data (Table 1), a graphs showed in Figure 2, in which the point of intersection of the data for a given material surface (char) with the X axis represents the PZC and that is the pH value at which this surface has a neutral charge [21, 17]. PZC was obtained from the plot of ΔpH = pHf – pHi against pHi. In the view of the fact that pH regulates the degree of ionization of basic and acidic compounds in the adsorbate solution, it also determines the adsorption efficiency [22]. Therefore, it may affect the increase or decrease of the adsorption degree and that is attributed to the change in the charge of the adsorbent surface with the change in the pH value [23, 24, 25].

The pH of solution from which adsorption occurs may influence the extent of adsorption. pH affects adsorption in that it governs the degree of ionization of the acidic and basic compounds
Therefore in general, initial pH value may increase or decrease the uptake and this is attributed to the change of the charge of the adsorbent surface with the change in pH value [15]. The surface of studied material adsorb anions only if it has positive charge at solution pH values less than the PZC. Such situation occurs when an acidic solution promotes protonation of surface hydroxyl groups and resulting in positively surface charging. Whereas, at solution pH > PZC of material surface will have negative charge therefore opposite trend is observed and such surface adsorb cations and that is attributed to the ionization of acidic groups, mostly phenolic, carboxylic

![Figure 2. Plots of ΔpH against pH\textsubscript{i} for PZC suspension method for 0.1M NaNO\textsubscript{3} for CH-1 (blue) and CH-2 (orange) chars](image)

<table>
<thead>
<tr>
<th>pH\textsubscript{i}</th>
<th>pH\textsubscript{f}</th>
<th>Δ pH</th>
<th>pH\textsubscript{i}</th>
<th>pH\textsubscript{f}</th>
<th>Δ pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.15</td>
<td>2.44</td>
<td>0.29</td>
<td>2.09</td>
<td>2.34</td>
<td>0.25</td>
</tr>
<tr>
<td>3.10</td>
<td>6.31</td>
<td>3.21</td>
<td>3.11</td>
<td>5.73</td>
<td>2.62</td>
</tr>
<tr>
<td>4.14</td>
<td>7.16</td>
<td>3.02</td>
<td>4.02</td>
<td>6.45</td>
<td>2.43</td>
</tr>
<tr>
<td>4.92</td>
<td>7.54</td>
<td>2.62</td>
<td>4.99</td>
<td>6.76</td>
<td>1.77</td>
</tr>
<tr>
<td>6.10</td>
<td>7.77</td>
<td>1.67</td>
<td>6.09</td>
<td>7.01</td>
<td>0.92</td>
</tr>
<tr>
<td>6.98</td>
<td>7.88</td>
<td>0.90</td>
<td>7.11</td>
<td>7.13</td>
<td>0.02</td>
</tr>
<tr>
<td>8.06</td>
<td>7.98</td>
<td>-0.08</td>
<td>8.08</td>
<td>7.25</td>
<td>-0.83</td>
</tr>
<tr>
<td>9.10</td>
<td>8.24</td>
<td>-0.86</td>
<td>8.96</td>
<td>7.37</td>
<td>-1.59</td>
</tr>
<tr>
<td>9.87</td>
<td>8.63</td>
<td>-1.24</td>
<td>9.80</td>
<td>7.46</td>
<td>-2.34</td>
</tr>
<tr>
<td>10.96</td>
<td>8.64</td>
<td>-2.32</td>
<td>10.98</td>
<td>10.22</td>
<td>-0.76</td>
</tr>
</tbody>
</table>

Table 1. The pH values calculated form the ΔpH = pH\textsubscript{f} − pH\textsubscript{i} expression for CH-1 and CH-2 chars.
and hydroxyl groups [26, 27, 28]. Taking into account the possibility of forming hydrogen bonds and electrostatic adsorbent-adsorbate interactions, the NO₃ anions are more strongly adsorbed by materials with a positively charged surface. In this study CH-1 char indicated higher tendency to absorb NO₃ anions (pH_PZC = 8.06 and solution pH was approximately 7.0) compared to CH-2 char (pH_PZC = 7.11) and that was confirmed in equilibrium studies, presented below.

**Table 2. Mathematical isotherm equations of used for modelling of adsorption equilibrium**

<table>
<thead>
<tr>
<th>Isotherm name</th>
<th>Abb.</th>
<th>Equation formula</th>
<th>Eq. no</th>
<th>Isotherm name</th>
<th>Abb.</th>
<th>Equation formula</th>
<th>Eq. no</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>L</td>
<td>( q_e = \frac{q_mK_Ce}{1 + K_Ce} )</td>
<td>(1)</td>
<td>Freundlich</td>
<td>F</td>
<td>( q_e = \frac{1}{K_Ce} )</td>
<td>(6)</td>
</tr>
<tr>
<td>Toth</td>
<td>T</td>
<td>( q_e = \frac{q_mK_Ce}{(1 + (K_Ce)^n)^{\frac{1}{n}}} )</td>
<td>(2)</td>
<td>Redlich-Peterson</td>
<td>R-Pet</td>
<td>( q_e = \frac{q_mK_Ce}{1 + K_Ce} )</td>
<td>(7)</td>
</tr>
<tr>
<td>Dubinin-Radushkevich</td>
<td>D-R</td>
<td>( \log q_e = -n(\log(K \cdot C_e)) + \log q_m )</td>
<td>(3)</td>
<td>Radke-Prausnitz</td>
<td>R-Pr</td>
<td>( q_e = \frac{q_mK_Ce}{(1 + K_Ce)^n} )</td>
<td>(8)</td>
</tr>
<tr>
<td>Fritz-Schlunder</td>
<td>F-S</td>
<td>( q_e = \frac{q_mK_Ce^\nu}{1 + K_Ce^\nu} )</td>
<td>(4)</td>
<td>Langmuir-Freundlich</td>
<td>L-F</td>
<td>( q_e = q_m(K_Ce)^n )</td>
<td>(9)</td>
</tr>
<tr>
<td>Marczewski-Jaroniec</td>
<td>M-J</td>
<td>( q_e = \frac{q_mK_Ce}{1 + (K_Ce)^n} )</td>
<td>(5)</td>
<td>Bi-Langmuir</td>
<td>Bi-L</td>
<td>( q_e = \frac{q_mK_Ce}{1 + K_Ce} + \frac{q_mK_Ce}{1 + K_Ce} )</td>
<td>(10)</td>
</tr>
</tbody>
</table>

The efficiency percentage of removed nitrates, was obtained according to Eq. 12 and shown in Figure 4.

\[
\text{% removal efficiency} = \left( \frac{C_0 - C_f}{C_0} \right) \times 100 \tag{12}
\]

where: \( C_0 \) – the initial NO₃ concentration in solution (mg/L); \( C_f \) – the final (equilibrium) NO₃ concentration in aqueous solution (mg/L).

The adsorption capacity \( (q_{mod}) \) and the adsorption equilibrium constant \( (K) \) determining heterogeneity of sorbent surface \( (n) \) in equations were key parameters of considered isotherms. Different 10 commonly known mathematical equations of isotherms were used (Table 2, Eq. 1–10) for calculation. The original form of nonlinear isotherm equations was used to model the experimental data for modeling and to maintain the integrity of experimental data (estimated modeling results). The rationale for using nonlinear equations is to avoid errors that may result from using a linearized form of equations that have already been transformed, which in turn leads to errors [29, 30]. Using math computer software Maplesoft (version 16.2), a models fitting were made using a nonlinear regression method based on the Levenberg–Marquardt algorithm [31] applied to minimize the sum of the squares of the error (SSE) function (Eq. 13).

\[
SSE = \sum_{i=1}^{N}(q_e - q_{emod})^2 \tag{13}
\]

where: \( N \) – the experimental points (samples) number; \( q_e \) – the NO₃ equilibrium
Adsorption isotherms constants and error functions for examined chars CH-1 and CH-2 are presented in Table 3, respectively. The fitting quality of the experimental data to the modelled isotherms was assessed based on the analysis of the modeling results, namely on the basis of the value of sorption capacity \((q_{\text{emod}})\) obtained in the calculations, which was closest to the maximum adsorption capacity \((q_{\text{emal}})\) obtained in the experimental part. Additionally, the adequacy and quality of model in relation to the experimental data were assessed and evaluated based on error functions: Fisher test \((F)\) – evaluated by achieved highest value, mean error – evaluated by calculated highest value, \((ME)\) and approximation of the standard deviation – evaluated as obtained lowest value \((\sigma)\).

\[
F = \frac{(N-1)\sum_{i=1}^{N}(q_{e,i} - \frac{1}{N}\sum_{i=1}^{N}q_{e,i})^2}{(N-1)\sum_{i=1}^{N}(q_{e,i} - q_{\text{mod},i})^2}
\]

\[
\sigma = \sqrt{\frac{1}{N} \sum_{i=1}^{N}(q_{e,i} - q_{\text{mod},i})^2}
\]

\[
ME = \frac{1}{N} \sum_{i=1}^{N} \left| q_{e,i} - q_{\text{mod},i} \right|
\]

All calculated empirical model (Eq. 1–10) parameters and determination of error functions values (Eq. 14–16) are tabulated in Table 3. Figure 3 shows plot comparing experimental data (dot line) to selected best fitted isotherms for both CH-1 and CH-2 chars (line), respectively.

**Table 3.** Equilibrium isotherm parameters for CH-1 (grey rows) and CH-2 (white rows) chars

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>K</th>
<th>(q_{\text{emal}}) [mg/g]</th>
<th>n</th>
<th>F</th>
<th>ME</th>
<th>(\sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>0.047</td>
<td>12.932</td>
<td>-</td>
<td>24.014</td>
<td>619.654</td>
<td>0.672</td>
</tr>
<tr>
<td></td>
<td>0.0116</td>
<td>11.161</td>
<td>-</td>
<td>22.714</td>
<td>273.577</td>
<td>0.473</td>
</tr>
<tr>
<td>F</td>
<td>1.464</td>
<td>-</td>
<td>2.196</td>
<td>6.378</td>
<td>995.012</td>
<td>1.305</td>
</tr>
<tr>
<td></td>
<td>0.290</td>
<td>-</td>
<td>1.515</td>
<td>11.963</td>
<td>440.302</td>
<td>0.652</td>
</tr>
<tr>
<td>T</td>
<td>4.111</td>
<td>1.05E + 08</td>
<td>0.036</td>
<td>6.453</td>
<td>970.728</td>
<td>1.297</td>
</tr>
<tr>
<td></td>
<td>0.0001</td>
<td>1.05E + 08</td>
<td>0.049</td>
<td>9.891</td>
<td>574.216</td>
<td>0.717</td>
</tr>
<tr>
<td>R-Pet</td>
<td>0.005</td>
<td>77.032</td>
<td>1.396</td>
<td>44.884</td>
<td>489.541</td>
<td>0.491</td>
</tr>
<tr>
<td></td>
<td>0.0002</td>
<td>619.491</td>
<td>1.823</td>
<td>42.768</td>
<td>223.746</td>
<td>0.345</td>
</tr>
<tr>
<td>D-R</td>
<td>0.013</td>
<td>9.794</td>
<td>0.517</td>
<td>73.150</td>
<td>323.889</td>
<td>0.385</td>
</tr>
<tr>
<td></td>
<td>0.0085</td>
<td>6.011</td>
<td>0.934</td>
<td>88.664</td>
<td>14.844</td>
<td>0.240</td>
</tr>
<tr>
<td>R-Pr</td>
<td>0.012</td>
<td>40.944</td>
<td>2.043</td>
<td>37.403</td>
<td>528.020</td>
<td>0.538</td>
</tr>
<tr>
<td></td>
<td>0.0004</td>
<td>284.129</td>
<td>16.924</td>
<td>29.769</td>
<td>256.466</td>
<td>0.413</td>
</tr>
<tr>
<td>F-S</td>
<td>0.012</td>
<td>7.945</td>
<td>(n_1 = 1.843, n_2 = 1.791)</td>
<td>125.598</td>
<td>233.932</td>
<td>0.294</td>
</tr>
<tr>
<td></td>
<td>0.0003</td>
<td>78.069</td>
<td>(n_1 = 1.492, n_2 = 1.975)</td>
<td>92.525</td>
<td>72.226</td>
<td>0.234</td>
</tr>
<tr>
<td>L-F</td>
<td>0.075</td>
<td>10.056</td>
<td>1.707</td>
<td>124.550</td>
<td>255.315</td>
<td>0.295</td>
</tr>
<tr>
<td></td>
<td>0.028</td>
<td>6.754</td>
<td>1.911</td>
<td>68.868</td>
<td>37.957</td>
<td>0.272</td>
</tr>
<tr>
<td>M-J</td>
<td>0.086</td>
<td>9.014</td>
<td>(m = 1.791, n = 1.843)</td>
<td>125.598</td>
<td>233.902</td>
<td>0.294</td>
</tr>
<tr>
<td></td>
<td>231.709</td>
<td>0.008</td>
<td>(m = 2.880, n = 3.536)</td>
<td>10.122</td>
<td>440.301</td>
<td>0.709</td>
</tr>
<tr>
<td>Bi-L</td>
<td>(K_1 = 0.047, K_2 = 0.048)</td>
<td>(q_e = 7.323, q_e = 5.610)</td>
<td>-</td>
<td>22.413</td>
<td>619.654</td>
<td>0.696</td>
</tr>
<tr>
<td></td>
<td>(K_1 = 0.012, K_2 = 0.012)</td>
<td>(q_e = 5.581, q_e = 5.581)</td>
<td>-</td>
<td>19.222</td>
<td>273.577</td>
<td>0.515</td>
</tr>
</tbody>
</table>

**Note:** \(K\) – the equilibrium constant (dimensionless); \(q_{\text{emal}}\) – concentration of NO\(_2\) in the sorbent at equilibrium calculated from model (mg/g); \(n\) and \(m\) – constants determining heterogeneity of adsorbent surface (-); \(ME\) – mean error; \(F\) – Fisher test; \(\sigma\) – approximation of the standard deviation. For distinction: CH-1 char – obtained data in grey rows in the above table \((q_{\text{emal}}\) from experiment 10.07 mg/g); CH-2 char – obtained data in white rows in the above table \((q_{\text{emal}}\) from experiment 5.87 mg/g).
Analyzing the obtained experimental data and its correlation to estimated values, best correlation were indicated by the three-parameters isotherm equations analyzed, namely L-F and D-R isotherms. Obtained results indicate that the adsorption of NO$_3^-$ on CH-1 and CH-2 char sorbents occurs including both physical adsorption and chemical adsorption. Fundamentally, the surface interactions take place through intermolecular Van der Waal forces and induced dipole interactions and chemical reactions which are related to the saturation of active sites on the adsorbent surface occur between the adsorbate and the adsorbent.

Considering NO$_3^-$ sorption onto CH-1 char, the best fit of the L-F model (Eq. 9) is evidenced by error functions $\sigma = 0.295$, $ME = 255.315$ and $F = 124.550$. Another parameter collaborating L-F model is the calculated value of the maximum achievable adsorption capacity ($q_{\text{mod}} = 10.06$ mg/g) resulting from mathematical modelling which is the closest to $q_{\text{emax}} = 10.07$ g/mg.

Whereas according to CH-2 char, the D-R isotherm practically, was most consistent with the experimental conditions including error functions values ($ME = 14.844$, $F = 88.664$, and $\sigma = 0.240$) and adsorption capacity parameter $q_{\text{emax}} = 5.87$ mg/g close to $q_{\text{mod}} = 6.01$ mg/g. However, both correlation results for D-R and L-F isotherm regarding to CH-2 char are very similar. Namely, estimated adsorption capacity parameter resulting from mathematical modelling for L-F model was $q_{\text{mod}} = 6.75$ mg/g and error functions values $ME = 37.957$, $F = 68.868$, and $\sigma = 0.272$, respectively. The last criterion of best L-F model correlation to experimental data was a visual assessment of the course of isotherm modeled as a measure of fit based on the graphs prepared, for both considered chars. Therefore, according to L-F isotherm assumptions it can be assumed that most likely the adsorption mechanism indicate both monolayer and multilayer adsorption effects of adsorbent by adsorbate molecules. The L-F isotherm was created by combining L
and F isotherms, and its purpose was to create the possibility of predicting adsorption in heterogeneous systems. In addition, L-F isotherm also solved the problem of the limitation of the rising adsorbate concentration, related to the original form of the F isotherm. In the view of that fact, at high adsorbate concentrations L-F isotherm predicts maximum coverage of the adsorbent surface and at low adsorbate concentrations reduces to the Freundlich isotherm [32]. Therefore, the interpretation of parameters for the most suitable models is another crucial step in accurately understanding the nature of adsorption on char surface. As the investigation of the $NO_3$ adsorption mechanism revealed that Freundlich-Langmuir and D-R models demonstrate a high degree of precision in predicting the adsorption behaviour of $NO_3$ ions on the CH-1 and CH-2 surface, thus confirming most probably the occurrence of multilayer sorption on the energetically heterogeneous surface.

Figure 4 shows percentage removal of nitrates efficiency for CH-1 and CH-2 chars. According to the obtained calculations based on experimental studies, the highest percentage of $NO_3$ removal efficiency was attained for the initial concentration of 26.44 mg/L, which was 80.74% for CH-1, whereas for CH-2 the maximum percentage value is lower and obtained 50.00% for the initial concentration 53.2 mg/L. Comparing obtained results for both series, the highest percentage of $NO_3$ removal efficiency was for CH-1 achieved for $NO_3$ initial concentration range from 26.44 to 66.55 mg/L, respectively reaching values in the range of from 80.74 to 78.7% (including eight consecutive experimental points), while for CH-2 char in the range of 26.74–53.20 mg/L, efficiency trend obtained values were from 47.0 to 49.99% (including three consecutive experimental points). The difference in the highest percentage of $NO_3$ removal efficiency between two examined chars was 30% obtained for CH-1.

**CONCLUSION**

In this work, the two types of chars CH-1 and CH-2 derived from used tires obtained through commercial-scale pyrolysis for $NO_3$ capture application have been studied towards $NO_3$ removal form water solutions for the first time. Conducted studies indicated that suspension method was suitable to determine the PZC for investigated chars. CH-2 char with close to neutral pH$_{PZC}$ (7.11) most probably could be used to remove both cation or anion species from aqueous solutions depend on pH on tested solution, whereas for CH-1 pH$_{PZC}$ (8.06) indicated slightly higher tendency to absorb anions which was confirmed in experimental studies.

Adsorption studies showed that the Freundlich-Langmuir isotherm may be dependable method for predicting $NO_3$ adsorption mechanism for both CH-1 and CH-2 chars. This conclusion was based on calculated error functions and the dependency between experimentally established adsorption capacity parameter ($q_{max} = 10.07$ mg/g and $q_{mod} = 5.87$ mg/g) to estimated adsorption capacity ($q_{max} = 10.07$ g/mg and $q_{mod} = 6.01$ mg/g), for CH-1 char and CH-2 char respectively.

This investigation revealed that L-F and D-R models demonstrated a high degree of precision in predicting the $NO_3$ ions adsorption behaviour onto CH-1 and CH-2 char surface, and confirming the occurrence of multilayer sorption on the heterogeneous char surface.
In conclusion, this study investigated the potential for chars obtained from the industrial-scale pyrolysis, which yields a valuable product in the form of char which may be used as an adsorbent (eg. to remove NO$_3$ ions form water). However, both materials require further extended studies in batch and column experiments to assess their efficiency in different conditions to establish most optimal removal capacity towards NO$_3$ ions. Thus further studies and interpretation may be necessary to fully understand the relationship between adsorbate and adsorbent in this context. In overall, this research may be assigned to sustainable waste management practices for repurposing globally discarded wasted tires.

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