AST RJ Advances in Science and Technology Research Journal

Advances in Science and Technology Research Journal 2024, 18(3), 246–256
https://doi.org/10.12913/22998624/186760
ISSN 2299-8624, License CC-BY 4.0

Received: 2024.03.27
Accepted: 2024.04.08
Published: 2024.04.20

Adsorption Equilibrium Studies on the Example of Nitrate Removal onto Char Produced from Waste Tires

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ABSTRACT

There have been investigated potential evaluation of equilibrium adsorption isotherm 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. Liquid phase adsorption studies were performed under batch conditions and maximum adsorption capacity was determined. Equilibrium data were mathematically modelled using two-parameters Langmuir, Freundlich, three-parameters Redlich-Peterson, Toth, Dubinin-Radushkevich, Radke-Praushnitz, combined Langmuir-Freundlich and four-parameters Fritz-Schlunder, Marczewski-Jaroniec, Bi-Langmuir adsorption models. Obtained results revealed the potential use of the studied char adsorbents for nitrates removal from aqueous media (the maximum adsorption capacity at equilibrium 10.07 mg/g, have been achieved for CH-1 char). The Langmuir-Freundlich isotherm had the best fit for the adsorption experimental data over the whole concentration range. The highest percentage of NO_3 removal efficiency onto CH-1 char achieved in NO_3 initial concentration range from 26.44 to 66.55mg/L reaching values in the range of from 80.74 to 78.7%.

Keywords: char, nitrates, sorption, waste tires, isotherm, equilibrium.

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, masterbatches, 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 nitrates 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 m^2/g and for CH-2 char reached the value 66 m^2/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 (HNO_3), potassium nitrate (KNO_3), sodium nitrate ($NaNO_3$) were supplied in analytical grade.

Used NO_3 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-NO_3-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 $NaNO_3$ (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 HNO_3) 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 (pH_i 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 (pH_f 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 (Elektronic model WL-2000 JW, Warsaw, Poland) and optimization of the experimental conditions like contact time for 24 h and stirring with a constant speed 110 rpm at room temperature. The stock nitrate solution with initial concentration 132.86 $mgNO_3/L$ (after conversion to nitrate ion 30.00 mgN-NO_3/L) was prepared by dissolving 0.2166 g of KNO_3 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-NO_3-B). The required initial concentrations of used nitrate solutions were prepared by several dilutions in order to obtain series of samples with initial concentration values for CH-1 (112.5; 93.0; 75.3; 46.5; 35.4; 36.3; 26.6; 21.3; 20.8; 18.2; 17.7; 14.2; 11.5; 8.4; 8.0; 5.3; 5.1; 3.1; 2.7 mgNO$_3$/L) and CH-2 (120.9; 108.9; 97.4; 74.4; 65.1; 56.7; 48.7; 39.9; 33.2; 26.6; 20.8; 14.2; 8.9; 5.8; 2.6 mgNO$_3$/L) using previously prepared stock solution. The experiment was carried out as follows: two series of 0.5g sample doses for each CH-1 and CH-2 char adsorbent were shaken for 24 hours at room temperature in the volume of 50 mL of decreasing initial solutions. All samples were agitated for predetermined times until equilibrium was attained.

In the next step, the samples were left to settle (sedimentation process) for 60 minutes. Subsequently, the samples were filtered using 0.2 μm cellulose filters (MCE, Whatman, Maidstone, UK) to separate the solid phase from the liquid phase. This allowed for the determination of the nitrates content (concentration) in the filtered liquid phase (adsorbat) using the above described method for each sample and given as mean values from three measurements. Figure 1 shows schematically the subsequent stages of laboratory tests.

Expressing the relationship between adsorbate concentration present in the surrounding phase (pollution removed form water solution e.g. nitrate ions) and adsorbate adsorbed concentration on the surface of the adsorbent at equilibrium (per unit mass of adsorbent, e.g. chars) and constant temperature is known and called as the adsorption isotherm. All adsorption isotherm assumes that every adsorption active site is equivalent and does independent of either or not adjacent sites are occupied [20]. All conducted tests and examinations were repeated 3 times to confirm the reliability of the obtained results. The data presented in the paper are the arithmetic average of the performed repetitions.

RESULTS AND DISSCUSION

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 $\Delta pH = pH_f - pH_i$ against pH_i. 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

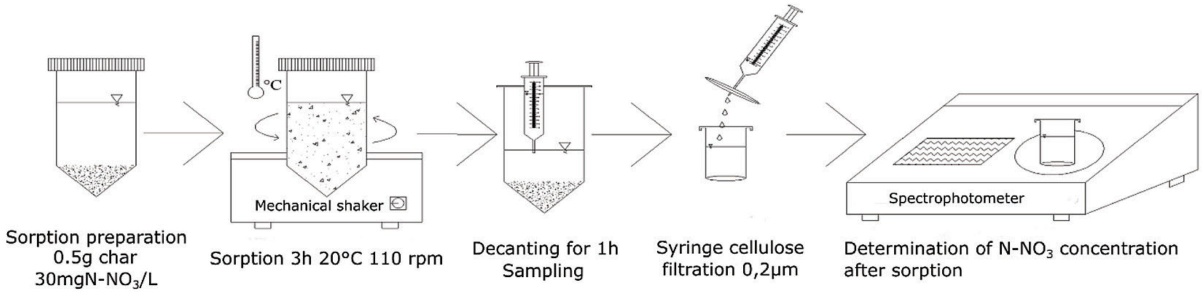

Figure 1. Scheme of analysed batch adsorption system - the subsequent major steps of conducted experiments on the NO$_3$ adsorption onto tires char form water solutions (self-made drawing - modified) [19]

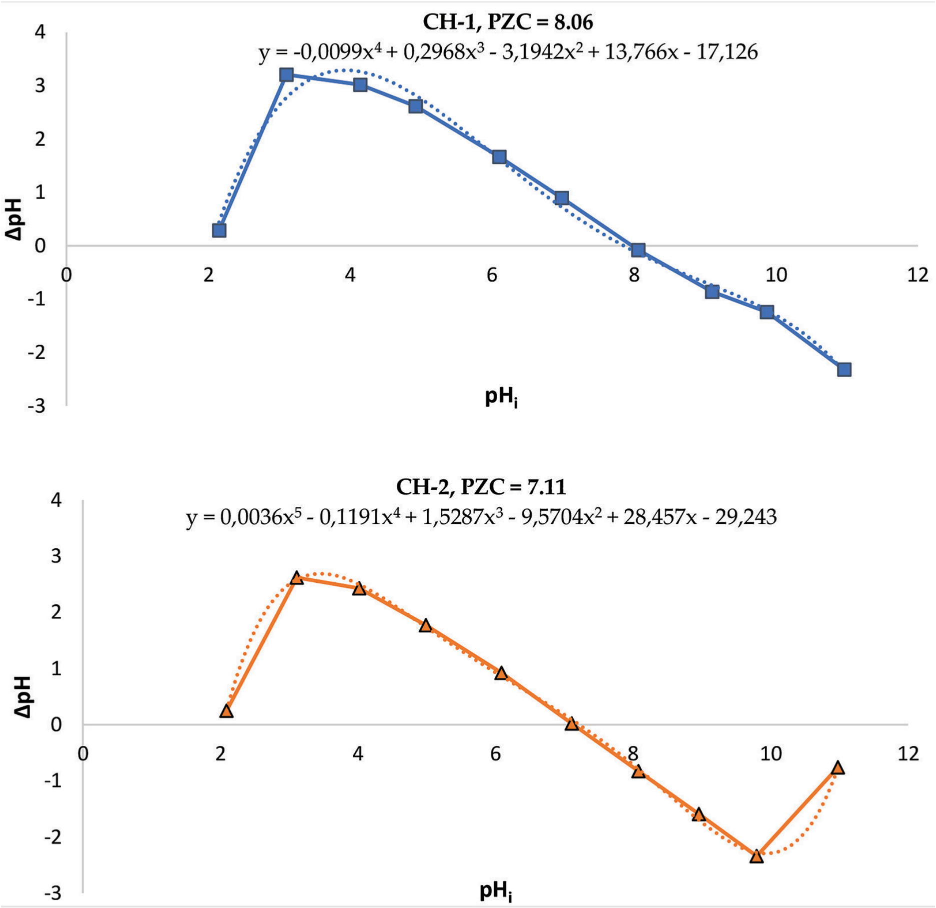

Figure 2. Plots of ΔpH against pH_i for PZC suspension method for 0.1M; $NaNO_3$ for CH-1 (blue) and CH-2 (orange) chars

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

Table 1. The pH values calculated form the $\Delta pH = pH_f - pH_i$ expression for CH-1 and CH-2 chars

CH-1			CH-2		
pH_i	pH_f	Δ pH	pH_i	pH_f	Δ pH
2.15	2.44	0.29	2.09	2.34	0.25
3.10	6.31	3.21	3.11	5.73	2.62
4.14	7.16	3.02	4.02	6.45	2.43
4.92	7.54	2.62	4.99	6.76	1.77
6.10	7.77	1.67	6.09	7.01	0.92
6.98	7.88	0.90	7.11	7.13	0.02
8.06	7.98	-0.08	8.08	7.25	-0.83
9.10	8.24	-0.86	8.96	7.37	-1.59
9.87	8.63	-1.24	9.80	7.46	-2.34
10.96	8.64	-2.32	10.98	10.22	-0.76

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

Isotherm name	Abb.	Equation formula	Eq. no	Isotherm name	Abb.	Equation formula	Eq. no
Langmuir	L	$q_e = \frac{q_m K C_e}{1 + K C_e}$	(1)	Freundlich	F	$q_e = K C_e^{\frac{1}{n}}$	(6)
Toth	T	$q_e = \frac{q_m K C_e}{(1 + (K C_e)^n)^{1/n}}$	(2)	Redlich-Peterson	R-Pet	$q_e = \frac{q_m K C_e}{1 + K C_e^n}$	(7)
Dubinin-Radushkevich	D-R	$log\, q_e = -n(log^2(K \cdot C_e)) + log\, q_m$	(3)	Radke-Praushnitz	R-Pr	$q_e = \frac{q_m K C_e}{(1 + K C_e)^n}$	(8)
Fritz-Schlunder	F-S	$q_e = \frac{q_m K C_e^{n_1}}{1 + K C_e^{n_2}}$	(4)	Langmuir-Freundlih	L-F	$q_e = \frac{q_m (K C_e)^n}{1 + (K C_e)^n}$	(9)
Marczewski-Jaroniec	M-J	$q_e = \frac{q_m (K C_e)^m}{1 + (K C_e)^n}$	(5)	Bi-Langmuir	Bi-L	$q_e = \frac{q_{m.1} K_1 C_e}{1 + K_1 C_e} + \frac{q_{m.2} K_2 C_e}{1 + K_2 C_e}$	(10)

and hydroxyl groups [26, 27, 28]. Taking into account the possibility of forming hydrogen bonds and electrostatic adsorbent-adsorbate interactions, the NO_3 anions are more strongly adsorbed by materials with a positively charged surface. In this study CH-1 char indicated higher tendency to absorb NO_3 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.

Isotherm parameters determination – modelling part

Experiments on adsorption and determination of the relationship between sorbed and aqueous concentration of NO_3 ions onto CH-1 and CH-2 chars were implemented under bath conditions. Different 10 adsorption isotherms were selected based on their possible ability to accurately predict NO_3 adsorption (Langmuir, Bi-Langmuir, Freundlich, Langmuir-Freundlich, Dubinin-Radushkewich, Toth, Redlich-Peterson, Radke-Praushnitz, Fritz-Schlunder and Marczewski-Jaroniec) and elaborated based on the calculated results. The non-linear form of isotherm equations (Eq. 1–10) are presented in the Table 2. Using mass balance equation (Eq. 11) values of the concentration of NO_3 adsorbate ions in the solid phase (q_e) were determined to perform adsorption isotherms. Considered isotherms let to interpret relation between the changes in equilibrium concentration (C_e) of nitrate ions in the solution (liquid phase) and the equilibrium adsorption capacity (q_e) of nitrate ions in the adsorbent (solid phase) at particular adsorption equilibrium.

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \tag{11}$$

where: q_e – equilibrium concentration of adsorbate (NO_3) in the adsorber, (mg/g); C_0 – initial adsorbate concentration in water solution, (mg/L); C_e – equilibrium adsorbate concentrations in the aqueous solution, (mg/L); V – NO_3 solution volume, (L); m – mass of CH-1 and CH-2 adsorbent used, respectively (g).

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

$$\%\, removal\ efficiency = \frac{(C_0 - C_f) \cdot 100}{C_0} \tag{12}$$

where: C_0 – the initial NO_3 concentration in solution (mg/L); C_f – the final (equilibrium) NO_3 concentration in aqueous solution (mg/L).

The adsorption capacity (q_{emod}) 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).

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

where: N – the experimental points (samples) number; q_e – the NO_3 equilibrium concentration in the adsorbent – solid phase, (mg/g); $q_{e\,mod}$ – equilibrium concentration of NO_3 in the adsorbent obtained (calculated) from the model, (mg/g).

Adsorption isotherms constants and error functions for exanimated 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_{emod}) obtained in the calculations, which was closest to the maximum adsorption capacity (q_{emax}) 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 (σ).

$$F = \frac{(N-l)\sum_{i=1}^{N}\left(q_{e,i}-\frac{1}{N}\sum_{i=1}^{N}q_{e,i}\right)^2}{(N-1)\sum_{i=1}^{N}\left(q_{e,i}-q_{mod,i}\right)^2} \tag{14}$$

$$\sigma = \sqrt{\frac{1}{N-l}\sum_{i=1}^{N}\left(q_{e,i}-q_{mod,i}\right)^2} \tag{15}$$

$$ME = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{q_{e,i}-q_{mod,i}}{q_{e,i}}\right| \tag{16}$$

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

Isotherm	*K*	q_{emod} [mg/g]	*n*	*F*	ME	*σ*
L	0.047	12.932	-	24.014	619.654	0.672
	0.0116	11.161	-	22.714	273.577	0.473
F	1.464	-	2.196	6.378	995.012	1.305
	0.290	-	1.515	11.963	440.302	0.652
T	4.111	1.05E + 08	0.036	6.453	970.728	1.297
	0.0001	1.05E + 08	0.049	9.891	574.216	0.717
R-Pet	0.005	77.032	1.396	44.884	489.541	0.491
	0.0002	619.491	1.823	42.768	223.746	0.345
D-R	0.013	9.794	0.517	73.150	323.889	0.385
	0.0085	6.011	0.934	88.664	14.844	0.240
R-Pr	0.012	40.944	2.043	37.403	528.020	0.538
	0.0004	284.129	16.924	29.769	256.466	0.413
F-S	0.012	7.945	n_1 = 1.843, n_2 = 1.791	125.598	233.932	0.294
	0.0003	78.069	n_1 = 1.492, n_2 = 1.975	92.525	72.226	0.234
L-F	0.075	10.056	1.707	124.550	255.315	0.295
	0.028	6.754	1.911	68.868	37.957	0.272
M-J	0.086	9.014	m = 1.791, n = 1.843	125.598	233.902	0.294
	231.709	0.008	m = 2.880, n = 3.536	10.122	440.301	0.709
Bi-L	K_1 = 0.047, K_2 = 0.048	q_1 = 7.323, q_2 = 5.610	-	22.413	619.654	0.696
	K_1 = 0.012, K_2 = 0.012	q_1 = 5.581, q_2 = 5.581	-	19.222	273.577	0.515

Note: *K* – the equilibrium constant (dimensionless); q_{emod} –concentration of NO_3 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; *σ* – approximation of the standard deviation. For distinction: CH-1 char – obtained data in grey rows in the above table (q_{emax} from experiment 10.07 mg/g); CH-2 char – obtained data in white rows in the above table (q_{emax} from experiment 5.87 mg/g).

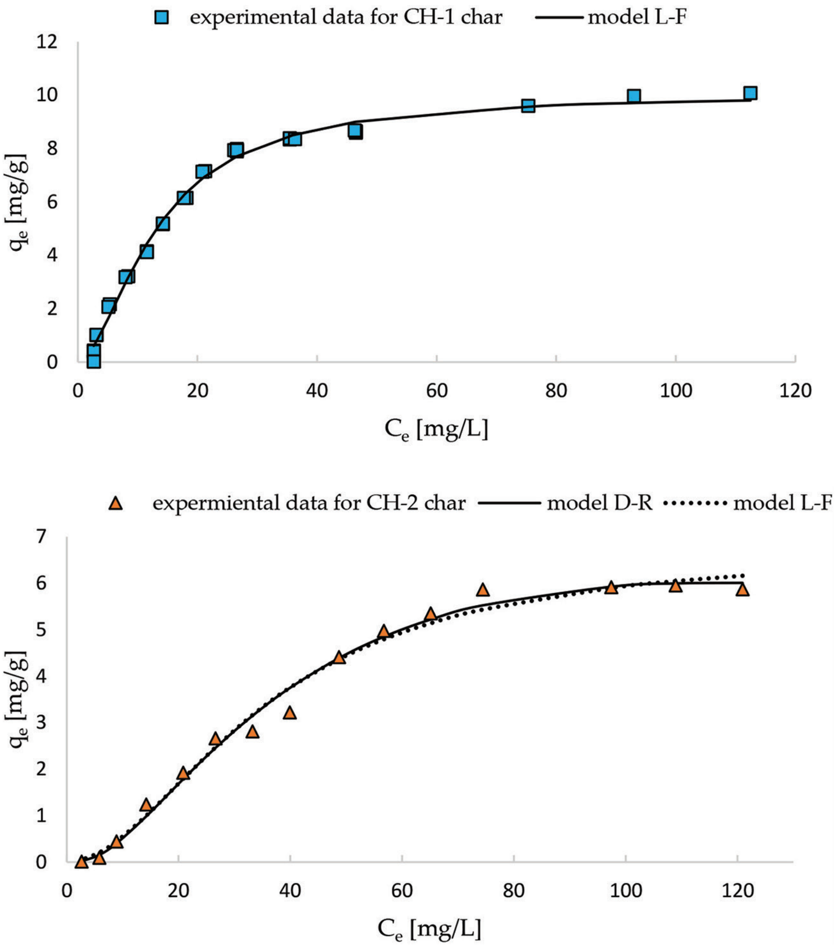

Figure 3. Adsorption isotherms plot of NO_3 on CH-1 and CH-2 chars fitted to the Langmuir-Freundlich nonlinear adsorption model isotherm

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_{emod} = 10.06 mg/g) resulting from mathematical modelling which is the closest to q_{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 σ = 0.240) and adsorption capacity parameter q_{emax} = 5.87 mg/g close to q_{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_{emod} = 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

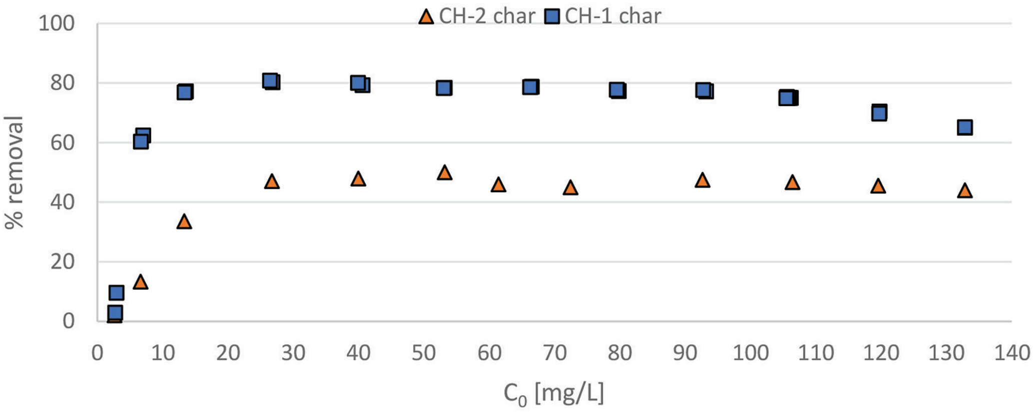

Figure 4. Removal efficiency for CH-1 and CH-2 chars for C_0 form 2.66 to 132.86 mg/L

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 exanimated 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_{emax} = 10.07 mg/g and q_{emax} = 5.87 mg/g) to estimated adsorption capacity (q_{emax} = 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.

Acknowledgements

The research leading to these results has received funding from the commissioned task entitled "VIA CARPATIA Universities of Technology Network named after the President of the Republic of Poland Lech Kaczyński contract no. MEiN/2022/DPI/2578 action entitled "In the neighbourhood – inter-university research internships and study visits".

REFERENCES

1. Hejna, A., Korol, J., Przybysz-Romatowska, M., Zedler, L., Chmielnicki, B., Formela, K. Waste tire rubber as low-cost and environmentally-friendly modifier in thermoset polymers - A review. Waste Management 2020; 108: 106–118. doi:10.1016/j.wasman.2020.04.032.
2. Szatyłowicz, E., Edizsoy, G., Öztürk, O., Yanaşık, I., Siemiończyk, E., Tabor, A., Skoczko, I. Multidimensional Analysis of Air Pollution Measurements Concentration with PM10 and PM2.5 on the Campus of the Bialystok University of Technology Adv. Sci. Technol. Res. J. 2023; 17(3): 226–235. doi:10.12913/22998624/166384.
3. Saleh, T.A., Gupta, V.K. Processing methods, characteristics and adsorption behavior of tire derived carbons: A review. Advances in Colloid and Interface Science 2014; 211: 93–101. doi:10.1016/j.cis.2014.06.006.
4. Mui, E.L.K., Cheung, W.H., McKay, G. Tyre char preparation from waste tyre rubber for dye removal from effluents 2010; 175(1–3): 151–158. doi:10.1016/j.jhazmat.2009.09.142.
5. Dyrektywa Rady (91/676/EWG) z dnia 12 grudnia 1991 r. dotycząca ochrony wód przed zanieczyszczeniami powodowanymi przez azotany pochodzenia rolniczego Dz.U.UE.L.1991.375.1 z dnia 1991.12.31
6. Ustawa z dnia 20 lipca 2017 r. Prawo wodne (Dz. U. 2017, poz. 1566 z późn. zm.)
7. Bhatnagar, A., Kumar, E., Sillanpaa, M., Nitrate removal from water by nano-alumina: characterization and sorption studies. Chem. Eng. L. 2010; 163(3): 317–323.
8. Chow, C.K., Hong, C.B.,. Dietary vitamin E and selenium and toxicity of nitrite and nitrate. Toxicology 2002; 180(2): 195–207.
9. Yukiyoshi, T., Yusuke, Y., Yoshimasa, A., Motoi, M. Effect of two types of adsorption sites of activated carbon fibers on nitrate ion adsorption. Journal of Environmental Management, 2021. doi: 10.1016/j.jenvman.2021.112484.
10. Wettstein, Z.S., Yarid, N.A., Shah, S. "Fatal methaemoglobinemia due to intentional sodium nitrite ingestion". BMJ Case Reports. 2022 15(12): e252954. doi: 10.1136/bcr-2022-252954.
11. Rozporządzenie Ministra Zdrowia z dnia 7 grudnia 2017 r. w sprawie jakości wody przeznaczonej do spożycia przez ludzi, Dz.U RP Poz. 2294 (Regulation of the Minister of Health of December 7, 2017 on the quality of water intended for human consumption; 2294)
12. Skoczko, I., Guminski, R. Tests on the Application of Various Types of Biomass for Activated Carbon Production, J. Ecol. Eng. 2024; 25(1): 285–302. doi: https://doi.org/10.12911/22998993/174223
13. Modrzejewska, Z., Skwarczyńska, A., Zarzycki, R. Process kinetics and equilibrium in Cu2+ sorption in hydrogel chitosan granules, Environmental Engineering III 2010. EID:2-s2.0-85055377531. Part of DOI: 10.1201/b10566
14. Lin, C.-I., Wang, L-H. Rate equations and isotherms for two adsorption models, J. Chin. Inst. Chem. Eng. 2008: 39579–585.
15. Langmuir, I. The adsorption of gases on plane surfaces of glass, mica and platinum, J. Amer. Chem. Soc. 1918; 40: 1361–1403.
16. Dabrowski, A. Adsorption—from theory to practice, Adv. Colloid Interface Sci. 93 (2001) 135–224
17. https://www.manualslib.com/manual/1202264/Hach-Dr2400.html?page=421#manual
18. Kosmulski " Surface charging and points of zero charge", Surfactant science series, CRC. Press/Taylor & Francis Group 2009; 145.
19. Skwarczyńska-Wojsa, A., Puszkarewicz, A. Removal of Acetaminophen from Aqueous Solutions in an Adsorption Process Materials 2024, 17(2): 431. doi: 10.3390/ma17020431.
20. Katal, R., Baei, S.M., Rahmati, H.T., Esfandian, H. Kinetic, isotherm and thermodynamic study of nitrate adsorption from aqueous solution using modified rice husk. 2012; 18(1): 295–302. 10.1016/j.jiec.2011.11.035.

21. Wieland E., Stumm W. Dissolution kinetics of kaolinite in acidic aqueous solutions at 25 °C. 1992; 56(9): 3339–3355. doi:10.1016/0016-7037(92)90382-s.
22. Karaca S., Gürses A., Açıkyıldız M., Ejder M. (Korucu). Adsorption of cationic dye from aqueous solutions by activated carbon. 2008; 115(3): 376–382. doi: 10.1016/j.micromeso.2008.02.008.
23. Bakatula, E.N., Richard, D., Neculita, C.M., Zagury, G.J. Determination of point of zero charge of natural organic materials. Environmental Science and Pollution Research 2018; 25(8): 7823–7833. doi:10.1007/s11356-017-1115-7.
24. Sakurai, K., Ohdate, Y., Kyuma, K.. Comparison of salt titration and potentiometric titration methods for the determination of Zero Point of Charge (ZPC). Soil Science and Plant Nutrition 1988; 34(2), 171–182. doi: 10.1080/00380768.1988.10415671.
25. Emad N. El Qada; Stephen J. Allen; Gavin M. Walker. Adsorption of Methylene Blue onto activated carbon produced from steam activated bituminous coal: A study of equilibrium adsorption isotherm 2006; 124(1–3): 103–110. doi:10.1016/j.cej.2006.08.015.
26. Soco, E., Domon, A., Papciak, D., Michel, M., Pająk, D., Cieniek, B., Azizi, M. Characteristics of Adsorption/Desorption Process on Dolomite Adsorbent in the Copper(II) Removal from Aqueous Solutions. Materials 2023, 16(13): 4648. doi: 10.3390/ma16134648.
27. Cardenas-Peña, A.M., Ibanez, J.G., Vasquez-Medrano, R. Determination of the Point of Zero Charge for Electrocoagulation Precipitates from an Iron Anode. Int. J. Electrochem. Sci. 2012; 7: 6142–6153.
28. Railsback's Some Fundamentals of Mineralogy and Geochemistry. https://railsback.org/Fundamentals/8150PointofZeroCharge05Pt1P.pdf
29. Skwarczynska-Wojsa, A.L., Chacuk, A., Modrzejewska, M., Puszkarewicz, A. Sorption of calcium by chitosan hydrogel: Kinetics and equilibrium. Desalination 2022; 540: 116024. doi: 10.1016/j.desal.2022.116024.
30. Joseph, I.V., Tosheva, L., Miller, G., Doyle, A.M. FAU-Type Zeolite Synthesis from Clays and Its Use for the Simultaneous Adsorption of Five Divalent Metals from Aqueous Solutions, Materials 2021; 14(13): 3738.
31. Marquardt, D.W. An algorithm for last-squares estimation of nonlinear parameter, J. Soc. Indust. Appl. Math 1963; 11(2): 431.
32. Saied Azizian, Setareh Eris, Chapter 6 - Adsorption isotherms and kinetics, Interface Science and Technology 2021; 33: 445–509. doi: 10.1016/B978-0-12-818805-7.00011-4.