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Adsorption of Naphthol Green B on unburned carbon: 2- and 3-parameter linear and non-linear equilibrium modelling☆

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ABSTRACT

The study deals with adsorption of Naphthol Green B on two unburned carbons and the parent coal, from which the UCs have been created in a fluidised-bed power station. Particular attention has been paid to the adsorption equilibrium modelling: experimental data has been analysed using 2-parameter (Langmuir, Freundlich) and 3-parameter (Redlich–Peterson) isotherms – both linear and non-linear regressions have been used for the estimation of the isotherm parameters. In the case of both UCs, the Langmuir isotherm model provides the worst fit, whereas 2-parameter Freundlich and 3-parameter Redlich–Peterson models are both good, from which 3-parameter Redlich–Peterson isotherm provides slightly better results (despite the penalty used for the higher number of parameters). In the case of both UCs, the linear regression of Freundlich and Redlich–Peterson models provides good results (comparable with non-linear regressions). Unlike both UCs, the best fit of the experimental data from the adsorption on the coal has been achieved by the Langmuir isotherm model. The results based on the Freundlich or Redlich–Peterson model were (in this case) somewhat worse.

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1. Introduction

Dyes are widely used not only in textile or leather manufacturing, but also in the rubber and plastics industry, paper printing, food processing, cosmetics or the pharmaceutical industry. Such an extensive utilization of dyestuff leads to a huge annual production, which is estimated to be 7×10^5 tonnes [1,2]. It is assumed that there is about 1%–2% loss in production and 1%–10% loss in use [3]. Furthermore, even 1×10^{-6} concentration is highly visible; thus, only a small release of dye can colour a vast amount of the receiving water environment [4]. Apart from the undesirable colour, contaminated waters reduce the transmission of sunlight into streams, which consequently reduces the photosynthetic activity of living organisms.

There is a wide range of destructive (biodegradation, oxidation/ozonization) or non-destructive (sedimentation, filtration, coagulation, adsorption) methods designed for the removal of the dye [1]. However, since most synthetic dyes are of an aromatic character, their chemical

structure is rather stable and resistant to biodegradation. Therefore, the adsorption on suitable adsorbent provides an attractive alternative, which can be very efficient.

There is extensive literature dealing with wastewater cleaning and many adsorbents have been studied in this context, such as wood [5], fruit peel [6], tree fern [7], plant seeds [8], peat [9], coal [10,11], aluminosilicates [12,13], and power station ashes [14–16].

One of the most widely used adsorbents is activated carbon which is used not only for the cleaning of effluents [17–19] but also for the retention of pollutants from flue gas during coal combustion or municipal solid waste incineration [20–22].

The main drawbacks of activated carbon are its rather high cost in combination with some difficulties associated with its regeneration; therefore, low-cost precursors and alternative materials are being sought, from which unburned carbon (UC) belongs to the most promising ones. Moreover, the utilization of unburned carbon as an adsorbent is beneficial because it is present in all coal combustion ashes and therefore a huge amount of UC is produced annually on a worldwide scale.

Depending on the UC origin, some UCs exhibit a high degree of turbostratic structural order, for which it has been studied as a potential precursor for the preparation of various carbon artefacts (synthetic graphite, electrodes etc.) [23–26]. Moreover, UC grains or pyrolysis chars typically provide good adsorption properties [26–29] and for this reason it has been widely used for the retention of pollutants from coal combustion flue gas [30–32] where promising results have

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been achieved. However, studies based on UC utilization as an adsorbent for the retention of dye from effluents are scarce [33–37] and UCs have been tested predominantly for the retention of the basic (cationic) dyes and so far, there is the only paper dealing with the adsorption of acid (anionic) dye of UC [37]. Moreover, all these unburned carbons [33–37] originated from the combustion of coal without any other materials. Despite the trend toward the co-combustion of coal with biomass or various waste materials [38–44], it is quite surprising that the study (in this context) of UC originating from the co-combustion of coal and wastes has not been published yet.

For the reasons described above, this study deals with the adsorption of Naphthol Green B (Acid Green 1) onto two unburned carbons and the parent coal, from which the UCs have been created in the fluidised-bed power station. This study deals with the adsorption equilibrium modelling – experimental data has been analysed using 2-parameter (Langmuir, Freundlich) and 3-parameter (Redlich–Peterson) isotherms. As some recent adsorption studies indicated that linear regression widely used for the analysis of the adsorption process might not always provide reliable results [45–49], both linear and non-linear regressions have been used for the estimation of the isotherm parameters.

2. Equilibrium Isotherms Description

Due to its simplicity and software availability, the linearization of kinetic and equilibrium adsorption data is often used to estimate the parameters of non-linear models. However, transformations of non-linear equations to linear forms may alter the error distributions and violate the normality assumptions of the least-square method [45–49]. Therefore, non-linear regression is more complex and is usually recommended for the estimation of the model parameters [45–49].

In this study, for the description of the adsorption equilibrium, Langmuir, Freundlich and Redlich–Peterson isotherm equations were applied to the experimental data – both non-linear and linearized forms were used for the comparison and for the calculation of the isotherm parameters. The non-linear and linearized forms of the adsorption isotherm models used in this study are summarized in Table 1.

2.1. Statistical calculations and comparison of the models

Non-linear regression and the calculation of the regression characteristics were performed using QC Expert statistical-analysis software (TriloByte) using Gauss–Newton, Marquardt, Gradient-Cauchy, Simplex and other algorithms ($\alpha = 0.05$) including advanced statistical methods

specified by various international standards and regulations, such as ISO 9000, ISO 14000 or ISO 9000.

Two-parameter (Langmuir, Freundlich) and three-parameter (Redlich–Peterson) models were tested in terms of their ability to describe the experimental kinetic data.

The comparison of the accuracy of the fit of the tested model to experimental data was evaluated by means of the coefficient of determination (R^2), Chi-square statistic test (χ^2) and Akaike's criterion (AIC). Akaike's information criterion is an advantageous statistical approach for the comparison of the kinetic models with different number of parameters [55]. Generally speaking, the more parameters used in the model, the better the fit achieved is (resulting e.g. in the higher coefficient of determination). For this reason, AIC has been used with the aim of finding the model with the lowest number of parameters but still providing a good fit (this is achieved by a penalty used for each parameter used).

Values χ^2 were calculated by MS Excel using the formula:

$$\chi^2 = \sum_{i=1}^n \frac{(q_{e,calc} - q_{e,meas})^2}{q_{e,meas}}$$

where $q_{e,calc}$ and $q_{e,meas}$ are the calculated and the measured amounts of NGB adsorbed at equilibrium.

R^2 and AIC values come from the aforementioned statistical software that offers two different modes of operation. The first (and more common one) is based on further approximation of the input (estimated) parameter values. When iteration procedure is finished, the statistical characteristics are calculated for the actual (improved) parameter values. This procedure has been used for the non-linear regression calculations (for the calculation of the R^2 and AIC values). The second mode of the operation enables to calculate the statistical characteristics (R^2 , AIC) for any input values of the isotherm parameters without any other iteration or approximation. This procedure has been used for the testing of the isotherm parameters calculated from the linear regression coefficients (MS Excel). This approach has been preferred due to quite problematic comparison of the R^2 values if originating from the linear and the non-linear regression. The principle of the aforementioned approach is not to test the closeness of the “linearized” experimental data to the equation of the line (in MS Excel) but to test the goodness of the fit of the isotherm (based on these “linearized” parameters) to the original experimental data. In other words, e.g., for the Freundlich isotherm, the two series of the isotherm parameters were obtained (one from the non-linear and one from the linearized model in MS

Table 1

Equilibrium isotherms used for the description of the adsorption of Naphthol Green B onto coal and two unburned carbons

	Non-linear form	Linear form	Plot	Reference
Langmuir	$q_e = \frac{q_m K_L c_e}{1 + K_L c_e}$	$\frac{c_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} \cdot c_e$ $\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m} \cdot \frac{1}{c_e}$ $\frac{q_e}{c_e} = K_L \cdot q_m - K_L \cdot q_e$ $q_e = q_m - \frac{1}{K_L} \cdot \frac{q_e}{c_e}$	c_e/q_e vs. c_e $1/q_e$ vs. $1/c_e$ q_e/c_e vs. q_e q_e vs. q_e/c_e	[50,51] [50,51] [50,51] [50,51]
Freundlich	$q_e = K_F \cdot c_e^{\frac{1}{n}}$	$\lg(q_e) = \lg(K_F) + \frac{1}{n} \cdot \lg(c_e)$	$\lg(q_e)$ vs. $\lg(c_e)$	[51,52]
Redlich–Peterson (R–P)	$q_e = \frac{A c_e}{1 + B c_e^g}$	$\ln(A \cdot \frac{c_e}{q_e} - 1) = g \cdot \ln(c_e) + \ln(B)$	$\ln(A \cdot \frac{c_e}{q_e} - 1)$ vs. $\ln(c_e)$	[51,53,54]

Abbreviations and symbols:

q_e	adsorbed amount at equilibrium, mol·g ^{−1}
c_e	equilibrium concentration (in solution), mol·L ^{−1}
q_m	Langmuir monolayer saturation capacity, mol·g ^{−1}
K_L	Langmuir isotherm constant, L·g ^{−1}
K_F	Freundlich isotherm constant, $\frac{\text{mol}}{\text{g}} \cdot (\frac{\text{L}}{\text{mol}})^{\frac{1}{n}}$
n	Freundlich exponent
A	Redlich–Peterson isotherm constant, L·g ^{−1}
B	Redlich–Peterson isotherm constant, (L·mol ^{−1}) ^g
g	Redlich–Peterson isotherm exponent

Excel). Then, both calculated Freundlich isotherms were tested for their ability to describe the experimental data using the same procedure. Therefore, such R^2 values can be compared and used for the evaluation of the goodness of the fit.

3. Experimental

3.1. Adsorbents

Three adsorbents were collected at a circulating fluidised-bed power station – parent coal and two unburned carbons originating from its combustion along with waste materials (and limestone due to desulphurization of flue gas) at the temperature of 850 °C. Unburned carbon grains were separated manually from bottom ashes (using tweezers) and ground to a particle size of <0.09 mm. The parent coal was also studied for comparison with both unburned carbons to evaluate the improvement of the adsorption efficiency of the coal during its incomplete combustion in a real power station.

Ash content (determined gravimetrically in muffle furnace at 815 °C) in UC1, UC2 and the coal was 66%, 62% and 22%. The major mineral phases (identified on the PANalytical X'Pert³ Powder X-ray diffraction spectrometer) in both UCs were quartz, anatase and magnetite and the dominant minerals in the coal were quartz, kaolinite, anatase, siderite and pyrite. Specific surface areas (determined by the adsorption of nitrogen and the BET method on Sorptomatic 1990) of UC1, UC2 and the coal were 183, 123 and 21 m²·g⁻¹. The most abundant pores in UC1 and UC2 (determined by the BJH method, Sorptomatic 1990) are mesopores falling approximately within the range of 10–16 nm and in the case of the coal it was 8–12 nm (but with a somewhat lower pore volume). The degree of graphitization and carbon disorder studied by Raman spectroscopy (DXR Smart Raman Spectrometer) revealed the presence of both G (graphite) and D (disorder) bands indicating some disorder of the crystallites and a relatively low degree of the graphitization of both UCs.

3.2. Adsorbate

The adsorbate used in this study was Naphthol Green B (Sigma Aldrich); the molecular formula is given in Fig. 1 ($M = 878.46 \text{ g} \cdot \text{mol}^{-1}$, $\lambda_{\text{max}} = 714 \text{ nm}$). Stock solutions were prepared by dissolution of Naphthol Green B in demineralised water. The spectrogram of Naphthol Green B is shown in Fig. 2.

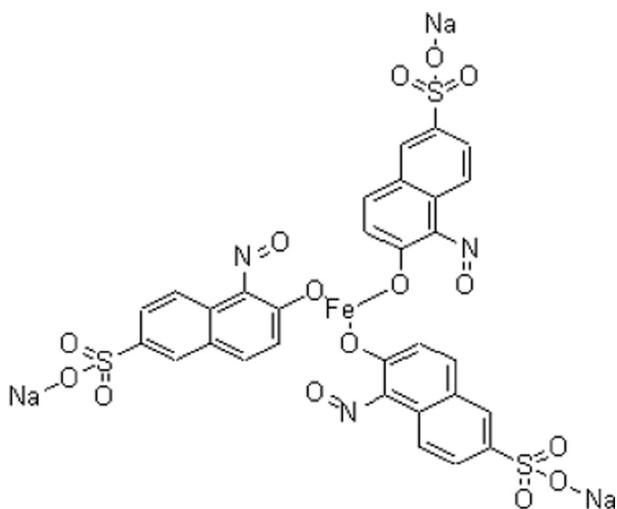


Fig. 1. Molecular formula of Naphthol Green B.

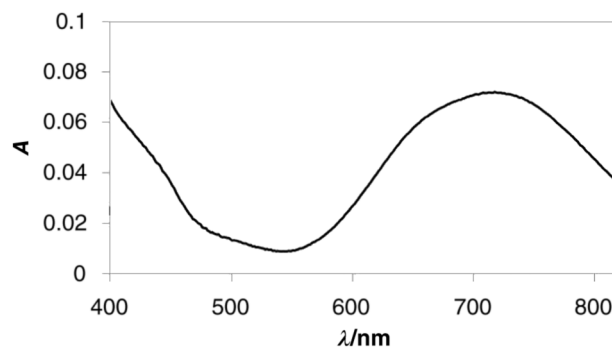


Fig. 2. Spectrogram of Naphthol Green B (the visible region of the spectrum).

3.3. Adsorption procedure

Batch adsorption experiments were performed in 150 ml of the studied dye solution (in demineralized water) in 250 ml PP bottles with 0.0375 g of unburned carbon.

All adsorption tests were carried out at laboratory temperature using Multi-shaker PSU 20 (Biosan) at 200 r·min⁻¹. Then the solutions were centrifuged in a laboratory centrifuge for 30 min at 3500 g and the concentration of the dye in the supernatant solution was measured spectrophotometrically with UV–VIS spectrophotometry (UV-1601, Shimadzu).

The amount of adsorbed dye was calculated using Eq. (1):

$$q_e = \frac{(c_0 - c_e)V}{m} \quad (1)$$

where:

q_e the adsorbed amount at equilibrium, mol·g⁻¹
 c_0, c_e the initial and equilibrium concentration of Naphthol Green B solution, mol·L⁻¹
 V volume of the solution, L
 m mass of the unburned carbon, g

4. Results and Discussion

4.1. Non-linear regression of equilibrium isotherm models

Equilibrium data were analysed using 2-parameter (Langmuir, Freundlich) and 3-parameter (Redlich–Peterson) adsorption isotherm models. The parameter values were calculated by means of the non-linear regression (which provides a mathematically rigorous method for determining isotherm parameters using the original form of the isotherm equation). The comparison of the non-linear isotherm models and the fit of the experimental data were performed by R^2 and namely by χ^2 and Akaike's information criterion (AIC statistic test).

The calculated parameters as well as the values of R^2 , AIC and χ^2 for the two unburned carbons and the parent coal are summarized in Table 2. The fit of the experimental data can also be checked visually in Figs. 3–5.

The data given in Table 2 and the comparison of the applied models suggest that the highest R^2 and the lowest χ^2 and AIC values have been calculated for both UCs using the Redlich–Peterson isotherm model. Hence, the best fit of the experimental data of the adsorption of Naphthol Green B on UCs has been achieved by the Redlich–Peterson isotherm equation – the AIC values for this model were the lowest ones even if some penalty has been used due to higher number of the parameters (when compared to 2-parameter models). Nevertheless, some caution is needed due to quite broad confidence interval of some parameters calculated by Redlich–Peterson (R–P) model.

Table 2

Parameters and statistics of nonlinear isotherm models

Model		Parameter 1 (stand. dev.) L: $q_m/\text{mol} \cdot \text{g}^{-1}$ F: $K_F / \left(\frac{\text{mol}}{\text{g}} \cdot \left(\frac{\text{L}}{\text{mol}} \right)^{\frac{1}{n}} \right)^{\frac{1}{n}}$ RP: $A/L \cdot \text{g}^{-1}$	Parameter 2 (stand. dev.) L: $K_L/L \cdot \text{g}^{-1}$ F: $1/n$ RP: $B/(L \cdot \text{mol}^{-1})^g$	Parameter 3 (stand. dev.) L: – F: – RP: g	R^2	χ^2	AIC
UC1	Langmuir	2.60×10^{-5} (6.08×10^{-7})	1641981 (329081.2)	–	0.870	5.49×10^{-7}	–212.1
	Freundlich	7.06×10^{-5} (9.0×10^{-6})	0.099 (0.012)	–	0.930	3.80×10^{-7}	–217.2
	Redlich–Peterson	73.22 (33.70)	1562665.9 (485602.0)	0.942 (0.022)	0.956	1.83×10^{-7}	–219.0
UC2	Langmuir	1.70×10^{-5} (3.47×10^{-7})	255248.3 (25824.2)	–	0.956	3.32×10^{-7}	–223.2
	Freundlich	1.27×10^{-4} (1.8×10^{-5})	0.213 (0.014)	–	0.978	1.37×10^{-7}	–228.7
	Redlich–Peterson	14.89 (9.57)	187430.0 (73242.3)	0.838 (0.032)	0.989	7.48×10^{-8}	–232.3
Coal	Langmuir	4.83×10^{-6} (1.39×10^{-7})	40628.8 (3142.7)	–	0.960	9.13×10^{-8}	–273.2
	Freundlich	1.61×10^{-4} (1.1×10^{-4})	0.401 (0.069)	–	0.872	2.39×10^{-7}	–262.6
	Redlich–Peterson	0.22 (0.08)	40629.4 (66022.2)	0.984 (0.215)	0.963	6.99×10^{-8}	–271.7

In the case of the parent coal, the highest R^2 and the lowest χ^2 were calculated for the Redlich–Peterson and the Langmuir models indicating comparable results with slightly better fit achieved by the R–P model. However, the AIC value for the R–P isotherm is higher than that of the Langmuir model. It can be explained by a similar closeness of the fit by the Langmuir and the R–P model but in the latter case, the penalty applied for the third parameter increased the final AIC value suggesting

that there is no justification of using the 3-parameter model in this case. Moreover, the observation is consistent with a very high standard deviation calculated for the parameter B that is even higher than the parameter itself. The conclusion can also be checked in Fig. 5 where the R–P and the Langmuir isotherms exhibit nearly the same shape – therefore, there is no justification for using the R–P isotherm for the description of the NGB adsorption on the coal (using the Langmuir isotherm is absolutely sufficient in this case).

The visual check of the quality of the fit of the experimental data in the case of the unburned carbons (Figs. 3 and 4) is consistent with the worst fit by the Langmuir isotherm, whereas 2-parameter Freundlich and 3-parameter R–P are both good.

An extensive literature survey on the Redlich–Peterson (R–P) isotherm was presented by Wu *et al.* [56]. In thirty evaluated papers, R–P isotherm was more accurate than the Langmuir and the Freundlich ones; twelve papers reported that both R–P and Langmuir isotherms had equally high accuracy. It has been mentioned in this context that the R–P isotherm is unlikely to provide worse fit than Langmuir or Freundlich isotherms because if exponent g is adjusted to 1 it is the same as the Langmuir isotherm and if $1/A \rightarrow 0$ it is the same form as the Freundlich isotherm [56]. Therefore, the question is whether using the 3-parameter model instead of the 2-parameter ones is justified. For this reason, in the case of the unburned carbons, AIC has been used for such evaluation (despite the penalty for the third parameter, R–P model provided the lowest AIC values for both unburned carbons).

The comparison of the values of the exponent g (from the R–P model) is interesting as well. In the aforementioned study [56] (based on the evaluation of 35 studies of the dye adsorption systems), it was reported that 31 exponent values were lower than 1 (with most values falling within the range of 0.82–0.98). Such g values were explained as

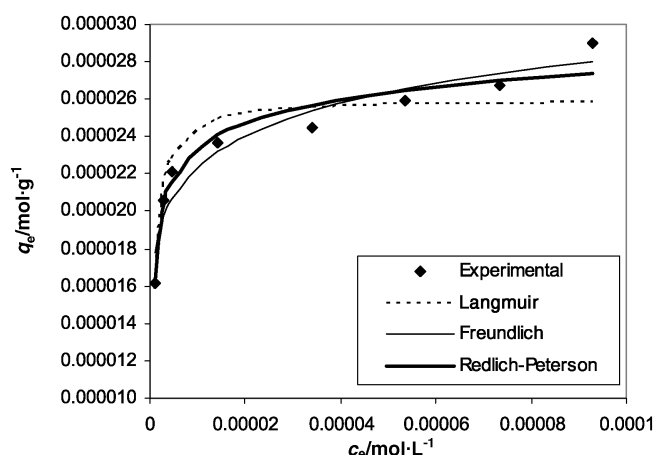


Fig. 3. Langmuir, Freundlich and Redlich–Peterson equation isotherms for the adsorption of Naphthol Green B on UC1 (based on nonlinear regression).

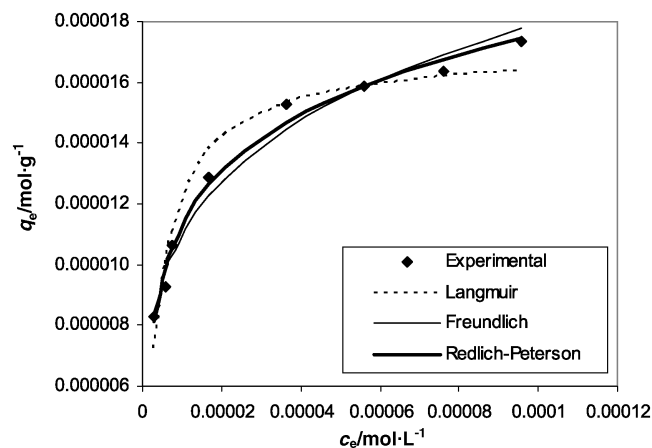


Fig. 4. Langmuir, Freundlich and Redlich–Peterson equation isotherms for the adsorption of Naphthol Green B on UC2 (based on nonlinear regression).

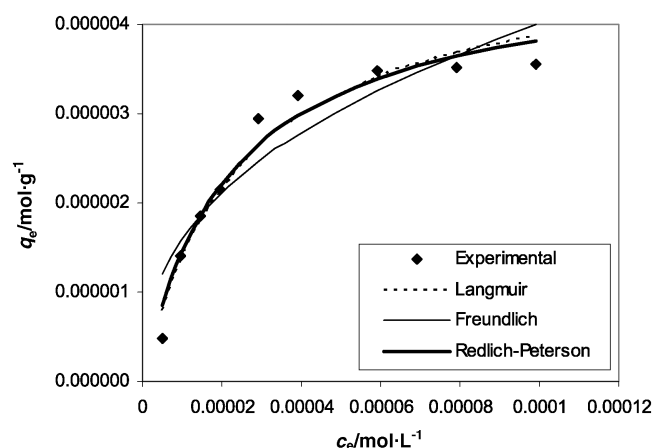


Fig. 5. Langmuir, Freundlich and Redlich–Peterson equation isotherms for the adsorption of Naphthol Green B on coal (based on nonlinear regression).

the existence of a solid impediment between pores and a large molecule of the adsorbate (dye). In the case of the unburned carbons, g values of 0.84 and 0.94 have been calculated, which is in an agreement with the adsorption of a large-molecule adsorbent (the molecular weight of Naphthol Green B is $878.46 \text{ g} \cdot \text{mol}^{-1}$).

Moreover, the value of the exponent g (from the R–P isotherm) affects the shape of the isotherm; according to Wu *et al.* [56], the higher the g value (up to $g = 1$), the more significant the curvature of the isotherm (*i.e.*, the sharper the increase of the adsorbed amount at the beginning with more horizontal end of the curve). Then, if g value in the R–P equation reaches 1, its form is the same as the Langmuir equation exhibiting the nearly horizontal end of the curve [56]. In the case of the unburned carbons, the g values were calculated as 0.94 and 0.84 indicating the more obtuse (open) bend angle (the less significant curvature) in relation to the Langmuir isotherm. At any case, the more obtuse bend angle (brought about by $g < 1$) helped to achieve the better fit of the experimental data.

As far as the adsorbed amount of Naphthol Green B is concerned, the papers in literature are quite scarce. For example, metal hydroxides sludge from hot dipping galvanizing plant (low-cost adsorbent) have been used for this purpose – the adsorption capacity was $10 \text{ mg} \cdot \text{g}^{-1}$ [57]. The polymeric xerogel (with amino groups) was tested as well and the retention of Naphthol Green B was $15.9 \text{ mg} \cdot \text{g}^{-1}$ [58]. Both these values are comparable with the adsorption capacity on the unburned carbons received in this study – 25.5 and $15.2 \text{ mg} \cdot \text{g}^{-1}$. It is worth mentioning in this context that the parent coal adsorbed only $3 \text{ mg} \cdot \text{g}^{-1}$ and that the increased adsorption on the unburned carbons corresponds preferentially with the (natural) release of the volatile combustibles out of the coal particles during the incomplete combustion at the power station (creating the porous texture). Higher adsorbed amount has been presented by Bezak-Mazuk and Adamczyk [59] for a commercial activated carbon ($130 \text{ mg} \cdot \text{g}^{-1}$); however, the cost of such adsorbent is rather high.

4.2. Calculation of isotherm parameters by linearization

Due to its simplicity (and often also due to software availability), the linear regression is widely used for the evaluation of the non-linear models. In the case of Langmuir and Freundlich isotherm, the linearized models (Table 1) are generally known and easy to use. However, as R–P isotherm is a 3-parameter model, the trial-and-error method is to be used [54] because the linear equation still contains parameter A . The principle of this optimization is to plot

$$\ln \left(A \cdot \frac{c_e}{q_e} - 1 \right) \text{ vs. } \ln(c_e)$$

and to find the optimized value of A (characterized by the highest correlation coefficient value). This linear equation (for the optimized parameter A) is then used for the calculation of the other two parameters of the R–P isotherm. In this study, due to its good availability, it has been done in an MS Excel spreadsheet.

The effect of parameter A on the correlation coefficient values in the dependence of

$$\ln \left(A \cdot \frac{c_e}{q_e} - 1 \right) \text{ vs. } \ln(c_e)$$

can be visually evaluated in Figs. 6–8. The regression equations of the linearized R–P model for the given values of parameter A are documented in Figs. 9–11. The regression equations with the highest correlation coefficients are highlighted.

Isotherm parameters calculated by linearized models (along with the values of the given statistic characteristics) are summarized in Table 3.

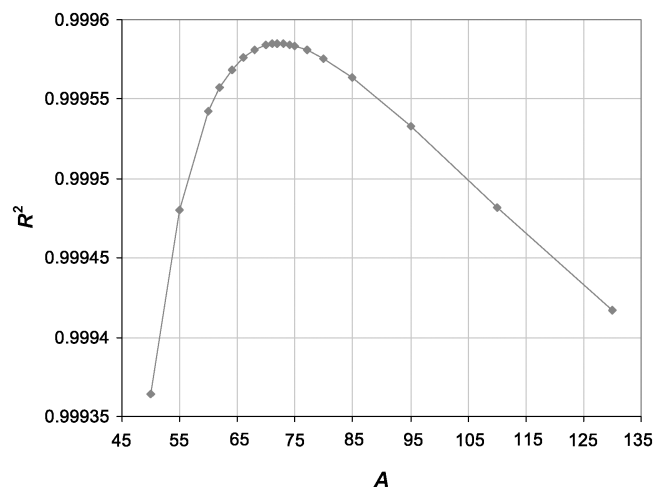


Fig. 6. Linearized Redlich–Peterson isotherm model for UC1 – shift of the determination coefficient R^2 in dependence of the actual value of parameter A .

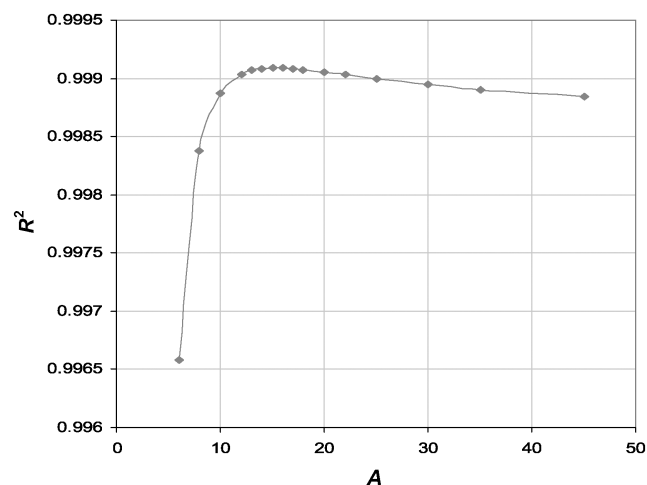


Fig. 7. Linearized Redlich–Peterson isotherm model for UC2 – shift of the determination coefficient R^2 in dependence of the actual value of parameter A .

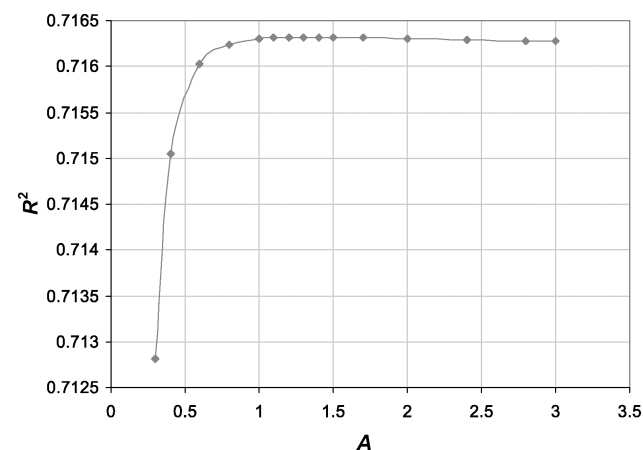


Fig. 8. Linearized Redlich–Peterson isotherm model for the coal – shift of the determination coefficient R^2 in dependence of the actual value of parameter A .

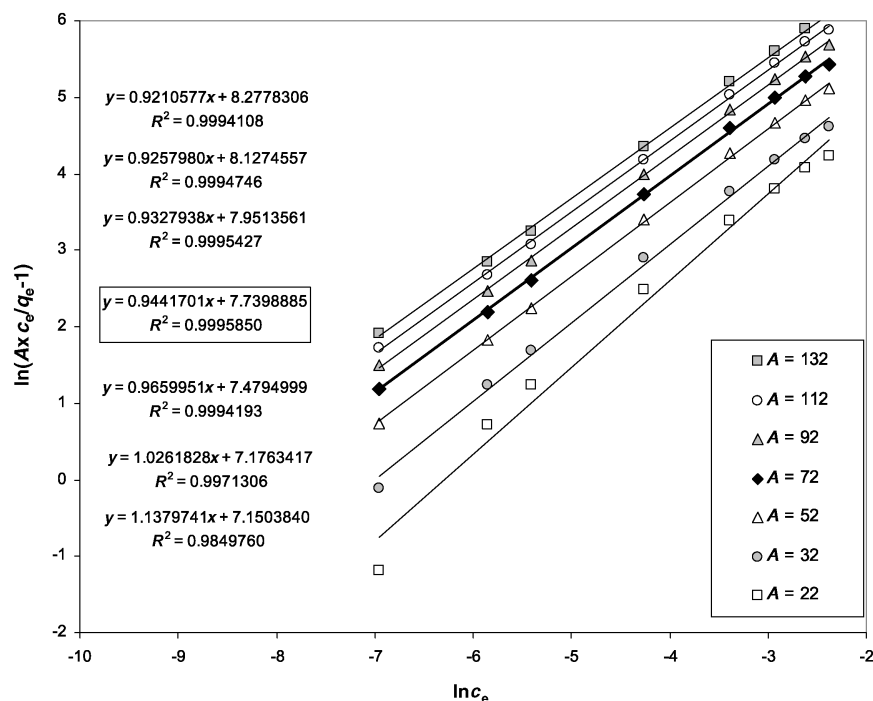


Fig. 9. Linearized Redlich–Peterson isotherm model for UC1 — regression equations and the determination coefficients R^2 for selected values of parameter A .

The direct comparison of the R^2 values coming from the linear and the non-linear regression is quite problematic because R^2 values in the linear regression correspond with the closeness of the “linearized” experimental data to the regression line and in the non-linear regression they relate to the fit of the original measured data to the isotherm (which is not a line). For this reason, the isotherm parameters calculated by the linear regression (in MS Excel) have been introduced into the statistical software (where all the non-linear regressions have been calculated) and the R^2 and AIC values were calculated directly for these input parameters using the original non-linear isotherm model (i.e., without any other iteration or further approximation). Such R^2

values were calculated in the same way as in the case of the non-linear isotherm parameters; therefore, the mutual comparison is possible.

In the case of the Langmuir and Freundlich isotherm, the data summarized in Tables 2 and 3 suggest that the parameters and the statistical characteristics calculated by the non-linear and the linear regression are roughly comparable. In other words, in this case, the linearized models of the Langmuir and Freundlich isotherm provide relatively good results and can also be used for the description of the adsorption process (the only exception is the Langmuir linearization #2 if calculated for the coal).

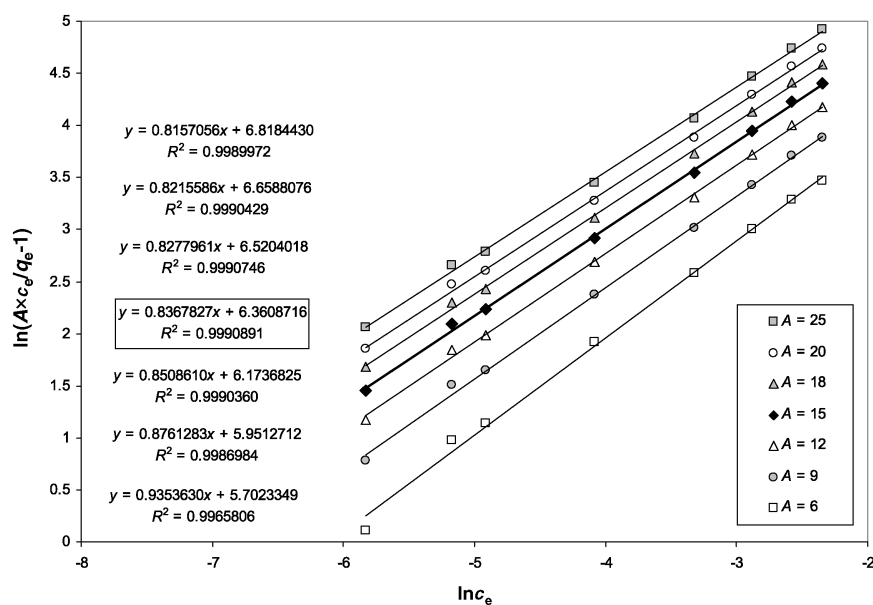


Fig. 10. Linearized Redlich–Peterson isotherm model for UC2 — regression equations and the determination coefficients R^2 for selected values of parameter A .

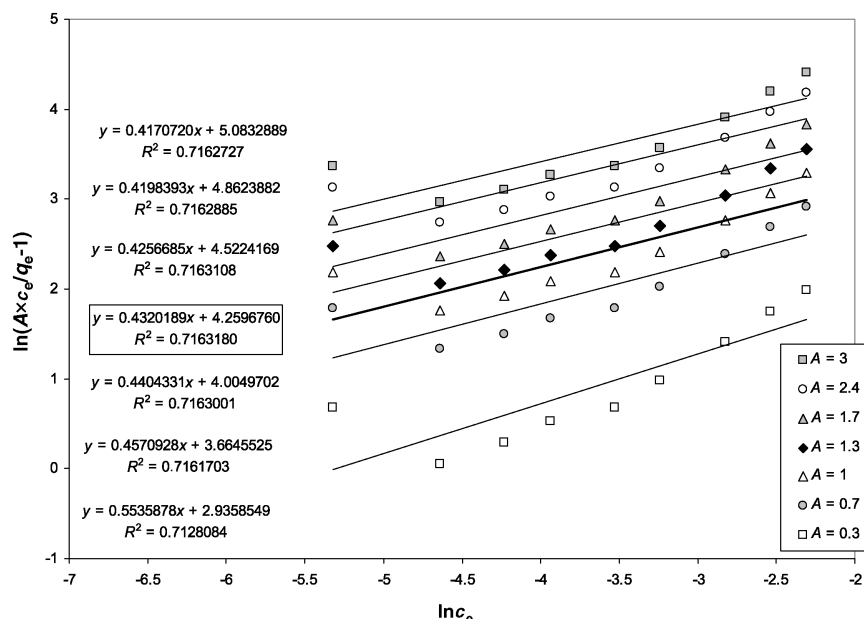


Fig. 11. Linearized Redlich–Peterson isotherm model for the coal – regression equations and the determination coefficients R^2 for selected values of parameter A .

Moreover, even linearization of the 3-parameter R–P model provides good results if calculated for the UCs (for which the R–P equation is a suitable model). In the case of the parent coal, the R–P linearization provides somewhat worse results, which is also the case of its original non-linear form, where the Langmuir model exhibited better results. Hence, the results indicate that the linearized R–P isotherm can be used in its linearized form with good results as well; at least in the cases where this (non-linear) model is suitable for the description of the adsorption process on a given adsorbent.

5. Conclusions

The study deals with the adsorption of Naphthol Green B on two unburned carbons and the parent coal, from which the UCs have been created in a fluidised-bed power station. Particular attention has been paid to the adsorption equilibrium modelling – experimental data has been analysed using 2-parameter (Langmuir, Freundlich) and 3-parameter (Redlich–Peterson) isotherms. As some recent adsorption

studies indicated that linear regression might not always provide reliable results, both linear and non-linear regressions have been used for the estimation of the isotherm parameters.

In the case of both UCs, the Langmuir isotherm model provides the worst fit, whereas 2-parameter Freundlich and 3-parameter Redlich–Peterson models are both good, from which 3-parameter Redlich–Peterson isotherm provides slightly better results despite the penalty used for the higher number of parameters (applied in the Akaike's information criterion). The comparison of the linear regression of the Freundlich and Redlich–Peterson models with the non-linear calculation procedures documents that (at least in this case) the linearized models provide good results and can be used for the calculation of the isotherm parameters (e.g., if the software needed for the non-linear calculations is not available).

Unlike both UCs, the best fit of the experimental data from the adsorption of Naphthol Green B on the coal has been achieved by the Langmuir isotherm model. The results based on the Freundlich or Redlich–Peterson model were (in this case) somewhat worse.

Table 3

Parameters of linearized isotherm models (parameters 1–3 are the same as in Table 2)

Isotherm type			Parameter 1	Parameter 2	Parameter 3	R^2 ^①	χ^2	AIC
UC1	Langmuir	Lin 1	2.84×10^{-5}	427345.8	–	0.828	5.99×10^{-6}	–196.2
		Lin 2	2.60×10^{-5}	1641973.0	–	0.867	5.50×10^{-7}	–212.1
		Lin 3	2.66×10^{-5}	1338909.0	–	0.875	5.65×10^{-7}	–212.6
		Lin 4	2.62×10^{-5}	1562500.0	–	0.873	5.36×10^{-7}	–212.5
	Freundlich		7.38×10^{-5}	0.104	–	0.928	3.77×10^{-7}	–217.1
UC2	Redlich–Peterson		72	1562659.9	0.944	0.956	1.84×10^{-7}	–218.9
	Langmuir	Lin 1	1.79×10^{-5}	186866.7	–	0.940	5.55×10^{-7}	–220.7
		Lin 2	1.62×10^{-5}	313982.8	–	0.926	4.66×10^{-7}	–219.0
		Lin 3	1.71×10^{-5}	255249.5	–	0.956	3.35×10^{-7}	–223.1
		Lin 4	1.67×10^{-5}	286533.0	–	0.946	3.79×10^{-7}	–221.5
Coal	Freundlich		1.28×10^{-4}	0.213	–	0.978	1.37×10^{-7}	–228.6
	Redlich–Peterson		15	187430.2	0.837	0.989	7.50×10^{-8}	–232.3
	Langmuir	Lin 1	4.68×10^{-6}	40628.7	–	0.953	2.91×10^{-7}	–271.6
		Lin 2	1.41×10^{-5}	8140.2	–	②	3.75×10^{-6}	②
		Lin 3	5.97×10^{-6}	25950.7	–	0.884	4.19×10^{-7}	–263.4
		Lin 4	4.50×10^{-6}	45126.4	–	0.955	3.18×10^{-7}	–272.1
	Freundlich		1.13×10^{-3}	0.594	–	0.707	1.06×10^{-6}	–255.1
	Redlich–Peterson		1.3	1399.6	0.432	0.710	8.58×10^{-7}	–235.2

① The R^2 values do not relate to the equation of the regression lines; the calculation procedure is described in the text (Section 4.2).

② The calculation with the given parameters cannot be completed.

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