Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon
Part II. Models with more than two parameters

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Abstract

The adsorption equilibrium isotherms of five phenolic compounds, phenol, 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol, from aqueous solutions onto granular activated carbon were studied and modeled. In order to determine the best-fit isotherm, the experimental equilibrium data were analyzed using thirteen adsorption isotherm models with more than two-parameter; nine three-parameter equations – the Redlich–Peterson, Sips, Langmuir–Freundlich, Fritz–Schlunder, Radke–Prasnitz (three models), Tóth, and Jossens isotherms – three four-parameter equation – the Weber–van Vliet, Fritz–Schlunder, and Baudu isotherms – and one five-parameter equation – the Fritz–Schlunder isotherm. The results reveal that the adsorption isotherm models fitted the experimental data in the order: Baudu (four-parameter) > Langmuir–Freundlich (three-parameter) > Sips (three-parameter) > Fritz–Schlunder (five-parameter) > Tóth (three-parameter) > Fritz–Schlunder (four-parameter) > Redlich–Peterson (three-parameter). The influence of solution pH on the adsorption isotherms of 4-CP was investigated. It was shown that the solution pH has not an effect on the adsorption isotherms for $pH < pK_a$. The pH at which the uptake decreased was found to be dependent on the adsorptive pK_a and the pH_{PZC}.
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1. Introduction

Activated carbon, the most important commercial adsorbent, is a carbonaceous material with a large surface area and high porosity. Adsorption of organic solutes from the aqueous phase is a very important application of activated carbons. This covers a wide spectrum of systems such as drinking water and waste water treatments, and applications in the food, beverage, pharmaceutical and chemical industries. Activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best available environmental control technologies [1].

Adsorption of phenols on carbons is an important subject especially because of ecological aspects. Phenol and its derivatives belong to a group of ordinary contaminants of water. They cause an unpleasant taste and odor even at low concentrations in water. Most of these compounds are recognized as toxic carcinogens. The European Union and US Environmental Protection Agency have listed phenol and phenolic compounds on the priority-pollutants list.

Adsorption equilibria information is the most important piece of information in understanding an adsorption process. No matter how many components are present in the system, the adsorption equilibria of pure components are the essential ingredient for the understanding of how much those components can be accommodated by a solid adsorbent. The description of the adsorption isotherms onto activated carbon can be based on models with two, three, even with more parameters [2–6]. Despite the progress in computer simulations, it is still necessary to look for the elegant analytical formulas describing adsorption isotherms and being suitable for a wide range of scientist and engineers. Additionally, the two-parameter models habitually showed a limit of application. Moreover, the models with more than two parameters were developed to mitigate deficiencies of the simple models with two-parameter [2,3,5,6].

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Nomenclature

A	the Redlich–Peterson isotherm constant $(\mathrm{L\,g^{-1}})$ and the Fritz–Schlunder model parameter
b	Langmuir constant related to the free energy of adsorption $(\mathrm{L\,mg^{-1}})$
b_0	the Baudu isotherm equilibrium constant
B	the Redlich–Peterson isotherm parameter $(\mathrm{L\,mg^{-1}})^{\beta}$ and the Fritz–Schlunder model parameter
C_e	the equilibrium concentration of the solute in the bulk solution $(\mathrm{mg\,L^{-1}})$
F	the Jossens equation parameter
GAC	granular activated carbon
H	the Jossens equation parameter
K_F	Freundlich constant indicative of the relative adsorption capacity of the adsorbent $(\mathrm{mg^{1-1/n}\,L^{1/n}\,g^{-1}})$
K_{FS}	the Fritz–Schlunder equilibrium constant $(\mathrm{L\,mg^{-1}})$
K_{LF}	the equilibrium constant for a heterogeneous solid
K_{RPI}	the Radke–Prausnitz-I equilibrium constant
K_{RPII}	the Radke–Prausnitz-II equilibrium constant
K_{RPIII}	the Radke–Prausnitz-III equilibrium constant
K_S	the Sips equilibrium constant $(\mathrm{L\,mg^{-1}})^m$
K_T	the Tóth equilibrium constant
K_1, K_2	the Fritz–Schlunder equation parameter
m_{FS}	the Fritz–Schlunder model exponent
m_{LF}	the heterogeneity parameter, lies between 0 and 1
m_{RPI}	the Radke–Prausnitz-I model exponent
m_{RPII}	the Radke–Prausnitz-II model exponent
m_{RPIII}	the Radke–Prausnitz-III model exponent
m_S	the Sips model exponent
m_T	the Tóth model exponent
m_1, m_2	the Fritz–Schlunder equation exponents
n	Freundlich constant indicative of the intensity of the adsorption
N	the number of experimental points
p	the Jossens equation parameter
P_1	parameter of the Weber–van Vliet equation
P_2	parameter of the Weber–van Vliet equation
P_3	parameter of the Weber–van Vliet equation
P_4	parameter of the Weber–van Vliet equation
q_e	the amount of solute adsorbed per unit weight of adsorbent $(\mathrm{mg\,g^{-1}})$
$q_{m_{FS}}$	the Fritz–Schlunder maximum adsorption capacity $(\mathrm{mg\,g^{-1}})$
$q_{m_{FS5}}$	the maximum adsorption capacity $(\mathrm{mg\,g^{-1}})$ in the five-parameter Fritz–Schlunder model
q_{m_L}	the Langmuir maximum adsorption capacity $(\mathrm{mg\,g^{-1}})$
$q_{m_{LF}}$	the Langmuir–Freundlich maximum adsorption capacity $(\mathrm{mg\,g^{-1}})$
$q_{m_{RPI}}$	the Radke–Prausnitz-I maximum adsorption capacity $(\mathrm{mg\,g^{-1}})$
$q_{m_{RPII}}$	the Radke–Prausnitz-II maximum adsorption capacity $(\mathrm{mg\,g^{-1}})$
$q_{m_{RPIII}}$	the Radke–Prausnitz-III maximum adsorption capacity $(\mathrm{mg\,g^{-1}})$
q_{m_S}	the Sips maximum adsorption capacity $(\mathrm{mg\,g^{-1}})$
q_{m_T}	the Tóth maximum adsorption capacity $(\mathrm{mg\,g^{-1}})$
q_{m0}	the maximum adsorption capacity $(\mathrm{mg\,g^{-1}})$ in the Baudu isotherm equation
r	coefficient of correlation
x	the Baudu isotherm parameter
y	the Baudu isotherm parameter

Greek letters

α	exponent in the Fritz–Schlunder model that lies between 0 and 1
β	exponent in the Redlich–Peterson and Fritz–Schlunder isotherms that lies between 0 and 1

For the second part of this study, thirteen adsorption isotherms, nine three-parameter equations – the Redlich–Peterson, Sips, Langmuir–Freundlich, Fritz–Schlunder, Radke–Prasnitz (three models), Tóth, and Jossens isotherms – three four-parameter equation – the Weber–van Vliet, Fritz–Schlunder, and Baudu isotherms – and one five-parameter equation – the Fritz–Schlunder isotherm – were examined for phenol and chlorophenols adsorption onto GAC for their ability to model the equilibrium adsorption data. The influence of solution pH on the adsorption isotherms of 4-CP onto GAC was investigated.

2. Materials and methods

2.1. Adsorbent and adsorbates

The adsorbent and adsorbates used were presented in the first part of this work.

2.2. Equilibrium isotherms

The procedure for the determination of the adsorption isotherms of the five phenolic compounds onto GAC was described in the first part of this study. The solution pH for the five phenolic compounds was 5.5. At this pH all the tested phenolic compounds are in their protonated forms.

For the study of the effect of pH on equilibrium data, adsorption isotherms experiments were carried out with accurately weighted amount of GAC $(0.05–1\,\mathrm{g\,L^{-1}})$ that were continuously stirred at 400 rpm with 90 mL of $100\,\mathrm{mg\,L^{-1}}$ of 4-CP at different pH (2.3, 5.5, 8, and 11). The temperature was controlled at $21\,^{\circ}\mathrm{C}$. Agitation was provided for 4 days, which is more than sufficient time to reach equilibrium.

All experiments were conducted in triplicate, and sometimes repeated again and the mean values have been reported.

2.3. Boehm titration

The surface functional groups containing oxygen were determined according to Boehm titration [7]. A 1 g carbon sample was placed in 50 mL of 0.1 N of the following solutions: sodium hydroxide, sodium carbonate, sodium bicarbonate, and hydrochloric acid. The vials were sealed and agitated for 24 h and then filtered; 5 ml of the filtrate was pipetted, and the excess base or acid was titrated with HCl (0.1 N) or NaOH (0.1 N), respectively. The number of acidic sites was determined under the assumption that NaOH neutralizes carboxylic, lactonic, and phenolic groups; and Na_2CO_3 neutralizes carboxylic and lactonic groups; and $NaHCO_3$ neutralizes only carboxylic groups. The number of basic sites was calculated from the amount of hydrochloric acid that reacted with the carbon.

3. Theoretical background

3.1. Three-parameter models

3.1.1. Redlich–Peterson model

The Redlich–Peterson [8] isotherm is an empirical isotherm incorporating three parameters. It combines elements from both the Langmuir and Freundlich equations, and the mechanism of adsorption is a hybrid and does not follow ideal monolayer adsorption:

$$q_e = \frac{AC_e}{1 + BC_e^{\beta}} \tag{1}$$

where A is the Redlich–Peterson isotherm constant $(L\,g^{-1})$, B is also a constant having unit of $(L\,mg^{-1})^{\beta}$, and β is an exponent that lies between 0 and 1. C_e is the equilibrium liquid-phase concentration of the adsorbate $(mg\,L^{-1})$ and q_e is the equilibrium adsorbate loading onto the adsorbent $(mg\,g^{-1})$.

At high liquid-phase concentrations of the adsorbate, Eq. (1) reduces to the Freundlich equation, i.e.:

$$q_e = \frac{A}{B} C_e^{1-\beta} \tag{2}$$

where A/B and $(1 - \beta)$ present, respectively, the parameters K_F and $1/n$ of the Freundlich model.

For $\beta = 1$, Eq. (1) reduces to the Langmuir equation, with $b = B$ is the Langmuir adsorption constant $(L\,mg^{-1})$ related to the energy of adsorption and $A = bq_{m_L}$, where q_{m_L} signifies the Langmuir maximum adsorption capacity of the adsorbent $(mg\,g^{-1})$.

For $\beta = 0$, Eq. (1) reduces to the Henry's equation, with $A/(1 + B)$ is the Henry's constant.

3.1.2. Sips model

Recognizing the problem of the continuing increase in the adsorbed amount with an increase in concentration in the Freundlich equation, Sips [9] proposed an equation similar in form to the Freundlich equation, but it has a finite limit when the concentration is sufficiently high:

$$q_e = \frac{q_{m_S} K_S C_e^{m_S}}{1 + K_S C_e^{m_S}} \tag{3}$$

where q_e is the adsorbed amount at equilibrium $(mg\,g^{-1})$, C_e the equilibrium concentration of the adsorbate $(mg\,L^{-1})$, q_{m_S} the Sips maximum adsorption capacity $(mg\,g^{-1})$, K_S the Sips equilibrium constant $(L\,mg^{-1})^m$, and m_S is the Sips model exponent.

3.1.3. Langmuir–Freundlich model

The Langmuir–Freundlich equation is given by [9]:

$$q_e = \frac{q_{m_{LF}} (K_{LF} C_e)^{m_{LF}}}{1 + (K_{LF} C_e)^{m_{LF}}} \tag{4}$$

where q_e is the adsorbed amount at equilibrium $(mg\,g^{-1})$, $q_{m_{LF}}$ the Langmuir–Freundlich maximum adsorption capacity $(mg\,g^{-1})$, C_e the adsorbate equilibrium concentration $(mg\,L^{-1})$, K_{LF} the equilibrium constant for a heterogeneous solid, and m_{LF} is the heterogeneity parameter, lies between 0 and 1.

3.1.4. Fritz–Schlunder model

The Fritz–Schlunder [10] equation has the following form:

$$q_e = \frac{q_{m_{FS}} K_{FS} C_e}{1 + q_m C_e^{m_{FS}}} \tag{5}$$

where q_e is the adsorbed amount at equilibrium $(mg\,g^{-1})$, C_e the equilibrium concentration of the adsorbate $(mg\,L^{-1})$, $q_{m_{FS}}$ the Fritz–Schlunder maximum adsorption capacity $(mg\,g^{-1})$, K_{FS} the Fritz–Schlunder equilibrium constant $(L\,mg^{-1})$, and m_{FS} is the Fritz–Schlunder model exponent.

3.1.5. Radke–Prausnitz models

The three Radke–Prausnitz [11] isotherms can be represented as

$$q_e = \frac{q_{m_{RPI}} K_{RPI} C_e}{(1 + K_{RPI} C_e)^{m_{RPI}}} \tag{6}$$

$$q_e = \frac{q_{m_{RPII}} K_{RPII} C_e}{1 + K_{RPII} C_e^{m_{RPII}}} \tag{7}$$

$$q_e = \frac{q_{m_{RPIII}} K_{RPIII} C_e^{m_{RPIII}}}{1 + K_{RPIII} C_e^{m_{RPIII}-1}} \tag{8}$$

where q_e is the adsorbed amount at equilibrium $(mg\,g^{-1})$, $q_{m_{RPI}}$, $q_{m_{RPII}}$, and $q_{m_{RPIII}}$ are the Radke–Prausnitz maximum adsorption capacities $(mg\,g^{-1})$, C_e the adsorbate equilibrium concentration $(mg\,L^{-1})$, K_{RPI}, K_{RPII}, and K_{RPIII} are the Radke–Prausnitz equilibrium constants, and m_{RPI}, m_{RPII}, and m_{RPIII} are the Radke–Prausnitz models exponents.

3.1.6. Tóth model

Tóth [12] has modified the Langmuir equation to reduce the error between experimental data and predicted values of equilibrium adsorption data. The application of his equation is best suited to multilayer adsorption similar to BET isotherms which

is a special type of Langmuir isotherm and has very restrictive validity [3]. The Tóth correlation is given as

$$q_e = \frac{q_{m_T} C_e}{(1/K_T + C_e^{m_T})^{1/m_T}} \qquad (9)$$

where q_e is the adsorbed amount at equilibrium (mg g^{-1}), C_e the equilibrium concentration of the adsorbate (mg L^{-1}), q_{m_T} the Tóth maximum adsorption capacity (mg g^{-1}), K_T the Tóth equilibrium constant, and m_T is the Tóth model exponent.

3.1.7. Jossens model

The model of Jossens et al. [13] is based on a distribution of the energy of interactions adsorbate–adsorbent on adsorption sites. It considers that the activated carbon surface is heterogeneous, with respect to the interactions which it engages with the adsorbate:

$$C_e = \frac{q_e}{H} \exp(F q_e^p) \qquad (10)$$

where q_e is the adsorbed amount at equilibrium (mg g^{-1}), C_e the equilibrium concentration of the adsorbate (mg L^{-1}), and H, F, and p are the parameters of the equation of Jossens. H and F depend only on temperature.

This equation can be reduced to Henry's law at low capacities.

3.2. Four-parameter models

3.2.1. Weber–van Vliet model

Weber and van Vliet [14] have proposed an empirical relation with four parameters to describe equilibrium data:

$$C_e = P_1 q_e^{(P_2 q_e^{P_3} + P_4)} \qquad (11)$$

where q_e is the adsorbed amount at equilibrium (mg g^{-1}), C_e the equilibrium concentration of the adsorbate (mg L^{-1}), and P_1, P_2, P_3, and P_4 are the isotherm parameters.

3.2.2. Fritz–Schlunder model

Another four-parameter equation of Langmuir–Freundlich type was developed empirically by Fritz and Schlunder [10]. It is expressed by the equation:

$$q_e = \frac{A C_e^\alpha}{1 + B C_e^\beta} \quad \text{with } \alpha \text{ and } \beta \leq 1 \qquad (12)$$

where q_e is the adsorbed amount at equilibrium (mg g^{-1}), C_e the equilibrium concentration of the adsorbate (mg L^{-1}), A and B are the Fritz–Schlunder parameters, and α and β are the Fritz–Schlunder equation exponents.

At high liquid-phase concentrations of the adsorbate, Eq. (12) reduces to the Freundlich equation, i.e.:

$$q_e = \frac{A}{B} C_e^{\alpha - \beta} \qquad (13)$$

where A/B and $(\alpha - \beta)$ present, respectively, the parameters K_F and $1/n$ of the Freundlich model.

For $\alpha = \beta = 1$, Eq. (12) reduces to the Langmuir equation, with $b = B$ is the Langmuir adsorption constant (L mg^{-1}) related

to the energy of adsorption and $A = b q_{m_L}$, where q_{m_L} signifies the monolayer adsorption capacity of the adsorbent (mg g^{-1}).

3.2.3. Baudu model

Baudu [15] has remarked that the calculation of the Langmuir coefficients, b and q_{m_L}, by the measurement of tangents at different equilibrium concentrations shows that they are not constants in a broad concentration range. Their variations can be written in the following forms:

$$b = b_0 C_e^x \qquad (14)$$

$$q_{m_L} = q_{m0} C_e^y \qquad (15)$$

Graphical study of $\ln b = f(\ln C_e)$ and $\ln q_{m_L} = f(\ln C_e)$ gives access to b_0, q_{m0}, x, and y.

Baudu has transformed the Langmuir equation to the following expression:

$$q_e = \frac{q_{m0} b_0 C_e^{(1+x+y)}}{1 + b_0 C_e^{(1+x)}} \quad \text{with } (1+x+y) \text{ and } (1+x) < 1 \qquad (16)$$

where q_e is the adsorbed amount at equilibrium (mg g^{-1}), C_e the equilibrium concentration of the adsorbate (mg L^{-1}), q_{m0} the Baudu maximum adsorption capacity (mg g^{-1}), b_0 the equilibrium constant, and x and y are the Baudu parameters.

For lower surface coverage, Eq. (16) reduces to the Freundlich equation, i.e.:

$$q_e = \frac{q_{m0} b_0 C_e^{(1+x+y)}}{1 + b_0} \qquad (17)$$

3.3. Five-parameter models

3.3.1. Fritz–Schlunder model

Fritz and Schlunder [10] have proposed a five-parameter empirical expression which can represent a broad field of equilibrium data:

$$q_e = \frac{q_{m_{FS5}} K_1 C_e^{m_1}}{1 + K_2 C_e^{m_2}} \quad \text{with } m_1 \text{ and } m_2 \leq 1 \qquad (18)$$

where q_e is the adsorbed amount at equilibrium (mg g^{-1}), C_e the equilibrium concentration of the adsorbate (mg L^{-1}), $q_{m_{FS5}}$ the Fritz–Schlunder maximum adsorption capacity (mg g^{-1}) and K_1, K_2, m_1, and m_2 are the Fritz–Schlunder parameters.

4. Results and discussion

4.1. Equilibrium isotherms modeling

The adsorption equilibrium data for phenol and chlorophenols onto GAC were analyzed by non-linear curve fitting analysis, using Microcal(TM) Origin® software, to fit the three-parameter, four-parameter, and five-parameter isotherm models.

The experimental values of q_e and C_e are initially treated with the models in order to determine the equations parameters

and the isotherms are reconstituted using the determined values. The isotherm curves showed the superposition of experimental results (points) and the theoretical calculated points (lines). The correlation coefficients (r) showed the fit between experimental data and isotherm equations while the average percentage errors (APE) calculated according to Eq. (19) indicated the fit between the experimental and predicted values of adsorption capacity used for plotting isotherm curves:

$$\text{APE } (\%) = \frac{\sum_{i=1}^{N} |((q_e)_{\text{experimental}} - (q_e)_{\text{predicted}})/(q_e)_{\text{experimental}}|}{N} \times 100 \qquad (19)$$

where N is the number of experimental data.

4.1.1. Three-parameter models

The abilities of the three-parameter equations, Redlich–Peterson, Sips, Langmuir–Freundlich, Fritz–Schlunder, Radke–Prausnitz (three models), Tóth, and Jossens isotherms, to model the equilibrium adsorption data were examined. Table 1 shows the isotherms parameters obtained using the non-linear fitting analysis. The worse fits of the equilibrium isotherms are given in grey frames (Table 1).

Among the tested three-parameter equations, the better and perfect representation of the experimental results of the adsorption isotherms is obtained using the Langmuir–Freundlich model (Fig. 1). According to Table 1, the coefficients of correlation are very good (≥ 0.994) and the mean value of the average percentage error for the studied compounds is 2.01%. The values of the maximum adsorption capacity obtained using the Langmuir–Freundlich equation are higher than those calculated by the Langmuir and Freundlich models and lower than the theoretical values. For TCP, the calculated maximum adsorption capacity is higher than the theoretical value. This indicates that, according Langmuir–Freundlich isotherms, TCP is not adsorbed in flat on the adsorbent surface. An agreement is obtained between the parameter m_{LF} and the constant $1/n$ of the Freundlich equation, except for Ph and 2-CP. The parameter

K_{LF} evolves in the same manner as the constant b of Langmuir, except for Ph and 2-CP.

The prediction of adsorption isotherms of phenol and chlorophenols onto GAC by the Sips model is shown on Fig. 2. The Sips equation fits adequately the experimental results. On the basis of the average percentage error values (Table 1), the Langmuir–Freundlich equation seems slightly better than that of Sips. The maximum adsorption capacities are identical to those obtained using the Langmuir–Freundlich isotherm. The parameter K_S and m_S change in the same manner as the constants K_{LF} and m_{LF} of the equation of Langmuir–Freundlich.

The Tóth model correctly simulates the adsorption isotherms of the studied phenolic compounds (Fig. 3). The coefficients of correlation are good ($r \geq 0.991$) for all the tested molecules. The average percentage error values lie between 0.9 and 4.16%. On the basis of the coefficients of correlation as well as the average percentage error values (Table 1), the Sips equation seems slightly preferable than that of the Tóth isotherm. The adsorption maximum capacities determined using the Tóth model are higher than those of Sips, Langmuir–Freundlich, Freundlich and Langmuir. For Ph and 2-CP, the maximum adsorption capacities are lower than the theoretical values, while, they are higher than the theoretical maximum capacities, for 4-CP, DCP, and TCP. This indicates that, according to the Tóth model, 4-CP, DCP,

Fig. 2. Comparison of experimental and predicted adsorption isotherms of phenol and chlorophenols onto GAC according to Sips model.
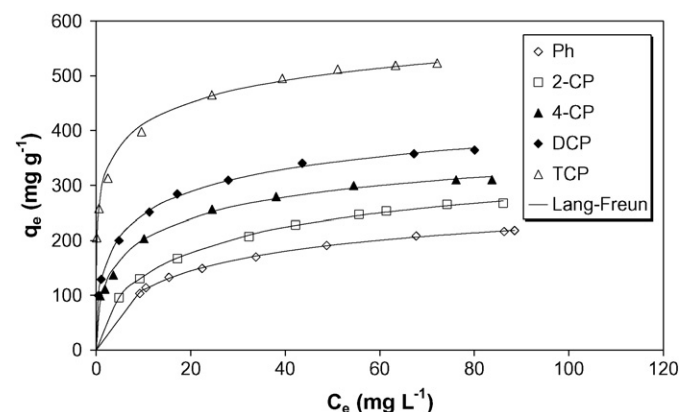

Fig. 1. Comparison of experimental and predicted adsorption isotherms of phenol and chlorophenols onto GAC according to Langmuir–Freundlich model.
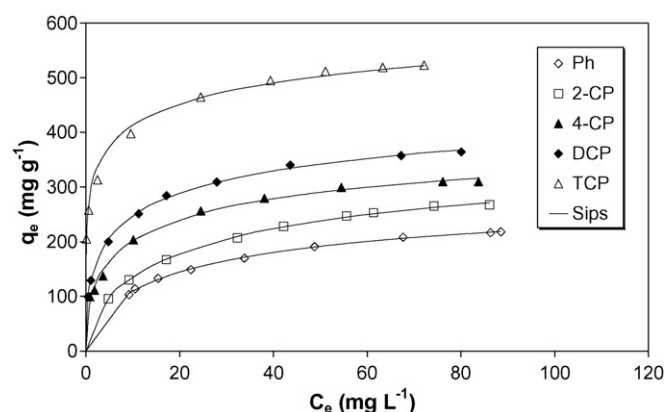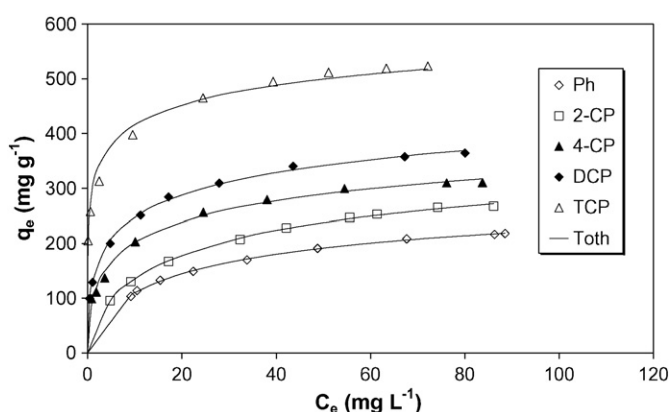

Fig. 3. Comparison of experimental and predicted adsorption isotherms of phenol and chlorophenols onto GAC according to Tóth model.

Table 1
Values of the parameters of the three-parameter models and correlation coefficients

Model	Parameters	Ph	2-CP	4-CP	DCP	TCP
Redlich-Peterson	A	29.999	41.636	275.695	554.710	2250.601
	B	0.2456	0.3103	1.9666	3.2427	7.2928
	β	0.8507	0.8232	0.8105	0.8208	0.8749
	r	0.999	0.999	0.994	0.998	0.956
	APE %	1.06	1.16	5.15	2.81	7.43
Sips	q_{mS} (mg·g^{-1})	313.652	401.387	460.237	551.037	854.806
	K_S (L^m·mg^{-m})	0.1157	0.1102	0.2540	0.2989	0.5140
	m_S	0.6668	0.6605	0.4873	0.4351	0.2610
	r	0.999	0.999	0.997	0.999	0.994
	APE %	1.04	0.82	3.77	1.40	3.11
Langmuir-Freundlich	q_{mLF} (mg·g^{-1})	313.654	401.321	460.093	550.968	847.114
	K_{LF} (L·mg^{-1})	0.0394	0.0355	0.0601	0.0623	0.0823
	m_{LF}	0.6668	0.6606	0.4875	0.4352	0.2712
	r	0.999	0.999	0.997	0.999	0.994
	APE %	1.04	0.82	3.77	1.40	2.99
Radke-Prausnitz-I	q_{mRPI} (mg·g^{-1})	140.814	151.676	113.876	130.889	154.528
	K_{RPI} (L·mg^{-1})	0.1830	0.2323	1.9326	3.2851	92.5845
	m_{RPI}	0.8237	0.7911	0.9755	0.8116	0.8598
	r	0.999	0.999	0.993	0.997	0.996
	APE %	1.07	1.29	5.45	3.07	2.65
Radke-Prausnitz-II	q_{mRPII} (mg·g^{-1})	122.159	134.185	140.194	171.066	283.254
	K_{RPII}	0.2456	0.3103	1.9664	3.2425	8.8159·10^{14}
	m_{RPII}	0.8507	0.8232	0.8105	0.8208	0.8520
	r	0.999	0.999	0.994	0.998	0.998
	APE %	1.06	1.16	5.15	2.81	2.75
Radke-Prausnitz-III	q_{mRPIII} (mg·g^{-1})	29.997	41.6084	274.780	553.789	4247.341
	K_{RPIII}	4.0727	3.2271	0.5107	0.3090	0.0723
	m_{RPIII}	0.1493	0.1767	0.1892	0.1791	0.1242
	r	0.999	0.999	0.994	0.998	0.980
	APE %	1.06	1.16	5.15	2.81	5.17
Tóth	q_{mT} (mg·g^{-1})	344.402	462.425	602.339	744.906	991.013
	K_T	0.3882	0.4274	1.4379	1.8912	4.8433
	m_T	0.5106	0.4724	0.2828	0.2407	0.1554
	r	0.999	0.999	0.996	0.999	0.991
	APE %	1.05	0.90	4.16	1.78	3.99
Jossens	H	24.587	34.209	122.577	340.912	644.845
	F	0.00067	0.00064	0.00082	0.00103	0.00102
	p	1.51168	1.46914	1.45082	1.41366	1.33643
	r	0.999	0.996	0.991	0.997	0.987
	APE %	3.16	4.89	17.43	10.50	/

and TCP are not adsorbed flat on the carbon surface. The order of the equilibrium constant K_T is similar to that of the parameter b of Langmuir. The same order as that of the equilibrium constant K_T is obtained for the parameter m_T.

The experimental results of the adsorption isotherms simulated by the model of Redlich–Peterson are presented on Fig. 4. From Table 1, the obtained coefficients of correlation are satisfactory and the average percentage error is about 3.52%. The Redlich–Peterson model describes with satisfaction the equilibrium data. A harmony is found between the ratio A/B of the Redlich–Peterson model and the constant K_F of the Freundlich equation. However, it is not the case for the parameter $1/n$ of the Freundlich model and the term $(1 - m_{RP})$.
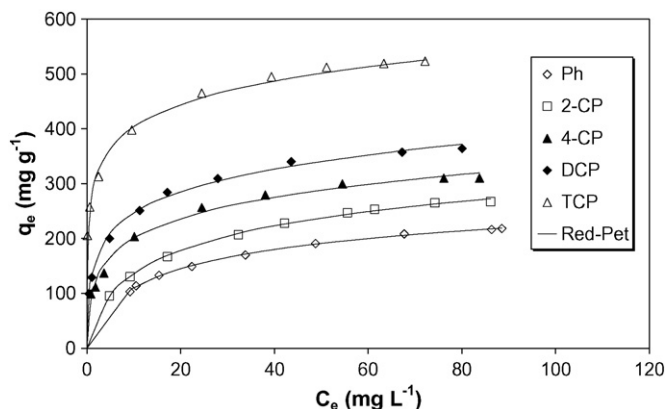
Fig. 4. Comparison of experimental and predicted adsorption isotherms of phenol and chlorophenols onto GAC according to Redlich–Peterson model.

Fig. 6. Comparison of experimental and predicted adsorption isotherms of phenol and chlorophenols onto GAC according to the four-parameter Fritz–Schlunder model.

The description of the adsorption isotherms by the model of Jossens is presented on Fig. 5. An appropriate prediction of the experimental results is obtained using the model of Jossens in the case of Ph and 2-CP (Table 1). For 4-CP and DCP, the simulation is worse because of the high average percentage error values (10.5 and 17.43%). In spite of the good coefficient of correlation for TCP, a very poor representation of the adsorption isotherm is obtained because of the high value of the average percentage error.

In spite of the good coefficients of correlation (≥ 0.98) and the low values of the average percentage error ($\leq 3.07\%$), the maximum adsorption capacities for the studied phenolic compounds determined using the three-parameter equations of Radke–Prausnitz (Table 1) are lower than the adsorbed amounts at equilibrium corresponding to the plateaus of the isotherms, except for DCP for which the value of the maximum adsorption capacity determined using the equation of Radke–Prausnitz-III is higher than those of Langmuir and Freundlich and lower than the theoretical value. For TCP, the maximum adsorption capacity obtained by the model of Radke–Prausnitz-III is abnormally high and inadmissible. Consequently, the three equations of Radke–Prausnitz cannot describe the experimental equilibrium data.
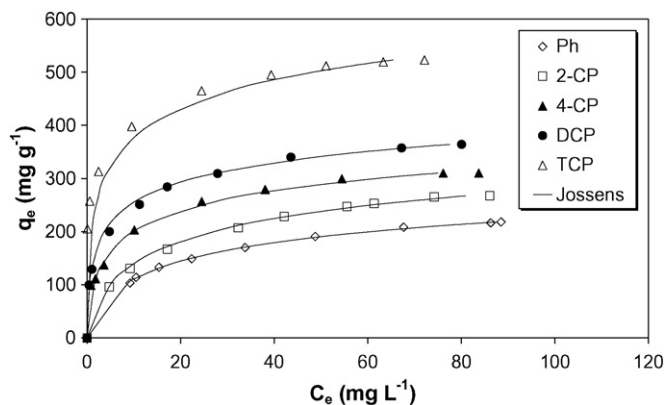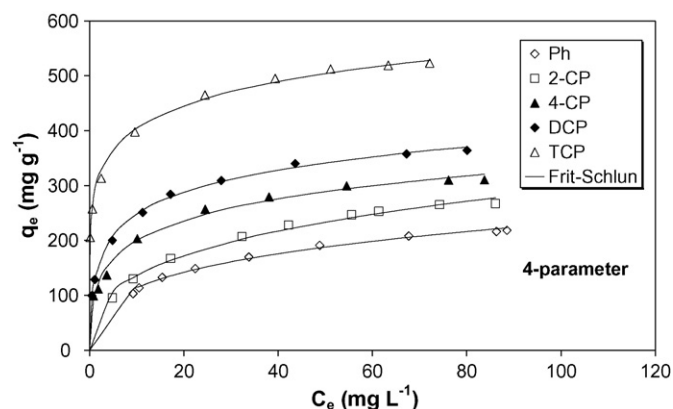

Fig. 5. Comparison of experimental and predicted adsorption isotherms of phenol and chlorophenols onto GAC according to Jossens model.

The results obtained using the three-parameter equations show that the best-fitted adsorption isotherm models were determined to be in the order: Langmuir–Freundlich > Sips > Tóth > Redlich–Peterson.

The models of Tóth, Radke–Prausnitz-I and II, Fritz–Schlunder, Langmuir–Freundlich, and Sips are reduced to the Langmuir model when the exponents m_T, m_{RPI}, m_{RPII}, m_{FS}, m_{LF}, and m_S are equal to unity. For higher liquid-phase concentrations, the model of Fritz–Schlunder and Radke–Prausnitz-I are converted to the Freundlich model. The equation of Radke–Prausnitz-III is reduced to Henry's law when the exponent $m_{RPIII} = 1$.

4.1.2. Four-parameter models

The adsorption data were analyzed according to the non-linear form of the four-parameter isotherm models.

An appropriate fitting of the experimental results of adsorption isotherms is obtained using the four-parameter model of Fritz–Schlunder (Fig. 6). From Table 2, the coefficients of correlation (≥ 0.994) are very good and the mean value of average percentage error for the studied compounds is 2.95%. An agreement has been noticed between the ratio A/B and the Freundlich constant K_F and between the term ($\alpha - \beta$) and the exponent $1/n$ of the Freundlich equation.

The prediction of equilibrium adsorption isotherms of phenol and chlorophenols on GAC by the Baudu model is presented on Fig. 7. An excellent description of the experimental results is obtained using the model of Baudu. On the basis of the average percentage error values (Table 2), the equation of Baudu seems better than that of Fritz–Schlunder. The values of the maximum adsorption capacity obtained using the Baudu isotherm are higher than those calculated by the Langmuir and Freundlich models and lower than the theoretical values. The equilibrium constant b_0 evolves in the same manner as the parameter b of the Langmuir equation. According to the results of Table 2, an accord between the term $[q_{m0} b_0 /(1 + b_0)]$ of the model of Baudu and the parameter K_F of Freundlich isotherm.

The worse fits of the equilibrium isotherms by the four-parameter equations are given in grey frames in Table 2.

Table 2
Values of the parameters of the four-parameter models and correlation coefficients

Model	Parameters	Ph	2-CP	4-CP	DCP	TCP
Weber-van Vliet	P_1	7.271	9.831	19.442	31.48969	62.587
	P_2	1.8057	1.8041	2.1617	1.9097	2.2244
	P_3	−0.4131	−0.4446	−0.5319	−0.5741	−0.6551
	P_4	0.4763	0.4968	0.4247	0.4012	0.3672
	r	0.999	0.997	0.910	0.871	0.300
	APE %	1.05	2.24	16.60	20.34	26.16
Fritz-Schlunder	A	218.632	225.024	259.902	312.737	893.805
	B	3.3199	2.9686	1.6728	1.4616	2.1436
	α	0.7596	0.7763	0.7570	0.7106	0.3166
	β	0.4799	0.4758	0.5834	0.5731	0.2227
	r	0.995	0.995	0.994	0.998	0.996
	APE %	2.38	2.88	4.73	2.29	2.45
Baudu	q_{m0} (mg·g^{-1})	292.166	327.199	407.073	469.981	671.182
	b_0	0.1597	0.1723	0.3016	0.3743	0.7441
	x	−0.4833	−0.5257	−0.5024	−0.5744	−0.9161
	y	0.04597	0.08337	0.01249	0.02321	0.10277
	r	0.998	0.997	0.996	0.999	0.997
	APE %	1.26	1.34	3.90	1.47	1.96

Adsorption equilibrium isotherms of the studied phenolic compounds onto GAC cannot be simulated correctly by the model of Weber–van Vliet because of the lower coefficients of correlation and higher average percentage error values (13.28%), especially for 4-CP, DCP, and TCP.

It was concluded for the fitting of the equilibrium adsorption data for the tested phenolic compounds onto activated carbon that the three-parameter models of Langmuir–Freundlich, Sips, and Tóth are better than that of the four-parameter equation of Fritz–Schlunder.

4.1.3. Five-parameter model

The adsorption data were analyzed according to the non-linear form of the five-parameter isotherm model of Fritz–Schlunder.

An adequate fitting of the experimental results of the adsorption isotherms is obtained using the five-parameter model of Fritz–Schlunder (Fig. 8). From Table 3, the coefficients of correlation are very good (≥0.994) and the average percentage error value for the studied compounds is 2.32%. The values of the maximum adsorption capacity obtained using the
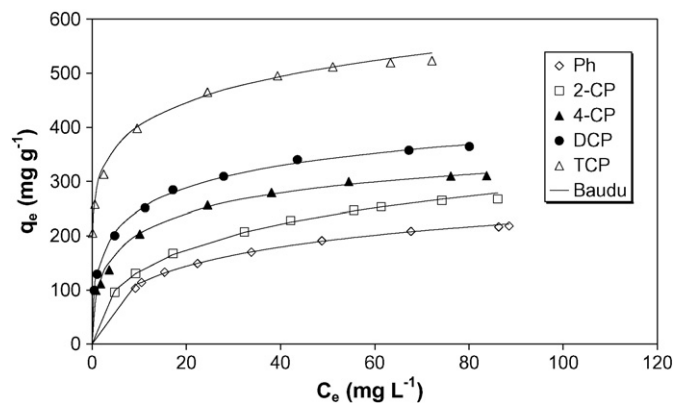
Fig. 7. Comparison of experimental and predicted adsorption isotherms of phenol and chlorophenols onto GAC according to Baudu model.
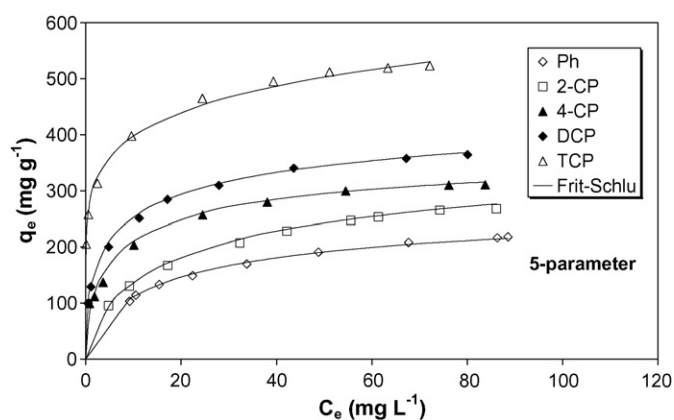

Fig. 8. Comparison of experimental and predicted adsorption isotherms of phenol and chlorophenols onto GAC according to the five-parameter Fritz–Schlunder model.

Fig. 9. Effect of pH on the adsorption isotherms of 4-CP onto GAC.

Fritz–Schlunder equation are higher than those calculated by the Langmuir model and lower than the theoretical values. The maximum adsorption capacities are higher than the values determined using the Freundlich model, except for 2-CP.

The five-parameter model of Fritz–Schlunder is reduced to the Langmuir model when the exponents m_1 and m_2 are equal to unity. For higher liquid-phase concentrations, the model of Fritz–Schlunder is converted to the Freundlich model.

By comparing the three-parameter, four-parameter, and five-parameter models, it seems that the model of Baudu is the most adapted for the fitting of adsorption isotherms because of the lower average percentage error value obtained for the five phenolic compounds (1.99%). The models of
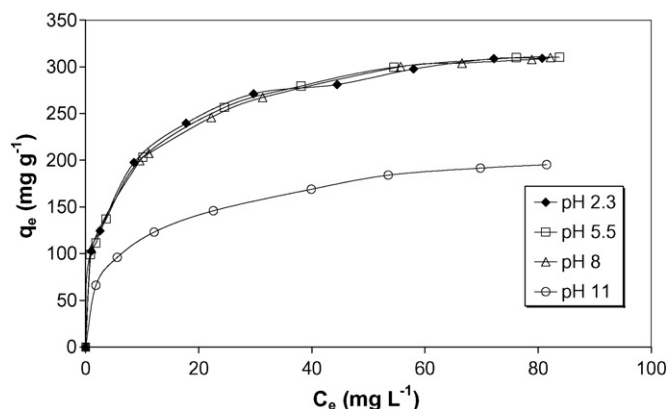
Langmuir–Freundlich and Sips (three-parameter) are better than that of Fritz–Schlunder (five-parameter). The four-parameter models of Baudu and Fritz–Schlunder are better than that of Fritz–Schlunder with five-parameter.

4.2. Effect of pH

The effect of pH on the equilibrium adsorption isotherms of 4-CP on activated carbon was investigated over a pH range of 2.3–11. The pH values were adjusted with dilute hydrochloric acid and sodium hydroxide solutions. Adsorption isotherms of 4-CP onto GAC at different pH are shown on Fig. 9. The obtained results show that there is no significant effect of the solution pH on adsorption equilibrium isotherms for pH 2.3, 5.5, and 8. On the other hand, the isotherm realized at pH 11 is characterized by an adsorption equilibrium capacity lower than those obtained at lower pH. At a solution pH lower than the pH_{PZC} (4.1 for the used GAC), the total surface charge will be on average positive, whereas at a higher solution pH it will be negative. In fact, the uptake was maximal at lower pH (pH < pK_a) because 4-CP was undissociated and the dispersion interactions predominated. At basic pH, however, the uptake was lower because of electrostatic repulsions between the negative surface charge and the chlorophenolate anions and between chlorophenolate–chlorophenolate anions in solution. High solubility of chlorophenolate anions may be another reason for lower adsorption at pH 11.

According to the numerical data listed in Table 4, the majority of functional groups on GAC surface were found to be acidic. Each $100 \, nm^2$ of the carbon surface thus contains 51 acidic and

Table 3

Values of the parameters of the five-parameter model and correlation coefficients

Model	Parameters	Ph	2-CP	4-CP	DCP	TCP
Fritz–Schlunder	$q_{m_{FS5}}$ (mg g^{-1})	257.627	283.869	481.777	580.254	664.226
	K_1	0.1288	0.1419	0.2362	0.2936	0.5651
	K_2	0.1606	0.1654	0.2819	0.3352	0.3202
	m_1	0.8048	0.8027	0.5920	0.4693	0.1574
	m_2	0.7520	0.7267	0.5969	0.4692	0.0450
	r	0.998	0.997	0.994	0.999	0.998
	APE%	1.33	1.78	4.67	1.95	1.86

Table 4
Results of Boehm titration

Carboxyl groups	0.06 mequiv. g^{-1}	0.06 µequiv. g^{-2}
Phenolic groups	0.22 mequiv. g^{-1}	0.24 µequiv. g^{-2}
Lactonic groups	0.5 mequiv. g^{-1}	0.54 µequiv. g^{-2}
Total acidic groups	0.78 mequiv. g^{-1}	0.84 µequiv. g^{-2}
Total basic groups	0.59 mequiv. g^{-1}	0.64 µequiv. g^{-2}
All groups	1.37 mequiv. g^{-1}	1.48 µequiv. g^{-2}
Groups $(100\,nm^2)^{-1}$		89
Number of adsorbed molecules (molecules $(100\,nm^2)^{-1}$)		
$\quad q_m$ (Baudu)		205
$\quad q_m$ (Langmuir–Freundlich)		232
$\quad q_m$ (Freundlich)		176

38 basic, or a total of 89 functional groups. Regarding the surface concentration of the titrated groups ($89\,(100\,nm^2)^{-1}$), the surface concentration of the adsorbed molecules (Table 4) is found in all cases to be significantly higher, i.e. adsorption occurs not only at the titrated functional groups. On the other hand, the surface area occupied by a single solute molecule is far higher than the theoretical value, i.e. the monolayer is not densely packed with adsorbed solute molecules.

The possible interactions between the carbon surface and phenols are (i) dispersion effect between the aromatic ring and the electrons of the graphitic structure; (ii) electron donor-acceptor interaction between the aromatic ring and the basic surface sites; (iii) electrostatic attraction and repulsion when ions are present.

At pH 2.3, both the functional groups on the carbon surface and the phenolic compound is in protonated form, that is, the surface groups are positively charged ($pH < pH_{PZC}$). At pH 5.5 and 8, surface functional groups are charged negatively, but the 4-CP is almost in its protanated form ($pH < pK_a$). Owing to the fact that the adsorption capacities at equilibrium at pH 2.3, 5.5 and 8 are practically identical, the interaction between the carbon surface and the 4-CP can be predominantly attributed to the dispersion effect.

At pH 11, 4-CP dissociate, forming negatively charged chlorophenolate anions, while the surface functional groups are negatively charged. The electrostatic repulsion between the like charges lowers the adsorption capacity and weakens the overall interaction. Deprotonated acidic groups along the edges of the graphitic layers repel the deprotonated chlorophenolate ions, thereby reducing access of chlorophenolate ions to the space between the turbostratic sheets. In addition to ionic repulsion, London dispersion also contributes. Competitive adsorption of water molecules must also be considered: the surface is more sparsely populated by the solutes at pH 11. Thus, the pH at which the uptake decreased was found to be dependent on the adsorptive pK_a and the pH_{PZC}. Additionally, surface acidic groups play a key role in the adsorption process [16,17].

5. Conclusion

Adsorption isotherms of phenolic compounds on activated carbon were studied and modeled using thirteen isotherm models with more than two-parameter.

An excellent prediction in all the studied concentration range can be obtained by the three-parameter equations. The classification of the three-parameter models according to the simulation of the adsorption isotherms is: Langmuir–Freundlich > Sips > Tóth > Redlich–Peterson.

Among all the tested equations, an excellent and perfect representation of the experimental results is obtained using the four-parameter model of Langmuir modified by Baudu. The five-parameter equation of Fritz–Schlunder simulates rightfully the experimental results, but the equations of Langmuir modified by Baudu (four-parameter), Langmuir–Freundlich (three-parameter), and Sips (three-parameter) were better.

It was concluded that the solution pH has not an influence on the 4-CP adsorption isotherms for $pH < pK_a$. When the pH increases beyond this value, a significant decrease of the adsorption capacity was observed. This decrease can be explained by the increase of negative charge on the activated carbon surface, because the solution pH is much higher than pH_{PZC} (4.1), and the predominance of chlorophenolate anions at this pH. Therefore, the electrostatic repulsion forces between the adsorbent surface and adsorbate anions increase. On the other hand, it seems that 4-CP solubility that varied considerably with the solution pH may be another reason for this decrease.

The classification of all the tested models for the description of adsorption equilibrium isotherms of phenol and chlorophenols on activated carbon is as follows: Baudu (four-parameter) > Langmuir–Freundlich (three-parameter) > Sips (three-parameter) > Fritz–Schlunder (five-parameter) > Tóth (three-parameter) > Fowler–Guggenheim > Fritz–Schlunder (four-parameter) > Hill–de Boer > Temkin > Freundlich (two-parameter) > Redlich–Peterson (three-parameter) > Kiselev > Langmuir (two-parameter).

In the literature, the researchers generally compare the equations with three, four, even with five parameters with the two-parameter equations of Langmuir and Freundlich. They generally concluded from their studies that the equations with more than two parameters are always better than those with two parameters.

In the two parts of this work, the comparison between the isotherm models is not limited to that with several parameters and those of Langmuir and Freundlich. The models allowing the determination of thermodynamic parameters (Fowler–Guggenheim, Kiselev, Hill–de Boer and Temkin) were also tested. The obtained results really show that the adjustment of more parameters makes possible a better fitting of the equilibrium isotherms. However, the mode of covering of the adsorption sites on the carbon surface is not possible by the models with more than two parameters owing to the fact that they do not adapt a thermodynamic model such those of Langmuir or Elovich. Nevertheless, the models of Fowler–Guggenheim, Hill–de Boer, and Temkin allow the determination of the energy of adsorption and the energies of interaction and complexation between the adsorbate molecules. These models are better than several models with four-parameter and three-parameter.

Acknowledgement

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