The isothermal adsorption of nicotine from an aqueous solution onto zeolite type USY at temperature range from 298 to 322 K was investigated. It was found that the adsorption isotherms can be described by the Freundlich adsorption isotherm. The density distribution function of adsorption centers has an exponential form and the adsorption isotherms can be fitted by the Freundlich isotherm. The changes of adsorption heats, free energy and entropy with the adsorption degree were determined on the base on the adsorption isotherms. The decrease of adsorption heat with the adsorption degree is explained by the presence of energetic heterogeneity of the adsorption centers on the interface. The increase of entropy with the adsorption degree can be explained with the change of the type of adsorption and with the phase state of adsorbed nicotine which has a structure different than liquid nicotine.

Numerous methods of elimination of nicotine from aqueous solutions have been developed: catalytic oxidation [1], microbiological degradation [2] and adsorption on solid adsorbents. The isothermal adsorption of nicotine from an aqueous solution onto different types of hydrophilic zeolite (NaA, NaX, NaY), hydrophobic zeolite (HZSM-5; silicate) and amorphous materials was investigated by Adnadjevic and co-workers [3].

Stošić et al. investigated adsorption of nicotine from an aqueous solution onto different types of zeolite: clinoptilolite, HZSM-5, FeZSM-5, CuZSM-5, β zeolite and activated carbon. The adsorption heats for nicotine adsorption onto β zeolite and activated carbon were in the range from 0.7 to 3.0 J/g and 0.7 to 2.5 J/g, respectively. It was found that during the adsorption of nicotine on the above mentioned solid, adsorbents did not produce any chemical transformation of nicotine molecules. The possible sites at which the nicotine molecules could be bonded to the surface of clinoptilolite and ZSM-5 zeolites were determined by NMR spectroscopy [4].

Adsorption of nicotine to magnesium-aluminium silicate was investigated by Sukseri et al. [5]. It was found that the isothermal adsorption of nicotine at different pH could be described by Langmuir and Freundlich models. The slopes of the Freundlich isotherms increase with the increase in the pH value, while the adsorption capacities decrease with the decrease in the pH value.

Saraydin et al. [6] investigated adsorption of nicotine onto poly(acrylamide/maleic acid) hydrogels. Based on the determined adsorption heats they concluded that nicotine was adsorbed by physical bonds onto the poly(acrylamide/maleic acid) hydrogel. The adsorption isotherm corresponds to S-type (sigmoidal) in the Giles classification system for adsorption of a co-solute from its solution.

The aim of this work was to investigate the ability of nicotine adsorption onto hydrophobic zeolite type USY, to determine the adsorption isotherm at different temperatures, heats of adsorption, changes of free energy and entropy and to propose a mechanism of nicotine adsorption.

**EXPERIMENTAL**

Nicotine (p.a.) was purchased from Merck, KGaA, Darmstadt, Germany. Zeolite type USY was synthesized at the Faculty of Physical Chemistry, Belgrade. Table 1 presents the basic physico-chemical properties of zeolite type USY. Distilled water was used in all experiments.

<table>
<thead>
<tr>
<th>Table 1. Basic physico-chemical properties of the zeolite type USY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical – chemical property</td>
</tr>
<tr>
<td>Degree of crystallinity (%)</td>
</tr>
<tr>
<td>SiO2, wt%, anhydrous basic</td>
</tr>
<tr>
<td>Al2O3, wt%, anhydrous basic</td>
</tr>
<tr>
<td>SiO2/Al2O3, molar ratio</td>
</tr>
<tr>
<td>Degree of hydrophobicity (%)</td>
</tr>
<tr>
<td>Lattice parameter (nm)</td>
</tr>
<tr>
<td>Crystal size SEM (μm)</td>
</tr>
<tr>
<td>Surface area BET, m²/g</td>
</tr>
<tr>
<td>Specific volume (cm³/g)</td>
</tr>
</tbody>
</table>

Determination of the adsorption isotherms of nicotine onto the zeolite

Batch adsorption experiments were carried out by using the zeolite type USY powder as the adsorbent. A series of adsorption vessels containing nicotine solutions with initial concentrations of 1 wt% and a determined dosage of the zeolite (1.0, 1.3, 2.0, 2.5, 3.3, 4.0, 4.4, 5.0, 5.9, 6.7, 7.7, 10.0, 13.3 and 20.0 g/L) were
placed in the thermostat at pre-determined temperature (298, 311 and 322 K) and left until the system reached equilibrium. Equilibrium was considered to be achieved when two consecutive nicotine concentrations in solution that were measured over a period time of 30 min between samples showed no significant difference in concentration. Our experiments indicated that 3 h were enough to ensure that equilibrium was reached at investigated temperatures. After that time, samples were taken from this adsorption system and centrifuged for 5 min at constant stirring speed of 400 rpm. The nicotine concentration in water solution was determined in accordance with the spectrometric method specified in ISO 2881 [7].

The specific adsorption capacity of zeolite USY for nicotine, $x_s (\%)$, is calculated at a given temperature from the equation:

$$x_s = \frac{V(c_0-c_i)}{m} \times 100$$  \hspace{1cm} (1)

where $c_0$ is the initial concentration of the nicotine solution before adsorption (g/L), $c_i$ is the concentration of the nicotine solution after reaching equilibrium (g/L), $V$ volume of solution (L) and $m$ is the mass of zeolite (g).

The adsorption isotherms of nicotine onto zeolite are presented in the form of $x_s = f(c_i)$.

**Determination of the adsorption degree of nicotine onto the zeolite**

The adsorption degree of nicotine onto the USY zeolite, $\theta$, is calculated at a given temperature from the equation:

$$\theta = \frac{x_s}{x_{\text{max}}}$$  \hspace{1cm} (2)

where $x_{\text{max}} (\%)$ is the maximum adsorption capacity of the USY zeolite for nicotine at a given temperature and is determined from experimental isotherms $x_s = f(c_i)$.

**Freundlich model of adsorption**

The Freundlich adsorption isotherm is an empirical equation based on adsorption on a heterogeneous surfaces or surfaces supporting sites of varied affinities. The Freundlich isotherm [8] is expressed as:

$$x_s = K_F c_i^{1/n}$$  \hspace{1cm} (3)

where $K_F$ and $n$ are Freundlich constants. The Freundlich constant $n$ indicates the favorability of the adsorption process and presents a measure of the deviation from the linearity of the adsorption and is used to verify the type of adsorption. The Freundlich constant $K_F$ is the adsorption capacity of the adsorbent and can be defined as the adsorption or distribution coefficient.

**RESULTS AND DISCUSSION**

The adsorption isotherms of nicotine from the aqueous solution onto zeolite type USY at investigated temperatures are shown in Figure 1.

![Figure 1. The adsorption isotherms of nicotine onto USY zeolite at different temperatures (■ 298, ● 311 and ▲ 322 K).](image)

As it can be seen from the results presented in Figure 1, the adsorption isotherms of nicotine onto zeolite type USY are of the same characteristic shape typical of so-called isotherms of type L [9] at all of the investigated temperatures. Two characteristic shapes of dependences can be observed from the presented isotherms, i.e. the nonlinear increase of the specific adsorption capacity with the increase in concentration and region of saturation (the maximum adsorption capacity). The rate of nonlinear changes of the adsorption capacity increases with the increase in adsorption temperature as well as the maximum of adsorption capacity.

The adsorption isotherms of type L, in this investigation, are characteristic for the microporous and energy heterogeneous adsorbent. With that in mind, in this paper the Freundlich empirical equation was used to describe the experimentally determined adsorption isotherms of nicotine onto zeolite type USY.

Figure 2 shows dependence of $\ln x_s$ on $\ln c_i$ for nicotine adsorption onto zeolite type USY at investigated temperatures. The dependence of $\ln x_s$ on $\ln c_i$ gives straight lines over the whole range of nicotine concentration and proves the possibility to describe the adsorption isotherm of nicotine onto the USY zeolite by Freundlich adsorption isotherm in entire range of nicotine concentration at all of the investigated temperatures. That enables to determine the Freundlich parameters $K_F$ and $n$.

The effect of the temperature on the changes of the parameters of Freundlich adsorption isotherms and correlation coefficients, $R^2$ are shown in Table 2. The increase in adsorption temperature leads to the increase in the Freundlich parameters, both $K_F$ and $n$. The increase in the Freundlich parameters indicates the change in the
energetical heterogeneity of the interface zeolite–nicotine solution.

Figure 2. The dependences of \( \ln x_s \) on \( \ln c_i \) at different temperatures (■ 298, ● 311 and ▲ 322 K).

Table 2. The changes of Freundlich parameters with temperature

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( K_F ) (%( c^{-1} ))</th>
<th>( n )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>35 ± 1</td>
<td>1.72 ± 0.01</td>
<td>0.994</td>
</tr>
<tr>
<td>311</td>
<td>36 ± 1</td>
<td>2.08 ± 0.01</td>
<td>0.992</td>
</tr>
<tr>
<td>322</td>
<td>40 ± 1</td>
<td>2.17 ± 0.04</td>
<td>0.992</td>
</tr>
</tbody>
</table>

In order to prove that hypothesis, the dependence of the isosteric heat of adsorption on the adsorption degree was examined. The isosteric heat of nicotine adsorption is determined using the experimental adsorption isosters, \( i.e. \) by the expression:

\[
\ln c_{\theta,T} = -\frac{Q_{\text{ads}}}{RT} + A
\]  

(4)

where \( c_{\theta,T} \) is the equilibrium concentration of nicotine in the solution and it is the value of concentration at which the adsorption degree \( \theta \) is achieved at a certain temperature.

Figure 3 shows dependence of \( \ln c_{\theta,T} \) on \( 1/T \) at different \( \theta \) values. Based on the results presented in Figure 3, all of the dependences of \( \ln c_{\theta,T} \) on \( 1/T \) for different adsorption degrees gave a straight line with a slope from which the isosteric heat of adsorption was obtained.

Figure 4 shows the dependence of the isosteric heat of adsorption on the adsorption degree.

The isosteric heat of nicotine adsorption onto the zeolite significantly changes, actually decreases with the increase in the adsorbed nicotine. The determined values of isosteric adsorption heat imply that the nicotine was adsorbed onto the adsorption centers by the hydrogen and van der Walls bonds (physical adsorption). The isosteric heat of adsorption \( \text{versus} \) adsorption degree dependence clearly reveals three characteristic shapes of the decrease in the isosteric adsorption heat with the increase in the adsorption degree: almost linear, non-linear and plateau.

The isosteric adsorption heat almost linearly decreases (from 30 to 18 kJ/mol) with the increase in the adsorption degree in the range \( 0.05 \leq \theta < 0.3 \). For the range of the adsorption degree \( 0.3 \leq \theta \leq 0.7 \), the isosteric adsorption degree decreases from the 18 to the 5 kJ/mol with the increase in the adsorption degree, while for the adsorption degree \( \theta \geq 0.7 \) isosteric adsorption heat is almost independent on the adsorption degree.

The changes in the adsorption heat with the adsorption degree are characteristic for adsorption onto energetically heterogeneous adsorbents. This directly proves the previously presented assumption about the energetical heterogeneity of the interface of the zeolite for nicotine adsorption and implies the presence of adsorption centers with different values of adsorption heat on the zeolite.
The density distribution function of adsorption centers on adsorption heat, $\rho(Q_{ads})$, was determined in order to define precisely the shape of the energetical heterogeneity of the interface zeolite–nicotine solution. The density distribution function $\rho(Q_{ads})$ is defined to satisfy [10]:

$$\int \rho(Q_{ads}) \, dQ = 1$$

It is clear that the dependence $\theta = f(Q_{ads})$ can be easily determined if the dependence of the isosteric heat of adsorption on the adsorption degree is known. The dependence of the $\rho(Q_{ads})$ is obtained by differentiating that dependence.

The plot of density distribution function $\rho(Q_{ads})$ versus isosteric heat of adsorption $Q_{ads}$ is given in Figure 5.

![Figure 5. The dependence of the function of density distribution on the adsorption heat and the plot of ln $\rho(Q_{ads})$ versus $Q_{ads}$.](image)

The function of density distribution of adsorption onto zeolite type USY decreases exponentially, which can be described by the following function:

$$\rho(Q_{ads}) = \alpha \exp(-mQ_{ads})$$

where $\alpha$ and $m$ are the parameters of the function of density distribution of adsorption. The values the function of density distribution are determined graphically from the plot $\ln \rho(Q_{ads})$ vs. $f(Q_{ads})$ which is also presented in Figure 5.

As shown in Figure 5, the plot of the $\ln \rho(Q_{ads})$ vs. the $Q_{ads}$ gives a straight line with slope and intercept from which the parameters of the function of density distribution of adsorption are determined. These values are shown in Table 3.

The data of the function of density distribution enables obtaining the functional form of the nicotine adsorption isotherms onto the zeolite. For an energetically heterogeneous surface the following equation should be valid [11]:

$$\theta = \int_{Q_p}^{Q_{max}} \rho(Q_{ads}) \, dQ_{ads}$$

where $Q_{max}$ is the maximum value of heat of adsorption, $Q_{ads} = -RT \ln (b_0c_{min})$, $Q_p = -RT \ln (b_0c_i)$, where $b_0$ is the coefficient of adsorption and $c_{min}$ is the minimal concentration of nicotine in the equilibrium.

![Table 3. The parameters of the density distribution function](image)

Accordingly, Eq. (7) gets the following form:

$$\theta = a\int_{Q_p}^{Q_{max}} \exp(-mQ_{ads}) \, dQ_{ads} = \alpha \left[ \frac{(b_0c_i)^{mRT}-(b_0c_{min})^{mRT}}{m} \right]$$

When $c_{min} << c_i$, i.e. when $Q_{max} >> Q_p$, the equation (8) is transformed to:

$$\theta = a\left( b_0 c_i \right)^{mRT} \frac{1}{m} = \alpha$$

where $a = \alpha(b_0)^{mRT} / m$ and $1/n = mRT$.

It is obvious that Eq. (9) corresponds to the Freundlich adsorption isotherm by mathematical form, which agrees with the previously established facts.

In order to determine the type of the adsorption of the investigated nicotine adsorption process onto zeolite (localized, delocalized), the change of entropy $\Delta S(\theta)$ of nicotine adsorption with the increase in the adsorption degree was examined. The change of entropy of adsorption is determined using the following equation:

$$\Delta S(\theta) = \frac{-Q_{ads}(\theta) - \Delta G(\theta)}{T}$$

where $\Delta G(\theta)$ is the change of the free energy of adsorption, which is given by the expression $G(\theta) = -RT \ln c_i$ [12].
heat with the adsorption degree. In the adsorption degree range of $0.05 \leq \theta < 0.3$, adsorption entropy has relatively high negative values (from $-64$ to $-16$ J/mol K) and almost linearly decreases with the increase in the adsorption degree. In the range of $0.3 \leq \theta \leq 0.5$, the values of the enthalpy of adsorption are still negative and decrease with the increase in the adsorption degree until down to 0 J/mol K, whereas when the $\theta > 0.5$, the enthalpies of the adsorption become positive values and increase with the increase of $\theta$.

Figure 6. The dependences of free energy on the adsorption degree at different temperatures (■ 298, ● 311 and ▲ 322 K).

Figure 7 shows the changes of the entropy of adsorption $\Delta S(\theta)$ with the adsorption degree at investigated temperatures.

Figure 7. The changes in entropy with the adsorption degree at ■ 298, ● 311 and ▲ 322 K.

By definition, the entropy of adsorption is given by the expression:

$$\Delta S_{\text{ads}}(\theta) = S_{\text{ads}}(\theta) - S_{\text{sol}}$$

where $S_{\text{ads}}(\theta)$ is the entropy of nicotine in the adsorbed layer for defined adsorption degree and $S_{\text{sol}}$ is the entropy of nicotine in the water solution.

Although $S_{\text{sol}}$ is an unknown value, it can be calculated by the assumption that the Sackur–Tetrode–Treuton equation is valid [13]:

$$S_{\text{sol}} = R \ln \left(\frac{M^{3/2}}{T^{5/2}}\right) - 101.60 = 80.17 \text{ J/mol K}$$

where $R$ is the universal gas constant, $M$ is the molar mass of nicotine and $T$ is the actual temperature.

When the molecules of adsorbate are completely localized on the adsorbent adsorption centre, entropy of the localized molecules ($S_{\text{loc}}$) is given by the equation [14]:

$$S_{\text{loc}} = R \ln \frac{\theta}{1-\theta}$$

The calculated values of the adsorption entropy, $\Delta S_{\text{ads}}$, applying Eqs. (11)–(13), are considerably lower than experimentally determined adsorption entropy, $\Delta S(\theta)$, implying that nicotine adsorption onto the zeolite is not localized.

If it is assumed that the adsorption centers of the zeolite are the potential cavity in which the adsorbed molecules have the limited freedom of translator move, then the following expression for the entropy of the adsorbed phase can be obtained [15,16]:

$$2D S_{\text{ads}} = R \ln \theta + R \ln (MT\sigma_0) + 267$$

where $\sigma_0$ is the area of the nicotine molecule in the adsorbed layer and that value is $36 \times 10^{-16} \text{ cm}^2$.

The calculated values of the adsorption entropies, the $\Delta S'_{\text{ads}}$, using Eqs. (11), (12) and (14) are in accordance with the experimentally determined values of the enthalpy adsorption, as well as with their change with the increase in the amount of the adsorbed nicotine.

It can be assumed that the adsorbed nicotine molecules for the $0.05 \leq \theta \leq 0.3$ are in the form of the two-dimensional clusters separated one from another. When the $\theta = 0.5$, the continual two-dimensional layer of nicotine adsorbed is formed, whereas when the $\theta \geq 0.7$, the three-dimensional layer of adsorbed nicotine with structure different from the liquid nicotine is created.

CONCLUSIONS

The Freundlich model was used to describe the experimentally determined adsorption isotherms of nicotine onto zeolite type USY. The reactive zeolite interface for the adsorption with the nicotine solution is energetically heterogeneous. The increase in adsorption temperature leads to the increase in Freundlich parameters, which implies the change in the energetic heterogeneity of the interface zeolite–nicotine solution. The density distribution function of adsorption centers on
adsorption heat has an exponential form, and the possibility of fitting the adsorption isotherms of nicotine onto the zeolite by Freundlich adsorption isotherm is a direct consequence of that. The determined increase in entropy with the increase in adsorption degree can be explained by the change of the type of adsorption and the phase state of adsorbed nicotine.

Acknowledgement

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Nomenclature

- $x_s$: Specific adsorption capacity (%)
- $c_0$: Initial concentration of the nicotine solution before adsorption (g/L)
- $c_i$: Nicotine solution concentration after reaching equilibrium (g/L)
- $V$: Volume of nicotine solution (L)
- $m$: Mass of zeolite (g)
- $\theta$: Adsorption degree of nicotine onto the zeolite
- $x_{max}$: Maximum adsorption capacity of the zeolite for nicotine (%)
- $K_{F,n}$: Freundlich constants
- $R^2$: Correlation coefficient
- $c_{0,T}$: Equilibrium concentration of nicotine solution at given adsorption degree and temperature (g/L)
- $Q_{ads}$: Isosteric heat of adsorption (kJ/mol)
- $\rho(Q_{ads})$: Density distribution function
- $\alpha, m$: Parameters of the function of density distribution
- $Q_{max}$: Maximum value of heat of adsorption (kJ/mol)
- $c_{min}$: Minimal nicotine concentration in the equilibrium (g/L)
- $R$: Universal gas constant (8.314 J/mol K)
- $T$: Temperature (K)
- $\Delta S(\theta)$: Experimentally determined adsorption entropy (J/mol K)
- $\Delta G(\theta)$: Change of the free energy of adsorption (kJ/mol)
- $\Delta S_{ads}$: Entropy of adsorption (J/mol K)
- $S_{ads}(\theta)$: Entropy of nicotine into the adsorbed layer for defined adsorption degree (J/mol K)
- $S_{sol}$: Entropy of nicotine in the water solution (J/mol K)
- $M$: Molar mass of nicotine
- $S_{loc}$: Entropy of the localized molecules (J/mol K)
- $2DS_{ads}$: Entropy of the adsorbed phase (J/mol K)
- $\sigma_0$: Area of the nicotine molecule in the adsorbed layer (36x10^-16 cm²)

REFERENCES

IZVOD

TERMODINAMIKA I MEHANIZAM ADSORPCIJE NIKOTINA IZ VODENOG RASTVORA NA HIDROFOBNOM ZEOLITU TIPA USY

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Ključne reči: Nikotin • Adsorpcija • Zeolit • Funkcija raspodele gustine • Entropija adsorpcije

Key words: Nicotine • Adsorption • Zeolite • Density distribution function • Entropy of adsorption