DETERMINATION OF THE STRUCTURAL AND CHEMISORPTION CHARACTERISTICS OF GRANULATED ACTIVE CHARCOAL ON THE BASIS OF COCONUT SHELL

Wastewater purification and the acquisition of drinking water from water streams that are in most cases recipients of various industrial plants, present a significant problem nowadays. The structural characteristics of granulated active charcoal (GAC) obtained by the carbonization of coconut shells and activated by steam are presented in this paper. The established kinetics of suspending cyanide from aqueous solution using GAC impregnated with copper(II) acetate were studied and a mathematical model established by a regression-correlation analysis.

Only hard porous materials with highly developed porosity are able to successfully adsorb gases and vapours. Among them is active charcoal (AC). The adsorption properties of active charcoal are related to their porous structure with micro pores (<10^-6 m) being the most important. Adsorption on GAC is physical sorption and, partly chemisorption, keeping in mind that the sorption depends to a great extent on the carbon-abiding raw-material that is activated (charcoal, anthracite, coconut shell, stones of various fruits, organic polymers) and on the conditions of activation [1]. According to M.M. Dubinin, it is possible to sort the activating methods into three categories: gas steam activation (H₂O and CO₂ with or without O₂), which can be considered as physical activation, activation in the presence of chemically activated inorganic materials (that can be deemed as chemical activation) and a combination of the two [2]. In the chemical activation process zinc chloride, potassium carbonate, potassium sulphate, phosphate acid, etc. are used in practice. Adsorption on GAC is mainly achieved by physical sorption. The character of physical sorption in micro pores is described in detail in the theory of the volumetric replenishment of adsorption space [3].

Active charcoal, which on the one hand possesses a very favorable surface chemical structure and, on the other hand, has a sufficiently developed transit (1-25 x 10^-3 m) and macro (>25 x 10^-3 m) pores, is very suitable for outlaying a surface (impregnation). The impregnation leads to significant transformations, in the structural, adsorption, as well as in the physico-chemical properties of the active charcoal. Besides changes in the transit- and macro porosity of the active charcoal carbon, it also leads to reduced porosity. The subsequent changes in the adsorption properties can be observed with the increase of chemisorption and decrease of adsorption abilities of the impregnated in relation to the non-impregnated active charcoal [4].

With the right choice of impregnation reagents, using the impregnation process, active charcoals of variable chemisorption and adsorption properties can be obtained, thus expanding the possibility of their application. For various organic vapours, the most suitable is non-impregnated active charcoal. Adsorbates of acid characteristics, bound by a hydrolysis mechanism and by product neutralization on the active charcoal, require impregnation using bases and basic salts, usually the salts of alkali metals [5]. Active charcoals impregnated with various salts of strong acids and heavy metal oxides, are applied for the retention of adsorbates of alkaline character. For some materials (HCN) that bind forming complex compounds, the most suitable impregnation is using hydroxides and heavy metal salts [6].

The need to quantify physical sorption, as well as chemisorption, has resulted in a large number of mathematical models that describe the conditions of equilibrium adsorption. The adsorbate quantity by adsorbent unit mass (qₑ) is a function of the initial quantity of adsorbate and temperature qₑ = f(T,c). A large number of models describing equilibrium adsorption conditions [7] can be found in the literature:

- Langmuir's model based on assumptions concerning the existence of a monomolecular layer of adsorbate, chemical linkings of adsorbents and adsorbate and a mutual non-responsiveness of the adsorbate molecule has the following form

  \[ Y = \frac{Y_c}{b+c}, \]

  where \( Y \) represents the concentration of an adsorptive by adsorbent unit mass, \( Y_c \) – the surface concentration of an adsorbate upon total saturation of the adsorbent surface, \( C \) – the adsorbate concentration in equilibrium,
b – a constant the value of which represents the adsorptive concentration at which one half of the activated locations on the adsorptive surface are taken up by adsorbate molecules;

- The Freundlich empirical model, which indicates the satisfactory layering on adsorbents of great adsorption power, has the form

\[ Y = kC^{1/n}, \]

where \( k \) and \( n \) are constants distinctive for each adsorption system;

- The BET model, according to which subsequent layers are formed on the surface of the first layer of adsorbed molecules and it has the form

\[ \frac{V}{V_m} = \frac{(C-x)}{(1-x)(1-x+Cx)}, \]

where \( x \) is the relative concentration, \( V \) – the adsorbed matter volume, \( V_m \) – the volume of matter taking up the whole monomolecular layer, \( C \) – a constant.

- The volumetric pore replenishment theory;
- The Dubinin–Astakhov (DA) model;
- The Dubinin – Redushkevich (DR) model, and
- The Dubinin – Stoeckli (DS) model, and many other models.

Chemisorptions process kinetics has a great importance from the aspect of plant design for wastewater treatment using the equipment based on chemisorption [3; 8]. The chemisorption of cyanides that could appear as non-specific drinking water pollutants, can be successfully performed by treating polluted water with active charcoal impregnated with copper(II) acetate, in batching or circulating systems [9]. Knowledge of the kinetic parameters of this process enables the prediction of basic plant parameters: the capacity, equipment dimensions, the allowed level of pollutant concentration, etc.

A mathematical description of the chemical processes, using experimental statistical methods and multivariable statistics, has had much broader application in the past years. The reason for this lies in the fact that statistical methods allow the development of a mathematical model that includes all the known variables, even though there is insufficient theoretical knowledge on the process mechanism [10].

Various methods can be applied to determine a mathematical model of the process with one or more independent variables: single and multiple regression analyses, correlative analyses and methods of experiment planning. Whatever the method, the main problem is choosing the appropriate type of model (linear or non-linear). In the studied process, considering that it combines chemisorption and physical sorption the individual dynamics of which are exponential, a complex exponential form of the dependence is shown:

\[ y = ax^b e^{bx} \]  

(1)

The definition of parameters of the supposed regression \((a; b; \text{and } b_0)\) is done by linearising the previous equation and transforming it into the following form:

\[ \ln y = \ln a + b + b_0x \]  

(2)

or by introducing the shift in the following form:

\[ Y = b_0 + b_1 \ln x + b_2x \]  

(3)

Parameters \( b_0; b_1; \text{and } b_2 \) can be determined by applying the least squares method to an equation that has been linearised in this way (3). The most adequate position of the line of the linearised regression with reference to the experimental points in the diagram is the one with the minimal square sum of all the errors of the individual experimental points:

\[ S^2 = \sum_{i=1}^{n} (Y_i - \bar{Y}_i)^2 = \sum_{i=1}^{n} (Y_i - b_0 - b_1 \ln x_i - b_2 x_i)^2 = \sum_{i=1}^{n} e_i^2 \rightarrow \text{min}. \]  

(4)

By partial differentiation of the function (4) with reference to the regression parameters and their individual equalization to zero, one obtains:

\[ \frac{\partial S^2}{\partial b_0} = 0 \]

\[ \frac{\partial S^2}{\partial b_1} = 0 \]

\[ \frac{\partial S^2}{\partial b_2} = 0 \]

A system of linear equations is obtained and by solving the parameters \( b_0; b_1; \text{and } b_2 \), are calculated

\[ \begin{align*}
    b_0 = \frac{\sum\Sigma Y_i}{n} & \\
    b_1 = \frac{\sum\Sigma \ln x_i Y_i - \Sigma\Sigma \ln x_i Y_i}{\Sigma\Sigma \ln x_i} & \\
    b_2 = \frac{\sum\Sigma(Y_i \ln x_i - Y_i \Sigma \Sigma Y_i)}{\Sigma\Sigma \ln x_i} & \\
\end{align*} \]  

(5)

Solution of the system of linear equations is possible with the inversion of the matrices into the following form:

\[ \begin{bmatrix}
    \Sigma\Sigma Y_i & \Sigma\Sigma Y_i \\
    \Sigma\Sigma \ln x_i & \Sigma\Sigma \ln x_i \\
\end{bmatrix} \begin{bmatrix} b_0 \\ b_1 \\ b_2 \end{bmatrix} = \begin{bmatrix} \Sigma Y_i \\ \Sigma \Sigma \Sigma Y_i \ln x_i \end{bmatrix} \]  

(6)

The correlation coefficient (R) was applied to estimate the intensity of the relation between variables in regression. It is defined as:

\[ R = \sqrt{\frac{\Sigma(y_i - \bar{y})^2}{\Sigma(y_i - \bar{y})^2}} = \sqrt{1 - \frac{\Sigma(y_i - \bar{y})^2}{\Sigma(y_i - \bar{y})^2}} = \sqrt{1 - \frac{S^2}{S_y}} \]  

(7)

where \( y \) – is the adding value of the absolute variable, \( \bar{y} \) – the arithmetical mean value of the result measurement and \( y_i \) – the measured value.

The significance estimate of the correlation coefficient (R), can be done with the R-test among others. Testing the hypothesis concerning the significance of the correlation coefficient (R) with the R-test consists of a comparison of the account value R and the appropriate critical value, or Rt. If \( R > R_t \), then the hypothesis of the significance of the correlation
The basic CN⁻ solution was prepared by dissolving the appropriate mass of KCN, in distilled water with the same quality. The basic adsorbent for the impregnating process was coconut GAC (using steam at 950°C), type KRF-H, produced by the Traylor Corporation, Krusevac, S.C.G. The characteristics of the used non-impregnated (I₀) and impregnated (I₁₀, I₂₀, I₃₀) GAC are listed in Table 1. The pH values of the CN⁻ solution were adjusted to pH = 12 with KOH.

THE COURSE OF THE EXPERIMENT

The experiments research performed in this study can be divided into three groups: determination of the characteristics of non-impregnated GAC, GAC impregnated with CuAc (GACCuAC) with determination of the adsorption isotherm type, CN⁻ sorption kinetics on GACCuAC with the determination of kinetic parameters and processing the obtained results. The determination of the GAC characteristics was performed using standard methods specified in Table 1. The parameters of the transient and macro pores of the GAC were determined by mercury porosimetry. Based on the obtained results, the integral and differential curve of the pore volume distribution by effective radiiuses is graphically shown in Figures 1 and 2.

The preparation of GACCuAC with three different impregnation indices, was performed by immersing 8.5 g of GAC into 250 cm³ of CuAc solution of the appropriate concentration for 24 hours. Before immersion, the GAC was dried to constant weight in a dryer at 110°C. With the goal of determining the parameters of the adsorption process of CuAc on GAC,

### EXPERIMENTAL

### Materials

All chemicals used in the paper were of analytical grade (p.a.). The solution for impregnating GAC was prepared by immersing into a solution obtained by dissolving CuAc in distilled water with a conductivity < 1 µS.
Langmuir and Freundlich adsorption isotherms were determined (Figure 3). The initial concentrations of the CuAc solution were: 0.050; 0.100; 0.200 and 0.250 g/dm³. GAC CuAc with 42.0 mg; 59.0 mg; 69 mg and 72.0 mgCu/gGAC were thus obtained. The deposited copper(II) mass per GAC unit mass (mCu) was obtained using the volume of the impregnation solution (V), the initial copper(II) concentration (C0), the copper(II) concentration after immersion (C1) and the immersed GAC mass (mGAC) according to the following equation:

\[ m_{\text{Cu}} = V (C_0 - C_1) / m_{\text{GAC}} \] (10)

The copper (II) concentrations in the impregnation solution before and after immersion were determined using atomic adsorption spectrophotometry (AAS) (Perkin Elmer 1100B) and iodometry. The basic CN⁻ solution was 3.86x10⁻⁵ mol/dm³. The CN⁻ concentration in the basic solution was determined using the Liebig method [11], by titrating the solution with NaNO2. The method sensitivity was 3.85x10⁻⁵ mol/dm³.

The working CN⁻ solution of 3.86x10⁻⁵ mol/dm³ was prepared by measuring an aliquot of the basic solution and diluting it to the working volume. Since the kinetics of the process are more advanced in the beginning and since more than half of the maximum capacity of GAC-CuAc was obtained within less than 30 minutes; it was not practical to observe the CN⁻ concentration in the solution during the GAC sorption process using classical methods. Thus, the electroanalytical method of direct potentiometry was applied, using an ion selective electrode (ISE) [12] for the CN⁻ (Radiometer, model F1024CN-O, Denmark). In the range of applied concentrations (0–3.85x10⁻⁵ mol/dm³), the electrode was subjected to Nernst’s theory. A saturated calomel electrode was used as the reference electrode. Continuous observation, numerical and graphical records of the experimental data were obtained using a MAS 345 type AD converter and the Mas View Software program set Version 1.1, produced by Mestrech. The working solution temperature was maintained constant (±0.1°C) using a Thermostat U1 colorstat, produced by VMP WERK, GDR.

RESULTS AND DISCUSSION

A greater selectivity and chemisorption capacity was achieved by impregnating GAC. The effused impregnant partially changed the GAC porous structure, depositing in macropores and transient pores; which confirm the results shown in Table 1. From the data presented, a partial GAC surface decrease with an increase in the impregnation index was noted. This results in a decrease in the effects in relation to the chemisorption of the physical sorption. This was also confirmed by the following results: benzene sorption decrease from 48.28% on non-impregnated GAC (l0) to 43.0% at GAC with 72 mg Cu/g of GAC (l2). This is the result of the fact that benzene binds to GAC exclusively by physical sorption under the given experimental conditions.

The results of determining the type of adsorption isotherm CuAc on GAC are presented in Figure 3.

A great concordance of the experimental data and data obtained using the Langmuir and Freundlich models was noted. Using a linear representation of the Langmuir and Freundlich models and by presenting them graphically, the parameters of these models were ob-

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**Figure 1.** Integral curve of the pore volume distribution using the GAC effective diameters

**Figure 2.** Differential curve of the pore volume distribution using the GAC effective diameters

**Figure 3.** Adsorption isotherms of copper(II)-acetate on GAC
tained: the Langmuir (equation 11) and the Freundlich (equation 12):

\[
q_e = 1.366 \frac{C_g}{1 + 22C_g} \quad (11)
\]

\[
q_e = 0.11C_g^{0.425} \quad (12)
\]

The range of obtained values indicated that CuAc adsorption on GAC occurred according to the assumptions made during the performance of these models. The process of binding chemical reagents to the impregnated GAC is a complex process depending on many factors. This is the result of the complexity of the phenomenon occurring in the impregnated GAC structure (chemical reaction, physical sorption, diffusion). The chemisorption of binding CN⁻ occurs in two phases [13]:

\[
\text{Cu}^{2+} + 2(\text{CN})_g \rightarrow \text{Cu(CN)}_{2g} \quad (13)
\]

\[
2\text{Cu(CN)}_{2g} + 6(\text{CN})_g \rightarrow 2[\text{Cu(CN)}]^{2+} + (\text{CN})_{3g} \quad (14)
\]

The results obtained while examining the effect of temperature on the CN sorption kinetics on GAC CuAc are presented in Figure 4.

Noticeable is the fact that CN⁻ binding is a relatively slow process considering the fact that the final equilibrium was established after several hours and that it was diffusion-controlled (the C/\text{C}_g dependence has an exponential character) [14]. The temperature that affects the process kinetics in the starting period (3 minutes) is less noted and more significant only in the latter phase. During the initial phase, when the reactant concentration is the highest (Cu^{2+}, CN⁻) and the Cu^{2+} ions are most available, bearing in mind that there is an ionic reaction happening in a very short time (max 2 sec) [13], the diffusion processes of this phase are less significant. In the subsequent phase, when the availability of Cu^{2+} ions is protracted, and to some extent precluded because of an entrance blockade into the micropores by an already created deposition of Cu(CN)₂g and of [Cu(CN)]^{2+}.

Figure 4. Effect of temperature on CN⁻ sorption kinetics on GAC-CuAc (initial concentration of CN⁻: C^{0}_\text{CN} = 0.100 g/dm³; mass of GACCuAc, m_{GACCuAc} = 1.00 g; volume of the working solution of CN⁻, V = 0.100 dm³; used GAC with 42.0 mgCu/gGAC; pH = 12.00).

Figure 5. The effect of mass of the impregnate (CuAc) on the CN⁻ sorption kinetics on GACCuAc (initial concentration of CN⁻; C^{0}_\text{CN} = 0.100 g/dm³; mass of GACCuAc, m_{GACCuAc} = 1.00 g; volume of the working solution of CN⁻, V = 0.100 dm³; t = 20°C; pH = 12.00).

The diffusion processes are expressive and so is their temperature dependence. Cyanide sorption on the GACCuAc increases with an increase in temperature, which indicates the predominance of the chemisorption process and the absence of CN⁻ physical sorption on GAC, decreasing with the temperature increase.

The mass of impregnants, reduced to the GAC unit mass, regarding that it concerns a diffusion-controlled extreme chemisorption process, has a significant effect on the cyanide sorption rate on GACCuAc in all phases of the process. The results of effect of the impregnation index on CN⁻ sorption on GACCuAc are presented in Figure 5.

It is noted that the difference in the rate of the process in the initial period is more expressive with samples that have a lower impregnation content, while with the increase of the rate it is negligible. The equilibrium conditions are clearly expressed and the balance of the bound CN⁻ concentration per GAC unit mass increase with increase of the impregnant contents, which is in accordance with the well-known dependence of the reaction rate on the reactant concentration.

When designing the mathematical model, it is most difficult to select the appropriate type of starting equation [10]. Bearing in mind that we have a process where the chemical reaction is dominant, models of complex exponential forms have been tested as the most credible form of mathematical models (equation 1).

The experimental data obtained by CN⁻ sorption on GACCuAc impregnated with 42; 59 and 72 mgCu/gGAC at 40°C and pH = 12 in a batch system with intensive stirring was tested. The working solution volume was 0.100 dm³ and the GACCuAc mass was 1.00 g. Three regression equations for different Cu^{2+} contents per GAC unit mass were obtained:

\[
[1(c_0 - c)]_t = 0.137 t^{0.031} e^{-0.022t} \quad (15)
\]

\[
[1(c_0 - c)]_t = 0.246 t^{0.425} e^{-0.0122t} \quad (16)
\]
Table 2. Numerical and statistical characteristics of the regression equations

<table>
<thead>
<tr>
<th>Numerical and statistical characteristics</th>
<th>Designation</th>
<th>Regression equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Arithmetical mean of the independent variable</td>
<td>$\bar{x}$</td>
<td>Eq. 15</td>
</tr>
<tr>
<td>2 Arithmetical mean of the dependent variable</td>
<td>$\bar{y}$</td>
<td>-0.759</td>
</tr>
<tr>
<td>3 Linearized regression parameter</td>
<td>$b_0$</td>
<td>-1.984</td>
</tr>
<tr>
<td>4 Linear and exponential regression parameter</td>
<td>$b_1$</td>
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<tr>
<td>5 Linear and exponential regression parameter</td>
<td>$b_2$</td>
<td>-0.0212</td>
</tr>
<tr>
<td>6 Exponential regression parameter</td>
<td>$a$</td>
<td>0.137</td>
</tr>
<tr>
<td>7 Explained variation</td>
<td>$S_e^2$</td>
<td>9.860</td>
</tr>
<tr>
<td>8 Unexplained dispersion</td>
<td>$S_u^2$</td>
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</tr>
<tr>
<td>9 Unexplained variation</td>
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<td>0.07525</td>
</tr>
<tr>
<td>10 Correlation coefficient</td>
<td>$R$</td>
<td>0.996</td>
</tr>
<tr>
<td>11 Tabular value of $R$-test for significance estimation</td>
<td>$R_t$</td>
<td>0.250</td>
</tr>
<tr>
<td>12 Mean relative error of the exponential of regression</td>
<td>$\alpha_{rel}$</td>
<td>2.64%</td>
</tr>
</tbody>
</table>

The experimentally obtained results and the data obtained using the corresponding regression equations 15, 16 and 17 are presented in Figure 6.

It is noted that the mentioned equations describe the kinetics of the studied process with satisfactory precision, which was confirmed by the correlation coefficients $R_{cc} = 0.996$, $R_{sc} = 0.990$ and $R_{ss} = 0.996$ as well as by the mean relative errors of the experiment $\bar{\alpha}_{rel} = 2.64\%$, $\bar{\alpha}_{rel} = 0.88\%$ and $\bar{\alpha}_{rel} = 1.61\%$, respectively. The numerical and statistical characteristics of the established regressions are presented in Table 2 [15].

CONCLUSIONS

Granulated active charcoal obtained by activating coconut shells using steam, has exceptionally good properties. The expressive transient and macroporosity and high total active surface provide high grade impregnation. This fact results in a very efficient process of cyanide ion removal from aqueous solutions. Copper (II) acetate can be successfully used, as an impregnant, considering its very favorable physical and chemical properties. The kinetics of cyanide sorption from aqueous solutions keeping in mind the expressed positive temperature dependence of the rate of this process indicate the dominance of chemisorption in the overall process. In some cases this can be a useful fact, regarding the irreversible character of this reaction.

The mathematical models obtained by regression and correlation analysis can be successfully applied to describe the kinetics of cyanide binding from aqueous solutions in a relatively long time interval (30 minutes), which is of great practical importance. During that interval more than 90% of the GACCuAc capacity was exploited, providing its use in wastewater refining of both batch and circulating systems.

REFERENCES

IZVOD

KARAKTERIZACIJA GRANULISANOG AKTIVNOG UGLJA NA BAZI LJUSKE KOKOSOVOG OREHA

(Naučni rad)

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