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PRINCIPLES FOR CALCULATION OF THE ADSORPTIVE COLUMNS WITH THE FIXED BED

A method has been presented for design of the activated carbon columns, applied for the water reuse. The method is based on real distribution of changes in adsorbate concentration in the effluent from the column. By determining this distribution as the functions of the column's height H , flow velocity V , time of column's operation t , and kind of adsorbate it was possible to calculate the basic design parameters, i.e.: height of the adsorption front and velocity of front shifting down the column. Principles of the procedure were discussed on the example of adsorption on the activated carbon Carbolpol Z-4 (1-3 mm) from the biologically treated municipal sewage after their coagulation and filtration.

1. INTRODUCTION

Adsorption on the solution-solid state interface is one of the basic processes used in technology of water treatment and its reuse. The course of this process is determined by such factors as: structure of adsorbent, concentration and characteristics of the adsorbate, multicomponent structure, pH, and temperature of the solution as well as the way of its contact with the adsorbent [1, 5-8].

The very number of these factors proves that adsorption is so complicated that examination of its course brings many difficulties. It is especially difficult in case of multicomponent solutions such as water and wastewater. Neither their total identification nor determination of the size of particles present in them is possible, although, this plus knowledge about porous structure of the adsorbate is very important for the analysis of kinetics of the processes and determination of its design parameters.

Design of the process for treatment or reuse of water should be preceded by model tests carried out for the given kind of solution and adsorbent. Effects of adsorption can be presented as function of such generalized pollution indices as: TOC, COD, BOD, and permanganate COD.

The paper presents some principles for calculation of the basic design parameters of the sorptive columns with the fixed bed.

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2. ADSORPTION PROCESS ON THE FIXED BED

Conventional method of adsorption on activated carbon bed is used for purification and reuse of water. In the initial stage of the process the sorbed compounds are most effectively removed in the upper carbon layer. Small amounts of the adsorbate that were not adsorbed in that layer are removed from the solution in the lower parts of the carbon bed. In fact, at the beginning of the process the effluent should not contain dissolved sorptive substances.

The part of the deposit in which concentration decreases from the initial value to the minimal one is defined as the adsorptive zone. At the constant wastewater or water inflow into the column the upper carbon layers are more and more saturated with the sorbate and their sorptive capacity is reduced. Thus, adsorption zone shifts down the bed to the carbon regions less depleted. The more the zone is shifted the larger amounts of substances get into the effluent.

The diagram of the zone displacement and the resulting exchange isoplane are shown in fig. 1. The breakthrough point on the curve proves that mass, adsorbed by the carbon filling the column, is in dynamic equilibrium with the inflow concentration. At that moment the column operation should be stopped to regenerate or exchange the activated carbon filling the column.

Adsorption process on a fixed bed depends to high extent on the shape of the curve $c_i/c_o = f(t)$ (fig. 1). For most water and wastewater pollutants the isoplanes are S-shaped but their slopes and position of the breakthrough points are different.

The time of column operation till the breakthrough point is the shorter the greater are the sorbent particles, the higher sorbate concentrations, pH of the medium and flow

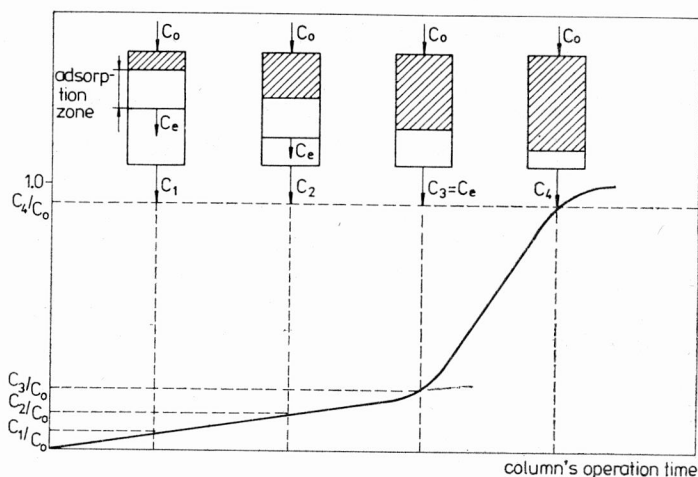


Fig. 1. Movement of the adsorption zone and the resulting exchange isoplane

Rys. 1. Ruch strefy adsorpcji i wynikająca z niego krzywa przebiecia

rate, and the lower is the sorption column height. These factors also influence the shape of isoplanes.

The sorptive column should be higher than the initial zone of adsorption.

3. DESIGN PRINCIPLES

Design of the flow-through adsorptive systems is based on two parameters: height of the adsorption front and rate of its moving down the column. The height of the carbon layer is equal to the adsorption front when the concentration in the effluent reaches the value characteristic of the breakthrough point in time $t = H/V$.

To achieve the breakthrough point of the column means that the lower edge of the front is in line with the bottom of the bed. Hence, the rate at which adsorption front is shifted can be calculated from the formula:

$$V_{fr} = \frac{H - H_0}{t_p - t_{fr}}, \quad (1)$$

where:

H — height of the column [m],

t_p — time at which the breakthrough point is achieved [h],

H_0 — height of the adsorption front [m],

$t_{fr} = H_0/V$ — time at which the adsorption front is formed [h],

V — linear velocity of water or wastewater flow [m/h].

The indispensable height of the column at the assumed duration of the cycle t_d is calculated from the modified formula (1):

$$H = V_{fr}(V \times t_p - H_0)V^{-1} + H_0. \quad (2)$$

3.1. DETERMINATION OF THE DESIGN PARAMETERS

The principles for determining the design parameters were discussed on the example of the given solutions and for the activated carbon Carbolpol Z-4 of granulation 1-3 mm. In order to determine these parameters the distribution of the adsorbate concentration changes in the effluent from the adsorptive column should be known. This distribution was determined as functions of the operation time, height of the carbon layer and flow velocity for TOC and COD in municipal sewage after various degrees of their treatment. Processes of adsorption were conducted on wastewater biologically treated after its coagulation with aluminium sulphate or ferric sulphate and after filtration. The average, maximal and minimal, concentrations of the biologically treated sewage for TOC, COD, BOD and permanganate COD were equal to: 16.5, 21.7, 10.0 c/m^3 ; 45.0, 65.0, 30.5 $\text{g O}_2/\text{m}^3$; 25.0, 40.0, 17.0 $\text{g O}_2/\text{m}^3$, and 18.0, 26.8, 12.0 $\text{g O}_2/\text{m}^3$, respectively.

Coagulation was conducted in the model of contact sedimentation tank. The application of optimal dosages $200 \text{ g Al}_2(\text{SO}_4)_3 \cdot 18 \text{ H}_2\text{O}/\text{m}^3$ or $150 \text{ g Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}/\text{m}^3$ and filtration yielded the decrement of the organic compounds concentration by 55% on the average.

Adsorption process was conducted in the columns filled with carbon layers of different heights applying different linear velocities of wastewater flow. The obtained exchange isoplanes $c_i/c_0 = f(t)$ were expressed by mathematical equations. Four functions, whose graphic forms resemble those of isoplanes, were taken into consideration [2]:

$$c_i/c_0 = y = \frac{t}{\sqrt{1+t^2}}; y = \frac{1}{1+e^{-t}}; y = \frac{t}{1+|t|}; y = \text{tg } ht.$$

In order to determine the equation parameters describing adequately the experimental isoplanes, the anti-function were used, i.e. $y = f(t)$ was replaced by $t = g(y)$ and the parameters a, b, c, d were chosen so that the function $t = a \cdot g(c[y-d]) + b$ approximate optimally in the sense of least squares, i.e.

$$\sum_i t_i - a \cdot g(c[y_i - d]) + b = \min,$$

the set of experimental points. Anti-functions were employed since initial values of parameters c and d can be easily determined and since the variables, when analyzed by means of library programs, appeared to be more sensitive to the change of these parameters, what warranted a better convergence with the experiment. The parameters c and d were determined by Powell and Smith's method (library programs for digital computer ODRA IZO4: minif, minig, minis) [3, 4]. The parameters a and b being of the first degree were calculated by solving the system m of equations with two unknowns. Subsequently, in order to obtain the result as a function of time, $t = a \cdot g(c[y-d]) + b$ was transformed to $y = 1/c \cdot f((t-b/a) + d)$. The parameters of equations and their final forms printed by digital computer are given in tab. 1.

Table 1

Forms of the functions analyzed and their parameters
Postacie analizowanych funkcji oraz ich parametrów

| Function | Parameters |
|--|--|
| $y = C \frac{t-B}{\sqrt{A^2+(t-B)^2}} + D$ | $a = A; b = B; 1/c = C; d = D$ |
| $y = C \frac{Be^{At}}{1+Be^{At}} + D$ | $1/a = A; e^{b/a} = B; 1/c = C; d = D$ |
| $y = C \frac{t-B}{A+\text{sgn } A(t-B)} + D$ | $a = A; b = B; 1/c = C; d = D$ |
| $y = C \frac{Be^{At}-1}{Be^{At}+1} + D$ | $2/a = A; e^{-2b/a} = B; 1/c = C; d = D$ |

From the analysis of the mean square deviations it follows that the isoplanes described by equations (1) and (2) are mostly close to the real ones. In first equation the mean square deviations amounted to 3.911×10^{-2} and 5.1702×10^{-2} for TOC and COD, respectively; the corresponding values in the equation (2) being 3.8257×10^{-2} and 4.801×10^{-2} . In third and fourth equations the respective values were amounting to 4.6292×10^{-2} and 6.1769×10^{-2} ; 4.0073×10^{-2} and 5.5619×10^{-2} .

In further consideration equation (1) was taken as determinant since it was relatively easy to present its parameters in dependence on flow velocity V or the carbon layer height H . In this way change of adsorbate c_i concentration in the effluent could be described by a general equation

$$c_i = c_0 \left\{ \left(0.5 - \frac{0.5V}{fV+g} \right) \frac{t - \left(\frac{mH}{kV+n} + p \right)}{\sqrt{\left(\frac{rH}{V} + S \right)^2 + \left[t - \left(\frac{mH}{kV+n} + p \right) \right]^2}} + \frac{V}{WV+z} \right\}. \quad (3)$$

The values of the parameters are set in tab. 2. Exemplary course of isoplanes described by the equation (3) is presented in fig. 2.

Height of the adsorption front is calculated from the transformed equation (3) by putting the ordinate of the breakthrough point. This point is found at the point of intersec-

Table 2

The parameters of the equation of distribution of changes in the concentration of the effluent
Zestawienie parametrów równania rozkładu zmian w stężeniu odpływu z kolumny adsorpcyjnej

| Parameter | Kind of wastewater | | | | | |
|-----------|----------------------|-------|--|--------|---|--------|
| | Treated biologically | | Treated biologically and coagulated with $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ and filtration | | Treated biologically and coagulated with $\text{Fe}(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$ and filtration | |
| | Index | | Index | | Index | |
| | TOC | COD | TOC | COD | TOC | COD |
| f | 2.0 | 8.0 | 1.8 | 2.0 | 1.8 | 2.0 |
| g | 25.0 | 30.0 | 5.5 | 3.75 | 5.5 | 3.75 |
| k | 0.5 | 1.0 | 0.6 | 0.375 | 0.6 | 0.375 |
| m | 333.0 | 400.0 | 1000.0 | 1000.0 | 1000.0 | 1000.0 |
| n | 6.0 | 7.0 | 10.0 | 10.0 | 10.0 | 10.0 |
| p | 10.0 | 10.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| r | 30.0 | 32.0 | 21.0 | 25.0 | 21.0 | 25.0 |
| s | 14.0 | 14.0 | 5.0 | 10.0 | 5.0 | 10.0 |
| w | 1.32 | 1.34 | 1.36 | 1.35 | 1.36 | 1.36 |
| z | 1.15 | 0.95 | 0.6 | 0.5 | 0.6 | 0.5 |

V [m/h]; t [H]; H [m]; c_i [g/m³]; c_0 [g/m³].

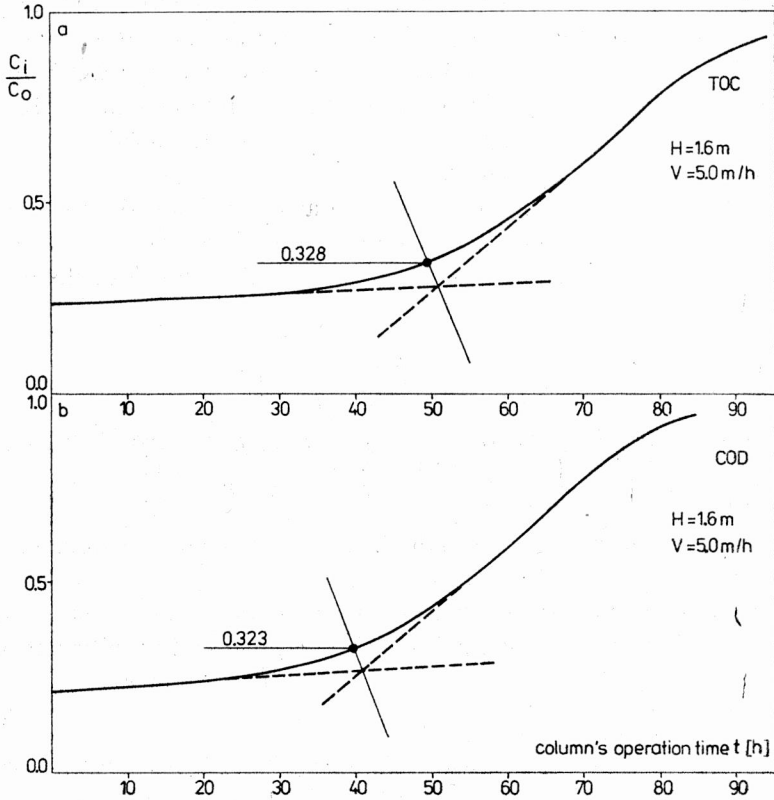


Fig. 2. Isoplanes of the sorptive column — biologically treated wastewaters.

$$a. \frac{C_i}{C_0} = \left(0.5 - \frac{0.5V}{2V+25}\right) \frac{t - \left(\frac{333H}{0.5V+6} + 10\right)}{\sqrt{\left(\frac{30H}{V} + 14\right)^2 + \left[t - \left(\frac{333H}{0.5V+6} + 10\right)\right]^2}} + \frac{V}{1.32V+1.15}$$

$$b. \frac{C_i}{C_0} = \left(0.5 - \frac{0.5V}{8V+30}\right) \frac{t - \left(\frac{400H}{V+7} + 10\right)}{\sqrt{\left(\frac{32H}{V} + 14\right)^2 + \left[t - \left(\frac{400H}{V+7} + 10\right)\right]^2}} + \frac{V}{1.34V+0.55}$$

Rys. 2. Izoplany kolumny sorpcyjnej — ścieki oczyszczone biologicznie

$$a. \frac{C_i}{C_0} = \left(0.5 - \frac{0.5V}{2V+25}\right) \frac{t - \left(\frac{333H}{0.5V+6} + 10\right)}{\sqrt{\left(\frac{30H}{V} + 14\right)^2 + \left[t - \left(\frac{333H}{0.5V+6} + 10\right)\right]^2}} + \frac{V}{1.32V+1.15}$$

$$b. \frac{C_i}{C_0} = \left(0.5 - \frac{0.5V}{8V+30}\right) \frac{t - \left(\frac{400H}{V+7} + 10\right)}{\sqrt{\left(\frac{32H}{V} + 14\right)^2 + \left[t - \left(\frac{400H}{V+7} + 10\right)\right]^2}} + \frac{V}{1.34V+0.55}$$

tion of the bisector of the angle formed by the tangent to isoplane at its initial point 0, $f(O)$ and the tangent at the point

$$\frac{mH}{kV+n} + p, \frac{V}{wV+z}$$

(fig. 2).

The mean values of c_i/c_0 at the breakthrough point depending on the kinds of wastewater and adsorbate and on flow velocity are given in tab. 3. By the following substitutions in equation (3):

$$\frac{rH}{V} + S = aH + S,$$

$$\frac{mH}{kV+n} + p = \beta H + p,$$

$$\left(\frac{c_i}{c_0} \frac{V}{wV+z} \right)^2 \left(0.5 - \frac{0.5V}{fV+g} \right)^{-2} = \gamma$$

(c_i/c_0 values from tab. 3) and suitable transformations, an equation of the second degree with respect to H has been obtained.

Table 3

Values of concentrations ratio at the breakthrough point of the column
Wartości stosunku stężeń w punkcie przebiecia kolumny

| Flow velocity V [m/h] | Breakthrough point c_i/c_0 | | | | | |
|----------------------------|------------------------------|-------|---|-------|--|-------|
| | Treated biologically | | Treated biologically and coagulated with $Al_2(SO_4)_3 \cdot 18 H_2O$ and filtration | | Treated biologically and coagulated with $Fe_2(SO_4)_3 \cdot 9 H_2O$ and filtration | |
| | Index | | Index | | Index | |
| | TOC | COD | TOC | COD | TOC | COD |
| 2.5 | 0.231 | 0.251 | — | — | — | — |
| 5.0 | 0.328 | 0.323 | 0.401 | 0.456 | 0.401 | 0.456 |
| 10.0 | 0.382 | 0.382 | 0.458 | 0.489 | 0.458 | 0.489 |
| 15.0 | — | — | 0.495 | 0.517 | 0.495 | 0.517 |

By neglecting the value t in this equation, as being insignificant with respect to the duration of the whole cycle of adsorption, the final form of equation from which the height of adsorption front can be calculated is the following:

$$[a^2\gamma + \beta(\gamma-1)]H_0^2 + 2[\alpha\gamma s - \beta p(\gamma-1)]H_0 + \gamma(s^2 + (p+1)p-2) + p^2 = 0. \quad (4)$$

The solution of the equation yields two values of H_0 of which $-H_0$ has no physical meaning. The calculated values of H_0 are presented in tab. 4.

Table 4

The heights of adsorption fronts
Zestawienie wysokości frontów adsorpcji

| Flow velocity V [m/h] | Height of the adsorption front H_0 [m] | | | | | |
|----------------------------|--|-------|--|-------|---|-------|
| | Treated biologically | | Treated biologically and coagulated with $Al_2(SO_4)_3 \cdot 18 H_2O$ and filtration | | Treated biologically and coagulated with $Fe_2(SO_4)_3 \cdot 9 H_2O$ and filtration | |
| | Index | | Index | | Index | |
| | TOC | COD | TOC | COD | TOC | COD |
| 2.5 | 0.137 | 0.120 | — | — | — | — |
| 5.0 | 0.165 | 0.158 | 0.109 | 0.137 | 0.109 | 0.137 |
| 10.0 | 0.357 | 0.168 | 0.141 | 0.176 | 0.141 | 0.176 |
| 15.0 | — | — | 0.148 | 0.179 | 0.148 | 0.179 |

The time t_p of the column's breakthrough, indispensable to determine the velocity of shifting the adsorption front (equation (1)) depending on the column height, was determined from the transformed equation (3)

$$t_p = (aH + s) \sqrt{\frac{\gamma}{1-\gamma}} + \beta H + p. \quad (5)$$

The calculated values V_{fr} are given in tab. 5.

Table 5

The velocities of the adsorption front shift
Zestawienie szybkości przesuwania się frontu adsorpcji

| Flow velocity V [m/h] | Velocity of the adsorption front shift V_{fr} [m/h] | | | | | |
|----------------------------|---|-------|--|--------|---|--------|
| | Treated biologically | | Treated biologically and coagulated with $Al_2(SO_4)_3 \cdot 18 H_2O$ and filtration | | Treated biologically and coagulated with $Fe_2(SO_4)_3 \cdot 9 H_2O$ and filtration | |
| | Index | | Index | | Index | |
| | TOC | COD | TOC | COD | TOC | COD |
| 2.5 | 0.03 | 0.033 | — | — | — | — |
| 5.0 | 0.03 | 0.036 | 0.0109 | 0.0125 | 0.0109 | 0.0125 |
| 10.0 | 0.03 | 0.047 | 0.0154 | 0.0141 | 0.0154 | 0.0141 |
| 15.0 | — | — | 0.0192 | 0.0158 | 0.0192 | 0.0158 |

4. CONCLUSIONS

The presented design method for the columns of activated carbon is based on real distribution of changes in adsorbate concentration in the effluent obtained during technological tests. For the assumed concentration of c_i/c_0 in the effluent the technology of waste-waters treatment before the inflow to the columns and linear flow velocity (tab. 3) should be chosen. For these parameters the values H_0 and V_{fr} (tabs. 4 and 5) are chosen. The values of the column's operation time t_p are chosen on the basis of technical-economical analysis. The analysis should first of all include:

- way of carbon regeneration,
- place of carbon regeneration (inside or outside the water reuse plant),
- frequency of regeneration (related to the efficiency of the regeneration system).

The height of the column is determined from the equation (2). It seems optimal to use the columns the layer heights of which do not exceed two meters and which are connected in series. In such system one of the columns can be always regenerated.

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ZASADY OBLICZANIA KOLUMN ADSORPCYJNYCH ZE ZŁOŻEM USTALONYM

Przedstawiono metodę projektowania kolumn z wypełnieniem z węgla aktywnego zastosowanych dla potrzeb odnowy wody. Metoda oparta jest na rzeczywistym rozkładzie zmian w stężeniu adsorbentu w odpływie z kolumny. Określenie tego rozkładu w funkcji wysokości kolumny H , prędkości przepływu V , czasu pracy kolumny t i rodzaju adsorbentu pozwoliło na wyznaczenie podstawowych parametrów projektowych — wysokości frontu adsorpcji oraz szybkości przesuwania się frontu w dół kolumny. Zasada postępowania została omówiona na przykładzie adsorpcji na węglu aktywnym Carbpol Z-4 (1-3 mm) zanieczyszczeń z biologicznie oczyszczonych ścieków miejskich po ich koagulacji i filtracji.

ZUR BERECHNUNG VON ADSORPTIONSKOLONNEN MIT EINEM FIXBETT

Dargestellt wird eine Entwurfsmethode von Kolonnen mit einer Aktivkohle-Schüttung zur Wasserrückgewinnung. Diese Methode stützt sich auf der wirklichen Verteilung der variablen Adsorbatkonzentration im Abfluß aus dem Filterbett. Die Bezeichnung dieser Verteilung als Funktion der Filterbetthöhe H , der Filtrationsgeschwindigkeit V , der Filtrationsperiode t und der Adsorbatart, gestattete die Aufstellung von grundlegenden Prozeßgrößen: der Höhe der Adsorptionsfront sowie der Geschwindigkeit der Verschiebung dieser Front nach unten. Das Verfahren wird anhand der Adsorption von Schmutzstoffen aus biologisch nachgereinigtem Abwasser (mittels Koagulation und Filtration) in einem A-Kohlefilter welcher mit granulierter Kohle Carbopol Z-4 (Körnung 1-3 mm) gefüllt war, erläutert.

ПРИНЦИПЫ РАСЧЁТА АДСОРБЦИОННЫХ КОЛОНН
СО СТАЦИОНАРНЫМ СЛОЕМ

Предложен метод проектирования колонн с заполнением из активированного угля, использованных для нужд обновления воды. Отмеченный метод основан на действительном распределении изменений в концентрации адсорбата в сливе из колонны. Определение этого распределения в функции высоты колонны H , скорости потока V , времени работы колонны t и вида адсорбата позволило определить основные проектные параметры — высоты фронта адсорбции, а также скорости перемещения фронта вниз колонны. Принцип действия описан на примере адсорбции на активированном угле Карбопол Z-4 (1-3 мм) загрязнений с биологически очищенных городских сточных вод после их коагуляции и фильтрации.