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REMOVAL OF SURFACTANT SUBSTANCES FROM AQUEOUS SOLUTION BY ADSORPTION

USUWANIE SUBSTANCJI POWIERZCHNIOWO CZYNNYCH Z ROZTWORÓW WODNYCH W PROCESIE ADSORPCJI

W artykule przedstawiono wyniki badań laboratoryjnych dotyczących możliwości wykorzystania węgli aktywnych produkcji polskiej (WD-ekstra, WG-12, WG-15, AG-5 i DTO) do usuwania substancji powierzchniowo czynnych z wody. Celem przeprowadzonych badań było ilościowe sformułowanie procesu adsorpcji, oraz ustalenie wpływu różnych czynników na jego przebieg. Nakreślone w celu pracy zadania próbowano rozwiązać posługując się modelowymi układami doświadczalnymi. Jako adsorptyw stosowano roztwór modelowy z anionową substancją powierzchniowo czynną o nazwie Aerosol OT-100 stężeniu 5 g/m^3 sporządzony na bazie wody destylowanej. Procesy adsorpcji prowadzone w układzie porcjowym najlepiej opisywały izotermy Freundlicha. Na podstawie izoterm wyliczono zdolność adsorpcyjną testowanych węgli aktywnych. Warunki przepływowe realizowano metodą filtracji kolumnowej. Na podstawie uzyskanych wyników sporządzono krzywe przebicia – izoplany, które posłużyły do wyznaczenia pojemności adsorpcyjnych w warunkach przepływowych. Największe wartości pojemności sorpcyjnych wyznaczone zarówno w warunkach nieprzepływowych jak i przepływowych posiadał węgiel DTO. Krzywe wyjścia (izoplany) wykorzystano również do określenia strefy przenikania masy (wysokości frontu adsorpcji) oraz do obliczenia prędkości przesuwania się strefy wymiany masy. Wysokość frontu adsorpcji dla badanych węgli była pięciokrotnie niższa niż wysokość złoża adsorpcyjnego, co świadczy o dużej skuteczności węgli aktywnych w usuwaniu detergentów.

1.   Introduction

The main sources of surfactants in natural waters include: wastewaters from households and farms, those form laundry businesses, fire-fighting extinguishers and from the industry, including: textile, paper, leather, petroleum, nonferrous metal and rubber industries [5].

Surfactants, being well soluble in water, may infiltrate to underground waters. In wells located near polluted rivers, the concentration anionic detergents reached 0.29

mg/l, while the totals of surfactants reached up to 1.47 mg/l. Underground waters from intakes on not threatened areas contained surfactants in trace quantities from 0.006 to 0.007 mg/l [3].

Presence of surfactants in larger amounts (1-3 $g \cdot m^{-3}$) in rivers has negative effect on self-purifying properties of natural waters as well as makes drinking water purification processes more difficult [5].

The negative effect of detergents on human life may occur in consequence of water consumption or when bathing. Detergents undergo bio-accumulation in internal organs of humans and animals, while changing their protein structure. They may cause allergies and skin changes. Toxicity of detergents depends on their type; non-ionic compounds are least toxic, whereas anionic ones are the most toxic [4, 9].

The limit values of anionic surfactants in surface waters taken in for drinking are as follows: categories A_1 and A_2 - 0,2 mg/l, category A_3 - 0,5 mg/l [8].

Sorption on active carbon is an effective process of removing many organic impurities, including surfactants. The effectiveness of the sorption process depends on many factors. In case of surfactants the presence of divalent cations, especially calcium ions Ca^{+2}, in conditioned water is worthy of attention, because they react with sorbent surface and increase its adsorptive capacity. Another sorbent used for sorption of surfactants, in addition to active carbon, is the aluminum oxide [6]. Mineral clays were also successfully applied as sorbents [7].

Powdery active carbon was applied for removing anionic and cationic surfactants. The adsorptive capacity of carbon was 1.1 mmol/g for anionic surfactant and 0.5 mmol/g for cationic surfactant. Particles of powdery carbon were removed in the micro-filtration process. Obtained results of purification were as follows: anionic surfactants were reduced by 34-38%, cationic surfactants were reduced by 68-98% [1].

The above results were confirmed by other tests, which have shown that, in the process of adsorption on active carbon, anionic and non-ionic surfactants were removed in a range of 31.7 – 67.4% [2].

2. Study objective

The objective of this study was to assess effectiveness of five grades of active carbon (WD-ekstra, WG-12, WG-15, AG-5 and DTO) produced in Poland in removing anionic surfactants from water. The assessment was made on the basis of adsorptive capacity values as determined in non-flow and flow conditions, as well as the height of adsorption front and the rate of mass exchange zone advance.

3. Study methods

The initial (model) solution of *detergents, Da,* was prepared by adding anionic surfactant, named Aerosol OT-100 of chemical formula $C_2H_{37}NaO_7S$, to distilled water in such quantity that detergent concentration in the solution is 5 mg/l. The determination of detergents was carried out by method using methylene blue. The determination is based on producing blue colored organic compound as a result of reaction of the methylene

blue with anion-active surfactant substance. The resulting complex is extracted with chloroform in alkali environment, and the intensity of coloring, as determined by photo-colorimetric measuring method at the wavelength $\lambda=652$ nm, is proportional to the detergent concentration.

Granulated active carbon, grades: WD-ekstra, WG-12, WG-15, AG-5 and DTO) pro-duced by Gryfskand company (refer to Table 1), were used in the tests.

Tab. 1.   Characteristic of activated carbons

Designation	Unit	WD-ekstra	WG-12	WG-15	AG-5	DTO
Specific surface area (BET,N_2)	m^2/g	950-1050	1250	980	950-1050	-
Iodine number	mg/g	900-1000	1160	1090	900-1000	min 750
Methylene number	cm^3	min 22	35	32	min. 25	min 50
Granulation	mm	1,0-1,5	-	-	0,75-1,2	-
Coefficient of grain-size distribution unevenness		1,2	-	-	1,2	-
Total volume of pores	cm^3/g	0,85-0,95	-	-	0,8-0,9	-
Adsorption of phenol	%	4-5	4	-	-	-

Adsorption kinetics was determined a dose of 1 g/l. A suitable adsorbent was added to a number of conical flasks each containing 300 cm^3 of model solution and shaken (at 150 r.p.m.) for 10, 20, 30, 40, 50, 60, 80, 100, 120 and 180 minutes. Testing was con-ducted with pH oscillating around neutral (pH=7.0). The clarification time was one hour. These parameters were optimized in preliminary technological research. The control determination was carried out in decanted solutions.

The effect of pH of adsorptive solutions on the adsorption process was studied with the use of sorbents and thier doses such as those for the determination of adsorption kinetics. The pH value of model solutions was varied within 5 – 10. The shaking time was 30 minutes and the decanting time – 1 hour.

In order to determine the adsorption isotherms, increasing doses (0,3 – 3,0 g/l) were added to eight conical flasks containing each 300 cm^3 of model solutions. Sample temperature was stabilized at 15°C, and the samples were shaken for 30 minutes in insulation. Then they were left for one hour and surfactants was determined in the decanted solution.

Dynamic conditions were realized (defined) by the column filtration method. The adsorption columns were made of organic glass of diameter 32 mm. The filling height was 700 mm and the adsorbent quantities in the column were: WD – ekstra 210 g, WG-12 245 g, WG-15 239 g, AG-5 210g i DTO 202 g. Filtration was performed from the top downwards. At the beginning of each filtration cycle the filtration rates were changed consecutively to 6, 8, 12, 18 and 20 m/h, while the optimum rate was deter-mined. Further testing in a given cycle was performed at filtration rates of 20 m/h. After each hour of bed operation, samples were taken in order to carry out control analyses. Filtration lasted each time until the moment of bed exhaustion, i.e., at the point where the concentration in the discharge becomes equal to that of the initial solution.

3. Results and discussion

As indicated in Fig. 1, data on adsorption kinetics showed that the process took place quite rapidly. A complete sorption balance became established after about 1 hour, but the process proceeded with great intensity for 20 – 30 minutes. In further testing, the shaking time of 30 minutes was accepted as the optimum.
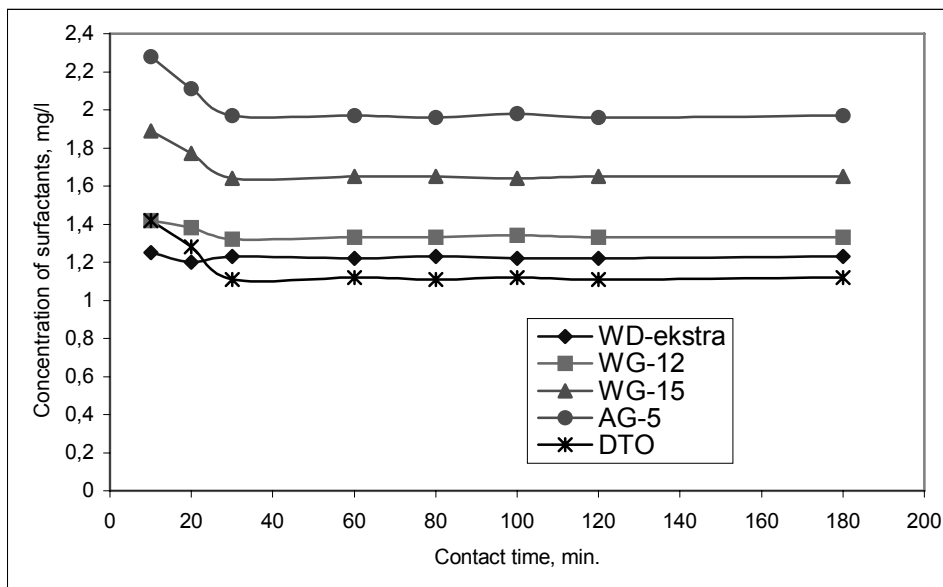

Fig.1.   *Effect of contact time on adsorption process*

As shown in Tab. 2, the pH value of adsorbates had a strong effect on the adsorption process. Adsorption of surfactants impurities proceeded best at reaction more than 8,0.

Tab. 2.   *Effect of pH adsorbate solutions the effectiveness of the adsorption process*

Value of pH of adsorbate solution	Concentration of surfactants, mg/l				
	WD-ekstra	**WG-12**	**WG-15**	**AG-5**	**DTO**
5,0	1,25	1,28	1,51	1,80	1,02
6,0	1,20	1,29	1,59	1,81	1,05
7,0	1,23	1,32	1,64	1,97	1,11
8,0	1,21	1,32	1,62	1,96	1,09
9,0	1,19	1,28	1,59	1,88	1,00
10,0	1,18	1,26	1,57	1,87	0,08

The results obtained in a successive series of experiments performed in static conditions were described with basic equations of isotherms, i.e., those of Freundlich, Langmuir and BET. Langmuir's and BET isotherms exhibited low matching to empirical values (coefficients of correlation ranged within 0.50-0.70). The adsorption processes were best described by Freundlich's isotherms. Their choice was dictated by a high correlation coefficient, R approx. equal to 0.9 (Table 3).

The Freundlich isotherms were determined in linear form, approximated with the least-squares method, described with mathematic equations and isotherm constants, n and K, were determined on their basis (Table 3).

Analysing the course of isoterms (Fig. 2) was found that activated carbons WD-ekstra i DTO exceeded the rest of adsorbents in respect of adsorption ability. Values of capacity adsorption were compiled in Table 4.

Tab. 3.   *Constants of Freundlich adsorption isotherms*

Adsorbent type	Constant of isotherms		Correlation coefficient R
	K	**n**	
WD-ekstra	3,3304	2,5813	0,9524
WG-12	3,0019	2,6490	0,9264
WG-15	2,4660	2,3277	0,9058
AG-5	2,0137	2,0288	0,9537
DTO	3,6141	2,9078	0,9120

The adsorptive capacity was calculated, based on determined isotherms (Fig. 2 and Table. 3).

As shown in Fig. 3, the breakthrough curves (isoplanes) were plotted based on results obtained from column filtration tests.
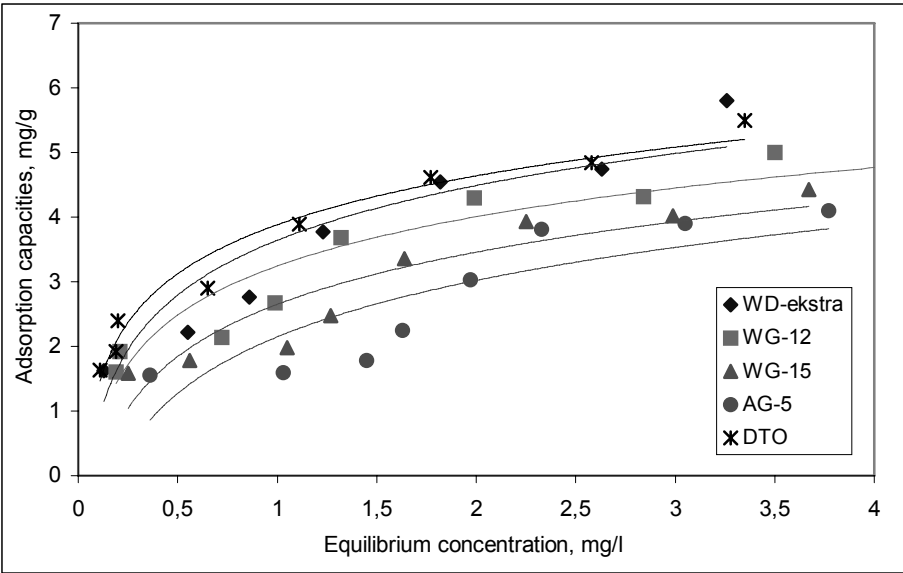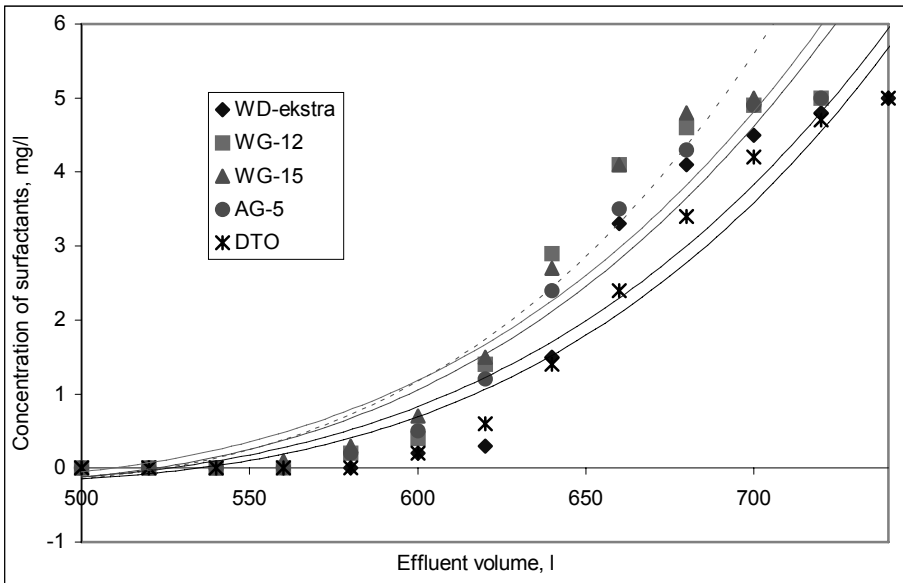
Fig.2.   Adsorption isotherms

Fig. 3.   Adsorption breakthrough curves (isoplanes)

These isoplanes served for the determination of sorption capacites under dynamic conditions (Table 4).

Calculations were performed to determine the total adsorptive capacity (until the bed exhaustion point) and usable adsorptive capacity (until the bed breakthrough point) using the filtration curves (isoplanes) plotted during the process and described by means of mathematic equations (1), (2), (3), (4) and (5):

(1) WD-ekstra: $y=2E-10x^4-2E-07x^3+5E-05x^2-0,0056x+0,1287$,
    $R=0,9349$,
(2) WG-12: $y=2E-10x^4-2E-07x^3+5E-05x^2-0,0055x+0,1186$,
    $R=0,9419$,
(3) WG-15: $y=3E-10x^4-3E-07x^3+0,0001x^2-0,0128x+0,3711$,
    $R=0,9666$,
(4) AG-5: $y=-1E-13x^5+4E-10x^4-3E-07x^3+0,0001x^2-0,0122x+0,3309$,
    $R=0,9632$,
(5) DTO: $y=2E-10x^4-2E-07x^3+7E-05x^2-0,0081x+0,2253$,
    $R=0,9688$.

The calculation were carried out in accordance with the diagram presented in Fig. 4.
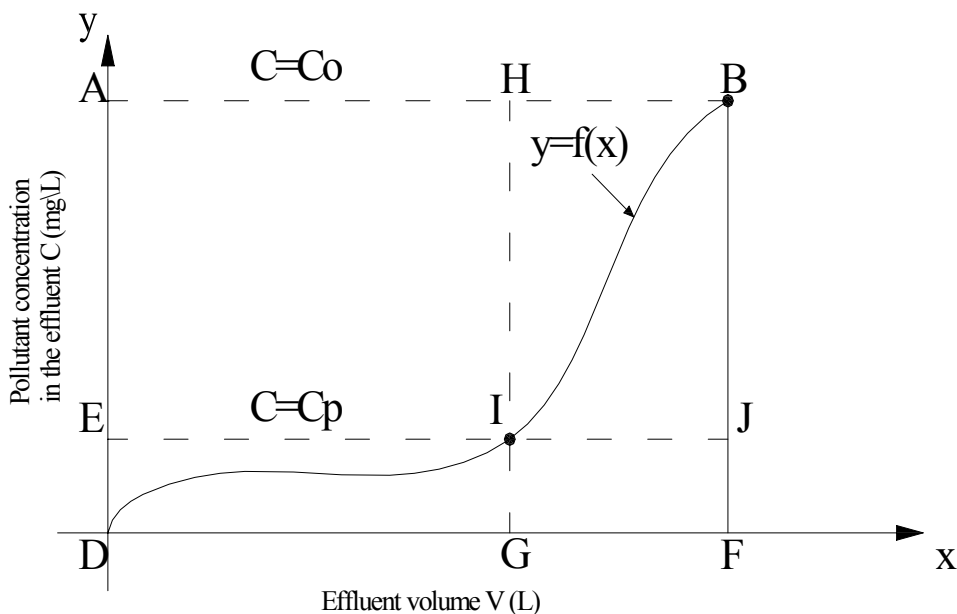
C = Co - point of bed exhaustion
C = Cp - breakthrough point

Fig. 4.   *Supporting drawing for calculation of total and usable adsorptive capacity*

Total adsorptive capacity PAc (g/kg), of specific material was calculated from the following formula, eq. (6):

(6)   PAc = Oc : M

were M is the mass of bed prior to filtration process [g]. The total amount of surfactants retained in the column, Oc, was calculated from the formula (7):

$$(7) \quad Oc = P_{DFBA} - P_{DFB} = P_{DFBA} - \int_{D}^{F} f(x)$$

where P_{DFBA} is the area representing the quantity of compounds introduced to filtration system (the point of bed exhaustion, $C = C_o = 5,0$ mg/l), P_{DFB} is the area representing the quantity of compounds not retained on the bed (the point of bed exhaustion, $C = C_o$).

The usable adsorptive capacity PAu (g/kg), was calculated as follows, eq. (8):

(8)   PAu = Ou : M [g/kg]

The amount of surfactants retained in the column to the break-through point (Ou), was calculated from the formula (9):

$$(9) \quad Ou = P_{DGHA} - P_{DGI} = P_{DGHA} - \int_{D}^{G} f(x)$$

where P_{DGHA} is the area representing the quantity of compounds introduced to the filtration system (the breakthrough point, $C = C_p = 0$ mg/l), P_{DGI} – area representing the quantity of compounds not retained on the bed (the breakthrough point, $C=C_p = 0$ mg/l).

Tab. 4.   Adsorption capacities of used materials

Adsorbent type	Adsorptions capacities (mg/g) determined in conditions		
	No-flow	**Flow**	
		PAu	**PAc**
WD-ekstra	1,7851	13,8100	15,6100
WG-12	1,6321	11,4280	13,4440
WG-15	1,2351	11,2970	14,0290
AG-5	0,9109	13,3330	15,3390
DTO	2,0697	14,3560	16,9230

The isoplanes, determined in tests conducted in flow conditions, also called the exit curves, served for defining the mass transfer zone, which was calculated using the equation of Michaels and Treybal [10]:

$$(10) \quad Ho = H \; \frac{tw - tp}{tw - (1-\varphi) \cdot (tw - tp)}$$

where: Ho – the adsorption front height, cm,
H – the adsorbent bed height, cm,
tw – bed operation time until exhausted, min,
tp – bed operation time until breakthrough, min,

φ - coefficient of sphericity of exit curves was calculated by dividing the surface area of the rectangle HBI J - $\int_{G}^{F} f(x)\,\mathrm{d}x$ by the surface area of the rectangle HBIJ (Fig. 3, Table 5).

Mass exchange zone moving rate, u (cm/min), was calculated from the formula [11] (Table 5):

(11) $u = H_o/(tw - tp)$.

Tab. 5.   The heights of adsorption fronts and the mass exchange moving rates

Adsorbent type	Coefficient of sphericity of exit curves, φ	Heights of adsorption fronts, Ho (cm)	Mass exchange moving rates, u (cm/min)
WD-ekstra	0,472	13,971	0,0154
WG-12	0,549	14,710	0,0157
WG-15	0,525	14,397	0,0155
AG-5	0,526	14,993	0,0159
DTO	0,577	13,700	0,0151

Materials having lower heights of mass exchange fronts, Ho, and lower rates of their moving across bed heights, exhibit the best adsorptive properties.

Having in mind the above parameters, as well as the values adsorption capacities determined in both non-flow and flow conditions, the tested adsorbents may ordered as follows:

DTO>WD-ekstra>WG-15>WG-12>AG-5.

4. Conclusions

- The adsorptive equilibrium between adsorbate solutions and the adsorbents established itself within 1 hour, but the adsorption process was most intensive during the first 20 – 30 minutes.

- The pH value of adsorbates had a strong effect on the adsorption process. Adsorption of surfactants impurities proceeded best at reaction more than 8,0.

- The Freundlich isotherm served best for describing the adsorption process. ● Izoterma Freundlicha najlepiej opisywała zachodzące procesy adsorpcji. Analiza stałych tej izotermy wykazała, że najlepszymi adsorbentami są węgle aktywne WD-ekstra i DTO. Podobną zależność potwierdziły pojemności adsorpcyjne wyznaczone w warunkach statycznych.

- With respect to the height of adsorption fronts and the rate of mass exchange zone advance, as well as the values of adsorption capacities determined in non-flow and flow conditions, the tested adsorbents may be rated in the following order:

  DTO>WD-ekstra>WG-15>WG-12>AG-5.

- The agreement of almost all empirical data from static tests with Freundlich's equation indicates the physical character of the studied phenomena.

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