JADWIGA KALETA*

EVALUATION OF EFFECTIVENESS OF ADSORPTION PROCESS IN REMOVAL OF SURFACTANTS FROM WATER

The paper presents the results of laboratory tests on the possibilities of utilizing active carbons produced in Poland (WD-ekstra, WG-12, WG-15, AG-5 and DTO) for removing surfactant substances from water. The objective of the tests was to arrive at quantitative formulation of the adsorption process as well as to determine the effect of various factors on the process. Attempt was undertaken to cope with the tasks set in the study purpose using model experimental setups. Model solution with anionic surfactant, Aerosol OT-100, in the concentration of 5.00 mg/dm^3, prepared using distilled water, was applied as adsorbate.

The processes of adsorption, conducted in a batch mode, were best described by Freundlich isotherms. The adsorption capacity of the active carbons tested was calculated on the basis of the isotherms.

The flow conditions were created by column filtration method. On the basis of the results obtained, the breakthrough curves, the so-called isoplanes, were prepared and served in turn to determine the adsorption capacities under flow conditions. The DTO carbon exhibited the highest values of adsorption capacities, as determined under both no flow and flow conditions.

The exit curves (isoplanes) were also utilized to determine the mass penetration zone (the adsorption front height), as well as to calculate the rate of mass-exchange zone advance. The adsorption front height for the carbons tested was five times lower than the adsorption bed height, thus confirming a high effectiveness of active carbons in detergent removing.

1. INTRODUCTION

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

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

_____

* Department of Water Protection and Purification, Technical University of Rzeszów, al. PowstancóW Warszawy 6, 35-959 Rzeszów, Poland. E-mail: jkaleta@prz.edu.pl

0.29 mg/dm^3, while the total amount of surfactants approached 1.47 mg/dm^3. Underground waters from the intakes in nonthreatened areas contained surfactants in trace quantities, i.e. from 0.006 to 0.007 mg/dm^3 [3].

Surfactants present in larger amounts (1–3 mg/dm^3) in rivers have negative effect on self-purifying properties of natural waters and make drinking water purification processes more difficult [5].

The consumption of water polluted with detergents or its use for bath may adversely affect human life. Detergents undergo bioaccumulation in internal organs of humans and animals and change the structure of proteins. They may cause allergies and skin changes. The toxicity of detergents depends on their type; non-ionic compounds are less toxic, whereas anionic ones are most toxic [4], [9].

The permissible values of anionic surfactants in surface waters taken in for drinking are as follows: the categories A$_1$ and A$_2$ – 0.2 mg/dm^3, the category A$_3$ – 0.5 mg/dm^3 [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 the case of surfactants, divalent cations, especially calcium ions (Ca^{2+}) present in conditioned water are 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].

Powdered active carbon was applied in 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. The particles of powdered carbon were removed in the microfiltration process. The results of purification were as follows: anionic and cationic surfactants were reduced by 34–38% and 68–98%, respectively [1]. The above results were confirmed by other tests, which have shown that due to adsorption on active carbon both anionic and non-ionic surfactants were removed in a range of 31.7–67.4% [2].

The objective of this study was to assess the 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 based on adsorption capacity values determined under no flow and flow conditions as well as on the height of adsorption front and the rate of mass exchange zone advance.

2. MATERIALS AND METHODS

The initial (model) solution of detergent was prepared by adding anionic surfactant, named Aerosol OT-100 of chemical formula C$_2$H$_{37}$NaO$_7$S, to distilled water in such a quantity that the detergent concentration in the solution reached 5.0 mg/dm^3. The detergent concentration was determined by using methylene blue, which reacts

with anion-active surfactant substance, producing blue-colored organic complex. This complex is extracted with chloroform in alkali environment, and the intensity of coloring, as determined by photocolorimetric method at the wavelength $\lambda = 652$ nm, is proportional to the detergent concentration.

Granular active carbon of five grades, i.e. WD-ekstra, WG-12, WG-15, AG-5 and DTO produced by Gryfskand company (table 1), was used in the tests.

Table 1

Characteristic of active 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	750
Methylene number	cm^3	22	35	32	25	50
Granulation	mm	1.0–1.5	–	–	0.75–1.2	–
Coefficient of grain-size-distribution uniformity		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 analyzed at a carbon dose of 1.0 g/dm³. A suitable adsorbent was placed to conical flasks, each containing 300 cm³ 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 conducted at near neutral pH. The clarification lasted one hour. These parameters were optimized for the detergent and active carbons in previous technological tests. The control analysis was carried out in decanted solutions.

The effect of pH of adsorptive solutions on adsorption was studied with the sorbents whose doses were the same as those for the determination of adsorption kinetics. The pH value of model solutions was varied within 5–10, the shaking lasted 30 minutes and the decanting – 1 hour.

In order to determine the adsorption isotherms, increasing surfactant doses (0.3–3.0 g/dm³) were added to eight conical flasks, each containing 300 cm³ of model solutions. A 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 the surfactant content was determined in the decanted solution.

The column filtration method ensured dynamic conditions (under flow conditions). The adsorption columns with 32-mm diameters were made of organic glass. The height of their filling was 700 mm and the adsorbent quantities in the column were as follows: WD-ekstra, 210 g; WG-12, 245 g; WG-15, 239 g; AG-5, 210 g and DTO, 202 g. The solution subjected to filtration was passed down the column. At the beginning of each filtration cycle the filtration rates were changed consecutively to 6, 8, 12, 20 and 25 m/h, while the optimum rate was determined. The filtration rate was deter-

mined with dosing pump. Further testing in a given cycle was performed at filtration rates of 20 m/h, the highest rate allowing a total detergent removal.

After each hour of bed operation, the samples were taken in order to carry out control analyses. Each time filtration lasted 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

The data on adsorption kinetics showed that the process took place quite rapidly (figure 1). A complete sorption balance became established after about 1 hour, but the process proceeded very rapidly for 20–30 minutes. In further testing, the shaking time of 30 minutes was accepted as the optimum.
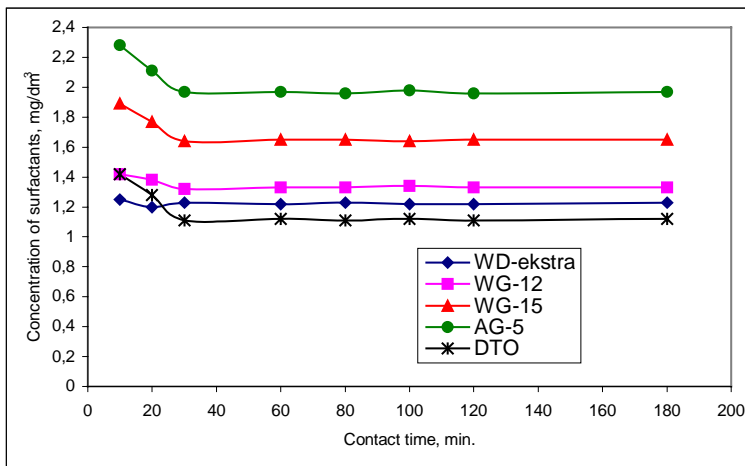

Fig. 1. Effect of contact time on adsorption process (initial surfactant concentration of 5.00 mg/dm^3, adsorbent dose of 1.0 g/dm^3)

pH value of adsorbates had a strong effect on the adsorption process (see table 2). Surfactant impurities were adsorbed most efficiently at pH higher than 8.0.

The results obtained in a successive series of experiments performed under static conditions (in no flow conditions) were described by basic equations of isotherms, i.e., those of Freundlich, Langmuir and BET. The Langmuir and BET isotherms did not matched well empirical values (the coefficients of correlation ranged between 0.50 and 0.70). The adsorption processes were best described by the Freundlich isotherms. Their choice was explained by a high correlation coefficient R (approx. equal to 0.9) (table 3).

The effect of model-solution pH on the adsorption process
(initial surfactant concentration of 5.00 mg/dm^3, adsorbent dose of 1.0 g/dm^3)

pH of adsorbate solution	Concentration of surfactant, mg/dm^3				
	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 equation representing the Freundlich isotherm is expressed by the following general formula:

$$\frac{X}{m} = K \cdot C^{1/n} . \tag{1}$$

The amount of the surfactant absorbed X was calculated from the difference between the initial concentration C_0 (mg/dm^3) and the equilibrium concentration C (mg/dm^3); m is the weight of adsorbent (g/dm^3), while K and n are constants.

After correcting the logarithm, it assumes a linear form:

$$\log \frac{X}{m} = \log K + \frac{1}{n} \cdot \log C . \tag{2}$$

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

Constants of Freundlich adsorption isotherms

Adsorbent type	Constants of isotherms		Correlation coefficient R
	K	$1/n$	
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

Analysing the shapes of isotherms (figure 2) is can be inferred that active carbons WD-ekstra and DTO exceed the rest of adsorbents in respect of adsorption ability.
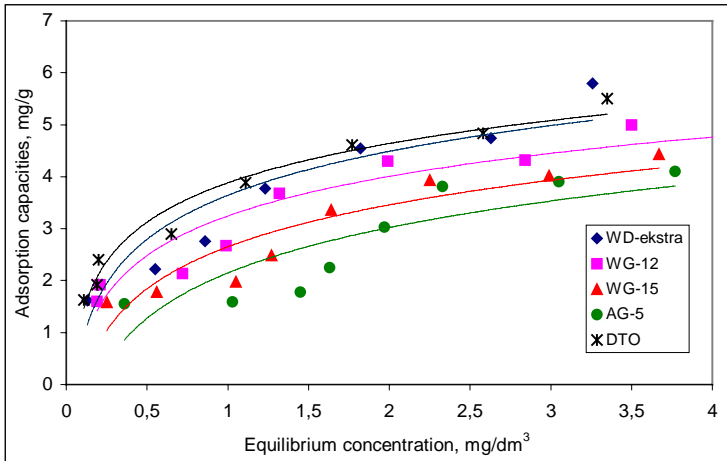
Fig. 2. Adsorption isotherms

The analysis of the adsorption process intensity ($1/n$) leads to the conclusion that active carbons of DTO and WD-ekstra grades showed the best adsorption potential. Maximum adsorption capacities were read from adsorption isotherms (see figure 2) and specified in table 4.
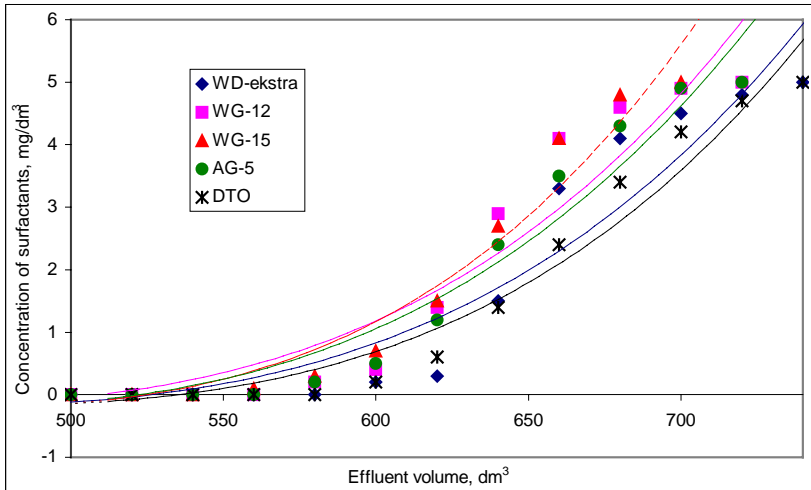

Fig. 3. Adsorption breakthrough curves (isoplanes) (initial surfactant concentration of 5.00 mg/dm^3, filtration rate of 20 m/h)

The breakthrough curves (isoplanes, figure 3) were plotted based on the results obtained from column filtration tests. These isoplanes served for the determination of adsorption capacity under dynamic conditions (table 4).

Adsorption capacities of the materials used

Adsorbent type	Adsorption capacity (mg/g)		
	No flow (batch)	Flow (column)	
		PAu	PAc
WD-ekstra	5.2113	13.8100	15.6100
WG-12	4.8224	11.4280	13.4440
WG-15	4.1289	11.2970	14.0290
AG-5	3.7566	13.3330	15.3390
DTO	5.3120	14.3560	16.9230

Calculations were performed to determine the total adsorption 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 the following mathematic equations

$$y = 2E-10x^4 - 2E-07x^3 + 5E-05x^2 - 0.0056x + 0.1287, \quad R = 0.9349, \text{ WD-extra}, \quad (3)$$

$$y = 2E-10x^4 - 2E-07x^3 + 5E-05x^2 - 0.0055x + 0.1186, \quad R = 0.9419, \text{ WG-12}, \quad (4)$$

$$y = 3E-10x^4 - 3E-07x^3 + 0.0051x^2 - 0.0128x + 0.3711, \quad R = 0.9666, \text{ WG-15}, \quad (5)$$

$$y = 1E-13x^5 + 4E-10x^4 - 3E-07x^3$$
$$+ 0.0001x^2 - 0.0122x + 0.3309, \quad R = 0.9632, \text{ AG-5}, \quad (6)$$

$$y = 2E-10x^4 - 2E-07x^3 + 7E-05x^2 - 0.0081x + 0.2253, \quad R = 0.9688, \text{ DTO}. \quad (7)$$

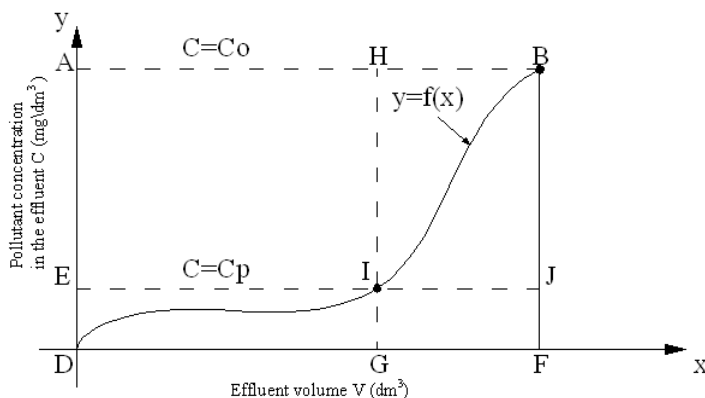The calculations were carried out in accordance with the diagram presented in figure 4.

Fig. 4. Supporting drawing for calculating total and usable adsorptive capacities
$C = C_0$ – point of bed exhaustion, $C = Cp$ – breakthrough point

Total adsorptive capacity PAc (g/kg) of a specific material was calculated from the following formula

$$PAc = Oc : M, \tag{8}$$

were M is the mass of bed prior to filtration process (g). A total amount of surfactants retained in the column (Oc) was calculated as follows:

$$Oc = P_{DFBA} - P_{DFB} = P_{DFBA} - \int_{D}^{F} f(x), \tag{9}$$

where P_{DFBA} is the area representing the quantity of compounds introduced to filtration system (the point of bed exhaustion, $C = C_0 = 5.0$ mg/dm^3), P_{DFB} is the area representing the quantity of compounds not retained on the bed (the point of bed exhaustion, $C = C_0$). The usable adsorptive capacity PAu (g/kg) was calculated as follows:

$$PAu = Ou : M \text{ (g/kg)}. \tag{10}$$

The amount of surfactants retained in the column until the breakthrough point (Ou) was calculated from the formula:

$$Ou = P_{DGHA} - P_{DGI} = P_{DGHA} - \int_{D}^{G} f(x), \tag{11}$$

where P_{DGHA} is the area representing the quantity of compounds introduced to the filtration system (the breakthrough point, $C = C_p = 0$ mg/dm^3), P_{DGI} – the area representing the quantity of compounds not retained on the bed (the breakthrough point, $C = C_p = 0$ mg/dm^3).

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

$$H_0 = H \frac{t_w - t_p}{t_w - (1 - \varphi) \cdot (t_w - t_p)}, \tag{12}$$

where:

H_0 – the adsorption front height, cm,

H – the adsorbent bed height, cm,

t_w – the time of bed operation until exhaustion, min,

t_p – the time of bed operation until breakthrough, min,

φ – the coefficient of sphericity of exit curves; it was calculated by dividing the surface area of the rectangle $HBIJ - \int_{G}^{F} f(x)\, dx$ by the surface area of the rectangle $HBIJ$ (figure 3, table 5).

The moving rate u (cm/min) of mass exchange zone was calculated from the following formula (table 5):

$$u = \frac{H_0}{t_w - t_p} .$$ (13)

<div align="right">T a b l e 5</div>

The heights of adsorption fronts and the moving rates of mass exchange zone

Adsorbent type	Coefficient of sphericity φ of exit curves	Heights H_0 of adsorption fronts (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, whose heights of mass exchange fronts H_0 and the rates of moving across bed heights are lower, exhibit the best adsorptive properties.

Bearing in mind the above parameters and the values of adsorption capacities determined under both no flow and flow conditions, we can arrange the adsorbents tested in the following descending order:

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

4. CONCLUSIONS

• The adsorption of the detergent onto active carbons tested under conditions of no through flow was most intensive during the first 20–30 minutes.

• The pH value of adsorbate solution had a strong effect on the adsorption process. The optimum pH of detergent adsorption exceeded 8.0.

• The Freundlich adsorption isotherm described best the adsorption processes. The analysis of the isotherm constants showed that active carbons of DTO and WD-ekstra grades were the best adsorbents. Adsorption capacities determined under static conditions confirmed a similar relationship.

• 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 under no flow and flow conditions, the adsorbents tested may be arranged in the following descending order:

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

• The conformity of almost all empirical data from static tests with the Freundlich equation testifies to the physical character of the phenomena studied.

REFERENCES

[1] BASAR C.A., KARAGUNDUZ A., CAKICI A., KESKINLER B., *Removal of surfactants by powdered activated carbon and microfiltration*, Wat. Res., 2004, No. 38, 2117–2124.

[2] CSERHATI T., FORGACS E., OROS G., *Biological activity and environmental impact of anionic surfactants*, Environmet International, 2002, No. 28, 337–348.

[3] GALASSIS S., GUZZELLA L., MINGAZZINI M., VIGANO L., CAPRI S., SORA S., *Toxical and chemical characterization of organic micropollutants in rivier Po waters (Italy)*, Wat. Res., 1992, No. 1, 19–27.

[4] GRANT R.L., YAO C., GABOLDON D., ACOSTA D., *Evaluation of surfactant cytotoxicity potential by primary cultures of ocular tissues:* I. *Characterization of rabbit corneal epithelial cells and initial injury and delayed toxicity studies*, Toxicology, 1992, No. 76, 153–176.

[5] KALETA J., *Detergenty w środowisku wodnym*, Inżynieria i Ochrona Środowiska, Politechnika Częstochowska, Częstochowa, 2005, t. 8, nr 1, 99–115.

[6] KOWAL A.L., ŚWIDERSKA-BRÓŻ M., *Oczyszczanie wody*, PWN, Warszawa–Wrocław, 1996.

[7] NARKIS N., BEN-DAVID B., *Adsorption of non-ionic surfactants on activated carbon and mineral clay*, Wat. Res., 1985, No. 19, 815–824.

[8] Rozporządzenie Ministra Środowiska z dnia 27 listopada 2002 r w sprawie wymagań, jakim powinny odpowiadać wody powierzchniowe wykorzystywane do zaopatrzenia ludności w wodę przeznaczoną do spożycia (DzU, Nr 204, poz. 1728).

[9] VERGE C., MORENO A., *Effects of anionic surfactants on Daphna magna*, Tenside Surfactants Deterg., 2000, No. 37, 172–175.