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ANDRZEJ BIELSKI (ORCID: 0000-0001-5703-0348)1

PAC ADSORPTION EFFICIENCIES IN THE FILTER AND IN THE HOMOGENEOUS FLOCCULATOR. A FULL-SCALE COMPARATIVE STUDY

The paper investigates the efficiency of adsorption of organic pollutants present in natural water on powdered activated carbon (PAC). A PAC adsorption capacity is related to the mass exchange driving force between water and sorbent. During the study, it was confirmed that the mass transfer driving force in the homogeneous flocculator with simultaneous PAC adsorption was lower than in the filter column. The filter showed a better utilization of PAC adsorption capacity than the volume system, for the optimal PAC dose. The authors proposed a new method where adsorption was carried out in the filter column with PAC applied to its upper layer. The powdered sorbent was applied to the bed at the end of a backwashing cycle. Two models of PAC adsorption in transient states for the homogeneous flocculator and the column mass exchanger were presented. The simulation calculations confirmed that there was still a possibility to double the PAC adsorption capacity concerning commonly used adsorption with coagulation in the homogeneous flocculator.

1. INTRODUCTION

Organic compounds are present in natural waters used as potable water sources. They may be responsible for unpleasant odor and taste, can negatively affect the consumer's health, and finally may act as precursors of harmful oxidation by-products (THM). To improve removal of organic compounds from water, adsorption on granular or powdered activated carbon (PAC) is used. In the first case, particulate or granular activated carbon is placed in a filter, while adsorption on PAC may be carried out inside of a coagulation system. Application of PAC is preferred when risks of failure to meet drinking water quality parameters occurs only occasionally [1, 2]. PAC as a method of removal of natural organics from water has been reported in numerous

¹Cracow University of Technology, Faculty of Environmental and Power Engineering, Department of Water Supply, Sewerage and Environmental Monitoring, Warszawska 24, 31-155 Cracow, Poland, email address: abielski@riad.usk.pk.edu.pl

research works [2–9]. If PAC works just as a supplementary agent, its doses stay within the range of a few grams per cubic meter while if it is used for a regular adsorption, the doses may vary from tens to hundreds of grams per cubic meter.

PAC adsorption may also be carried out in a filter bed with two or three layers [13, 14]. A PAC suspension is applied to the top layer (a two-layer bed: anthracite/sand) or either to the middle or top layer (a three-layer bed: anthracite/sand/garnet) at the end of filter backwashing. The efficiency of PAC adsorption was determined using two filter columns operating with and without a PAC dosing [14].

2. EXPERIMENTAL

The study was carried out at the Dłubnia WTP in Krakow; the plant takes water from the Dłubnia river. The treatment process comprises coagulation, clarifiers, rapid filters, and contact chambers for disinfection with chlorine dioxide.

PAC adsorption in a filter bed. The PAC adsorption experiments were carried out in the two-layer (anthracite/sand) filter. A PAC suspension was introduced into the anthracite layer. The granulometric characteristics of the filtering material was kept identical to that of the Dłubnia Water Treatment Plant (WTP), Kraków, where the tests were carried out. Another filter with the same filter bed and no PAC dosing was used as a reference unit [14]. A detailed description of the experimental set and its operation is presented in [14].

PAC adsorption with simultaneous coagulation. Currently, the WTP combines coagulation with PAC adsorption and PAC is dosed immediately after the PAX-16 coagulant. The PAC adsorption effects were determined based on the content of dissolved organic substances in water after coagulation and after coagulation and adsorption. The water samples settled for 5 min and then the solids were removed by centrifugation. The organic content was assumed as proportional to UV_{254nm} absorbance. Rapid mixing of water with coagulant and possibly with PAC takes place in three rapid mixers with a total volume of 42.6 m³. After rapid mixing, the water passes through the overflow into the main pipeline that distributes water between the flocculation. The flocculation process as well as flocculation combined with occasional PAC adsorption were carried out with the use of five two-chamber flocculators, 160 m³ in volume each. The minimum retention time was 40 min. Each chamber was equipped with a mechanical stirrer. Water from the flocculation chambers was discharged to the settling tanks. The PAC contact times varied according to flow rates through the slow mixing chambers. The retention times in the flocculation chambers calculated for the chemicals varied from 0.4 to 1.0 h (Table 1) while the PAC doses varied from 10.2 to 31.0 g PAC/m³ (Table 1).

Adsorption in the PAC filter. Water after coagulation and sedimentation passed through two identical filters filled with sand and anthracite. During the operation of two parallel filters, a PAC suspension was fed to an anthracite layer of only one filter. The doses of PAC applied to the filter were 21, 42, and 63 g. In the anthracite layer 0.5 m high and located in a column with a diameter of 0.15 m, the following apparent sorbent densities were obtained 2376.71, 4753.43, 7130.14 g/m³. A detailed description of the filter columns operation is presented in [14]. The influent and effluent samples from both columns were automatically collected and then analyzed.

3. ADSORPTION MODELS

The adsorption models presented in the following sections analyze the concentration of the adsorbate C in a liquid phase. $UV_{254 nm}$ absorbance (A254) is used to determine dissolved organic pollutants; it is assumed that absorbance A is approximately proportional to the organics concentration C [13, 14].

3.1. ADSORPTION IN A HOMOGENEOUS FLOCCULATOR

In a homogeneous flocculator operating in transient states, a set of three differential balance equations has to be integrated to calculate the concentration C and effluent adsorption a. The balance equations are as follows

• mass balance equation for adsorbate in a liquid

$$Q_0 C_0 - \frac{ka_m}{\varepsilon_m} D \frac{\rho_w}{\rho_u} (C - C_i) V_r = V_r \frac{dC}{dt} + Q_0 C$$
(1)

• mass balance equation for adsorbate in adsorbent

$$Q_0 D_0 a_0 + \frac{ka_m}{1 - \varepsilon_m} D \frac{1}{\rho_u} (C - C_i) M_{\text{sorb}} = M_{\text{sorb}} \frac{da}{dt} + Q_0 Da$$
(2)

• mass balance equation for adsorbent (PAC dosing)

$$Q_0 D_0 = V_r \frac{dD}{dt} + Q_0 D \tag{3}$$

where: C_0 – adsorbate concentration in a flocculator feed, g/m³ of water, C – adsorbate concentration in a flocculator and its effluent, g/m³ of water, a_0 – adsorption capacity in a flocculator feed, g/g of sorbent, a – adsorption capacity in a flocculator and its effluent, g/g of sorbent, D_0 – sorbent concentration in a flocculator feed (sorbent dose), g of sorbent/m³ of a unit, D – sorbent concentration in a flocculator and its effluent, g of

sorbent/m³ of a unit, C_i – equilibrium concentration of adsorbate calculated from the adsorption isotherm f for a current adsorption capacity a ($C_i = f(a)$, g/m^3 of water, Q_0 – flow in a sorbent-water system, m³ of a unit/s, V_r – volume of a water-sorbent unit (volume of a flocculator), m³ of a unit, ρ_w – water density (10⁶ g/m³), ρ_u – density of a water-sorbent system, g/m^3 of a unit, $\rho_u \approx \rho_w + D$, ε_m – mass share of water in a water-sorbent system, $\varepsilon_m \approx \rho_w/(\rho_w + D)$, k – mass transfer rate constant across a water-sorbent interface, m/s, a_m – specific outer surface of sorbent particles, m²/g of sorbent, M_{sorb} – mass of sorbent in a reactor, g, $M_{sorb} = V_r \rho_u (1 - \varepsilon_m)$, t – time, s.

The set of equations (1)–(3) was integrated using Euler's method at $\Delta t = 0.001$ h.

3.2. ADSORPTION IN A PAC FILTER

Transport of adsorbate in an adsorption column can be described by the advection and diffusion equation that includes the adsorption rate. The equation is as follows [10–14]

$$\frac{\partial C}{\partial t}\varepsilon + V_x \frac{\partial C}{\partial x} = D_x \frac{\partial^2 C}{\partial x^2} - ka_m \rho_{p, \text{ sorb}} \left(C - C_i \right)$$
(4)

where C – adsorbate concentration, g/m³ of water, C_i – equilibrium adsorbate concentration, g/m³ of water, a_m – specific outer surface of sorbent particles, m²/g of sorbent, V_x – empty bed (column) velocity, m/s, D_x – mass dispersion coefficient for an empty bed, m²/s, ε – filter bed porosity, $\rho_{p,\text{sorb}}$ – apparent density of sorbent fed to a column, g of sorbent/m³, m_{sorb} – mass of sorbent fed to a column, g, V – volume of an adsorption column, m³, x – linear coordinate, m, other symbols as in equations (1)–(3).

Adsorption capacity a^* , g/m³ of sorbent, in a fixed adsorption layer is described by an equation

$$\frac{\partial a^*}{\partial t}(1-\varepsilon) = ka_m \rho_{p, \text{ sorb}} \left(C - C_i\right), a^* = \frac{a\rho_{p, \text{ sorb}}}{1-\varepsilon}$$
(5)

where all symbols are as above.

To integrate equations (4) and (5), the adsorption isotherm has to be identified. It may be Henry's isotherm:

$$a^* = \Gamma^* C_i \tag{6}$$

where Γ^* is Henry's constant, m³ of water/m³ of sorbent, and

$$\Gamma^* = \frac{\Gamma \rho_{p, \, \text{sorb}}}{1 - \varepsilon} \tag{7}$$

 Γ is Henry's constant expressed in m³ of water/g of sorbent, other symbols as above.

Equation (7) makes it possible to accommodate the Henry coefficient expressed in different units.

Different isotherms can be used in calculations. If the Langmuir isotherm is used

$$a^* = \frac{a^*_{\max}C_i}{b+C_i} \tag{8}$$

where a_{max}^* – maximum adsorption capacity (asymptote of the Langmuir isotherm), g/m³ of sorbent, *b* – Langmuir isotherm's constant, g/m³ of water, other symbols as above).

Then the maximum adsorption capacity can be expressed in other units, using the formula:

$$a_{\max}^* = a_{\max} \frac{\rho_{p, \text{ sorb}}}{(1 - \varepsilon)}$$
(9)

 a_{max} – maximum adsorption capacity, g/g of sorbent.

The set of equations (4) and (5) may be solved numerically, together with the iso-therm (6) [12].

3.3. OPERATION OF A PAC FILTER

Concentrations of the pollutants adsorbed on PAC and captured on the other layers within the PAC filter can be calculated based on the column adsorption model and the effluent concentrations from the filter with no PAC. If the effluent concentrations from the filter with no PAC are known at intervals Δt , then after a time equal to $i\Delta t$ the effluent concentration from the filter with PAC will be

$$C_{i, \text{ PWA}} = C_0 - \left(C_i - C_{i, \text{ PWA}}^*\right)$$
(10)

where C_0 – influent concentrations to the filter without and with PAC, g/m³, C_i – effluent concentrations from the filter without PAC after $i\Delta t$, g/m³, $C_{i,PWA}$ – effluent concentrations from the filter with PAC after $i\Delta t$) if the filter had only a PAC layer, g/m³, $C_{i,PWA}^*$ – effluent concentrations from the filter with PAC after $i\Delta t$, g/m³, Q_0 – flow rate to the filters, m³/s, Δt – time interval, s.

Equation (10) determines the adsorbate concentrations in the effluent from the PAC filter, as a result of PAC adsorption, only. It also describes the difference in operation efficiency between the filter with PAC and without PAC. The concentrations $C_{i,PWA}$ can be used to estimate parameters of the adsorption model in the PAC filter.

4. RESULTS AND DISCUSSION

4.1. ADSORPTION ON PAC WITH A SIMULTANEOUS COAGULATION IN A FULL-SCALE HOMOGENOUS FLOCCULATOR

Full-scale experiments on PAC adsorption during coagulation in the homogeneous flocculator enabled one to determine the adsorption model parameters. A PAX-16 coagulant dose of 2 g Al^{3+}/m^3 and a PAC dose (Dose PAC, changing with time) were fed to the flocculator (Fig. 1). Over time, the PAC concentration in the changed to reach finally the PAC dosage value. At the end of each test, absorbances in the effluent from the flocculator were measured after previous sedimentation and centrifugation (Fig. 2, Data).



Fig. 1. PAC doses fed to the homogeneous flocculator (HP) and PAC concentrations (C PAC) in the flocculator vs. the experiment time (*t*)



Fig. 2. Absorbances (A) measured (Data) and calculated with the model vs. the experiment time (t)

The parameters of the adsorption model were determined with the least-squares method (eqs. (1)–(3)). The time dependences of absorbance A calculated from the model (eqs. (1)–(3)) are shown in Fig. 2. The absorbance values, measured and calculated at the end of each test, are summarized in Table 1.

Table 1

			A [1/m]		a [(1	AC]	
t	D	С				Theoretical	
[h]	[g PAC/m ³]	[g PAC/m ³]	Measured	Theoretical	Measured	Henry's	Langmuir's
						isotherm	isotherm
0.40	31.00	30.79	1.1500	1.2499	0.0277	0.0254	0.0255
0.80	20.70	20.94	1.2980	1.3883	0.0336	0.0282	0.0282
0.97	25.60	25.39	1.3720	1.3313	0.0248	0.0271	0.0271
0.41	18.80	18.66	1.4994	1.4696	0.0269	0.0298	0.0298
0.59	20.70	20.69	1.4360	1.4113	0.0274	0.0286	0.0287
1.00	19.90	19.94	1.5140	1.4227	0.0245	0.0289	0.0289
0.40	10.20	10.20	1.6300	1.6603	0.0365	0.0335	0.0336
0.60	10.20	10.20	1.6560	1.6601	0.0339	0.0335	0.0336
1.00	10.20	10.20	1.7280	1.6599	0.0269	0.0335	0.0336
		Henry's	Langmuir's isotherm				
ka_m , [(m/h)·(m ² /g PAC)]				25.33941	ka_m , [(m/h)·(m ² /g PAC)]		25.05244
Henry's isotherm Γ [m ³ /g PAC]				0.020319 (0.020960)	A_{max} , (1/m)·m ³ /g PAC]		0.949359
(for Langmuir's isotherm A_{max}/b)				(0.0-0700)		8]	
Mean relative error of the model				0.0382	b, 1/m		45.2932

Summary of PAC adsorption with simultaneous coagulation in the homogeneous flocculator at the WTP

Homogenous flocculator, PAX-16 dose 2 g Al³⁺/m³, $A_0 = 2.002$ m⁻¹ after coagulation with D = 0.



Fig. 3. Absorbance A vs. PAC concentration C in the homogenous flocculator

The ka_m product was 25.33941 (m/h)·(m²/g PAC), Henry's constant (eqs. (6) and (7)) was 0.020319 m³/g PAC. For Langmuir's isotherm (eq. (8)), *b* was high (45.2932 1/m) compared to the measured absorbances, that the isotherm stayed almost linear within the range of observed absorbances. The A_{max}/b ratio (0.020996) was close to Henry's

coefficient. A small average relative error (0.0382) proved the good model fit. The model can determine changes in both absorbances in the aqueous solution and PAC adsorption capacities (over time and for different sorbent doses) (Table 1).

Since adsorption in the flocculator proceeded fast, absorbance changed approximately linearly with the PAC concentration in the flocculator following the linear adsorption isotherm (Fig. 3). The absorbance drop per unit of a PAC concentration was $-0.0242 \text{ m}^2/\text{g}$ PAC (Fig. 3).

4.2. FILTRATION ON THE FILTER WITH PAC

Figures 4, 5, and 6 illustrate changes of absorbance A in the effluent from the filter without PAC and with PAC (as a result of PAC adsorption). The data were obtained from direct measurements and the model calculations for various PAC doses. The theoretical curves fit well to the recorded absorbance measurements. Points marked were used to determine the parameters of the adsorption model according to equation (10). They describe magnitude of absorbance in the effluent from the filter with PAC only. The studies enabled one to find parameters ka_m and Γ^* for the adsorption model (4)–(6) in a column system. The average model parameters varied with the dose of PAC fed to the filter

 $ka_m = 0.002678 \pm 0.0005958 \text{ (m/h)} \cdot (\text{m}^2/\text{g PAC})$ $ka_m \rho_{p, \text{sorb}} = 0.001768 \pm 0.0003933 \text{ 1/s}$ $I^* = 73.137 \pm 25.440 \text{ m}^3 \text{ of water/m}^3 \text{ of sorbent}, \varepsilon = 0.4425$ $\Gamma = 0.017156 \pm 0.005967 \text{ m}^3 \text{ of water/g PAC}$ $\rho_{p, \text{ sorb}} = 2376.71 \text{ g PAC/m}^3$ • for 42 g PAC: $ka_m = 0.004106 \pm 0.001500 \text{ (m/h)} \cdot (\text{m}^2/\text{g PAC})$ $ka_m \rho_{p, \text{sorb}} = 0.005422 \pm 0.001981 \text{ 1/s}$ $I^* = 239.17 \pm 88.662 \text{ m}^3 \text{ of water/m}^3 \text{ of sorbent}, \varepsilon = 0.4425$ $\Gamma = 0.028051 \pm 0.010399 \text{ m}^3 \text{ of water/g PAC}$ $\rho_{p, \text{ sorb}} = 4753.43 \text{ g PAC/m}^3$ • for 63 g PAC: $ka_m = 0.002382 \pm 0.0009037 \text{ (m/h)} \cdot (\text{m}^2/\text{g PAC})$ $ka_m \rho_{p, \text{sorb}} = 0.004718 \pm 0.001790 \text{ 1/s}$ $I^* = 169.43 \pm 9.8737 \text{ m}^3 \text{ of water/m}^3 \text{ of sorbent}, \varepsilon = 0.4425 \text{ m}^3/\text{m}^3$ $\Gamma = 0.013247 \pm 0.000772 \text{ m}^3 \text{ of water/g PAC}$ $\rho_{p, \text{ sorb}} = 7130.14 \text{ g PAC/m}^3$

The above model parameters were reported during bench scale experiments. They can be achieved when PAC was evenly distributed in the filter, so their actual values slightly exceed the ones reported elsewhere [14].



Fig. 4. Absorbance A vs. time in the effluent from the filters without PAC, with PAC and adsorption on PAC only for the measurements (Data) and model calculations (flow 0.087 m³/h, x = 0 and x = L stand for the top and the bottom cross-section of the filter, respectively), the dose of PAC 42 g



Fig. 5. Absorbance A vs. time in the effluent from the filters without PAC, with PAC and adsorption on PAC only for the measurements (Data) and model calculations (flow 0.087 m³/h, x = 0 and x = L stand for the top and the bottom cross-section of the filter, respectively), the dose of PAC 21 g



Fig. 6. Absorbance A vs. time in the effluent from the filters without PAC, with PAC and adsorption on PAC only for the measurements (data) and model calculations (flow 0.087 m³/h, x = 0 and x = L stand for the top and the bottom cross-section of the filter, respectively), the dose of PAC 63 g

The actual PAC doses resulted in different apparent PAC densities $\rho_{p, \text{ sorb}}$ in the filter; the values of ka_m and Γ^* varied with $\rho_{p, \text{ sorb}}$. The highest values of ka_m were found

for 42 g of PAC and such a PAC dose was therefore strongly preferred if adsorption efficiency was considered. If the PAC dose is too low, the sorbent molecules located in pore corners have a smaller external mass exchange surface since they are covered with the filter particles; when the PAC doses are too high, the sorbent molecules cover each other (multilayer coatings) and the external surface of mass exchange also decreases, comparing to the lower dose of PAC.

4.3. REMOVAL OF ORGANIC POLLUTANTS FROM WATER WITH PAC IN THE FILTER AND THE HOMOGENOUS FLOCCULATOR

Parameters of the adsorption model described determined previously were used to simulate the PAC filter operation. Absorbances A measured in the effluent in the function of time at a PAC dose of 42 g are shown in Fig. 7. At the lower influent absorbances, the effluent absorbances (after the same time of 24 h) are closer to influent ones but their ratios (A (t = 24 h)/ A_0) are similar (ca. 0.83).



Fig. 8. Absorbance A and adsorption capacity along the filter column after 24 h of filtration

Absorbances A and the adsorption capacity along the filter column after 24 h of operation at a dose of 42 g of PAC are shown in Fig. 8. For all $A_0 = \{2, 3, 4\}$ m⁻¹, the

effluent absorbances were ca. 17% lower than the A_0 . Therefore, the ratios of influent/effluent absorbances remained approximately the same (ca. 1.2) regardless of the influent absorbance. It means that exhaustion of the PAC sorption capacity in the filter takes place regardless of the influent absorbance (organic matter) within the value range from 2.00 to 4.00 m⁻¹ (Figs. 7, 8).

For all absorbances $A_0 = \{2, 3, 4\}$ m⁻¹, adsorptions *a* in the bottom cross-section of the filter are about 31% lower than those in the upper cross-section (Fig. 8) which means that PAC adsorption capacity in the lower part of the filter is about 1.45 times less than in the upper one.

Table 2

t	<i>m</i> [g]	<i>A</i> ₀ [1/m]	A'_{PAC} [1/m]	D_1 [g PAC/m ³]	a_1 [(1/m)·m ³ /g PAC]	<i>a</i> ₂	$D_2 _ a_1$
[h]	Filte	r bed wit	h PAC 0.5 m, $\rho_{p,s}$	[(1/m)·m ³ /g PAC]	$\overline{D_1} - \overline{a_2}$		
	flow	through	the filter $Q = 0.08$				
12	42	2.00	0.77 (62%)	39.61	0.032	0.016	1.99
		3.00	1.15 (62%)		0.048	0.023	2.01
		4.00	1.53 (62%)		0.064	0.031	2.02
24	42	2.00	1.10 (45%)	19.81	0.047	0.022	2.04
		3.00	1.64 (45%)		0.070	0.033	2.07
		4.00	2.19 (45%)		0.093	0.044	2.12
48	42	2.00	1.46 (27%)	9.90	0.055	0.030	1.85
		3.00	2.20 (27%)		0.082	0.045	1.82
		4.00	2.93 (27%)		0.110	0.059	1.83
		Filter be	ed with PAC 0.75				
12	63	3.00	0.676 (77%)	59.42	0.040	0.014	2.86
24	63	3.00	1.15 (62%)	29.71	0.063	0.023	2.67
48	63	3.00	1.82 (39%)	14.85	0.080	0.037	2.16

Adsorption in the PAC filter and the homogeneous flocculator for different filtration times and inflow absorbances

m – PAC mass, A'_{PAC} – average absorbance in the effluent from the PAC filter, $\eta = 100(A_0 - A'_{PAC})/A_0$, D_1 – equivalent sorbent dose, $D_1 = m/(Qt)$, (PAC filter), a_2 – average adsorption for the HP, ($\Gamma = 0.020319 \text{ m}^3/g$, $a_2 \approx \Gamma A'_{PAC}$).

Monitoring changes of absorbance A in time made it possible to make a mass balance of substances identified by UV_{254 nm} absorbance A at different filtration times, PAC doses, and influent absorbances (Table 2). Based on the mass balances and the volume of filtered water in the filtration cycle, the average amounts of organic compounds removed a_1 were determined ($a_1 = (A_0 - A_{PAC})/D_1$)) as well as the equivalent doses D_1 of sorbent (Table 2). The doses D_1 were expressed as a ratio of PAC mass fed to the filter to the water volume produced during the filter cycle.

Table 3

<i>t</i> [h]	<i>m</i> [g]	A ₀ [1/m]	A'_{PAC} [1/m] (η)	D ₁ [g PAC/m ³]	a_1 [(1/m)·m ³ /g PAC]	<i>a</i> ₂	$\frac{D_2}{a_1} = \frac{a_1}{a_1}$
	Filter bed with PAC 0.5 m, $\rho_{p, \text{ sorb}} = 4753.43 \text{ g PAC/m}^3$, flow through the filter $Q = 0.08835 \text{ m}^3/\text{h}$					$[(1/m) \cdot m^3/g PAC]$	$D_1 a_2$
24	21	2.00	1.68 (16%)	9.90	0.032	0.034	0.95
		3.00	2.52 (16%)		0.049	0.051	0.95
		4.00	3.36 (16%)		0.065	0.068	0.95
	42	2.00	1.10 (45%)	19.81	0.047	0.022	2.04
		3.00	1.64 (ŋ=45%)		0.070	0.033	2.07
		4.00	2.19 (45%)		0.093	0.044	2.12
	63	2.00	1.30 (35%)	29.71	0.024	0.026	0.89
		3.00	1.94 (35%)		0.036	0.039	0.91
		4.00	2.59 (35%)		0.048	0.052	0.91

Adsorption in the PAC filter and the homogeneous flocculator for different PAC doses and inflow absorbances

m - PAC mass, A'_{PAC} – average absorbance in the effluent from the PAC filter, $\eta = 100(A_0 - A'_{PAC})/A_0$, D_1 – equivalent sorbent dose, $D_1 = m/(Qt)$, (PAC filter), a_2 – average adsorption for the HP, ($\Gamma = 0.020319$ m³/g PAC, $a_2 \approx \Gamma A'_{PAC}$)



Fig. 9. Absorbance A in the effluent from the PAC filter for different doses of PAC

Parameters of a PAC adsorption model (Table 1) for the homogenous flocculator were used to calculate PAC dose D_2 that would be required to keep a flocculator effluent absorbance equal to the average absorbance A'_{PAC} in the PAC column effluent. The D_2/D_1 ratios are summarized in Table 2. At the PAC dose of 42 g applied to the homogenous flocculator, the dose D_1 doubled the equivalent one in the filter, regardless of a filtration time and an influent absorbance A_0 ; it proves that a PAC sorption capacity is better utilized in the filter bed.

Due to a high adsorption rate in the homogeneous flocculator, adsorption a_2 is almost equal to the one resulting from the adsorption isotherm for the average absorbance A'_{PAC} in the PAC filter effluent ($a_2 \approx \Gamma A'_{PWA}$, $\Gamma = 0.020319$ m³/g PAC, Table 1).

Since in the homogeneous flocculator, $a_2 = (A_0 - A_{PAC})/D_2$ so $D_2/D_1 = a_1/a_2$ (Tables 2 and 3).

The D_2/D_1 ratio represents a measure of PAC utilization in the PAC filter concerning that in the homogeneous flocculator. Therefore, the ratio can be used as a general comparative measure of PAC utilization in various systems with similar average effluent concentrations.

The D_2/D_1 ratios show a strong dependence on the PAC dose applied to the filter bed. The maximum ratios were observed at the PAC dose of 42 g; they ranged from 1.82 to 2.12 (the average of about 2.0) for different filtration times (12, 24, and 48 h) (Table 2). The D_2/D_1 ratios decreased with a PAC filter operation for the filter bed of 0.5 m and 0.75 m and also the adsorption efficiency $\eta (A_0 - A'_{PAC})/A_0$ (Table 2) decreased over time. The D_2/D_1 ratios indicated that adsorption effects in the PAC filter predominated over the same effects in the homogeneous flocculator.

If the PAC dose introduced into the filter is too low (21 g), the equivalent sorbent dose D_1 is about 5% higher than the dose D_2 in the homogenous flocculator, necessary to achieve the same absorbance ($D_1 \approx D_2/0.95 = 1.05D_2$, Table 3). If the PAC dose introduced into the filter is too large (63 g), the equivalent sorbent dose D_1 is only about 11% higher than the dose D_2 for the homogenous flocculator, necessary to achieve the same absorbance ($D_1 \approx D_2/0.9 = 1.11D_2$, Table 3). Hence, the adsorbent utilization in the filter is just slightly higher than that in the homogeneous flocculator, for the PAC doses of 21 g and 63 g; in this case, the filter cannot be a competitive solution over the homogeneous flocculator. A higher PAC filter bed (from 0.5 m to 0.75 m) results in an increase of the D_2/D_1 ratio – e.g., from 2.07 to 2.67 at a 24-hour filter cycle (Table 2).

The observations lead to the conclusion that adsorption on the PAC filter is more efficient than in the homogeneous flocculator. It better utilizes the PAC sorption capacity for the optimal PAC dose introduced into the filter (42 g) ($\rho_{p,\text{sorb}} = 4753.43$ g PAC/m³ of empty filter bed). At the influent absorbance $A_0 = 3 \text{ m}^{-1}$, the slowest increase of the effluent absorbance is observed for the PAC dose of 42 g (Fig. 9); for 21g and 63 g of PAC, the absorbance increases faster proving poorer adsorption.

The experiments showed that utilization of a PAC adsorption capacity in PAC filter (bed height of 0.5 m) is approximately twice as high as in the currently used method with simultaneous PAC adsorption in a homogeneous flocculator. A higher PAC filter layer (increase up to 0.75 m) results in a 2.7 times better utilization of PAC absorption capacity, compared to the homogeneous flocculator.

5. CONCLUSIONS

• The PAC filter better utilizes adsorption capacity of the sorbent comparing to the homogeneous flocculator.

• The tests and simulation calculations showed that if a small organic mass was removed from water, the adsorption capacity in the PAC filter (filter bed 0.5 m and 0.75 m) was 2.0–2.7 times higher than in the flow homogeneous system with PAC dosing.

• The maximum PAC adsorption efficiency was observed at the optimal PAC dose applied to the filter bed (ca. 4753.43 g PAC/m^3).

• The mathematical models of adsorption for the homogeneous flocculator and the PAC filter showed a very good agreement with the measured results.

• The good removal of organic compounds in the PAC filter resulted in the equivalent PAC dose several times lower than for the homogeneous flocculator, at the same average effluent adsorbate concentration.

• An excessive dose of PAC introduced into the filter did not contribute to a higher PAC utilization in this system.

• Simulation calculations showed that the D_2/D_1 dose ratio (for the PAC filter and the homogeneous flocculator, respectively) was ca. 2.0 and remained practically unchanged for the inflow absorbance 2–4 m⁻¹, a filtration time up to 24 h, a sorbent dose of 4753.43 g/m³ and a filter bed of 0.5 m; it started to slowly decrease after 24 h.

• The adsorption efficiency decreased along with a PAC filter operation time. For the PAC dose of 4753.43 g PAC/m³ and the bed height of 0.5 m, the adsorption efficiency was 62-45% and the D_2/D_1 was ca. 2.0.

• For the PAC dose of 4753.43 g PAC/m³ and the bed height of 0.75 m, the adsorption efficiency was 77–39% and the D_2/D_1 decreased from 2.86 to 2.16.

• An increase of a PAC filter height from 0.5 m to 0.75 m resulted in a significant increase of the D_2/D_1 ratio (from 2.07 to 2.67) at a 24-hour filter cycle and a better utilization of a PAC sorption capacity.

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