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Adsorption of Trihalomethanes (THMs) on Activated Carbons**

1. Introduction

Water chlorination is the widely used disinfection method. It is a cheap and efficient and easy to use method, however due to its by-products less and less recommended. Trihalomethanes (THMs) are the main by-products of this method, they are being generated during the reaction of chlorine with natural organic matter, such as fulvic and humic acids, which naturally occur in raw water. The total trihalomethanes (TTHMs) are the sum of four compounds: trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and tribromomethane (TBM). Other authors have reported that the THMs presence in potable water rises the risk of urinary bladder and colon cancer, they also cause reproductive defects [5, 6], and low birth weight, cleft defects, cardiac defects, central nervous system defects [2]. The trihalomethanes concentration in potable water depends on natural organic matter concentration in disinfected water, chlorine dose, pH, temperature and contact time. The THMs formation is a long process, it is why THMs concentration can not be measured just after the disinfection process, but the THMs formation dynamism in time is calculated basing on natural organic matter concentration and other factors.

In the water distribution system, because of the secondary microbiologically contamination risk, disinfected water should have an overdose of the disinfectant. In a case of water disinfection in the food industry, chlorine in water is undesirable due to the bad taste and smell, and it is removed with different methods. Dechlorination could be realized by chemical methods; by adding to water chemical substances to bind chlorine, for instance sodium thiosulfate. The physical

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methods could be applied as well; the most popular is adsorption on activated carbons. During the chemical dechlorination THMs are not being bound, however by removing the overdose of chlorine, the THMs formation process is stopped. Dechlorination on activated carbons removes chlorine and the disinfection by-products as well. The article presents the results of researches on the application activated carbons to minimize the THMs concentration in disinfected water.

2. Materials and Methods

2.1. Activated Carbons Characteristic

Two kinds of activated carbons have been used in the researches: AG-5 and N-C I, both produced by the GRYFSKAND Ltd. in Hajnówka. The basic parameters of the activated carbons porous structure have been determined basing on the densimetric analysis results and on the measurements of the nitrogen vapors adsorption in the liquid nitrogen temperature (77 K) and their desorption. The densimetric analysis has been conducted with the helium and mercury pycnometer. The adsorption analysis has been carried out with the Quantasorb Jr. apparatus by Quantachrome Co. The porous structure parameters of the activated carbons have been presented in the table 1.

Table 1. The Characteristics of the activated carbons porous structure

Activated carbon	AG-5	N-C I
Surface area [m^2/g]	1003	750
Total pores volume [cm^3/g]	1.079	0.862
Macropores volume [cm^3/g]	0.382	0.310
Mezzopores volume [cm^3/g]	0.140	0.131
Micropores volume [cm^3/g]	0.556	0.421

2.2. Activated Carbons Beds and THMs Solutions

The dynamic method has been applied to determine the efficiency of the activated carbons to remove THMs from water. The model filters have been constructed – each of them consists the 35 mm diameter cylinder and a precisely dosed amount of an activated carbon (50 g). For the AG-5 activated carbon the bed height has been 140 mm, for the NC-I carbon – 130 mm). The water solutions of THMs have been passed through the beds with the peristaltic pump PP1B-05A by the Zalimp company. The following flow rates have been applied: 2; 3; 6; 9; 11 and 15 m/h. The THMs solutions have been prepared from redistilled water and the THMs chromatography standards by the Ultra Scientific (concentration 5000 μg/ml).

2.3. Methodology of THMs Analysis

The THMs concentration has been analyzed with the gas chromatograph with a mass spectrometer detector (GC-MS) Trace Ultra and DSQ-II by the Thermo, with helium as carrier gas. The Rxi™-1ms capillary column by Restek has been used (100% polydimethylsiloxane; film thickness 0.25 μm; column length 30 m; column diameter 0.25 mm).

The THMs have been extracted with the Head-Space method and determined on GS-MS due to the Polish Standard PN-EN ISO 10301. The samples have been incubated in 90°C for 40 minutes, the column has been heated from 31°C (0 min) to 200°C (0 min) with the temperature rate of 16°C/min.

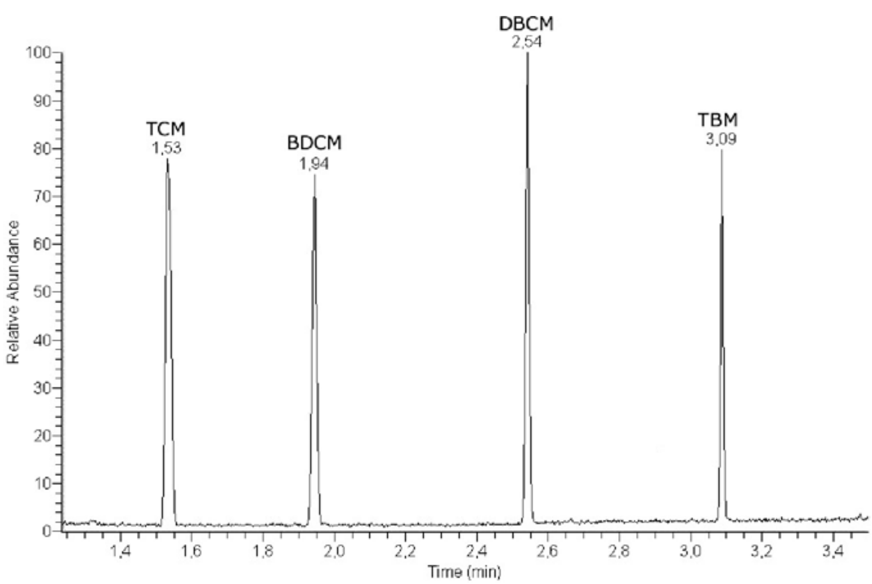

Fig. 1. THMs standard solution chromatogram

The figure 1 presents the chromatogram of the chromatography standard solution used in the analyses.

3. Results and Discussion

The results of THMs removal on activated carbons have been presented in tables 2 and 3 and shown on the figures 2–7.

Table 2. Activated carbon AG-5
– trihalomethanes removal efficiency

Flow rate [ml/min]	THMs concentration in filtrate [µg/dm³]					THMs adsorption [µg/g]				
	TCM	BDCM	DBCM	TBM	TTHM	TCM	BDCM	DBCM	TBM	TTHM
Initial THMs concentration [µg/dm³]	21.05	13.21	14.97	9.17	58.40	21.05	13.21	14.97	9.17	58.40
15	0.12	0.01	0.04	0.01	0.18	0.419	0.264	0.299	0.183	1.164
11	0.08	0.01	0.02	0.00	0.11	0.419	0.264	0.299	0.183	1.166
9	0.06	0.02	0.02	0.00	0.09	0.420	0.264	0.299	0.183	1.166
6	0.02	0.01	0.00	0.02	0.05	0.421	0.264	0.299	0.183	1.167
3	0.01	0.02	0.01	0.04	0.07	0.421	0.264	0.299	0.183	1.167
2	0.00	0.00	0.01	0.02	0.04	0.421	0.264	0.299	0.183	1.167
Initial THMs concentration [µg/dm³]	30.92	38.47	46.71	50.60	166.70	30.92	38.47	46.71	50.60	166.70
15	0.25	0.15	0.22	0.36	0.98	0.613	0.766	0.930	1.005	3.314
11	0.14	0.03	0.09	0.15	0.41	0.616	0.769	0.932	1.009	3.326
9	0.06	0.00	0.00	0.07	0.12	0.617	0.769	0.934	1.011	3.332
6	0.05	0.05	0.01	0.00	0.11	0.617	0.768	0.934	1.012	3.332
3	0.03	0.00	0.03	0.00	0.06	0.618	0.769	0.934	1.012	3.333
2	0.01	0.00	0.03	0.00	0.04	0.618	0.769	0.934	1.012	3.333
Initial THMs concentration [µg/dm³]	49.15	63.57	78.29	89.48	280.50	49.15	63.57	78.29	89.48	280.50
15	0.38	0.37	0.39	0.55	1.69	0.975	1.264	1.558	1.779	5.576
11	0.26	0.19	0.20	0.27	0.92	0.978	1.268	1.562	1.784	5.592
9	0.10	0.12	0.11	0.14	0.46	0.981	1.269	1.564	1.787	5.601
6	0.07	0.06	0.07	0.09	0.30	0.982	1.270	1.564	1.788	5.604
3	0.01	0.03	0.01	0.06	0.11	0.983	1.271	1.566	1.788	5.608
2	0.02	0.00	0.04	0.00	0.07	0.983	1.271	1.565	1.790	5.609

Table 3. Activated carbon NC-I – trihalomethanes removal efficiency

Flow rate [m/h]	THMs concentration in filtrate [μg/dm³]					THMs adsorption [μg/g]				
	TCM	BDCM	DBCM	TBM	TTHM	TCM	BDCM	DBCM	TBM	TTHM
Initial THMs concentration [μg/dm³]	10.83	8.16	7.28	8.73	35.00	10.83	8.16	7.28	8.73	35.00
15	5.36	3.29	3.32	3.27	15.24	0.109	0.097	0.079	0.109	0.395
11	4.11	2.63	2.34	2.84	11.92	0.134	0.111	0.099	0.118	0.462
9	3.89	2.49	2.48	3.17	12.03	0.139	0.113	0.096	0.111	0.459
6	3.19	1.73	1.84	2.09	8.85	0.153	0.129	0.109	0.133	0.523
3	1.87	1.07	1.19	1.28	5.41	0.179	0.142	0.122	0.149	0.592
2	0.01	0.30	0.30	0.45	1.07	0.216	0.157	0.140	0.166	0.679
Initial THMs concentration [μg/dm³]	21.05	13.21	14.97	9.17	58.40	21.05	13.21	14.97	9.17	58.40
15	9.62	3.80	4.54	3.00	20.96	0.229	0.188	0.209	0.123	0.749
11	7.43	2.92	3.69	2.55	16.59	0.272	0.206	0.226	0.132	0.836
9	7.82	3.01	3.34	2.76	16.92	0.265	0.204	0.233	0.128	0.830
6	6.69	2.67	3.04	2.12	14.53	0.287	0.211	0.239	0.141	0.877
3	3.19	0.85	1.18	0.86	6.08	0.357	0.247	0.276	0.166	1.046
2	1.47	0.26	0.43	0.44	2.61	0.392	0.259	0.291	0.175	1.116
Initial THMs concentration [μg/dm³]	30.92	38.47	46.71	50.60	166.70	30.92	38.47	46.71	50.60	166.70
15	14.15	14.56	18.35	20.16	67.22	0.335	0.478	0.567	0.609	1.990
11	12.49	13.98	14.06	17.89	58.42	0.369	0.490	0.653	0.654	2.166
9	10.70	12.19	0.00	16.84	39.73	0.404	0.526	0.934	0.675	2.539
6	9.61	10.60	12.39	12.66	45.25	0.426	0.557	0.686	0.759	2.429
3	5.97	4.69	5.90	8.02	24.58	0.499	0.676	0.816	0.852	2.842
2	2.19	1.61	2.30	2.37	8.47	0.575	0.737	0.888	0.965	3.165
Initial THMs concentration [μg/dm³]	49.15	63.57	78.29	89.48	280.50	49.15	63.57	78.29	89.48	280.50
15	26.40	32.28	39.16	43.53	141.37	0.455	0.626	0.783	0.919	2.783
11	24.37	28.40	34.09	38.39	125.25	0.496	0.703	0.884	1.022	3.105
9	21.72	26.79	30.91	35.31	114.72	0.549	0.736	0.948	1.083	3.316
6	18.03	21.07	25.25	28.61	92.96	0.622	0.850	1.061	1.217	3.751
3	7.24	7.84	9.54	11.62	36.23	0.838	1.115	1.375	1.557	4.885
2	5.59	3.66	5.06	6.60	20.91	0.871	1.198	1.465	1.658	5.192

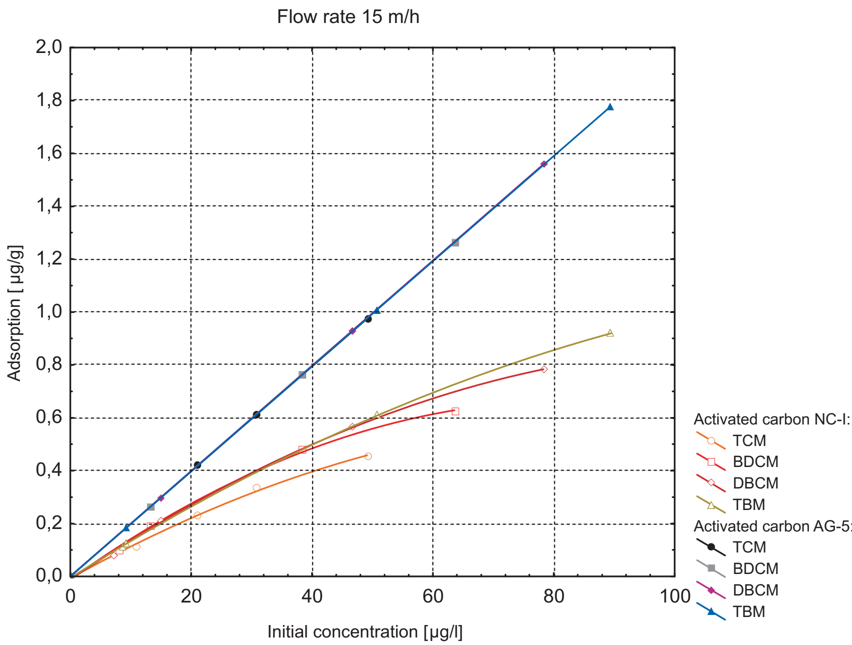

Fig. 2. Trihalomethanes adsorption on activated carbon NC-I and AG-5 – flow rate 15 m/h

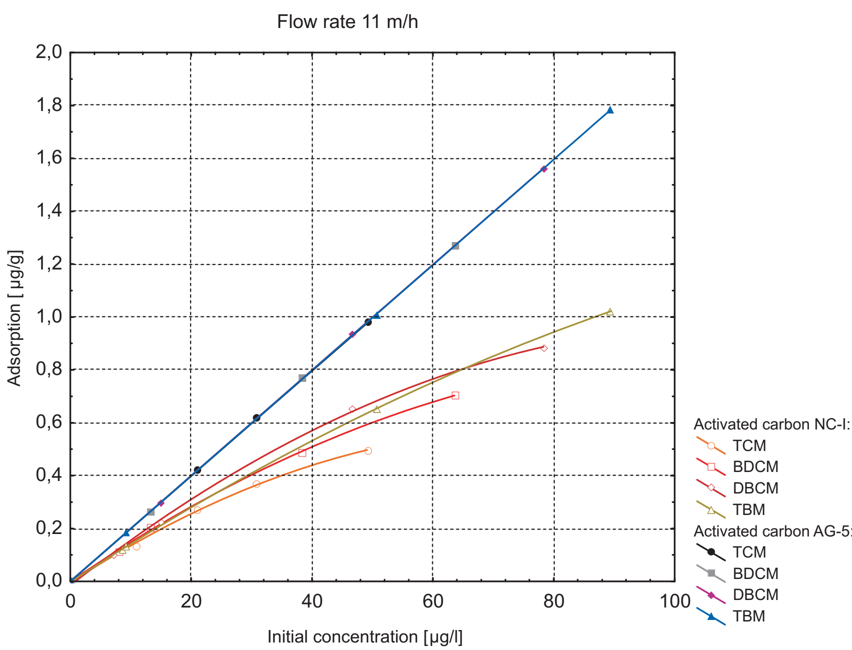

Fig. 3. Trihalomethanes adsorption on activated carbon NC-I and AG-5 – flow rate 11 m/h

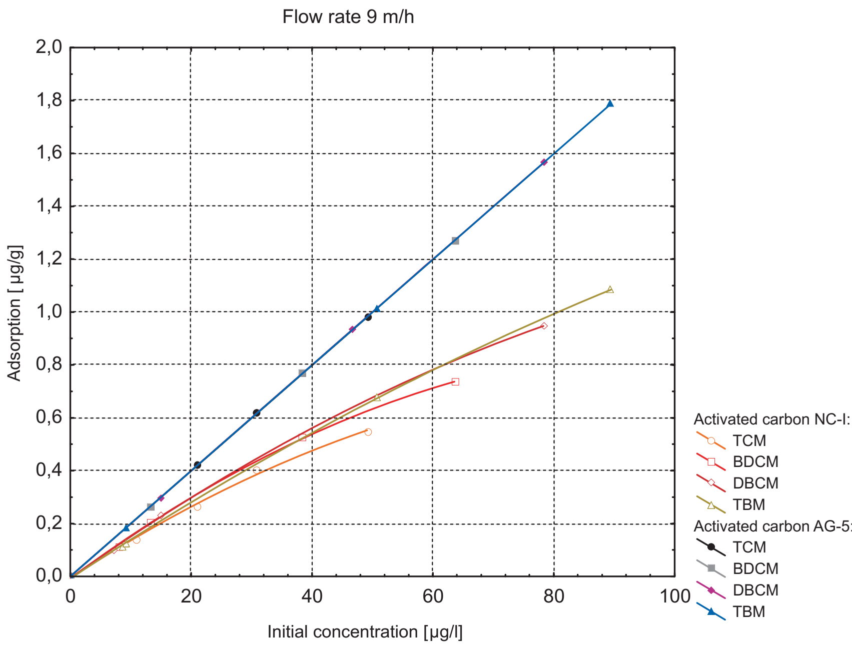

Fig. 4. Trihalomethanes adsorption on activated carbon NC-I and AG-5 – flow rate 9 m/h

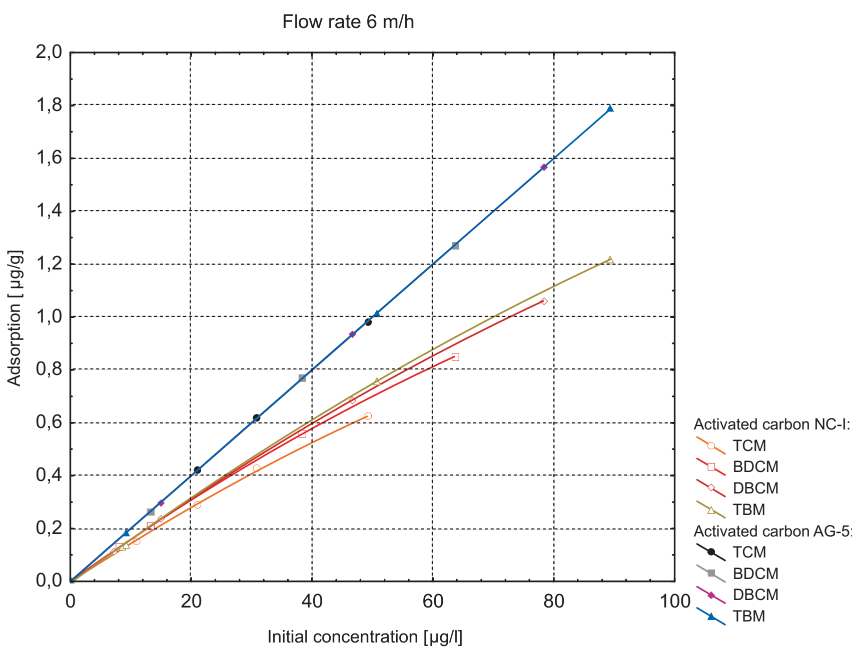

Fig. 5. Trihalomethanes adsorption on activated carbon NC-I and AG-5 – flow rate 6 m/h

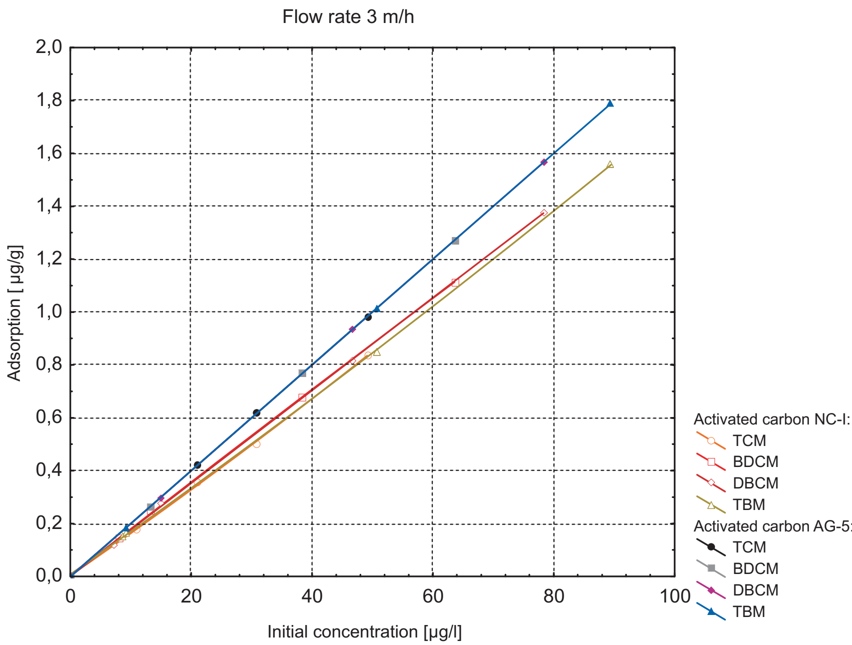

Fig. 6. Trihalomethanes adsorption on activated carbon NC-I and AG-5 – flow rate 3 m/h

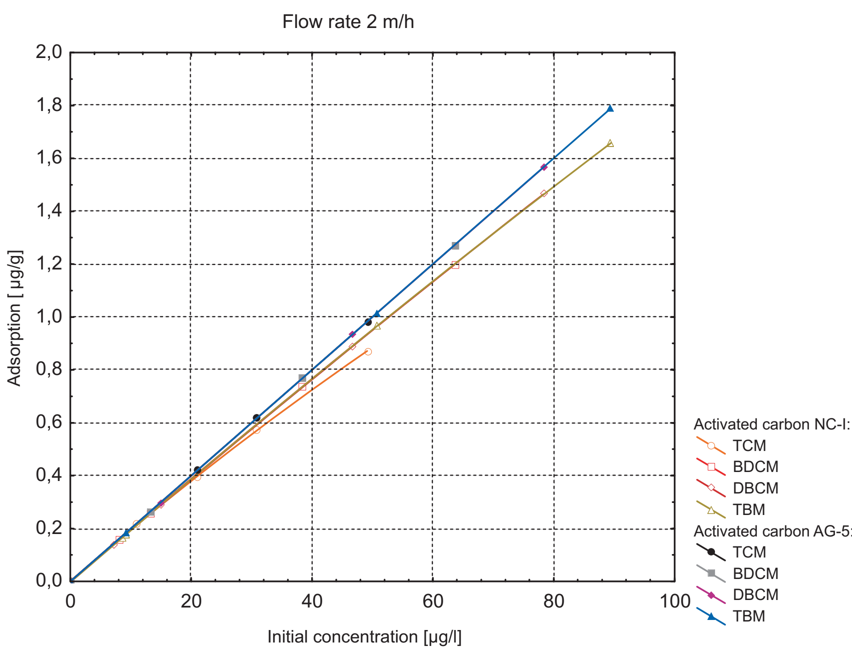

Fig. 7. Trihalomethanes adsorption on activated carbon NC-I and AG-5 – flow rate 2 m/h

The AG-5 activated carbon, which has the higher surface area and pores volume, has shown its higher efficiency to remove THMs from water. AG-5 has reached the 99% level of efficiency for all tested THMs initial concentrations and for all flow rates. For the NC-I activated carbon the strong relation between the THMs removal and the flow rate has been observed. For the lowest rate 2 m/h – the THMs removal efficiency was between 96–99%, for the highest rate 15 m/h – the efficiency was 50–64% and generally it was increasing with an increase of the initial THMs concentration in water. In the researches different TTHMs concentrations have been analyzed – starting from very low concentrations, below the Polish standard for potable water, which is 100 μg/dm^3 (*Rozporządzenie Ministra Zdrowia z dnia 29 marca 2007 r. w sprawie jakości wody przeznaczonej do spożycia przez ludzi*. Dz.U. Nr 61, poz. 417), to the very high ones, higher than 280 μg/dm^3 – much above the standard. For AG-5 the TTHMs concentrations in all filtrates have been much lower than the Polish standard – the highest observed TTHMs concentration has been 1.69 μg/dm^3. For NC-I the Polish standards TTHMs level has been exceeded only for the highest TTHMs initial concentration 280.50 μg/dm^3, for the flow rates: 9, 11 and 15 m/h.

For the AG-5 activated carbon is difficult to observe a difference in an adsorption of separate THMs (Figs 2–7). It is caused by its very big surface area, and the easy access of THMs to it. For highest flow rates of THMs through the NC-I bed (6–15 m/h) the significant trend could be observed (Figs 2–5); compounds with the higher bromine ions level have been better adsorbed than the THMs with the higher chlorine ions level. Regarding the separate THMs; TBM has been most-efficiently adsorbed, than DBCM, BDCM, the lowest efficiency has been observed for TCM. These differences have been most distinct for the high flow rates 11–15 m/h (Figs 2–3). For lower flow rates (and higher contact times) these differences have been smaller (Figs 4–5). For flow rates 2 and 3 m/h the separate THMs adsorption results have been very similar, however worse than results for the activated carbon AG-5 (Figs 6–7).

4. Conclusions

The researches on the efficiency of activated carbons to remove THMs from water have proved their high effectiveness and their potential to minimize the chlorine disinfection by-products. The very high efficiency of THMs adsorption has been observed for different flow rates (2 to 15 m/h) of the solutions with different TTHMs concentrations (34.50 to 280.50 μg/dm^3). The activated carbon AG-5, which has the higher surface area and pores volume than the NC-I, has shown the higher efficiency in THMs removal from water. Out of four THMs, TCM has been best adsorbed, than DBCM, than BDCM, and TCM has been adsorbed on the lowest level. These differences in adsorption effectiveness of separate THMs were higher for higher flow rates.

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