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The effect of the water pre-treatment method on the adsorption process in a surface water treatment system

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ABSTRACT

This article presents the results of research on the effect of the water pretreatment method on the adsorption process in the surface water treatment system. In the first, water undergoing adsorption was pre-treated during coagulation, sedimentation and filtration through a sand bed. In the second one, in place of filtration, water was subjected to ultrafiltration. The study was conducted on partially depleted and on fresh active carbon. Thanks to the replacement of the carbon during the study period, it was possible to evaluate the effect of the pre-treatment method on the adsorption process at different stages in the cycle and to also evaluate bed bioactivity. These studies have shown, that a lower contamination level of water undergoing adsorption allowed for obtaining slightly higher effectiveness in removing organic substances during adsorption on beds with partially depleted adsorption potential. In the adsorption process, mainly colored and UV-absorbing organic substances were removed. It was also shown that the effectiveness in removing dissolved organic substances, irrespective of the quality of water undergoing adsorption, was directly proportional to the reduction in watercolor and UV absorbance. The active carbon bed bioactivity was observed only in the system supplied by water after sand filtration characterized by a higher concentration of biodegradable dissolvent organic carbon. Studies have shown a reduction in the number of microorganisms in water reaching the beds delays the development of microorganisms on the bed surface, and consequently delays biodegradation. It has also been shown that the level of water pre-treatment has no effect on adsorption effectiveness on fresh active carbon.

Keywords: Adsorption process; Organic substances; Microcontaminants; Biogenic substances; Biodegradation

1. Introduction

The increase in water pollution levels, especially for surface water, contributes to the need to expand water treatment systems. Most often adsorption is included in water treatment systems for removing dissolved organic substances. The most popular absorbent used for treating water intended for consumption is granulated or formed activated carbon [1,2]. Activated carbon has long been used in order to decrease the concentrations of heavy metals [3] and micro contaminants such as pesticides [4,5] or pharmaceuticals [6,7]. Such large effectiveness of this adsorption material and its relatively easy operation contributed to the development of technologies for the production of activated carbon. Currently, various modifications of activated carbon are available on the market. An example of this is impregnated carbons [8] for example, with nanosilver, which limits the development of a biofilm and ensures water disinfection. These modifications also consist of shaping the surface and pore size inside the carbon structure, which is to ensure a greater affinity for individual contaminant groups [9,10].

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Increasing adsorption effectiveness is achieved by the use of ozonation prior to adsorption [11], however, this improvement in the effectiveness is small and significant only in the context of considering the length of the adsorption cycle. Extending the time between subsequent regenerations is ensured by the biofilm, which develops on the activated carbon surface [12,13], which allows for not only the biodegradation of organic substances but also the assimilation of inorganic food substrates [14,15].

As numerous studies have shown, the effectiveness in removing organic substances depends above all on the water-absorbent contact time [16], water temperature [17], the water pH value [18], and also on the composition of the treated water [17,19], including the properties of the present organic substances. Water before adsorption should have low turbidity because the suspended particles blocked active centers on the active carbon. The efficiency of removal particle pollutants increased with their higher concentration. There is no information about the influence of pre-treatment water quality on adsorption efficiency and granular active carbon (GAC) bioactivity [20].

Therefore it was justified to conduct studies concerning the impact of the quality of water undergoing adsorption (i.e. the filtration method) on the course of this process and the bed bioactivity.

2. Subject and methods of study

The research was carried out in two pilot-scale surface water treatment systems, which included coagulation, sedimentation, filtration, adsorption and disinfection steps. Both systems worked inflow conditions with a capacity of 1 m^3/h. Studies were performed in two adsorption beds with a throughput of 1 m^3/h each. In the first, water undergoing adsorption was pre-treated during coagulation, sedimentation and filtration through a sand bed. In the second one, in place of filtration, water was subjected to ultrafiltration. The difference in the pre-treatment method included the filtration step. The main goal of the research was a comparison of adsorption efficiency after sand filtration or ultrafiltration.

Operating parameters of sand filters and ultrafiltration modules are shown in Table 1.

The objects of study were water samples taken after filtration (SFO), ultrafiltration (UFP) and at the outflow from the adsorption columns in the first and second systems respectively (GAC1, GAC2). Samples were collected once a week from April to July. More frequent water sampling took place in the period of activated carbon exchange, that is, from May 14. Thus, the study was conducted on partially depleted active carbon (April–May, after 12 months of operation) and fresh carbon (the remaining study period). Thanks to the replacement of the carbon during the study period, it was possible to evaluate the effect of the filtration method on the adsorption process at different stages in the cycle and to also evaluate bed bioactivity.

In both systems, the adsorption process was carried out on an adsorption bed of formed activated carbon. The adsorption column had a diameter of 0.5 m, with a bed height of 1.5 m, which resulted in a water flow speed through the adsorption bed of 5 m/h, with the water bed contact time of about 20 min. Due to the need to maintain continuous system operation, these parameters may have undergone slight fluctuations, however, no more than 2%.

In the water samples, the following were determined: pH, temperature, concentrations of dissolved oxygen, total organic carbon (TOC), dissolved organic carbon (DOC), and biodegradable organic carbon (BDOC), nitrate and ammonia nitrogen, phosphates, turbidity, color at 340 and 410 nm, and UV_{254} and UV_{272} absorbance. In addition, the total number of psychrophilic and mesophilic microorganisms (TNMpsych, TNMmeso) as well as the total number of cells (TCC) were determined.

All physical and chemical indicators were determined in accordance with Polish Norms. Biodegradable DOC was determined based on the decrease in DOC in a sample incubated with microorganisms typical for the given environment. The TCC was determined by the use of a flow cytometer BD6 with DNA dying. For this purpose SYBR Green dye was used.

3. Results and discussion

The water undergoing adsorption was characterized by a low variability in quality during the study period, as evidenced by the values of individual parameters (Table 2).

Differences in the composition of water undergoing adsorption concerned mainly turbidity and the number of microorganisms (TNMpsych, TNMmeso) and cells (TCC).

Table 1
Parameters of rapid filtration and ultrafiltration processes

Parameter	Filtration	Ultrafiltration
Filtration surface, m^2	0.2	102
Throughput, m^3/h	1	1*
Filtration speed, m/h	5	–
Pressure, MPa	0.1	0.08**
Frequency of rinsing,	1 d	30 min.; additionally the membranes were chemically cleaned with sodium hypochlorite and citric acid at a frequency of once a week
Pore size	0.3–1.5 mm***	30 kDa
Material	Sand	Poly(vinylidene fluoride)

*applies to permeate, **transmembrane pressure, ***grain range;

Table 2
Ranges of water quality indicator values before and after adsorption

No	Parameter	Unit	System 1						System 2					
			SFO (before adsorption)			GAC1 (after adsorption)			UFP (before adsorption)			GAC2 (after adsorption)		
			min.	max.	av.	min.	max.	av.	min.	max.	av.	min.	max.	av.
1	Turbidity	NTU	0.01	0.37	0.11	0.02	0.19	0.08	0.01	0.13	0.11	0.01	0.29	0.07
2	pH	–	7.25	7.82	7.56	7.39	8.55	7.65	7.40	7.93	7.68	7.49	8.62	7.74
3	Dissolved oxygen	gO_2/m^3	6.56	9.97	7.95	3.02	9.14	6.41	7.84	11.04	9.09	4.15	9.42	7.04
4	DOC	gC/m^3	2.20	3.03	2.65	0.09	2.66	1.24	2.43	3.39	2.81	0.09	2.71	1.21
5	TOC	gC/m^3	2.35	4.42	2.78	0.21	4.40	1.71	2.39	3.70	2.91	0.12	3.46	1.63
6	BDOC	gC/m^3	0.08	0.68	0.31	0.04	1.18	0.31	0.23	0.86	0.43	0.02	0.65	0.26
7	UV_{254}	1/m	5.24	7.07	5.85	0.13	4.87	2.08	5.89	7.78	6.43	0.10	5.32	2.16
8	UV_{272}	1/m	4.27	5.74	4.76	0.09	3.83	1.64	4.80	6.36	5.25	0.08	4.31	1.72
9	$Color_{340}$	gPt/m^3	4.61	6.26	5.01	0.04	3.32	1.43	4.87	6.77	5.43	0.01	3.82	1.51
10	$Color_{410}$	gPt/m^3	5.88	8.81	7.12	0.00	3.88	1.69	5.72	9.27	7.76	0.00	4.64	1.81
11	Nitrates	gNO_3^-/m^3	1.72	12.30	6.52	2.54	12.40	6.44	1.27	12.40	6.21	2.14	20.10	6.66
12	Phosphates	gPO_4^{-3}/m^3	0.01	0.05	0.03	0.01	1.13	0.13	0.01	0.04	0.03	0.01	0.49	0.09
13	Ammonium ion	gNH_4^+/m^3	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.07	0.05	0.05	0.05	0.05
14	TNMpsych	cfu/mL	22	980	236	18	5,500	582	23	660	237	14	5,200	1,002
15	TNMmeso	cfu/mL	1	230	54	1	720	137	18	270	88	1	4,800	639
16	TCC	cell/mL	841	19,625	9,291	783	11,545	4,088	66	7,722	953	64	2,794	971

Water after ultrafiltration was characterized by lower values of these parameters. The parameters caused by the nature of the ultrafiltration process and the ultrafiltration membrane that was used. Additionally in the context of evaluating the adsorption beds bioactivity, it is significant that in the second system, the water reaching adsorption beds had higher oxygen saturation. Therefore oxygen was not a factor limiting the growth of microorganisms on the bed surface.

However, no difference was found in the inorganic substance content in water which was supplied to both adsorption beds.

The nature of organic substances in the water feeding the adsorption beds of both systems was different. In water supplying the first system, a larger amount of DOC, BDOC was found, this being a higher organic food substrate content. On the other hand, water supplying the second system was characterized by larger values of UV absorption, which corresponds to the presence of chlorinated disinfection by-product precursors [21,22], and higher color intensity at 340 nm, which testifies to the presence of humic substances.

Although the differences in the composition of the water supplying both systems were small, they had an impact on the adsorption process, especially when the process was conducted on partially depleted beds. This is shown by the higher effectiveness in removing DOC in the second analyzed system (Fig. 1). The maximum difference in the efficiency achieved was 19%, which may already significantly affect sufficient water treatment in the event of a temporary deterioration of input water quality. This difference was not found after bed replacement, where, irrespective of the input water quality, 100% of the DOC was adsorbed.

The effectiveness in removing organic substances in both systems was directly proportional to the effectiveness in reducing color intensity (at both analyzed wavelengths) and absorption UV_{254} and UV_{272} (Table 3).

The correlations that were found indicate the removal of mainly colored organic substances that absorb UV radiation. For all of these indicators, greater reduction effectiveness was found in the second system despite lower contamination levels of water undergoing adsorption, which is the opposite of what was found in other studies [23].

During the study period with partially depleted adsorption beds, greater effectiveness in reducing phosphate concentration was found in the second analyzed system. On the other hand, during the first month of fresh bed operation, phosphate flushing was found, as evidenced by the multiple increases in 8 this parameter with respect to its amount in water supplying the beds. The maximum phosphate content amounted to 1.12 and 0.49 gPO_4/m in the first and second systems respectively. The increase in phosphate ion content decreased along with the duration of bed operation time. However during the study period a state of decrease in the parameter was not noted, which occurred before the replacement of adsorption beds.

During the entire study period, there were no changes found in the ammonia ion content in post-adsorption water in both systems (Table 2). On the other hand, nitrate concentrations increased in the majority of water samples from both systems. This increase was larger in the first system, and in the second system it was smaller than the analysis error. The increase in nitrate concentration in the first system could indicate the presence of nitrification, which is confirmed by a decrease in the dissolved oxygen content.

Fig. 1. Variability of DOC removal efficiency during adsorption.

Table 3
Linear correlations between the dissolved organic substance removal effectiveness and color and UV absorbance

System 1		System 2	
Correlation equation	*R*	Correlation equation	*R*
$\eta DOC = 1.2400\eta Color_{340} - 32.032$	0.98	$\eta DOC = 1.2234\eta Color_{340} - 27.918$	0.97
$\eta DOC = 1.4429\eta Color_{410} - 52.002$	0.95	$\eta DOC = 1.2287\eta Color_{410} - 32.427$	0.89
$\eta DOC = 1.0668\eta UV_{254} - 13.641$	0.99	$\eta DOC = 1.0104\eta UV_{254} - 8.397$	0.96
$\eta DOC = 1.0899\eta UV_{272} - 16.224$	0.99	$\eta DOC = 1.0173\eta UV_{272} - 9.7026$	0.95

However, this is contradicted by a lack of change in ammonia ion concentrations and an increase in nitrates after carbon replacement, that is, during a period of no bed bioactivity. The lack of nitrification is also supported by very varied decreases in dissolved oxygen during the entire study period (Fig. 2a), which can in no way be correlated with changes in nitrate ions (Fig. 2b).

Similarly, changes in the content of biodegradable DOC did not have one direction throughout the study period. In both systems, BDOC was adsorbed by fresh carbon, yet in the earlier and later study periods its content increased in the majority of samples from the second system and had no clear direction of change in the first system. Such variability in BDOC may indicate bed bioactivity in the first system, and limited bed bioactivity in the second system (Fig. 3).

Generally the variability in the food substrate content and dissolved oxygen may indicate the presence of microorganisms of the surface of both beds, yet higher activity was exhibited by the bed supplied by the water of worse quality and lower organic food substrate content. (Table 2).

Microorganisms were flushed out from the fresh bed in the second system, which caused multiple increases in the number of psychrophilic organisms and the total cell count (Fig. 4). This indicates a possibility of colonization of beds with microorganisms and film development on the carbon surface. In the first system, such an increase was found only in three samples after bed replacement, and in the remainder of samples a decrease in the number of microorganisms and cells was found [24]. The different variations in the numbers of microorganisms and cells indicate a different mechanism of changes taking place during adsorption. Probably in the first system, the bed bioactivity had a greater impact on the process. Inhibition of microorganism flushing from this bed may also indicate the formation of a biofilm on the bed surface [25].

As a result of the increase in the number of microorganisms and cells and the phosphate concentration the water quality deteriorated, with respect to microbiological contamination in the system supplied by water after ultrafiltration, this relationship was not found for the first system, where water after adsorption was characterized by a lower number of microorganisms. Despite the reduction in the number of microorganisms the values of these indicators were larger than those found in the second system (Fig. 5), due to their accumulation on the adsorption bed surface in the first system.

This was a consequence of the small number of microorganisms and cells in water supplying the second system. This means that the effective elimination of microorganisms from the water before adsorption inhibits bed colonization and delays the biodegradation process [26].

A probable consequence of this was a larger dissolved oxygen concentration in water after adsorption, as it was not consumed by microorganisms populating the bed.

The larger effectiveness in removing organic substances before bed replacement in the second system resulted in an increase in the differences in the content of total and DOC between post-adsorption water in both systems (Fig.1). As colored, UV absorbing substances dominated among organic substances, there was a decrease in the differences in the

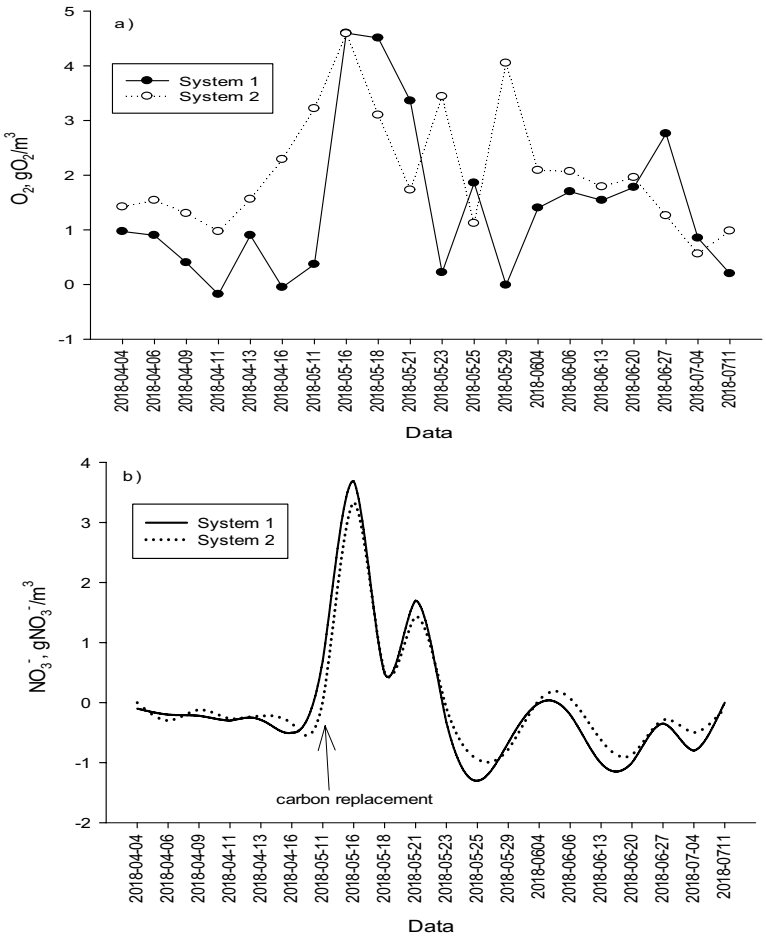

Fig. 2. Effectiveness of changes in (a) dissolved oxygen and (b) nitrate ions concentration in both systems.

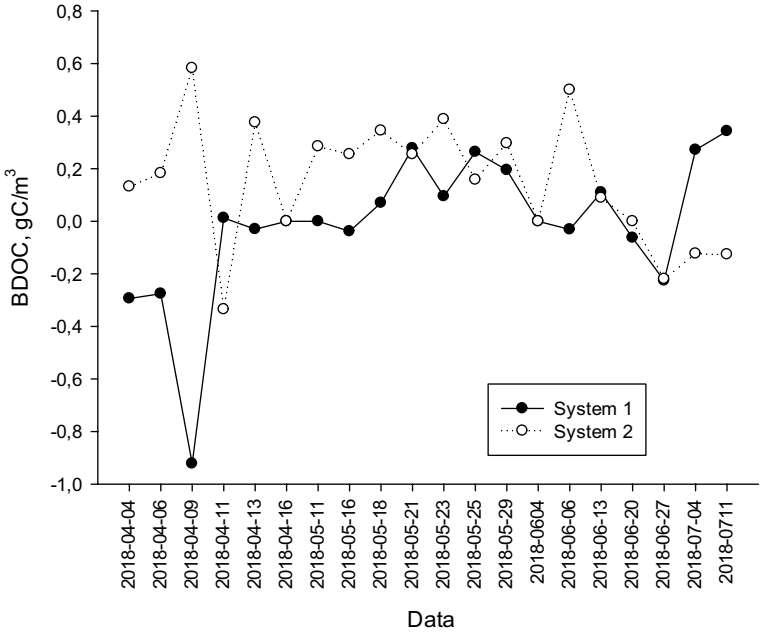

Fig. 3. Variability of BDOC in both systems.

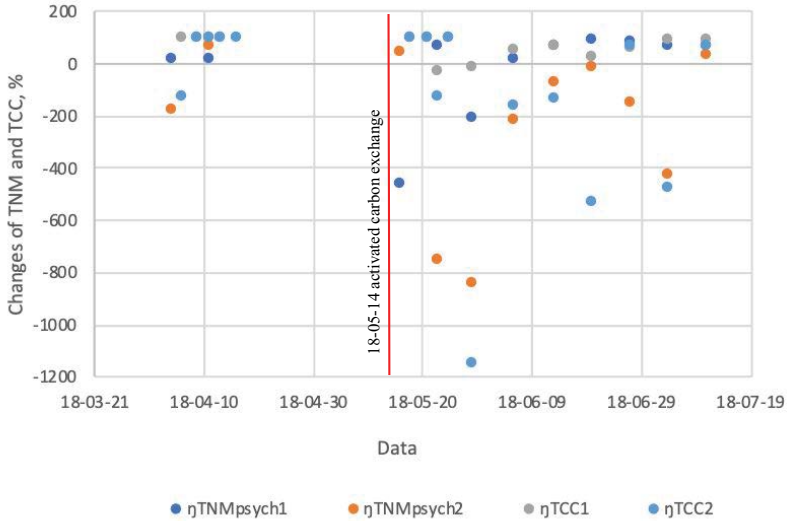

Fig. 4. Effectiveness of changes in the number of microorganisms and cells during the adsorption process.

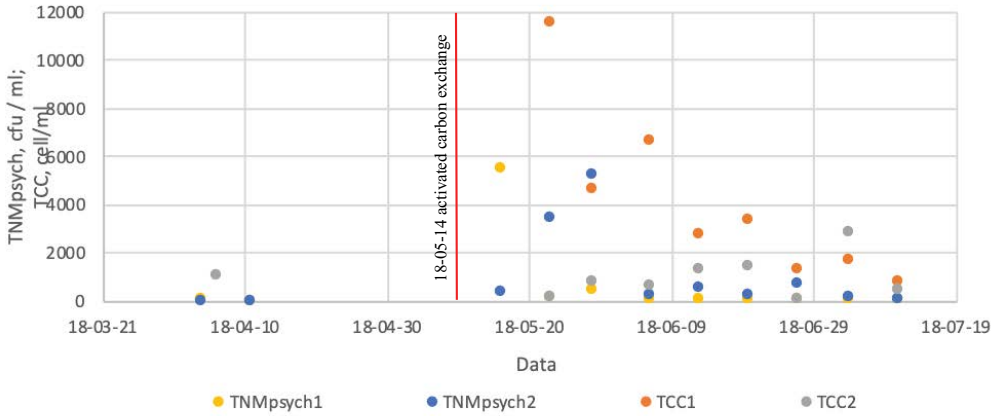

Fig. 5. Variability of the total number of psychrophilic bacteria and the total cell count in water after the adsorption process.

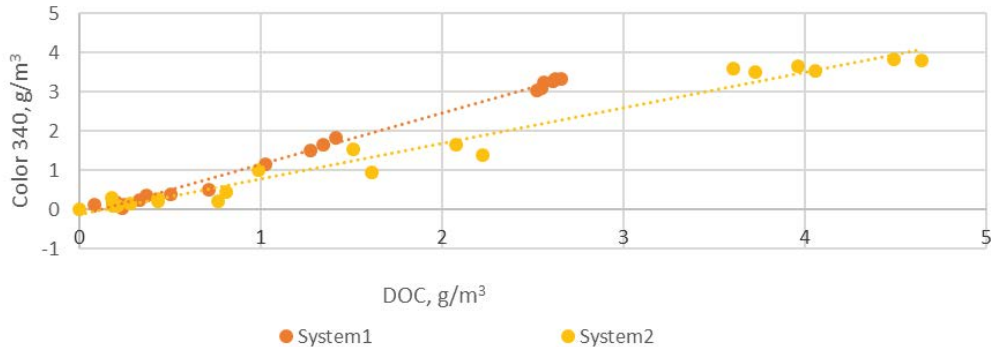

Fig. 6. Relationship between DOC values and color at 340 nm in water after the adsorption process.

values of UV absorbance and color between water from the two analyzed systems.

A consequence of removing colored substances was the relationship that was found between DOC values and color at 340 nm in water after adsorption in both systems (Fig. 6). This means that regardless of the pre-treatment method, the adsorption process caused a change in the number of organic substances, but did not change their form or structure.

The bed bioactivity in the first system caused the BDOC concentration before and after adsorption was higher in the first system.

4. Conclusions

- A lower contamination level of water undergoing adsorption, after ultrafiltration pre-treatment, allowed for obtaining slightly higher effectiveness in removing organic substances during adsorption on beds with partially depleted adsorption potential. The efficiency of organic substance removal was similar after the replacement of adsorption beds.
- Mainly colored and UV-absorbing organic substances were removed during the adsorption process in both systems and both parts of research (before and after the replacement of adsorption beds).
- The effectiveness in removing dissolved organic substances, irrespective of the quality of water undergoing adsorption, was directly proportional to the reduction in watercolor and UV absorbance.
- Bed bioactivity was observed only in the system supplied with water with a higher biodegradable organic fraction content.
- Limiting the number of microorganisms in water reaching the beds (their more effective elimination during the ultrafiltration process) delays the development of microorganisms on the bed surface, and consequently delays biodegradation.
- The level of water pre-treatment (efficiency of filtration steps) has no effect on adsorption effectiveness on fresh activated carbon.

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