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Comparison of Ultrasound-Assisted Sorption under Different Conditions of the Process

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The study presents the results of the research which aimed to estimate the opportunities for increasing the efficiency of humic substances (HS) adsorption on active carbon (AC). The modification was carried out through exposure of HS solution to 20 kHz ultrasonic field (amplitude 114 μm, time 1 min.). The processes of sonication of the solution caused disintegration of high-molecular compounds into compounds of lower mass (more easily adsorbed and biodegraded), and creation of highly-oxidizing radicals. The research was conducted in four systems: sorption, sono-sorption, biosorption and sono-biosorption. A solution of the humic substances was provided by a commercial formulation of humic acid salt concentration of 20 mg/L. The substrate was sonicated partially, each time by 0,25 L. The research was conducted in filtration columns (diameter 25 x 10^{-2} m), packed with AC (ROW 08 Supra), up to the level of 0.5 m. The process of HS biodegradation, which was conducted on biological filters with AC layer inoculated with suspension of microorganisms and left for 60 days in order to be colonized (oxygen conditions and access to nutrients was ensured). The biological filter was created based on microorganisms from biopreparation and activated sludge. Analysis of efficiency of these processes was verified by parameters such as: DOC, absorption at UV_{254}, oxygen consumption, colour, pH. The bacterial count on three levels of the bed and in the eluate from columns was also measured. In the solutions where biodegradation occurred the amount of the dissolved oxygen was measured in order to evaluate the EMS index (which defines intensity of sorption and biosorption processes). The results obtained in the study demonstrated that carbon filters colonized by microflora operated 100 % longer. Furthermore, no significant improvement in the process was observed after using the method of sorption combined with exposure to ultrasounds. DOC analysis revealed that after the same flow time, through the column, depletion of HS is higher in beds sorbing HS solution modified with ultrasounds. Advantageous influence of ultrasound modification was confirmed in the effects of work of the column with biopreparation.

1. Introduction

One of the classical methods of removal of organic and inorganic compounds during water treatment is sorption process (Lavecchia et al., 2006). The most popular sorbent used for this purpose is activated carbon (AC), which is considered as a relatively cheap, non-selective with respect to adsorbates and susceptible to regeneration and modification. The porous structure of carbon and its rough surface provide a perfect base for colonization of AC molecules by microorganisms. The phenomenon of growth of microorganisms in the bed, with particular focus on bacteria, was extensively documented, Papciak (2004). The basic precondition for colonization of a filter is constant supply of oxygen and contaminants, which perform the role of nutrients. After several-month operation of the carbon filter, a biofilm can be observed on its surface. Microorganisms take part in biodegradation of the contaminants adsorbed inside AC pores, thus elongating the bed's life and providing a natural barrier protecting from development of pathogenic microflora (competing for substrates). Humic substances (HS) are high molecular compounds which "lock" AC pores. For this reason, the efficiency of HS adsorption is low. On the other hand, these substances are known to exhibit strong sorption properties with respect to other organic compounds (pesticides, PAH) and heavy metals. The aggregates that are created in this manner are highly toxic, mutagenic and carcinogenic. The process of oxidation and disinfection of water with higher content of HS

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leads to creation of oxidation/disinfection by-products during chlorination of water, such as trihalomethans (THMs). Kusiak et al. (2012) demonstrated that HS in waters cause increased oxidability, content of organic carbon (DOC/TOC) and elevated absorbance under ultraviolet conditions. It is also observed that organoleptic properties of waters with HS (colour, smell, taste) deteriorate. HS reduce surface tension of water and they cause, similar to surface active agents, increased solubility of organic toxic compounds. Furthermore, HS are little susceptible to biodegradation and resistant to chemical oxidation (Kaleta, 2004). Removal of humic substances from water is typically carried out by means of coagulation, adsorption, ion exchange, membrane processes and chemical oxidation and biodegradation. The combined processes, which use two or more methods for intensification of the basic process, are also used. One example of this solution is using physical method of modification of particles through effect of ultrasound field i.e. HS sonication. Distribution of the ultrasound waves in water causes macroscopic changes in the agent. These changes are irreversible and cause activation of chemical reactions and their acceleration. Sonochemical processes consist in degradation of polymers, decomposition of chemical compounds and oxidation. Sonochemical reactions have been demonstrated to be caused by free radicals (OH°) hydrogen peroxide and ozone created as a result of dissociation of water molecules (Stępniak et al., 2009). The aim of HS sonication is to obtain compounds with lower molecular mass, which are easier to adsorb in micropores (full utilization of carbon sorption capacity) and easier to biodegrade as they are better assimilated by microorganisms. Different organic compounds have been extensively researched by the scientists who test the usefulness of exposure to ultrasounds. Effect of ultrasound field on saccharin was studied by Bernardo et al. (2006). The study demonstrated that ultrasounds have effect on improved sorption of saccharin. Increased sonication time causes a reduced concentration of total organic carbon (TOC). A study by Liu et al. (2005) evaluated the effect of ultrasound field on efficiency of biological filters. An advantageous effect of ultrasounds with power of 10 W on bacterial count in the bed was also demonstrated: it caused improved biodegradation of organic compounds in a bioreactor. The focus in a study by Mason et al. (2003) was on evaluation of the efficiency of removal of microbiological contaminants from water by means of ultrasounds and the combined methods. Sonication of bacterial cells allowed for purification of water at higher efficiency. A research on using ultrasound field for carbon regeneration was documented by Breitbach and Bathen (2001), who found that ultrasounds promote desorption of compounds more effectively than sorption. The aim of the study was to evaluate the efficiency of ultrasound-assisted sorption and biosorption of humic substances.

2. Method

1 m high filtration columns with internal diameter of 26 x 10^{-2} m, filled with a carbon bed were used in the study. An adsorbent was provided by granulated activated carbon ROW 08 Supra (Norit) with majority of mesopores with alkaline water extract and high mechanical strength. Height of the carbon bed amounted to 0.5 m and the support layer (slag) was 3 x 10^{-2} m thick. The solution was fed to the column by means of a peristaltic pump. The flow rate of the solution flowing through the column from top towards bottom was constant (1 m/h), which gave a 30 min contact time of sorbent with adsorbate. Adsorbate was provided by a commercial preparation of sodium salt of humic acids. For this purpose, the authors prepared a model solution of HS with concentration of 20 mg/L. In order to increase the process efficiency, the HS solution was modified with ultrasound field. An ultrasonic disintegrator VCX 750 (Sonics) with frequency of 20 kHz was used. Sonication was carried out for 1 min at the amplitude of 100 % (114 μm, intensity: 60 W/cm^2). Biological carbon filter, which simulated the conditions present in water treatment plants was obtained using microflora: a commercial biopreparation and activated sludge. The tests were carried out in 6 columns. K - AC and inflow of basic solution of HS, 0 - AC and inflow of the solution modified with ultrasounds (US), A - AC colonized with microflora of the biopreparation and inflow of the basic solution, B - AC colonized with microflora of the activated sludge and inflow of the basic solution, C - AC inoculated with microflora of biopreparation and inflow of the solution modified with ultrasounds, D - AC inoculated with microflora of the activated sludge and inflow of the solution modified with ultrasounds. In order to evaluate quantitative changes of microflora during the process, the samples of eluates from the three levels of the bed (0.15; 0.30; 0.45 m) were taken for microbiological inoculation. Furthermore, in order to evaluate process efficiency in six columns, the samples of eluates, taken every hour, were analysed through determination of dissolved organic carbon (DOC), absorbance UV (254 nm), oxidability, colour (436 nm) and pH. The DOC determination was made using a Multi N/C 2100 Analytic Jena analyzer (PN-EN 1484:1999). The spectrophotometric measurements were made on a Thermo Electron Corporation Helios α SpectroLab apparatus. The oxygen consumption (Ox.) was measured by the permanganate index determination method (PN-EN ISO 8467:2001). In the case of the columns with biological bed, the authors also determined the level of dissolved oxygen in order to calculate the EMS index (EMS = $\Delta COD_{Mn}/\Delta O_{2,}$

COD_{Mn} = Ox.). EMS index (Eberhardta, Madsena i Sontheimera) which allows determination of the prevailing processes in a column, sorption and biodegradation (EMS = 1 – balance of sorption and biodegradation, EMS < 1 – advantage of biodegradation, EMS > 1 advantage of sorption). The process was carried out in a non-continuous manner, 5 to 8 hours per day. In the results, the changes of the parameters after the determined flow time (T) through the column (operation time) were researched. The experiment took 23 days. At his time, inside the columns, the researched processes of HS sorption and biosorption were occurring.

3. Results and discussion

The effect of ultrasounds on increased effectiveness of sorption of organic contaminants on AC and support for other processes, such as coagulation, has been the focus of studies carried out by a great number of scientists. Results were presented by e.g. Kusiak et al. (2011), who studied sonosorption of HS on granulated activated carbon and demonstrated that sonication of a solution of HS leads to increased efficiency of the process. A combined sono-oxidation method was analysed in a study by Chemat et al. (2001). The results obtained in their study showed that degradation of HS, determined by the content of TOC was possible just after one hour. Kim et al. (2007) studied the rate of removal of HS as TOC and they demonstrated the relationship between increased dose of H_2O_2 and TOC removal rate. A method of oxidation combined with sonication or ultrasonic effect for removal of humic acids was also used by Mahvi et al. (2009). They demonstrated that photodegradation occurs at increased efficiency and at shorter time than the simultaneous ultrasonic degradation. Kaleta (2004) discussed HS sorption on biological filters using AC with initial ozonation which increased the process efficiency by 10 %. As mentioned above, biodegradation of HS with support of microorganisms in the activated sludge occurred with high efficiency. The results obtained in the study demonstrated that carbon filters colonized by microflora operated 100 % longer, and, these beds were not fully depleted yet. Furthermore, no significant improvement in the process was observed after using the method of sorption combined with exposure to ultrasounds. Analysis of the content of DOC (Figure 1) revealed that biological bed considerably improved operation of the filters i.e. it elongated life of the columns and allowed for removal of HS in a more efficient manner.

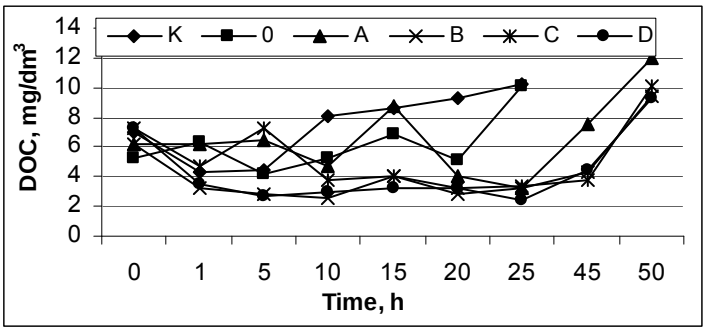

Figure 1: DOC times profiles (K - AC, 0 - AC + US, A - biopreparation, B –activated sludge, C - biopreparation + US, D - activated sludge + US).

Comparison of K and 0 samples demonstrated that ultrasounds cause higher depletion of DOC after the same flow time. However the life time of both columns was the same. A high increase in the content of DOC in the bed 0 was observed in the final phase of the process. The effect of ultrasound field on biological beds was also observed. After the same time of the flow for the columns, higher depletion of DOC was observed in the columns C and D. The bed which sorbed HS better, both as a basic solution and as a solution modified with ultrasounds, was AC colonized with microflora of activated sludge. Advantageous influence of ultrasound modification was confirmed in the effects of work of the C column (with biopreparation). Described effects were obtained at the short sonification time of HS solution, which is 1 min. It is important because of economical respects, in the case of the use of ultrasonic modification of processes. Analysis of absorbance in ultraviolet (Figure 2) allows for conclusion that ultrasounds elongate operating time with AC by ca. 30 %. Presence of microorganisms also considerably elongates the operating time of the columns. No considerable differences in operation of columns colonized by microorganisms from the biopreparation and activated sludge were observed. There was also no effect of ultrasounds on improvement in the process. Analysis at UV_{254} of the samples from different biological filters after the same operating time shows the same levels. Analysis of oxidability of the samples

subjected to sorption on AC and AC+US (Figure 3) revealed considerable decline in this parameter. Although ultrasound modification did not cause such a substantial decline in oxidability as it was the case in the control sample (K), the eluates sampled from columns filled with biological filter were characterized by reduced value of oxidability in the first phase of the process. After ca. 20 - 25 h, an increase in oxidability (over the values of zero samples) was observed. This might have been caused by presence of microorganisms on filters and the processes of biodegradation with generation of metabolites. Ultrasonic modification of biological filters allowed, to an insignificant degree, for obtaining a decline in oxidability, which might also have been a result of a reducing number of microorganisms as an effect of toxic O_3, H_2O_2 and R°. Lower number of microflora causes that the compounds are decomposed slower and fewer metabolites are present in the eluate. Analysis of the colour change (Figure 4) shows that ultrasounds have beneficial effect on reduction in UV_{436}.

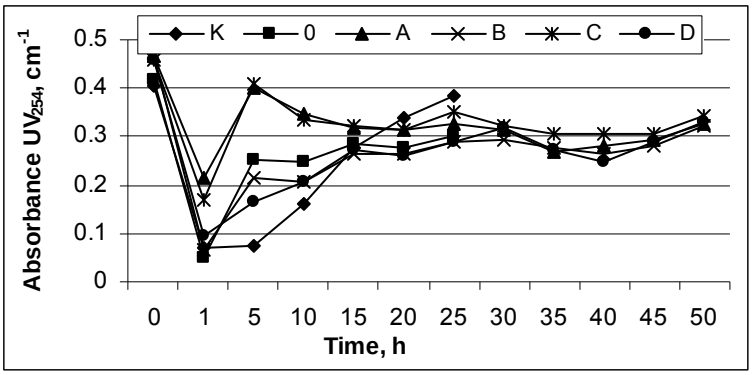

Figure 2: Absorbance UV_{254} times profiles (K -AC, 0 -AC + US, A -biopreparation, B –activated sludge, C - biopreparation + US, D - activated sludge + US).

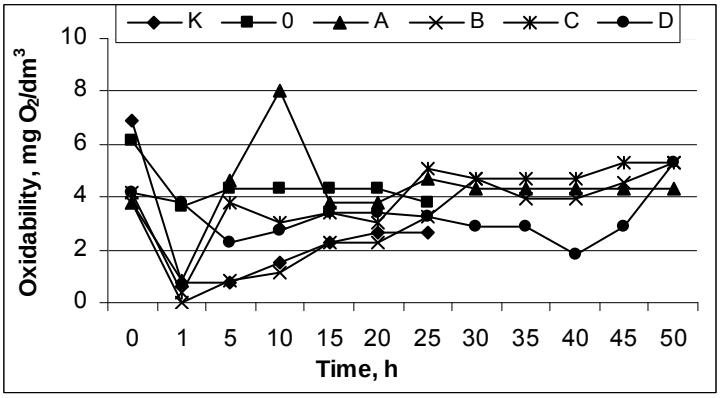

Figure 3: Oxidability times profiles (K -AC, 0 -AC + US, A -biopreparation, B –activated sludge, C - biopreparation+ US, D - activated sludge + US).

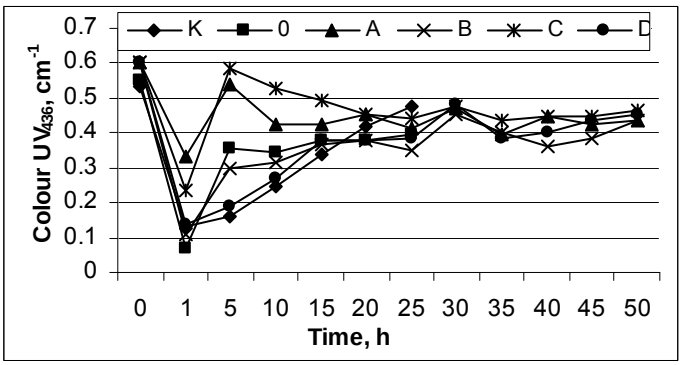

Figure 4: Colour times profiles (K -AC, 0 -AC + US, A -biopreparation, B –activated sludge, C - biopreparation+US, D - activated sludge + US).

Since ca. 30th hour of the process, these changes were insignificant, but, in the initial hours, they were even 50 %. It was also observed that the filter colonized by microorganisms of the activated sludge reduced the colour more intensively. The tests of turbidity of the samples taken for the analysis revealed that all the samples after sorption were deteriorated with respect to the control samples. This concerns ultrasonic modification, biological filters and the combined effect of microorganisms and exposure to ultrasounds. Analysis of pH of the solutions showed similar results, with all the samples exhibiting a slightly alkaline reaction i.e. pH = 7-9. Quantitative analysis of microorganisms in eluates from different heights of the bed revealed (Table 1) that the most of the bacteria are found in upper layer of the bed, where supply of oxygen is the most intensive. Deeper layers of the bed contained fewer bacteria. A reducing number of microorganisms on consecutive day of the experiment was also observed. This is likely to have been a result of reducing concentration of HS on the surface of AC, which might have had a toxic effect on microbes. A reduction in the number of microorganisms after sorption of solution modified with ultrasounds was also observed. This can be explained by the oxidative products of sonochemical reactions. Analysis of EMS index (Figure 5), which reveals either domination or balanced processes of sorption and biodegradation, leads to the conclusion that a dominant process in the bed is biodegradation (EMS<1).

Table 1: The number of bacteria at different bed heights (CFU x 10^3 in 1 mL)

Bad heights	**A**	**B**	**C**	**D**	day*
W	15	0	48	6	
X	63	55	67	13	2
Y	99	112	94	19	
Z	uc	uc	uc	29	
W	14	0	56	0	
X	30	7	40	0	7
Y	43	14	72	2	
Z	61	19	uc	14	
W	24	0	18	0	
X	50	2	23	0	12
Y	76	5	51	1	
Z	142	7	95	3	
W	12	12	4	1	
X	12	12	6	5	16
Y	15	18	6	5	
Z	16	20	7	7	

W- effluent of the bottom of column; X-15 cm, Y-30 cm, Z- 45 cm; uc-uncountable, day*- another day of the process

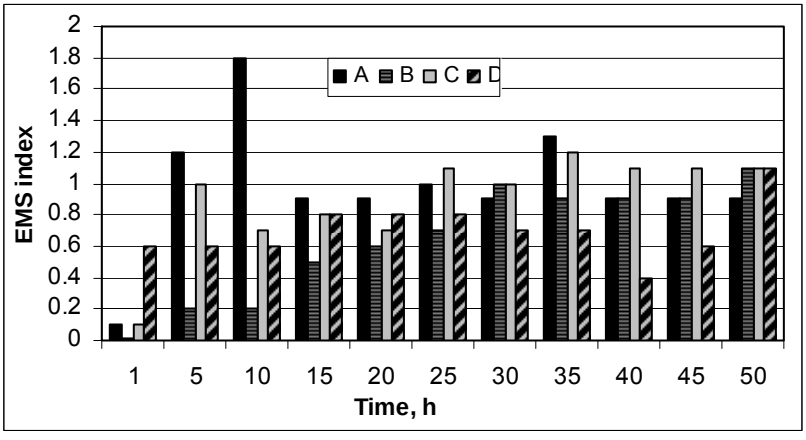

Figure 5: The changes of EMS (A -biopreparation, B –activated sludge, C -biopreparation + US, D - activated sludge + US).

After some time of the process, biodegradation was replaced by sorption. A reducing number of microorganisms was also observed at the same time. Contribution of the processes of sorption and

biodegradation in A and B systems was varied. The bed A is characterized by advantage of biodegradation, but it remained at the borderline of balance between both the processes and, in certain points of the process, an advantage of sorption was also observed. The B bed exhibited the dominance of biodegradation throughout the whole process. An insignificant advantage of sorption was observed only after 50 h of the process. No unequivocal relationship between the ultrasound effect and EMS index was found.

4. Conclusions

a) A considerable elongation of operating time was observed in the beds with biological filters. It was also found, especially during the first hours of filter's operation, that a dominant process was biodegradation. This led to a reduced number of microorganisms in the beds at the end of operation of the filters. Insignificantly better results of the study were obtained in the bed inoculated with activated sludge.
b) An insignificant improvement in the process of sorption combined with ultrasound effect was observed. DOC analysis revealed that, for the same time, depletion of HS is higher in the beds that sorbed HS solution modified with ultrasounds. Advantageous influence of ultrasound modification was confirmed in the effects of work of the column with biopreparation. Beneficial effects of sonosorption were also confirmed by the analysis of colour of HS solutions.

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