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Evaluation of the efficiency of humic substances adsorption on activated carbon in ultrasound assisted process

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ABSTRACT

The study presents results regarding an ultrasound-assisted adsorption process of humic acids from prepared water solution on activated carbon (AC). The experimental matrix created in accordance with Box–Behnken design for three independent variables was used in the research. The impact of changes in process temperature, time, and the mass ratio of solution to AC on the purification degree of that water mixture was examined. The dependence of the purification degree on the ultrasound treatment was also determined. After conducting the experiment, defined by the generated experimental matrix, the statistical evaluation of the ultrasound-assisted adsorption process was performed. Response surface plots, as well as contour plots describing the relationship between the values of several independent variables and the purification degree of water solution of humic substances, were generated. Pareto chart of standardized effect estimates of changes in the mass ratio of the prepared solution of HAs to the AC, adsorption process temperature, and its duration was created. That effects assessment was also defined for particular process variables. The final stage of the research was the obtainment of the polynomial model specifying the response dependence on the values of independent variables.

Keywords: Humic acids; Adsorption; Activated carbon; Ultrasound

1. Introduction

Humic substances (HS) are specific organic compounds. In nature, they may occur not only in soil but also in surface water and sediments. They are formed in the soil during the humification process as a result of dead organic matter transition. Humic compounds may typically be divided into three main fractions: fulvic acids (FAs), humic acids (HAs), and humins. An important feature that allows to distinguish these groups is their solubility. Scientists state that the fulvic fraction is soluble in water in the entire pH range, whereas humic fraction creates aggregates, that look like a gel, in acidic media. Humins, by contrast, are characterized by a good solubility in non-aqueous liquids. Generally, fractions of HS are presented as yellow, brown, or even black colored compounds and differ in their properties. It is important to stress that their features are strongly influenced by environmental conditions under which they were formed. The same principle to their molecular structure. There are two main theories of it. The first one describes HS as supramolecular

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substances when the second one claims they are similar to polymers. Unfortunately, it is not possible to determine one chemical formula which would be appropriate for all samples of particular HS fractions. Humic compounds are frequently shown as consisting of aromatic nuclei, aliphatic chains, and many functional groups, including hydroxyl, phenolic, or carboxyl groups. These structural elements ensure numerous specific properties of described organic substances [1–6].

HS, especially fulvic and HAs, are extensively used in agriculture, horticulture and many other branches of the industry. They constitute one of the most significant components of the soil because of their impact on its productivity. HAs commercial preparation is applied for improvement of soil water holding, sorption, and buffering capacity. Moreover, their dark color supports the thermal properties of soils. The presence of HS modifies soil structure, creating aggregates with mineral particles. These organic acids are also characterized by their biological activity. They may stimulate the life processes of living organisms located in the soil. A really important function of HS is their significant role in supporting nutrients uptake by plants. The use of mentioned organic acids may also guarantee a more efficient livestock production. HS is characterized by their anti-inflammatory, antioxidant, or bactericidal activity. They improve animals appetite. Proposals of HAs applications in cosmetics and medicine are getting more popular and are being still examined. Furthermore, dietary supplements form a significant part of the HAs market. HS is present in therapeutic peat which are used in the sanatorium. Research aimed at the utilization of HS for environmental protection and remediation was also done by scientists. HS may be applied as components of filters and sorbents to remove, for example, odorants or xenobiotics. They are also used as the colorant of paper or cardboard. What is more, they are useful in the construction and production of ceramics and polymers [7–16].

However, despite all the beneficial effects of HS, they can be harmful for human organism. Due to the mobility of described organic compounds, they may be leach out to surface waters and, subsequently, the groundwater and be a cause of their contamination. The water coloration and the deterioration of its organoleptic characteristics are some of the possible results of such contamination. The HS presence could be far more dangerous, for example, in a form of compounds with heavy metals, therefore water purification plants are commonly used in order to prevent the risk of high HS content in water. Traditional water treatment methods maybe not efficient enough to solve the problem of HS presence in the water. Humic compounds are undesirable because of the fact that they can be precursors for trihalomethanes (THMs) formation in chlorinated water. THMs are methane derivatives. Their general chemical formula is CHX_3, where X can be atoms of four elements located in the 17th group of the periodic table, namely iodine, bromine, chlorine, or fluorine. There are studies, although some of their outcomes are inconsistent or insufficient, which states that THMs may cause cancer or reproductive disorders. For that reason, it is necessary to remove THMs precursors, such as HS, from water intended for purification and disinfection [17–22].

One of the possible methods of HS removal from water is adsorption. Basically, the adsorption is mostly an exothermic process of adhesion of some substance particles (called adsorbate) present in gas or liquid phase to the liquid or solid surface of another substance (called adsorbent). During that process, the concentration of adsorbed compound declines

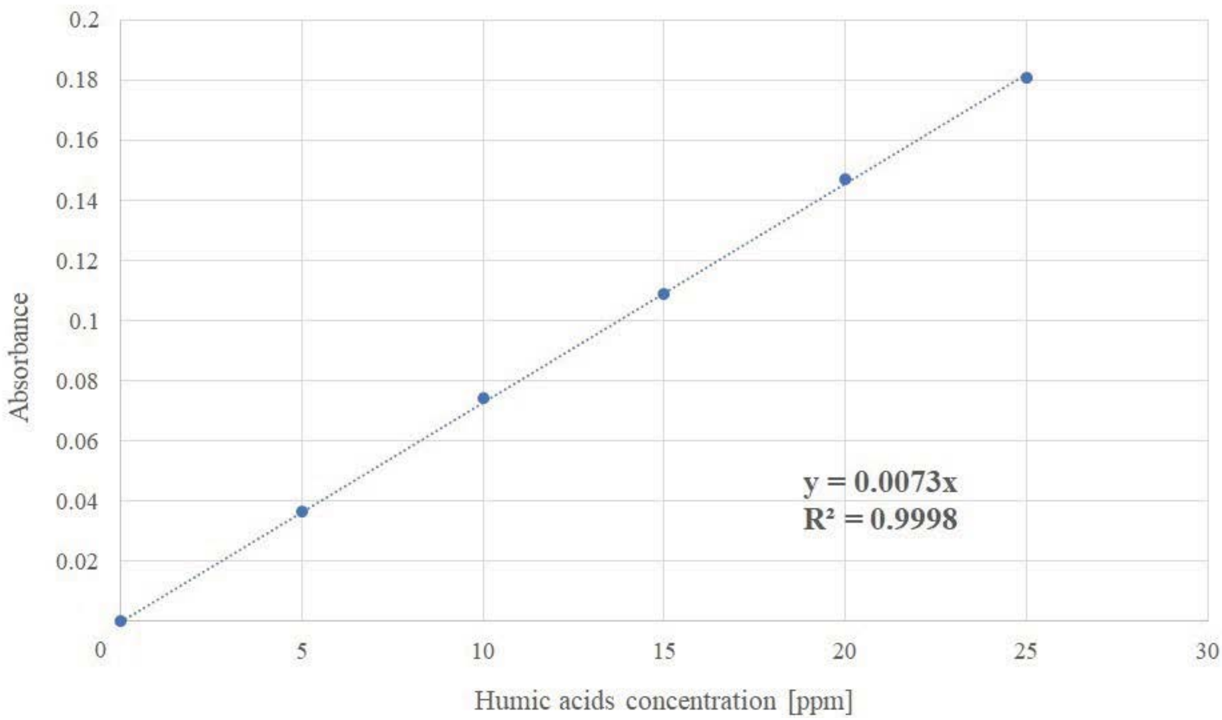

Fig. 1. Calibration curve for defining the concentration of HAs in prepared solution.

in the environment from which it is adsorbed but increases its concentration on the surface of an adsorbent. The adsorption is widely used in various industrial processes, such as water and wastewater treatment, gases, and other substances separation or catalytic processes. Really popular and often utilized adsorbents are silica gels, zeolites, and activated carbons (ACs), which are porous materials. There are many scientific papers about studies on the use of AC for water purification. Main benefits of AC are its good porosity and a high surface area, which makes AC widely used adsorbent. AC is also an easily accessible and relatively low-cost sorbent. AC can be produced from various cheap raw materials like seeds, peels, shells, many other agricultural wastes, or biomass. AC may be sold in several forms such as pellets, granules, or powder [23–33].

The aim of present examinations was the assessment of the purification efficiency of prepared water solution from HS using commercial AC. Two types of purification processes were compared. In the first variant, the water solution of HAs was exposed to an ultrasound before the purification process, the second variant excluded sewage was not prepared for adsorption by the ultrasound-assisted process. The impact of purification time, temperature, and water solution to AC mass ratio on the degree of purification were also examined.

Due to the assessment of the impact of independent process parameters on the purification efficiency of water solution, experimental matrix, and statistical assessment were done. Statistical part of this paper was based on the Box–Behnken design of an experiment. Dependency between process parameters values and the effect of the adsorption process, that was the efficiency of initial water solution purification from HS, was also described using response surface plots with contour chart and polynomial, which are specifying interactions between independent variables.

2. Materials and methods

Water solution of humic compounds was prepared by dissolving technical HAs in demineralized water. HAs concentration in prepared solution was about 15 mg/dm^3. HAs, that were used to prepare a solution, were defined as a mixture, obtained from two typed of carbon raw materials (peat and soft coal) by the producer (Sigma-Aldrich, Poland). To obtain good solubility of HAs, the pH of demineralized water was raised to nine by adding 1 M solution of NaOH. Next, 15 mg of technical HAs was mixed with 1 dm^3 of the mixture of water and NaOH and stirred with a magnetic stirrer for 1 h at 40°C.

2.1. HAs concentration measurement

For the precise determination of HAs concentration in prepared feed for the purification process, the spectrophotometric method was used. For that part of the research, the calibration curve, which defined HAs concentration as a function of absorbance, was made. Five model solutions of HAs were prepared using demineralized water for calibration purposes. These samples had HAs concentrations of 5, 10, 15, 20, and 25 mg/dm^3. Procedure for model humic acid solutions preparation was the same as for water solution, that was previously prepared as feed for the purification process.

Absorbance was measured for a wavelength of 420 nm by using spectrophotometer JASCO type V-670 (Poland). The initial concentration of HAs in water solution for the purification process amounted to 15.12 mg/dm^3. HAs content in water after adsorption also was defined by absorbance measurement.

2.2. Characteristic of the AC

For the adsorption-based purification of water from HAs, commercial AC NORIT SX 2, supplied by Chempur Company, was used. That type of AC is often used in industrial water and wastewater treatment processes. That AC has been produced from hard coal. Specific surface area of that mesoporous AC equals 1,010 m^2/g. Size range of NORIT SX 2 carbon granules used for the sewage purification process was between 0.5 and 1.6 mm. Only granules with size exceeding 1.2 mm were used for the adsorption process. In order to ensure the correct minimal size, a sieve with a suitable mesh size was used.

2.3. Preparing of HS water solution using ultrasound process

One part of the presented research was focused on comparing the efficiency of HAs removal from water in traditional adsorption and for process and in the process that was preceded by the ultrasound preconditioning of water solution using an ultrasonic bath Emmi 40 HC. After the solution was prepared, a part of it was subjected to ultrasounds with a power of 250 W and a frequency of 45 kHz. Initial solution for the purification process, containing 15.12 mg/dm^3 of HAs, was poured into 500 ml conical flasks and placed into an ultrasonic bath for 1 h at 40°C. After that, water was purified using the traditional adsorption.

2.4. Adsorption process

The main part of the presented study was focused on the adsorption-based water purification from HAs using commercial AC as adsorbent. An additional effect of temperature, time, and water to AC mass ratio on the efficiency of HAs removal was defined. Experimental points were specified based on the experimental matrix for Box–Behnken design. According to that experimental plan, each one of the independent variables has three values. For the Box–Behnken plan, the lowest value of process parameters was marked as –1, medium value as 0, and the highest value of process parameters as +1. Values for time, temperature, and solution to adsorbent mass ratio are presented in Table 1.

For each experiment, 2 ± 0.01 g of AC was weighted. Next, the adsorbent was transferred to polyethylene bottles and mixed with 40, 80, or 120 cm^3 of water solution of HAs, which was depending on experimental points in the Box–Behnken matrix. Depending on the adopted variant, the process was carried out for 2, 4, or 6 h. Values of adsorption temperature were also different. That parameter depended on the experimental point from the matrix and had three values: 30°C, 40°C, or 50°C.

The Purification process was carried out using a water bath shaker Elpin+ type 357. After the adsorption, samples

Table 1
Independent variables values and codes for Box–Behnken design levels

Independent variable	Mark	Levels and values		
		–1	0	1
Time of process (h)	X_1	2	4	6
Temperature (°C)	X_2	30	40	50
Wastewater to activated carbon mass ratio	X_3	20:1	40:1	60:1

were pulled out from the shaker and filtered twice, using quality hard filter paper. Humic acid content in solutions was determined by a comparison of the results of the measurement and the absorbance curve. Based on the difference of HAs concentration before and after the adsorption process, the degree of purification was calculated.

3. Results and discussion

Table 2 presented the Box–Behnken matrix of the experiment for the process of HAs removal from water. The highest degree of purification (86.96%) was obtained for point 10, The lowest (2.87%) for run number 8.

Based on results from Table 2, statistical analysis for the process of HAs removal from water solution was made. Pareto chart was used to illustrate the impact of changing values of independent variables on the purification degree. Fig. 2 presents the significant factors for independent variables as a form of Pareto chart of standardized effects for HAs removal from the initial solution.

Pareto chart describes the effect of linear (L) and quadratic (Q) changing of independent variables values on the results of the experiment. It also includes interactions of L effects between process parameters (e.g., $X_1^L \cdot X_2^L$) on the removal of HAs. According to the obtained results presented in Fig. 2, it is possible to define which independent variable values have the most important role for the results of the adsorption process. The highest absolute value of effect estimates for the independent variable was for changing of a solution of HAs to AC mass ratio. Effect estimates with negative values mean that the lowest mass ratio provides better water purification.

Three-dimensional response surface charts were created in order to accurately determine the impact of a value change for process parameters on the purification degree of the prepared solution. Based on these figures, it is possible to compare the influence of process parameters on the experiment. Charts present the degree of purification, that was the response for the experiment, as a function of two selected independent variables. Value for the third variable was specified as an average for the range for Box–Behnken experimental matrix, which was coded as 0.

The mass ratio of water solution to AC had the biggest impact on the efficiency of the purification process. A higher degree of HAs removal was obtained for a lower value of X_3. Significant impact of water solution to AC mass ratio changing confirms Pareto chart for standardized effect estimates, but also the shape of charts presented as Figs. 3 and 4, where an increase of purification degree is observed, with the decrease of water to AC mass ratio. Results for experimental points of the matrix, which had the same values for temperature and adsorption time (X_1 and X_2), but different mass ratio (X_3), for example, points 5 and 7 or 9 and 11. For the results for points 5 and 7, where the purification process was carried out for 2 h at 40°C, it is clear that decreasing mass ratio of water solution of HAs to AC allows to obtain a considerably higher degree of purification (from 55.04 to 14.50 mass%). For processes carried out for 4 h at 30°C (points 9 and 11) decreasing water solution to AC mass ratio, from 60:1 to 20:1, allows to increase removal degree of HAs from 3.24 to 65.96 mass%.

Influence of temperature and time manipulation on the obtained results were similar. Based on the analysis of Fig. 5, that defines the influence of temperature and time of adsorption on the results of experiments, it can be concluded that,

Table 2
Degree of solution purification from HAs for experimental points, that were created according to Box–Behnken design of experiment

Run	Process time (X_1) [h]	Temperature (X_2) [°C]	Wastewater to activated carbon mass ratio (X_3)	Degree of purification (Y) [mass%]
1	2	30	40:1	11.97
2	6	30	40:1	50.34
3	2	50	40:1	5.66
4	6	50	20:1	7.17
5	2	40	20:1	55.04
6	6	40	20:1	82.70
7	2	40	60:1	14.50
8	6	40	60:1	2.87
9	4	30	20:1	65.96
10	4	50	20:1	86.96
11	4	30	60:1	3.24
12	4	50	60:1	9.68
13	4	40	40:1	42.22
14	4	40	40:1	44.28
15	4	40	40:1	38.55

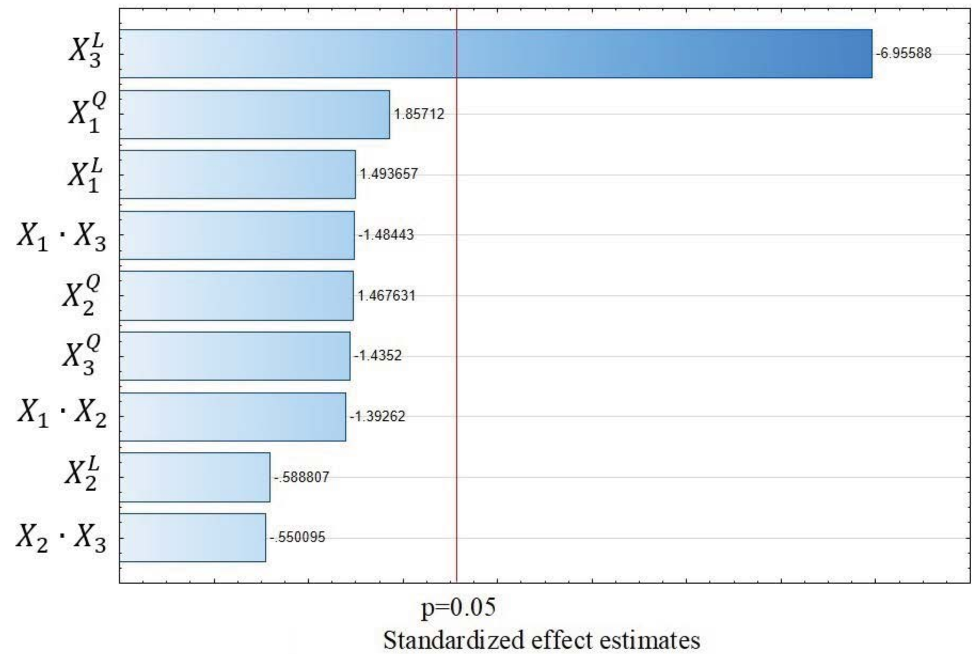

Fig. 2. Pareto chart for standardized effect estimates of HAs removal from an initial solution of HAs.

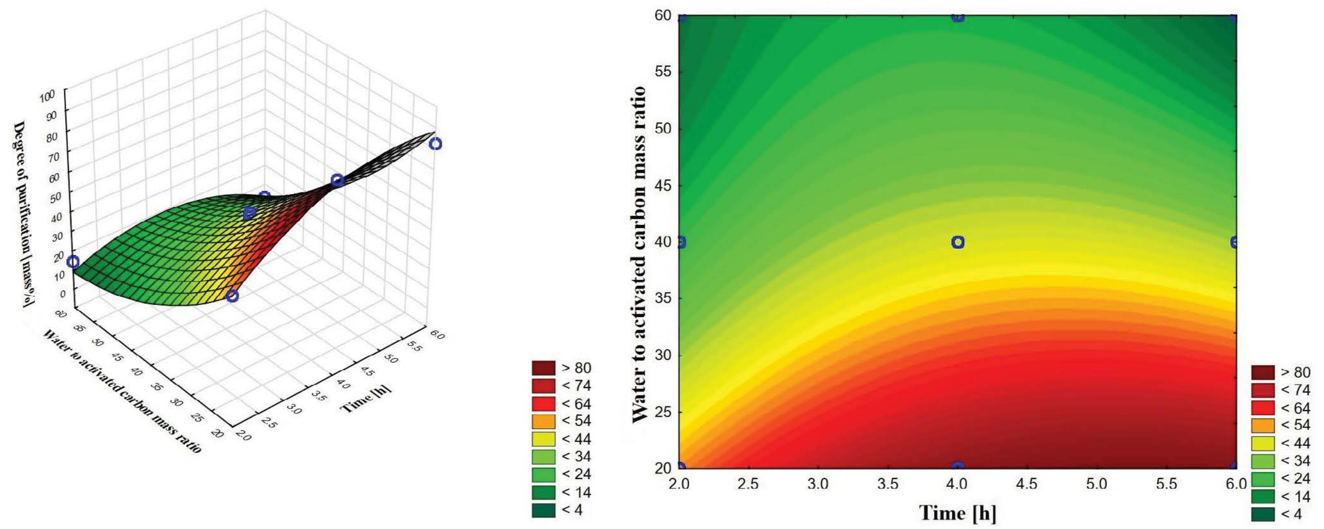

Fig. 3. Response surface chart with a contour plot of the influence of time (X_1) and water solution to AC mass ratio (X_3) on the degree of purification of the water solution from HAs for temperature (X_2) = 40°C.

after exceeding a certain value of time and temperature for the purification process, the efficiency of purification begun to decrease. That fact may be related to the establishing of adsorption-desorption equilibrium, and also with the exothermic process of adsorption.

The last step of statistical analysis was to create a polynomial Eq. (1), that describes the impact of independent variables (X) on the results of the experiment (Y). The created formula defines the influence of L, Q process parameters factors and also interactions between process conditions. Generated model was compared with experimental results for individual experimental points.

$$Y = -211.66 + 57.33X_1 - 3.20X_1^2 + 10.38X_2 - 0.10X_2^2 - 1.89X_3 + 0.03X_3^2 - 0.46X_1X_2 - 0.25X_1X_3 - 0.02X_2X_3 \quad (1)$$

The statistical fit of the model, described as Eq. (1), was 92.70% (R^2 = 95.47%). Based on the generated polynomial equation, it is possible to perform an initial determination of HAs removal degree based on the values of process parameters. Differences between results obtained from the polynomial model and from the experiment are shown in Fig. 6.

Due to the heterogeneity structure of HS, that type of organic chemical compounds may change the structure, for example, at high temperatures. This work shows the impact

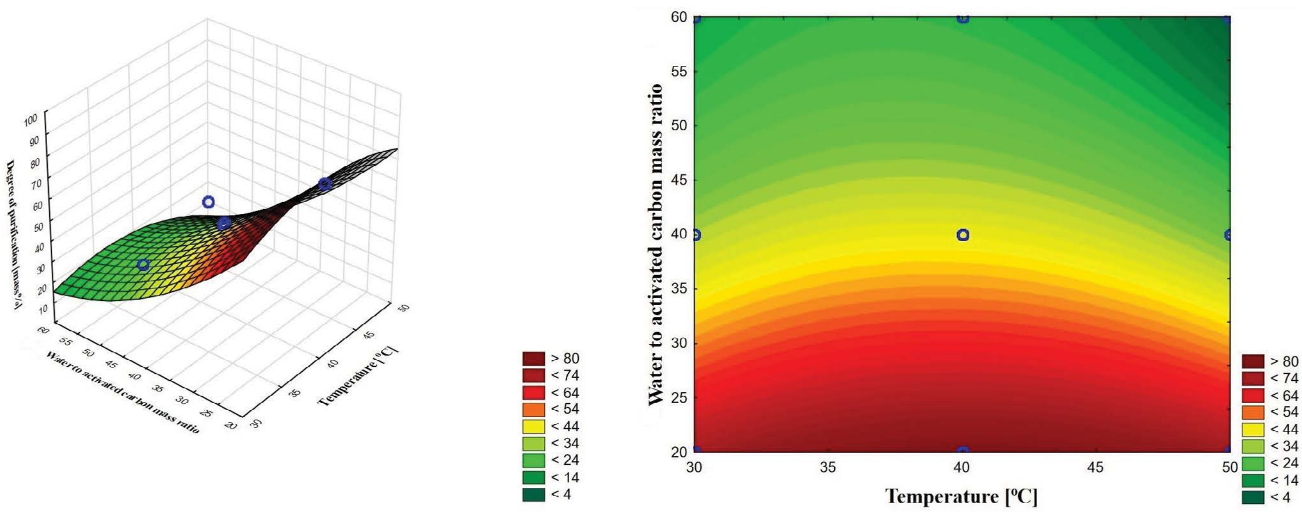

Fig. 4. Response surface chart with a contour plot of the influence of temperature (X_2) and water solution to AC mass ratio (X_3) on the degree of purification of the water solution from HAs for time (X_1) = 2 h.

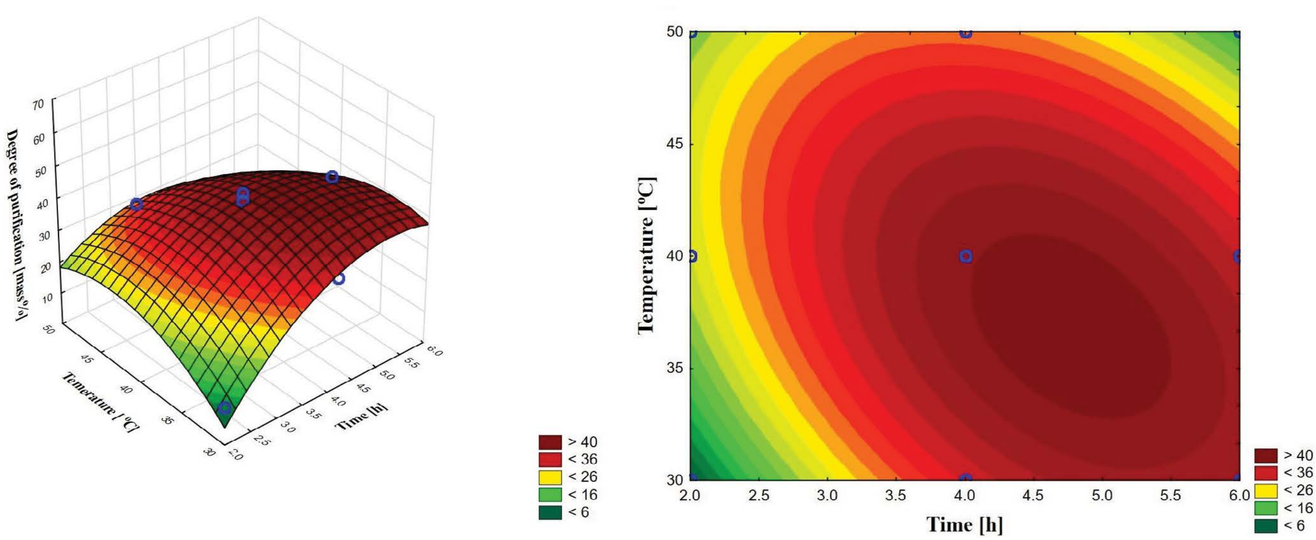

Fig. 5. Response surface chart with a contour plot of the influence of time (X_1) and temperature (X_2) on the degree of purification of the water solution from humic acids for water solution to AC mass ratio (X_3) = 40:1.

Table 3
Degree of water purification in samples with and without the pretreatment process using ultrasound

Time (h)	Temperature (°C)	Wastewater to activated carbon mass ratio	Preparing wastewater in the ultrasound process	Degree of purification (mass%)
2	30	40:1	Yes	32.55
			No	11.97
4	50	20:1	Yes	91.81
			No	86.96
6	40	60:1	Yes	9.44
			No	2.87

of ultrasound energy on the efficiency of HAs removal from water. The comparison of the purification degree of HAs solution samples with and without pretreatment with ultrasound before the adsorption process is presented in Table 3. Points for experimental matrix, which were compared in Table 3, were selected randomly. For each of these points, the initial solution prepared in the ultrasound process had a positive effect on HAs removal from sewage. The largest increase of purification degree after ultrasonic water treatment was recorded for HAs adsorption for 2 h at 30°C. The highest solution purification degree after the ultrasonic process can be associated with changes of HAs structure under the influence of ultrasound. During the sonification of water solution for adsorption of HAs on AC increase of temperature was observed. Therefore, HAs structure may have been affected. Due to that, HAs removal using AC was easier.

4. Conclusions

Due to the harmful influence of HS and primarily their chemical transformation products (mainly oxidation), it is necessary to remove that type of chemical compounds from water. A small concentration of HS causes water coloring, negatively impacting the useful properties of water. A cheap and well-known method of water treatment is the adsorption of pollutants using AC. Presented results confirmed that this process, for some values of process parameters, is effective for HAs removal from water. Purification degrees from HS may be improved by ultrasonic processes. In that research, the direct ultrasound-assisted purification process in an ultrasonic bath was also tested. That one-step ultrasound-assisted adsorption caused destruction of the adsorbent structure. Due to that, a two-stage purification was proposed. The two-step process of water treatment from HAs, using ultrasounds, gave better results, that were presented in Table 3. However, it is required to further research of process optimization in order to maximize the degree of water purification from HS.

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