A study on adsorption of metals by activated carbon in a large-scale (municipal) process of surface water purification

Marzena Dabioch1*, Robert Skorek1, Andrzej Kita1, Piotr Janoska2, Katarzyna Pytlakowska1, Piotr Zerzucha1, Rafal Sitko1

1Department of Analytical Chemistry, Institute of Chemistry, University of Silesia, 40-006 Katowice, Poland
2Department of Probability Theory, Institute of Mathematics, University of Silesia, 40-007 Katowice, Poland

Abstract: Elements that enter the aquatic environment may pose a health risk to wildlife and humans. The aims of this study were: to determine how the introduction of activated carbon for a water purification system will improve the quality of the water produced; and to investigate the sorption of metals on activated carbons, including determination of the accumulation, as well as changes in concentrations of elements in carbons. The tests were carried out on three types of activated carbons with different granular structure. All samples were collected from Water Treatment Plant Goczalkowice, Poland. Concentrations of elements were measured using an optical emission spectrometer with inductively coupled plasma. The experiment showed that metals accumulating in the activated carbons during the operation included: Ca, Mn, Zn, and Cu. In each of the three types of carbons, it can distinguish such elements as Ba, Al, Cr, Ni, Ti, which are characterized by irregular accumulation during the operation of the filter. The introduction of carbon sorbent for water treatment largely contributed to improvement in the quality of raw material supplied to customers, mainly with regard to taste and smell, as well as to reduction of basic parameters: color, absorbance in the UV range and oxidability.

Keywords: Carbon sorbent • Heavy metals • Drinking water • ICP-OES • PCA

1. Introduction

Surface intakes, which are a raw material for production of water, are exposed to numerous pollutants. Progressive chemicalization from all areas of life (washing powders, detergents, whiteners), especially agriculture (pesticides, fertilizers), together with increasing pollution of the atmosphere, makes the water quality in lakes and rivers significantly worse. The water is sometimes polluted with compounds posing high hazards to living organisms, including humans.

Activated carbons are applied in separation and purification technologies, catalytic processes, biomedical developments, pollution control, and energy storage, among other uses [1]. Specifically, the use of activated carbon in surface water purification is nowadays considered an effective purification process for reducing trace amounts of several pollutants in order to reach environmental standards and regulations. The extensive application of activated carbon in water treatment is mainly due to its relatively low cost compared to other adsorbents, wide availability, high performance in adsorption processes and surface reactivity. This adsorbent offers good versatility and flexibility to modify its physical and chemical properties, thus opening the possibility of preparing materials with tailored characteristics [2,3]. Until now, several types of activated carbons have been used for the removal of
priority pollutants from water. It turned out that they may be successfully used to remove inorganic compounds, such as heavy metals, but also organic compounds – among others, dyes, pesticides, detergents, aromatic and aliphatic hydrocarbons, phenols, drugs and their metabolites, and even viruses resistant to chlorination [4-7]. It is important to recall that water pollution by both heavy metals and organic compounds is considered a serious environmental problem because these pollutants modify the chemical properties of water and are toxic to aquatic flora, animals and human beings [8-11]. For example, heavy metals are toxic even at relatively low concentrations, while some may be carcinogenic, e.g. Cr(VI). Although only one form of chromium is toxic, both forms of Cr are removed on activated carbons, due to the fact that Cr(III) can be oxidized in the water treatment process to form toxic Cr(VI) [12,13]. We also ascertained the major influence of the initial oxidation of the above mentioned groups of compounds with strong oxidants, such as ozone, on the subsequent filtration process and its effectiveness. Use of activated carbon to remove excess chlorine remaining from the process of chlorination is also noteworthy. Among the known methods, adsorption on activated carbon is the simplest, most effective and economical one, because activated carbon used in water treatment processes may be reused after regeneration [14,15]. Therefore, the water producers face a task of continuous modernization of technical systems based on activated carbons used for water treatment and purification.

Understanding the phenomenon of adsorption, research on carbon surface modification and other work aimed at understanding the physico-chemical properties of activated carbons have made activated carbons the material which is widely used in the process of water purification. Ion adsorption on activated carbon depends on the ion size and charge, as well as pH [16-19]. Specific properties of the ion, connected with the interaction of the cation with the surface of activated carbon, may also have a large impact. Alkali metal cations are bound to the surface of carbon practically only by electrostatic forces [20]. Ions prone to polarization, such as Fe(III), Cr(III), Al(III), Cu(II), Ni(II), form complexes on the carbon surface containing coordination bonds [18,21]. Often, activated carbons are modified and impregnated to increase the active groups which retain metal cations. The role of the modifier or impregnation may be met by pyrocatechol violet [22], pyrogallol red [23], sodium dimethyldithiocarbamate [24], potassium manganate(VII) [25] or potassium bromate(V) [26]. Studies have investigated the adsorption of metals on activated carbons by physically activated - carbon(IV) oxide, water vapour [16], air [27] and chemically activated - zinc chloride, phosphoric(V) acid [16], sulfuric(VI) acid [28] or nitric(V) acid [29]. Some metal ions are adsorbed on the carbon surface of a different character and opposite ion-exchange properties. Non-oxidized activated carbon with anion-exchange properties may adsorb heavy metal ions such as Hg and Ag [30]. Ion adsorption on activated carbon is also accompanied by the oxidation and reduction processes which are connected with the redox properties of carbon. In contact with carbon, cations of metals such as Au, Ag, Hg, Fe, Cr, Mn may be reduced to ions at lower oxidation states and even to metallic form [31].

The present study used granular activated carbons from anthracite, which were obtained during the first year of operation inside filters, as well as new, unused activated carbon. The main objectives of the present study were: (1) to determine how the introduction of activated carbon for a water purification system will improve the quality of the water produced; (2) to investigate the sorption of metals on activated carbons including determination of the accumulation, as well as changes in concentrations of elements in activated carbons used in the water treatment process, and comparison of these values with new carbons not used in this process; (3) to characterize the correlation between the content of elements in different activated carbons; (4) to trace the similarities and differences between the analyzed carbons.

2. Experimental procedure

2.1. Stages in water purification

The first technological system in Water Treatment Plant Goczałkowice (southern Poland), called Go-cza I, uses raw water from the Goczalkowice reservoir located on the Vistula river. It utilizes pre-ozonation (Fig. 1, step 1), coagulation with alum (Al₂(SO₄)₃) (step 3), and flocculation and sedimentation units. After a rapid sand filtration (step 4), water flows trough the pumps (step 7) and is mixed with the water passing through the second filtering system. The second filtering system, Go-cza II, uses raw water from both the Goczalkowice and the Czaniec reservoir. Technologically, it consists of analogous water treatment units, i.e., of preozonation (step 2), coagulation with Al₂(SO₄)₃ at step 5 and the rapid sand filtration of water (step 6). However, a more effective, advanced and compact clarifier/flocculator unit (Degremont) is employed for the coagulation process. The consecutive step is a common secondary ozonation (step 8). Then the water passes through the granular activated carbon filtration unit (step 9) and finally, the process of chlorination (step 10) takes place.
Eventually, the water enters the municipal pipeline system. The consecutive steps involved in water filtering are schematically shown in Fig. 1.

2.2. Sampling
All samples of activated carbons were collected after the first year of operation inside filters from Water Treatment Plant Goczalkowice. Of the sixteen filtration chambers filled with carbon sorbent, activated carbons from nine selected filters were tested. The tests were carried out on three types of activated carbons with different granular structure – Chemviron F-300 (grain shape; filter No. 1, 2), Norit ROW 08 (cylindrical shape; filter No. 4), WG-12 (cylindrical shape; filter No. 9, 10, 11, 12, 15, 16). New, unused Chemviron F-300, Norit ROW 08 and WG-12 activated carbons constituted the comparative materials. Used and unused materials were purchased and delivered at the same time.

2.3. Reagents
All reagents used in the analysis of activated carbons were analytically pure. High purity double-distilled and deionized water for dilution was obtained using a Millipore Milli-Q system. All solutions of multielemental standards (Merck, Germany) were prepared daily in water obtained from the Milli-Q System (Millipore, USA) and used for the calibration. Ultrapure concentrated nitric(V) acid (65%, Merck, Germany) was used for adjusting acidity of the samples and standard solutions.

2.4. Analytical methods
0.1 g-in-weight samples of crushed activated carbon were quantitatively transferred into teflon crucibles, and then 6 mL of 65% nitric(V) acid were added. The conditions for the digestion of activated carbons were determined by optimization. The digestion process was carried out using a Uniclever BM-1z mineralizer working in four stages: I – heating: 3 min, pressure: 17-20 atm, 60% microwave involved, II – heating: 5 min, pressure: 27-30 atm, 80% microwave involved, III – heating: 10 min, pressure: 42-45 atm, 100% microwave involved, IV – cooling: 10 min When the mineralization was completed, the samples were quantitatively transferred to flasks and volumes were made up to 10 mL with demineralized water. The concentrations of elements, such as Ca, Mg, Ba, Sr, Mn, Ti, Al, Cr, Cu, Fe, Ni, K, Na, P, and Zn was determined using optical emission spectrometry with excitation by argon inductively coupled plasma (ICP-OES). All assays were performed six times for each type of activated carbon and evaluated statistically. The optimum measurement conditions are shown in Table 1. The wavelength, detection and quantification limits of the elements analyzed are shown in Table 2. Quality control for this procedure was carried out using the standard recovery test. The recovery was studied for two different concentrations of the elements analyzed and ranged from 88% for Cr to 109% for K.
2.5. Data processing methods

Analysis of the interdependence of variables was carried out by calculating linear Pearson correlation coefficients. It has been assumed that the regression modeling of the potential usefulness of the selected variable (explanatory) to model another variable (explained variable) determines the absolute value of the high correlation coefficient between these two variables. The statistical analysis usually assumes that if the correlation coefficient is >0.9, a very strong linear dependence exists; 0.7-0.9 – significant linear dependence; 0.4-0.7 – moderate linear dependence; 0.2-0.4 – distinct linear dependence, but low; <0.2 – no linear dependence [32]. Applications of the Pearson correlation coefficients may be found in literature [33,34].

Measurement series were obtained by statistical correlation analysis using the variance correlation test and Spearman’s test. Spearman’s rank correlation coefficient is a non-parametric measure of the statistical dependence between two variables. If there are no repeated data values, a perfect Spearman correlation of +1 or −1 occurs when each of the variables is a perfect monotonic function of the other. The Spearman correlation coefficient is often thought of as being the Pearson correlation coefficient between the ranked variables. The variance test of the correlation is a kind of F-test. The F-test was used to compare the variance associated with linear regression to the residual variance. The estimated variance was compared with the array F distribution critical values. If the estimation of the variance is greater or equal than the critical value [35], the alternative hypothesis must be adopted by correlating results of determination of elements. If the absolute value of Spearman’s rank correlation coefficient is greater than the critical value [36], the

| Element   | Wavelength [nm] | Limit of detection in solution [µg mL⁻¹] | Limit of quantification in the sample [µg g⁻¹] | Limit of detection in solution [µg mL⁻¹] | Limit of quantification in the sample [µg g⁻¹] |
|-----------|----------------|------------------------------------------|-----------------------------------------------|------------------------------------------|-----------------------------------------------|
| Ca        | 318.128        | 0.0481                                   | 4.819                                         | 0.0964                                   | 9.638                                         |
| Al        | 167.080        | 0.0304                                   | 3.044                                         | 0.0609                                   | 6.087                                         |
| Fe        | 273.955        | 0.0196                                   | 1.958                                         | 0.0392                                   | 3.917                                         |
| P         | 178.287        | 0.0603                                   | 6.033                                         | 0.1207                                   | 12.07                                         |
| Mg        | 279.079        | 0.0256                                   | 2.555                                         | 0.0511                                   | 5.111                                         |
| K         | 766.490        | 0.0861                                   | 8.614                                         | 0.1723                                   | 17.23                                         |
| Na        | 589.592        | 0.0082                                   | 0.819                                         | 0.0164                                   | 1.639                                         |
| Ba        | 233.527        | 0.0051                                   | 0.510                                         | 0.0102                                   | 1.019                                         |
| Sr        | 421.552        | 0.0001                                   | 0.011                                         | 0.0003                                   | 0.030                                         |
| Cu        | 324.754        | 0.0023                                   | 0.232                                         | 0.0046                                   | 0.464                                         |
| Ti        | 334.941        | 0.0007                                   | 0.067                                         | 0.0014                                   | 0.136                                         |
| Mn        | 257.610        | 0.0004                                   | 0.038                                         | 0.0008                                   | 0.075                                         |
| Ni        | 232.003        | 0.0464                                   | 4.637                                         | 0.0927                                   | 9.274                                         |
| Zn        | 213.856        | 0.0202                                   | 2.024                                         | 0.0405                                   | 4.047                                         |
| Cr        | 267.716        | 0.0056                                   | 0.558                                         | 0.0112                                   | 1.116                                         |
alternative hypothesis must be adopted by correlating results of determination of elements. Otherwise, the null hypothesis of no such correlation must be adopted [37,38].

Next, we examine the diversity of the elements analyzed in all activated carbons using one-way ANOVA and Kruskal-Wallis one-way analysis of variance. Kruskal-Wallis one-way analysis of variance by ranks is a non-parametric method for testing equality of population medians among groups. It is identical to a one-way analysis of variance with the data replaced by their ranks. The null hypothesis \( (H_0) \) implies that there is no statistical difference in the element across all activated carbons. The opposite hypothesis \( (H_1) \) means that the test element varies across all activated carbons [39,40]. Applications of one-way ANOVA [38,41,42] and Kruskal-Wallis one-way analysis [38,43,44] abound in the literature.

The Mann-Whitney U test is a non-parametric statistical hypothesis test for assessing whether two independent samples of observations have equally large values [40]. This test can be used to investigate the differences between any two activated carbons for all analyzed elements. This test was used only in one type of activated carbon – Norit ROW 08 - because our comparison concerns only two series, so we compared this new activated carbon with the carbon used in filter No. 4. Moreover, these activated carbons have been examined in the t-Student test. A t-test was used to compare the average obtained for the new activated carbon with the average obtained for the used activated carbon [45,46]. A t-test is any statistical hypothesis test in which the test statistics follows a Student's t distribution if the null hypothesis is supported. Statistical equality of the average means accepting the null hypothesis. However, acceptance of the alternative hypothesis is supported in the absence of equality of averages. Other applications of the Mann-Whitney U test are presented in the literature [37,38] and of the t-Student test in articles [41,42,47].

Principal component analysis (PCA) has been widely applied in data mining to investigate data structure. In PCA, new orthogonal variables (latent variables or principal components) are obtained by maximising the variance of the data. The number of latent variables (factors) is much lower than the number of original variables, so that the data can be visualised in a low-dimensional PC space. Several algorithms can be used to perform PCA, such as the singular value decomposition (SVD) approach [48] and the non-linear iterative partial least squares (NIPALS) algorithm [49]. In recent years, the so-called kernel PCA approach has gained a lot of attention in chemometrics due to its computational efficiency [50]. PCA allows to reveal similarities and differences between individual samples and the relationship among the measured parameters [51].

3. Results and discussion

15 elements were determined in all activated carbon samples. Table 3 shows the element content in different activated carbons from various filters – Chemviron F-300 (CH), Norit ROW 08 (N), and WG-12 (WG) used for one year in relation to new activated carbons.

The analysis determined the impact of operating time on the concentrations of selected elements in the three types of activated carbons examined, which were located in various chambers of the filter. The points of reference were new, unused activated carbons.

In the case of Chemviron F-300, collected from filter No. 1 (CH1), we observed a gradual increase of Ca, Mg, Ba, Mn, Al, Cr, Cu, Fe, Ni, Zn, and P in carbon after the first year of operation in comparison to new activated carbon. The largest increases in the concentrations of these elements was found for Mn (1623%), Zn (855%), Ca (301%), Cu (253%), and P (237%). Other elements of this group are adsorbed by activated carbon to a lesser extent and their growth reaches the following values: Mg – 160%, Ba – 133%, Ni – 131%, Cr – 119%, Al – 110%, Fe – 105%. In the case of K, Na, Sr and Ti, concentrations are highest in new carbon and after the first year of operation, white the concentrations of these metals in F-300 from filter No. 1 are clearly decreasing. Analysis of Chemviron F-300, located in filter No. 2 (CH2), showed an increase in element concentrations over time during exploitation of the carbon only for Ca, Mg, Mn, Cu, Fe, Zn, and P. Increments are as follows: Mn – 1874%, P – 525%, Zn – 181%, Ca – 155%, Cu – 130%, Fe – 127% and Mg – 103% in relation to new activated carbon. The content of such metals as K, Na, Ba, Sr, Ti, Al, Cr, and Ni decreased in the first year of the carbon filter operation, proving their leaching from new carbon.

Filter No. 4 contained Norit ROW 08 (N4) sorbent. The study showed a gradual increase of Ca, Ba, Sr, Mn, Ti, Al, Cr, Cu, Ni, Zn, and P during the first year of operation in relation to new activated carbon. However, in unused carbon, Ni is below the detection limit. The largest increases in the contents of these elements in used activated carbon compared to the unused activated carbon were found for Cu (1965%), Mn (807%), Ba (425%), Zn (203%), Al (203%). Other elements of this group are adsorbed by activated carbon to a lesser extent, with concentration increases reaching 164% for
### Table 3a. Mean concentration [µg g⁻¹] and standard deviation for all samples of activated carbon (n = 6).

|        | Ca   | Mg   | Ba   | Sr   | Mn   | Ti   | Al   | Cr   |
|--------|------|------|------|------|------|------|------|------|
| CH new | Mean | 1297 | 282  | 50.2 | 131  | 13.1 | 189  | 3862 | 17.1 |
|        | SD   | 188  | 42   | 4.8  | 5    | 1.0  | 10   | 358  | 4.1  |
| CH1    | Mean | 3905 | 452  | 66.9 | 75.7 | 213  | 172  | 4253 | 20.3 |
|        | SD   | 301  | 49   | 3.5  | 1.8  | 16   | 4    | 186  | 1.6  |
| CH2    | Mean | 2010 | 291  | 33.4 | 68.2 | 246  | 135  | 3718 | 7.7  |
|        | SD   | 390  | 64   | 8.7  | 2.4  | 34   | 8    | 514  | 3.1  |
| N new  | Mean | 1552 | 1060 | 8.3  | 26.6 | 14.4 | 19.2 | 121  | 8.8  |
|        | SD   | 203  | 127  | 1.4  | 2.0  | 1.4  | 1.4  | 14   | 1.3  |
| N4     | Mean | 2392 | 237  | 35.2 | 30.0 | 116  | 20.3 | 244  | 10.5 |
|        | SD   | 273  | 67   | 9.9  | 3.4  | 28   | 3.4  | 53   | 3.2  |
| WQ new | Mean | 1948 | 554  | 11.1 | 204  | 31.7 | 104  | 6250 | 16.6 |
|        | SD   | 242  | 54   | 12   | 13   | 2.7  | 6    | 427  | 2.0  |
| WQ9    | Mean | 2318 | 336  | 29.4 | 31.3 | 193  | 113  | 3914 | 9.4  |
|        | SD   | 154  | 11   | 3.0  | 1.0  | 9.0  | 3    | 93   | 0.4  |
| WQ10   | Mean | 2411 | 290  | 31.6 | 34.0 | 311  | 105  | 4150 | 9.3  |
|        | SD   | 215  | 26   | 3.6  | 2.4  | 36   | 7    | 332  | 1.2  |
| WQ11   | Mean | 2771 | 314  | 37.0 | 33.8 | 194  | 103  | 3651 | 13.4 |
|        | SD   | 513  | 52   | 8.2  | 4.3  | 24   | 11   | 486  | 3.0  |
| WQ12   | Mean | 2856 | 357  | 40.9 | 37.0 | 291  | 138  | 3809 | 8.83 |
|        | SD   | 243  | 24   | 4.0  | 2.3  | 18   | 6    | 128  | 0.57 |
| WQ15   | Mean | 2811 | 374  | 38.5 | 35.3 | 183  | 105  | 3866 | 8.88 |
|        | SD   | 265  | 30   | 4.3  | 2.3  | 29   | 7    | 173  | 1.30 |
| WQ16   | Mean | 3168 | 391  | 45.5 | 36.4 | 276  | 116  | 3790 | 9.46 |
|        | SD   | 1100 | 104  | 16.9 | 7.1  | 50   | 19   | 623  | 3.10 |

### Table 3b. Mean concentration [µg g⁻¹] and standard deviation for all samples of activated carbon (n = 6).

|        | Cu   | Fe   | Ni   | K    | Na   | P    | Zn   |
|--------|------|------|------|------|------|------|------|
| CH new | Mean | 23.2 | 2827 | 22.6 | 581  | 346  | 120  | 4.69 |
|        | SD   | 1.9  | 167  | 7.08 | 93   | 43   | 13   | 1.05 |
| CH1    | Mean | 58.8 | 2962 | 29.6 | 500  | 313  | 285  | 40.1 |
|        | SD   | 2.9  | 115  | 1.6  | 55   | 28   | 14   | 2.4  |
| CH2    | Mean | 30.2 | 3603 | 13.7 | 357  | 305  | 217  | 24.6 |
|        | SD   | 1.9  | 341  | 5.2  | 61   | 36   | 29   | 3.0  |
| N new  | Mean | 1.3  | 704  | <4.6 | 347  | 550  | 169  | 7.3  |
|        | SD   | 1.3  | 72   | <4.6 | 22   | 18   | 15   | 1.7  |
| N4     | Mean | 25.8 | 631  | 4.4  | 75.7 | 193  | 277  | 27.8 |
|        | SD   | 2.9  | 149  | 1.6  | 26.7 | 26   | 45   | 5.0  |
| WQ new | Mean | 84.6 | 3092 | 21.0 | 16808| 3538 | 589  | 13.9 |
|        | SD   | 5.6  | 221  | 1.7  | 510  | 108  | 31   | 2.2  |
| WQ9    | Mean | 74.5 | 2617 | 21.0 | 705  | 177  | 394  | 33.2 |
|        | SD   | 3.0  | 126  | 1.6  | 4    | 12   | 9    | 1.3  |
| WQ10   | Mean | 94.2 | 2472 | 20.5 | 613  | 153  | 471  | 37.7 |
|        | SD   | 6.5  | 220  | 1.4  | 41   | 13   | 33   | 1.7  |
| WQ11   | Mean | 64.0 | 2775 | 21.3 | 581  | 140  | 409  | 31.1 |
|        | SD   | 3.5  | 348  | 2.1  | 48   | 16   | 32   | 2.0  |
| WQ12   | Mean | 96.1 | 2542 | 24.0 | 658  | 166  | 434  | 35.5 |
|        | SD   | 12.1 | 84   | 1.0  | 50   | 12   | 22   | 2.8  |
| WQ15   | Mean | 62.5 | 2723 | 23.2 | 632  | 170  | 428  | 30.4 |
|        | SD   | 5.7  | 167  | 1.0  | 27   | 13   | 17   | 1.6  |
| WQ16   | Mean | 66.2 | 2813 | 21.8 | 525  | 144  | 435  | 31.8 |
|        | SD   | 1.9  | 575  | 1.8  | 70   | 15   | 61   | 3.8  |
A study on adsorption of metals by activated carbon in a large-scale (municipal) process of surface water purification

P, 154% for Ca, 120% for Cr, 113% for Sr, and 106% for Ti. During the study, in the case of this activated carbon, desorption of some elements during the filter operation was also observed. This applies in particular to Na, K, Mg, and Fe.

In the remaining filter chambers No. 9, 10, 11, 12, 15 and 16, which contained activated carbon of the WG-12 type, we observed a gradual increase in the concentrations of Ca, Mn, and Zn in used carbon in relation to new carbon after the first year of operation. In the case of Mn, the increase in all the filters was in the range of 577-982%, for Zn, 218-270%, and for Ca 119-163%. Moreover, in used activated carbon in comparison to new carbon, we observed a slight increase in the concentrations of Ti and Ni in most filters, and a slight decrease only in filter No. 11 (WG11) for Ti and in filter No. 10 (WG10) for Ni. In the case of Cu, the experiments showed irregular adsorption of this metal on the activated carbon, a small increase in filters No. 10 (WG10) and 12 (WG12) and a slight drop in filters No. 9 (WG9), 11 (WG11), 15 (WG15), 16 (WG16). Additionally, leaching of metals from the surface of activated carbon during its operation was observed in the filter test chamber. Desorption mainly of light elements such as K, Na, Mg, Ba, Sr, Fe, Al, Cr, and P occurred in all the filter chambers.

3.1. Statistical analysis

Tables of Pearson correlation coefficients show the dependences of the analyzed elements. The values of correlation coefficients for all sampling points and the selected explanatory variables are shown in Table 4. Summary of the data allows selecting specific elements for explanatory variables repeated in various activated carbons. During the test the correlation between the elements, the following conclusions were arrived at: the strongest line correlations depending on the level of the Pearson correlation coefficients $r \geq 0.90$ are observed between Na and K. Significant correlations ($r = 0.70-0.90$) are also found in the case of Fe, which is most strongly correlated with Al and Ti. P has the highest correlation coefficient for Cu. Then, Zn has the highest correlation coefficient for Mn and Ca. Sr correlates well with Ba. Na correlates to the greatest degree with Sr and Ba. K is particularly strongly correlated with Ba and Sr. Similarly, Ni shows a correlation with Ti, Al, and Fe. On the other hand, in the case of Al, the strongest correlation was observed for Ti and Ba. A linear relationship exists also for Cu and Al.

Measurement series were obtained by statistical correlation analysis using the variance correlation test (a kind of F-test) and Spearman’s test. Results of this statistical analysis are summarized in Table 5. The carbons characterized by the highest correlation (for $r_s > 0.95$) due to the concentration of studied elements are as follows: WG9 and WG11 (1.000), WG12 and WG15 (1.000), WG12 and WG16 (1.000), WG15 and WG16 (1.000), and WG9 and WG10 (0.988), WG9 and WG12 (0.988), WG9 and WG15 (0.988), WG9 and WG16 (0.988), WG10 and WG11 (0.988), WG11 and WG12 (0.988), WG11 and WG15 (0.988), WG11 and WG16 (0.988), and CH1 and CH2 (0.964), and CHn and CH2 (0.952). On the other hand, WGN and N4 (0.370) are activated carbons showing a low correlation (with

---

Table 4. Pearson correlation coefficients in all samples.

|   | Ca     | Mg     | Ba     | Sr     | Mn     | Ti     | Al     | Cr     | Cu     | Fe     | Ni     | K     | Na     | P     | Zn     | Pearson |
|---|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|-------|--------|-------|--------|---------|
|Ca | 0.58   | 0.74   | 0.50   | 0.65   | 0.48   | 0.43   | 0.51   | 0.52   | 0.77   | 0.24   | 0.34   | 0.45   | 0.46   | 0.21   | 0.85    |
|Mg | 0.74   | 0.58   | 0.74   | 0.50   | 0.65   | 0.48   | 0.51   | 0.52   | 0.77   | 0.24   | 0.34   | 0.45   | 0.46   | 0.21   | 0.85    |
|Ba | 0.50   | 0.74   | 0.58   | 0.74   | 0.50   | 0.65   | 0.48   | 0.51   | 0.77   | 0.24   | 0.34   | 0.45   | 0.46   | 0.21   | 0.85    |
|Sr | 0.65   | 0.50   | 0.74   | 0.58   | 0.74   | 0.50   | 0.65   | 0.48   | 0.51   | 0.77   | 0.24   | 0.34   | 0.45   | 0.46   | 0.21    |
|Mn | 0.48   | 0.43   | 0.65   | 0.50   | 0.74   | 0.58   | 0.74   | 0.50   | 0.65   | 0.48   | 0.43   | 0.51   | 0.52   | 0.77   | 0.24    |
|Ti | 0.51   | 0.48   | 0.51   | 0.65   | 0.48   | 0.43   | 0.51   | 0.52   | 0.77   | 0.24   | 0.34   | 0.45   | 0.46   | 0.21   | 0.85    |
|Al | 0.52   | 0.52   | 0.52   | 0.52   | 0.52   | 0.52   | 0.52   | 0.52   | 0.77   | 0.24   | 0.34   | 0.45   | 0.46   | 0.21   | 0.85    |
|Cr | 0.41   | 0.44   | 0.44   | 0.44   | 0.44   | 0.44   | 0.44   | 0.44   | 0.77   | 0.24   | 0.34   | 0.45   | 0.46   | 0.21   | 0.85    |
|Cu | 0.54   | 0.54   | 0.54   | 0.54   | 0.54   | 0.54   | 0.54   | 0.54   | 0.77   | 0.24   | 0.34   | 0.45   | 0.46   | 0.21   | 0.85    |
|Fe | 0.22   | 0.22   | 0.22   | 0.22   | 0.22   | 0.22   | 0.22   | 0.22   | 0.22   | 0.77   | 0.24   | 0.34   | 0.45   | 0.46   | 0.21    |
|Ni | 0.23   | 0.23   | 0.23   | 0.23   | 0.23   | 0.23   | 0.23   | 0.23   | 0.23   | 0.77   | 0.24   | 0.34   | 0.45   | 0.46   | 0.21    |
|K  | 0.54   | 0.54   | 0.54   | 0.54   | 0.54   | 0.54   | 0.54   | 0.54   | 0.54   | 0.77   | 0.24   | 0.34   | 0.45   | 0.46   | 0.21    |
|Na | 0.48   | 0.48   | 0.48   | 0.48   | 0.48   | 0.48   | 0.48   | 0.48   | 0.48   | 0.48   | 0.77   | 0.24   | 0.34   | 0.45   | 0.46    |
|P  | 0.22   | 0.22   | 0.22   | 0.22   | 0.22   | 0.22   | 0.22   | 0.22   | 0.22   | 0.22   | 0.22   | 0.77   | 0.24   | 0.34   | 0.45    |
|Zn | 0.21   | 0.21   | 0.21   | 0.21   | 0.21   | 0.21   | 0.21   | 0.21   | 0.21   | 0.21   | 0.21   | 0.21   | 0.77   | 0.24   | 0.34    |
Similar conclusions as in the case of Spearman’s test were received using the variance correlation test (e.g., high correlation: 4143 for carbons WG11 and WG15, low correlation: 0.004 for WGn and Nn).

Next, we analyzed the diversity of the elements in all carbons using one-way ANOVA and the Kruskal-Wallis one-way analysis of variance. The results are shown in Table 6. The Kruskal-Wallis test gives similar results as a more powerful one-way ANOVA. Values of F and chi gathered in Table 6 are the critical values for the corresponding levels of significance (5% and 1%) for the distribution of F and the distribution of chi-square. If the calculated value is larger than F or chi critical value, we should reject the null hypothesis (H0 – no differences between the carbons), and adopt the alternative hypothesis (H1) of the statistical variation for the elements in all carbons. In both new and used Chemviron carbons (CH), the biggest differences appear for strontium and the smallest ones for aluminum. From the point of view of the contents in Chemviron, all elements exhibit statistical variability, except for Al and Na. In new and used WG carbons, the largest differences appear for potassium and the lowest ones for iron. Contents of all elements in WG carbon are statistically different. Analysis of new carbons of Chemviron, Norit and WG types suggests that the largest differences occur for potassium and the lowest ones for calcium. In all the new carbons analyzed, concentrations of all elements show statistical differences.

In the case of Norit carbon, we have not applied the Kruskal-Wallis test or one-way ANOVA, because these methods are not recommended for only two series (Nn and N4). Therefore, in this type of carbon, elements were tested by the Mann-Whitney U test and the t-Student test (Table 7). The null hypothesis is that there is no difference between Nn and N4 activated carbons (H0), while the alternative hypothesis is differentiation of Nn and N4 activated carbons (H1). Using these tests, we notice statistical differences in all analyzed elements, except for Sr, Ti, Cr, and Fe.

### Table 5. Spearman’s rank correlation coefficient and variance correlation test.

|        | CHn | CH1 | CH2 | Nn | N4 | WGn | WG9 | WG10 | WG11 | WG12 | WG15 | WG16 | Sp test |
|--------|-----|-----|-----|----|----|-----|-----|------|------|------|------|------|----------|
| CHn    |     | 0.939 | 0.952 | 0.612 | 0.576 | 0.830 | 0.842 | 0.806 | 0.842 | 0.830 | 0.830 | 0.830 | CHn      |
| CH1    | 28.8 | 0.964 | 0.673 | 0.721 | 0.782 | 0.927 | 0.891 | 0.927 | 0.939 | 0.939 | 0.939 | 0.939 | CH1      |
| CH2    | 150 | 46.2 | 0.588 | 0.648 | 0.806 | 0.891 | 0.879 | 0.891 | 0.879 | 0.879 | 0.879 | 0.879 | CH2      |
| Nn     | 0.152 | 2.08 | 0.584 | 0.697 | 0.491 | 0.515 | 0.430 | 0.515 | 0.539 | 0.539 | 0.539 | 0.539 | Nn       |
| N4     | 0.473 | 5.81 | 1.40 | 15.2 | 0.370 | 0.758 | 0.733 | 0.758 | 0.770 | 0.770 | 0.770 | 0.770 | N4       |
| WGn    | 0.515 | 0.137 | 0.168 | 0.004 | 0.081 | 0.697 | 0.673 | 0.697 | 0.685 | 0.685 | 0.685 | 0.685 | WGn      |
| WG9    | 115 | 116 | 116 | 0.671 | 1.98 | 0.437 | 0.988 | 1.000 | 0.988 | 0.988 | 0.988 | 0.988 | WG9      |
| WG10   | 88.1 | 112 | 79.0 | 0.545 | 1.96 | 0.346 | 1462 | 0.988 | 0.976 | 0.976 | 0.976 | 0.976 | WG10     |
| WG11   | 56.2 | 335 | 104 | 1.26 | 3.51 | 0.257 | 438 | 284 | 0.988 | 0.988 | 0.988 | 0.988 | WG11     |
| WG12   | 49.5 | 413 | 69.6 | 1.19 | 3.54 | 0.298 | 459 | 437 | 1.434 | 1.000 | 1.000 | 1.000 | WG12     |
| WG15   | 59.8 | 323 | 90.9 | 1.18 | 3.26 | 0.296 | 679 | 448 | 4143 | 3669 | 1.000 | 1.000 | WG15     |
| WG16   | 39.4 | 874 | 70.7 | 1.60 | 4.52 | 0.172 | 218 | 189 | 1672 | 1272 | 1133 | 1133 | WG16     |
| F test | CHn | CH1 | CH2 | Nn | N4 | WGn | WG9 | WG10 | WG11 | WG12 | WG15 | WG16 | Sp test |
| F test - estimation of the variance: critical values: $F_{0.05} = 5.32; F_{0.01} = 11.26$ | CHn | CH1 | CH2 | Nn | N4 | WGn | WG9 | WG10 | WG11 | WG12 | WG15 | WG16 | Sp test |

3.2. Principal component analysis

Principal component analysis allowed us to find the relationship among all measured elements and activated carbon samples. All analytical results were put together in one 12×15 matrix (samples×elements) and were autoscaled. Then, the singular value decomposition (SVD) algorithm was adopted. After calculating the cumulative percentage of variance it was possible to see the percentage of the variability, described by all principal components. The first principal component (PC1) describes about 40% of the total variance, the first two PCs more than 70% and the first three PCs more than 80% of the total variance. Subsequent factors explain less and less volatility. Therefore, data analysis was conducted based on the first three main factors. Then, in order to examine the interactions between the elements analyzed, projections of weights of selected pairs of the main factors (PC 1 to PC 2 and PC 1 to PC 3) were drawn (Fig. 2). Elements, which are characterized by high absolute values of weights for the main component, contribute substantially to the creation of this factor. From the analysis of the projection of elements on the plane spanned by PC 1 and PC 2, it can be concluded that the variables that make the greatest contribution to the creation of the first principal component (PC 1) are the content of Mg and the contents of Al, Fe, Ni, Ba. The greatest contribution to the second principal component (PC 2) are the contents of Na, K, Sr and the contents of Mn and Zn. In the formation of
A study on adsorption of metals by activated carbon in a large-scale municipal process of surface water purification

the third factor (PC 3), the greatest contributions are the content of P and the content of Ti. A positive correlation can be noticed between the content of elements in the activated carbons, as follows: Na–K, Fe–Ni–Al–Ti and Zn–Mn–Ca. Additionally, there appears to be a lack of correlation between the contents of Mg, Na and K.

The projection of the main component scores (PC 1 to PC 2 and PC 1 to PC 3) was also plotted (Fig. 3). This projection shows the relations between all the analyzed activated carbon samples. When two data points on the plot are closer together, they are more similar to each other. The differences are larger when the distance increases [51]. On the PCA score plots, especially PC 1 to PC 3, there is an evident division into 3 groups: Nnew–N4 (first group); CH1–CH2 (second group); WG9–WG10–WG11–WG12–WG15–WG16 (third group). It may be noted that the unused activated carbon WGnew deviates significantly from the third group, much like the unused activated carbon CHnew deviates from the second group. In the third group, there are many activated carbons and, as shown by the analysis, they are similar to each other. The biggest differences within this group can be observed between the WG10 and WG11 activated carbons. In the case of first and second groups, the similarity within the group is smaller.

### Table 6. The results of one-way ANOVA and Kruskal-Wallis one-way analysis of variance for three types of activated carbons.

| CHn, Nn | Ca  | Sr  | Ba  | Mg  | Al  | Fe  | Zn  | Mn  | Cr  | Ni  | Cu  | P   | K   | Na  | Ti  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| K-W.    |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| ANOVA   |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
|         |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| WGn     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| K-W.    |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| ANOVA   |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
|         |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |

*K-W. – Kruskal-Wallis test

### Figure 2. Loading plots – projection of elements on the plane spanned by: (a) PC 1 and PC 2, (b) PC 1 and PC 3.
4. Conclusion

The method presented for determination of elements in the activated carbons studied using ICP-OES techniques allowed simultaneous determination of Ca, Mg, Ba, Sr, Mn, Ti, Al, Cr, Cu, Fe, Ni, K, Na, Zn, and P. It thereby allowed us to determine the degree of accumulation, as well as changes in concentrations of these elements in activated carbons used for more than one year in the water treatment process in Water Treatment Plant in Goczków, compared to new activated carbons. The experiment showed that metals usually accumulating in the activated carbons during the operation included Ca, Mn, Zn, and Cu.

Moreover, in each of the three types of activated carbons used in the study, we can distinguish such elements as Ba, Al, Cr, Ni, Ti, characterized by irregular accumulation during the operation of the filter. During
A study on adsorption of metals by activated carbon in a large-scale (municipal) process of surface water purification

Operation of a carbon filter under a constant flow of water, leaching of mainly light metals, such as K and Na, occurs. Other metals, in the form of easily soluble salts, are also leached, which is reflected in the results obtained by ICP-OES. On the basis of the results one may conclude that K and Na are the most mobile elements, because their losses caused by leaching from the surface of activated carbons in the first year of operation are observed for each type of carbon.

The introduction of carbon sorbent for water treatment in Water Treatment Plant Goczalkowice largely contributed to improvements in the quality of raw material supplied to customers, mainly with regard to taste and smell, as well as to reduction of basic parameters: color by 85%, absorbance in the UV range by 79%, oxidability by 54% (Table 8). Furthermore, use of ozonation and filtration by carbon adsorption beds allowed for 44% reduction in the dose of chlorine used in the final disinfection of water and resulted in reduced levels of THMs, especially chloroform, by ca. 80% [52].

This study showed that heavy metals are still present in the aquatic environment. Further analyses of activated carbons in subsequent years of filter operation needs to be undertaken to improve the water purification process, thereby improving the quality of treated water.

Acknowledgments

The authors would like to thank management and employees of Water Treatment Plant Goczalkowice for their valuable assistance and suggestions.

References

[1] H. Jankowska, A. Świątkowski, J. Choma, Węgiel aktywny - Activated carbon (WNT, Warsaw, 1985) (in Polish)
[2] H. Trevino-Cordero, L.G. Juárez-Aguilar, D.I. Mendoza-Castillo, V. Hernández-Montoya, A. Bonilla-Petriciolet, M.A. Montes-Morán, Ind. Crop. Prod. 42, 315 (2013)
[3] M. Haro, B. Ruiz, M. Andrade, A.S. Mestre, J.B. Parra, A.P. Carvalho, C.O. Ania, Micropor. Mesopor. Mater. 154, 68 (2012)
[4] C. Ingram, The Drinking Water Book: How to Eliminate Harmful Toxins from Your Water (Celestial Arts, Berkeley, 2006)
[5] S. Altenor, B. Carene-Melane, S. Gaspard, IJETM 10, 308 (2009)
[6] A. Demirbas, J. Hazard. Mater. 167, 1 (2009)
[7] J.M. Dias, M.C.M. Alvim-Ferraz, M.F. Almeida, J. Rivera-Utrilla, M. Sánchez-Polo, J. Environ. Manage. 85, 833 (2008)
[8] A. Demirbas, J. Hazard. Mater. 157, 220 (2008)
[9] F. Fu, Q. Wang, J. Environ. Manage. 92, 407 (2011)
[10] I. Gueguze, S. Dridi-Dhaouadi, F. Mhenni, Ind. Crop. Prod. 29, 197 (2009)
[11] W. Li, L. Zhang, J. Peng, N. Li, S. Zhang, S. Guo, Ind. Crop. Prod. 28, 294 (2008)
[12] J. Lach, E. Okoniewska, E. Neczaj, M. Kaczprzak, Desalination 206, 259 (2007)
[13] R.M. Schneider, C.F. Cavalin, M.A.S.D. Barros, C.R.G. Tavares, Chem. Eng. J. 132, 355 (2007)
[14] S.M. Manocha, Sadhana 28, 335 (2003)
[15] L. Dąbek, J. Hazard. Mater. B101, 191 (2003)
[16] M. Pérez-Candela, J.M. Martin-Martinez, R. Torregrosa-Maciá, Water Res. 29, 2174 (1995)
[17] K. Kadivelu, K. Thamaraiselvi, C. Namasivayam, Bioresour. Technol. 76, 63 (2001)
[18] M. Pasavento, A. Profumo, G. Alberti, F. Conti, Anal. Chim. Acta 480, 171 (2003)
[19] R. Leyva Ramos, L.A. Bernal Jacome, J. Mendoza Barron, L. Fuentes Rubio, R.M. Guerrero Coronado, J. Hazard. Mater. B90, 27 (2002)
[20] J. Rivera-Utrilla, M.A. Ferro-Garcia, I. Bautista-Toledo, Coll. Interface Sci. 5, 191 (2002)
[21] P.Y. Chang, Y.L. Wei, Y.W. Yang, J.F. Lee, Bull. Environ. Contam. Toxicol. 71, 791 (2003)
[22] M. Soylak, I. Narin, L. Elci, M. Dogan, Asian J. Chem. 13, 1097 (2001)
[23] A.A. Ensafi, T. Khayamian, M.H. Karbasi, Anal. Sci. 19, 953 (2003)
[24] L. Monser, N. Adhoum, Sep. Purif. Technol. 26, 137 (2002)
[25] E. Okoniewska, J. Lach, M. Kaczprzak, E. Neczaj, Desalination 206, 251 (2007)
[26] D. Satapathy, G.S. Natarajan, Adsorption 12, 147 (2006)
[27] E. Sikorska-Sobiegraj, S. Zieliński, Przem. Chem. 85, 189 (2006) (in Polish)
[28] H. Hasar, Y. Cuci, Environ. Technol. 21, 1337 (2000)
[29] S.E-S. Ghazy, S.E-S. Samra, A.E-F.M. Mahdy, S.M. El-Morsy, Anal. Sci. 22, 377 (2006)
[30] A.J. Groszek, Carbon 35, 1329 (1997)
[31] H. Jankowska, A. Świątkowski, L. Starostin, J. Ławrinienko-Omiecyńska, Adsorpcja jonów na węglu aktywnym - Ion adsorption on activated carbon (PWN, Warsaw, 1991) (in Polish)
[32] S. Ostasiewicz, Z. Rusnak, U. Siedlecka, Statystyka. Elementy teorii i zadania - Statistics. Elements of theory and jobs (University of Economics Press, Wroclaw, 1998) (in Polish)
[33] R. Shimura, T. Nikaido, M. Yamauti, M. Ikeda, J. Tagami, Dent. Mater. J. 24, 70 (2005)
[34] F. Nedel, F.N. Soki, M.C.M. Conde, B.D. Zeittin, S.B.C. Tarquino, J.E. Nör, F.K. Seixas, F. Demarco, Int. Endod. J. 44, 59 (2011)
[35] W. Volk, Statystyka stosowana dla inżynierów - Applied statistics for engineers (WNT, Warsaw, 1973) (in Polish)
[36] P.H. Ramsey, J. Educ. Behav. Stat. 14, 245 (1989)
[37] Y. Cohen, J.Y. Cohen, Statistics and Data with R: An applied approach through examples (John Wiley&Sons, London, 2008)
[38] D. Inal-Ince, S. Savci, H. Arikanto, M. Saglam, N. Vardar-Yaglı, M. Bosnak-Guclu, D. Dogru, Spine J. 9, 981 (2009)
[39] W.H. Kruskal, W.A. Wallis, J. Am. Stat. Assoc. 47, 583 (1952)
[40] A. Łomnicki, Wprowadzenie do statystyki dla przyrodników - Introduction to statistics for scientists (PWN, Warsaw, 1995) (in Polish)
[41] M. Ikeda, K. Tsubota, T. Takamizawa, T. Yoshida, M. Miyazaki, J.A. Platt, Oper. Dent. 33, 702 (2008)
[42] M. Marcondes, M.P.G. Panahos, A.M. Spohr, E.G. Mota, I.N.L. Da Silva, A.A. Souto, L.H. Burnett Jr, J. Biomed. Mater. Res. B 90, 388 (2009)
[43] D. Laguna, C. Lopez-Cortijo, I. Millan, F.M. Gonzalez, J.R. Garcia-Berrocal, J. Otolaryngol-Head N. 37, 324 (2008)
[44] V.E. Méndez, C.M. Bacon, M. Olson, S. Pechers, D. Herrador, C. Carranza, L. Trujillo, C. Guadarrama-Zugasti, A. Cordón, A. Mendoza, Renew. Agr. Food Syst. 25, 236 (2010)
[45] Student, Biometrika 6, 1 (1908)
[46] Student, Biometrika 6, 302 (1908)
[47] R. Gupta, T. Ahmed, B. Banerjee, M. Bhatia, J. Headache Pain 10, 161 (2009)
[48] B.M.G. Vandeginste, D.L. Massart, L.M.C. Buydens, S. de Jong, P.J. Lewi, J. Smeyers-Verbeke, Handbook of Chemometrics and Qualimetrics, Part B (Elsevier, Amsterdam, 1998)
[49] W. Wu, D.L. Massart, S. de Jong, Chemometr. Intell. Lab. 36, 165 (1997)
[50] W. Wu, D.L. Massart, S. de Jong, Chemometr. Intell. Lab. 37, 271 (1997)
[51] I. Stanimirova, M. Polowniak, R. Skorek, A. Kita, E. John, F. Buhl, B. Walczak, Talanta 74, 153 (2007)
[52] B. Walczuk, M. Zin, K. Gawlik, A. Szostak, In: Z. Dębowski (Ed.), Wprowadzenie procesów ozonowania wtórnego i filtracji na granulowanym węgle aktywnym w Zakładzie Produkcji Wody Goczałkowice - The introduction of secondary ozonation and filtration on granular activated carbon processes in Water Treatment Plant Goczałkowice. Węgiel aktywny w ochronie środowiska i przemyśle - Activated carbon in environmental protection and industrial (Czestochowa University of Technology Press, Czestochowa, 2004) 290