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Enhancement of coagulation process with powdered activated carbon in PCB and heavy metal ions removal from drinking water

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ABSTRACT

Suitability of powdered activated carbon CWZ-30 for enhancing the coagulation process used for the removal of contaminants from surface water was evaluated. Aluminium sulphate, aluminium chloride and pre-hydrolysed polyaluminium chloride (PAX18 and PAX-XL1905) were used as coagulants, and the following parameters were analysed in water sampled from the Kozłowa Góra dam reservoir (Poland): concentrations of heavy metals (Cu, Cd, Ni, Pb) and indicator PCBs (28, 52, 101, 118, 138, 153, 180). The highest reduction in heavy metal concentration was obtained with the use of PAX-XL1905. It amounted, in case of copper, cadmium, nickel and lead, to 64, 39, 18 and 85%, respectively. Enhancement of coagulation with powdered activated carbon CWZ-30 in the amount of 30 mg L^{-1}, increased the efficiency of these metals removal up to 79, 53, 26 and 95%, respectively. The best results for total PCB concentration removal were obtained with the use of PAX18. Application of powdered activated carbon also allowed to obtain better effects of PCB removal from water. Therefore, the coagulation process enhanced with powdered activated carbon had crucial impact on the reduction of analysed heavy metals concentration and indicator PCBs.

Keywords: Heavy metals; Polychlorinated biphenyls; Coagulation process; Powdered activated carbon; Drinking water

1. Introduction

Negative impact of micropollutants on water consumers' health causes the necessity for removal of these substances from drinking water. Choice of micropollutant removal processes is determined by their type, properties and form of occurrence. Organic micropollutants present in surface water are mainly surface active substances, pesticides, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, whereas inorganic are heavy metal ions. In the course of removal method selection, more attention is paid to the properties of the pollutants contained in the treated water. Different technologies are not equally effective in removing substances with different properties.

According to the literature data, for organic micropollutants removal, adsorption on activated

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carbons is essential. Adsorption properties of carbons result from microporous structure and developed specific surface area, on which there are a number of reactive centres. In the literature, many factors determining the efficiency of adsorption are described, in particular chemical properties of the adsorbed compound, pH of the solution and the type of chemical surface formations of the carbon. In the literature there are few examples of research on PCB removal from polluted water, despite the fact that they are harmful chemical compounds. The level of PCB toxicity depends on the number and the substitution location of chlorine atoms in the biphenyl molecule. These compounds condense in the subsequent stages of movement in the food chain and become dangerous to humans and animals. PCB in the environment usually occur as a mixture of congeners. On a technological scale, these compounds were obtained from a direct reaction of biphenyl with chlorine, obtaining a mixture of congeners with a composition depending on the proportion of chlorine and biphenyl and the conditions of the synthesis. PCB as non-ionic, hydrophobic organic compounds are very poorly soluble in water and soluble in fats, oils and non-polar solvents (hexane, isooctane) [1,2]. PCB lipophilicity increases with the increasing number of chlorine atoms in the biphenyl molecule. PCB congeners solubility in water is varied and ranges from 1.3×10^3 μg L^{-1} for monochlorobiphenyl to 0.02 μg L^{-1} for decachlorobiphenyl. PCB solubility in water and in organic solvents affects, amongst others, their stability in the environment, and plays an important role in their degradation. Lipophilic properties and low pressure of PCB saturated vapour [3,4] determine sorption on polar surface of solids, especially rich in organic compounds [5–7]. Sorption process intensifies with increasing number of chlorine atoms in the biphenyl molecule. This indicates that higher chlorinated biphenyls sorb better than lower chlorinated, however coplanar congeners containing from four to six chlorine atoms sorb stronger than higher chlorinated biphenyls due to their flat spatial structure. The presence of PCB in drinking water may result for example from water disinfection with chlorine. It has been shown that the side effect of chlorine usage is formation of new organic compounds, such as: halomethanes, acetonitriles, chlorophenols, chloropicrin, PCB and a variety of other organic compounds with significant toxicity. According to the EPA regulations, maximum PCB concentration in drinking water is 0.5 μg L^{-1}. In Polish legislation on the quality of drinking water, PCB content is not included. Literature data show high efficiency of activated carbon in removal of disinfection by-product precursors [8], and other organic micropollutants [9].

Adsorption efficiency is not always satisfactory, and it depends on the type of adsorbates being removed. This process should be preceded by preliminary water treatment processes, in which coagulation plays an important role. Efficiency of the coagulation process depends on physico-chemical composition of water, pH value, type and dosage of coagulants. For coagulation of contaminants, salts of aluminium and iron are mainly used. The most often used aluminium coagulants are aluminium sulphate $Al_2(SO_4)_3$ and aluminium chloride $AlCl_3$. In recent years, the usage of pre-hydrolysed coagulants is more and more popular, e.g. alkaline polyaluminium chlorides with general formula $Al_n(OH)_mCl_{3n\text{-}m}$. In solutions of polyaluminium chlorides, besides monomers Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, which are also present in solutions of non-hydrolysed aluminium coagulants, presence of many polymerized aluminium hydroxyl complexes with general formula $Al_p(OH)_q^{(3p-q)+}$, e.g. $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$, $Al_13O_4(OH)_{24}^{7+}$, was identified. Polycationic products of preliminary hydrolysis of aluminium, after addition of polyaluminium chlorides to the treated water, undergo the hydrolysis to $Al(OH)_3$ far more slowly than aluminium present in the solution of aluminium sulphate. This results in the fact that the usage of polyaluminium chlorides is more effective in destabilization of negatively charged colloids, which cause mainly water colour and turbidity, in comparison to the results obtained with the usage of aluminium sulphate. Properly conducted coagulation can also provide removal of heavy metal ions [10,11], and organic micropollutants [12–14].

In order to intensify the removal of organic matter from water, the coagulation process can be conducted in combination with adsorption on activated carbon. The efficiency of organic contaminant removal in the combined process of coagulation and adsorption on powdered activated carbon is limited by the value of the dissociation constant of removed organic compounds, the chemical nature of the adsorbent surface, its pore structure, and also the type of developed products of used coagulant hydrolysis. Fabris et al. [15] analysed the efficiency of aluminium sulphate coagulation supported by powdered activated carbon in the removal of dissolved organic compounds. In the study, three types of carbon were used, with different pore structure, i.e. microporous carbon, mesoporous, and carbon with diverse pores. The highest rate of removal of dissolved organic carbon (44%) was obtained using the carbon with diverse pore structure. Moreover, after introduction of carbonaceous adsorbents into the system with coagulation, an increase in the degree of removal of organic compounds with lower molecular weights was observed. Applying the coagulation process and then the filtration on granular activated carbon has proven to be very effective in the removal of certain organic micropollutants in the treatment of drinking water [14,16,17].

Li et al. [18] conducted studies on assessing the effectiveness of the coagulation process in removal of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) from suspended particulate matter and treated water. 99% removal efficiency of PCDD/Fs was demonstrated, after application of ferric chloride and polyaluminium chloride, slightly lower (97–98%) was obtained for aluminium sulphate. Used coagulants were selective in removal of particular PCDD/Fs. Better removal of PCDD with a low degree of chlorine substitution (tetra and penta-substituted) was demonstrated. In the literature, there are few examples of research on PCB removal from contaminated water, and this applies to both unit as well as combined processes [19]. Kawashima et al. [20] studied the effect of physicochemical characteristics of carbonaceous adsorbent for dioxin-like polychlorinated biphenyl adsorption. Considering the similarity of chemical properties of PCB and PCDD, for polychlorinated biphenyl elimination from water, research achievements in PCDD/Fs removal can be used [18,21].

The aim of this research was to evaluate the efficiency of coagulation process, adsorption on activated carbon, and coagulation enhanced by powdered activated carbon, in removal from surface water of turbidity, dissolved organic carbon, heavy metal ions (copper, nickel, cadmium and lead), and PCB with codes: 28, 52, 101, 118, 138, 153 and 180, with the use of non-hydrolysed and pre-hydrolysed coagulants.

2. Materials and methods

2.1. Materials

For the research surface water from Kozłowa Góra dam reservoir was used, which is the source of water for Water Treatment Plant in Wymysłów (Poland, Silesian voivodeship). The water composition was modified in order to obtain concentration of copper, nickel, cadmium, and lead ions equal approx. 0.4 mg L^{-1}, by introducing to water appropriate amount of solution prepared with $Cu(NO_3)_2{\cdot}3H_2O$, $NiCl_2{\cdot}6H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$ and $Pb(NO_3)_2$ salts. Standard mixture PCB MIX 24 was also added to water in order to obtain 500 ng L^{-1} concentration of each congener. PCB MIX 24 mixture was composed with solution of congeners: 28, 52, 101, 118, 138, 153 and 180. The amount of PCB MIX 24 standard added to analysed water was selected, so that the concentration was equal to the limit value of PCB in drinking water, recommended by the EPA.

Non-hydrolysed salts $Al_2(SO_4){\cdot}18H_2O$ and $AlCl_3{\cdot}6H_2O$ were used as coagulants, produced by POCH company in Gliwice city (Poland), and hydrolysed salts, polyaluminium chlorides with commercial names PAX18 and PAX-XL1905, produced by KEMIPOL company in Police city (Poland). Commercial solutions of polyaluminium chlorides had alkalinity equal respectively 41 and 85%. The alkalinity is determined by the ratio of the number of OH^- moles to Al^{3+} in the coagulant, defined as the coefficient $r = [OH^-]/[Al^{3+}]$. The relation between the "r" value and the alkalinity of the coagulant is as follows: alkalinity (%) = $r/0.03$. Commercial solution of PAX18 contained 17.0% of Al_2O_3, while PAX-XL1905 11.3% of Al_2O_3. Polyaluminium chlorides were chosen based on previously conducted research [22]. For the analyses, coagulant solutions were prepared by diluting commercial products so that they contained 1.0 gAl L^{-1}.

In the study, powdered activated carbons were also used, with trade names AKPA-22, CWZ-22, CWZ-30, manufactured by GRYFSKAND company in Hajnówka city. The characteristics of the carbons are shown in Table 1. The carbons were characterized by the specific surface area 1,134–914 g m^{-2}, iodine number 1,190–940 mg g^{-1} and methylene number 30–28 cm^3.

2.2. Jar test procedure

The process of adsorption and coagulation was conducted in laboratory conditions. In the first stage

Table 1
Selected properties of powdered activated carbons

Properties	Unit	Powdered acivated carbon		
		AKPA-22	CWZ-22	CWZ-30
Specific surface area	$m^2\ g^{-1}$	914	960	1,134
Iodine number	$mg\ g^{-1}$	940	1,032	1,190
Methylene number	cm^3	28	29	30
Granulation < 0.06 mm	%	98	93	90

of the research, the adsorption process was conducted. One litre of analysed modified water was measured into glass beakers with a volume of 2 L, and powdered activated carbons were introduced. Applied dose of carbons was equal to 30 mg L^{-1}. Using a mechanical stirrer, mixing was performed with 200 RPM for 15 min. Then the carbon was separated from the water by filtration of the samples through a paper filter.

In the second stage, the coagulation process was conducted in glass beakers with 3-L volume, to each beaker 2 L of analysed water was measured. The coagulants were introduced in the amount of 3 mgAl L^{-1}, and with the use of a mechanical stirrer fast stirring was executed for 2 min (applying 200 RPM), and then slow stirring for 15 min (20 RPM). After this time, the samples were subjected to 1 h of sedimentation. Afterwards 0.7 L of water was decanted and analysed.

In the third stage, the coagulation process was combined with the adsorption on powdered activated carbon. The study was conducted in the way described above, with following modifications: fast stirring was applied for 4 min and activated carbon was introduced during that stirring, 2 min after the coagulant. In this stage, powdered activated carbon CWZ-30 was used. The carbon dosage amounted to 30 mg L^{-1} of water.

2.3. Analytical methods

Water quality indicators, before and after the coagulation process and/or the adsorption process, were determined by means of the following methods: pH—potentiometric, turbidity—nephelometric, dissolved organic carbon DOC—after water filtration through a 0.45-μm membrane filter, infrared spectrophotometry (carbon analyser multi N-C, Analytic Jena), heavy metal ions—atomic absorption spectrometry (spectrometer novAA 400, Analytic Jena), aluminium—Aquaquant 14413 test.

PCB analysis methodology was described in the literature [23]. For PCB separation from water, solid phase extraction (SPE) was used, using Bakerbond columns with Octadecyl C_{18} filling. The extract was condensed in vacuum and then subjected to qualitative and quantitative analysis by gas chromatography and mass spectrometer (GC-MS).

3. Results and discussion

Surface water was characterized by alkaline reaction (pH 7.5), and turbidity equal 7.9 NTU. DOC content amounted to 13.3 mgC L^{-1}. Concentration of heavy metal ions: copper, nickel, cadmium, lead before water modification amounted to respectively 0.08, 0.01, <0.01, 0.06 mg L^{-1}, after the modification approx. 0.4 mg L^{-1}. Total concentration of PCB in raw water amounted to 326.8 ng L^{-1}. Dominant congeners were higher chlorinated PCB: 138 (54.8 ng L^{-1}), 153 (55.4 ng L^{-1}), and 180 (70.9 ng L^{-1}). The lowest concentration was shown for PCB 28 (10.9 ng L^{-1}).

3.1. Turbidity

The results of turbidity measurement showed that the most effective for its removal under coagulation operation conditions (temperature 21–22°C, pH 7.5–7.0) was PAX-XL1905, usage of which decreased turbidity from 7.9 down to 1.5 NTU. Conducting coagulation with PAX18, value of 2.8 NTU was obtained, whereas with aluminium sulphate and aluminium chloride 3.4 and 2.3 NTU were obtained, respectively. The highest efficiency of PAX-XL1905 coagulant could result from the fact that in solution of this reagent products of preliminary hydrolysis with high positive charge are present, which create good conditions for destabilization of negatively charged pollutions that cause water turbidity. This is confirmed by the research [24,25]. An advantageous aspect of coagulation conducted with the use of PAX-XL1905 was also low concentration of aluminium remaining after the process (below 0.05 mg L^{-1}).

3.2. DOC and heavy metals

The effects of reduction of organic substances content determined as DOC, and concentration of copper, nickel, cadmium, and lead ions, depending on the type of used powdered activated carbon (AKPA-22, CWZ-22, and CWZ-30), coagulant, and coagulant + powdered activated carbon CWZ-30 are presented in Table 2.

The use of carbons CWZ-30, CWZ-22, as well as AKPA-22 resulted in a slight increase in the water pH, from 7.5 up to max 7.7. An approx. 9–14% reduction in DOC content was obtained. Better results were obtained using AKPA-22 carbon than with the use of carbons CWZ-22 and CWZ-30. In case of heavy metals, an approx. 31–38% removal from water for copper was obtained, 18–24% for cadmium, 13–18% for nickel, and 38–46% for lead, with an indication for achieving better results with the use of carbon CWZ-30.

In the presented study, unmodified carbons (obtained from the manufacturer) were used, therefore their suitability for the removal of heavy metals was limited. Sorption capacity and exchangeable capacity

Table 2
Effect of powdered activated carbon addition on DOC and heavy metal ions in water during adsorption and coagulation

Coagulant, powdered carbon	DOC mg L^{-1}	Al mg L^{-1}	Heavy metal ions, mg L^{-1} Copper	Nickel	Cadmium	Lead
Raw water	13.3	<0.05	0.39[a]	0.38[a]	0.38[a]	0.39[a]
AKPA-22	11.4	–	0.27	0.33	0.31	0.24
CWZ-22	11.9	–	0.25	0.31	0.30	0.22
CWZ-30	12.1	–	0.24	0.31	0.29	0.21
$Al_2(SO_4)_3$	9.5	0.25	0.24	0.31	0.30	0.25
$AlCl_3$	9.3	0.30	0.22	0.32	0.28	0.21
PAX18	9.8	0.45	0.17	0.34	0.28	0.19
PAX-XL1905	9.0	<0.05	0.14	0.31	0.23	0.06
$Al_2(SO_4)_3$ + CWZ-30	8.6	0.15	0.16	0.30	0.29	0.07
$AlCl_3$ + CWZ-30	8.3	0.15	0.15	0.29	0.30	0.08
PAX18 + CWZ-30	7.4	0.10	0.11	0.31	0.27	0.04
PAX-XL1905 + CWZ-30	6.3	<0.05	0.08	0.28	0.18	0.02

[a] Water was modified.

of activated carbon depends on the amount and the degree of dissociation of oxygen functional groups present on its surface. Surface oxides with acidic nature exchange cationic metal forms, while the exchange of anionic forms is determined by alkaline functional groups. Technical activated carbons possess relatively few surface oxygen connections, which can be involved in metal adsorption. Creating favourable conditions for the process, e.g. correction of water pH, change in the chemical form of pollution or the use of specially prepared adsorbents, can significantly improve the efficiency of heavy metal removal. By modifying the activated carbon, its sorptive capacity was improved, regarding lead, copper, cadmium and nickel ions [26,27].

Reduction in DOC content during the coagulation process amounted to 26–32%, with powdered activated carbon enhancement 35–53%.

In case of heavy metal ions, the best effects were obtained during the coagulation process for lead removal. Concentration of this metal ions was decreased from approx. 0.4 mg L^{-1} down to respectively 0.25, 0.21, 0.19 and 0.06 mg L^{-1} with the use of respectively $Al_2(SO_4)_3$, $AlCl_3$, PAX18 and PAX-XL1905, which gives efficiency equal respectively 36, 46, 51 and 85%. In case of other metals, removal efficiency of copper ions amounted to 38–64%, cadmium 21–39% and nickel 11–18%. Heavy metal concentration reduction is the highest in pH range in which exists the possibility of formation of poorly soluble heavy metal compounds. During the conducted study, in pH range of 7.7–7.0, analysed metals occurred mainly in cationic forms (Cu^{2+}, Cd^{2+}, $CdCl^{+}$, Pb^{2+}, $Pb(OH)^{+}$, Ni^{2+}), in case of copper also $CuCO_3$ [28,29]. Therefore, metal removal was determined by adsorption, surface complexation, and ionic exchange.

Comparison of the percentage removal of ions of copper, nickel, cadmium and lead, using 3 mg Al L^{-1} coagulant dosage, and CWZ-30 powdered activated carbon in the amount of 30 mg L^{-1}, is shown in Fig. 1.

Evaluating the importance of adsorption in analysed heavy metal removal, only in case of lead ion's removal, significant influence of coagulation enhancement by powdered activated carbon was discovered. Using activated carbon CWZ-30 and respectively $Al_2(SO4)_3$, $AlCl_3$, PAX18 and PAX-XL1905, a decrease in lead ion concentration by 82, 79, 90 and 95% was obtained. The removal of copper, cadmium and nickel, with the usage of PAX-XL1905 and carbon CWZ-30 amounted to 79, 53 and 26%, respectively. The best

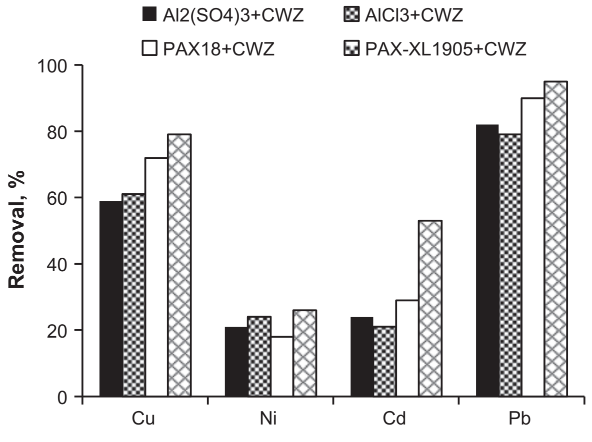

Fig. 1. Percentage of removal of heavy metals from surface water.

results obtained in case of lead ion removal can result both from adsorption, as well as from precipitation of poor solubility in water of lead compounds during the coagulation process, and micro-precipitation in the pores of activated carbon.

3.3. PCB

The results for PCB removal from water in the coagulation process, the adsorption process, and the coagulation enhanced by powdered activated carbons are presented in Table 3. Selectivity of chosen PCB congeners removal, depending on used coagulant, was demonstrated. Using $AlCl_3$ and PAX18, removal of all PCB congeners in analysed water was obtained, in the range from 17 up to 82%. The usage of PAX-XL1905 and $Al_2(SO_4)_3$ coagulants did not cause the removal of hexa- and heptachlorobiphenyls. Amongst analysed coagulants, the most efficient was PAX18, which usage allowed for decreasing congener content from 44 (PCB 28) to 82% (PCB 153).

The coagulation effectiveness in removing PCB arises from the fact that these compounds sorb well on the organic matter, which is confirmed by the literature data. According to [21,30], coagulation preference for PCDD/Fs removal from water results primarily from the fact that these compounds are bond to natural organic matter (NOM), and during coagulation will be removed together with the NOM particles. The obtained results confirm a relation between PCB hydrophobicity (expressed by the n-octanol–water partition coefficient—$K_{o/w}$) and the coagulation effectiveness in removal of these contaminants from water. According to the publication [31], for compounds demonstrating log $K_{o/w} > 3.2$, a high efficiency of their removal in the coagulation process is achieved. The log $K_{o/w}$ value of analysed PCB equals to from 5.80 to 8.27, which explains the high efficiency of the coagulation process in their removal. For all analysed coagulants, it has been demonstrated that with increasing log $K_{o/w}$ of PCB, the removal efficiency of indicator congeners increases in the range from PCB 28 to PCB 138. This relation was not observed for PCB 153, indicating that the coagulation is also influenced by the structure of the compound [32], i.e. the spatial arrangement of chlorine atoms in the biphenyl molecule.

The adsorption onto the powdered activated carbon allowed to reduce the concentration of analysed congeners max. to 82%. A correlation between PCB adsorption effectiveness and specific surface area of the powdered activated carbon was demonstrated. According to the publication [20], activated carbon with a surface area of 700–1,200 $m^2 g^{-1}$ and micropores with a diameter of 0.7–0.8 nm, exhibited a high activity for PCB adsorption, and the capacity of mesopores of the activated carbon affected the rate of the adsorption and the adsorption equilibrium. Liyan et al. [21] demonstrated the efficiency of powder-activated carbon, granular-activated carbon in hydrophobic organic chemicals (HOCs) removal in the range of 73.4–89.2%, which is confirmed by the obtained research results. Used in the study powdered activated carbons AKPA-22, CWZ-22 and CWZ-30 were characterized by specific surface area of, respectively, 914, 960 and 1,134 $m^2 g^{-1}$. AKPA-22 was characterized by the smallest iodine number, while CWZ-30 the highest, granulation decreased in the following order:

Table 3
Concentration of indicator PCB in water after enhancement of coagulation process with powdered activated carbon

	Concentration, ng L^{-1}						
Coagulant, powdered carbon	PCB 28	PCB 52	PCB 101	PCB 118	PCB 138	PCB 153	PCB 180
Raw water[a]	510.9	517.0	529.6	553.8	554.8	554.7	570.9
AKPA-22	511.0	517.2	530.1	553.8	555.1	571.0	590.1
CWZ-22	125.9	192.0	262.3	184.0	279.1	294.9	336.0
CWZ-30	105.0	182.2	216.0	142.0	250.3	279.2	316.0
$Al_2(SO_4)_3$	270.2	280.0	231.3	211.0	203.1	210.0	679.0
$AlCl_3$	300.1	251.9	210.0	271.1	245.2	280.8	504.7
PAX18	289.4	229.3	159.9	192.1	149.4	162.0	306.1
PAX-XL1905	390.3	349.3	289.9	393.6	568.8	382.9	512.3
$Al_2(SO_4)_3$ + CWZ-30	51.9	88.2	99.1	65.9	94.9	97.2	197.9
$AlCl_3$ + CWZ-30	113.0	194.4	176.6	93.7	174.0	173.8	162.5
PAX18 + CWZ-30	58.5	105.3	99.4	100.6	118.5	113.6	97.9
PAX-XL1905 + CWZ-30	33.8	47.5	52.4	78.0	79.4	83.2	131.5

[a] Water was modified with PCB MIX 24 standard.

AKPA-22, CWZ-22, CWZ-30. The iodine number is commonly used as a parameter of quality control in the production and regeneration of activated carbon, and usually it is not a measure of the carbon capability of compound adsorption. The basic parameters determining the efficiency of adsorption of pollutants with different sizes include specific surface area of activated carbon, which was confirmed by the conducted studies. The best results were obtained using activated carbon CWZ-30, which was characterized by the highest specific surface area. PCB congener concentration in water after the adsorption process onto the CWZ-22 carbon were the lowest and ranged from 105.0 to 316.0 ng L^{-1}. For this sorbent, a reduction in analysed PCB congener concentration in water was obtained in the range of 55 (PCB 180)–82% (PCB 118). Satisfactory results were also obtained for the powdered activated carbon CWZ-22 with specific surface area of 960 m^2 g^{-1}, where the PCB removal efficiency amounted to from 51 (PCB 180) to 77% (PCB 28). The least effective activated carbon in sorbing PCB (0–43%) was AKPA-22, with the smallest specific surface area.

Improved efficiency of PCB adsorption was obtained for lower chlorinated congeners, which does not confirm the rule that with an increase in the molecular weight of chemical compounds, their adsorption increases [33]. However it should be noted that the adsorption is affected not only by the molecular weight, but also by the spatial structure of the molecule, solubility, ionic strength and the temperature of the solution in which the adsorption process occurs [16,17]. According to the publications, dioxins and non-*ortho* PCB with a planar structure have a higher adsorption rate in comparison to *ortho*-substituted DL-PCB [20,34]. Analysed PCB congeners have a different arrangement of the chlorine atoms in the biphenyl molecule, i.e. in the *ortho*, *meta* and *para* positions, which may limit the interaction of PCB congener molecules with carbon surface area. The phenyl rings in the PCB molecule can undergo a rotation around the central carbon–carbon bond. Depending on the site of substitution and the amount of chlorine atoms, the two rings adopt different spatial configuration. The greatest influence on limiting the freedom of rotation has the substitution of chlorine in at least one *ortho* position in both rings. Increasing the number of substituents in *ortho* positions, affects the reduction in the rotation of PCB molecule. The analysed congeners were divided into two groups, depending on the number of chlorine atoms, the mono-*ortho* PCB (28, 118) and di-*ortho* PCB (52, 101, 138, 153, 180). The efficiency of the mono-*ortho* PCB adsorption ranged from 43 to 82%, and was higher than the efficiency of the di-*ortho* PCB adsorption (0–67%). Similar results were obtained by Kawashima et al. [20]. The authors obtained the highest adsorption rate for non-*ortho* PCB (34–100%), the mono-*ortho* PCB rate was in the range of 4–89%, and for di-*ortho* PCB the lowest adsorption rates were achieved (0–23%).

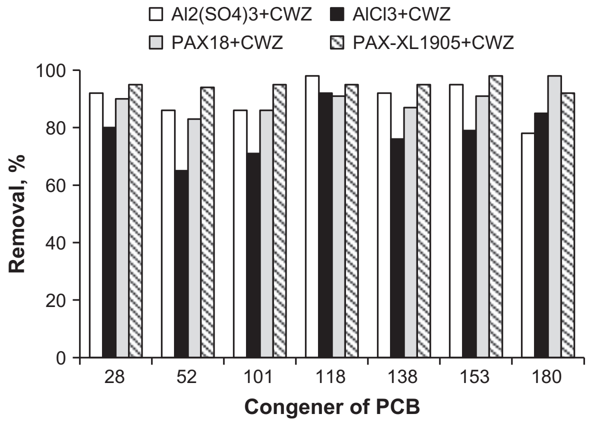

Fig. 2. Percentage of removal of PCBs from surface water.

Using the obtained results and the experience of other authors [9,35], in further studies the coagulation process enhanced by the adsorption on CWZ-30 carbon, which demonstrated the best efficiency for sorbing PCB, was implemented.

The best results were obtained applying an enhancement of the coagulation process with powdered activated carbon (Fig. 2), using the coagulation process with PAX-XL1905 coagulant, enhanced by CWZ-30 activated carbon, where concentration of all analysed PCB congeners in water was decreased by the range of 92 (PCB 180)–98% (PCB 153). Acceptable results were also obtained for other samples with addition of $Al_2(SO_4)_3$ + CWZ-30, $AlCl_3$ + CWZ-30 and PAX18 + CWZ-30, for which the efficiency of PCB removal amounted to respectively: 78–98, 65–92 and 83–98%.

The coagulation plays an important role in the water treatment technology, but its ability to remove PCB is lower than in case of combined processes. Only a combination of the coagulation and the adsorption creates a new quality in the removal of these organic micropollutants from water.

4. Conclusions

Conducted research allow to draw the following conclusions:

(1) Removal selectivity of chosen PCB congeners was demonstrated, depending on the used coagulant; with the usage of $AlCl_3$ and PAX18

removal of all PCB congeners was obtained, whereas with the use of PAX-XL1905 and $Al_2(SO_4)_3$ hexa- and heptachlorobiphenyls were not removed.

(2) The adsorption on powdered activated carbon allowed to reduce the concentration of analysed congeners max. to 82%; the best results were obtained using activated carbon CWZ-30, which was characterized by the highest specific surface area.

(3) Application of pre-hydrolysed salts (PAX-XL1905 and PAX18) in the coagulation process was more effective in reducing the concentration of copper and lead ions with respect to the usage of non-hydrolysed salts ($Al_2(SO_4)_3$ and $AlCl_3$).

(4) The best effects for removal of analysed micropollutants were obtained after the coagulation process with the use of polyaluminium chloride PAX-XL1905 and powdered activated carbon; a decrease in concentration of indicator PCB congeners in water was obtained in the range of 92–98%, lead ions 95%, and dissolved organic carbon content 53%.

(5) The advantageous aspect of the coagulation enhanced by activated carbon was obtaining lower concentration of aluminium remaining in purified water.

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