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-hydrolyzed polyaluminium chloride (PAX18 and PAX-XL1905) were used as coagulants, and the following parameters were analysed in water samples from the Kozłowa Góra dam reservoir (Poland): turbidity, concentrations of heavy metals (Cu, Cd, Ni, Pb) and indicator PCBs (28, 52, 101, 118, 138, 153, 180).

Composition of water was modified in order to obtain concentrations of each heavy metal of ca. 0.4 mg L^{-1} with implementation of particular amounts of cadmium-, cooper-, lead nitrate and nickel chloride. In order to obtain concentration of 500 ng L^{-1} in case of each congener, a standard mixture PCB MIX 24, which consisted of indicator congeners, was added to water.
By applying coagulants: $Al_2(SO_4)_3$, $AlCl_3$, PAX18, PAX-XL1905, in amount of 3 mg Al L^{-1}, 57, 71, 65, and 81% removal of water turbidity was obtained, respectively. 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. The best results for total PCB concentration removal was obtained with the use of PAX18. Selectivity of chosen PCB congeners removal were, depending on applied coagulant, was demonstrated. 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 97%, respectively. Application of powdered activated carbon allowed also to obtain better effects of PCB removal from water. Therefore the coagulation process enhanced with powdered activated carbon had crucial impact on reduction of analyzed 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 cause 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. According to the literature data, for organic micropollutants removal, adsorption on activated carbon is essential. Adsorption efficiency is not always satisfactory, and it depends on type of adsorbates being removed. This process should be preceded by preliminary water treatment processes, in which coagulation plays an important role. Efficiency of coagulation process depends on physico-chemical composition of water, pH value, type and dosage of coagulants. The effect of an efficient coagulation is a decrease mainly in turbidity, and in water colour. Properly conducted coagulation can also provide removal of heavy metal ions (El Samrani A.G. *et al*., 2008; Hilal *et al*., 2008), and organic micropollutants (Alexander *et al*., 2012; Reungoat *et al*., 2010; Ternes *et* *al*., 2002). In the literature there are few examples of research on PCB removal from polluted water. Considering the similarity of chemical properties of PCB and PCDD, for polychlorinated biphenyls elimination from water, research achievements in PCDD/Fs removal can be used(Li *et al*., 2009; Liyan *et al*., 2009).

The aim of the research was to evaluate the efficiency of coagulation process, 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 nonhydrolyzed and prehydrolyzed coagulants.

2. Methods

For the research surface water from Kozłowa Góra dam reservoir was used (Poland, Silesian voivodeship), which is the source of water for Water Treatment Plant in Wymysłów. 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.

Nonhydrolyzed salts $Al_2(SO_4){\cdot}18H_2O$ and $AlCl_3{\cdot}6H_2O$ were used as coagulants, produced by POCH in Gliwice, and hydrolyzed salts, polyaluminium chlorides with commercial names PAX18 and PAX-XL1905, produced by KEMIPOL in Police (Poland). Commercial solutions of polyaluminium chlorides had alkalinity equal respectively 41 and 85%, and contained 17 and 13% of Al_2O_3. Polyaluminium chlorides were chosen based on previously conducted research (Sperczyńska *et al*., 2014).

In the first stage, the coagulation process was conducted in glass beakers with 3 L volume, to each beaker 2 L of analysed water was measured. Coagulants were introduced in the amount of 3 mgAl L^{-1}, and with the use of mechanical stirrer fast stirring was executed for 2 minutes (applying 200 RPM), and then slow stirring for 15 minutes (20 RPM). After this time the samples were subjected to 1 hour sedimentation. Afterwards 0.7 L of water was decanted and analysed. In the second stage the coagulation process was combined with adsorption on powdered activated carbon. Study was conducted in the way described above, introducing activated carbon during fast stirring, 2 minutes after the coagulant. Powdered activated carbon with commercial name CWZ-30 was used, produced by Gryfskand in Hajnówka (Poland). The carbon had surface area equal 1134 m^2 g^{-1} and iodine number – 1190 mg g^{-1}. The carbon dosage amounted to 30 mg L^{-1} of water. Water quality indicators before and after the coagulation process were determined by means of the following methods: pH – potentiometric, turbidity – nephelometric, dissolved organic carbon DOC – infrared spectrophotometry, heavy metal ions – atomic absorption spectrometry, aluminium – Aquaquant 14413 test.

PCB analysis methodology was described in the literature (Rosińska, and Dąbrowska, 2013). 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 subject to qualitative and quantitative analysis by gas chromatography and mass spectrometer (GC-MS).

3. Results

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 0.008; <0.001; <0.001; 0.006 mg L^{-1}, after the modification approx. 0.4 mg L^{-1}. Presence of all analysed PCB congeners in water was confirmed, their total concentration amounted to 326.8 ng L^{-1}. Dominant congeners were higher chlorinated PCB: 153 (70.9 ng L^{-1}), and 180 (89.9 ng L^{-1}). The lowest concentration was shown for PCB 28 (10.9 ng L^{-1}).

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 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 (Yan *et al*., 2008; Yang *et al*., 2010). 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}).

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 coagulant, and coagulant +powdered activated carbon are presented in Table 1.

Table 1: Effect of powdered carbon CWZ addition on DOC and heavy metal ions of water during 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	0.38	0.38	0.39
$Al_2(SO_4)_3$	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	8.6	0.15	0.16	0.30	0.29	0.07
$AlCl_3$+CWZ	8.3	0.15	0.15	0.29	0.30	0.08
PAX18+CWZ	7.4	0.10	0.11	0.31	0.27	0.03
PAX-XL1905+CWZ	6.3	<0.05	0.08	0.28	0.18	0.01

*- water was modified

In case of heavy metal ions, the best effects were obtained 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; 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 7.5-7.0, analysed metals occurred mainly in cationic forms (Cu^{2+}, Cd^{2+}, $Pb(OH)^+$, Ni^{2+}), in case of copper also $Cu(OH)_2$ (Genc-Fuhrman *et al*., 2007). Therefore metals removal was determined by adsorption, surface complexation, and ionic exchange. Reduction in DOC content during the coagulation process amounted to 26-32%, with powdered activated carbon enhancement 35-53%.

Evaluating the importance of adsorption in analysed heavy metal removal, only in case of lead ions removal significant influence of coagulation enhancement by powdered activated carbon was discovered. Using activated carbon and respectively $Al_2(SO_4)_3$, $AlCl_3$, PAX18, and PAX-XL1905, a decrease in lead ion concentration by 82; 79; 92; and 97% was obtained. Whereas removal of copper, nickel, and cadmium with the usage of PAX-XL1905 and powdered carbon amounted to 79; 26; and 53%, respectively. An advantageous aspect of coagulation enhanced by activated carbon was obtaining lower concentration of aluminium remaining in purified water.
The results for PCB removal from water in the coagulation process, and the coagulation enhanced by powdered activated carbon CWZ are presented in Table 2. 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 congeners content from 44 (PCB 28) to 82% (PCB 153). Obtained

results confirm literature data about polyaluminium chloride effectiveness in dioxins and dioxin-like compounds removal. Li *et al*. (2009) demonstrated 99% effectiveness in PCDD/Fs removal after application of ferric chloride and polyaluminium chloride, slightly lower (97-98%) was obtained for aluminium sulfate. Used coagulants were selective in chosen PCDD/Fs removal.
Better effects of PCB removal were obtained using coagulation enhancement by powdered activated carbon CWZ. Application of powdered activated carbon allowed for decrease in concentration of analysed congeners by 45 to 77%. The best results were obtained using the coagulation process with PAX-XL1905 coagulant, enhanced by activated carbon, where concentration of all analysed PCB congeners in water was decreased by the range of 92 (PCB 180) to 98% (PCB 153). Acceptable results were also obtained for other samples with addition of $Al_2(SO_4)_3$+CWZ, $AlCl_3$+CWZ, and PAX18+CWZ, for which the efficiency of PCB removal amounted to respectively: 78-98%, 65-92%, 83-98%.

Table 2: Concentration of indicator PCB in water after enhancement of coagulation process with powdered activated carbon.

Coagulant, powdered carbon	Concentration, ng L^{-1}							
	PCB 28	PCB 52	PCB 101	PCB 118	PCB 138	PCB 153	PCB 180	∑PCB
Water was modified	510.9	517.0	529.6	553.8	554.8	554.7	570.9	3826.7
$Al_2(SO_4)_3$	270.2	280.0	231.3	211.0	203.1	210.0	679.0	2084.6
$AlCl_3$	300.1	251.9	210.0	271.1	245.2	280.8	504.7	2063.8
PAX18	289.4	229.3	159.9	192.1	149.4	162.0	306.1	1488.2
PAX-XL1905	390.3	349.3	289.9	393.6	568.8	382.9	512.3	2887.1
$Al_2(SO_4)_3$+CWZ	51.9	88.2	99.1	65.9	94.9	97.2	197.9	695.1
$AlCl_3$+CWZ	113.0	194.4	176.6	93.7	174.0	173.8	162.5	1088.0
PAX18+CWZ	58.5	105.3	99.4	100.6	118.5	113.6	97.9	693.8
PAX-XL1905+CWZ	33.8	47.5	52.4	78.0	79.4	83.2	131.5	505.8

Liyan *et al*. (2009) demonstrated the efficiency of powder-activated carbon, granular-activated carbon in hydrophobic organic chemicals (HOCs) removal in the rage of 73.4 to 89.2%, which is confirmed by obtained research results.

4. Conclusions

Conducted research allow to draw the following conclusions:

- 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,
- 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 to 98%, lead ions 97%, and dissolved organic carbon content 53%,
- the advantageous aspect of the coagulation enhanced by activated carbon was obtaining lower concentration of aluminium remaining in purified water.

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