Selection of coagulants for the removal of chosen micro-pollutants from drinking water

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Abstract. In order to evaluate the efficiency of PAH removal, water was modified with PAH MIX A standard solution. Benzo(a)pyrene, in the amount of 0.02 μg/L, and four recommended PAH, ie. benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene, which total concentration amounted to 0.2 μg L^{-1}, were introduced into water. In order to evaluate the efficiency of PCB removal, water was modified with PCB standard mixture, composed of seven indicator congeners: 28, 52, 101, 118, 138, 153 and 180. The concentration of each congener amounted to 0.3 μg/L. With regard to heavy metals, modifications were made by introducing into water a solution containing nickel, cadmium and lead ions, providing their initial concentration in water equal to 0.2 mg L^{-1}.

It was demonstrated that the use of $Al_2(SO_4)_3$ allowed to obtain better results of PCB removal from water than in case of using hydrolysed polyaluminium chlorides. The total concentration of PCB decreased by 71%. Whereas the highest efficiency of reduction of the sum of four standardized PAH in water after coagulation (by 84%) was obtained using polyaluminium chloride PAX-19F. Also in case of heavy metal ions removal, best results were obtained using PAX-19F, respectively for Ni, Cd, Pb, concentration was reduced by 21; 44; 78%.

Keywords: polycyclic aromatic hydrocarbons, polychlorinated biphenyls, coagulants, heavy metal ions, water.

1. Introduction

Polycyclic aromatic hydrocarbons (PAH) constitute a group of chemical compounds containing from two to seven condensed aromatic rings (Arey and Atkinson, 2003; Boström *et al*., 2002; Di-Toro *et al*., 2000). At present, in the environment there are recognized over 300 different compounds classified as polycyclic aromatic hydrocarbons (Armstrong *et al*., 2004; Kim *et al*., 2013), including 33 of them considered by the Scientific Committee on Food (SCF) to be particularly toxic.

The permissible PAH content in water intended for human consumption is the sum of benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene, and it amounts to 0.1 μg/ L^{-1}. The permissible content of benzo(a)pyrene, which amounts to 0.01 μg L^{-1}, is stated separately. In Polish legislation, the permissible levels of benzo(a)pyrene concentration and the sum of the four PAH in drinking water are stated in The Ministry of Health Regulation of 13 November 2015 on the quality of water intended for human consumption, while in the European legislation in the Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption.

209 polychlorinated biphenyl (PCB) congeners are known, a number of which are characterized by high bioaccumulation, toxicity or potential carcinogenicity, and simultaneously high persistence in the environment. According to the U.S. Environmental Protection Agency, 7 indicator congeners should be determined in the environment, with codes: 28, 52, 101, 118, 138, 153, and 180 (Howell *et al*., 2008). Negative influence of micropollutants on water consumers health causes the need to remove these substances from drinking water. The choice of micropollutant removal processes is determined by their type, properties, and form of occurrence. Coagulation is the most commonly used process for removing inorganic and organic colloidal contaminants and difficult to settle suspensions from water. Decrease of turbidity, color of water, content of organic matter (e.g. humic substances, which are precursors of oxidation by-products) is the result of effective coagulation (Matilainen *et al*., 2010; Siéliéchi *et al*., 2008). Properly performed coagulation can also ensure heavy metal ions removal (Hilal *et al*., 2008).

The aim of the research was to select a coagulant for efficient removal of polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) and heavy metal ions from surface water. As the coagulants, aluminium sulphate and pre-hydrolyzed salts, polyaluminium chlorides, were used. For the study, surface water was used, taken from a water reservoir, which is a source of supply for water treatment plant for drinking water.

2. Materials and methods

2.1.Materials

For the research, surface water from Kozłowa Góra dam reservoir was used. The Kozłowa Góra dam Reserovir is located on the south-east outskirts of Świerklaniec commune (Poland). This reservoir was formed due to the raised water level of the Brynica River. At present, the Kozłowa Góra dam Reservoir is a water source for the Water Treatment Plant in Wymysłów which belongs to the Upper Silesia Water Supply Company.

Water was modified with PAH MIX A standard solution, in order to obtain total concentration of standardized PAH higher than the permissible level in water intended for human consumption. Four PAH were introduced to water: benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene, which are enclosed in the Directive (total concentration amounted to 0.20 μg L^{-1}), benzo(a)pyrene (0.05 μg L^{-1}).

In order to evaluate the efficiency of PCB removal, water was modified with PCB standard mixture, composed of seven indicator congeners: 28, 52, 101, 118, 138, 153 and 180. The concentration of each congener amounted to 0.3 μg L^{-1}.

The water composition was modified in order to obtain concentration of nickel, cadmium, and lead ions equal approx. 0.2 mg L^{-1}, by introducing to water appropriate amount of solution prepared with $NiCl_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$ and $Pb(NO_3)_2$ salts.

Nonhydrolyzed salt $Al_2(SO_4)_3 \cdot 18H_2O$ was used as coagulant, produced by POCH in city Gliwice, and hydrolyzed salts, polyaluminium chlorides, with commercial names PAX-XL19F, PAX-XL1910 produced by KEMIPOL company in city Police (Poland). Aluminium sulphate is a commonly used coagulant in water treatment plants in Poland. However, more and more often it is replaced by pre-hydrolyzed coagulants, i.a. due to the fact that they allow to reduce the dose of the applied reagents. Commercial solutions of polyaluminium chlorides had alkalinity equal to 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 follow: alkalinity (%) = r/0.03. Commercial solution of PAX-XL19F contained 16.0% of Al_2O_3, while PAX-XL1910 19.8% of Al_2O_3. For the analyses, coagulant solutions were prepared by diluting commercial products so that they contained 1.0 gAl L^{-1}.

2.2.Jar test procedure

The coagulation process was conducted in glass beakers with 3 L volume, to each beaker 2.5 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 minutes (applying 250 RPM), and then slow stirring for 15 minutes (25 RPM). After this time the samples were subjected to 1 hour sedimentation. Afterwards 1 L of water was decanted and analysed.

2.3.Analytical procedure

For PAH and PCB separation from water, solid phase extraction (SPE) method was applied, using Bakerbond company columns with Octadecyl C_{18} filling. For this purpose, 0.5 L of modified surface water was collected and 0.5 L of water after the coagulation. The samples were then passed through preconditioned Octadecyl C_{18} columns PAH and PCB. The obtained eluate was gently evaporated to dryness under a stream of nitrogen and then acetonitrile was added to the test tube in the amount of 1 mL. The sample, prepared this way, was analyzed by means of gas chromatography and mass spectrometer (GC-MS).

The concentration of heavy metals (Ni, Cd, Pb) was determined by means of the atomic absorption spectrometry method with four repetitions.

3. Results and discussion

PAH, PCB and heavy metals concentration in modified surface water and in water after the coagulation process, are presented in Table 1.
In the results discussion, the analyzed were divided into following groups:

- standardized in the Council Directive 98/83/EC on the quality of water intended for human consumption: benzo(a)pyrene and the total of: benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene (compounds classified as 5- and 6-ring PAH),
- PCB (28, 52, 101, 118, 138, 153 and 180),
- nickel, cadmium, lead ions.

In unmodified surface water, total concentration of analyzed PAH amounted to 21.44 ng L^{-1}. The concentration of PAH included in the Council Directive 98/83/EC on the quality of water intended for human consumption, i.e. benzo(a)pyrene and the sum of benzo(k)fluoranthene, benzeno(g,h, i)perylene and indeno(1,2,3-cd)pyrene, were below the permissible level value i.e. 0.05 μg L^{-1}. Using the coagulation process, the highest efficiency of reduction of benzo(a)pyrene concentration (by 84.2%) from modified water was obtained after the application of $Al_2(SO_4)_3$, and the lowest (by 63.9%) after the application of PAX-XL19F coagulant. The highest efficiency of the reduction of the sum of four standardized PAH, i.e. benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene, was obtained in case of PAX-XL19F coagulant application (by 84.5%). With the usage of the remaining coagulants, $Al_2(SO_4)_3$ and PAX-XL1910, the efficiency of reduction of total concentration of these compounds amounted to 59.4 and 67.4%, respectively.

The obtained results indicate that the coagulation is effective in removal from water of polycyclic aromatic hydrocarbons, including benzo(a)pyrene, and four standardized in the Council Directive 98/83/EC on the quality of water intended for human

consumption.

The highest removal rates for indicator PCBs were obtained with use of $Al_2(SO_4)_3$. Concentrations of PCB congeners with codes: 28, 52, 101, 118, 138, 153 decreased from ~300 ng L^{-1} to 129.0, 117.1, 62.0, 44.1, 31.4, 31.3 ng L^{-1} respectively. Total concentration of PCBs was reduced by 71%. Removal efficiency for particular congeners amounted from 57% (PCB 28) to 90% (PCB 153).

Using $Al_2(SO_4)_3$ was insufficient only in case of removal of heptachlorobiphenyl – congener with code 180, which concentration was reduced by 34%. Best results for this congener elimination were obtained with use of PAX-XL19F. The smallest degree of removal from water for indicator was stated for coagulants PAX-XL1910 and PAX-XL19F. After the application of these coagulants, decrease in PCB concentration in the range of 4 to 60%.

Table 1. The concentration of PAH, PCB and heavy metal ions in water before and after the coagulation process

Micropollutants	Water after modification	$Al_2(SO_4)_3$	PAX-XL1910	PAX-XL19F
PAH [ng L^{-1}]				
Benzo(a)pyrene	50.85	8.06	15.96	18.33
Benzo(b)fluoranthene	49.76	18.03	10.01	11.50
Benzo(k)fluoranthene	51.99	26.44	9.62	8.83
Benzo(g,h,i)perylene	51.26	20.25	20.93	6.46
Indeno(1,2,3-cd)pyrene	50.85	18.06	25.97	4.83
Σ	203.86	82.78	66.53	31.62
PCB [ng L^{-1}]				
28	301.6	129.0	278.9	258.9
52	301.2	117.1	274.8	261.9
101	301.1	62.0	215.6	164.0
118	300,6	44.1	202.7	134.9
138	300.4	31.4	192.6	134.9
153	300.6	31.3	263.0	230.0
180	300.5	198.0	170.3	118.8
Heavy metal ions [mg L^{-1}]				
Nickel	0.204	0.184	0.168	0.161
Cadmium	0.205	0.167	0.120	0.114
Lead	0.208	0.112	0.052	0.046

According to the literature, the efficiency of the coagulation process is influenced by: the type and dose of the coagulant, treated water composition, including content and properties of organic contamination, pH, water alkalinity and physicochemical properties of removed organic micropollutants (Alexander *et al.*, 2012).The application of $Al_2(SO_4)_3$ or polyaluminum chloride as coagulants for organic contaminant removal is recommended by many authors (Li *et al*., 2009; Alexander *et al*., 2012). The obtained results suggest that in case of organic micropollutant removal from water with the usage of polyaluminium chlorides, their alkalinity is important, which should be equal to ca. 70%. Li and co-authors studies (2009) demonstrated that during the coagulation of organic micropollutants, sorption of these compounds on particles of organic matter naturally occurring in water (NOM) plays an important role. The authors demonstrated that polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) occur in water in a form bound to NOM and during coagulation will be removed along with the NOM particulates. PAH strongly bound to suspended solids and particulates surface include: indeno(1,2,3-cd)pyrene, benzo(g,h,i)perylene, dibenzo(a,h)antracene and benzo(k)fluoranthene. The obtained results confirm the correlation between PAH and PCB hydrophobicity (expressed by the partition coefficient n-octanol/water i.e. $K_{o/w}$) and the coagulation effectiveness in removal of these pollutants from water. According to Tadkaew and co-authors (2011) for compounds demonstrating log $K_{o/w}>3.2$, higher efficiency of their removal in the coagulation process is achieved.

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 0.208 mg L^{-1} down to respectively 0.112; 0.052; and 0.046 mg L^{-1} with the use of respectively $Al_2(SO_4)_3$, PAX-XL1910, and PAX-XL19F, which gives efficiency equal respectively 46; 75; 78%. In case of other metals, removal efficiency of cadmium ions amounted to 18-44%, and nickel 10-21%. 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 7.7-7.0, analysed metals occurred mainly in cationic forms (Cd^{2+}, $CdCl^+$, Pb^{2+}, $Pb(OH)^+$, Ni^{2+}, $CdCO_3$ and $PbCO_3$) (Genc-Fuhrman *et al*., 2007; Powell *et al*., 2009; Powell *et al*., 2011). Therefore metals removal was determined by adsorption, surface complexation, and ionic exchange.

4. Conclusions

Based on the obtained results the following conclusions were drawn:
- in the coagulation process high efficiency of reduction of the sum of the four standardized PAH, i.e. benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene, was obtained using PAX-XL19F coagulant (84.5%); the usage of $Al_2(SO_4)_3$ or PAX-XL1910 allowed to obtain an efficiency of removal of these compounds by 59.4 and 67.4%, respectively,
- a good efficiency of removal of benzo(a)pyrene (84.2%) was obtained during coagulation using $Al_2(SO_4)_3$,
- best results of indicator PCB removal (71%) were observed with application of $Al_2(SO_4)_3$,
- application of pre-hydrolyzed salts (PAX-XL1910 and PAX-XL19F) in the coagulation process was more effective in reducing the concentration of cadmium and lead ions (41-78%) with respect to the usage of $Al_2(SO_4)_3$ (18-46%).

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References

Alexander J.T., Hai F.I. and Al-aboud T.M. (2012), Chemical coagulation-based processes for trace organic contaminant removal: Current state and future potential, *Journal Environmental Management*, **111**, 195-207.

Arey J. and Atkinson R. (2003), Photochemical reactions of PAH in the atmosphere. In: PAHs: An ecotoxicological perspective. P.E.J. Douben (ed), John Wiley and Sons Ltd, New York, USA.

Armstrong B.G., Hutchinson E., Unwin J. and Fletcher T. (2004), Lung cancer risk after exposure to polycyclic aromatic hydrocarbons: a review and meta-analysis. *Environmental Health Perspectives*, **112**, 970–978.

Boström C.-E., Gerde P., Hanberg A., Jernström B., Johansson C., Kyrklund T., Rannug A., Törnqvist M., Victorin K. and Westerholm R. (2002), Cancer risk assessment, indicators and guidelines for polycyclic aromatic hydrocarbons in ambient air, *Environmental Health Perspectives*, **110**, 451–89.

Di-Toro D.M., McGrath J.A. and Hansen D.J. (2000), Technical basis for narcotic chemicals and polycyclic aromatic hydrocarbon criteria. I. Water and tissue, *Environmental Toxicology and Chemistry*, **19**, 1951-1970.

Genc-Fuhrman H., Mikkelsen P.S., Ledin A. (2007), Simultaneous removal of As, Cd, Cr, Cu, Ni and Zn from stormwater: Experimental comparison of 11 different sorbents, *Water Research*, **41**, 591-602

Hilal N., Al-Abri M., Moran A. and Al-Hinai H. (2008), Effects of heavy metals and polyelectrolytes in humic substance coagulation under saline conditions, *Desalination*, **220**, 85-95

Howell N.L., Suarez M.P., Riafi H.S. and Koenig L. (2008), Concentration of polychlorinated biphenyls (PCBs) in water, sediment and aquatic biota in the Huston Ship Chanel, Texas, *Chemosphere*, **70**, 593-606.

Kim K.-H., Jahan S.A., Kabir E. and Brown R.J.C. (2013), A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects, *Environment International*, **60**, 71–80

Li X., Peng P., Zhanga S., Man R., Sheng G.J. and Fu J. (2009), Removal of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans by three coagulants in simulated coagulation processes for drinking water treatment, *Journal Hazardous Materials*, **162**, 180–185.

Matilainen A. Vepsäläinen M. and Sillanpää M. (2010), Natural organic matter removal by coagulation during water treatment: A review, *Advance in Colloid and Interface Science*, **15**, 189-197.

Powell K.J., Brown P.L., Byrne R.H., Gajda T., Hefter G., Leuz A-K., Sjöberg S. and Wanner H. (2009), Chemical speciation of environmentally significant metals with inorganic ligands. Part 3: The Pb^{2+} + OH, Cl^-, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-} systems (IUPAC Technical Report), *Pure and Applied Chemistry*, **81**, 2425-2476.

Powell K.J., Brown P.L., Byrne R.H., Gajda T., Hefter G., Leuz A-K., Sjöberg S., and Wanner H. (2011), Chemical speciation of environmentally significant metals with inorganic ligands. Part 4: The Cd^{2+} + OH^-, Cl^-, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-} systems (IUPAC Technical Report), *Pure and Applied Chemistry*, **83**, 1163-1214.

Siéliéchi J.M., Lartiges B.S., Kayem G.J., Hupont S., Frochot C., Thieme J., Ghanbaja J., d'Espinose de la Caillerie J.B., Barrés O., Kamga R., Levitz P. and Michot L.J. (2008), Changes in humic acid conformation during coagulation with ferric chloride: Implications for drinking water treatment, Water Research, **42**, 2111-2123.

Tadkaew N., Hai F.I., McDonald J.A., Khan S.J. and Nghiem L.D. (2011), Removal of trace organics by MBR treatment: the role of molecular properties, *Water Research*, **45**, 2439-2451.